A TREATISE ON CHEMISTRY

A

TREATISE ON CHEMISTRY

Henry Enfield — BY — Karl

SIR H. E. ROSCOE F.R.S. AND C. SCHORLEMMER F.R.S.

VOLUME III

THE CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES

OR

ORGANIC CHEMISTRY

PART VI

> "*Chymia, alias Alchemia et Spagirica, est ars corpora vel mixta, vel composita, vel aggregata etiam in principia sua resolvendi, aut ex principiis in talia combinandi.*"—STAHL, 1723

NEW YORK
D. APPLETON AND COMPANY
1892

Authorized Edition.

PREFACE TO VOL. III. PART VI.

THIS part of the Treatise on Organic Chemistry contains a description of the derivatives of naphthalene and the allied hydrocarbons, as well as of the compounds consisting of two or more Benzene-nucleï directly connected. The next part, now in the press, will complete the description of the hydrocarbons and their derivatives properly so called. The authors are much indebted to Dr. H. G. Colman and Dr. A. Harden for the assistance which they have given them in passing this volume through the press.

H. E. R.
C. S.

January, 1892.

CONTRACTIONS EMPLOYED IN THIS PART

ac = alicyclic.
as = asymmetric.
ar = aromatic.
m = meta.
n = normal.
o = ortho.
p = para.
s = symmetric.
v = adjacent.

Am. Chem. Journ. = American Chemical Journal.
Annalen = Liebig's Annalen der Chemie.
Ann. Chim. Phys. = Annales de Chemie et Physique.
Ber. = Berichte der Deutschen Chemischen Gesellschaft.
Bull. Soc. Chim. = Bulletin de la Société Chimique de Paris.
Chem. Centr. = Chemisches Centralblatt.
Chem. Zeit. = Chemiker Zeitung.
Compt. Rend. = Comptes Rendues de l'Académie des Sciences.
Gazzetta = Gazzetta Chimica Italiana.
Journ. Chem. Soc. = Journal of the Chemical Society.
J. Pr. Chem. = Journal für Praktische Chemie.
Journ. Soc. Chem. Ind. = Journal of the Society of Chemical Industry.
Monatsh. = Monatshefte für Chemie.
Phil. Mag. = Philosophical Magazine.
Phil. Trans. = Philosophical Transactions of the Royal Society.
Pogg. Ann. = Annalen der Physik und Chemie (Poggendorf).
Proc. Chem. Soc. = Proceedings of the Chemical Society.
Proc. Roy. Soc. = Proceedings of the Royal Society.
Rec. Trav. Chim. = Recueil des Travaux Chimiques des Pays-Bas.
Wied. Ann. = Annalen der Physik (Wiedemann).
Zeit. analyt. Chem. = Zeitschrift für analytische Chemie.
Zeit. angew. Chem. = Zeitschrift für angewandte Chemie.
Zeit. phys. Chem. = Zeitschrift für physikalische Chemie.
Zeit. physiol. Chem. = Zeitschrift für physiologische Chemie.

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ORGANIC CHEMISTRY

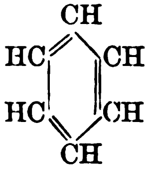
OR THE CHEMISTRY OF THE HYDROCARBONS AND THEIR DERIVATIVES.

PART VI.

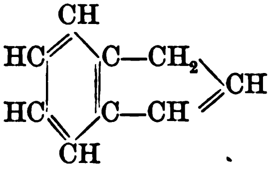
THE INDENE GROUP.

2552 The compounds of this group are derived from indene, a hydrocarbon which occurs in coal-tar. It is intermediate in constitution between benzene and naphthalene.

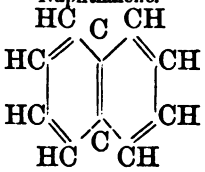
Benzene.



Indene.



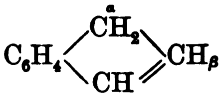
Naphthalene.



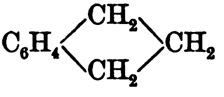
The ortho-position is assigned to the carbon atoms combined with the benzene nucleus in indene and its derivatives, because they are either obtained from naphthalene or phthalic acid, or are converted into the latter by oxidation.

All the indene derivatives at present known are derived from the following:

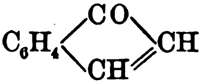
Indene.



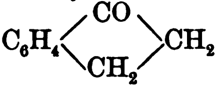
Hydrindene.



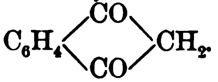
Indone.



Hydrindone.



Diketohydrindene.



The letters of the Greek alphabet are used as shown to denote the position of the carbon atoms in the indene chain.[1]

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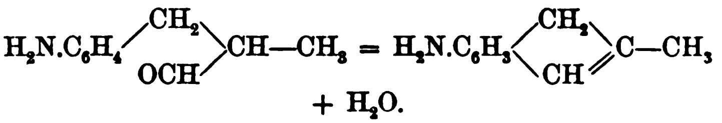
[1] Roser, *Annalen*, **247**, 129.

DERIVATIVES OF INDENE.

2553 *Indene*, C_9H_8, occurs in the fraction of crude benzene boiling at about 176—182°, from which it is isolated by means of the picrate.[1] The latter forms golden-yellow needles melting at 98°, and is decomposed by steam. Indene is a colourless oil which has a sp. gr. of 1·040 at 15° and boils at 179·5—180·5° (corr.). It combines with bromine to form a *dibromide*, which melts at 43—45°, and on treatment with water yields *indene bromhydrin*, which crystallizes in long white needles melting at 130—131°. On oxidation with nitric acid indene is converted into phthalic acid.

m-Amido-β-methylindene, $C_9H_6(NH_2)CH_3$, is formed by the action of tin and hydrochloric acid on *m*-nitro-*a*-methylcinnamic aldehyde. *m*-Amido-*a*-methylhydrocinnamic aldehyde is first formed, and then loses the elements of water:



$$H_2N.C_6H_4\left<\begin{matrix}CH_2\\OCH\end{matrix}\right>CH{-}CH_3 = H_2N.C_6H_3\left<\begin{matrix}CH_2\\CH\end{matrix}\right>C{-}CH_3 + H_2O.$$

It crystallizes from ether in small lustrous plates, melting at 98°, sublimes readily, and boils in an atmosphere free from oxygen at 271—272°, under a pressure of 718 mm. Its hydrochloride also crystallizes in small lustrous plates, and dissolves readily in water, with some difficulty in cold hydrochloric acid. Acetic anhydride converts the base into the *acetyl derivative*, $C_9H_6(NH.CO.CH_3)CH_3$, which crystallizes from a mixture of ether and alcohol in aggregates of concentrically arranged prisms and melts at 148°.[2]

The base is converted by Sandmeyer's diazoreaction into *chloro-β-methylindene*, $C_9H_6Cl(CH_3)$, a dark yellow liquid, boiling at about 240°, which is oxidized by nitric acid to *as*-chlorophthalic acid.[3]

The following compounds have been prepared by similar methods:

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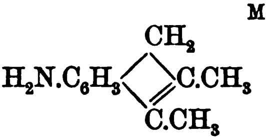
[1] Krämer and Spilker, *Ber.* **23**, 3276.

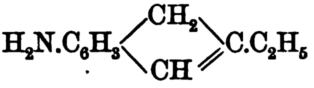
[2] v. Miller and Kinkelin, *Ber.* **19**, 1249.

[3] v. Miller and Rohde, *Ber.* **22**, 1830.

Melting-point.

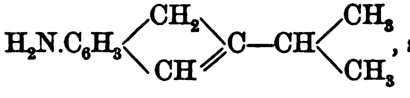
m-Amido-β-γ-dimethylindene, 

lustrous plates . . . . 62—63°

m-Amido-β-ethylindene, 

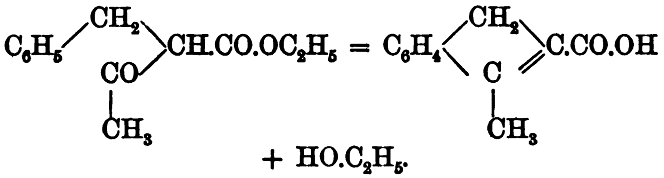
micaceous plates . . . . 89°

m-Amido-isopropylindene,



, small plates . 84°

γ-Methylindene-β-carboxylic acid, $C_{11}H_{10}O_2$, is formed when a mixture of ethyl benzylaceto-acetate with 8 parts of concentrated sulphuric acid is allowed to stand for several hours:



The acid separates out when the mixture is poured into water. It is almost insoluble in water, but readily dissolves in hot alcohol, from which it crystallizes in small white needles, melting at 200°. On heating with soda-lime it decomposes into carbon dioxide and *γ-methylindene*, $C_6H_4{:}C_3H_2.CH_3$, a highly refractive liquid, which boils at 205—206°, has a disagreeable smell resembling that of naphthalene, and changes on exposure to the air into a yellow resinous mass. It is also formed in very small quantity when benzylacetone is dissolved in concentrated sulphuric acid.[1] The acid is converted by oxidation into phthalic acid; when it is fused with caustic potash and a little water, the surface of the mass becomes coloured blue with a greenish yellow metallic lustre, and a potassium salt is formed, which is only stable in alkaline solution and appears to be a derivative of complex constitution.

The *methyl ester*, $C_{10}H_9.CO.OCH_3$, crystallizes from methyl alcohol in small, lustrous needles, melting at 78°.

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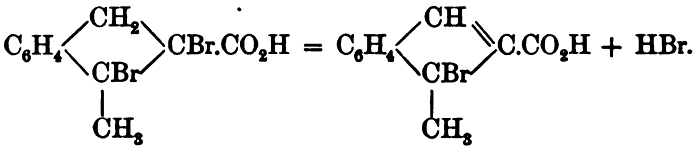
[1] Miller and Rohde, *Ber.* **23**, 1883.

If the acid be exposed to the vapour of bromine, its *dibromide* is formed; it separates from ether in white crusts and melts with decomposition at 215°.

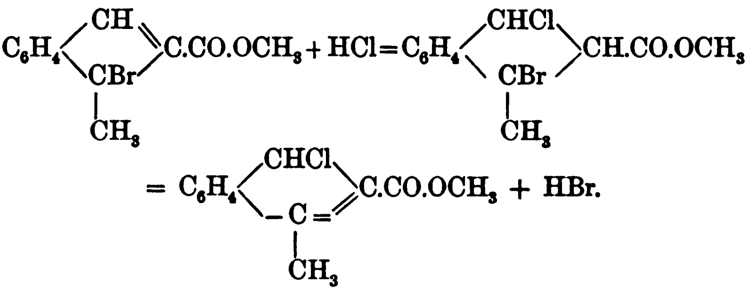
Its *methyl ester*, $C_{10}H_9Br_2.CO.OCH_3$, forms long, white needles melting at 157°.

a-Brom-a-methylindenecarboxylic acid, $C_{11}H_9BrO_2$, is prepared by adding the calculated quantity of bromine to methylindenecarboxylic acid suspended in glacial acetic acid, the dibromide which is first formed being decomposed in the following manner:



It is insoluble in water, but is slightly soluble in alcohol, and crystallizes from acetic acid in small, white needles, melting at 245°. Its *methyl ester*, $C_9H_8Br.CO.OCH_3$, is formed by the action of hydrobromic acid on a solution of the acid in methyl alcohol or may be prepared by dissolving the ester of the unbrominated acid in chloroform, adding the calculated amount of bromine and allowing to evaporate. It forms small, flat crystals, melting at 98—100°.

When the solution of the acid in methyl alcohol is saturated with hydrochloric acid, the methyl ester of *chloromethylindenecarboxylic acid* is formed, perhaps according to the following equation:

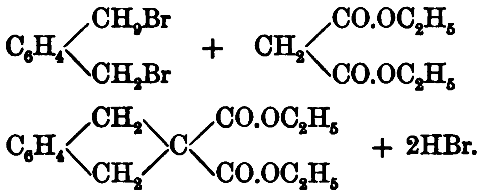


It crystallizes in long, silky needles, melting at 84°, and, like the ester of the brominated acid, gives with alcoholic caustic soda a splendid blue colouration, which on standing becomes green and finally changes to brown (Roser).

DERIVATIVES OF HYDRINDENE.

2554 *Hydrindene*, C_9H_{10}, is obtained by reducing indene with sodium in boiling alcoholic solution. It is a colourless oil which has a sp. gr. of 0·957 at 15° and boils at 173·5—174·5° (corr.).[1]

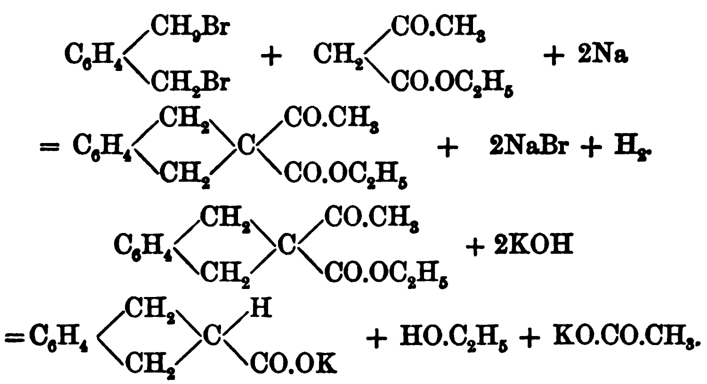
Hydrindene-β-carboxylic acid, $C_{10}H_{10}O_2$, has already been described as hydrindonaphthenecarboxylic acid (Pt. V. p. 263). It was obtained by Baeyer and Perkin by adding *o*-xylylene bromide to an alcoholic solution of ethyl malonate and sodium, the ethyl ester of *hydrindene-β-dicarboxylic acid* being formed:



$$C_6H_4\left\langle\begin{matrix}CH_2Br\\CH_2Br\end{matrix}\right. + CH_2\left\langle\begin{matrix}CO.OC_2H_5\\CO.OC_2H_5\end{matrix}\right. =$$

$$C_6H_4\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle C\left\langle\begin{matrix}CO.OC_2H_5\\CO.OC_2H_5\end{matrix}\right. + 2HBr.$$

The free acid liberated from this ester forms rhombic plates or tablets, melts at 199°, and when heated above its melting point decomposes into carbon dioxide and hydrindenecarboxylic acid.[2] The latter may also be prepared by dissolving two atoms of sodium in eight parts of alcohol, adding three parts of absolute ether, then a molecule of ethyl acetoacetate and finally a molecule of *o*-xylylene bromide dissolved in five times its weight of ether. After standing for a few hours the product is hydrolized with alcoholic caustic potash:



$$C_6H_4\left\langle\begin{matrix}CH_2Br\\CH_2Br\end{matrix}\right. + CH_2\left\langle\begin{matrix}CO.CH_3\\CO.OC_2H_5\end{matrix}\right. + 2Na$$

$$= C_6H_4\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle C\left\langle\begin{matrix}CO.CH_3\\CO.OC_2H_5\end{matrix}\right. + 2NaBr + H_2.$$

$$C_6H_4\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle C\left\langle\begin{matrix}CO.CH_3\\CO.OC_2H_5\end{matrix}\right. + 2KOH$$

$$= C_6H_4\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle C\left\langle\begin{matrix}H\\CO.OK\end{matrix}\right. + HO.C_2H_5 + KO.CO.CH_3.$$

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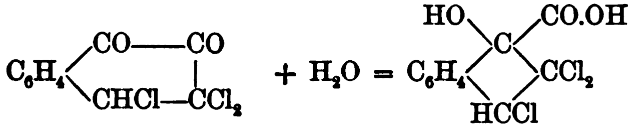
[1] Krämer and Spilker, *Ber.* **23**, 3281.

[2] *Ber.* **17**, 122.

Hydrindenecarboxylic acid crystallizes from boiling water in fascicular groups of needles, melts at 130°, and can be sublimed without decomposition. It is oxidized by potassium permanganate to *o*-carboxyphenylglyoxylic acid,[1] $CO_2H.C_6H_4.CO.CO_2H$.

γ-Methylhydrindene-β-carboxylic acid, $C_{11}H_{12}O_2$, is prepared by adding a large excess of sodium amalgam to a boiling alcoholic solution of methylindenecarboxylic acid. It crystallizes from hot water in small needles, melts at 80°, and boils without decomposition at 300—310°. The *silver salt* is a crystalline precipitate, and the *barium salt*, $(C_{11}H_{11}O_2)_2Ba + 4H_2O$, crystallizes from alcohol in needles, which are very soluble in water.[2]

Trichlorohydroxyhydrindenecarboxylic acid, $C_{10}H_7Cl_3O_3$, is formed when trichlorodiketohydronaphthalene is dissolved in cold, dilute caustic soda solution:

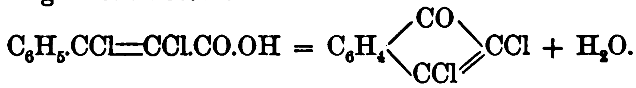


It is an oily liquid and yields a *methyl ester* which forms lustrous monosymmetric crystals, melting at 150°. When heated to 100° with acetyl chloride, a compound of the formula $C_9H_5Cl_3(OCO.CH_3)CO.OCH_3$ is obtained, which crystallizes in small needles and melts at 114—115°.[3]

The acid is oxidized to trichlorohydrindone by a dilute solution of chromic acid.

DERIVATIVES OF INDONE.

2555 *Dichlorindone*, $C_9H_4Cl_2O$, was obtained by Zincke and Fröhlich by the oxidation of dichlorohydroxyindenecarboxylic acid.[4] Roser and Haselhoff then found that it can readily be prepared from dichlorocinnamic acid, which is itself obtained by passing chlorine into a solution of phenylpropiolic acid in chloroform. When the product is dissolved in sulphuric acid, the following reaction occurs:



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[1] Scherke, *Ber.* **18**, 378; Perkin, *Journ. Chem. Soc.* 1888, **1**, 7.

[2] Roser, *Annalen*, **247**, 165.

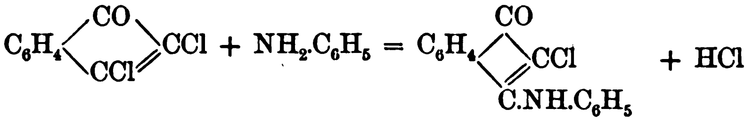
[3] Zincke, *Ber.* **20**, 2894.

[4] *Ber.* **20**, 1267.

The pure substance is obtained by precipitation with water and distillation with steam.[1] It crystallizes from alcohol or acetic acid in long, golden yellow, lustrous needles, has a characteristic smell, somewhat resembling that of quinone, and melts at 90°. When its alcoholic solution is boiled with potassium bromide, *chlorobromindone*, C_9H_4ClBrO, is obtained; it crystallizes in small yellow needles and melts at 105°.

Dichlorindone-oxime, $C_9H_4Cl_2(N.OH)$, is formed when an alcoholic solution of dichlorindone is gently heated with hydroxylamine hydrochloride; it crystallizes in long, light yellow needles, which are readily soluble in alkalis and warm alcohol.

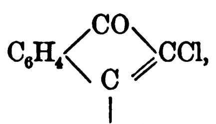
Anilidochlorindone, $C_9H_4Cl(NH.C_6H_5)O$, is prepared by heating dichlorindone or chlorobromindone with aniline dissolved in alcohol or acetic acid:



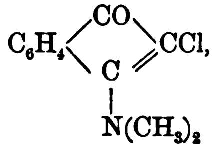
It is only slightly soluble in alcohol and acetic acid, and crystallizes in slender, deep red needles, melting at 203—204°, which dissolve without decomposition in dilute alkalis, forming red solutions; when such a solution is boiled, however, chlorohydroxyindone is formed.

The amines act upon dichlorindone in a similar manner to aniline: methylamine and dimethylamine, for example, form the following compounds:

Melting-point.



long dark red needles . . . . . 195°



thick red tablets . . . . 140°

Chlorohydroxyindone, $C_9H_4(OH)ClO$, is formed when the preceding compounds are heated with alkalis or acids, and may also

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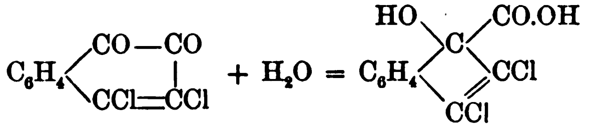
[1] *Annalen*, **247**, 129.

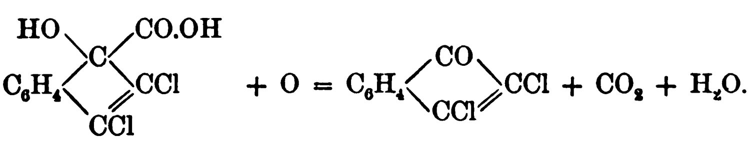
be prepared by suspending dichlorindone in alcohol and gradually adding caustic soda solution, the liquid being well stirred and cooled throughout the operation; the mixture is allowed to stand for a day and the chlorohydroxyindone then precipitated by hydrochloric acid. It crystallizes from dilute alcohol in broad, thin plates, with a satin lustre, and separates from light petroleum in small compact crystals, melting at 114°. It forms a red solution in alkalis, from which it is precipitated by acids. If its solution in alcohol or acetic acid be heated with aniline, the anilido-compound described above is formed.

The chlorine atom which is removed in the formation of chlorohydroxyindone and other derivatives from dichlorindone is that which occupies the γ-position. This follows from the fact that chlorohydroxyindone is converted by the action of chlorine into dichlorodiketohydrindene, $C_6H_4(CO)_2CCl_2$, which is described below, a substance which can also be obtained from naphthoquinone and can readily be converted into phthalic acid.

Dichlorohydroxyindenecarboxylic acid, $C_{10}H_6Cl_2O_3$, is formed when dichloro-β-naphthoquinone is treated with cold dilute caustic soda solution, the mixture being frequently shaken until it has dissolved:



It crystallizes in slender white needles containing water, which are readily soluble in alcohol, but only slightly in water.[1] As already mentioned, it is oxidized to dichlorindone by chromic acid:



Its *methyl ester*, $C_9H_5Cl_2O.CO_2CH_3$, crystallizes from alcohol in thick plates, and from ether in lustrous, six-sided tablets, which melt at 137—138°.

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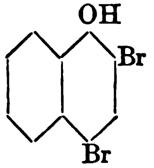
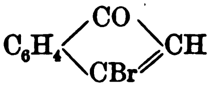
[1] Zincke, *Ber.* **19**, 2493.

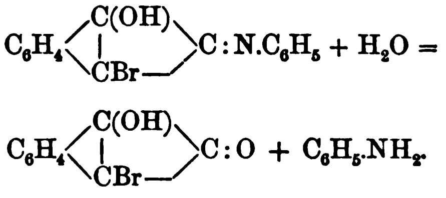
γ-Bromindone, C_9H_5BrO, is formed when dibrom-*a*-naphthol is brought into well cooled fuming nitric acid. It forms small ochreous scales, melting at 127—128°. Its constitution follows from that of the dibrom-*a*-naphthol from which it is obtained:





$$C_6H_4\left\langle\begin{matrix} CO \\ \\ CBr \end{matrix}\right\rangle CH$$

Anilido-γ-bromindone, $C_9H_5BrO(NC_6H_5)$, is obtained by boiling the bromindone in concentrated alcoholic solution with aniline; the hydro-derivative, which can be obtained by the action of reducing agents on the amido-compound, is probably first formed and is then oxidized on exposure to the air. It dissolves very sparingly in boiling alcohol, readily in benzene chloroform and sulphuric acid, with a magenta-red colour, and separates in deep red scales, melting at 190°; it is therefore isomeric with the compound obtained by Roser (see below) which melts at 170°. It readily forms salts with alkalis, but is decomposed on boiling with caustic soda solution, with formation of a *bromohydroxyindone*, isomeric with that obtained by Roser and Haselhoff:



$$C_6H_4\left\langle\begin{matrix} C(OH) \\ | \\ CBr \end{matrix}\right\rangle C{:}N.C_6H_5 + H_2O =$$

$$C_6H_4\left\langle\begin{matrix} C(OH) \\ | \\ CBr \end{matrix}\right\rangle C{:}O + C_6H_5.NH_2.$$

This substance crystallizes from hot water, in dull orange coloured stumpy needles, melting at 191—192°. It forms a characteristic barium salt, crystallizing in slender orange needles.

γ-Bromindone also reacts with other amido-compounds forming bodies which resemble the anilide.[1]

Dibromindone, $C_9H_4Br_2O$, is obtained from dibromocinnamic acid, and crystallizes from alcohol in orange-yellow needles, which melt at 123°; in its other properties it closely resembles dichlor-

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[1] Meldola and Hughes, *Journ. Chem. Soc.* 1890, **1**, 393.

indone. When its alcoholic solution is boiled with potassium iodide, *bromo-iodindone*, C_9H_4BrIO, is formed; this substance crystallizes in short, yellowish red pointed prisms, which are odourless and melt at 163°.

Dibromindone-oxime, $C_6H_4.C_3Br_2(N.OH)$, crystallizes from alcohol in fascicular groups of yellow, silky needles, and melts at 198° with decomposition. Its *sodium salt* forms well-developed yellow needles and is readily soluble in water, less easily in caustic soda solution.

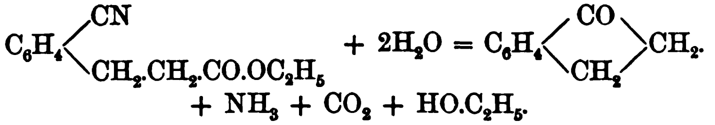
Tribromindone-oxime, $C_6H_3Br.C_3Br_2(N.OH)$, is the product of the action of bromine on the preceding compound, and crystallizes from alcohol in small, golden-yellow, silky needles.

Anilidobromindone, $C_9H_4Br(NH.C_6H_5)O$, crystallizes in light red needles and melts at 170°; it is readily soluble in alcohol and acetic acid, and resembles the chlorine compound in its other properties.

Bromohydroxyindone, $C_9H_4(OH)BrO$, is formed by the action of caustic soda on dibromindone and crystallizes in slender needles, which have a very slight yellow tint. It melts at 119°, is readily soluble in alcohol, acetic acid and benzene, and forms red solutions in the alkalis (Roser and Haselhoff).

HYDRINDONE AND ITS DERIVATIVES.

2556 *Hydrindone*, C_9H_8O, is prepared by gently heating ethyl *o*-cyanobenzylacetate with concentrated hydrochloric acid:



$$C_6H_4\left\langle\begin{matrix}CN\\CH_2.CH_2.CO.OC_2H_5\end{matrix}\right. + 2H_2O = C_6H_4\left\langle\begin{matrix}CO\\CH_2\end{matrix}\right\rangle CH_2 + NH_3 + CO_2 + HO.C_2H_5.$$

As soon as the evolution of carbon dioxide has ceased, the liquid is neutralized and distilled with steam. The hydrindone passes over as an oil, which soon solidifies, and that which has dissolved in the aqueous distillate separates on cooling in well-developed rhombohedral tablets, which melt at 40°. It boils at 243—245°, has a characteristic smell resembling that of phthalide, and is readily taken up by most solvents.

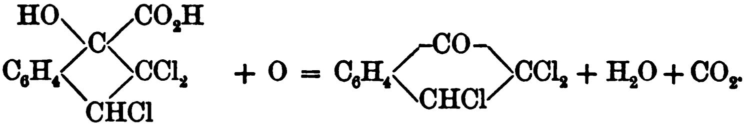
When hydrindone is heated to 100° for some hours with concentrated hydrochloric acid, it is converted into tribenzylenebenzene, $C_{27}H_{18}$, water being eliminated. The formation of this substance, which will be subsequently described, is quite analogous to that of mesitylene from acetone.

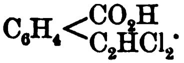
Phosphorus pentachloride acts upon hydrindone when the two are heated together with formation of *dichlorindene*, $C_9H_6Cl_2$, which crystallizes from methyl alcohol in lustrous prisms melting at 29°.

Hydrindone-oxime, $C_9H_8N.OH$, crystallizes from alcohol in lustrous white needles, melting at 146°.

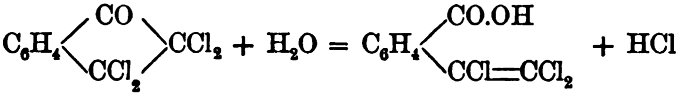
Hydrindonephenylhydrazone, $C_9H_8N.NH.C_6H_5$, separates from alcohol in white prisms, which turn brown at 120° and melt at a few degrees above this temperature. It changes in the air into a brown oil, and when boiled with hydrochloric acid is converted into benzylene-indol, $C_{18}H_{11}N$, which will be subsequently described.[1]

Trichlorohydrindone, $C_9H_5Cl_2O$, is formed by the oxidation of trichlorohydroxyhydrindenecarboxylic acid:



It crystallizes from alcohol in thick, pointed needles or prisms, melts at 58—59°, and has a characteristic smell, resembling that of benzophenone. It is converted by methylamine into dichlorindone, which then combines with the excess of the amine to form the substance already described (Zincke). Caustic soda solution dissolves it and thereby converts it into *dichlorovinylbenzoic acid*,  $C_6H_4{<}^{CO_2H}_{C_2HCl_2}$.

Tetrachlorohydrindone, $C_9H_4Cl_4O$, is prepared by passing chlorine into a warm solution of dichlorindone in acetic acid, and forms colourless transparent monosymmetric crystals or thick white striated needles, which melt at 107—108°, and sublime at a somewhat lower temperature, yielding a vapour which has a peculiar smell, resembling that of hexchlorethane. When its solution in caustic soda, to which a little alcohol has been added, is heated, trichlorovinylbenzoic acid is formed:



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[1] Hausmann, *Ber.* 22, 2019.

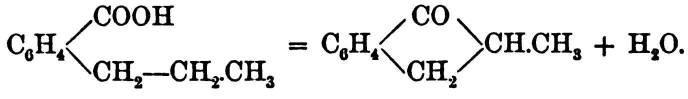
This substance crystallizes from dilute alcohol in needles or long plates, and melts at 163°. It is converted by the continued action of sodium amalgam and water into *o*-ethylbenzoic acid.[1]

Dibromohydrindone, $C_9H_6Br_2O$, is obtained when bromine diluted with chloroform is gradually added to a boiling solution of hydrindone in chloroform. It crystallizes from alcohol in white prisms, melts at 133—134°, and is readily taken up by the usual solvents on heating.

Tetrabromohydrindone, $C_9H_4Br_4O$, is prepared by adding chloroform and an excess of bromine to dibromindone. On evaporating the solution it crystallizes in colourless, lustrous prisms, which melt at 124° with decomposition. Its alcoholic solution becomes coloured yellow on heating, and dibromindone is again formed when it is boiled. If however it be added to an excess of caustic soda solution, *tribromovinylbenzoic acid*, $CBr_2 = CBr.C_6H_4.CO_2H$, is formed. This substance crystallizes from alcohol in lozenge-shaped tablets and melts at 196—198°.

Dichlorodibromohydrindone, $C_9H_4Cl_2Br_2O$, has been obtained from both dichlorindone and dibromindone. It crystallizes in white prisms and is converted into dichlorindone by sulphurous acid or boiling alcohol.

β-Methylhydrindone, $C_{10}H_{10}O$, is formed when *a*-methylhydrocinnamic acid is brought into concentrated sulphuric acid heated to 150°. The reddish-brown solution is rapidly cooled, poured into cold water, and made alkaline with caustic soda, the methylhydrindone being then distilled off in a current of steam.[2]



$$C_6H_4\Big\langle{}^{COOH}_{CH_2-CH_2.CH_3} = C_6H_4\Big\langle{}^{CO}_{CH_2}\Big\rangle CH.CH_3 + H_2O.$$

It is a colourless oil, somewhat heavier than water, which has a strong characteristic odour resembling that of peppermint, and boils at 244—246° at a pressure of 719 mm., with slight decomposition. It is only slightly soluble in water but readily in other solvents. Dilute nitric acid converts it into phthalic acid.

Its *phenylhydrazone* crystallizes from alcohol in yellowish plates, melting at 116°.

A series of other substituted hydrindones has been prepared in

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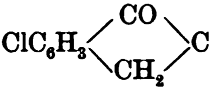
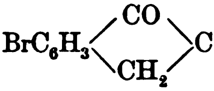
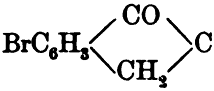
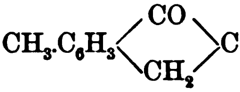
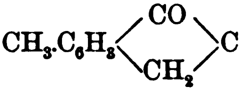
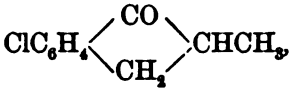
[1] Zincke and Fröhlich, *Ber.* **20**, 2053.

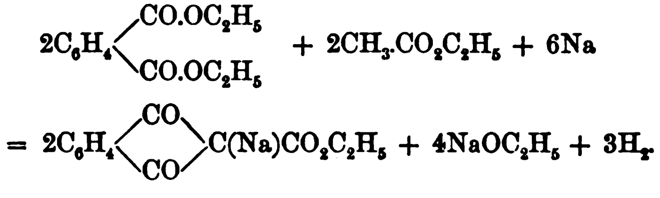
[2] Miller and Rohde, *Ber.* **23**, 1888.

a similar manner from the corresponding hydrocinnamic acids by the same chemists.

	Boiling-point.	Melting-point.
m-Chlorohydrindone,  $ClC_6H_3{<}\begin{smallmatrix}CO\\CH_2\end{smallmatrix}{>}CH_2$, white needles	274°	95°
m-Bromohydrindone,  $BrC_6H_3{<}\begin{smallmatrix}CO\\CH_2\end{smallmatrix}{>}CH_2$, white needles	—	122-123°
p-Bromohydrindone,  $BrC_6H_3{<}\begin{smallmatrix}CO\\CH_2\end{smallmatrix}{>}CH_2$, white microscopic needles	—	111-112°
m-Methylhydrindone,  $CH_3.C_6H_3{<}\begin{smallmatrix}CO\\CH_2\end{smallmatrix}{>}CH_2$, long white needles	—	59°
p-Methylhydrindone,  $CH_3.C_6H_3{<}\begin{smallmatrix}CO\\CH_2\end{smallmatrix}{>}CH_2$, white needles	—	63°
m-Chloro-β-methylhydrindone,  $ClC_6H_4{<}\begin{smallmatrix}CO\\CH_2\end{smallmatrix}{>}CHCH_3$, colourless oil	265-268°	—

DIKETOHYDRINDENE AND ITS DERIVATIVES.

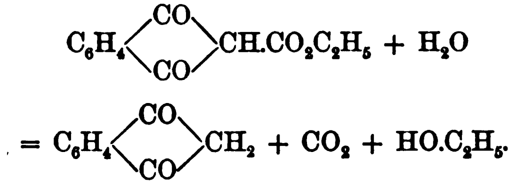
2557 *Diketohydrindene*, $C_9H_6O_2$. The sodium compound of ethyl diketohydrindenecarboxylate is prepared by heating 10 grms. of ethyl phthalate and 2 grms. of sodium, or the corresponding amount of sodium ethylate, on the water-bath, and gradually adding 7—10 grms. of ethyl acetate. The reaction is probably expressed by the following equation:



$$2C_6H_4{<}\begin{smallmatrix}CO.OC_2H_5\\CO.OC_2H_5\end{smallmatrix} + 2CH_3.CO_2C_2H_5 + 6Na$$

$$= 2C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C(Na)CO_2C_2H_5 + 4NaOC_2H_5 + 3H_2.$$

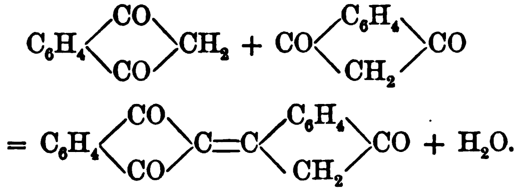
This substance crystallizes from water in slender, yellow needles. The ester, which also crystallizes in fine yellow needles, is precipitated by the addition of sulphuric acid to the aqueous solution of the sodium salt, and on heating with an alkali decomposes into diketohydrindene, alcohol and carbon dioxide, a change which also occurs when its solution in ether which contains water is allowed to stand:



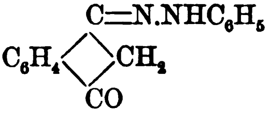
$$C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}CH.CO_2C_2H_5 + H_2O$$
$$= C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}CH_2 + CO_2 + HO.C_2H_5.$$

It is, however, best to heat the acidified aqueous solution for half an hour on the water-bath and filter the hot liquid. Diketohydrindene forms colourless, lustrous needles, which melt with decomposition at 129—130°. It is readily soluble in hot alcohol and benzene, less readily in ether and hot light petroleum, and is only very slightly soluble in water. Dilute alkalis dissolve it readily, the solutions being of a deep yellow colour.

Bidiketohydrindene, $C_{18}H_{10}O_3$, is formed when diketohydrindene is boiled with water. It crystallizes in difficultly-soluble, yellowish rhombic tablets, which melt with decomposition at 206—208°. All its salts are coloured deep red to violet, and it dyes wool a violet red in a faintly acid bath, but not very readily. Its formation is probably represented by the following equation:



$$C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}CH_2 + CO{<}\begin{smallmatrix}C_6H_4\\CH_2\end{smallmatrix}{>}CO$$
$$= C_6H_4{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C{=}C{<}\begin{smallmatrix}C_6H_4\\CH_2\end{smallmatrix}{>}CO + H_2O.$$

Diketohydrindenephenylhydrazone,  $C_6H_4{<}\begin{smallmatrix}C{=}N.NHC_6H_5\\CO\end{smallmatrix}{>}CH_2$, is obtained as a yellow flocculent precipitate when phenylhydrazine hydrochloride is added to a solution of the diketone in alcohol which contains a little water. It crystallizes from dilute alcohol in yellow, hair-like, matted needles, melting at 162—163°, and yields a solution in concentrated sulphuric acid which is coloured a deep bluish green by ferric chloride.

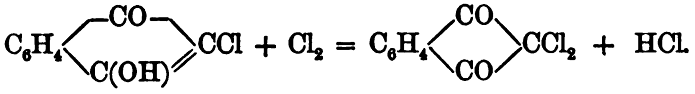
Diketohydrindenediphenylhydrazone, $C_7H_6(C{=}N_2H.C_6H_5)_2$, is formed when the diketone is heated on the water-bath with the necessary amount of phenylhydrazine. It crystallizes from alcohol in matted, light flesh-coloured needles, melting at 171°, and its solution in cold sulphuric acid is also coloured dark bluish green by a trace of ferric chloride.

Diketohydrindenedioxime, $C_6H_4(CH_2)(C{=}N.OH)_2$, is formed when a solution of hydroxylamine hydrochloride is added to a solution of diketohydrindene in carbonate of sodium. It crystallizes from hot dilute alcohol in very fine, matted needles, which are readily soluble in alkalis.

Isonitrosodiketohydrindene, $C_6H_4(CO)_2.C{=}N.OH$, is obtained by the addition of dilute sulphuric acid to a solution of the diketone and sodium nitrite in dilute caustic soda. It crystallizes from glacial acetic acid in triangular plates, which melt with decomposition at 197—198° and dissolve in alkalis, forming solutions of a delicate pink colour.

Tri-isonitrosodiketohydrindene, $C_6H_4(C{=}N.OH)_3$, is the product of the action of hydroxylamine on the preceding compound, and is a crystalline substance, melting at 197° with evolution of gas.[1]

Dichlorodiketohydrindene, $C_9H_4Cl_2O_2$, is formed by the action of chlorine on a solution of chlorohydroxyindone in acetic acid :



$$C_6H_4\left\langle\begin{matrix}-CO-\\ C(OH)\end{matrix}\right\rangle CCl + Cl_2 = C_6H_4\left\langle\begin{matrix}CO\\ CO\end{matrix}\right\rangle CCl_2 + HCl$$

It may also be obtained by the oxidation of dichloroketohydroxyhydrindic acid, a substance which is described later on. In order to avoid the purification of this substance the preparation is most conveniently carried out by dissolving chlorohydroxynaphthoquinone in sodium carbonate solution, passing in chlorine until the liquid becomes colourless, acidifying with acetic acid and filtering. Hydrochloric acid is then added to the filtrate and this heated with chromic acid.

Dichlorodiketohydrindene crystallizes from dilute alcohol in small lustrous plates and from a mixture of ether and light petro-

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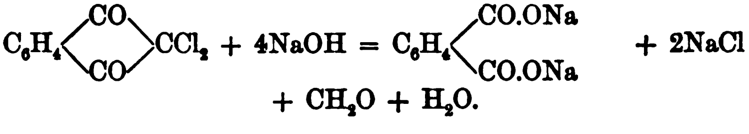
[1] Wislicenus, *Annalen*, **246**, 347; Wislicenus and Kötzle, *Annalen*, **252**, 72.

leum in large, thin tablets, the corners of which are truncated; it melts at 125°.

When it is dissolved in caustic soda, phthalic acid and dichloromethane are formed, the latter of which is converted by the alkali into formaldehyde, so that the solution obtained reduces ammoniacal silver nitrate:



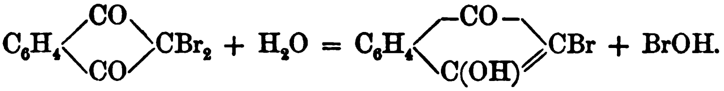
$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle CCl_2 + 4NaOH = C_6H_4\left\langle\begin{matrix}CO.ONa\\CO.ONa\end{matrix}\right. + 2NaCl + CH_2O + H_2O.$$

Alcoholic potash, on the other hand, converts it into dichloracetophenonecarboxylic acid:

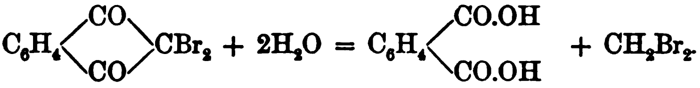
$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle CCl_2 + HOK = C_6H_4\left\langle\begin{matrix}CO.CHCl_2\\CO.OK\end{matrix}\right. .$$

When this substance is dissolved in sodium carbonate and treated with chlorine, trichloracetophenonecarboxylic acid is formed (Pt. V., p. 149).[1]

Dibromodiketohydrindene, $C_9H_4Br_2O_2$, is formed by the action of bromine on diketohydrindene (Wislicenus) or on bromohydroxyindone (Roser and Haselhoff), as well as by the oxidation of dibromoketohydroxyhydrindic acid (Zincke and Gerland). It crystallizes from acetic acid in thick white plates, which melt at 176°. Dilute alkalis convert it into bromohydroxyindone, phthalic acid and bromoform, the reactions which occur being represented by the following equations:



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle CBr_2 + H_2O = C_6H_4\left\langle\begin{matrix}CO-\\C(OH)=\end{matrix}\right\rangle CBr + BrOH.$$



$$C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle CBr_2 + 2H_2O = C_6H_4\left\langle\begin{matrix}CO.OH\\CO.OH\end{matrix}\right. + CH_2Br_2.$$

$$CH_2Br_2 + BrOH = CHBr_3 + H_2O.$$

Chlorobromodiketohydrindene, $C_9H_4ClBrO_2$, is obtained by the oxidation of chlorobromoketohydroxyhydrindic acid and also by the action of chlorine on bromohydroxyindone or of bromine on chlorohydroxyindone. It crystallizes from alcohol or acetic acid in lustrous plates, melting at 147°, and is converted by

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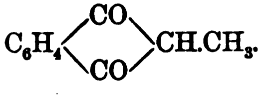
[1] Zincke, *Ber.* **21**, 491; Zincke and Gerland, *Ber.* **20**, 3216; **21**, 2379 and 2396.

alkalis into a mixture of phthalic acid, dibromochloromethane and chlorohydroxyindone.

2558 *β-Methyldiketohydrindene*, $C_{10}H_8O_2$, is prepared from ethyl phthalate and ethyl propionate and has, therefore, the constitution:



$$C_6H_4\begin{matrix}\diagup CO \diagdown \\ \diagdown CO \diagup\end{matrix}CH.CH_3.$$

In this way the *sodium compound*, $C_6H_4(CO)_2CNa.CH_3$, is obtained, which crystallizes from hot water in small garnet red or dark red prisms. When an acid is added to its solution, methyldiketohydrindene separates out as a colourless oil, which soon solidifies. It crystallizes from alcohol in small obtuse pyramids, and from light petroleum in pointed needles, which melt at 84—85° and form red solutions in the alkalis. It can be distilled without alteration, no condensation product being formed as is the case with diketohydrindene.

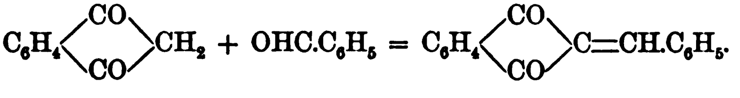
Methyldiketohydrindenephenylhydrazone forms small yellowish crystals and melts at 142—162°.

Methyldiketohydrindenedioxime crystallizes from alcohol in fine needles and melts at 116—117° with evolution of gas.

Methylbromodiketohydrindene, $C_6H_4(CO)_2CBr.CH_3$, is formed when a solution of methyldiketohydrindene in acetic acid is heated with bromine. It crystallizes from alcohol in small white needles, melts at 90—91° and forms yellowish red solutions in alkalis.

Dimethyldiketohydrindene, $C_6H_4(CO)_2C(CH_3)_2$, may be obtained by heating the sodium compound of methyldiketohydrindene with methyl alcohol and methyl iodide to 100°. It crystallizes from alcohol in small white needles, melts at 107—108°, and boils almost without decomposition at 250°. It has no acid properties, both the hydrogen atoms of the methylene group having been replaced by methyl. The *diphenylhydrazone* forms thin, yellowish prisms, melting at 184—187°.[1]

Benzidenediketohydrindene, $C_{16}H_{10}O_2$, is prepared by heating together molecular proportions of benzaldehyde and diketohydrindene:



$$C_6H_4\begin{matrix}\diagup CO \diagdown \\ \diagdown CO \diagup\end{matrix}CH_2 + OHC.C_6H_5 = C_6H_4\begin{matrix}\diagup CO \diagdown \\ \diagdown CO \diagup\end{matrix}C{=}CH.C_6H_5.$$

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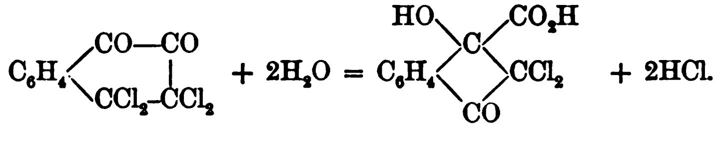
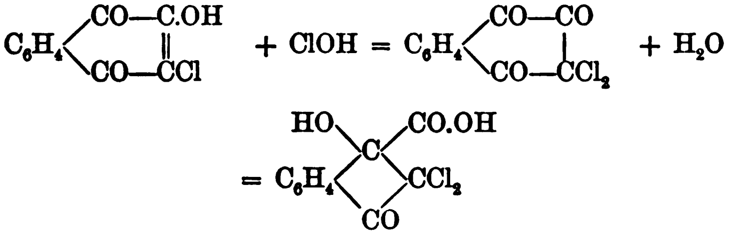
[1] Wislicenus and Kötzle, *Annalen*, **252**, 80.

It separates from alcohol in yellowish, lancet-shaped crystals, which melt at 150—151°. On heating with alkalis it is decomposed into its constituents.

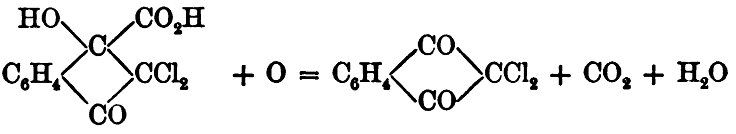
Dichloroketohydroxyhydrindic acid, $C_{10}H_6Cl_2O_4$. Zincke obtained this acid by the action of sodium carbonate solution on tetrachlorodiketohydronaphthalene :



It may also be prepared from dichlorotriketohydronaphthalene, which need not be isolated, by simply passing chlorine into an alkaline solution of chlorohydroxynaphthoquinone ; the triketone is thus formed and is converted into the acid by the alkali present :



It crystallizes from hot water in small prisms or thick needles, and from hot hydrochloric acid in long, almost rectangular prisms, while it separates from a mixture of ether and light petroleum in lustrous monosymmetric prisms. All these crystals contain a molecule of water which can be removed by careful heating, but is very readily re-absorbed. As already mentioned, the acid is easily oxidized to dichlorodiketohydrindene :



Its *methyl ester*, $C_9H_4Cl_2O(OH)CO_2.CH_3$, forms large, lustrous, transparent monosymmetric crystals, which melt at 121—122°, and its acetyl compound, $C_9H_4Cl_2O(OC_2H_3O)CO_2H$, crystallizes in small prisms, melting at 126°.[1]

Dibromoketohydroxyhydrindic acid, $C_{10}H_6Br_2O_4$, has been obtained from bromohydroxynaphthoquinone, and crystallizes in needles or large monosymmetric prisms containing water of crystallization, which become anhydrous at 130° and melt at about 170°. Its *methyl ester* resembles the corresponding chlorine compound, and melts at 137°.

Chlorobromoketohydroxyhydrindic acid, $C_{10}H_6ClBrO_4$, is formed by the action of bromine on an alkaline solution of chlorohydroxynaphthoquinone and by that of chlorine on the corresponding bromine compound; it forms crystals which are similar to those of the preceding compound and also lose a molecule of water on heating. The anhydrous acid separates from a mixture of ether and light petroleum in crystals, which melt at 190°. The *methyl ester* melts at 134—135°.

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[1] Zincke, *Ber.* **21**, 491 ; Zincke and Gerland, *Ber.* **21**, 2379.

THE NAPHTHALENE GROUP

NAPHTHALENE, $C_{10}H_8$.

2559 ON December 15th, 1819, A. Garden sent to T. Thomson a short account of a peculiar crystalline substance which had been formed in the distillation of coal-tar and which appeared to be a kind of camphor.[1] Thomson ascertained that it was a hydrocarbon, and concluded from the results of his analyses that it consisted of three atoms of carbon and two atoms of hydrogen or of one atom of olefiant gas and one atom of carbon.[2] J. Kidd then obtained the same substance by passing the vapours of coal-tar through a red-hot tube and gave it the name of naphthalene,[3] soon after which Chamberlain showed that it could be obtained in large quantity by simply distilling the tar, the naphthalene being found in that portion of the distillate which comes over towards the end of the operation.[4] Its correct composition was first determined by Faraday,[5] and although at first doubted, was eventually confirmed. Dumas assumed that the naphthalene existed as such in the coal, but Reichenbach showed that this idea was not accurate, but that the naphthalene is a product formed by the dry distillation.[6] Faraday, Berzelius, and more especially Laurent, were the next to turn their attention to this substance. The last named found that it unites with chlorine to form a tetrachloride, $C_{10}H_8Cl_4$, which on oxidation yields dibasic phthalic acid, $C_8H_6O_4$, a fact which led Marignac to assume that naphthalene is a compound of two hydrocarbons,[7] $C_8H_4 + C_2H_4$. This chemist subsequently showed that phthalic acid on heating with lime decomposes into carbon dioxide and benzene, from which it follows that naphtha-

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[1] Thomson's *Ann. Phil.* **15**, 74.

[2] *Ann. Phil.* **16**, 85.

[3] *Phil. Trans.* **1821**, 209.

[4] *Ann. Phil.* II. **6**, 135.

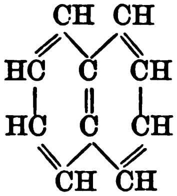
[5] *Phil. Trans.* **1826**, II. 140.

[6] *Pogg. Ann.* **28**, 484.

[7] *Annalen*, **38**, 18.

lene is derived from the latter by the substitution of two hydrogen atoms by the divalent group, C_4H_4.

Erlenmeyer then proposed the following formula:



According to this it consists of two aromatic nuclei, which have two carbon atoms in common.[1] The accuracy of this view was experimentally proved by Gräbe, who showed that phthalic acid can be obtained by the destruction of either of the two nuclei. This cannot be ascertained in the case of the hydrocarbon itself, since there is no way of distinguishing between the two nuclei. One of them must therefore first be marked by replacing one or more hydrogen atoms by other elements or radicals, and it then becomes possible to ascertain which nucleus has been destroyed by oxidation. Gräbe actually found that dichloronaphthoquinone, $C_{10}H_4Cl_2O_2$, is converted by oxidation into phthalic acid, so that its formula may be written $C_6H_4.C_4Cl_2O_2$. Phosphorus pentachloride converts the dichloro-compound into pentachloronaphthalene:

$$C_{10}H_4Cl_2O_2 + 2PCl_5 = C_{10}H_3Cl_5 + 2POCl_3 + HCl$$

This substance is converted on oxidation into tetrachlorophthalic acid, so that its formula can be written $C_4H_3Cl.C_6Cl_4$, and from these facts it follows that naphthalene must have the symmetrical constitution assigned to it by Erlenmeyer.[2]

In addition to this proof several others have been brought forward.

When the tetrachloride, $C_{10}H_8Cl_4$, which we have already mentioned and which is converted by oxidation into phthalic acid,[3] is heated, it decomposes into hydrochloric acid and two dichloronaphthalenes, one of which is oxidized to dichlorophthalic acid,[4] which has also been obtained from monochloronaphthalene tetrachloride,[5] $C_{10}H_7Cl.Cl_4$, while monochloro-

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[1] *Annalen*, **137**, 346.

[2] *Annalen*, **149**, 20.

[3] Laurent, *Ann. Chim. Phys.* **61**, 113.

[4] Atterberg, *Ber.* **9**, 547.

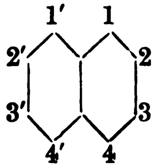
[5] J. and E. Depouilly, *Bull. Soc. Chim.* **4**, 10; Widman, *ibid.* **28**, 505.

naphthalene itself is converted by nitric acid into chloronitrophthalic acid (Atterberg). When monochloronaphthalene tetrachloride is heated with alcoholic caustic potash, trichloronaphthalene, $C_{10}H_5Cl_3$, is obtained, and on oxidation yields trichlorophthalic acid (Widman).

Mononitronaphthalene, $C_{10}H_7NO_2$, is oxidized by chromic acid to mononitrophthalic acid.[1] The same nitro-compound is converted by reduction into amidonaphthalene, $C_{10}H_7.NH_2$, which is oxidized by potassium permanganate or chromic acid to phthalic acid and not to amidophthalic acid.[2]

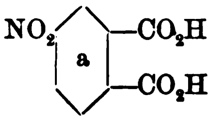
Amidonaphthalene can also be readily converted into dinitronaphthol, which also yields phthalic acid on oxidation.

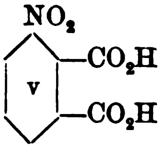
2560 Erlenmeyer's formula, moreover, explains the fact that naphthalene differs from benzene, inasmuch as it yields two isomeric mono-substitution products, which are distinguished as α and β.[3]



$$\alpha = 1 = 4 = 4' = 1'$$
$$\beta = 2 = 3 = 3' = 2'$$

The α-compounds on oxidation yield naphthoquinone, $C_{10}H_6O_2$, which so closely resembles benzo-quinone that an analogous constitution was assigned to it and the oxygen atoms assumed to occupy the position 1 : 4. The discovery of a second naphthoquinone, however, rendered this conclusion somewhat doubtful until its accuracy was fully proved by the following observations. Phthalic acid yields two isomeric nitrophthalic acids of known constitution :





The latter of these is, however, also formed by the oxidation of α-nitronaphthalene and the α-position must therefore be next to a carbon atom which is common to both nuclei. This also

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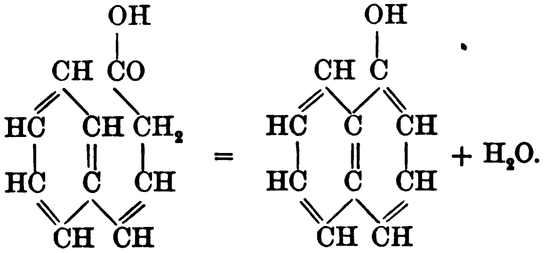
[1] Beilstein and Kurbatow, *Ber.* **12**, 688.

[2] Reverdin and Nölting, *Constitution des Naphthalins*. Genf, 1880; *Constitution de la Naphthaline*, Mulhouse, 1888.

[3] Merz, *Zeitsch. Chem.* **1868**, 394.

follows from the synthetical formation of *α*-naphthol by heating phenylisocrotonic acid :[1]



It follows from the formula given above that the *α*- and *β*-positions each occur four times. Atterberg proved this for the *α*-position after Liebermann had showed that it occurs twice. *α*-Nitronaphthalene, $C_{10}H_7.NO_2$, is converted by reduction into *α*-amidonaphthalene, $C_{10}H_7.NH_2$, which can readily be converted into *α*-amidonitronaphthalene, $C_{10}H_6(NO_2)NH_2$. When the amido-group of this compound is replaced by hydrogen, the product is the original *α*-nitronapthalene. Moreover, the *α*-amidonitronaphthalene can easily be converted into *α*-naphthoquinone, which on oxidation yields phthalic acid, thus proving that both the substituent groups are situated in the same nucleus.[2] If, however, the amido-group of amidonitronaphthalene be replaced by chlorine, *α*-chloronitronaphthalene, $C_{10}H_6Cl(NO_2)$, is formed, which is converted by phosphorus pentachloride into dichloronaphthalene, $C_{10}H_6Cl_2$. A substance which is isomeric with this is obtained in a similar manner from *α*-nitronaphthalenesulphonic acid, $C_{10}H_6(NO_2)SO_3H$. The latter, however, is formed both by the action of sulphuric acid on *α*-nitronaphthalene and of nitric acid on *α*-naphthalenesulphonic acid. The two substituent groups and therefore the two chlorine atoms in the dichloronaphthalene which is derived from it are consequently both in the *α*-position. This is also the case in a third dichloronaphthalene, obtained by the action of chlorine on *α*-nitronaphthalene, for if another atom of hydrogen be replaced by chlorine in each of these three dichloro-compounds, one and the same trichloronaphthalene is obtained. This proves the proposition that the *α*-position occurs four times, Liebermann's experiments showing that it is found twice in one nucleus, and Atterberg's that it also occurs twice in the other :[3]

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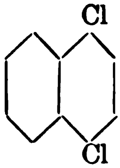
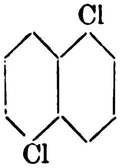
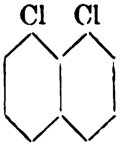
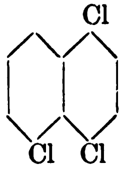
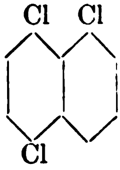
[1] Fittig and Erdmann, *Annalen*, **227**, 245. [2] Liebermann, *Annalen*, **183**, 235.
[3] Atterberg, *Ber.* **9**, 1734 ; **10**, 547.

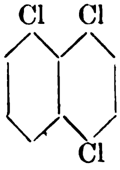












Naphthalene yields α-compounds when treated with chlorine, bromine, or nitric acid, whilst both the α- and β-monosulphonic acids, as was found by Faraday, are formed by the action of sulphuric acid. The substitution products of naphthalene are naturally much more numerous than those of benzene. If two hydrogen atoms are replaced by the same element or radical, ten isomerides are possible :

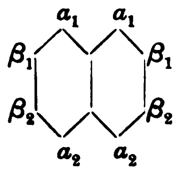


FIG. A.

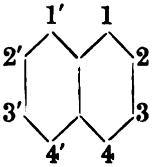


FIG. B.

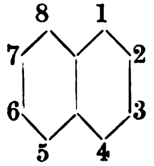


FIG. C.

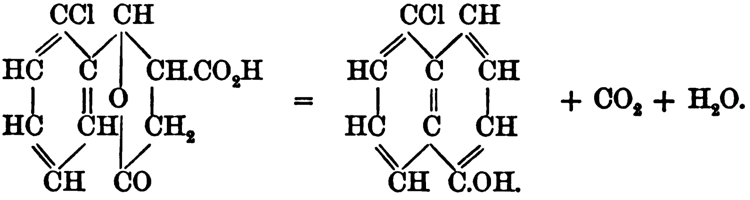
1 : 2
1 : 3
1 : 4
1 : 1′
1 : 2′

1 : 3′
1 : 4′
2 : 3
2 : 2′
2 : 3′

To express these relations three plans have been proposed, which are exemplified in the above figures. When the Greek letters are employed, these are written close together when the two substituents are both in the same nucleus, and separated by a hyphen or sometimes by a double line when they are in different nuclei. The dichloronaphthalenes mentioned above would therefore be $\alpha_1\alpha_2$; α_1—α_2 (or $\alpha_1 = \alpha_2$), α_1—α_1. As this method is very likely to cause mistakes both in writing and printing, it is better to make use of numbers. The plan shown in Fig. B is that adopted by the English chemists, while that shown in Fig. C is frequently employed on the Continent.

In order to determine the constitution of the di-substitution products, Erdmann has employed the following method.[1] In the naphthylaminesulphonic acids, $C_{10}H_6(NH_2)SO_3H$, either the amido- or the sulphonic-group is replaced by hydrogen, the products thus obtained being either *α*- or *β*-naphthylamine or *α*- or *β*-naphthalenesulphonic acid. The naphthalenesulphonic acids are converted into dichloronaphthalenes, naphtholsulphonic acids, dihydroxynaphthalenes, &c.; the oxidation of the dichloronaphthalenes, &c., to phthalic acid or a substituted phthalic acid, decides whether the two substituents are in the same nucleus (homonucleal) or in different nuclei (heteronucleal). To determine the constitution of the heteronucleal di-substitution derivatives, Armstrong and Wynne start with *α*-chloro-*β*-naphthylamine,which is converted by sulphonation into a mixture of chloronaphthlaminesulphonic acids.[2] These can be converted into dichloronaphthalenes by two methods; either by reducing the substance and thus replacing the chlorine by hydrogen and then converting the resulting *β*-naphthylaminesulphonic acid into a dichloro-compound by means of the diazo-reaction followed by treatment with phosphorus pentachloride, or by first replacing the amido-group by hydrogen and then treating the chloronaphthalenesulphonic acid thus obtained with phosphorus pentachloride. They have thus succeeded in connecting the chloronaphthylaminesulphonic acids with compounds of known constitution, and in establishing the constitutional formulae both of the acids themselves and of numerous di- and tri-substitution products which are derived from them.

Another method for the determination of the constitution of the di-substitution products of naphthalene is their synthesis from benzene derivatives of known constitution. Phenylparaconic acid, for example, yields *α*-naphthol on distillation, and the chlorophenylparaconic acids in the same manner yield chlorinated *α*-naphthols of known constitution.[3]



o-Chloroparaconic Acid. 1 : 4' Chlorohydroxynaphthalene.

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[1] *Annalen*, **247**, 306.

[2] *Proc. Chem. Soc.* **1889**, pp. 34, 48.

[3] *Annalen*, **247**, 366.

An important factor in all these conclusions is the supposition that no intermolecular changes take place in the reactions employed. Erdmann has carefully investigated this question, and has found that the di-substitution products of naphthalene are very stable and show no tendency to isomeric change.

Five naphtholsulphonic acids, or the corresponding naphthalenedisulphonic acids, for example, are converted by fusion with caustic potash into five different dihydroxynaphthalenes, while the three phenolsulphonic acids, on the other hand, are thereby converted into the same dihydroxybenzene (resorcinol). Moreover the dihydroxynaphthalenes are converted into five different diamidonaphthalenes by heating with ammonia.

The sulphonic acids of naphthalene, of the naphthols and of the naphthylamines appear to form an exception, as they are converted into isomerides when heated with sulphuric acid, water being probably taken up, the sulpho-group split off, and fresh sulphonation then taking place.[1] A similar tendency to isomeric change has been observed in the sulphonic acids of the halogen-substituted naphthalenes.[2]

In the replacement of the sulphonic acid group by chlorine by means of phosphorus pentachloride, however, no such isomeric change appears to occur, even in the apparently somewhat violent reaction in which the nitroxyl group is also replaced by chlorine. This is shown by the fact that the nitronaphthalenesulphonic acids yield the same dichloronaphthalenes as are obtained from the corresponding diamidonaphthalenes by converting these into diazo-compounds and decomposing the latter by a boiling solution of cuprous chloride in hydrochloric acid. It follows, therefore, that the reactions carried out by Atterberg (p. 25), yield correct results, and that the method adopted by Armstrong and Wynne is also reliable. The results obtained by Erdmann's synthetical methods are, moreover, in perfect agreement with those obtained by the last-named chemists.

Substitution products which contain the substituents in the position 1 : 1′ = 4 : 4′ show a very characteristic behaviour, and in many respects are very similar to ortho-compounds. Bamberger and Philip have therefore proposed to give the prefix "peri" (περί, round about) to such substances.[3]

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[1] Weinberg, *Ber.* **20**, 3354.

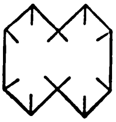
[2] Armstrong and Wynne, *Proc. Chem. Soc.* **1889**, 119, &c.

[3] *Ber.* **20**, 237.

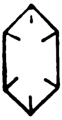
When more than two atoms of hydrogen are replaced in naphthalene by the same element or radical, the following cases of isomerism are possible:

Triderivatives	14
Tetraderivatives	22
Pentaderivatives	14
Hexderivatives	10
Heptaderivatives	2
Octoderivative	1

2561 Bamberger[1] has been led by the study of the reduction products of naphthalene and its derivatives to propose a formula for this hydrocarbon, which differs from that of Erlenmeyer in the same way as the centric formula for benzene differs from that of Kekulé (Part III., p. 67).



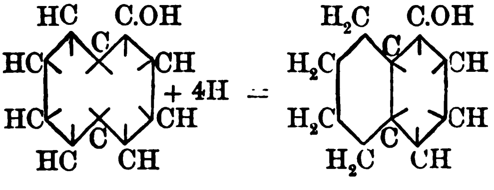
Naphthalene.



Benzene.

He has found that the tetrahydro-derivatives of naphthalene, in which the four hydrogen atoms have been added to the same nucleus, behave as true benzene substitution products, whereas the unreduced naphthalene compounds, although they behave in a general way like those derived from benzene, yet differ from the latter in many important respects.

He therefore assumes that naphthalene consists of two similar nuclei, neither of which is a benzene nucleus, and that when four atoms of hydrogen are added to one of these the other becomes a true benzene nucleus. The reduction of α-naphthol, for example, is represented by the following equation:



2562 *Naphthalene* is frequently found among the products of the decomposition of organic substances by heat. It was even

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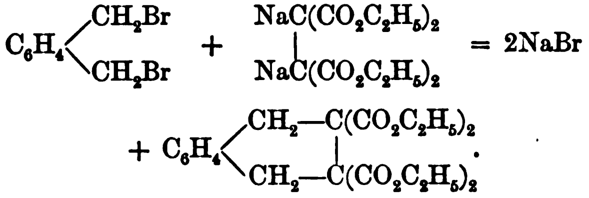
[1] *Annalen*, **257**, 1; *Ber.* **23**, 1124.

observed by Reichenbach that it is formed when the vapour of alcohol is passed through a red-hot tube, and it is obtained in the same way from ether, acetic acid, ethereal oils, camphor, &c.,[1] as well as from ethylene, acetylene, toluene, and especially from a mixture of benzene and acetylene.[2] When the vapour of wood-tar is passed through an iron tube filled with coke and heated to a bright red heat, a product resembling coal-tar is formed, which in addition to benzene hydrocarbons contains much naphthalene.[3] The same compounds are formed when the residues obtained from the distillation of Baku petroleum are employed.[4] Naphthalene is also found in wood-tar, in bone-oil and in rock-oil from Rangoon.[5]

Aronheim obtained it synthetically by passing the vapour of phenyl-β-butylene bromide over red-hot lime:[6]

$$C_6H_5.C_4H_7Br_2 = C_6H_4.C_4H_4 + 2HBr + H_2.$$

It has been obtained in a similar manner from phenyl-α-butylene bromide,[7] and is also formed when the vapour of isobutylbenzene is passed over heated oxide of lead[8] and when equal molecules of dimethylaniline and bromine are heated together to 120°.[9] The following synthesis, carried out by Baeyer and Perkin, is of theoretical interest on account of the ease with which the reactions proceed.[10] When *o*-xylylene bromide is heated with the sodium compound of ethyl acetylenetetracarboxylate, the ethyl ester of tetrahydronaphthalenetetracarboxylic acid is formed:



$$C_6H_4\left\langle\begin{array}{l}CH_2Br\\ CH_2Br\end{array}\right. + \begin{array}{l}NaC(CO_2C_2H_5)_2\\ \quad|\\ NaC(CO_2C_2H_5)_2\end{array} = 2NaBr$$

$$+ C_6H_4\left\langle\begin{array}{l}CH_2-C(CO_2C_2H_5)_2\\ \qquad\quad|\\ CH_2-C(CO_2C_2H_5)_2\end{array}\right..$$

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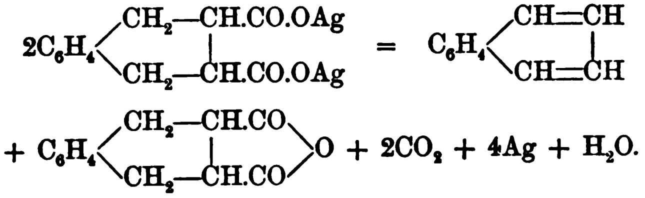
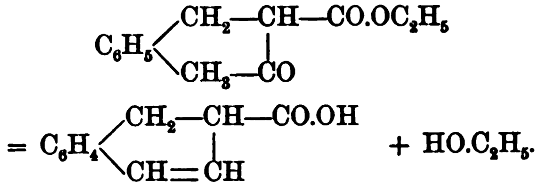
[1] Berthelot, *Jahresb. Chem.* **1851**, 437, 504.
[2] Berthelot, *Bull. Soc. Chim.* **7**, 218, 278 and 306.
[3] Atterberg, *Ber.* **11**, 1222.
[4] Letux, *Ber.* **11**, 1210.
[5] Warren and Storer, *Zeitsch. Chem.* **1868**, 232.
[6] *Annalen*, **171**, 233.
[7] Radziszewski, *Ber.* **9**, 260.
[8] Wreden and Znatowicz, *Ber.* **9**, 1606.
[9] Brauner and Brandenburg, *Ber.* **11**, 697.
[10] *Ber.* **17**, 448.

This is converted by saponification into tetrahydronaphthalene-dicarboxylic acid, and the silver salt of the latter decomposes on heating into the anhydride and naphthalene:



A considerable amount of naphthalene is also formed when the vapour of the anhydride is passed through a red-hot tube.

Pechmann[1] has also succeeded in obtaining naphthalene by a different method. Dihydronaphthoic acid is formed by the action of sulphuric acid on ethyl benzylacetacetate:



This substance is converted by loss of carbon dioxide into dihydronaphthalene, which can be readily converted by the elimination of hydrogen into naphthalene.

Naphthalene is obtained on the large scale from the fraction of coal tar which boils between 180—250°, and which partially solidifies on cooling and standing, owing to the crystallization of naphthalene. It is then treated with caustic soda solution to remove phenol, and again distilled; the distillate thus obtained solidifies to a crystalline mass which is separated from adhering oils by the filter-press. The crude naphthalene still contains quinoline bases and it is therefore successively washed with dilute sulphuric acid, water and caustic soda solution, after which it is again distilled or sublimed by means of superheated steam.

The product still contains impurities which cause it to turn red in the air. To remove these it may be heated with a little sulphuric acid to 185°, and distilled in steam, this treatment

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[1] *Ber.* **16**, 516.

being repeated until a sample dissolves in sulphuric acid without colouration.[1] The admixed substances may also be removed by heating it with sulphuric acid and a little manganese dioxide.[2] In this process, however, a large amount of sulphur dioxide is evolved and a considerable loss of naphthalene is experienced. A pure product can easily be prepared by boiling crude naphthalene with 0·5—2 per cent. of sulphur, according to the purity of the sample; the impurities are thus converted into substances of high boiling point and can then be easily separated. A little sulphuretted hydrogen is evolved during the reaction, which is absorbed in caustic soda solution or milk of lime.[3]

2563 *Properties.* Naphthalene crystallizes in plates or monosymmetric tablets, and has a characteristic, unpleasant smell and a burning taste. It melts at 79·2°, boils at 218°, and readily sublimes below this temperature, condensing in such a voluminous mass when the sublimation is slowly carried out that 0·25 grammes of it are sufficient to fill a litre flask.[4] Its specific gravity compared with water at 4° is:

At 4°	80°	98°
1·145	0·9777	0·9621

One hundred parts of absolute alcohol dissolve 5·29 parts at 15°, whilst 100 parts of toluene dissolve 31·94 parts at 16·5°, and the two substances are miscible in all proportions at the boiling point; it is also readily soluble in ether and benzene, but only slightly in light petroleum. In the liquid state it dissolves indigo, sulphur, phosphorus and other substances.

A characteristic property of naphthalene is the formation of the compound $3SbCl_3 + 2C_{10}H_8$ when it is fused with antimony trichloride;[5] this substance crystallizes in deliquescent monosymmetric tablets. If the naphthalene contains the least trace of impurity the fused mass becomes coloured carmine red.[6] When pure naphthalene is dissolved in chloroform and the solution heated with anhydrous aluminium chloride, a deep greenish blue colouration is produced, and the liquid then solidifies to a brown mass.[7]

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[1] Stenhouse and Groves, *Ber.* **9**, 683.

[2] Lunge, *Ber.* **14**, 1755.

[3] Dehnst, *Ber.* **22**, 362 c.

[4] *Handwörterbuch*, 1st Edition, **5**, 432.

[5] Watson Smith and Davis, *Journ. Chem. Soc.* 1882, **1**, 411.

[6] Smith, *Ber.* **12**, 142.

[7] Schwarz, *Ber.* **14**, 1532.

Naphthalene is technically employed for the manufacture of phthalic acid and colouring matters, and is also used for carburetting water-gas, which is manufactured by passing steam over red-hot coke, and is then passed over melted naphthalene, which imparts illuminating power to the flame.

Naphthalene is a powerful antiseptic and is used for preventing mould, and also, as it is fatal to the lower animals, for driving away moths and phylloxera and to protect specimens of butterflies. It is also employed as a dressing for wounds, and a mixture of equal parts of naphthalene and vaseline is used as a remedy for the itch.

In 1857 Fritsche found that naphthalene combines with picric acid, yielding a substance of the formula $C_{10}H_8 + C_6H_3(NO_2)_3O$, which crystallizes from ether in golden-yellow needles or monosymmetric prisms, melting at 149° and only slowly decomposed by boiling water.[1] It has since then been found that it also combines with the following nitro-derivatives :[2]

	Melting-point.
m-Dinitrobenzene, thick prismatic needles . .	52—53°
p-Dinitrobenzene, long, fine, white needles . .	118—119°
Trinitrobenzene, very long, fine, white needles .	152°
m-Dinitrotoluene, thick prismatic needles . .	60—61°
a-Trinitrotoluene, needles	97—98°
β-Trinitrotoluene, yellowish-white needles . .	100°
γ-Trinitrotoluene, fine, yellowish-white needles	98—99°
Trinitro-aniline, thick orange-yellow prisms . .	168—169°
m-Dinitrophenol, yellow needles	213°
β-Trinitrophenol, yellow needles	72—73°
γ-Trinitrophenol, golden-yellow needles . . .	100°
Trinitro-*o*-cresol, small yellowish needles . . .	106°
Trinitro-*m*-cresol, lemon-yellow needles . . .	126—127°

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[1] *Jahresb. Chem.* **1857**, 456 ; Bodewig, *Jahresb. Chem.* **1879**, 376.

[2] Hepp, *Annalen*, **215**, 357 ; Henriques, *Annalen*, **215**, 321 ; Gruner, *Zeitsch. Chem.* **1868**, 213 ; Liebermann and Palm, *Ber.* **8**, 377 ; Willgerodt, *Ber.* **11**, 601 ; Nölting and Salis, *Ber.* **15**, 1858 ; Nölting and Collin, *Ber.* **17**, 268.

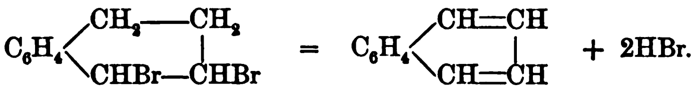
ADDITION PRODUCTS OF NAPHTHALENE.

THE HYDRONAPHTHALENES.

2564 *Dihydronaphthalene*, $C_{10}H_{10}$, occurs, according to Berthelot, in coal-tar, and is formed when naphthalene is heated to 280° with hydriodic acid. It is probably formed in this reaction by the action of the liberated iodine on the higher reduction products which are first formed.[1] Gräbe and Guye obtained dihydronaphthalene by adding rather more than a molecule of bromine to one molecule of tetrahydronaphthalene dissolved in carbon disulphide and treating the product with alcoholic potash.[2] It may also be prepared by treating an alcoholic solution of naphthalene with sodium, and is obtained, together with tetrahydro-α-naphthomethylamine, $C_{10}H_{11}.CH_2.NH_2$, from α-naphthonitrile:[3]

$$C_{10}H_7.CN + 4H = C_{10}H_{10} + HCN.$$

It is a liquid, which has a faint odour of naphthalene, boils at 212°, and on cooling solidifies in large tablets, which have a vitreous lustre and melt at 15·5°. At a red heat it decomposes into hydrogen and naphthalene; it combines with bromine to form *dihydronaphthalene dibromide*, $C_{10}H_{10}Br_2$, which crystallizes in large, monosymmetric prisms with a vitreous lustre, melts at 73·5—74°, and decomposes into hydrobromic acid and naphthalene when it is heated above its melting-point or treated with alcoholic potash:



$$C_6H_4\left\langle\begin{array}{l}CH_2—CH_2\\ CHBr—CHBr\end{array}\right. = C_6H_4\left\langle\begin{array}{l}CH{=}CH\\ CH{=}CH\end{array}\right. + 2HBr.$$

α-*Tetrahydronaphthalene*, $C_{10}H_{12}$. was obtained by Baeyer by heating naphthalene to 170—190° with phosphonium iodide.[4] It is also formed when 10 grms. of naphthalene are heated with 3 grms. of amorphous phosphorus and 9 grms. of hydriodic acid of boiling-point 127° for 7—8 hours at 210—225°. The product of these reactions is a liquid which has a characteristic,

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[1] *Ber.* **16**, 3032.

[2] *Ibid.*

[3] Bamberger and Lodter, *ibid.* **20**, 1703, 3075.

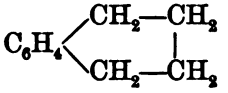
[4] *Annalen*, **155**, 276.

but not penetrating odour, boils at 205°, and has a sp. gr. of 0·981 at 12·5°. It does not combine with picric acid, absorbs oxygen from the air, is more readily oxidized than naphthalene to phthalic acid and decomposes into naphthalene and hydrogen at a red heat. When it is heated with sulphuric acid, *tetrahydronaphthalenesulphonic acid*, $C_{10}H_{11}SO_3H$, is formed as a crystalline substance which is decomposed into the hydrocarbon and sulphuric acid, when it is mixed with three parts of sulphuric acid and one of water and heated to 170° by superheated steam.[1] Since the sulphonic acid of naphthalene itself is decomposed by water at 160°, this process can be used to separate tetrahydronaphthalene from naphthalene. The *barium sulphonate*, $2(C_{10}H_{11}SO_3)_2Ba + H_2O$, crystallizes in tablets.[2]

β-Tetrahydronaphthalene, is formed when α-tetrahydronaphthylhydrazine is suspended in boiling water and a hot saturated solution of copper sulphate slowly added until the liquid is permanently coloured blue:

$$C_{10}H_{11}.NH{-}NH_2 + 2CuO = C_{10}H_{12} + N_2 + Cu_2O + H_2O.$$

It is also obtained when sodium is added to a boiling solution of naphthalene in amyl alcohol.[3] It is a transparent, colourless oily liquid, which has a strong smell of naphthalene, boils at 205°, and has a sp. gr. of 0·978 at 17°. It dissolves in hot sulphuric acid, forming a monosulphonic acid, the soluble *barium salt* of which crystallizes in small hemispherical aggregates which effloresce in the air. Its constitution follows from that of tetrahydro-α naphthylamine, which will be subsequently discussed, and is expressed by the following formula:[4]



On oxidation it yields *o*-carboxyhydrocinnamic acid, $C_6H_4(CO.OH)CH_2.CH_2.COOH$.

Hexhydronaphthalene, $C_{10}H_{14}$, was first obtained by Wreden and Znatowicz who heated 4 grms. of naphthalene with 20 grms. of hydriodic acid saturated at 0° and 0·5 grms. of amorphous

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[1] Gräbe, *Ber.* **5**, 677 ; Gräbe and Guye, *Ber.* **16**, 3028.

[2] Friedel and Crafts, *Bull. Soc. Chim.* **42**, 66.

[3] Bamberger and Kitschelt, *Ber.* **23**, 1561.

[4] Bamberger and Bordt, *Ber.* **22**, 625.

phosphorus.[1] According to Gräbe and Guye it is prepared by heating 6·7 grms. of naphthalene with 10 grms. of hydriodic acid of boiling-point 127° and 3 grms. of phosphorus to 240—250° for 8—10 hours. It is a liquid which boils at 200°, has a specific gravity of 0·942 at 0°, absorbs oxygen from the air, and does not combine with picric acid. On treatment with sulphuric acid it yields two sulphonic acids.[2]

Octohydronaphthalene, $C_{10}H_{16}$, was obtained by Guye by heating 5 grms. of naphthalene with 9 grms. of hydriodic acid and phosphorus to 260—265° for 15—20 hours. It is a liquid which boils at 185—190°, has a specific gravity of 0·910 at 0°, and has a smell resembling that of oil of turpentine.

Dekahydronaphthalene, $C_{10}H_{18}$, is formed, according to Wreden, when naphthalene is heated with 5 parts of hydriodic acid saturated at 0° and some phosphorus for 36 hours to 260°. It smells like petroleum, boils at 173—180°, and has a specific gravity of 0·851 at 0°.

When naphthalene is heated with aluminium chloride, a series of hydrocarbons is formed which boil between 70° and 250°. The fraction, boiling at about 200°, chiefly contains tetrahydro- and dekahydronaphthalene, in addition to some unaltered naphthalene. The mixture is then repeatedly treated with sulphuric acid which converts the naphthalene and its tetrahydro-derivative into sulphonic acids, but does not attack the deka-compound. In order to obtain the hydrocarbons from their sulphonic acids, the latter are converted into their sodium salts which are mixed with a concentrated solution of phosphoric acid and distilled in steam. This method is much better adapted for the decomposition of sulphonic acids in general than the older one, because when sulphuric acid is employed a portion of the monosulphonic acid is converted into the very stable disulphonic acid. If several sulphonic acids are present which are decomposed with different degrees of readiness, the temperature is raised at intervals, and the products at each temperature collected separately.[3]

Dodekahydronaphthalene, $C_{10}H_{20}$, is formed when naphthalene is heated with an excess of saturated hydriodic acid for 50 hours to 280°. It is a colourless, mobile liquid, which smells like petroleum, boils at 153—158°, and has a specific gravity of

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[1] Beilstein's *Lehrbuch*, **2**, 137.

[2] *Ber.* **16**, 796.

[3] Friedel and Crafts, *Compt. Rend.* **109**, 95.

0·802 at 0°. Wreden gave it the name of hexhydrocymene.[1] It certainly contains an open carbon chain, and may be butylhexhydrobenzene, $C_6H_{11}.C_4H_9$; *o*-diethylhexhydrobenzene, $C_6H_{10}(C_2H_5)_2$, or *o*-methylpropylhexhydrobenzene, $C_6H_{10}(CH_3)C_3H_7$.

CHLORIDES OF NAPHTHALENE AND THEIR DERIVATIVES.

2565 *Naphthalene dichloride*, $C_{10}H_8Cl_2$, is obtained, together with naphthalene tetrachloride and substitution products, by the direct action of chlorine on naphthalene.[2] It is more conveniently prepared by making a mixture of naphthalene and potassium chlorate into pellets by the aid of a little water and bringing them into hydrochloric acid. A mixture of the two chlorides is thus formed from which the liquid dichloride can be separated by pressing; the crude product is then cooled to a low temperature at which it is kept until the greater part of the residual tetrachloride has crystallized out. The last traces of this are separated by mixing the liquid with ether and alcohol and fractionally precipitating with water, which causes the separation of the tetrachloride before the dichloride.

The latter is a light yellow oil which has a characteristic smell somewhat resembling that of naphthalene. It begins to lose hydrochloric acid at 40—50°, and at 250° decomposes completely into *a*-chloronaphthalene and hydrochloric acid.[3]

Naphthalene tetrachloride is also formed when chlorine is passed into a solution of naphthalene in chloroform.[4] To prepare it, dry chlorine is passed into a glass bell jar in which a number of shallow basins containing naphthalene are arranged one above the other.[5] The oily product is freed from dichloride and other products by extraction with light petroleum and with alcohol, the residue being then recrystallized from chloroform. The tetrachloride is thus obtained in large rhombohedra, which melt at 182°,[6] are only slightly soluble in boiling alcohol and light petroleum, but dissolve somewhat more readily in ether.

[1] *Annalen*, **187**, 164.

[2] Laurent, *Annalen*, **8**, 8.

[3] E. Fischer, *Ber.* **11**, 735.

[4] Schwarzer, *Ber.* **10**, 379.

[5] Grimaux, *Bull. Soc. Chem.* **18**, 207; **19**, 396.

[6] Faust and Saame, *Annalen*, **160**, 65.

When it is heated alone or with alcoholic potash, three isomeric dichloronaphthalenes are formed (p. 41).

Dichloronaphthydrene glycol, $C_{10}H_8Cl_2(OH)_2$, is obtained by the continued boiling of the tetrachloride with a large quantity of water. It crystallizes from dilute alcohol in small, indistinct prisms, melting at 155—156°, whilst larger crystals of the same character are deposited from its solution in ether. Zinc and dilute sulphuric acid convert it into *a*-naphthol,[1] $C_{10}H_7.OH$.

Naphthalenedichlorohydrin, $C_{10}H_8Cl_2(OH)_2$, is isomeric with the preceding compound and is formed when naphthalene is brought into a tolerably concentrated solution of hypochlorous acid and allowed to stand for a considerable time. It crystallizes from alcohol in prisms which melt at a low temperature. When it is heated with a solution of caustic potash in dilute alcohol, *naphthene alcohol*, $C_{10}H_8(OH)_4$, is formed. This substance crystallizes in prisms, which are soluble in alcohol and ether, and rapidly turns brown in the air. It is oxidized by very dilute nitric acid to naphthoxalic acid, $C_{10}H_8O_6$, and on heating with hydriodic acid is converted into naphthalene.[2]

CHLORINE SUBSTITUTION PRODUCTS OF NAPHTHALENE.

MONOCHLORONAPHTHALENES.

2566 *a-Chloronaphthalene*, $C_{10}H_7Cl$, is formed when the dichloride is heated or boiled with alcoholic potash.[3] It is also obtained by the action of phosphorus pentachloride on *a*-naphthalenesulphonic acid,[4] and on *a*-nitronaphthalene:[5]

$$C_{10}H_7NO_2 + PCl_5 = C_{10}H_7Cl + POCl_3 + NOCl.$$

Atterberg prepared it by saturating *a*-nitronaphthalene with chlorine and distilling the oily addition-product.[6] It is also formed, together with *a*-naphthol, when *a*-naphthylamine is

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[1] Grimaux, *Bull. Soc. Chim.* **18**, 207; **19**, 396.
[2] Neuhoff, *Annalen*, **136**, 342.
[3] Laurent, *loc. cit.*; Faust and Saame, *Annalen*, **168**, 68.
[4] Carius, *Annalen*, **114**, 145.
[5] De Koninck and Marquart, *Ber.* **5**, 11.
[6] Atterberg, *Ber.* **9**, 316 and 926.

diazotized and the product heated with hydrochloric acid.[1] It is best obtained by passing the calculated amount of chlorine through boiling naphthalene and fractionating the product[2] or by acting with chlorine in the cold in the presence of antimony chloride.[3] It is an oily liquid, which does not solidify in a freezing mixture, boils at 263°[4] and has a specific gravity of 1·2025 at 15°. Its compound with picric acid crystallizes in lemon yellow needles,[5] melting at 137°.

a-Chloronaphthalene tetrachloride, $C_6H_4.C_4H_3Cl_5$, is obtained when chlorine is passed into fused naphthalene (Faust and Saame) or into α-chloronaphthalene.[6] It crystallizes from chloroform in monosymmetric prisms, melts at 131·5°, and is oxidized by nitric acid to phthalic acid.

β-Chloronaphthalene has been prepared by the action of phosphorus pentachloride on β-naphthol[7] and by the diazo-reaction from β-naphthylamine.[8] It is best obtained by triturating equal molecules of sodium β-naphthalenesulphonate and phosphorus pentachloride together, and as soon as the reaction is over distilling the product with another molecule of phosphorus pentachloride (Rymarenko).

β-Chloronaphthalene crystallizes from alcohol in nacreous plates, melts at 56°, boils at 264—266°, and has a specific gravity of 1·2656 at 16°. It is also formed, accompanied by a large amount of tarry products, when the α-compound is heated with aluminium chloride.

On treatment with chlorine it yields the tetrachloride, $C_6H_4Cl_4.C_4H_3Cl$.

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[1] Gasiorowski and Wayss, *Ber.* **18**, 1936.

[2] Rymarenko, *Beilstein's Handb.* **2**, 139.

[3] Reverdin and Nölting, *Const. de la Naphthaline, &c.*, 30.

[4] Atterberg, *Bull. Soc. Chim.* **28**, 509.

[5] Roux, *Bull. Soc. Chim.* **45**, 515 ; *Ann. Chim. Phys.* VI. **12**, 347.

[6] Widman, *Bull. Soc. Chim.* **28**, 506.

[7] Cleve and Juhlin, *Bull. Soc. Chim.* **25**, 258 ; Rymarenko, *Ber.* **9**, 663.

[8] Liebermann and Palm, *Annalen*, **183**, 267 ; Gasiorowski and Wayss, *Ber.* **18**, 1936 ; Reverdin and Nölting, *Const. de la Naphthaline, &c.*

THE DICHLORONAPHTHALENES, $C_{10}H_6Cl_2$.

α-α-DICHLORONAPHTHALENES.

2567 1 : 4-*Dichloronaphthalene.* Faust and Saame by boiling naphthalene tetrachloride with alcoholic potash obtained α-dichloronaphthalene,[1] which was more closely examined by Widman.[2] It crystallizes in needles, melting at 38°, and combines with chlorine to form two tetrachlorides, one of which is solid, the other liquid. Armstrong and Wynne have however shown that it is a mixture of 1 : 3- and 1 : 4-dichloronaphthalenes.[3] The latter was obtained by Faust and Saame, who named it β-dichloronaphthalene, by the continued and vigorous boiling of naphthalene tetrachloride. It is also formed, according to Widman, when chlorine is passed into a solution of α-chloronaphthalene in chloroform,[4] and by the action of phosphorus pentachloride on 1 : 4-chloronitronaphthalene,[5] 1 : 4-nitronaphthol,[6] 1 : 4-chloronitronaphthalenesulphonic acid,[7] 1 : 4-bromonaphthalenesulphonic acid,[8] and 1 : 4-diazonaphthalenesulphonic acid.[9]

1 : 4-Dichloronaphthalene crystallizes from alcohol, in which it is only slightly soluble, in silky needles. It is more readily soluble in glacial acetic acid, and very readily in acetone, from which it separates on the spontaneous evaporation of the solvent in large needles or prisms. It melts at 67—68°, readily sublimes, boils at 286—287°, and is oxidized by nitric acid to dichlorophthalic acid.

It combines with chlorine to form the tetrachloride, $C_{10}H_6Cl_6$, which crystallizes in monosymmetric prisms, melting at 172°.

1 : 4′-*Dichloronaphthalene* was obtained by Atterberg, who named it γ-dichloronaphthalene, by the action of chlorine on fused α-nitronaphthalene, and by heating α-dinitronaphthalene with phosphorus pentachloride.[10] Cleve prepared it in a similar

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[1] *Annalen*, **160**, 65 ; Krafft and Becker, *Ber* **9**, 1089.

[2] *Ber.* **15**, 2160.

[3] *Proc. Chem. Soc.* **1888—1889**, 104.

[4] Reverdin and Nölting, *loc. cit.* 18.

[5] Atterberg, *Ber.* **9**, 1157 ; Gasiorowski and Wayss, *loc. cit.*

[6] *Ibid.*

[7] Cleve, *Bull. Soc. Chim.* **26**, 242.

[8] Jolin, *Bull. Soc. Chim.* **28**, 561.

[9] Erdmann, *Annalen*, **247**, 350.

[10] *Ber.* **9**, 316 and 1187.

manner from the corresponding chloronaphthalenesulphonic acid, and Erdmann from 1 : 4-diazonaphthalenesulphonic acid, and from 4′-chloro-α-naphthol.[1] It crystallizes from alcohol or glacial acetic acid in small plates, melts at 107°, and sublimes in very thin, broad prisms. When chlorine is passed into its solution in chloroform, the tetrachloride is formed,[2] which crystallizes in large prisms, and melts at 85°. Chromic acid oxidizes 1 : 4′-dichloronaphthalene in acetic acid solution to v-chlorophthalic acid.[3] The constitution of this dichloronaphthalene follows from its formation from α-dinitronaphthalene (Atterberg), and from 4′ : 1-chloronaphthol (Erdmann).

1 : 1′-*Dichloronaphthalene*, was prepared by Atterberg, who distinguished it as ζ-dichloronaphthalene, from 1 : 1′- or β-dinitronaphthalene by treatment with phosphorus pentachloride, and also by the diazo-reaction from the corresponding chloro-α-naphthylamine. It forms large, rhombohedral crystals and melts at 83°.[4]

α-β-DICHLORONAPHTHALENES.

2568 1 : 2-*Dichloronaphthalene*, was prepared by Cleve from α-chloro-β-naphthylamine by means of the diazo-reaction. It crystallizes from alcohol in rhombic tablets, melts at 34—35°,[5] and does not form an additive product with chlorine.[6]

1 : 3-*Dichloronaphthalene* was termed θ-dichloronaphthalene by Cleve, who obtained it from the corresponding nitronaphthalenesulphonic acid and from dichloronaphthylamine.[7] As already mentioned, it is formed, together with 1 : 4- and 2 : 3-dichloronaphthalenes, when naphthalene tetrachloride is boiled with alcoholic potash, and Erdmann has obtained it from 2′-4′-dichloro-α-naphthol.[8] It crystallizes from alcohol in fine white needles, which melt at 61·5° (Armstrong and Wynne), and is oxidized to phthalic acid by nitric acid, whilst chromic acid converts it into monochloronaphthoquinone and phthalic acid.[9]

1 : 3′-*Dichloronaphthalene*, which Cleve termed η-dichloronaphthalene, is obtained by treating the corresponding nitro-

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[1] *Annalen*, **247**, 363 and 1187.

[2] Atterberg and Widman, *Ber.* **10**, 1841.

[3] Guareschi, *Ber.* **20**, Ref. 509.

[4] *Ber.* **9**, 1730; **10**, 547.

[5] *Ber.* **20**, 1989.

[6] Hellström, *Ber.* **21**, 3267.

[7] *Ber.* **19**, 2179; **20**, 448.

[8] *Ber.* **21**, 3444.

[9] Cleve, *Ber.* **23**, 954.

naphthalenesulphonic acid[1] and 3′-chloro-*a*-naphthol[2] with phosphorus pentachloride. It crystallizes in long, slender, lustrous ribbons, melting at 48°. On oxidation with nitric acid it yields *a*-chlorophthalic acid. Its constitution follows from its synthesis by Erdmann and Kirchhoff from the chloronaphthol obtained by the distillation of *m*-chlorophenylparaconic acid, and has been confirmed by Armstrong and Wynne,[3] who have obtained this dichloronaphthalene from chloronaphthylaminesulphonic acid, ($SO_3H : NH_2 : Cl = 1 : 3' : 4'$), by acting upon it with sodium amalgam to replace the chlorine by hydrogen, and then converting the 3′ : 1-naphthylaminesulphonic acid thus formed into dichloronaphthalene.

1 : 2′-*Dichloronaphthalene* was considered to be identical with the 1 : 3-compound until Armstrong and Wynne showed that this was not the case. It is formed when *β*-naphthol-*a*-sulphonic acid,[4] *β*-chloronaphthalene-*a*-sulphonic acid,[5] and 2′-chloro-*a*-naphthol,[6] are treated with phosphorus pentachloride, and crystallizes from alcohol in small, lustrous plates, melts at 63—63·5° (Armstrong and Wynne), and boils at 286°.

β-*β*-DICHLORONAPHTHALENES.

2569 2 : 3-*Dichloronaphthalene* or *ι*-*Dichloronaphthalene* is formed in small quantity, accompanied by the 1 : 3- and 1 : 4-isomerides, when naphthalene tetrachloride is boiled with alcoholic potash (Widmann), or heated to 200° with moist silver oxide.[7] It crystallizes from alcohol in thin scales and melts at 119·5°. Its constitution is proved by the fact that it is formed by the partial reduction of 1 : 2 : 3-trichloronaphthalene (Armstrong and Wynne).

2 : 3′-*Dichloronaphthalene* was obtained by Cleve, who named it *ε*-dichloronaphthalene, from *β*-naphthalenedisulphonic acid.[8] Claus and Zimmermann prepared it from *β*-naphthol-*β*-sulphonic

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[1] *Bull. Soc. Chim.* **26**, 448 ; **29**, 499 ; *Ber.* **20**, 75.

[2] Erdmann and Kirchhoff, *Annalen*, **247**, 379.

[3] Armstrong and Wynne, *Proc. Chem. Soc.* **1889**, 34, 48 ; *Chem. News*, 1889, **59**, 140, 188.

[4] Claus and Volz, *Ber.* **18**, 3154 ; Forsling, *Ber.* **20**, 2100.

[5] Arnell, *Bull. Soc. Chim.* **45**, 184.

[6] Erdmann and Kirchhoff, *Annalen*, **247**, 379.

[7] Leeds and Everhart, *Am. Chem. Journ.* **2**, 211.

[8] *Bull. Soc. Chim.* **26**, 244.

acid,[1] and Arnell from β-chloronaphthalenesulphonic acid. It crystallizes from alcohol in long narrow ribbons, and from benzene in large monosymmetric tablets, melting at 135°. It boils at 285°, and is converted by nitric acid into a-chlorophthalic acid.

Its constitution has been determined by Armstrong and Wynne, who obtained it from chloronaphthylaminesulphonic acid ($NH_2 : SO_3H : Cl = 2 : 3' : 1$) by eliminating chlorine and then replacing the amido- and sulphonic-groups by chlorine.[2]

2 : 2′-*Dichloronaphthalene,* termed the δ-compound by Cleve, was prepared by him from α-naphthalenedisulphonic acid, and by Erdmann from β-diazonaphthalene-δ-sulphonic acid[3] by heating with phosphorus pentachloride. It crystallizes from alcohol in large, thin, rhomboid tablets, melting at 114°. It is also oxidized by nitric acid to a-chlorophthalic acid.

Armstrong and Wynne have obtained it from chloronaphthylaminesulphonic acid ($NH_2 : SO_3H : Cl = 2 : 2' : 1$) in the manner described above, and have thus determined its constitution.

TRICHLORONAPHTHALENES, $C_{10}H_5Cl_3$.

2570 1 : 2 : 3- or *α-Trichloronaphthalene* was obtained by Faust and Saame from α-chloronaphthalene tetrachloride by heating with alcoholic potash. It is also formed when α-naphtholdisulphochloride[4] or α-β-dichloro-β-naphthol[5] is heated with phosphorus pentachloride. It crystallizes from alcohol in long slender needles, melting at 81°. Nitric acid converts it into trichloronitrophthalic acid,[6] its constitution being thus proved.

1 : 2 : 4- or *ι-Trichloronaphthalene,* was prepared by Cleve from dichloro-α-naphthol by the action of phosphorus pentachloride, and has also been obtained from the corresponding dichloro-α-naphthylamine (Armstrong and Wynne), and by the action of chlorine on 1 : 3-dichloronaphthalene dissolved in chloroform.[7] It is only slightly soluble in alcohol, from which it crystallizes in tufts of slender flat needles, melting at 92°.[8]

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[1] *Ber.* **14**, 1477

[2] *Proc. Chem. Soc.* **1889**, 34, 48.

[3] *Ber.* **20**, 3185 ; **21**, 637.

[4] Claus and Mielke, *Ber.* **19**, 1182.

[5] Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 76 ; *Chem. News,* 1890 **61**, 272.

[6] Widman, *Bull. Soc. Chim.* **28**, 511.

[7] Cleve, *Ber.* **23**, 954.

[8] *Ber.* **21**, 891.

1 : 2 : 2′-*Trichloronaphthalene* is formed by the action of phosphorus pentachloride on the dichloronaphthalenesulphonic acid which is prepared from chloronaphthylaminesulphonic acid.[1] ($Cl : NH_2 : SO_3H = 1 : 2 : 2'$). It crystallizes from alcohol in hemispherical aggregates of microscopic needles, melting at 83—84°.

1 : 2 : 3′-*Trichloronaphthalene* is obtained in a similar manner from 1 : 2 : 3′-chloronaphthylaminesulphonic acid (Armstrong and Wynne), and by the action of phosphorus pentachloride on the corresponding chloro-β-naphtholsulphonic acid. It crystallizes from alcohol in tufts of short, slender needles, melting at 91°.

1 : 2 : 4′-*Trichloronaphthalene* has been prepared by Armstrong and Wynne from 1 : 2 : 4′-chloronapthylaminesulphonic acid. It crystallizes from alcohol in long slender needles, melting at 78·5°.

1 : 3 : 2′- or η-*Trichloronaphthalene* was obtained by Alén from nitronaphthalene-β-disulphonic acid.[2] Armstrong and Wynne have obtained it from the monosulphonic acids yielded by 3 : 2′- and 1 : 3-dichloronaphthalenes and from β-naphthylaminedisulphonic acid G (2 : 1′ : 3′), and have thus settled its constitution. It is readily soluble in hot alcohol and benzene, and crystallizes from glacial acetic acid in needles, melting at 112·5—113°.

1 : 3 : 4′- or γ-*Trichloronaphthalene* is formed by the action of chlorine on heated α-nitronaphthalene,[3] and by the action of phosphorus pentachloride on dichloronaphthalene-α-sulphonic acid.[4] Its constitution follows from the fact that it can be obtained from the monosulphonic acids of both 1 : 3- and 1 : 4′-dichloronaphthalene (Armstrong and Wynne). It crystallizes in lustrous, brittle prisms, or from alcohol in long slender needles, melting at 103°.

1 : 4 : 1′- or δ-*Trichloronaphthalene* has been prepared by the action of phosphorus pentachloride on β-dinitronaphthalene (1 : 1′), nitro-γ-dichloronaphthalene (4 : 1′), the α-dinitrochloronaphthalene melting at 106°, β-dinitrochloronaphthalene,[5] nitro-β-dichloronaphthalene[6] (1 : 4), and 1 : 1′-dichloronaphtha-

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[1] Armstrong and Wynne, *Proc. Chem. Soc.* **1889**, 48.

[2] *Beilstein's Handb.* 2nd Edit. **2**, 140.

[3] Atterberg, *Ber.* **9**, 316 and 926.

[4] Widman, *Bull. Soc. Chim.* **12**, 2228

[5] Atterberg, *Ber* **9**, 1187 and 1730.

[6] Widman, *loc. cit.*

lenesulphonic acid. It crystallizes from hot alcohol in soft, very long flat needles, melting at 131°. Nitric acid converts it into dichloropthalic acid.

1 : 4 : 2′-*Trichloronaphthalene* has been obtained by Armstrong and Wynne from the monosulphonic acids of 1 : 4-, 1 : 2′-, and 1 : 3′-dichloronaphthalenes. It crystallizes from alcohol in slender flat needles, which, on standing in the solvent, become opaque, and melt at 66°. If the melting point be redetermined immediately after solidification, it is found to be 56°, but after a longer interval it becomes 66°, as at first. This substance is identical with that obtained by Widman[1] from dichloronaphthalene-β-sulphonic acid[2] (ζ-trichloronaphthalene), and with the ε-trichloronaphthalene obtained by Cleve from nitro-η-dichloronaphthalene[3] (1 : 3′). It is converted by nitric acid into nitrodichlorophthalic acid.

2 : 3 : 1′-*Trichloronaphthalene* is prepared from the monosulphonic acid of 2 : 3-dichloronaphthalene. It crystallizes from alcohol in long, very slender needles, melting at 109·5° (Armstrong and Wynne). Only two heteronucleal trichloronaphthalenes derived from 2 : 3-dichloronaphthalene are possible, and since the compound described below has the constitution 2 : 3 : 2′, the constitution of this substance is fixed.

2 : 3 : 2′-*Trichloronaphthalene* has been obtained by the same chemists from 2 : 2′-dichloronaphthalenemonosulphonic acid, and from β-naphthylaminedisulphonic acid R. ($NH_2 : SO_3H : SO_3H =$ 2 : 3 : 2′). It crystallizes from alcohol in minute plates, and melts at 90·5—91°.

β-*Trichloronaphthalene* was obtained by Atterberg by the action of chlorine on heated α-nitronaphthalene; it crystallizes from hot alcohol in long, lustrous needles, melting at 90°.[4] A trichloronaphthalene which is dimorphous, crystallizing from alcohol in long needles, melting at 87°, or large flat prisms, melting at 90°, has been prepared by Armstrong and Wynne from the so-called α-naphthylamine-ε-disulphonic acid (1 : 3 : 1′).

θ-*Trichloronaphthalene* was obtained by Alén from nitronaphthalene-α-disulphonic acid; it crystallizes from glacial acetic acid in small needles, which are readily soluble in alcohol, very readily in benzene, and melt at 75·5—76°.[5]

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[1] *Ber.* **12**, 926.

[2] Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 81; *Chem. News*, **61**, 93.

[3] *Bull. Soc. Chim.* **29**, 500.

[4] *Bull. Soc. Chim.* **9**, 316 and 926.

[5] *Beilstein's Handb.* 2nd Edit. **2**, 140.

a-Trichloronaphthalene dichloride, $C_{10}H_5Cl_5$, was obtained by Atterberg and Widman, together with 1 : 4-dichloronaphthalene tetrachloride; it forms large lustrous crystals, melting at 93°.

β-Trichloronaphthalene dichloride, is formed when chlorine is passed into a solution of *a*-monochloronaphthalene in acetic acid; it crystallizes in short prisms, melting at 152°.[1]

TETRACHLORONAPHTHALENES, $C_{10}H_4Cl_4$.

2571 *a-Tetrachloronaphthalene* is obtained by boiling 1 : 4-dichloronaphthalene tetrachloride with alcoholic potash (Faust and Saame), or in the same manner from *β*-trichloronaphthalene dichloride (Widman). It crystallizes in long needles, melting at 130°, and is oxidized by nitric acid to dichlorophthalic acid.

β-Tetrachloronaphthalene was obtained by Atterberg together with 1 : 4′-dichloronaphthalene and *β*-trichloronaphthalene; it crystallizes in needles, and melts at 194°.

γ-Tetrachloronaphthalene is also formed by the action of alcoholic potash on 1 : 4-dichloronaphthalene tetrachloride, and crystallizes in flat needles, melting at 176° (Widman).

δ-Tetrachloronaphthalene was obtained in a similar manner from the tetrachloride of 1 : 4′-dichloronaphthalene and from *a*-trichloronaphthalene dichloride; it forms slender, pliable needles, melting at 141°.

ε-Tetrachloronaphthalene is formed when dinitro-*γ*-dichloronaphthalene is heated with phosphorus chloride, and crystallizes in long needles, melting at 180° (Atterberg and Widman).

ζ-Tetrachloronaphthalene, which is obtained from *ε*-dichlorodinitronaphthalene, forms needles, melting at 160°.[2]

2572 *a-Pentachloronaphthalene*, $C_{10}H_3Cl_5$, is formed when *a*-dichloronaphthoquinone is heated with phosphorus pentachloride,[3] the temperature being gradually raised to 250°, and then maintained for several hours at 200—250°.[4] It crystallizes from hot alcohol in needles, melts at 168·5°, and boils above 360°. It is oxidised by nitric acid to tetrachlorophthalic acid.

β-Pentachloronaphthalene was obtained by Atterberg and Widman from nitro-*δ*-tetrachloronaphthalene by the action of

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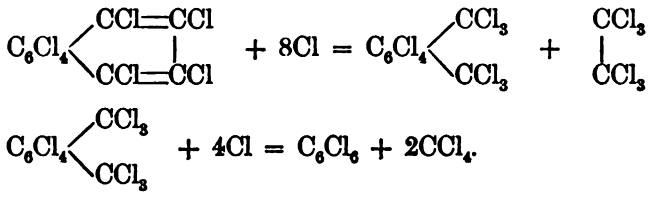
[1] Widman, *Bull. Soc. Chim.* **28**, 507.
[2] Alén, *Bull. Soc. Chim.* **36**, 435.
[3] Gräbe, *Annalen*, **149**, 1.
[4] Claus and v. der Lippe, *Ber.* **16**, 1016.

phosphorus pentachloride. It crystallizes in spherical aggregates of needles, melts at 177°, and is oxidised by nitric acid to trichlorophthalic acid.

Hexchloronaphthalene, $C_{10}H_2Cl_6$, is, according to Laurent, contained in the products of the continued action of chlorine on heated naphthalene, and crystallizes in six-sided prisms, which can be moulded like wax, melts at 143°, and may be distilled without decomposition.[1]

Heptachloronaphthalene, $C_{10}HCl_7$, is formed when tetrachloro-α-naphthoquinone is heated to 250° with phosphorus pentachloride and crystallizes in small needles, which melt at 194°. Nitric acid oxidises it to tetrachlorophthalic acid.[2]

Perchloronaphthalene, $C_{10}Cl_8$, was first obtained by Laurent, but not in the pure state. It is formed when naphthalene is treated for a long time with chlorine in presence of antimony chloride,[3] and when α-naphtholtrisulphochloride is heated to 150° with chloride of phosphorus (Claus and Mielke). It crystallizes in long, thin needles, melting at 203°, boils at 403°, and is soluble in benzene, light petroleum and chloroform, less readily in alcohol and acetic acid. When it is heated with antimony pentachloride to 200—300°, tetrachloromethane, hexchlorethane and hexchlorobenzene are formed.[4]



$$C_6Cl_4\left\langle\begin{matrix}CCl=CCl\\ \qquad\ \ |\\ CCl=CCl\end{matrix}\right. + 8Cl = C_6Cl_4\left\langle\begin{matrix}CCl_3\\ \\ CCl_3\end{matrix}\right. + \begin{matrix}CCl_3\\ |\\ CCl_3\end{matrix}$$

$$C_6Cl_4\left\langle\begin{matrix}CCl_3\\ \\ CCl_3\end{matrix}\right. + 4Cl = C_6Cl_6 + 2CCl_4.$$

BROMINE SUBSTITUTION PRODUCTS OF NAPHTHALENE.

2573 *α-Bromonaphthalene*, $C_{10}H_7Br$, is formed by the action of bromine on naphthalene,[5] and on mercury naphthyl.[6] It is also obtained when naphthalene is heated to 250° with cyanogen

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[1] *Gmelin's Handb.* **4**, 60.

[2] Claus and v. der Lippe, *Ber.* **16**, 1019; Claus and Wenzlik, *Ber.* **19**, 1165.

[3] Berthelot and Jungfleisch, *Bull. Soc. Chim.* **9**, 446.

[4] Ruoff, *Ber.* **9**, 1486.

[5] Laurent, *Ann. Chim. Phys.* **59**, 215; Wahlfors, *Zeitsch. Chem.* **1865**, 3.

[6] Otto, *Annalen*, **147**, 175.

bromide,[1] and has been prepared from *a*-naphthylamine by means of the diazo-reaction.[2] It is best obtained by adding the calculated quantity of bromine to a solution of naphthalene in carbon disulphide,[3] or by covering finely-powdered naphthalene with a solution of bromine in caustic soda and then allowing dilute hydrochloric acid to flow to the bottom of the well-stirred mixture.[4]

It is a strongly refractive liquid which boils at 280°, mixes with absolute alcohol, ether and benzene in every proportion and has a specific gravity of 1·503 at 12°. It solidifies in a freezing mixture and then melts at 4—5°.[5] Sodium amalgam added to its alcoholic solution converts it into naphthalene; it is not attacked by alcoholic potash, and is oxidised to phthalic acid by a solution of chromium trioxide in acetic acid.[6] When it is dissolved in hot toluene and treated with aluminium bromide, double decomposition occurs, *p*-bromotoluene and naphthalene being formed (Roux). Its compound with picric acid crystallizes from benzene in lemon-yellow needles, melting at 134—135°.

a-Bromonaphthalene dichloride, $C_{10}H_7BrCl_2$, was obtained by Laurent from bromonaphthalene by the action of chlorine; it crystallizes from ether in rhombic tablets, and melts at 165°.

β-Bromonaphthalene was prepared by Liebermann from *β*-naphthylamine by means of the diazo-reaction,[7] whilst Brunel obtained it by the action of phosphorus pentabromide on *β*-naphthol.[8] When a solution of *a*-bromonaphthalene in carbon disulphide is heated with a little aluminium chloride, it is partially converted into the *β*-compound, dibromonaphthalene, a small amount of naphthalene and other products being also formed (Roux).

β-Bromonaphthalene crystallizes in lustrous white rhombic plates, which melt at 59°. It boils at 281—282°, has a specific gravity of 1·605 at 0°, and is readily soluble in ether, chloroform and benzene, less readily in alcohol. Its compound with picric acid crystallizes from alcohol in yellow needles and melts at 79°.

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[1] Merz and Weith, *Ber.* **10**, 753.

[2] Rother, *Ber.* **4**, 850.

[3] Glaser, *Annalen*, **135**, 41.

[4] Gnehm, *Ber.* **15**, 2721.

[5] Roux, *Bull. Soc. Chim.* **45**, 511; *Ann. Chim. Phys.* II. **12**, 342.

[6] Beilstein and Kurbatow, *Annalen*, **202**, 216.

[7] *Annalen*, **183**, 268; Gasiorowski and Wayss, *Ber.* **18**, 1941.

[8] *Ber.* **17**, 1179.

DIBROMONAPHTHALENES, $C_{10}H_6Br_2$

2574 Laurent was the first to obtain a substance having the composition of dibromonaphthalene, but this was subsequently shown to be a mixture.

a-*a*-DIBROMONAPHTHALENES.

1 : 4-*Dibromonaphthalene* was found by Glaser among the products of the bromination of naphthalene.[1] It is also formed by the action of bromine on *a*-nitronaphthalene,[2] as well as by heating 1 : 4-bromonitronaphthalene or 1 : 4-bromonaphthalenesulphonic acid with phosphorus pentabromide,[3] and has also been obtained from 1 : 4-bromonaphthylamine by means of the diazo-reaction.[4] In order to prepare it, air saturated with bromine vapour is passed over naphthalene, contained in a long, well-cooled tube; the isomerides formed at the same time are separated by recrystallization from alcohol.[5]

It forms long needles, which melt at 81—82°, and dissolve in 76 parts of alcohol of 93·5 per cent. at 11·4°, and in 16·5 parts at 56°. It is converted by nitric acid into dibromophthalic acid and by an acetic acid solution of chromic acid into dibrom-*a*-naphthoquinone and dibromophthalide, $C_8H_4Br_2O_2$ (Part IV. p. 444).

a-Dibromonaphthalene tetrabromide, $C_{10}H_6Br_2.Br_4$, is formed, together with the *β*-compound, when 1 : 4-dibromonaphthalene is treated with bromine at 0°. It is insoluble in ether, and crystallizes from chloroform in rhombic prisms, melting at about 100°.

β-Dibromonaphthalene tetrabromide is soluble in ether and crystallizes in prisms, which melt with decomposition at 173—174°.[6]

1 : 4′-*Dibromonaphthalene* is, according to Guareschi, obtained, together with the 1 : 4-compound and an isomeride melting at

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[1] *Annalen*, **135**, 40 ; Gasiorowski and Wayss, *Ber.* **18**, 1936.

[2] Guareschi, *Ber.* **10**, 294

[3] Jolin, *Bull. Soc. Chim.* **28**, 514.

[4] Meldola, *Journ. Chem. Soc.* 1883, **1**, 1 ; 1885, **1**, 508.

[5] Guareschi, *Annalen*, **222**, 262.

[6] Guareschi, *Ber.* **19**, 554 R.

67·5—68° by allowing bromine to drop on to naphthalene. The product is first washed with alcohol to remove α-bromonaphthalene and then dissolved in boiling alcohol. On cooling this solution, 1 : 4-dibromonaphthalene is first deposited and then a mixture of the two other isomerides. This mixture is warmed with alcohol to remove the compound melting at 68°, and the residue finally purified by recrystallization from alcohol.

1 : 4′-Dibromonaphthalene is also formed by the action of phosphorus pentabromide on α-dinitronaphthalene and 1 : 4′-bromonaphthalenesulphonic acid.[1] It crystallizes in lustrous tablets, which melt at 130·5—131·5°, and dissolve at 56° in 50 parts of alcohol of 93·5 per cent. It is oxidized by nitric acid to bromonitrophthalic acid, and by an acetic acid solution of chromium trioxide to v-bromophthalic acid.[2] It forms no addition compound with bromine.

α-β-DIBROMONAPHTHALENES.

2575 1 : 2-*Dibromonaphthalene* was obtained by Meldola from bromo-β-amidonaphthalene. It crystallizes from alcohol in oblique rhombic prisms and melts at 63°.

It is probably identical with the dibromonaphthalene described above as melting at 68°.

1 : 3-*Dibromonaphthalene* has been prepared by Meldola from dibrom-α-naphthylamine; it crystallizes from alcohol in needles, melting at 64°.

1 : 2′-*Dibromonaphthalene* is formed, together with the 1 : 4′-compound, by the action of bromine on α-naphthalenesulphonic acid,[3] as well as by the distillation of 1 : 2′-bromonaphthalenesulphonic acid with phosphorus pentabromide.[4] It crystallizes from alcohol in needles, melting at 76—77°.

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[1] Jolin, *Bull. Soc. Chim.* **28**, 54.

[2] Guareschi, *Ber.* **21**, 528 *c.* This acid melts at 178·5° and not at 138—140° as stated by Faust and Pechmann (Pt. IV. p. 472), who actually had a mixture of the v- and a-acids.

[3] Darmstädter and Wichelhaus, *Annalen*, **152**, 303.

[4] Forsling, *Ber.* **22**, 1400.

β-β-DIBROMONAPHTHALENE.

2 : 2′-*Dibromonaphthalene* was obtained by Försling from the bromide of the corresponding bromonaphthalenesulphonic acid; it crystallizes from a mixture of ether and chloroform in four-sided tablets, melting at 158°.

TRIBROMONAPHTHALENES, $C_{10}H_5Br_3$

2576 *α-Tribromonaphthalene* is obtained, together with other products, when naphthalene is treated with bromine. It crystallizes from alcohol in needles, melts at 75°, and solidifies in rosettes resembling the mineral wavellite.[1]

β-Tribromonaphthalene (1 : 4 : 1′) was prepared by Jolin from nitro-β-dibromonaphthalene by the action of phosphorus pentabromide. It is very readily soluble in alcohol and crystallizes in long, pliable needles, melting at 85°.

γ-Tribromonaphthalene was obtained by the same chemist in a similar manner from dibromo-β-naphthalenesulphonic acid; it crystallizes in short, brittle needles, and melts at 86·5°.

δ-Tribromonaphthalene (1 : 2 : 4) was prepared by Meldola from the corresponding dibromonaphthylamine. It is also formed when nitrobromonaphthylamine is heated with hydrobromic acid and glacial acetic acid to 130°.[2] It is readily soluble in ether, less readily in alcohol, crystallizes in small lustrous needles and melts at 113—114°.

ε-Tribromonaphthalene (1 : 3 : 2′ or 1 : 3 : 3′) was obtained by Meldola from dibromo-β-amidonaphthalene. It crystallizes from alcohol in short needles, melting at 110°.

ζ-Tribromonaphthalene (1 : 3 : 1′ or 1 : 3 : 4′) was obtained in the same way from dibrom-α-amidonaphthalene; it forms small needles, melting at 105°.

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[1] Gräbe, *Annalen*, **135**, 43.

[2] Prager, *Ber.* **18**, 2163.

[3] *Journ. Chem. Soc.* 1885, **1**, 497.

TETRABROMONAPHTHALENES, $C_{10}H_4Br_4$

2577 *a-Tetrabromonaphthalene* (1 : 4 : 3′ : 2′) is formed by the action of an alcoholic solution of sodium ethylate on β-dibromonaphthalene tetrabromide, and crystallizes from hot alcohol in long, silky needles, which melt at 175°, sublime in pearly tablets, and are only slightly soluble in ether. An acetic acid solution of chromium trioxide oxidises it to tetrabrom-α-naphthoquinone and dibromophthalide.

β-Tetrabromonaphthalene is obtained, together with the α-compound, from α-dibromonaphthalene tetrabromide. It is readily soluble in ether and crystallizes from alcohol in small needles, melting at 119—120°.[1]

2578 *Pentabromonaphthalene*, $C_{10}H_3Br_5$, is obtained by heating α-tetrabromonaphthalene with bromine to 150°, in the form of colourless crystalline granules, which are insoluble in alcohol (Gräbe).

Hexbromonaphthalene, $C_{10}H_2Br_6$, is formed by very gradually heating naphthalene to 350° with bromine and a little iodine. It forms slender needles, melts at 245—246°, and may be sublimed. It is insoluble in alcohol and ether, and only slightly soluble in benzene and chloroform.[2]

Bromochloronaphthalene, $C_{10}H_6BrCl$, is only known in three isomeric forms.

α-Bromochloronaphthalene (Br : Cl = 1 : 4′) is obtained from the corresponding bromonaphthalenesulphochloride by the action of phosphorus pentachloride; it crystallizes in needles, and melts at 115°.[3]

β-Bromochloronaphthalene is formed, together with the γ-compound, by the action of chlorine on α-bromonaphthalene or of bromine on α-chloronaphthalene. It crystallizes in thin, lustrous tablets, and yields chlorophthalic acid on oxidation.

γ-Bromochloronaphthalene is more readily soluble in alcohol, melts at 66—67°, boils at 303°, and sublimes in needles. On oxidation it yields bromochlorophthalide.[4]

Several other substitution and addition products containing both chlorine and bromine, most of which were prepared by Laurent, are also known.

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[1] Guareschi, *Gazzetta.* **16**, 142.

[2] Gessner, *Ber.* **9**, 1510.

[3] Cleve, *Bull. Soc. Chim.* **26**, 540.

[4] Biginelli and Guareschi, *Chem. Centralbl.* **1887**, 518.

IODINE SUBSTITUTION PRODUCTS OF NAPHTHALENE.

2579 *a-Iodonaphthalene*, $C_{10}H_7I$, was obtained by Otto by the action of iodine on a solution of mercury dinaphthyl in carbon disulphide,[1] and by Nölting from diazonaphthalene sulphate by boiling its solution with the calculated quantity of hydriodic acid, or by simply heating the solution with potassium iodide.[2] It is a thick oily liquid, which does not solidify in a freezing mixture, is miscible with alcohol, ether, benzene, &c., and boils at 305°.[3] On boiling with hydriodic acid it is quantitatively converted into naphthalene (Nölting), which is also formed, together with tarry products, when its solution in carbon disulphide is boiled with aluminium chloride (Roux). Its *picric acid compound* forms golden yellow needles, which melt at 127°.

β-Iodonaphthalene was prepared by Jacobsen from β-naphthylamine by the diazo-reaction; it crystallizes in small plates, melts at 54·5°, is volatile with steam, and readily dissolves in alcohol, ether, &c.[4]

1 : 4-*Di-iodonaphthalene*, $C_{10}H_6I_2$, was obtained by Meldola from 1 : 4-iodonaphthylamine by the diazo-reaction; it crystallizes from alcohol in needles, melting at 109—110°.

1 : 2-*Di-iodonaphthalene* is formed in a similar manner from 2 : 1-iodonaphthylamine; it forms white scales, melting at 81°.

Meldola has also prepared the following bromiodonaphthalenes from the corresponding bromonaphthylamines:[5]

Br : I		Melting-point.
1 : 4	long flat needles	83·5°
1 : 3	long needles	68°
1 : 2	thick white needles	94°

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[1] *Annalen*, **147**, 173.

[2] *Ber.* **19**, 135.

[3] Roux, *Bull. Soc. Chim.* **45**, 517; *Ann. Chim. Phys.* VI. **12**, 350.

[4] *Ber.* **14**, 803.

[5] *Journ. Chem. Soc.* 1885, **1**, 521.

FLUORINE SUBSTITUTION PRODUCTS OF NAPHTHALENE.

2580 *α-Fluonaphthalene*, $C_{10}H_7F$, is formed when α-naphthylamine is dissolved by the aid of heat in strong hydrofluoric acid and sodium nitrite gradually added to the mixture. The reaction is accompanied by a vigorous evolution of gas, and considerable quantities of resinous products are formed. α-Fluonaphthalene is a colourless liquid, smelling like the chlorine compound; it boils at 212°, has the specific gravity of 1·135 at 0°, and is readily soluble in alcohol, benzene, chloroform and glacial acetic acid.

β-Fluonaphthalene has been prepared in a similar manner from β-naphthylamine; it crystallizes from alcohol in lustrous plates, melting at 59°, boils at 212·5°, and dissolves in the same solvents as the α-compound.[1]

NITROSO-SUBSTITUTION PRODUCTS OF NAPHTHALENE.

2581 *Nitrosonaphthalene*, $C_{10}H_7NO$, was obtained by Baeyer by acting upon a solution of mercury dinaphthyl in carbon disulphide with the calculated amount of a mixture of bromine and carbon disulphide saturated with nitric oxide at 20°:

$$(C_{10}H_7)_2Hg + NOBr = C_{10}H_7NO + C_{10}H_7HgBr.$$

It forms yellow granular crystals, which melt at 89°, rapidly become red in the air, and decompose at 134° with energetic evolution of gas. It volatilizes with steam, forming a vapour which has a sharp odour, very similar to that of nitrosobenzene, and its solution in phenol is coloured blue by sulphuric acid.[2]

1 : 2-*Dinitrosonaphthalene*, $C_{10}H_6(NO)_2$, is formed when an alcoholic solution of 1 : 2-naphthoquinonedioxime, $C_{10}H_6(N.OH)_2$, is oxidised with potassium ferricyanide or bromine. It crystallizes in lustrous, flat needles, which melt at 127° and readily volatilize with steam. It is insoluble in water and

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[1] Ekbom and Mauzelius, *Ber.* **22**, 1846.

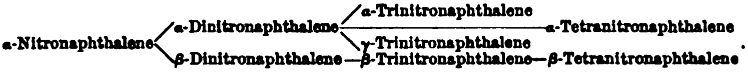
[2] *Ber.* **7**, 1639; **8**, 615.

alkalis, but is slightly soluble in alcohol and light petroleum, and does not give Liebermann's reaction.[1]

1 : 4-*Dinitrosonaphthalene* is formed by the oxidation of 1 : 4-naphthoquinonedioxime. It is a yellow odourless powder, which detonates on heating.[2]

NITRO-SUBSTITUTION PRODUCTS OF NAPHTHALENE.

2582 The direct nitration of naphthalene yields as first product, α-nitronaphthalene, from which the higher substitution products are derived in the following manner :



α-Nitronaphthalene, $C_{10}H_7NO_2$, was obtained by Laurent in 1835 by boiling naphthalene with nitric acid.[3] Piria then showed that it is also formed in the cold,[4] and Beilstein and Kuhlberg then pointed out that in this case it is the only product.[5] It has also been obtained from α-, γ- and δ-nitronaphthylamine by means of the diazo-reaction. It is best prepared on the small scale by adding concentrated nitric acid to a solution of naphthalene in glacial acetic acid and heating the mixture for half-an-hour.[6] Technically it is prepared in a similar manner to nitrobenzene (Pt. III. p. 101), 10 parts of naphthalene, 10 parts of sulphuric acid of sp. gr. 1·84 and 8 parts of nitric acid of sp. gr. 1·4 being employed. After removing the excess of acid, the still liquid product is run into cold water and washed with water and dilute caustic soda solution.

α-Nitronaphthalene crystallizes in long, fine, lustrous, yellow needles or prisms, melts at 61°[7] and boils at 304°.[8] It has a

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[1] Koreff, *Ber.* **19**, 183 ; Ilinski, *Ber.* **19**, 349.
[2] Nietzki and Guitermann, *Ber.* **21**, 428.
[3] *Ann Chim. Phys.* **59**, 376 ; **66**, 152.
[4] *Ann. Chim. Phys.* III. **31**, 217.
[5] *Annalen*, **169**, 81.
[6] Fittig, *Grundriss*, **2**, 892.
[7] Aguiar, *Ber.* **5**, 370.
[8] De Koninck and Marquart, *Ber.* **5**, 11.

characteristic, unpleasant smell, readily dissolves in benzene, ether, carbon disulphide and hot alcohol. One hundred parts of alcohol of 87·5 per cent. dissolve 2·81 parts at 15° (Beilstein and Kuhlberg). Chromium trioxide in acetic acid solution oxidizes it to v-nitrophthalic acid and *o*-nitrophthalide.

The following addition-products, accompanied by some substitution-products, are formed by the action of bromine.[1]

a-Nitronaphthalene a-tetrabromide, $C_{10}H_7NO_2Br_4$, crystallizes in druses of needles, which melt at 130·5°.

a-Nitronaphthalene β-tetrabromide is formed, accompanied by monobromonitronaphthalene when the substance just described is heated to 135—137°. It crystallizes from boiling alcohol in short prisms, which melt at 142—143·5°.

a-Nitronaphthalene γ-tetrabromide is obtained together with the *a*-compound, which is itself converted by continued boiling with alcohol into the γ- derivative. The latter forms short prisms and melts with decomposition at 172—173°.

β-Nitronaphthalene, $C_{10}H_7NO_2$, is not formed by the action of nitric acid on naphthalene. Lellmann and Remy obtained it from *a*-naphthylamine by converting the latter into acetonaphthalide, $C_{10}H_7.NH(COCH_3)$ and nitrating this, the 1 : 2- and 1 : 4-nitro-compounds being formed. The two nitronaphthylamines, $C_{10}H_6(NO_2)NH_2$, were then prepared from the mixture and separated; the amido-group of the 1 : 2-compound being finally replaced by hydrogen by means of the diazo-reaction.[2]

It can be much more simply prepared from β-naphthylamine, which is manufactured by heating β-naphthol with ammonia. Seven parts of the amido-compound are dissolved in a boiling mixture of 15 parts of nitric acid of specific gravity 1·4 and 250 parts of water, the solution rapidly cooled and a solution of 12 parts of sodium nitrite in 40 parts of water added to the paste thus formed. A clear solution of β-diazonaphthyl nitrite is thus obtained, which is added to cuprous oxide suspended in water, prepared by the reduction of copper sulphate by means of grape sugar and caustic soda solution. A vigorous evolution of nitrogen occurs, and the solution is allowed to stand for some time; a little alcohol is then added to remove the voluminous froth which has been formed, and the β-nitronaphthalene finally distilled off with steam. Sandmeyer assumes that a compound of β-diazonaphthyl nitrite with cuprous

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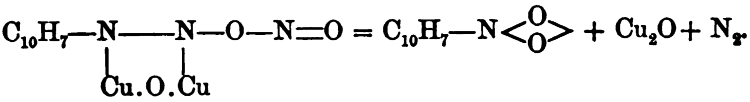
[1] Guareschi, *Annalen*, **222**, 284.

[2] *Ber.* **19**, 236; **20**. 891.

oxide is formed, which readily decomposes with loss of nitrogen, the oxynitrosyl group being converted into nitroxyl:[1]



$$C_{10}H_7-\underset{\underset{\text{Cu}.\text{O}.\text{Cu}}{|\qquad\;|}}{N-\!\!-\!\!-N}-O-N{=}O = C_{10}H_7-N{<}^{O}_{O}{>} + Cu_2O + N_2.$$

β-Nitronaphthalene is readily soluble in alcohol and glacial acetic acid and crystallizes in small, yellow needles, which have a smell of cinnamon and melt at 79°.

2583 *Dinitronaphthalene*, $C_{10}H_6(NO_2)_2$, was obtained by Laurent by boiling naphthalene with nitric acid and further investigated by Marignac and other chemists, who considered the substance to be homogeneous, until Darmstädter and Wichelhaus proved that it is a mixture of two isomerides.[2]

a-Dinitronaphthalene (1 : 4′) is prepared by covering 100 grms. of naphthalene with 200 cc. of crude nitric acid, adding 160 cc. of sulphuric acid after 24 hours and heating the mixture for a day on the water-bath. The product is ground up, washed with water, and extracted with a little boiling carbon disulphide to remove a small amount of mononitronaphthalene; it is then washed with acetone and repeatedly boiled up with fresh quantities of the latter to free it from the β-compound, the residue being finally recrystallized from boiling xylene.[3]

a-Dinitronaphthalene is scarcely soluble in carbon disulphide and only slightly in the other usual solvents; it crystallizes from glacial acetic acid in six-sided needles, which melt at 216°.[4] It is converted by hot dilute nitric acid into v-nitrophthalic acid, δ-dinitrobenzoic acid and picric acid. On heating with phosphorus pentachloride it is converted into 1 : 4′-dichloronaphthalene.

β-Dinitronaphthalene (1 : 1′) is more readily soluble in acetone, glacial acetic acid, benzene and chloroform than the α-compound and crystallizes in rhombic tablets, melting at 170° (Aguiar). It is oxidized by dilute nitric acid, heated to 150°, to dinitrophthalic acid, δ-dinitrobenzoic acid and picric acid, whilst when treated with phosphorus pentachloride it yields δ-trichloronaphthalene (1 : 4 : 1′) accompanied by a small quantity of 1 : 1′-dichloronaphthalene.

γ-Dinitronaphthalene (1 : 3) has been prepared by Liebermann

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[1] *Ber.* **20**, 1494.

[2] *Annalen*, **152**, 298.

[3] Beilstein and Kurbatow, *Annalen*, **202**, 219.

[4] Aguiar, *Ber.* **5**, 370.

from dinitro-α-amidonaphthalene by means of the diazo-reaction. It crystallizes in small pale yellow needles, which melt at 144° and readily sublime.[1]

δ-Dinitronaphthalene is prepared in the same manner from dinitro-β-amidonaphthalene, and forms light yellow needles, melting at 161·5°.[2]

Naphthocyamic acid, $C_{28}H_{18}N_8O_9$, is obtained by boiling a mixture of α- and β-dinitronaphthalenes with a solution of potassium cyanide:

$$2C_{10}H_6N_2O_4 + 12CNH + 9H_2O = \\ C_{28}H_{18}N_8O_9 + 4CO_2 + 8NH_3.$$

The free acid, liberated from the potassium salt by hydrochloric acid, is a dark brown precipitate, which dries to a lustrous black mass. This is only slightly soluble in water, more readily in alcohol, to which it imparts a brownish-yellow colour, whilst it is freely soluble in amyl alcohol, forming a dark reddish brown solution. The solutions are coloured green or blue by a very small amount of any alkali.

Potassium naphthocyamate, $C_{28}H_{17}N_8O_9K + H_2O$, is a dark blue mass which has a cupreous lustre and explodes on heating. It forms beautiful blue solutions in hot water and alcohol, but is decomposed with evolution of ammonia when the solution is boiled with caustic potash.[3]

2584 *α-Trinitronaphthalene*, $C_{10}H_5(NO_2)_3$, is formed when α-dinitronaphthalene is boiled for several hours with 15 parts of nitric acid of specific gravity 1·42; it crystallizes from glacial acetic acid or chloroform in monosymmetric pyramids and from alcohol in serrated plates, which melt at 122°.[4]

β-Trinitronaphthalene is obtained in a similar manner from β-dinitronaphthalene (Aguiar); it has also been obtained from trinitro-α-amidonaphthalene and trinitro-β-amidonaphthalene,[5] but is best prepared by gently boiling 1 part of β-dinitronaphthalene with 5 parts of fuming nitric acid and 5 parts of sulphuric acid. The solution is then poured on to snow, the precipitate washed with ether and finally recrystallized from hot nitric acid.[6] It forms monosymmetric crystals and melts at 218°.

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[1] *Annalen*, **183**, 274.

[2] Gräbe and Drews, *Ber.* **17**, 1170.

[3] Mühlhäuser, *Annalen*, **141**, 214.

[4] Aguiar, *Ber.* **5**, 370 and 897.

[5] Städel, *Ber.* **14**, 898.

[6] Beilstein and Kuhlberg, *Annalen*, **169**, 96.

γ-*Trinitronaphthalene* is obtained by boiling α-dinitronaphthalene with a mixture of nitric and sulphuric acids (Beilstein and Kuhlberg). It crystallizes in light yellow lustrous plates, which melt at 154° (Aguiar).

α-*Tetranitronaphthalene*, $C_{10}H_4(NO_2)_4$, is formed by the further nitration of α-dinitronaphthalene (Aguiar), and is best prepared by boiling this substance for several hours with a mixture of 10 parts of fuming nitric acid and fuming sulphuric acid (Beilstein and Kuhlberg). It is only slightly soluble in the usual solvents, and separates from chloroform in rhombic crystals, which melt at 259° and detonate violently on heating.

β-*Tetranitronaphthalene* is obtained by heating β-dinitronaphthalene to 100° in a sealed tube with fuming nitric acid. It crystallizes from alcohol in very long, thin needles, which melt at 200° and explode violently when quickly heated.[1]

THE CHLORONITRONAPHTHALENES.

2585 1 : 4-*Chloronitronaphthalene*, $C_{10}H_6Cl(NO_2)$, was obtained by Atterberg by the action of cold nitric acid on α-chloronaphthalene. It crystallizes from alcohol in extremely slender light yellow needles, melting at 85°. It is gradually reduced to α-amidonaphthalene by tin and hydrochloric acid, and is converted into 1 : 4-dichloronaphthalene by phosphorus pentachloride.[2]

2′ : 1-*Chloronitronaphthalene* is formed when rather more than two molecules of nitric acid of specific gravity 1·42 are added to a solution of one molecule of β-chloronaphthalene in glacial acetic acid, and the mixture allowed to stand for a few days. It crystallizes from alcohol in sulphur-yellow needles, melting at 116°, and is converted into 1 : 2′-dichloronaphthalene by distillation with phosphorus pentachloride.[3]

α-*Chlorodinitronaphthalene*, $C_{10}H_5Cl(NO_2)_2(1 : 4 : 1')$, is obtained when α-chloronaphthalene is gently heated with nitric acid; it is readily soluble in alcohol and crystallizes in long, yellow, soft needles, which melt at 106° (Faust and Saame, Atterberg).

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[1] Aguiar and Lautemann, *Bull. Soc. Chim.* **3**, 261.

[2] *Ber.* **9**, 926.

[3] Armstrong and Wynne, *Proc. Chem. Soc.* **1889**, 71.

β-Chlorodinitronaphthalene (1 : 4 : 4′) is formed, together with the *a*-compound, when *a*-chloronaphthalene is strongly heated with fuming nitric acid. It is only slightly soluble in alcohol, and crystallizes from glacial acetic acid in short, pale-yellow, brittle needles, which melt at 180°.

Both these compounds are converted into δ-trichloronaphthalene (1 : 4 : 1′) by phosphorus pentachloride (Atterberg).

β-Dichloronitronaphthalene, $C_{10}H_5Cl_2NO_2$, (1 : 4 : 1′) has been prepared by the nitration of 1 : 4-dichloronaphthalene; it forms crystals which melt at 92°.[1]

γ-Dichloronitronaphthalene (1 : 4′ : 4) is formed when 1 : 4′-dichloronaphthalene is nitrated with cold nitric acid. It is only slightly soluble in alcohol, and crystallizes in short, sulphur-yellow prisms, melts at 142°, and also yields δ-trichloronaphthalene (Atterberg).

η-Dinitrochloronaphthalene was obtained by Cleve from 1 : 3′-dichloronaphthalene by the action of nitric acid on its solution in acetic acid. It crystallizes in golden-yellow needles, which melt at 119°, and are readily soluble in boiling alcohol and glacial acetic acid. Phosphorus pentachloride converts it into ε-trichloronaphthalene.[2]

Several other isomerides of unknown constitution have also been prepared.[3]

The most important of the other chloronitronaphthalenes are given in the following table:

DICHLORODINITRONAPHTHALENES, $C_{10}H_4Cl_2(NO_2)_2$

		Melting-point.
β-,	long yellow needles[4]	158°
γ-,	light-yellow prismatic needles[5]	246°
δ-,	light-yellow prisms[6]	246°
ε-,	pale-yellow, slender needles[7]	252°
	pale-yellow flat needles[8]	169·5°
	yellowish tabular crystals[9]	150°
	very small, white needles[9]	158°

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[1] Widman, *Bull. Soc. Chim.* **28**, 505.

[2] *Bull. Soc. Chim.* **29**, 499.

[3] Alén, *ibid.* **36**, 433.

[4] Widman, *ibid.* **28**, 510.

[5] Atterberg, *Ber.* **9**, 1730.

[6] Alén, *loc. cit.*

[7] *Ibid.*

[8] From 1 : 2-Dichloronaphthalene, Hellström, *Ber.* **21**, 3267.

[9] From 1 : 3-Dichloronaphthalene, Cleve, *Ber.* **23**, 956.

TRINITRODICHLORONAPHTHALENE, $C_{10}H_3Cl_2(NO_2)_3$

	Melting-point.
Pale-yellow compact needles[1]	178°

TRICHLORODINITRONAPHTHALENES, $C_{10}H_3Cl_3(NO_2)_2$

α-, yellow prisms[2]	178°
δ-, light-yellow, slender needles[3]	200°
ε-, light-yellow, flat needles[4]	200°

TETRACHLORONITRONAPHTHALENE, $C_{10}H_3Cl_4NO_2$

δ-, large rhombic tablets[5]	154°

THE BROMONITRONAPHTHALENES.

2586 1 : 4-*Bromonitronaphthalene*, $C_{10}H_6BrNO_2$, was obtained by Jolin by the nitration of α-bromonaphthalene; it crystallizes in yellow needles, melts at 85°, and is converted by phosphorus bromide into 1 : 4-dibromonaphthalene.[6]

1 : 3-*Bromonitronaphthalene*, was prepared by Liebermann and Scheiding from nitrobromamidonaphthalene. It forms yellow needles, melting at 132° and yields β-amidonaphthalene on reduction with tin and hydrochloric acid.[7]

3 : 1-*Bromonitronaphthalene*, which was prepared by Meldola from the isomeric nitrobromamidonaphthalene, crystallizes in needles and melts at 131°. It is converted into phthalic acid by oxidation, and yields 1 : 3-dibromonaphthalene when the nitroxyl group is replaced by bromine.[8]

m-Bromonitronaphthalene ($NO_2 : Br = 1 : 3'$ or $1 : 2'$) is formed by the action of bromine on α-nitronaphthalene, and crystallizes from alcohol in yellow needles, which are only slightly soluble in cold alcohol and melt at 122·5°. It is oxidized by potassium permanganate to a-bromophthalic acid and v-nitrophthalic acid.[9]

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[1] Cleve, *loc. cit.* [2] Widman, *loc. cit.* [3] Alén, *loc. cit.* [4] *Ibid.*

[5] Atterberg and Widman, *Ber.* **10**, 1842.

[6] *Bull. Soc. Chim.* **28**, 515.

[7] *Annalen*, **183**, 262.

[8] *Journ. Chem. Soc.* 1885, **1**, 507.

[9] Guareschi, *Annalen*, **222**. 290.

Bromodinitronaphthalene, $C_{10}H_5Br(NO_2)_2$, is formed in two modifications by the action of cold, fuming nitric acid on *a*-bromonaphthalene:

	Melting-point.
a-, slender needles with a vitreous lustre . .	170·5°
β-, slender needles or tablets	143°

Both these substances are oxidized by dilute nitric acid to v-nitrophthalic acid, whilst they are converted by the action of a mixture of concentrated sulphuric acid and nitric acid into the isomeric *bromotetranitronaphthalenes*,[1] $C_{10}H_3Br(NO_2)_4$.

	Melting-point.
a-, needles	189°
β-, lustrous needles	245°

Dibrom-a-nitronaphthalene, yellow needles,[2] melting at 98°
β-Dibromonitronaphthalene, yellow needles,[3] melting at 116·5°

THE IODONITRONAPHTHALENES, $C_{10}H_6INO_2$

2587 These substances were obtained by Meldola from the amidonitronaphthalenes.

2 : 1-*Iodonitronaphthalene* crystallizes from alcohol in yellow scales, melts at 108·5°, and is readily reduced to *β*-naphthylamine.

1 : 2-*Iodonitronaphthalene* forms light-yellow, lustrous needles, melting at 88·5°.

1 : 4-*Iodonitronaphthalene* crystallizes in microscopic needles, and melts at 123°.[4]

THE SULPHONIC ACIDS OF NAPHTHALENE.

2588 *a-Naphthalenesulphonic acid* is formed, as was found by Faraday, together with the *β*-compound, by the action of sulphuric acid on naphthalene,[5] and also when it is treated with sulphur trioxide[6] or chlorosulphonic acid.[7] In order to prepare

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[1] Merz and Weith, *Ber.* **15**, 2708.

[2] Guareschi, *loc. cit.*

[3] Jolin, *loc. cit.*

[4] *Journ. Chem. Soc.* 1885, **1**, 497.

[5] *Phil. Trans.* 1826, **2**, 140; *Pogg. Ann.* **7**, 104.

[6] Wöhler and Liebig, *Pogg. Ann.* **24** 169.

[7] Armstrong, *Zeitsch. Chem.* **1871**, 322; *Proc. Chem. Soc.* **1887-1888**, 146

it, 4 parts of naphthalene are heated to 80° with 3 parts of sulphuric acid for 8 to 10 hours, and the mixture then poured into ten times its weight of hot water. After cooling, the unaltered naphthalene is filtered off and the solution neutralized with lead carbonate. On evaporation, the salt of the β-acid crystallizes out first and then that of the α-acid, which is dissolved in 10 to 12 parts of boiling alcohol, the greater part of the adhering β-salt being thus left undissolved.[1] The acids can also be separated by means of their calcium salts, but these cannot, like the lead salts, be distinguished by their appearance.[2]

α-Naphthalenesulphonic acid is a deliquescent crystalline mass, which melts at 85—90°,[3] and dissolves readily in alcohol, but is almost insoluble in ether. When it is heated to 200° with concentrated hydrochloric acid it decomposes into sulphuric acid and naphthalene, and it is to a large extent converted into the β-acid by heating with sulphuric acid. Potassium permanganate oxidizes it to phthalic acid.[4]

Its salts have been investigated by Regnault and Merz.

Calcium α-naphthalenesulphonate, $(C_{10}H_7SO_3)_2Ca + 2H_2O$, crystallizes in plates, which dissolve at 11° in 16·5 parts of water and 19·5 parts of 85 per cent. alcohol.

Barium α-naphthalenesulphonate, $(C_{10}H_7SO_3)_2Ba + H_2O$, also crystallizes in plates, and dissolves at 10° in 87 parts of water and 350 parts of alcohol.

Lead α-naphthalenesulphonate, $(C_{10}H_7SO_3)_2Pb + 3H_2O$, forms small lustrous plates, and dissolves at 10° in 27 parts of water and 11 parts of alcohol.

α-Naphthalenesulphochloride, $C_{10}H_7SO_2Cl$, crystallizes from ether in small plates, which melt at 66° and are gradually decomposed by cold water.[5] When chlorine is passed into its solution in carbon disulphide, the *tetrachloride*, $C_{10}H_7Cl_4.SO_2Cl$, is formed as a yellow oil which is decomposed by alcoholic potash into hydrochloric acid and dichloronaphthalenesulphonic acid.[6]

When sodium amalgam is added to a hot ethereal solution of the sulphochloride, the sodium salt of *α-naphthalenesulphinic acid*, $C_{10}H_7.SO_2H$, is formed. The free acid crystallizes in lustrous scales, which are only slightly soluble in water acidulated with

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[1] Merz, *Zeitsch. Chem.* **1868**, 394; Merz and Weith, *Ber.* **3**, 195.

[2] Merz and Mühlhäuser, *Ber.* **3**, 709.

[3] Regnault *J. Pr. Chem.* **12**, 99.

[4] Beilstein and Kurbatow, *Annalen*, **202**, 216.

[5] Maikopar, *Zeitsch. Chem.* **1869**, 711; Kimberly, *Annalen*, **114**, 131.

[6] Widman, *Ber.* **12**, 2220.

hydrochloric acid and are decomposed at 180° by dilute hydrochloric acid into sulphur dioxide and naphthalene.[1]

a-Naphthalenesulphamide, $C_{10}H_7(SO_2.NH_2)$, is a crystalline mass, which melts at 150°, is very readily soluble in water and is oxidized by potassium permanganate to v-sulphophthalic acid and v-sulphaminephthalic acid.

β-Naphthalenesulphonic acid is obtained, according to Merz and Weith, when the mixture employed for the preparation of the *a*-acid is heated to 160°. The hot solution is diluted with water, treated with milk of lime and then with chalk until neutralized, and finally filtered. On cooling, calcium β-naphthalenesulphonate separates out, a further crop being deposited when the mother liquors are concentrated. The last deposit contains, in addition to the β- and *a*-salts, calcium naphthalenedisulphonate and tarry products.

β-Naphthalenesulphonic acid crystallizes in plates, which are not deliquescent, and is not decomposed by hydrochloric acid even at 200°. Potassium permanganate oxidizes it in acid or neutral solution to phthalic acid (Beilstein and Kurbatow).

Sodium β-naphthalenesulphonate, $C_{10}H_7SO_3Na$, is manufactured by heating equal parts of naphthalene and sulphuric acid for several hours to 200°, pouring the product into water, filtering and neutralizing the boiling solution with milk of lime. The filtrate is precipitated with a solution of sodium carbonate and the solution evaporated. The sodium salt is thus obtained in small plates which are freed from their mother liquor on the centrifugal drier. It is employed for the preparation of β-naphthol.

Calcium β-naphthalenesulphonate, $(C_{10}H_7SO_3)_2Ca$, crystallizes in small plates, which dissolve at 10° in 76 parts of water and 437 parts of 85 per cent. alcohol.

Barium β-naphthalenesulphonate, $(C_{10}H_7SO_3)_2Ba + H_2O$, dissolves at the same temperature in 290 parts of water and 1950 parts of alcohol; it also crystallizes in small plates.

Lead β-naphthalenesulphonate, $(C_{10}H_7SO_3)_2Pb$, crystallizes in small hard scales, which contain varying amounts of water. It dissolves at 10° in 113 parts of water and in 305 parts of alcohol.

β-Naphthalenesulphochloride, $C_{10}H_7(SO_2Cl)$, forms small plates, melting at 76°, which are less readily soluble in ether than those of the *a*-compound (Maikopar). Like the latter it forms a *tetrachloride*, which crystallizes from chloroform in hard, lustrous

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[1] Gessner, *Ber.* 9, 1500.

cubes, melting at 131°, and is converted by alcoholic potash into a dichlorosulphonic acid (Widman).

Sodium amalgam added to an ethereal solution of the sulphochloride converts it into *β-naphthalenesulphinic acid*, $C_{10}H_7SO_2H$, a dull, microcrystalline powder, which is rather freely soluble in pure water, and is decomposed into sulphur dioxide and naphthalene by hydrochloric acid at 170° (Gessner).

β-Naphthalenesulphamide, $C_{10}H_7(SO_2NH_2)$, crystallizes in small, thin plates, melting at 217°, which are only slightly soluble in water and ether, and are oxidized by potassium permanganate to a-sulphophthalic acid and a-sulphaminephthalic acid.[1]

2589 *Naphthalenedisulphonic acids*, $C_{10}H_6(SO_3H)_2$. Berzelius[2] obtained an acid of this composition by heating naphthalene with sulphuric acid, and Dusart,[3] employing a different method of purification, obtained a similar substance. This led Ebert and Merz to think that these acids were probably isomeric, a supposition which was confirmed by their investigations.[4] Later researches have shown that a third acid is simultaneously formed. In order to prepare them, naphthalene is heated to 160° for four hours with five times its weight of sulphuric acid, the product converted into a mixture of calcium salts, and the solution of these evaporated to a small bulk. Common salt is then added, and the liquid heated to boiling and filtered from the residue, which consists of the salt of the β-acid; the filtrate on cooling deposits the α-salt as a crystalline paste, and the mother liquors from this yield the γ-salt on further evaporation.[5] The pure acids are obtained by converting the calcium salts into potassium salts, and preparing from these the corresponding sulphochlorides, which are purified by recrystallization from benzene, and finally converted into the acids by the action of hydrochloric acid at 150°.

2 : 2′- or *a-Naphthalenedisulphonic acid*, is formed in large quantity when naphthalene is heated to 180° with sulphuric acid. It crystallizes in long deliquescent needles, which are only slightly soluble in cold concentrated sulphuric acid. Its salts are more readily soluble in water and alcohol than those of the β-acid. On fusion with caustic potash it yields 2 : 2′-hydroxynaphthalene.

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[1] Maikopar, *loc. cit.*; Cleve, *Bull. Soc. Chim.* **25**, 258.

[2] *Annalen*, **28**, 9.

[3] *Compt. Rend.* **64**, 859.

[4] *Ber.* **9**, 592.

[5] Landshoff and Meyer, *Chem. Zeit.* **13**, 1162.

a-Naphthalenedisulphochloride, $C_{10}H_6(SO_2Cl)_2$, is readily soluble in benzene, and crystallizes in transparent four- or six-sided tablets, melting at 162°.[1] When it is heated with phosphorus pentachloride it yields 2 : 2′-dichloronaphthalene.

The *amide* forms lustrous needles and melts at 242—243°.

2 : 3′- or *β-Naphthalenedisulphonic acid* crystallizes in small plates, which deliquesce slowly in the air. Like the *a*-compound, it is decomposed at 200° by water into sulphuric acid and naphthalene. Phosphorus pentachloride converts it into 2 : 3′-dichloronaphthalene.

β-Naphthalenedisulphochloride is slightly soluble in benzene, and crystallizes in small needles, which melt at 226°.

The *amide* is only very slightly soluble in water and does not melt below 305°.

1 : 4′- or *γ-Naphthalenedisulphonic acid* was obtained by Armstrong by the action of chlorosulphonic acid on naphthalene; it is also formed when an intimate mixture of naphthalene, sulphur trioxide and sand is well shaken up.[2] It crystallizes from water in lustrous, white plates, which are not hygroscopic.[3] On fusion with caustic potash it is converted into 1 : 4′-dihydroxynaphthalene, whilst with phosphorus pentachloride it yields 1 : 4′-dichloronaphthalene, melting at 107°.

The *sodium salt* of the acid crystallizes in thin tablets or forms large, monosymmetric crystals. When the acid is very gradually heated to 170—180°, naphthalene sublimes and *β*-naphthalenesulphonic acid remains behind.[4]

The *γ*-disulphonic acid is therefore formed at a low temperature from the *a*-naphthalenesulphonic acid, which is the first product, but passes at a higher temperature into the *β*-acid, from which the other disulphonic acids are then derived.

γ-Naphthalenedisulphochloride, forms small prisms, which become opaque in the air and melt at 183°.

1 : 3- or *m-Naphthalenedisulphonic acid* has been obtained by Armstrong and Wynne from *β*-naphthylaminedisulphonic acid *G*, by the replacement of the amido-group by hydrogen. It forms a very soluble *potassium salt*, which crystallizes with two molecules of water in small prisms.

m-Naphthalenedisulphochloride crystallizes from benzene in

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[1] Armstrong, *Ber.* **15**, 204.

[2] Armstrong and Wynne, *Proc. Chem. Soc.* **1886**, 42.

[3] Ewer and Pick, Schultz, *Steinkohlentheer*, **2**, 1012.

[4] Armstrong and Wynne, *Proc. Chem. Soc.* **1887**, 146.

prisms, and from acetic acid in prismatic needles, melting at 147°. On distillation with phosphorus pentachloride it yields 1 : 3-dichloronaphthalene.[1]

1 : 3′-*Naphthalenedisulphonic acid* is formed by the action of chlorosulphonic acid on β-naphthalenesulphonic acid.[2] Its *sodium salt* $C_{10}H_6(SO_3Na)_2 + 7H_2O$, crystallizes in long, broad needles and its *chloride* in aggregates of small needles, melting at 127°. On heating with phosphorus pentachloride it is converted into 1 : 3′-dichloronaphthalene, melting at 48°.

1 : 2′-*Naphthalenedisulphonic acid* has been obtained from 1 : 4 : 3′-naphthylaminedisulphonic acid by replacement of the amido-group by hydrogen. Its *chloride* crystallizes from benzene, in which it is readily soluble, in prismatic forms, and from acetic acid in beautiful glistening plates. It melts at 122·5°, and on distillation with phosphorus pentachloride yields 1 : 2′-dichloronaphthalene.[3]

Naphthalenetrisulphonic acid has been obtained by Baeyer's hydrazine reaction from α-naphthylaminetrisulphonic acid. Its *chloride* crystallizes from a mixture of benzene and light petroleum in small prisms melting at about 191°.[4]

Naphthalenetetrasulphonic acid, $C_{10}H_4(SO_3H)_4 + 4H_2O$, was obtained by Senhofer by heating naphthalene with sulphuric acid and phosphorus pentoxide to 260°.[5] It is also formed when naphthalene is heated for some time to 160° with five times its weight of fuming sulphuric acid, containing 40 per cent. of trioxide.[6]

It crystallizes in coarse prisms, which are readily soluble in water but with difficulty in cold alcohol, and are insoluble in ether. The *barium salt* forms oblique prisms containing water of crystallization.

Dinaphthylsulphone, $(C_{10}H_7)_2SO_2$, was obtained by Berzelius, together with naphthalenesulphonic acid by heating naphthalene with sulphuric acid.[7] It was, however, found by Stenhouse and Groves that two isomerides are thus formed, which separate out with the unaltered naphthalene in the preparation of β-naphthalenesulphonic acid.[8]

[1] Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 13 ; *Chem. News*, **61**, 92.
[2] *Proc. Chem. Soc.* **1886**, 231 ; **1889**, 10 ; **1890**, 17 ; *Chem. News*, **61**, 93.
[3] Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 126.
[4] Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 125.
[5] *Ber.* **8**, 1486 ; *Monatsh. Chem.* **3**, 112.
[6] *Farbenfab.* vorm. Baeyer and Co. ; Schultz, *Steinkohlentheer*, **2**, 1003.
[7] *Annalen*, **28**, 9 ; Gercke, *Annalen*, **100**, 216.
[8] *Ber.* **9**, 682.

In order to prepare them, naphthalene is heated with three times its weight of sulphuric acid to 180° until no more water is given off; the mixture is then allowed to cool to 100°, four parts of boiling water added and the upper layer distilled with steam until no more naphthalene comes over. The residue is finally extracted with boiling carbon disulphide.

α-β-Dinaphthylsulphone separates from this solution in oblique, hard, transparent prisms, which are moderately soluble in hot alcohol and melt at 123°.

β-β-Dinaphthylsulphone is insoluble in carbon disulphide and crystallizes from boiling alcohol, in which it is only slightly soluble, in silky needles, which melt at 177°. When it is heated to 180° with phosphorus pentachloride, β-naphthalenesulphochloride and β-chloronaphthalene are formed.[1]

The α-β- and β-β-sulphones can also be obtained by the oxidation of the corresponding sulphides.

α-α-Dinaphthylsulphoxide, $(C_{10}H_7)_2SO$, is obtained by the partial oxidation of the corresponding sulphide. It separates from alcohol in coarse white crystals and melts at 164·5°.

α-α-Dinaphthylsulphone melts at 187°.[2]

α-Naphthylphenylsulphone, $C_{10}H_7SO_2C_6H_5$, is formed, together with the following compound, when naphthalene is heated to 170—190° with benzenesulphonic acid and phosphorus pentoxide.[3] The two substances are separated by recrystallization from a mixture of ether and alcohol, from which the α-compound is the first to separate. It forms dull, rhombohedral crystals, melting at 99·5—100·5°.

β-Naphthylphenylsulphone is also obtained by heating β-naphthalenesulphonic acid with benzene and phosphorus pentoxide. It crystallizes in fan-shaped aggregates of lustrous needles, which melt at 115—116°.

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[1] Cleve, *Bull. Soc. Chim.* **25**, 25.
[2] Krafft, *Ber.* **23**, 2367. Cf. Ekstrand, *Ber.* **17**, 2601.
[3] Michael and Adair, *Ber.* **10**, 583.

CHLORONAPHTHALENESULPHONIC ACIDS.

2590 1 : 4-*Chloronaphthalenesulphonic acid*, $C_{10}H_6Cl(SO_3H)$, was obtained by Zinin by heating α-chloronaphthalene to 140° with sulphuric acid,[1] and has been prepared by Cleve from naphthionic acid.[2] It forms a soft, buttery mass, readily soluble in water and alcohol; its salts and other derivatives have been investigated by Arnell.[3]

1 : 4-*Chloronaphthalenesulphochloride*, $C_{10}H_6Cl(SO_2Cl)$, crystallizes from benzene in prisms, melting at 95°, and is converted into 1 : 4-dichloronaphthalene by heating with phosphorus pentachloride.

The *amide* melts at 196—197°. The *ethyl ester* forms monosymmetric tablets, melting at 67·5°, whilst the *methyl ester* crystallizes in needles and melts at 70°.

1 : 4'-*Chloronaphthalenesulphonic acid* has been obtained by Armstrong and Wynne from chloro-β-naphthylaminesulphonic acid (1 : 2 : 4') by replacing the amido-group by hydrogen[4] and by Cleve from diazo-α-naphthalenesulphonic acid.[5] It is also formed, together with the preceding compound, by the direct sulphonation of α-chloronaphthalene at 160°, and is probably derived from the 1 : 4-acid, which is formed at lower temperatures, by isomeric change.[6] Its *chloride* crystallizes from benzene in small prisms, melting at 95°. Phosphorus pentachloride converts it into 1 : 4'-dichloronaphthalene.

γ-*Chloronaphthalenesulphonic acid* was obtained by Cleve by heating γ-diazonaphthalenesulphonic acid with hydrochloric acid. Its *chloride* forms crystals, melting at 106°.[7] It is probably the 1 : 3-derivative.

1 : 1'-*Chloronaphthalenesulphonic acid* is formed by the action of phosphorus pentachloride on the potassium salt of 1 : 1'-nitronaphthalenesulphonic acid suspended in carbon disulphide.[8] The *barium salt* crystallizes with two molecules of water in soluble, pearly scales. The *sulphochloride* separates from benzene in thin, colourless plates, melting at 101°.

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[1] *J. Pr. Chem.* **33**, 36.

[2] *Ber.* **20**, 73.

[3] *Beilstein's Handb.* **2**, 153.

[4] *Proc. Chem. Soc.* **1888**, 105, 49.

[5] *Ber.* **20**, 72.

[6] Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 87; *Chem. News*, **61**, 285.

[7] *Ber.* **21**, 3271.

[8] Cleve, *Ber.* **23**, 962.

1 : 2′-*Chlorosulphonic acid* was obtained by Armstrong and Wynne from 1 : 2 : 2′-chloronaphthylaminesulphonic acid. It yields a *chloride* which crystallizes from a mixture of benzene and light petroleum in long prisms, melting at 93—94°, and is converted by phosphorus pentachloride into 1 : 2′-dichloronaphthalene.

1 : 3′-*Chloronaphthalenesulphonic acid* was prepared in a similar manner from 1 : 2 : 3′-chloronaphthylaminesulphonic acid, and has also been obtained from β-nitronaphthalenesulphonic acid.[1] Its *chloride* crystallizes from benzene in small plates which unite to form opaque hemispherical aggregates, melting at 112—113°, and yields 1 : 3′-dichloronaphthalene, melting at 48°, on treatment with phosphorus pentachloride.

2 : 3′-*Chloronaphthalenesulphonic acid* is formed, together with the following compound, when β-chloronaphthalene is heated with slightly fuming sulphuric acid; the two acids are separated by means of their lead salts, that of the 2 : 3′-acid being the less soluble.[2] Its *chloride* crystallizes in prisms, which melt at 108·5—109·5°, and is converted into 2 : 3′-dichloronaphthalene by heating with phosphorus pentachloride.

2 : 1′-*Chloronaphthalenesulphonic acid* has also been prepared from the corresponding naphthylaminesulphonic acid by the diazo-reaction.[3] Its *chloride* crystallizes in needles, melts at 129° and yields 1 : 2′-dichloronaphthalene.

This acid, accompanied by a smaller quantity of the 2 : 3′-acid, is the product of the action of chlorosulphonic acid on β-chloronaphthalene in the cold.

2 : 2′-*Chloronaphthalenesulphonic acid* has been obtained from the corresponding naphthylaminesulphonic acid by means of the diazo-reaction (Armstrong and Wynne). The *chloride* crystallizes from benzene in prisms, melting at 86°, and yields 2 : 2′-dichloronaphthalene (melting at 114°) on heating with phosphorus pentachloride.

2 : 4′-*Chloronaphthalenesulphonic acid* is prepared in the same way as the preceding compound. The *chloride* crystallizes from a mixture of benzene and light petroleum in prisms, melting at 70°. On heating with phosphorus pentachloride it is converted into 1 : 3′-dichloronaphthalene, melting at 48°.

1 : 4 : 2′-*Dichloronaphthalene-β-sulphonic acid,* $C_{10}H_5Cl_2(SO_3H)$

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[1] Cleve, *Ber.* **20**, 74.

[2] Arnell, *Bull. Soc. Chim.* **45**, 184.

[3] Forsling, *Ber.* **19**, 1715 ; **20**, 2100 ; **21**, 2802.

was obtained by Widman[1] from the tetrachloride of β-naphthalenesulphonic acid, $C_6H_4Cl_4.C_4H_3(SO_3H)$, by the action of alcoholic potash, and is also formed by the action of chlorosulphonic acid on 1 : 4-dichloronaphthalene.[2] It solidifies to a gelatinous mass when its solution is cooled and gives a *chloride* which melts at 132°, and is converted into 1 : 4 : 2′-trichloronaphthalene (ζ) by distillation with phosphorus chloride.

1 : 3 : 4′-*Dichlor-a-naphthalenesulphonic acid*, is obtained from the *a*-sulphonic acid in a similar manner,[3] and is also formed by the sulphonation of 1 : 3-dichloronaphthalene. It crystallizes in long, flat, lustrous needles, and is converted by phosphorus pentachloride into a chloride which crystallizes in prisms or needles, melting at 148·5°, and yields the corresponding 1 : 3 : 4′-trichloronaphthalene (γ).

The following dichloronaphthalenesulphonic acids are also known. They are formed by the sulphonation of the dichloronaphthalenes, and yield the corresponding trichloronaphthalenes on distillation with phosphorus pentachloride.[4]

Cl : Cl : SO_3H	Chloride.	Melting-point of chloride.
1 : 1′ : 4	minute aggregates	114°
1 : 4′ : 3	long thin plates	139·5°
1 : 2 : 4′	large prismatic crystals	104°
1 : 2 : 3′	aggregates of small prisms	167·5°
1 : 3 : 2′	long four-sided prisms	121°
1 : 2′ : 4	slender needles becoming opaque in the air	118°
1 : 3′ : 4	magnificent prisms	151°
2 : 3 : 1′	lustrous slender ribbons	142°
2 : 2′ : 3	elongated prisms	163·5°
2 : 3′ : 4	radiate groups of slender prismatic needles	136°

In addition, a number of chloronaphthalenedisulphonic acids has been prepared by the sulphonation of the chloronaphthalenesulphonic acids.[5]

Cl : SO_3H : SO_3H	Chloride.	Melting-point of chloride.
2 : 3′ : 4	bundles of slender needles	148°
2 : 2′ : 4	radiate groups of flat prismatic needles	174°

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[1] *Ber.* **12**, 963.

[2] Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 81; *Chem. News*, **61**, 273.

[3] *Ber.* **12**, 2231.

[4] Armstrong and Wynne, *loc. cit.*

[5] Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 131.

Several isomerides have moreover been obtained from the corresponding naphthylaminedisulphonic acids by means of the diazo-reaction:[1]

Cl : SO_3H : SO_3H	Chloride.	Melting-point of chloride.
1 : 4 : 3′	minute needles	126—127°
1 : 4 : 1′	glistening flat plates	135°
2 : 3 : 2′	small opaque aggregates . . .	176°
2 : 1′ : 3′	needles	169°
2 : 4′ : 2′	radiate groups of small prisms	156°
2 : 1 : 4′	flat needles	158°
2 : 1 : 3′	small prisms	124·5—125°

a-Chloronaphthalenetrisulphonic acid, $C_{10}H_4Cl(SO_3H)_3$, has been obtained from *a*-naphthylaminetrisulphonic acid by the diazo-reaction. Its *chloride* crystallizes from benzene in minute prisms, melting at 215°.

BROMONAPHTHALENESULPHONIC ACIDS.

2591 1 : 4-*Bromonaphthalenesulphonic acid*, $C_{10}H_6Br(SO_3H)$, was obtained by Laurent by heating *a*-bromonaphthalene with fuming sulphuric acid,[2] and was further investigated by Otto and Möries,[3] and by Darmstädter and Wichelhaus.[4] It crystallizes in broad, smooth needles, which melt at 138—139°, and are readily soluble in water and alcohol, but only very slightly in ether. When its potassium salt is heated with an excess of phosphorus bromide, 1 : 4-dibromonaphthalene is formed (Jolin).

1 : 4-*Bromonaphthalenesulphochloride*, $C_{10}H_6Br(SO_2Cl)$, crystallizes from benzene in well developed prisms, melting at 86—87°.[5] In attempting to prepare this substance by the action of phosphorus pentachloride on the sodium salt, Gessner obtained the isomeric *chloronaphthalenesulphobromide*, $C_{10}H_6Cl(SO_2Br)$, which crystallizes in needles and melts at 115—116°.[6]

1 : 4-*Bromonaphthalenesulphobromide*, $C_{10}H_6Br(SO_2Br)$, crystallizes in rhombic tablets which melt at 114·5° (Jolin).

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[1] Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, pp. 125 *et seq.*

[2] *Annalen*, **72**, 298.

[3] *Annalen*, **147**, 184.

[4] *Annalen*, **152**, 302.

[5] *Bull. Soc. Chim.* **28**, 516.

[6] *Ber.* **9**, 1514.

1 : 4′-*Bromonaphthalenesulphonic acid* is formed, together with 1 : 4′- and 1 : 2′-dibromonaphthalenes, when bromine is added to a solution of α-naphthalenesulphonic acid. On evaporation of the solution it remains as a syrup, which solidifies in a vacuum to a crystalline mass, readily soluble in alcohol but almost insoluble in ether (Darmstädter and Wichelhaus). When its potassium salt is heated with an excess of phosphorus pentabromide, 1 : 4′-dibromonaphthalene is formed (Jolin). Its *chloride* crystallizes from benzene in prisms, melting at 90°.

2 : 1′-*Bromonaphthalenesulphonic acid* was obtained from β-naphthylamine-α-sulphonic acid; its *potassium salt*, $C_{10}H_6Br(SO_3K) + H_2O$, forms a crystalline powder which is converted by phosphorus pentabromide into the *bromide*, $C_{10}H_6Br(SO_2Br)$. The latter crystallizes from chloroform in broad needles, melting at 151°, and when heated with phosphorus pentabromide yields 1 : 2′-dibromonaphthalene.[1]

The same acid is the chief product of the action of sulphuric acid on β-bromonaphthalene,[2] the 2 : 3′-acid being also formed in small quantity.

2 : 3′-*Bromonaphthalenesulphonic acid* has been prepared from β-naphthylamine-β-sulphonic acid; it is very soluble in water, but, on the other hand, its salts are only slightly soluble; the *potassium salt*, $2C_{10}H_6Br(SO_3K) + H_2O$, is a crystalline powder. The *bromide* crystallizes from a mixture of ether and chloroform in prisms, which melt at 118°, and are converted by phosphorus pentabromide into 2 : 3′-dibromonaphthalene (Forsling).

2 : 4′-*Bromonaphthalenesulphonic acid* was obtained by Sindall from β-naphthylamine-γ-sulphonic acid; its *chloride* crystallizes from light petroleum in small prisms melting at 77°.

2 : 2′-*Bromonaphthalenesulphonic acid* was prepared in the same way from the δ-sulphonic acid; its *chloride* separates from benzene in compact oblique prisms, and melts at 100°.

Bromo-β-naphthalenesulphonic acid is obtained, unaccompanied by any brominated naphthalenes, by the action of bromine on β-naphthalenesulphonic acid. It forms a crystalline mass, which is readily soluble in alcohol, water and ether, and melts at 62° (Darmstädter and Wichelhaus).

Dibromo-β-naphthalenesulphonic acid, $C_{10}H_5Br_2(SO_3H)$, is

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[1] Forsling, *Ber.* **22**, 1401.

[2] Sindall, *Proc. Chem. Soc.* **1889**, 118.

formed when an excess of bromine is employed, and is a crystalline mass which is converted by phosphorus bromide into γ-tribromonaphthalene (Jolin).

IODONAPHTHALENESULPHONIC ACIDS, $C_{10}H_6I(SO_3H)$.

2592 These compounds have been prepared from the corresponding naphthylaminesulphonic acids.

2 : 4′-*Iodonaphthalenesulphonic acid* is also formed in small quantity by the action of chlorosulphonic acid on β-iodonaphthalene; its *chloride* melts at 92·5°.

2 : 1′-*Iodonaphthalenesulphonic acid* is the chief product of the action of chlorosulphonic acid on β-iodonaphthalene; its *chloride* melts at 164—165°.

2 : 3′-*Iodonaphthalenesulphonic acid* forms a *chloride*, melting at 140°, and is the sole product when β-iodonaphthylamine is heated to 150° with chlorosulphonic acid, both of the preceding isomerides being converted into it at this temperature.

2 : 2′-*Iodonaphthalenesulphonic acid*, is not formed by the sulphonation of β-iodonaphthalene; its *chloride* crystallizes from benzene in small prisms, melting at 100°.[1]

FLUONAPHTHALENESULPHONIC ACID.

2593 1 : 4′-*Fluonaphthalenesulphonic acid* has been prepared from the corresponding amido-acid by means of the diazo-reaction. It crystallizes in small, lustrous plates, and is a strong acid, but gives salts which crystallize badly. Its *ethyl ester* forms large prisms, melting at 79°, and the *chloride*, which crystallizes in rhombic prisms, melts at 122—123°. When it is distilled with superheated steam, α-fluonaphthalene is formed.[2]

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[1] Houlding, *Proc. Chem. Soc.* **1889**, 74; Armstrong and Wynne, *Proc. Chem Soc.* **1889**, 119.

[2] Mauzelius, *Ber.* **22**, 1844.

NITRONAPHTHALENESULPHONIC ACIDS.

2594 1 : 4'-*Nitronaphthalenesulphonic acid*, $C_{10}H_6(NO_2)SO_3H + 4H_2O$, was obtained by Laurent by the action of fuming sulphuric acid on *a*-nitronaphthalene and by Cleve, who named it *a*-nitronaphthalenesulphonic acid, by the nitration of *a*-naphthalenesulphonic acid.[1] It is readily soluble in alcohol and water, less readily in dilute sulphuric acid, and crystallizes in light yellow, flat needles, which have a very bitter taste and lose two molecules of water over sulphuric acid. It is converted by the action of sodium amalgam and water into *a*-naphthylamine, whereas the nitrobenzenesulphonic acids when treated in the same manner form azo-compounds, unaccompanied by a trace of aniline.[2]

Its *chloride*, $C_{10}H_6(NO_2)SO_2Cl$, crystallizes from ether in yellowish needles, melting at 113°.

The *amide* crystallizes either in scales or octohedra, melting at 188°. The *methyl ester* forms small needles melting at 117°, whilst the *ethyl ester* crystallizes from alcohol in large prisms, melting at 101°.

1 : 4-*Nitronaphthalenesulphonic acid* is formed in small quantity together with the preceding compound, from which it is separated by the greater solubility of its calcium salt. It forms a readily soluble, yellowish crystalline mass, and yields a *chloride*, which crystallizes from benzene in large yellow prisms, melting at 99°. On reduction it yields 1 : 4-amidonaphthalenesulphonic acid (naphthionic acid).[3]

1 : 1'-*Nitronaphthalenesulphonic acid* is also formed by the nitration of *a*-naphthalenesulphonic acid, and is contained in the mother liquor from the calcium salt of the 1 : 4-acid. Its *potassium salt* crystallizes in pointed needles, and when suspended in carbon disulphide and treated with phosphorus pentachloride yields 1 : 1'-chloronaphthalenesulphonic acid (Cleve).

1 : 3'-*Nitronaphthalenesulphonic acid*, which was termed *β*-nitronaphthalenesulphonic acid, is formed, together with the *γ*- and *θ*-compounds when *β*-naphthalenesulphonic acid is nitrated, and is separated from the isomerides by means of

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[1] *Bull. Soc. Chim.* **24**, 507.

[2] Claus, *Ber.* **10**, 1303.

[3] Cleve, *Ber.* **23**, 958.

its difficultly soluble barium salt. It is also formed, together with the 1 : 4′- and 1 : 2′-acids, by the action of sulphuric acid on α-nitronaphthalene.[1] The acid is readily soluble in water and alcohol, and crystallizes in bitter tasting, yellow needles.

Its *chloride* is readily soluble in acetic acid, crystallizes from benzene in prisms, melting at 125·5°, and is converted by heating with phosphorus pentachloride into 1 : 3′-dichloronaphthalene.

1 : 2′-*Nitronaphthalenesulphonic acid*, termed by Cleve the θ-compound, forms yellow crystals, which are readily soluble in water. Its *chloride* is only slightly soluble in acetic acid, forms large prisms melting at 169°, and is converted by phosphorus pentachloride into 1 : 2′-dichloronaphthalene.[2]

1 : 3-*Nitronaphthalenesulphonic acid* was termed the γ-compound by Cleve, and is readily soluble in water, but forms salts which are only slightly soluble. Its *chloride* crystallizes in pale, yellow needles, which are soluble with difficulty in acetic acid, and melt at 140°.[3]

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[1] Palmaer, *Ber.* **21**, 3260.

[2] *Ber.* **19**, 1279; **20**, 72; **21**, 3271; *Bull. Soc. Chim.* **26**, 444; Armstrong and Wynne, *Proc. Chem. Soc.* **1889**, 71; *Chem. News*, **59**, 95.

[3] Cf. Armstrong and Wynne, *loc. cit.*

HYDROXYNAPHTHALENES AND ALLIED COMPOUNDS.

THE NAPHTHOLS, $C_{10}H_7.OH$.

2595 These compounds are very closely related in their chemical properties to the phenols, from which they differ in forming esters when they are heated with organic acids, and in some other respects in which they behave similarly to the alcohols.

a-Naphthol was first obtained by Griess, who termed it *naphthyl alcohol,* from α-naphthylamine by the diazo-reaction.[1] It is more readily formed when α-naphthalenesulphonic acid is heated with caustic potash.[2] On the large scale it is manufactured by fusing sodium α-naphthalenesulphonate with caustic soda. The melt is dissolved in water and the naphthol liberated by hydrochloric acid and purified by distillation. Schulze detected it in coal tar,[3] and it has been prepared synthetically by distilling phenylparaconic acid,[4] and by boiling phenylisocrotonic acid (p. 25). It crystallizes in lustrous monosymmetric prisms or needles, has an aromatic smell resembling that of phenol and a burning taste, and forms a powder which causes violent sneezing. It is slightly soluble in cold, more freely in hot water, and readily in alcohol, ether, &c., melts at 94°, boils at 278—280°, and has the specific gravity of 1·224 at 4°.[5] When it is boiled for some time in the air, dinaphthylene oxide, $C_{20}H_{12}O$, is formed. A splinter of pine wood dipped into an aqueous solution of α-naphthol and then into hydrochloric acid

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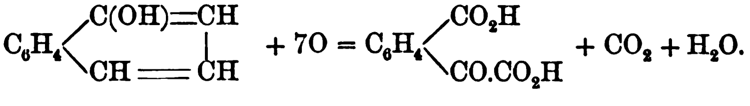
[1] *Journ. Chem. Soc.* **1867**, 89.
[2] Eller, *Annalen*, **152**, 275; Schäffer, *Annalen*, **152**, 279.
[3] *Annalen*, **227**, 143.
[4] Fittig and Erdmann, *Annalen*, **227**, 242.
[5] Schröder, *Ber.* **12**, 1613.

rapidly becomes coloured green when exposed to sunlight, more slowly in diffuse daylight, and then gradually changes to reddish-brown (Schäffer). Bleaching powder colours the aqueous solution deep-violet and forms a flocculent precipitate of the same colour. Ferric chloride produces a white precipitate of dinaphthol, $C_{20}H_{12}(OH)_2$, which soon turns grey. When α-naphthol is dissolved in an excess of caustic soda solution and a little ammonia and some 1 : 4-diazonaphthalenesulphonic acid added, a splendid dark-red colouration is produced.[1] If a solution of α-naphthol in strong caustic potash solution be heated to 50° with chloroform, a deep Prussian-blue colouration is produced, which changes in the air to green and then to brown.

α-Naphthol taken internally appears in the urine as α-naphtholglycuronic acid, $C_{16}H_{16}O_7$, which is decomposed by mineral acids into glycuronic acid, $C_6H_{10}O_7$, and α-naphthol.[2] At the same time a little α-naphthylsulphuric acid, $C_{10}H_7.O.SO_2.OH$, is also formed. When such urine is acidified with hydrochloric acid, distilled until half its volume has passed into the receiver, and the distillate extracted with ether, an ethereal solution is obtained which on evaporation yields a residue with which chloroform in alkaline solution gives the blue colouration already described, although in this case the shade produced is more inclined to green, the alkaline solution being generally tinged more or less deeply with brown. This reaction can also be made use of to detect chloroform in urine and other animal liquids, α-naphthol being used as the reagent (Lustgarten).[3]

Potassium permanganate oxidizes α-naphthol in cold alkaline solution to carboxyphenylglyoxylic acid (Pt. V. p. 153).[4]



$$C_6H_4\left<\begin{matrix}C(OH)=CH\\ \qquad\quad\vert\\ CH=CH\end{matrix}\right. + 7O = C_6H_4\left<\begin{matrix}CO_2H\\ CO.CO_2H\end{matrix}\right. + CO_2 + H_2O.$$

α-Naphthol is technically employed in the colour industry and as an antiseptic. Camille Köchlin states that putrefaction of the albumen employed in calico printing can be prevented by adding to every 100 parts of the latter 2 parts of a solution prepared by dissolving α-naphthol in an equal weight of alcohol,

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[1] Erdmann, *Annalen*, **247**, 330.

[2] Lesnik and Nencki, *Ber.* **19**, 1534.

[3] *Monatsh.* **3**, 715.

[4] Henriques, *Ber.* **21**, 1607.

diluting with 4 parts of water, and adding a little ammonia. When an alcoholic solution of picric acid which has been saturated in the cold and then heated to boiling is added to a solution of a-naphthol in a small quantity of alcohol, the compound $C_{10}H_8O + C_6H_2(NO_2)_3OH$ separates out on cooling in orange-coloured needles, melting at 189—190°.[1] a-Naphthol forms crystalline naphthates with the alkalis, but is precipitated from their solutions by carbon dioxide or ammonium chloride. When a-naphthol is treated with iodine and aluminium foil (Pt. III. p. 323), *aluminium a-naphthate*, $(C_{10}H_7O)_3Al$, is formed; this substance has not been obtained pure, and decomposes on heating into alumina, naphthalene, isodinaphthyl, and other compounds.[2]

2596 *a-Naphthyl methyl ether*, $C_{10}H_7.OCH_3$, was obtained by Hantzsch from a-naphthylamine by heating it with methyl alcohol and zinc chloride to 180—200°:[3]

$$C_{10}H_7.NH_2 + HO.CH_3 = C_{10}H_7.OCH_3 + NH_3.$$

Städel prepared it by heating a-naphthol with caustic potash, methyl iodide and methyl alcohol,[4] but it is best obtained by acting upon sodium naphthate at 280° with methyl chloride.[5] It is a strongly refractive liquid, which boils at 269—270°, and has a very pleasant odour like that of orange-flowers, so that it may, perhaps, be used as a perfume. It combines with picric acid to form a compound crystallizing in red needles.

a-Naphthyl ethyl ether, $C_{10}H_7.OC_2H_5$, is a liquid, boiling at 208·7°, which has a characteristic odour (Schäffer).

a-Naphthyl ethylene ether, $(C_{10}H_7O)_2C_2H_4$, is formed when a solution of a-naphthol in caustic soda is heated with alcohol and ethylene bromide; it crystallizes from alcohol in small plates, melting at 125—126°.[6]

a-Dinaphthyl ether, $(C_{10}H_7)_2O$, is formed, together with naphthylene oxide, when a-naphthol is heated to 180—200° with zinc chloride, and when hydrochloric acid is passed into boiling a-naphthol. It crystallizes from alcohol in plates, and from a mixture of ether and alcohol in thick, lustrous rhombic tablets, melting at 110°. With picric acid it forms the com-

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[1] Marchetti, *Gazzetta*, **12**, 502.

[2] Gladstone and Tribe, *Journ. Chem. Soc.* 1882, **1**, 5.

[3] *Ber.* **13**, 1347.

[4] *Annalen*, **217**, 40.

[5] *Bull. Soc. Chim.* **40**, 106.

[6] Kölle, *Ber.* **13**, 1953.

pound, $C_{20}H_{14}O + 2C_6H_3(NO_2)_3O$, which crystallizes in red plates or prisms, melting at 115°.[1]

Acid a-naphthyl sulphate, $C_{10}H_7O.SO_2.OH$, is obtained, together with the isomeric α-naphtholsulphonic acid, when a solution of α-naphthol in acetic acid is heated with sulphuric acid, the temperature being kept below 75°. The solution is diluted with water, neutralized with lead oxide and concentrated. Lead naphthyl sulphate separates out in small plates and yields the free acid, which crystallizes, when placed over sulphuric acid, in long, slender needles; it readily decomposes into α-naphthol and sulphuric acid.

Claus and Knyrim looked upon this substance as a sulphonic acid,[2] but Beilstein pointed out[3] that its properties clearly prove it to be naphthylsulphuric acid.

a-Naphthyl phosphate, $(C_{10}H_7)_3PO_4$, is formed when α-naphthol is heated with phosphorus pentachloride to temperatures below 100°, whilst α-chloronaphthalene is formed when an excess of chloride is used and the temperature allowed to rise to 150°.[4] It is best prepared by heating α-naphthol with the requisite quantity of phosphorus oxychloride until the mixture boils quietly.[5] It crystallizes from alcohol in lustrous needles, melting at 145°.

a-Naphthyl silicate, $(C_{10}H_7)_4SiO_4$, is obtained by the action of silicon chloride on α-naphthol. It crystallizes in needles, and distils at 425—430° under a pressure of 130 mm.[6]

a-Naphthyl acetate, $C_{10}H_7.O.CO.CH_3$, is formed by the action of acetyl chloride on α-naphthol (Schäffer), and also when the latter is heated to 200° with acetic acid.[7] It is however best prepared by heating α-naphthol with acetic anhydride and anhydrous sodium acetate.[8] It crystallizes in broad needles or tablets, melts at 49°, and is readily soluble in alcohol and ether.

a-Naphthyl ethylcarbonate, $CO(OC_2H_5)OC_{10}H_7$, is the product of the action of ethyl chlorocarboxylate on potassium α-naphthate. It is readily soluble in absolute alcohol and crystallizes, when this solution is diluted with sufficient water to produce a slight turbidity, in large rhombic tablets, melting at 31°. On boiling, it decomposes into carbon dioxide, alcohol, α-naphthol and

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[1] Merz and Weith, *Ber.* **14**, 195.

[2] *Ber.* **18**, 2924.

[3] *Handb.* **2**, 561.

[4] Schäffer, *loc. cit.*; Oehler, *Ber.* **15**, 312.

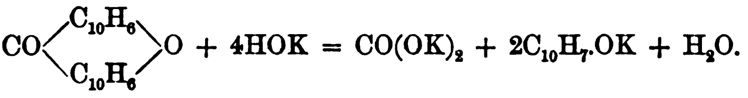
[5] Heim, *Ber.* **16**, 1769.

[6] Hertkorn *Ber.* **18**, 1696.

[7] Gräbe, *Annalen*, **209**, 156.

[8] Tasinari, *Gazzetta*, **10**, 491. See also Miller, *Annalen*, **208**, 247.

dinaphthyleneketone-oxide, $C_{21}H_{12}O_2$, which crystallizes from hot alcohol in sulphur-yellow needles, melts at 240°, is not attacked by caustic potash solution even at 280°, and on fusion with caustic potash only slowly decomposes into α-naphthol and carbon dioxide:[1]



$$CO\begin{cases}C_{10}H_6\\ \\C_{10}H_6\end{cases}O + 4HOK = CO(OK)_2 + 2C_{10}H_7.OK + H_2O.$$

α-Naphthyl phenylcarbamate, $C_{10}H_7O.CO.NH.C_6H_5$, is formed when α-naphthol is heated with phenyl carbimide. It crystallizes from alcohol in needles, which melt at 178·5°, and decomposes on distillation into its constituents.[2]

α-Naphthyl orthoxalate, $C_{10}H_7O.C(OH)_2.C(OH)_2.OC_{10}H_7$, is obtained by boiling α-naphthol and oxalic acid with acetic acid for some time; it is a crystalline powder, which melts with decomposition at 163°.[3]

α-Naphthoxyacetic acid, $C_{10}H_7O.CH_2.CO_2H$, was prepared by Spica by heating α-naphthol with chloracetic acid and caustic potash. It crystallizes in small prisms, which are slightly soluble in cold water, and melt at 190°. Its salts crystallize well; the *ethyl ester* forms small crystals, melting at 173—174°.[4]

α-Naphtholglycuronic acid, $C_{16}H_{16}O_7$, occurs in human urine and in that of dogs after the administration of α-naphthol, and crystallizes from water in long needles, melting at 202—203°. Its aqueous solution gives with concentrated sulphuric acid a deep emerald-green colouration, which gradually changes to a dirty greyish-green.[5] It is decomposed by mineral acids into α-naphthol and glycuronic acid, $C_6H_{10}O_7$.[6]

ar-Tetrahydro-α-naphthol, $C_{10}H_{11}.OH$, was first obtained from *ar*-tetrahydro-α-naphthylamine by means of the diazo-reaction.[7] It is also formed when 20 grms. of sodium are gradually added to a boiling solution of 10 grms. of α-naphthol in boiling amyl alcohol.[8] It melts at 68·5—69°, boils at 264·5—265·5° under a pressure of 705 mm., and solidifies in large silvery tablets,

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[1] Bender, *Ber.* **13**, 702; **19**, 2266.

[2] Leuckart and Schmidt, *Ber.* **18**, 2338; Snape, *Ber.* **18**, 2428.

[3] Staub and Smith, *Ber.* **17**, 1740.

[4] *Gazzetta*, **16**, 437.

[5] Lesnik and Nencki, *Ber.* **19**, 1534.

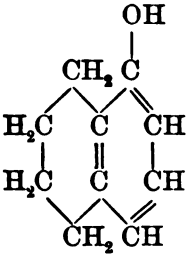
[6] Spiegel, *Ber.* **15**, 1964.

[7] Bamberger and Althausse, *Ber.* **21**, 1892.

[8] Bamberger and Bordt, *Ber.* **23**, 215.

resembling those of naphthalene, which have a strong smell of phenol. It is very slightly soluble in cold water and only slightly in hot water, but very readily in alcohol, from which it separates as an oily liquid, which soon solidifies in large crystalline masses. If these are carefully broken up, cavities are found lined by silvery rectangular monosymmetric tablets. In the air its surface becomes coloured pink. Bleaching powder produces a yellowish-white turbidity in its aqueous solution, and ferric chloride gives a faint turbidity after some time, more rapidly on warming: if the solution be boiled, the liquid becomes coloured yellowish-red and a yellowish-white flocculent precipitate is formed.

Its constitution is that shown in the following formula, and is proved by its formation from *ar*-tetrahydro-*a*-naphthylamine:



ar-Tetrahydro-*a*-naphthol is soluble in alkalis and is precipitated from solution in them by carbonic acid. It also combines with diazo-salts to form azo-colours. In its chemical relations therefore it behaves as an aromatic hydroxyderivative, and it has been found by Bamberger that whenever a tetrahydro-derivative of naphthalene contains the additional atoms of hydrogen and the substituent group (OH,NH_2, &c.) in different nuclei, the substance retains the properties of an aromatic compound, whereas when they are both in the same nucleus the compound behaves as a benzene derivative containing fatty side chains. To mark this difference of function, compounds of the first class are termed *aromatic*, and those of the second *alicyclic*-reduction-products (*ἄλειφαρ*, fat, *κύκλος*, a ring; in practice these terms are abbreviated to the prefixes *ar*- and *ac*-.)

ar-Tetrahydro-*a*-naphthol, like other *ar*-tetrahydro-derivatives (p. 29), is more closely related to phenol than to *a*-naphthol in several respects. Thus, like phenol, it does not readily form a substituted sulphuric acid, is not converted into an ether when heated with hydrochloric acid and alcohol to 150°, and does not form the oxide (dinaphthyl ether) when heated with dilute sulphuric acid, whereas α-naphthol undergoes all of these reactions.[1]

ar-Tetrahydro-α-naphthol ethyl ether, $C_{10}H_{11}.O.C_2H_5$, is formed by the action of alcoholic potash and ethyl iodide on hydronaphthol, and also by the reduction of α-naphthol ethyl ether. It is a viscid, heavy oil, which boils at 259° under a pressure of 705 mm., and has a pleasant odour.[2]

2597 *β-Naphthol*, $C_{10}H_7.OH$, was first obtained by Schäffer by fusing lead β-naphthalenesulphonate with caustic potash,[3] whilst Liebermann prepared it from β-amidonaphthalene by means of the diazo-reaction,[4] and it was found by Schulze to be contained in small quantity in coal-tar. It is manufactured by melting sodium β-naphthalenesulphonate with 2 parts of caustic soda and some water in an iron pot, heated by an air-bath, and finally raising the temperature to 300°. The melt is dissolved in water and the β-naphthol precipitated by hydrochloric acid and purified by distillation.

It crystallizes in very lustrous plates or rhombic tablets, which are almost odourless, have a burning taste, and form a powder which causes violent sneezing. Hot water only dissolves a small quantity of it, but it is readily soluble in alcohol, &c. It has a sp. gr. of 1·217 at 4° (Schröder), melts at 122°, boils at 285—290°, and readily sublimes; it is not readily volatile with steam, but can easily be distilled with superheated steam. When it is boiled for a considerable time in the air, β-dinaphthalene oxide, $C_{20}H_{12}O$, is formed. With a splinter of pine wood and hydrochloric acid it gives the same reaction as α-naphthol, but the colour is more rapidly produced (Schäffer). Bleaching powder only produces a yellowish colouration in its aqueous solution, whilst ferric chloride gives a faint greenish colour followed by a white flocculent precipitate of β-dinaphthol, $C_{20}H_{12}(OH)_2$. Its alkaline solution gives the same colouration as the α-compound with chloroform. When it is dissolved in glacial acetic acid at 110°, and a solution of nitrosodimethylaniline hydrochloride gradually added, a bluish-violet colouring matter is formed, the hydrochloride of which crystallizes in needles, which have a copper lustre.[5]

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[1] Bamberger, *Annalen*, **257**, 5; Bamberger and Longfeldt, *Ber.* **23**, 1128.

[2] Bamberger and Bordt, *loc. cit.*

[3] *Annalen*, **152**, 279.

[4] *Annalen*, **183**, 267.

[5] Meldola, *Ber.* **12**, 2065.

It differs from
this when heated
β-phenylnaphthyl
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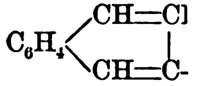

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[1] *Monatsh.* **9**, 527; Ehrlich, *Monatsh.* **10**, 115.

[2] Dyson, *Journ. Chem. Soc.* 1883, **1**, 466.

[3] Städel, *Annalen*, **217**, 40; Marchetti, *Gazzetta*, **9**, 544; Vincent, *Bull. Soc. Chim.* **40**, 106.

β-Naphthyl ethyl ether, $C_{10}H_7.OC_2H_5$, is a crystalline mass which has a pleasant smell of pineapple. It melts at 33°, boils at 274—275°,[1] and decomposes when heated for some time to 310—320° into α-naphthol and ethylene.[2]

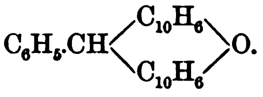
β-Naphthyl methylene ether, $(C_{10}H_7O)_2CH_2$, is formed when β-naphthol is heated with methylene iodide and caustic soda; it crystallizes from alcohol in brittle, silky needles, which melt at 133—134°.[3]

β-Naphthyl ethylene ether, $(C_{10}H_7O)_2C_2H_4$, crystallizes in lustrous plates, melting at 217° (Kölle).

β-Dinaphthyl ether, $(C_{10}H_7)_2O$, is obtained by heating β-naphthol with zinc chloride[4] and hydrochloric acid or dilute sulphuric acid, and is best prepared by boiling β-naphthol for some time with 15—20 parts of sulphuric acid of sp. gr. 1·4.[5] It crystallizes from hot alcohol in silvery plates, melting at 105°, sublimes with difficulty, and boils above 360°. Its compound with picric acid, $C_{20}H_{14}O + 2C_6H_3(NO_2)_3O$, crystallizes in orange-yellow plates, and melts at 122°.

β-Dinaphthylacetal or *Ethidene β-dinaphthyl ether*, $CH_3.CH(OC_{10}H_7)_2$, is formed when seven parts of β-naphthol and three parts of paraldehyde are dissolved in fifteen parts of glacial acetic acid and heated on the water-bath with one part of fuming hydrochloric acid. It is a snow-white, crystalline powder, which melts at 200—201°, and is only soluble with difficulty in all solvents, but with least difficulty in chloroform, from which it crystallizes in short prisms.

Benzidene β-dinaphthyl ether, $C_6H_5.CH(OC_{10}H_7)_2$, is formed when 7·2 parts of β-naphthol and 5·3 parts of benzaldehyde are dissolved in thirty parts of glacial acetic acid, two parts of fuming hydrochloric acid added to the well-cooled liquid, and the whole allowed to stand for a few days at a temperature of 0°. It forms hard, white, crystalline crusts or small tablets, melts at 204—205°, and is converted at 210°, or when heated with glacial acetic acid and hydrochloric acid, into benzidenedinaphthyl oxide, which is also invariably formed in its preparation and has the constitution:[6]



$$C_6H_5.CH{\left\langle\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}\right\rangle}O.$$

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[1] Hager and Liebermann, *Ber.* **15**, 1427.

[2] Bamberger, *Ber.* **19**, 1818.

[3] Kölle, *Ber.* **13**, 1953.

[4] Merz and Weith, *Ber.* **14**, 199.

[5] Gräbe *Annalen*, **209**, 47.

[6] Claisen, *Annalen*, **237**, 361.

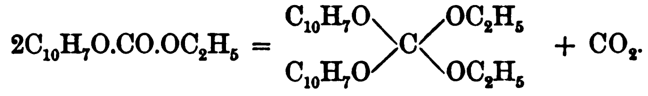
Acid β-naphthyl sulphate, $C_{10}H_7O.SO_2.OH$, was obtained by Armstrong by the action of chlorosulphonic acid on β-naphthol,[1] whilst Nietzki prepared it by dissolving the latter in concentrated sulphuric acid.[2] It is a crystalline mass, which is readily soluble in water, and easily decomposes in aqueous solution into sulphuric acid and β-naphthol. Its crystalline salts with the alkalis yield β-naphthyl ethyl ether on heating with sodium ethyl sulphate, and β-dinaphthyl ether with β-naphthol.

β-Naphthyl phosphate, $(C_{10}H_7)_3PO_4$, is prepared in the same way as the α-compound, and crystallizes from alcohol in small needles, melting at 111° (Schäffer, Heim).

β-Naphthyl silicate, $(C_{10}H_7)_4SiO_4$, forms warty crystals, and boils at about 430° (Hertkorn).

β-Naphthyl acetate, $C_{10}H_7O.CO.CH_3$, was obtained by Schäffer from β-naphthol by the action of acetyl chloride; it is also formed when β-naphthol is gently boiled with acetic anhydride for a few hours,[3] or heated to 240° with glacial acetic acid for some time.[4] It crystallizes from alcohol or acetic acid in small, soft needles, which have a faint smell of aniseed and melt at 70°.

β-Naphthyl ethyl orthocarbonate, is formed by the action of ethyl chlorocarboxylate on potassium β-naphthate; the normal carboxylate is the first product, as in the case of the α-compound, but immediately undergoes the following decomposition:



$$2C_{10}H_7O.CO.OC_2H_5 = \begin{matrix} C_{10}H_7O \\ C_{10}H_7O \end{matrix} \!\!>\! C \!<\!\! \begin{matrix} OC_2H_5 \\ OC_2H_5 \end{matrix} + CO_2.$$

It is an easily fusible, tallow-like mass, which has a faint but pleasant odour, boils at 298—300°, and on heating to 250° with hydrochloric acid decomposes into β-naphthol, carbon dioxide, and ethyl chloride. On continued boiling it decomposes into alcohol and *β-dinaphthylene ketone oxide*, $C_{21}H_{12}O_2$, which crystallizes from benzene in thin prisms, melting at 194°, and is, like the α-compound, a very stable substance (Bender).

β-Naphthyl phenylcarbamate, $C_{10}H_7O.CO.NHC_6H_5$, is obtained in the same way as the α-compound, and crystallizes in prisms melting at 230°.

β-Naphthyl orthoxalate, $C_{10}H_7O.C(OH)_2.C(OH)_2.OC_{10}H_7$, is, like the α-compound, a crystalline powder, which melts with

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[1] Armstrong, *Ber.* **15**, 203.

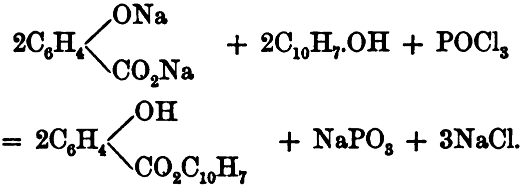
[2] Nietzki, *Ber.* **15**, 305.

[3] Miller, *Ber.* **14**, 1602.

[4] Gräbe *Annalen*, **209**, 147.

some decomposition at 167°, and on distillation is almost completely decomposed into formic acid and β-naphthol.

β-Naphthyl salicylate, $C_{10}H_7O.CO.C_6H_4.OH$, is formed when a mixture of salicylic acid and β-naphthol is heated with acid sodium sulphate.[1] This last can be replaced by phosphorus oxychloride, and it is then unnecessary to use free salicylic acid, since the basic sodium salt which is formed in the manufacture of the acid can be employed :[2]



$$2C_6H_4\begin{matrix}\diagup ONa \\ \diagdown CO_2Na\end{matrix} + 2C_{10}H_7.OH + POCl_3$$
$$= 2C_6H_4\begin{matrix}\diagup OH \\ \diagdown CO_2C_{10}H_7\end{matrix} + NaPO_3 + 3NaCl.$$

It forms odourless and tasteless crystals, which melt at 95°. It is used in medicine under the name of *naphthalol* or *naphthosalol* for the same purposes as phenylsalicylate or salol (Part IV. p. 307). α-Naphthyl salicylate can be prepared in the same manner.

β-Naphthoxyacetic acid, $C_{10}H_7O.CH_2.CO_2H$, is obtained in a similar manner to the α-compound and crystallizes in scales or rhombic prisms, which melt at 151—152°. Its *ethyl ester* forms large tablets melting at 48—49° (Spica).

β-Naphtholglycuronic acid, $C_{16}H_{16}O_7$, occurs in urine after the administration of β-naphthol, and crystallizes in long needles, which melt at 150°, and are decomposed by mineral acids into β-naphthol and glycuronic acid. When sulphuric acid is added to its aqueous solution a bluish-green colouration is produced at the contact of the two liquids, and this changes to dirty green when the liquid is agitated (p. 78).

2599 *ac-Tetrahydro-β-naphthol*, $C_6H_4 : C_4H_8.OH$, is formed, together with a smaller quantity of the *ar*-reduction product, when 20 grms. of sodium are added to a boiling solution of 10 grms. of β-naphthol in 200 grms. of amyl alcohol. The hot alkaline solution is poured into water, and the layer of amyl alcohol, in which the alicyclic derivative is dissolved, is separated, washed successively with caustic soda, water, and dilute hydrochloric acid, and distilled under diminished pressure. The

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[1] Schultz, *Steinkohlentheer*, **2**, 1043.

[2] Schultz, *Steinkohlentheer*, **2**, 987.

fraction passing over at 150—205° (at 40 mm.), contains the alicyclic compound together with the aromatic isomeride, and unaltered β-naphthol. To remove these the liquid is covered with caustic soda solution, and distilled with steam, a distillate being thus obtained which only contains traces of the aromatic compound, which may be removed by treatment with a solution of sodium diazobenzene-*p*-sulphonate. The aromatic compound unites with this to form an azo-colour, whilst the alicyclic derivative remains unaltered and is extracted by ether, and purified by distillation under diminished pressure.[1]

It is a clear, colourless, very viscid oil, which has a smell resembling that of sage, and boils without decomposition at 264°, under a pressure of 716 mm. It solidifies in a mixture of solid carbonic acid and ether to a hard, gummy mass. It is only very slightly soluble in water, but readily in alcohol and other solvents.

ac-Tetrahydro-β-naphthol is insoluble in alkalis and does not combine with diazo-salts. Sodium acts upon it as upon the fatty alcohols, and in nearly all its reactions it behaves as a substituted benzene derivative containing the hydroxyl group in a side chain, closely resembling borneol and menthol (Part V. pp. 428, 471), which have a similar constitution. This conclusion is confirmed by the fact that it forms *o*-carboxyhydrocinnamic acid on oxidation.

When heated with solid caustic potash it is decomposed into water and dihydronaphthalene:

$$C_{10}H_{11}(OH) = C_{10}H_{10} + H_2O.$$

ac-Tetrahydro-β-naphthol acetate, $C_{10}H_{11}O.CO.CH_3$, is obtained by heating tetrahydronaphthol with glacial acetic acid to 140—150°. It is a yellowish, very viscid oil, with a pleasant fruity odour, and boils at 169° under a pressure of 34 mm. When distilled under the atmospheric pressure it decomposes into acetic acid and dihydronaphthalene.

ac-Tetrahydro-β-naphthol benzoate crystallizes from alcohol in lustrous tablets, melting at 62—63°. It resembles the acetate in its behaviour on heating.

ac-Tetrahydro-β-naphthyl chloride, $C_{10}H_{11}Cl$, is obtained when tetrahydronaphthol is heated on the water bath with concentrated hydrochloric acid. It decomposes on heating, even under

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[1] Bamberger and Lodter, *Ber.* **23**, 197.

diminished pressure, into dihydronaphthalene and hydrochloric acid.

ac-Tetrahydro-β-naphthyl phenylcarbamate, $C_{10}H_{11}O.CO.NHC_6H_5$, is formed at the ordinary temperature when a mixture of 2 grms. of tetrahydronaphthol and 1·6 grms. of phenyl isocyanate is allowed to stand. It crystallizes from boiling alcohol in fascicular groups of needles, melting at 98·5°.

ac-Tetrahydro-β-naphthylxanthogenic acid, $C_{10}H_{11}O.CS.SH$, is readily obtained by the action of carbon disulphide on the sodium salt of tetrahydronaphthol at the ordinary temperature. Its *cuprous salt* crystallizes from carbon disulphide in light-yellow crusts.

ar-Tetrahydro-β-naphthol, $C_6H_3.C_4H_8.OH$, is also formed by the reduction of β-naphthol, and is thus obtained as a solution of its sodium salt, as already described. This is acidified with hydrochloric acid and distilled with steam, the distillate being extracted with ether and the residue from this purified by distillation and recrystallization from light petroleum. It has also been obtained from *ar*-tetrahydro-β-naphthylamine by the diazo-reaction.[1] It crystallizes in silver-white, lustrous flat needles, which have a faint odour of creosote, melts at 58°, and boils at 275° without decomposition (at 707 mm.). It is only slightly soluble in cold, more freely in hot water, and very readily in ether, alcohol, &c., readily dissolves in alkalis, and forms azo-colours.[2]

Bleaching powder produces a white flocculent precipitate, and ferric chloride a bluish-green colouration, accompanied by a slight turbidity, a brownish-yellow flocculent precipitate being formed when the solution is heated.

Like the corresponding α-compound, it is not acted upon by sulphuric acid or a mixture of sulphuric acid and alcohol, whereas β-naphthol is thereby converted into β-naphthylsulphuric acid and β-naphthyl ethyl ether respectively.[3]

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[1] Bamberger and Kitschelt, *Ber.* **23**, 884.

[2] Bamberger and Kitschelt, *Ber.* **23**, 885.

[3] Bamberger and Kitschelt, *Ber.* **23**, 1129.

HALOGEN SUBSTITUTION-PRODUCTS OF α-NAPHTHOL.

THE MONOCHLOR-α-NAPHTHOLS, $C_{10}H_6Cl(OH)$.

2600 The first monochloronaphthol was obtained by Grimaux from dichloronaphthydrene glycol (p. 38) by distilling it with hydrochloric acid:

$$C_{10}H_8Cl_2(OH)_2 = C_{10}H_6Cl.OH + HCl + H_2O.$$

It crystallizes in long needles, which melt at 109°, and are slightly soluble in cold, more freely in hot water.[1] An isomeric compound is formed when a salt of Schäffer's α-naphtholsulphonic acid (p. 105) is heated with phosphorus pentachloride. It is readily soluble in alcohol, crystallizes in reddish matted needles, melting at 57°, and is oxidized by chromic acid to phthalic acid, whilst concentrated nitric acid converts it into α-naphthoquinone.[2] This substance is probably identical with the first product of the action of chlorine on α-naphthol, which melts at about 54°, but has not yet been obtained pure.[3]

Chloronaphthols of known constitution have been prepared by Erdmann and Kirchhoff from the three chlorobenzaldehydes. These were heated with succinic anhydride and anhydrous potassium acetate, and thus converted into the corresponding chlorophenylparaconic acids, which were then submitted to dry distillation[4] (p. 27, and Part V. p. 364).

4′-Chlor-α-naphthol is formed from *o*-chlorophenylparaconic acid, and is only slightly soluble in water. It crystallizes from hot water in small, slender, white needles, and from carbon disulphide in yellowish plates. It melts at 131·5°, has a characteristic smell and a burning taste. With bleaching powder it gives a light-violet precipitate, and with ferric chloride a yellowish-white precipitate, the colour of which does not alter on standing. Its alkaline solution gives the same reaction as α-naphthol with 1 : 4-diazonaphthalenesulphonic acid. With picric acid it forms the compound $C_{10}H_7ClO + C_6H_3(NO_2)_3O$,

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[1] *Bull. Soc. Chim.* **18**, 208.

[2] Claus and Oehler, *Ber.* **15**, 312.

[3] Cleve, *Ber.* **21**, 891.

[4] *Annalen*, **247**, 366; **260**, 55.

which crystallizes in slender, matted, yellowish-red needles, melting at 160°, and forms a blood-red solution in chloroform.

4′-Chlor-a-naphthyl acetate, $C_{10}H_6ClO.CO.CH_3$, is prepared by boiling the chloronaphthol with acetyl chloride. It crystallizes from hot alcohol in white plates, melting at 53°.

3′-Chlor-a-naphthol was obtained from *m*-chlorophenylparaconic acid. It crystallizes from carbon disulphide in long, white prisms, which melt at 94°, and rapidly become coloured greyish-violet in the air. It gives the same reaction as 4′-chlor-*a*-naphthol with bleaching powder and diazonaphthalenesulphonic acid, whilst ferric chloride produces in its aqueous solution a yellowish precipitate, which rapidly becomes coloured greyish-violet and brown. The picric acid compound crystallizes in long, slender, bright-yellowish red, lustrous needles, and melts at 165°.

3′-Chlor-a-naphthyl acetate is formed when the chloronaphthol is boiled with acetic anhydride. It crystallizes from a mixture of alcohol and ether in rhombic tablets, melting at 47°.

2′-Chlor-a-naphthol is obtained by the distillation of *p*-chlorophenylparaconic acid, and crystallizes from hot water, in which it is only slightly soluble, in long, thin, white needles, and from carbon disulphide in small brownish needles. It melts at 123°, and has a faint smell of iodoform and a burning taste. Bleaching powder and diazonaphthalenesulphonic acid behave towards it as towards its isomerides, but ferric chloride produces a yellowish-white precipitate, which rapidly becomes a deep violet. Its picric acid compound forms slender yellowish-red silky needles, melting at 139°.

2′-Chlor-a-naphthyl acetate is an oily liquid, and has not been obtained in the solid form.

THE DICHLOR-α-NAPHTHOLS, $C_{10}H_5Cl_2(OH)$.

2601 *a*-Naphthylsulphuric acid on treatment with phosphorus pentachloride yields a dichloronaphthol which crystallizes in needles, melting at 101° (Claus and Knyrim); it is oxidized by chromic acid to dichlor-*a*-naphthoquinone, and by nitric acid to phthalic acid.[1]

2 : *4-Dichlor-a-naphthol* is formed by the action of chlorine on a well-cooled solution of *a*-naphthol in glacial acetic acid.[2] It

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[1] *Ber.* **18**, 2924. [2] Cleve, *Ber.* **21**, 891; Zincke and Kegel *Ber.* **21**, 1030.

crystallizes from alcohol or benzene in pliable, silky needles, melting at 107—108°, and from glacial acetic acid in thick, transparent needles or prisms, which contain a molecule of acetic acid and effloresce in the air. It is converted into phthalic acid by dilute nitric acid, and into monochlor-α-naphthoquinone by chromic acid. When it is heated with phosphorus pentachloride, ι-trichloronaphthalene is formed.

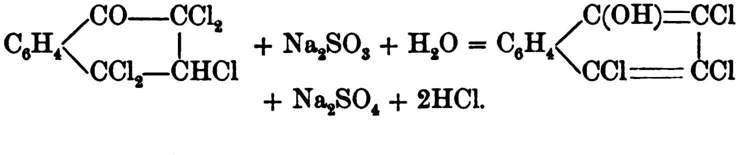
2 : 4-*Dichlor-α-naphthyl acetate*, $C_{10}H_5Cl_2O.C_2H_3O$, crystallizes from alcohol in thick needles, melting at 74—76°.

2′ : 4′-*Dichlor-α-naphthol*, was obtained by Erdmann by heating *o*-*p*-dichlorobenzaldehyde with succinic acid and fusing the dichlorophenylparaconic acid, $C_6H_3Cl_2.CH{=}CH.CH_2.CO.OH$, thus obtained. It crystallizes from carbon disulphide in large prisms, which melt at 132°. When heated with ammonia it yields the corresponding dichlor-α-naphthylamine, which is converted by the diazo-reaction into 1 : 3-dichloronaphthalene.[1]

In addition to the foregoing compounds, 1′-4′-*dichlor-α-naphthol*, melting at 114°, has been prepared from 2 : 5-dichlorophenylisocrotonic acid, and 1′ : 2′- and 2′ : 3′-*dichlor-α-naphthol* from 3 : 4-dichlorophenylisocrotonic acid.[2]

THE TRICHLOR-α-NAPHTHOLS, $C_{10}H_4Cl_3(OH)$.

2602 When a well-cooled solution of α-naphthol in acetic acid is saturated with chlorine, pentachloroketohydronaphthalene is formed (p. 125), and this substance is reduced to trichloronaphthol when sodium sulphite is added to its hot solution in acetic acid :



It crystallizes in long, silky needles, which melt at 159—160°, and are fairly soluble in hot glacial acetic acid or alcohol. It is oxidized in acetic acid solution by nitric acid to dichloro-β-naphthoquinone; a small quantity of dichlor-α-naphthoquinone is also formed in this reaction and is the chief product when chromic acid is employed as the oxidizing agent.

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[1] *Ber.* **21**, 3444.

[2] Erdmann and Schwichten, *Annalen*, **260**, 77.

Trichlor-a-naphthyl acetate, $C_{10}H_4Cl_3O.CO.CH_3$, crystallizes in long, white, silky needles, and melts at 123—124° (Zincke and Kegel).

THE BROM-α-NAPHTHOLS.

2603 *Brom-a-naphthol*, $C_{10}H_6Br(OH)$, has not yet been prepared. Its *ethyl ester*, $C_{10}H_6Br(OC_2H_5)$, was obtained by Marchetti from α-naphthyl ethyl ether by adding bromine diluted with chloroform to its solution in chloroform. It crystallizes in long, thick prisms, and melts at 48°.[1]

Dibrom-a-naphthol, $C_{10}H_5Br_2(OH)[Br : Br = 2 : 4]$ is formed by the bromination of α-naphthol in acetic acid solution,[2] and when dibrom-α-diazonaphthalene sulphate is boiled with water.[3] It crystallizes from alcohol or light petroleum in long, silky needles, which melt at 105·5°. On heating with alcoholic potash it is converted into trihydroxynaphthalene, and it is oxidized to phthalic acid by alkaline potassium permanganate.

Pentabrom-a-naphthol, $C_{10}H_2Br_5(OH)$, was obtained by Blümlein, who added 1 grm. of aluminium to 150 grms. of bromine and brought into this mixture, cooled to 0°, 10 grms. of α-naphthol, distilled off the excess of bromine, extracted the residue with cumene, and then recrystallized it from phenol. Pentabromonaphthol crystallizes from hot xylene in slender, matted needles, which are scarcely soluble in alcohol and ether, and only slightly in cumene. It melts at 238—239°, and is oxidized to dibromophthalic acid by continued boiling with nitric acid.[4]

HALOGEN SUBSTITUTION-PRODUCTS OF β-NAPHTHOL.

THE CHLORO-β-NAPHTHOLS.

2604 1-*Chloro-β-naphthol*, $C_{10}H_6Cl.OH$, was first obtained by Schall by the action of chlorine on sodium β-naphthate suspended in carbon disulphide.[5] It is also formed when

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[1] *Gazzetta*, **9**, 544.

[2] *Gazzetta*, **6**, 1117 ; Fittig and Erdmann, *Annalen*, **227**, 242.

[3] Meldola, *Journ. Chem. Soc.* 1884, **1**, 156.

[4] *Ber.* **17**, 2485.

[5] *Ber.* **16**, 1901.

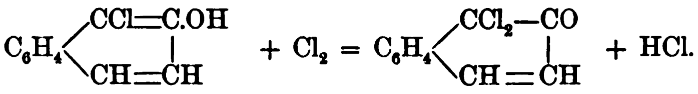
chlorine is passed into a solution of β-naphthol in acetic acid[1] and is quantitatively obtained when β-naphthol, suspended in three parts of carbon disulphide, is heated with one molecule of sulphuryl chloride.[2] It readily dissolves in alcohol or glacial acetic acid, crystallizes from hot water in micaceous scales, and from chloroform in monosymmetric prisms, melting at 70°. When it is heated with phosphorus chloride until hydrochloric acid ceases to be evolved, the product contains:

1 : 2-*Chloronaphthyl phosphate*, $(C_{10}H_6Cl.O)_3PO$, which is left when the mass is treated with water as a white powder. It is only slightly soluble in boiling alcohol, and crystallizes from it in microscopic needles, melts at 152°, and solidifies on cooling to a vitreous mass. On heating the chloronaphthol more strongly with phosphorus pentachloride, 1 : 2-dichloronaphthalene is formed.

4′-*Chloro-β-naphthol* is obtained from the corresponding β-naphthylaminesulphonic acid, and sublimes in long needles, melting at 128°.[3]

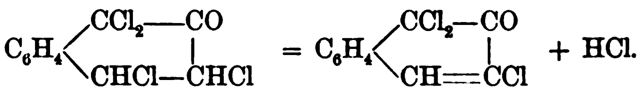
3′-*Chloro-β-naphthol* is formed, together with 2 : 3′-dichloronaphthalene, when potassium β-naphthol-β-sulphonate is heated to 165° with phosphorus pentachloride and the product distilled with water; the dichloronaphthalene is thus volatilized, and the chloronaphthylphosphoric acid, which is at first formed, decomposed. The chloronaphthol separates out, when the residue is allowed to cool, in fine needles, which melt at 115°, and sublime in lustrous, slender prisms. It is oxidized to a-chlorophthalic acid by nitric acid.[4]

1 : 3-*Dichloro-β-naphthol*, $C_{10}H_5Cl_2.OH$. When chlorine is allowed to act on β-naphthol, the 1-chloro-β-naphthol which is first formed is readily converted into dichloro-β-ketonaphthalene:



$$C_6H_4\begin{array}{l}\diagup CCl{=}C.OH\\ \qquad\quad\ |\\ \diagdown CH{=}CH\end{array} + Cl_2 = C_6H_4\begin{array}{l}\diagup CCl_2{-}CO\\ \qquad\quad\ |\\ \diagdown CH{=}CH\end{array} + HCl.$$

The latter then combines with chlorine to form tetrachloro-β-ketohydronaphthalene, which is converted by boiling with alcohol into trichloro-β-ketonaphthalene:



$$C_6H_4\begin{array}{l}\diagup CCl_2{-}CO\\ \qquad\quad\ |\\ \diagdown CHCl{-}CHCl\end{array} = C_6H_4\begin{array}{l}\diagup CCl_2{-}CO\\ \qquad\quad\ |\\ \diagdown CH{=}CCl\end{array} + HCl.$$

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[1] Cleve, *Ber.* **21**, 891.

[2] Armstrong and Rossiter, *Proc. Chem. Soc.* **1889**, 71.

[3] Claus, *J. Pr. Chem.* II. **39**, 315.

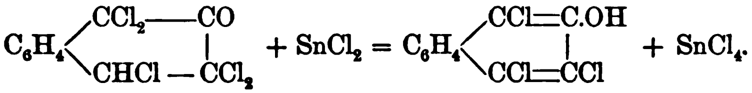
[4] Claus and Zimmermann, *Ber.* **14**, 1483; Claus and Dehn, *Ber.* **15**, 321.

This substance, on reduction with stannous chloride or sodium sulphite, yields 1 : 3-dichloro-β-naphthol, which crystallizes from hot, light petroleum in nodular masses of slender, lustrous needles, melting at 80—81°.

1 : 4-*Dichloro-β-naphthol* is formed, together with the preceding compound, by the reduction of tetrachloroketohydronaphthalene. The two substances are separated by adding a little water to the solution of the mixture in acetic acid; the precipitate thus formed consists chiefly of the 1 : 4-compound, which is purified by recrystallization from light petroleum. It forms long, hard, white needles, united to form masses resembling asbestos, and melts at 123—124°.[1]

A third dichloro-β-naphthol is formed when β-naphtholdisulphonic acid is heated with phosphorus pentachloride. It crystallizes from hot water, in which it is only slightly soluble, in small plates, melting at 125°.[2]

1 : 3 : 4-*Trichloro-β-naphthol*, $C_{10}H_4Cl_3.OH$. The trichloroketonaphthalene mentioned above combines with chlorine to form pentachloroketohydronaphthalene, which is reduced by stannous chloride to trichloro-β-naphthol:



$$C_6H_4\left\langle\begin{array}{l}CCl_2 — CO \\ \qquad\quad | \\ CHCl - CCl_2\end{array}\right. + SnCl_2 = C_6H_4\left\langle\begin{array}{l}CCl{=}C.OH \\ \qquad\quad | \\ CCl{=}CCl\end{array}\right. + SnCl_4.$$

It crystallizes from glacial acetic acid in needles, and melts at 162° (Zincke).

THE BROMO-β-NAPHTHOLS.

2605 1-*Bromo-β-naphthol*, $C_{10}H_6Br.OH$, is obtained by the action of bromine on a solution of β-naphthol in glacial acetic acid, and crystallizes in lustrous needles, which melt at 84°, and are readily soluble in alcohol. On oxidation it yields phthalic acid.[3]

Dibromo-β-naphthol, $C_{10}H_5Br_2.OH$, is formed when one molecule of β-naphthol is treated with two molecules of bromine. It crystallizes from light petroleum in woolly needles, melting at 106°, whilst it separates from acetic acid in prisms melting at 84°, and containing a molecule of acid which is lost in the air.

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[1] Zincke, *Ber.* **21**, 3378.

[2] Claus and Schmidt, *Ber.* **19**, 3172.

[3] A. J. Smith, *Journ. Chem. Soc.* 1879, **1**, 789.

On oxidation with potassium permanganate it yields bromophthalic acid.[1]

Tetrabromo-β-naphthol, $C_{10}H_3Br_4.OH$, was obtained by Smith by employing an excess of bromine. It crystallizes in white needles, melting at 156°, and is also oxidized by potassium permanganate to a bromophthalic acid.

Pentabromo-β-naphthol, $C_{10}H_2Br_5.OH$, is formed when a small quantity of aluminium is dissolved in bromine and β-naphthol gradually added. It is insoluble in alcohol, ether, and glacial acetic acid, slightly soluble in hot benzene, and more readily in nitrobenzene, from which it crystallizes in needles. It separates out as a crystalline precipitate, melting at 237°, when ether is added to its solution in phenol. When it is heated with dilute alcohol and caustic soda, the sodium salt is formed, and crystallizes on cooling in silky, elastic needles, which are often an inch in length. Nitric acid oxidizes it to tribromophthalic acid.[2]

2606 1-*Iodo-β-naphthol*, $C_{10}H_6I.OH$, was prepared by Meldola by dissolving 20 grms. of β-naphthol with an equal amount of lead acetate and anhydrous sodium acetate in glacial acetic acid, and dropping in a solution of 35·2 grms. of iodine in acetic acid :

$$2C_{10}H_8O + 4I + Pb(C_2H_3O_2)_2 = 2C_{10}H_7IO + PbI_2 + 2C_2H_4O_2.$$

It crystallizes from alcohol in prismatic needles, melts at 94·5°, and is oxidized to phthalic acid by potassium permanganate.[3]

NITRO-SUBSTITUTION-PRODUCTS OF α-NAPHTHOL.

2607 2-*Nitro-α-naphthol*, $C_{10}H_6(NO_2)OH$, is formed when the corresponding nitro-acetonaphthalide, $C_{10}H_6(NO_2)NH.CO.CH_3$, or nitrobenzonaphthalide, $C_{10}H_6(NO_2)NH.CO.C_6H_5$, is boiled with caustic potash solution,[4] and when sodium nitrite is added to an acid solution of α-diazonaphthalene sulphate.[5] It crystallizes in

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[1] Armstrong and Rossiter, *Proc. Chem. Soc.* **1889**, 71.

[2] Flessa, *Ber.* **17**, 1479.

[3] *Journ. Chem. Soc.* 1855, **1**, 525.

[4] Liebermann, *Annalen*, **183** 245 ; Lellmann and Remy, *Ber.* **19**, 801 ; Worms, *Ber.* **15**, 1873.

[5] Deninger, *Journ. Chem. Ind.* **8**, 538.

long, narrow, greenish-yellow plates, melting at 128°, is only slightly soluble in dilute alcohol, even less readily in water, and volatilizes with steam like *o*-nitrophenol.

Potassium 2-nitro-a-naphthate, $C_{10}H_6(NO_2)OK$, crystallizes in purple-red needles.

Barium 2-nitro-a-naphthate, $[C_{10}H_6(NO_2)O]_2Ba+3H_2O$, forms lustrous red needles.

4 : 1-*Nitronaphthol* was first obtained by Dusart in small quantity by the continued action of caustic potash and lime on *a*-nitronaphthalene in presence of air, and was named by him nitro-oxynaphthalenic acid.[1] Darmstädter and Nathan then recognised it as a nitronaphthol.[2] It is prepared in a similar manner to the preceding compound from the corresponding nitrated naphthalide.[3] It is readily soluble in alcohol, and crystallizes from hot water in golden-yellow needles, which melt at 164°, and are not volatile with steam.

$C_{10}H_6(NO_2)OK$, small, deep orange-red crystals.
$C_{10}H_6(NO_2)ONa + 2H_2O$, brilliant, carmine-red needles.
$(C_{10}H_6(NO_2)O)_2Ba + H_2O$, lustrous, dark-red needles, with a blue surface lustre.[4]

Its sodium salt was formerly manufactured and sold under the name of *French yellow* or *chryseïc acid*.

2-*Bromo-4-nitro-a-naphthol*, $C_{10}H_5Br(NO_2)OH$, was obtained by Meldola by heating the corresponding acetobromonitronaphthalide with concentrated caustic soda solution. It crystallizes from alcohol in silky-yellow needles, which melt with decomposition at about 136°.[5] An isomeric compound was obtained by Biedermann and Remmers from the acetobromonitronaphthalide, melting at 229°. It crystallizes in golden-yellow needles, melts at 142° and commences to decompose at 145°.[6]

4-*Iodo-2-nitro-a-naphthol*, $C_{10}H_5I(NO_2)OH(4:2:1)$, was prepared by Meldola from acetiodonitronaphthalide. It is insoluble in cold, and scarcely soluble in boiling water, crystallizes from alcohol in yellow needles, melting at 145—146°, and dyes silk or wool a fine yellow.

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[1] *Compt. Rend.* **52**, 1183.
[2] *Ber.* **3**, 943.
[3] Andreoni and Biedermann, *Ber.* **6**, 342; Hübner, *Annalen*, **208**, 325.
[4] Biedermann, *Ber.* **6**, 1117.
[5] *Journ. Chem. Soc.* 1885, **1**, 497.
[6] *Ber.* **7**, 538.

2608 *Dinitro-a-naphthol*, $C_{10}H_5(NO_2)_2OH(4:2:1)$. In 1856 Ganahl and Chiozza obtained a fine yellow colouring matter with acid properties, to which they provisionally assigned the formula $C_9H_6N_2O_4$, by the action of nitrous fumes on the nitrate of amidonaphthalene moistened with a little water;[1] this formula was changed to $C_{10}H_6NO_4$ by Gerhardt,[2] who looked upon the compound as the imide of a dibasic acid, $C_{10}H_7(NO_2)O_4$. It was then found by Martius in 1865 that when a solution of *a*-amidonaphthalene hydrochloride is treated in dilute solution with the amount of potassium nitrite necessary to form a diazo-salt, the calculated quantity of nitric acid added, and the whole gradually heated to boiling, a vigorous evolution of nitrogen takes place, and a yellow, frothy mass of dinitronaphthol separates out.[3]

Darmstädter and Wichelhaus have subsequently observed that the same compound is formed when a solution of *a*-naphtholsulphonic acid is brought into nitric acid and gently heated.[4] Resinous products are formed in considerable quantity in this reaction, whereas *a*-naphthol-2:4-disulphonic acid is quantitatively converted into dinitronaphthol under the same conditions.[5] According to Ballo it is also formed by the action of fuming nitric acid on *a*-naphthylamine,[6] and when the nitro-*a*-naphthols are boiled with nitric acid in dilute alcoholic solution.[7] It was also obtained by Darmstädter and Nathan by adding potassium nitrite to a solution of *a*-naphthol in sulphuric acid, and R. S. Dale observed that it is formed when a solution of *a*-naphthylamine in aqueous sulphuric acid is saturated with nitrogen trioxide, evolved by the action of sulphuric acid on sodium nitrite, and then heated to boiling.[8]

It was at first prepared on the large scale by adding sodium nitrite to an acid solution of *a*-naphthylamine until a small quantity of the liquid gave a cherry-red precipitate of diazo-amidonaphthalene with caustic soda, and then adding nitric acid and heating slowly to the boiling-point. Instead of following this process, Messrs. Roberts, Dale, and Co. dissolved the naphthylamine in an excess of tolerably concentrated sulphuric acid, added sodium nitrite, and heated the mixture; the froth of dinitronaphthol was then removed, and *a*-naphthlyamine

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[1] *Annalen*, **99**, 242.
[2] *Traité*, **4**, 1026.
[3] *Jahresb.* **1865**, 568.
[4] *Annalen*, **152**, 298.
[5] Bender, *Ber.* **22**, 969.
[6] *Ber.* **3**, 288.
[7] Darmstädter and Nathan, *Ber.* **3**, 943; Liebermann, *Annalen*, **183**, 249.
[8] Private communication.

together with the necessary quantities of sulphuric acid and sodium nitrite added to the cold mother-liquor. A fresh quantity of dinitronaphthol was formed on heating, and this process was continued until the mother-liquor became too concentrated. At the present time α-naphthol is cheaper than α-naphthylamine and is therefore used for the preparation of dinitronaphthol. It is either dissolved in an equal weight of sulphuric acid, and the solution, which contains 1 : 2 : 4-naphtholdisulphonic acid, heated with nitric acid or, more simply, heated to 100° with a mixture of nitric and sulphuric acids.

Dinitronaphthol is scarcely soluble in boiling water, only slightly in alcohol, ether, or benzene, and crystallizes in lemon-yellow needles or from glacial acetic acid in long prisms,[1] melting at 138°. It dissolves in cold concentrated nitric acid without decomposition, but is oxidized on heating to oxalic and phthalic acids.

Sodium dinitronaphthate, $C_{10}H_5(NO_2)_2ONa + H_2O$, is readily soluble in water and crystallizes in small yellowish-red needles.

Calcium dinitronaphthate, $[C_{10}H_5(NO_2)_2O]_2Ca + 6H_2O$, forms long, orange-yellow needles, which are not readily soluble in water.

Both of these salts occur in commerce under the name of *Martius Yellow* or *Manchester Yellow,* because dinitronaphthol was first manufactured by Roberts, Dale and Co. It is also known as *Safran Yellow* and *Jaune d'Or.* The acidified solution of these salts dyes silk or wool a brilliant golden-yellow, and in combination with red colours produces various shades of reddish-yellow to scarlet, whereas picric acid does not give such good mixed shades, inasmuch as when applied alone it dyes a greenish-yellow.

Naphthol yellow is poisonous to many animals. Rabbits are not much affected by it, but dogs are killed even by relatively small doses. A dog weighing 6,850 grms., for example, was killed by doses of 0·5 grm. of the sodium salt on two consecutive days, and 1 grm. on the third day, on which it died, whilst four doses of 0·1 grm. each per day, and 0·2 grms. administered by subcutaneous injection, sufficed to kill a dog weighing 8,800 grms.[2]

Ethyl dinitro-α-naphthate, $C_{10}H_5(NO_2)_2OC_2H_5$, was obtained by Martius from the silver salt by the action of ethyl iodide. It crystallizes from alcohol in long, yellow needles, and melts at 88°.

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[1] Ekstrand, *Ber.* **11**, 162.

[2] Weyl, *Ber.* **21**, 2191.

Naphthylpurpuric acid, $C_{11}H_7N_3O_4$, is not known in the free state. Its potassium salt is best prepared by dissolving 6 parts of dinitro-α-naphthol in 40 times its weight of boiling alcohol, and gradually adding a solution of potassium cyanide in dilute alcohol:

$$C_{10}H_6N_2O_5 + 2KCN + 2H_2O = C_{11}H_6KN_3O_4 + KHCO_3 + NH_3.$$

It crystallizes from hot water in irregular brown microscopic plates, which have a dull appearance after drying, whereas if it be pressed when damp it is obtained as a mass which has a green surface lustre, and forms a dark, reddish-brown solution in water. On heating with nitric acid, nitronaphthol, dinitronaphthol and oxalic acid are formed, whilst fusion with potash yields benzoic acid, phthalic acid, and hemimellitic acid.

Indophane, $C_{22}H_{10}N_4O_4$, is formed, together with the preceding compound, when aqueous solutions are employed, and is a violet mass which has a green metallic lustre, is insoluble in water, alcohol, &c., and forms purple-red solutions in sulphuric acid and hot glacial acetic acid. When it is heated with caustic potash, the insoluble compound $C_{22}H_9KN_4O_4 + H_2O$ is formed, which after drying shows the colour and lustre of indigo, a characteristic which is shared by the sodium salt.

On fusion with caustic potash it yields the same products as potassium naphthylpurpurate.[1]

Trinitro-α-naphthol, $C_{10}H_4(NO_2)_3OH$, which is also called *naphthopicric acid*, is formed by the action of nitric and sulphuric acids on dinitro-α-naphthol,[2] and is only slightly soluble in water, alcohol, and benzene. It crystallizes from hot glacial acetic acid in light-yellow, glittering plates or small prisms, which melt at 176°, and yield *v*-nitrophthalic acid on oxidation. Its yellow or red salts crystallize readily, and detonate on heating.

Ethyl trinitro-α-naphthate, $C_{10}H_4(NO_2)_3OC_2H_5$, was prepared by Städel from α-naphthyl ethyl ether by direct nitration; it crystallizes from alcohol in lustrous, yellow needles, which melt at 148°.[3]

Tetranitro-α-naphthol, $C_6H_3(NO_2)_4OH$, is formed when tetranitro-α-bromonaphthalene is heated with sodium carbonate solution, and crystallizes from hot glacial acetic acid or benzene

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[1] Sommaruga, *Annalen*, **157**, 327.

[2] Ekstrand, *Ber.* **11**, 161; Merz and Diehl, *Ber.* **11**, 1661.

[3] *Annalen*, **217**, 170.

in yellow, lustrous splinters or flat needles, melting at 180°. It is oxidized by dilute nitric acid to *a*-dinitrophthalic acid. Its yellow or red salts are only slightly soluble in water, readily in alcohol.[1] It dyes silk and wool a fine yellow, and was for some time sold under the name of "Sonnengold" or *Heliochrysine*; it was afterwards given up since it fades in the light.

NITRO-SUBSTITUTION-PRODUCTS OF β-NAPHTHOL.

2609 1-*Nitro-β-naphthol*, $C_{10}H_6(NO_2)OH$, was first obtained by Stenhouse and Groves by the oxidation of nitroso-β-naphthol.[2] Liebermann and Jacobsen then prepared it by boiling nitro-β-acetonaphthalide with dilute caustic soda solution.[3] It crystallizes from alcohol in small yellow plates, needles or prisms, melting at 103°. Its *sodium salt* crystallizes in red prisms, and is insoluble in caustic soda solution.

Nitro-β-naphthyl acetate, $C_{10}H_6(NO_2)O.C_2H_3O$, is formed by the action of acetyl chloride on the sodium salt, and crystallizes from light petroleum in long colourless needles, melting at 61°.[4]

Dinitro-β-naphthol, $C_{10}H_5(NO_2)_2OH$, is formed when an alcoholic solution of β-naphthol is heated with dilute nitric acid.[5] It is, however, best obtained from β-amidonaphthalene by dissolving 50 grms. of this with 30 grms of hydrochloric acid in 1 litre of water, cooling the solution to 30—40°, and adding a mixture of 100 grms. of sulphuric acid and 1 litre of water; the whole is then diluted to 3 litres, cooled to 15°, and treated with a solution of 25 grms. of sodium nitrite in water. When the precipitated β-amidonaphthalene sulphate has redissolved, the liquid is boiled with 400 c.c. of nitric acid of sp. gr. 1·35.[6]

It crystallizes in lustrous, light-yellow needles, which become brown, and melt at 195°, and are very slightly soluble in boiling water, more readily in alcohol, and readily in ether. It dyes wool and silk a fine yellow. Most of its salts are only slightly soluble in water. On oxidation it yields a-nitrophthalic acid, and can be converted into a triamido-compound which contains two amido-groups in the ortho- (1 : 2) position.[7]

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[1] Merz and Weith, *Ber.* **15**, 2708.

[2] *Annalen*, **189**, 145.

[3] Wallach and Wichelhaus, *Ber.* **3**, 846.

[4] Böttcher, *Ber.* **16**, 1933.

[5] Wallach and Wichelhaus, *loc. cit.*

[6] Gräbe and Drews *Ber.* **17**, 1170.

[7] Loewe, *Ber.* **23**, 2546.

Ethyl dinitro-β-naphthate, $C_{10}H_5(NO_2)_2.OC_2H_5$, crystallizes in light-yellow needles, and melts at 138°.

Ethyl trinitro-β-naphthate, $C_{10}H_4(NO_2)_3.OC_2H_5$, is obtained by the nitration of ethyl-β-naphthyl ether, and crystallizes in large, light-yellow, lustrous needles, melting at 186°.[1]

Dinitro-β-naphthol ethyl ether, $C_{10}H_5(NO_2)_2(OC_2H_5)$ (2 : 4′ : 1′), is obtained by the action of well-cooled fuming nitric acid on the diethyl ether of β-naphtholmonosulphide. It crystallizes from alcohol in long, slender, silky, light-yellow needles, melting at 215°. On oxidation with dilute nitric acid at 160° it yields dinitrophthalic acid ($CO_2H : CO_2H : NO_2 : NO_2 = 1 : 2 : 3 : 6$).[2]

Trinitrochloronaphthol is obtained by heating trinitrodichloronaphthalene with caustic soda solution and a little alcohol. It crystallizes from glacial acetic acid in light-yellow needles, which contain a molecule of acetic acid, and melt with decomposition at 156°.[3] It forms crystalline, orange-coloured salts.

THE SULPHONIC ACIDS OF α-NAPHTHOL.

α-NAPHTHOL-α-SULPHONIC ACIDS.

2601 1 : 4-*Naphtholsulphonic acid*, $C_{10}H_6(OH)SO_3H$, was obtained by Erdmann from 1 : 4-naphthylaminesulphonic acid, which is usually termed naphthionic acid, by converting it into the diazo-compound, and bringing this in the moist state into a boiling mixture of 100 grms. of concentrated hydrochloric acid and 400 grms. of water. It was then converted into the lead salt, and the latter decomposed by sulphuretted hydrogen in aqueous solution.[4] It crystallizes in transparent tablets, which become dark-coloured at 120°, and melt at 170° with evolution of gas when they are rapidly heated. Dilute nitric acid converts it into dinitro-α-naphthol, resinous products being also formed. Its aqueous solution has a strongly acid reaction, and an astringent taste; ferric chloride produces in it a fugitive blue colouration which becomes red on heating and disappears again when the solution cools. When potassium dichromate is added to the aqueous solution a brownish-red colouration is produced, and the liquid becomes turbid on heating; if sulphuric

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[1] Städel, *Annalen*, **217**, 171.

[2] Onufrowicz, *Ber.* **23**, 3361.

[3] Cleve, *Ber.* **23**, 957.

[4] *Annalen*, **247**, 341.

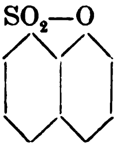
acid be now added a smell of α-naphthoquinone becomes perceptible, and this substance soon separates out in yellow, glittering crystals.

A solution of the acid gives with 1 : 4-diazonaphthalene sulphonic acid in presence of sodium acetate a bluish-red colouring matter (Azorubin S.), which is neither altered by acids nor alkalis. The acid is prepared on the large scale by heating 100 kilos of sodium naphthionate with 100 kilos of caustic soda solution of 50 per cent. for 8—10 hours to 240—260° under pressure.[1]

According to the patent of Dahl and Co., it is obtained by diazotising 20 kilos. of naphthionic acid with 7 kilos. of sodium nitrite, filtering off the diazo-acid formed, pressing, and then bringing it into 100 litres of boiling water acidified with sulphuric acid. As soon as the evolution of gas has ceased, the solution is neutralized with milk of lime, and the calcium salt converted into the *sodium salt*, which is soluble in alcohol of 90 per cent., from which it crystallizes in large needles. It is employed in the preparation of azo-colouring matters.[2]

1 : 4′-*Naphtholsulphonic acid* was prepared by Erdmann from the corresponding naphthylaminesulphonic acid; it forms an indistinctly crystalline mass, which melts at 110—120°, and yields with 1 : 4-diazonaphthalenesulphonic acid a colouring matter, which can only be distinguished from the corresponding 1 : 4-derivative by its somewhat bluer shade.

1 : 1′-*Naphtholsulphonic acid* is not formed in the free state when 1 : 1′-diazonaphthalenesulphonic acid is treated with water, alcohol, or dilute acids, but forms an anhydride which may be considered as a kind of lactone :[3]



Naphthosultone, $C_{10}H_6O_3$, as it is termed by Erdmann, is the first example of a new class of compounds, the *sultones* (contracted from sulpholactones), which are derived from the γ-hydroxysulphonic acids in the same way as the lactones from the γ-hydroxycarboxylic acids.

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[1] Actiengesellsch. Anilinfarb. Berlin. *Ber.* **22**, 116 c.

[2] Schultz, *Steinkohlentheer*, **1**, 629.

[3] Schultz, *Ber.* **21**, 3162.

Naphthosultone is scarcely soluble in water, slightly in alcohol, but readily in hot benzene, from which it crystallizes on gradual evaporation in very broad, transparent prisms, which have a vitreous lustre, and melt at 154°. It boils above 360°, and forms a vapour the specific gravity of which is 7·26 (Erdmann).

Its great stability towards alkalis is remarkable, as it is not altered by these in the cold, but forms 1 : 1′-naphtholsulphonates on heating, the solution simultaneously becoming yellow.

The free 1 : 1′-naphtholsulphonic acid is obtained by decomposing the lead salt, suspended in water, with sulphuretted hydrogen. The solution can be concentrated over the Bunsen flame without any alteration of the acid. If it be then allowed to evaporate in a vacuum over sulphuric acid, the 1 : 1′-naphtholsulphonic acid is obtained as a radiating brittle crystalline mass, which contains a molecule of water, is readily soluble in water, and has an acid reaction and a bitter taste. Its great stability on heating is exceptional; it melts at 106—107° and solidifies immediately on cooling. If it be more strongly heated it boils violently at 180° and gives off its water of crystallization, after which it does not solidify on cooling, but dissolves completely when brought into water. At a still higher temperature partial carbonization occurs, sulphur dioxide is given off and a slight sublimate of naphthosultone is formed.

Potassium 1 : 1′-naphtholsulphonate, $C_{10}H_6(OK)SO_3K$. When naphthosultone is heated under pressure with concentrated caustic potash solution, a basic salt separates out on cooling in needles, and is readily converted by hydrochloric acid into the soluble normal salt; the latter is precipitated from solution by potassium chloride in small lustrous plates.

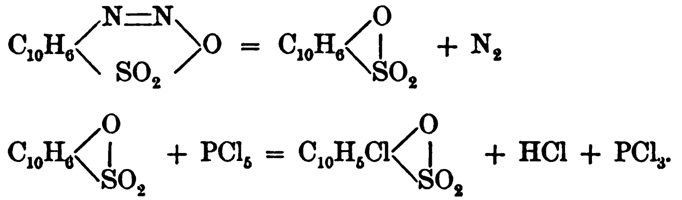
Basic Sodium 1 : 1′-naphtholsulphonate, $2C_{10}H_6(ONa)SO_3Na + 3H_2O$, has been obtained by boiling the ammonium salt with caustic soda; it is also readily soluble in water, and crystallizes from caustic soda solution, in which it is only slightly soluble even on heating, in masses of small needles.

Ammonium 1 : 1′-naphtholsulphonate, $C_{10}H_6(OH)SO_3NH_4$, is formed when the sultone is heated to 130° with dilute alcoholic ammonia; it crystallizes in lustrous plates, which are readily soluble in water.

Basic Lead 1 : 1′-naphtholsulphonate, $C_{10}H_6OPbSO_3 + 3H_2O$, is a white amorphous or microcrystalline precipitate, which is obtained by adding lead acetate to a hot solution of the ammonium salt and boiling up the liquid for an instant.

When sodium acetate and 1 : 4-diazonaphthalenesulphonic acid are added to a solution of the ammonium salt, a reddish-yellow azo-colouring matter is obtained, the colour of which is converted into yellow by acids and deep-violet by alkalis. Ferric chloride added to a solution of the acid or its ammonium salt produces a splendid dark-green colouration, which passes through yellow to red; the careful addition of hydrochloric acid renders the colour still finer, but it is destroyed by an excess of the acid.

Chloronaphthosultone, $C_{10}H_5ClSO_3$, is formed, instead of 1 : 1'-dichloronaphthalene (p. 41), when 1 : 1'-diazonaphthalenesulphonic acid is heated with phosphorus pentachloride:



$$C_{10}H_6\left<\begin{matrix}N{=}N\\SO_2\end{matrix}\right>O = C_{10}H_6\left<\begin{matrix}O\\|\\SO_2\end{matrix}\right. + N_2$$

$$C_{10}H_6\left<\begin{matrix}O\\|\\SO_2\end{matrix}\right. + PCl_5 = C_{10}H_5Cl\left<\begin{matrix}O\\|\\SO_2\end{matrix}\right. + HCl + PCl_3.$$

Chloronaphthosultone crystallizes from alcohol in long yellow needles, melts at 174—175°, and dissolves in a boiling concentrated solution of caustic potash; on cooling a yellow salt is deposited, the aqueous solution of which is coloured dark green by ferric chloride, the colour changing rapidly to a splendid magenta (Erdmann).

α-NAPHTHOL-β-SULPHONIC ACIDS.

2611 1 : 2-*Naphtholsulphonic acid* was obtained by Schäffer, who described it as *α-naphtholsulphonic* acid, by heating α-naphthol on the water-bath with twice its weight of sulphuric acid until it was completely dissolved and not precipitated by the addition of water; he then prepared the lead salt and decomposed this with sulphuretted hydrogen.[1]

1 : 2-Naphtholsulphonic acid crystallizes in radiating masses of long needles, is very deliquescent, and becomes brown and melts at 101°. Ferric chloride added to the aqueous solution produces a deep-blue colouration, which becomes green on heating, but changes back again to blue on cooling.

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[1] *Annalen*, **152**, 293.

Calcium 1 : 2-*naphtholsulphonate*, $(C_{10}H_7SO_4)_2Cu + 3H_2O$, crystallizes in small very lustrous plates, which are readily soluble in water, less readily in alcohol.

Lead 1 : 2-*naphtholsulphonate*, $(C_{10}H_7SO_4)_2Pb + 4H_2O$, forms aggregates of small needles, and is readily soluble in water.

The constitution of this acid follows from the fact that it is converted by the further action of sulphuric acid into a disulphonic acid, which is also obtained from 1 : 4-naphtholsulphonic acid, and which is quantitatively converted by nitric acid into dinitro-*a*-naphthol.[1]

Dinitro-a-naphtholsulphonic acid, $C_{10}H_4(NO_2)_2(OH)SO_3H$, was discovered by Caro, who obtained it by heating *a*-naphtholtrisulphonic acid with nitric acid. Lauterbach, who carefully investigated it, found that it is not formed by the action of sulphuric acid on dinitronaphthol.[2] It is also obtained when sulphuric acid is added to a boiling solution of calcium *a*-naphthylaminetrisulphonate, sodium nitrate, and sodium nitrite.[3]

Dinitronaphtholsulphonic acid crystallizes best from hydrochloric acid, in long yellow needles, and is an excellent yellow dye, which is superior to dinitronaphthol because it is not volatile and therefore adheres more firmly to the fibre and withstands steaming. It also differs from dinitronaphthol in not being poisonous (p. 99).

Grübe has shown that dinitronaphtholsulphonic acid is oxidized to a-sulphophthalic acid when its aqueous solution is heated with nitric acid, and it follows from this that the sulpho-group is in the position 2′ or 3′.[4] This point has been decided by Armstrong and Wynne, who have found that dinitronaphtholsulphonic acid is also obtained when *a*-naphthylamine -4 : 2′-disulphonic acid is diazotized and the product heated with nitric acid.[5] Its constitution is therefore $NO_2 : NO_2 : SO_3H = 2 : 4 : 2'$.

Potassium dinitronaphtholsulphonate, $C_{10}H_4(NO_2)_2(OK)SO_3K$, is slightly soluble in cold, more freely in hot water, and forms lemon-yellow crystalline crusts, which become coloured deep-red on heating and then detonate. It is found in the market under the names of *Naphthol yellow* S, or *Acid yellow* S. It is converted by dilute sulphuric acid into the more soluble *acid salt*, $C_{10}H_4(NO_2)_2(OH)SO_3K$.

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[1] Bender, *Ber.* **22**, 993.

[2] *Ber.* **13**, 2028.

[3] Farbwerke, vorm. Meister, Lucius and Brüning, *Ber.* **16**, 1517.

[4] *Ber.* **18**, 1126.

[5] *Proc. Chem. Soc.* **1889—1890**, 16.

α-NAPHTHOLDISULPHONIC ACIDS, $C_{10}H_5(OH)(SO_3H)_2$.

2612 Bender found that 1 : 2- and 1 : 4-naphtholsulphonic acids are the first products of the action of sulphuric acid on α-naphthol, and that these are then rapidly converted into

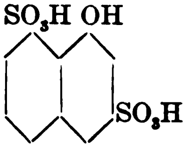
1 : 2 : 4-*Naphtholdisulphonic acid.* When much sulphuric acid is used, and especially when it is fuming sulphuric acid, this disulphonic acid is converted into a trisulphonic acid which passes into a new disulphonic acid as the temperature rises. If only a small amount of ordinary sulphuric acid be employed, the trisulphonic acid is formed in very small quantity, and the 1 : 2 : 4-disulphonic acid is converted into the isomeric acid, which yields azo-colours and is converted by nitric acid into dinitronaphtholsulphonic acid, resinous products being also formed. 1 : 2 : 4-Naphtholdisulphonic acid, on the other hand, does not yield azo-colours, and is quantitatively converted into dinitronaphthol by nitric acid, whilst on boiling with hydrochloric acid or dilute sulphuric acid a sulpho-group is lost and a mixture of 1 : 2- and 1 : 4-naphtholmonosulphonic acids formed.

1 : 3 : 1′-*Naphtholdisulphonic acid,* is prepared from the corresponding α-naphthylaminedisulphonic acid by converting the sodium salt into the diazo-compound, suspending this in water, adding a little sulphuric acid and boiling. Its *sodium salt,* $C_{10}H_5(OK)(SO_3Na)_2 + 6H_2O$, crystallizes in long prisms and is readily soluble in water; its solution is coloured deep-blue by ferric chloride. Concentrated nitric acid acts vigorously upon it on warming, but without the production of a colouring matter analogous to naphthol-yellow. With diazo-compounds it yields colouring-matters, which are remarkable for their purity of shade.

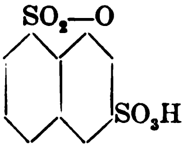
Naphthosultonesulphonic acid, $C_{10}H_5(O-SO_2)SO_3H$, is formed when the diazo-compound is only boiled until the evolution of nitrogen has ceased and the solution then rapidly cooled, the *sodium salt,* $C_{10}H_5(SO_3)SO_3Na + 3H_2O$, being thereby obtained in long needles. The free acid also crystallizes in needles, and, as well as its alkali salts, is readily converted into the disulphonic acid. When it is brought into a solution of ammonia, on the other hand, *naphtholsulphamidosulphonic acid,* $C_{10}H_5(OH)(SO_2.NH_2)SO_3H$, is formed. This acid crystallizes in coarse needles or long, slender prisms, and is moderately soluble in cold water.

These compounds have the following constitutions :[1]

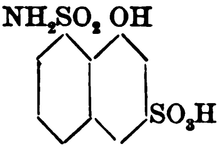
Disulphonic Acid.



Sultonesulphonic Acid.



Sulphamidosulphonic Acid.



1 : 4 : 1′-*Naphtholdisulphonic acid*, or *a-Naphtholdisulphonic acid δ*, may be obtained from 1 : 1′-amidonaphthalenesulphonic acid by either of two methods.[2]

The amido-acid may be converted by further sulphonation into *a*-naphthylaminedisulphonic acid δ, which is then diazotized, or the 1 : 1′ acid itself may be diazotized and the naphthosultone thus formed further sulphonated. The *sodium salt* is very readily soluble in water, crystallizes in plates, and gives a deep-blue colouration with ferric chloride.

1 : 4 : 1′-*Naphthosultonesulphonic acid*, $C_{10}H_5(SO_2.O)SO_3H$, is formed by the action of concentrated sulphuric acid on the preceding compound, and is the first product of the sulphonation of naphthosultone. It is prepared by bringing 1 part of the latter into 8 parts of cooled sulphuric acid, containing 5 per cent. of anhydride, allowing the mixture to stand for an hour, and then pouring it gradually into a mixture of 12 parts of ice and 16 parts of saturated salt solution, which must be well stirred and cooled. The *sodium salt*, which is thus formed, crystallizes from water, in which it is much less soluble than the salt of the disulphonic acid, in elongated hexagonal plates containing three molecules of water. It gives no colouration with ferric chloride. On boiling with an alkali, or for some time with dilute sulphuric acid or water, the corresponding salt of *a*-naphtholdisulphonic acid is formed.

a-Naphtholsulphamidosulphonic acid δ, $C_{10}H_5(OH)(SO_2NH_2)SO_3H$. The sodium salt of this acid is formed when sodium naphthosultonesulphonate is brought into concentrated ammonia solution. It crystallizes in rhomboid plates, containing two molecules of water (Bernthsen).

a-Naphtholtrisulphonic acid, $C_{10}H_4(OH)(SO_3H)_3$, is formed, as already mentioned, from the 1 : 2 : 4-disulphonic acid. It crystal-

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[1] Bernthsen, *Ber.* **22**, 3327.

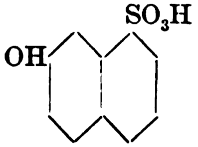
[2] German Patent 40571, December 23rd, 1885 ; Bernthsen, *Ber* **23**, 3090.

lizes with difficulty in slender needles, and forms a readily soluble potassium salt, which crystallizes well (Lauterbach). Nitric acid converts it quantitatively into dinitronaphtholsulphonic acid, so that the sulpho-groups must have the position 2 : 4 : 2′.

THE SULPHONIC ACIDS OF β-NAPHTHOL.

2613 The first product of the action of sulphuric acid on β-naphthol is β-naphthyl sulphate, which is then mainly converted into β-naphthol-α-sulphonic acid; this subsequently passes into the β- and δ-acids, from which the disulphonic acids are formed on further heating (p. 28).[1]

β-Naphthol-α-sulphonic acid, which is also known as croceïc acid, is formed, together with its isomerides, when β-naphthol is rapidly added to twice its weight of concentrated sulphuric acid, but the temperature not allowed to rise above 50—60°.[2] It has also been obtained from the corresponding β-naphthylamine-sulphonic acid by means of the diazo-reaction.[3] It is only known in solution, since it decomposes into β-naphthol and sulphuric acid on evaporation. It may be separated from the β-acid by means of its basic salts, which are readily soluble in alcohol. On heating its salts with phosphorus pentachloride, 1 : 2′-dichloronaphthalene is formed, whilst α-naphthalene-sulphonic acid is produced when the hydroxyl group is replaced by hydrogen;[4] on oxidation it yields v-sulphophthalic acid,[5] and has therefore the following constitution:



Normal sodium β-naphthol-α-sulphonate, $C_{10}H_6(OH)SO_3Na$, crystallizes in lustrous, six-sided plates, which are readily soluble in water, but only slightly in alcohol.

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[1] Armstrong, *Ber.* **15**, 200; Green, *Journ. Chem. Soc.* 1889, **1**, 33; Schultz, *Steinkohlentheer*, **1**, 642.

[2] Farbwerke, vorm. Bayer and Co., *Ber.* **15**, 1351, 1352.

[3] Bad. Anilin-und Sodafabrik, *Ber.* **16**, 448; Bayer and Duisberg, *Ber.* **20**, 1426.

[4] Pfitzinger and Duisberg, *Ber.* **22**, 396; Nietzki and Zübelin, *Ber.* **22**, 453.

[5] Nölting, *Ber.* **22**, 454.

Basic sodium β-naphthol-a-sulphonate, $C_{10}H_6(ONa)SO_3Na$, crystallizes from hot alcohol in spherical aggregates of slender needles, and is soluble in water in every proportion.

The normal and basic salts of calcium and barium are readily soluble in water, but not in absolute alcohol.

Lead β-naphthol-a-sulphonate, $2(C_{10}H_7O.SO_3)_2Pb + 5H_2O$, crystallizes in lustrous rhombohedra, and is soluble in water and dilute alcohol.

β-Naphthol-α-sulphonic acid and its isomerides are employed for the manufacture of colouring matters which will be subsequently described. It differs from the isomeric acids inasmuch as it is converted by heating with dilute nitric acid into *dinitro-β-naphthol-a-sulphonic acid*, $C_{10}H_4(OH)(NO_2)_2SO_3H$, the *potassium salt* of which, $C_{10}H_4(OK)(NO_2)_2SO_3K$, crystallizes in small golden-yellow plates, and is called croceïn yellow, but is not employed as a dye because it is dearer than naphthol yellow S. It is converted by dilute acids into the salt, $C_{10}H_4(NO_2)_2(OH)SO_3K$, which crystallizes in long yellow needles.[1]

β-Naphthol-β-sulphonic acid, was obtained by Schäffer, who termed it β-naphtholsulphonic acid, in the same way as α-naphtholsulphonic acid is obtained from α-naphthol. It is also formed when β-naphthalenedisulphonic acid is fused with caustic potash[2] and crystallizes in small plates, which have an unctuous touch, are not deliquescent, dissolve readily in water and alcohol, and melt at 125°. Its aqueous solution is coloured a faint green by ferric chloride, and deposits a brown flocculent precipitate on heating. When the salts of the acid are heated with phosphorus chloride, 2 : 3′-dichloronaphthalene is formed.[3]

Calcium β-naphthol-β-sulphonate, $(C_{10}H_7O.SO_3)_2Ca + 5H_2O$, crystallizes in light, silky plates, which are readily soluble in water and alcohol.

Lead β-naphthol-β-sulphonate, $(C_{10}H_7OSO_3)_2Pb + 6H_2O$, is, readily soluble in water, less freely in alcohol, and forms silvery plates.

β-Naphthol-δ-sulphonic acid, is formed, together with the β-β-acid when β-naphthol is heated to 100° with sulphuric acid,[4] and when α-naphthalenedisulphonic acid is heated with

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[1] Farbwerke, vorm. Bayer and Co., German Patent, No. 18027 ; Nietzki and Zübelin, *loc. cit.*

[2] Armstrong and Graham, *Journ. Chem. Soc.* 1881, **1**, 135.

[3] Claus and Zimmermann, *Ber.* **14**, 1447.

[4] Green, *loc. cit.* ; Armstrong and Graham, *loc. cit.*

caustic soda solution to 250°, and has also been prepared from the corresponding β-naphthylaminesulphonic acid.[1] It crystallizes from strong hydrochloric acid in needles containing water of crystallization, and decomposes on heating to 200° with the dilute acid into sulphuric acid and β-naphthol. Phosphorus pentachloride converts it into 2 : 2′-dichloronaphthalene.

Sodium β-naphthol-δ-sulphonate, $2C_{10}H_7O.SO_3Na + 5H_2O$ forms large plates, which readily dissolve in water, to which they impart a blue fluorescence, and are reprecipitated by common salt. The *barium salt* crystallizes in indistinct prisms, and is somewhat more readily soluble in water than that of the β-acid.

β-Naphthol-α-disulphonic acid, $C_{10}H_5(OH)(SO_3H)_2$, is obtained, together with the following compound, when β-naphthol is heated to 100—110° with 2—3 parts of fuming sulphuric acid until all the naphthol is attacked; the acids are then separated by means of their barium salts.[2]

The α-acid crystallizes in silky, deliquescent needles, which are insoluble in ether. With diazo-salts it forms deep-red or violet colouring matters, and the solutions of its salts have a bluish-green fluorescence, which is increased by the addition of ammonia. When the hydroxyl group is replaced by hydrogen, α-naphthalenedisulphonic acid is obtained (Pfitzinger and Duisberg).

Barium β-naphthol-α-disulphonate, $C_{10}H_5(OH)(SO_3)_2Ba + 6H_2O$, crystallizes in needles, which are slightly soluble in cold, more readily in hot water, and very slightly in alcohol.

β-Naphthol-β-disulphonic acid, also forms very deliquescent, silky needles, which are insoluble in ether. It gives orange or light-red colouring matters with diazo-salts, and forms salts which have a bluish-green fluorescence.

Barium β-naphthol-β-disulphonate, $C_{10}H_5(OH)(SO_3)_2Ba + 8H_2O$, crystallizes in small white prisms, which are very readily soluble in water, but only slightly in alcohol.

β-Naphthol-γ-disulphonic acid was obtained by Armstrong from β-naphthol by the action of chlorosulphonic acid. It forms a *barium salt*, which crystallizes in large, hard prisms, and is only slightly soluble in water.[3]

β-Naphtholtrisulphonic acid, $C_{10}H_4(OH)(SO_3H)_3$, is formed when β-naphthol is heated for a considerable time with

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[1] Bayer and Duisberg, *Ber.* **20**, 1456; Weinberg, *Ber.* **20**, 2906; Schultz, *Ber.* **20**, 3158.

[2] Griess, *Ber.* **13**, 1956.

[3] *Ber.* **15**, 203.

sulphuric acid, and is best obtained by heating one part of β-naphthol with two parts of sulphuric acid at 70—80°, in order that the monosulphonic acid may be obtained, then adding two parts of sulphuric acid and heating for some time at 120° and finally adding two parts of fuming sulphuric acid, containing 40 per cent. of sulphur trioxide, and raising the temperature to 150°. This acid, the properties of which have not yet been described, is employed for the preparation of azo-colours.[1]

THE THIONAPHTHOLS.

2614 *α-Thionaphthol* or *α-Naphthyl hydrosulphide*, $C_{10}H_7.SH$, is formed by the action of zinc and dilute sulphuric acid on α-naphthalenesulphochloride.[2] In order to prepare it, twenty parts of sodium α-naphthalenesulphonate are decomposed by 18·5 parts of phosphorus pentachloride, and the product of this reaction added to a cooled mixture of 40 parts of zinc dust and 240 parts of 25 per cent. sulphuric acid; the whole is then heated until the thionaphthol has separated out as an oil, which is then taken up with ether, and, after the evaporation of the latter, twice rectified under diminished pressure.[3]

α-Thionaphthol is a heavy, colourless, strongly refractive, oily liquid, which has a faint odour of the mercaptans, and solidifies to a crystalline mass at a low temperature. It boils under a pressure of 15 mm. at 152·5—153·5° and at 286° at the ordinary pressure. Its *lead salt*, $(C_{10}H_7S)_2Pb$, is a heavy, yellow precipitate.

α-Thionaphthyl ethyl ether, $C_{10}H_7.S.C_2H_5$, is formed when thionaphthol is heated with ethyl iodide, alcohol and caustic potash; it is an oily liquid, which boils at 167—167·5° under a pressure of 15 mm.

α-Thionaphthyl acetate, $C_{10}H_7.S.CO.CH_3$, is obtained by the action of acetyl chloride on thionaphthol as a liquid which boils at 188°, under a pressure of 15 mm.

α-Thionaphthyl benzoate, $C_{10}H_7.S.CO.C_6H_5$, forms crystals melting at 116—117°, and boils at 262° under a pressure of 15 mm.

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[1] Levinstein, *Ber.* **16**, 462; Limpach, *Ber.* **16**, 726.

[2] Schertel, *Annalen*, **132**, 91; Maikopar, *Zeitsch. Chem.* **1869**, 711.

[3] Krafft and Schönherr, *Ber.* **22**, 821.

a-Naphthyl sulphide, $(C_{10}H_7)_2S$, was obtained by Armstrong by distilling a mixture of potassium *a*-naphthalenesulphonate and potassium thiocyanate,[1] whilst Krafft and Schönherr prepared it by distilling lead *a*-thionaphthate at a very low pressure, and Kraft and Bourgeois,[2] by the action of bromonaphthalene on lead thionaphthate. It crystallizes from alcohol in white needles, melting at 110°, and boils at 289—290° under a pressure of 15 mm.

a-Naphthyl disulphide, $(C_{10}H_7)_2S_2$, was prepared by Schertel by allowing a solution of thionaphthol in alcoholic ammonia to stand in the air; it forms monosymmetric crystals melting at 85°.

4-*Nitro-a-naphthyl disulphide*, $(C_{10}H_6NO_2)_2S_2$, is obtained by boiling a solution of 1 : 4-nitronaphthalenesulphochloride in acetic acid with hydriodic acid. It forms greenish-yellow scales, which are very sparingly soluble in the ordinary solvents, and melt at 186°.[3]

1′-*Chlor-a-naphthyl disulphide*, $(C_{10}H_6Cl)_2S_2$, is prepared in a similar manner to the above. It separates from alcohol in tabular crystals, and melts at 110°.[4]

Phenyla-naphthyl sulphide, $C_6H_5.S.C_{10}H_7$, is prepared by heating lead thiophenate with *a*-bromonaphthalene. It forms hard and colourless, lustrous, odourless prisms, is slightly soluble in cold alcohol and ether, melts at 41·5°, and distils at 218° under a pressure of 14 mm. On oxidation it yields the corresponding sulphone[5] (p. 68).

β-Thionaphthol is obtained in a similar way to the *a*-compound, and crystallizes in lustrous scales, which have a faint odour of the mercaptans and are readily soluble in alcohol and ether. It melts at 81°, boils at 153·5° under a pressure of 15 mm., and at 286° under the ordinary pressure. Its *lead salt* is an orange-yellow crystalline precipitate.

β-Thionaphthyl ethyl ether is a crystalline mass which melts at 16° and boils at 170·5° under a pressure of 15 mm.

β-Thionaphthyl cyanate, $C_{10}H_7SCN$, is formed when a current of cyanogen chloride is passed into alcohol in which the lead salt is suspended. It is a snow-white, lustrous mass, melting at 35°, and is reconverted into thionaphthol by the action of potassium hydrosulphide.[6]

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[1] *Ber.* **7**, 407.

[2] *Ber.* **23**, 3045.

[3] Cleve, *Ber.* **23**, 960.

[4] Cleve, *Ber.* **23**, 963.

[5] Krafft and Bourgeois, *Ber.* **23**, 3046.

[6] Billeter, *Ber.* **8**, 426.

β-Thionaphthyl acetate is also crystalline, melts at 53·5°, and boils at 191° under a pressure of 15 mm.

β-Thionaphthyl benzoate melts at 108°, and boils at 267° under a pressure of 15 mm.

β-β-Dinaphthyl sulphide is formed when the lead salt is distilled under diminished pressure, and crystallizes from alcohol in thin plates, with a vitreous lustre. It melts at 151°, and boils at 295—296° under a pressure of 15 mm. (Krafft and Schönherr).

β-Dinaphthyl disulphide is obtained by the oxidation of thionaphthol and by heating the thiocyanate with sodium amalgam to 150—160°. It crystallizes in small needles, melting at 132° (Billeter), and on heating with copper powder is converted into the monosulphide (Krafft and Schönherr).

a-β-Dinaphthyl sulphide is formed when the lead salt of β-thionaphthol is heated with a slight excess of a-bromonaphthalene in a sealed tube for two to three hours at 200—220°, and then for an equal length of time at 240°.[1] It crystallizes from alcohol in lustrous plates, melts at 60—61°, and distils without decomposition at 290—291° (15 mm.). On oxidation it yields a-β-dinaphthylsulphone, melting at 123°.

Phenyl-β-naphthyl sulphide, $C_6H_5.S.C_{10}H_7$, is obtained by heating lead β-thionaphthate with bromobenzene. It crystallizes from alcohol in fan-shaped groups of small, white odourless needles, or, when the solution is rapidly cooled, in dull plates, melts at 51·5°, and boils at 224° (14 mm. pressure). On oxidation it yields the corresponding sulphone[2] (p. 68).

β-Dihydroxynaphthyl sulphide, $(HO.C_{10}H_6)_2S$, which is also termed *β-naphthol sulphide*, is formed by the action of sulphur dichloride on β-naphthol[3] and by heating the latter with sulphur, and gradually adding lead oxide.[4] It crystallizes from hot alcohol in white prisms, melts at 215°, and is readily soluble in ether, benzene and alkalis. The *sodium salt* forms aggregates of thick, colourless needles, containing six molecules of water of crystallization. On heating with copper powder it is converted into β-dinaphthol, $C_{20}H_{12}(OH)_2$. Dilute nitric acid converts it into phthalic acid. Mercuric oxide converts the sulphide in hot alcoholic solution into a ruby-red crystalline indifferent substance, melting at 164°, which has the formula, $C_{20}H_{12}SO_2$, and is reconverted into the sulphide by reducing agents.

[1] Krafft, *Ber.* **23**, 2368.

[2] Krafft and Bourgeois, *Ber.* **23**, 3048.

[3] Tassinari, *Ber.* **20**, Ref. 324.

[4] Onufrowicz, *Ber.* **21**, 3559.

Diacetoxynaphthyl sulphide, $(CH_3CO.O.C_{10}H_6)_2S$, is obtained by boiling naphthyl sulphide with acetic anhydride, and crystallizes in slender white needles, melting at 154°.

Dibenzoxynaphthyl sulphide, $(C_6H_5.CO.O.C_{10}H_6)_2S$, forms elongated white plates, and melts at 208°.

β-Diethoxynaphthyl sulphide, $(C_2H_5O.C_{10}H_6)_2S$, is obtained by heating a solution of the sulphide in alcoholic potash with ethyl iodide. It is almost insoluble in alcohol and ether, and sparingly soluble in cold, more readily in hot benzene; it crystallizes in long, thin needles, with a waxy lustre, and melts at 189°.[1]

β-Diethoxynitronaphthyl sulphide, $[C_2H_5O(NO_2)C_{10}H_5]_2S$, is formed by the action of concentrated nitric acid on a mixture of the preceding compound with ether and 10 parts of acetic acid cooled by ice. It forms thin, golden-yellow needles, melting at 235°. An isomeride, melting at 202°, is also formed by the reaction (Onufrowicz).

β-Dihydroxynaphthyl disulphide, or *β-Naphthol disulphide*, $(HO.C_{10}H_6)_2S_2$, was obtained by Lange from β-naphthol by boiling it with caustic soda and sulphur. It crystallizes in white needles, melting at 210°, which are only slightly soluble in alcohol, but readily form yellow solutions in the alkalis.[2]

An isomeric substance, which melts at 169°, is also formed in small quantity in the reaction mentioned above,[3] and may be obtained by heating β-naphthol with sulphur to 180°, or, accompanied by the monosulphide, by the action of sulphur chloride or bromide on β-naphthol dissolved in benzene. It crystallizes from benzene in thin, odourless, sulphur-yellow needles, is insoluble in water, slightly soluble in ether, and more readily in benzene. On heating with copper powder it is converted, like the monosulphide, into β-dinaphthol.

The *diethyl ether* forms greyish white needles, melting at 158·5°. The *diacetyl* derivative is a yellowish, hard, indistinctly crystalline mass, which becomes soft at 130° and melts at 140°. The *dibenzoyl* compound forms greenish crystalline granules or small tablets, is only very slightly soluble in alcohol and ether, sparingly in cold, but freely in hot benzene, and melts at 187°.[4]

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[1] Onufrowicz, *Ber.* **23**, 3355.

[2] Lange, *Ber.* **21**, 262.

[3] Onufrowicz, *Ber.* **21**, 260.

[4] Onufrowicz, *Ber.* **23**, 3363.

DIHYDROXYNAPHTHALENES, $C_{10}H_6(OH)_2$.

2615 1 : 4-*Dihydroxynaphthalene*, or *a-naphthoquinol*, was obtained by Groves from *a*-naphthoquinone by boiling it with concentrated hydriodic acid and amorphous phosphorus.[1] It is also readily formed when the quinone is brought into a boiling mixture of hydrochloric acid and tin.[2] It crystallizes from hot water in long, colourless needles, which melt at 176°, and dissolve freely in alcohol, ether, and glacial acetic acid, but only slightly in boiling benzene. Oxidizing agents reconvert it into *a*-naphthoquinone.

Diacet-a-naphthoquinol, $C_{10}H_6(OCO.CH_3)_2$, is formed when the quinol is heated with acetic anhydride and anhydrous sodium acetate, and crystallizes from alcohol in transparent, lustrous, six-sided tablets, melting at 128—130°.[3]

Dichlor-a-naphthoquinol, $C_{10}H_4Cl_2(OH)_2$, was prepared by Gräbe by heating dichlor-*a*-naphthoquinone with hydriodic acid and ordinary phosphorus. It crystallizes in colourless prisms, which rapidly become coloured reddish in the air, melt at 135°, and are only sparingly soluble in boiling water. Its *diacetate* crystallizes from alcohol in long, colourless, silky needles, which melt at 236°, and sublime in long prisms.[4]

3-*Brom-a-naphthoquinol*, $C_{10}H_5Br(OH)_2$, is formed by the action of sulphur dioxide on bromonaphthoquinone, and crystallizes in small needles, melting at 193°.[5]

1 : 4′-*Dihydroxynaphthalene* is obtained by fusing 1 : 4′-naphtholsulphonic acid[6] or 1 : 4′-naphthalenedisulphonic acid[7] with caustic potash. In order to prepare it, the former acid is heated to 200° with caustic potash for about a quarter of an hour, until a small portion of the mass dissolved in water no longer gives a red but a blue colouration with 1 : 4′-diazonaphthalenesulphonic acid.[8] It crystallizes in small prisms, which melt at 258—260°, sublime in long needles,[9] and are scarcely soluble in benzene and light petroleum, sparingly in water, and more readily in alcohol

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[1] *Annalen*, **167**, 357.

[2] Plimpton, *Journ. Chem. Soc.* 1880, **1**, 633.

[3] Korn, *Ber.* **17**, 3025.

[4] *Annalen*, **149**, 1 ; Claus, *Ber.* **19**, 1141.

[5] Brömme, *Ber.* **21**, 386.

[6] Cleve, *Bull. Soc. Chim.* **24**, 513 ; Bernthsen and Semper, *Ber.* **20**, 934.

[7] Armstrong and Wynne, *Proc. Chem. Soc.* **1887**, 42.

[8] Erdmann, *Annalen*, **247**. 356.

[9] Ewer and Pick, Schultz, *Steinkohlentheer*, **2**, 1012.

and glacial acetic acid. It reduces the salts of copper and silver, and its alkaline solutions take the colour of potassium permanganate solution when they are exposed to the air, finally becoming brown. The fine blue colouration which 1 : 4-diazonaphthalenesulphonic acid produces in its alkaline solution is converted by acids into a light-red. These colourations resemble those of litmus, but are much brighter; when the alkaline solution is saturated with carbon dioxide, the intermediate violet shade is produced, just as with litmus.

1 : 4′-*Diacetodihydroxynaphthalene* separates from alcohol in feathery crystals, which melt at 159—160°.

1 : 1′-*Dihydroxynaphthalene* was obtained by Erdmann by fusing 7 grms. of naphthosultone (p. 103) with 30 grms. of caustic potash and 10 cc. of water; potassium 1 : 1′-naphtholsulphonate is first formed, the whole mass becoming yellow, and the temperature is then raised to 200—230° for 15 to 20 minutes. The product is decomposed with 160 cc. of hydrochloric acid of 13 per cent., and brought into solution in 500 cc. of hot water. On cooling, 1 : 1′-dihydroxynaphthalene crystallizes out in long, white needles, melting at 140°. It is sparingly soluble in water and light petroleum, readily in ether and benzene, and crystallizes from a mixture of toluene and light petroleum in druses of small plates. It has a permanently biting taste, and forms a powder which causes sneezing. Its alkaline solution gives a deep-violet colouration with 1:4-diazonaphthalenesulphonic acid, which is converted by acids into a fine cherry-red.[1]

1 : 1′-*Diacetodihydroxynaphthalene* forms small, silvery plates, melting at 147—148°.

1 : 2-*Dihydroxynaphthalene*, or *β-naphthoquinol*, is readily formed when β-naphthoquinone is dissolved in concentrated sulphurous acid, and soon separates out in elongated, silvery plates, which melt at 60°. Its yellow alkaline solution becomes green in the air, and its aqueous solution irritates sensitive portions of the skin so violently that they become red and violently inflamed, and sometimes even ulcerated.[2]

Diaceto-β-naphthoquinol crystallizes from glacial acetic acid in small, well-developed, transparent plates, which melt at 104—106° (Korn).

Chloro-β-naphthoquinol, $C_{10}H_5Cl(OH)_2$, is obtained by the action of sulphur dioxide on a solution of chloro-β-naphtho-

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[1] Erdmann, *loc. cit.*

[2] Liebermann and Jacobsen, *Annalen*, **211**, 58.

quinone in acetic acid, and crystallizes from hot water in long needles, melting at 116—117°.[1]

Dichloro-β-naphthoquinol, $C_{10}H_4Cl_2(OH)_2$, forms slender needles, melting at 125°.[2]

Nitro-β-naphthoquinol, $C_{10}H_5(NO_2)(OH)_2$, is formed by the action of a hydrochloric acid solution of stannous chloride[3] or of sulphurous acid on nitro-β-naphthoquinone;[4] it crystallizes from alcohol or benzene in carmine-red tablets, and from acetic acid in prisms, melts at 159·5°, and sublimes without decomposition in long, red needles.

1 : 3′-*Dihydroxynaphthalene* was prepared from β-naphthylamine-γ-sulphonic acid by converting this into the corresponding naphtholsulphonic acid and fusing the latter with caustic potash.[5] It may also be obtained from the disulphonic acid, which is formed when β-naphthylamine is sulphonated at temperatures below 150°.[6] It crystallizes from hot water or benzene in short prisms, melting at 135·5°. Its alkaline solution has a splendid blue fluorescence, but rapidly acquires a reddish colour in the air.

1 : 3′-*Diacetodihydroxynaphthalene* crystallizes from alcohol in well formed prisms, and melts at 73°.

1 : 2′-*Dihydroxynaphthalene* is obtained by fusing β-naphthol-α-sulphonic acid with caustic potash. It crystallizes from boiling benzene in small, white needles, which melt at 178°, and dissolve very readily in alcohol, less easily in water. Its solutions become coloured brown in the air and give a deep-blue precipitate with ferric chloride. Its alkaline solution rapidly absorbs oxygen, the dihydroxynaphthalene being destroyed and the solution turned black.

Diethyl-1 : 2′-*dihydroxynaphthalene* is readily soluble in alcohol and ether, from which it crystallizes in needles or prisms, melting at 67°.[7]

Diaceto-1 : 2′-*dihydroxynaphthalene* crystallizes from benzene in rhombic tablets, which melt at 108°.

2 : 3′-*Dihydroxynaphthalene* is formed when β-naphthol-β-sulphonic acid is fused with caustic potash, and is sparingly soluble in water, readily in alcohol. It crystallizes in nacreous plates, melts at 215—216°, and sublimes without decomposition. Its alkaline solution becomes brown in the air (Emmert).

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[1] Fröhlich and Zincke, *Ber.* **19**, 2497.

[2] Zincke, *Ber.* **19**, 2493.

[3] Groves, *Journ. Chem. Soc.* 1884, **1**, 299.

[4] Zaertling, *Ber.* **23**, 177.

[5] Claus, *J. Pr. Chem.* II. **39**, 315.

[6] Ewer and Pick, *Ber.* **21**, 916 c.

[7] Emmert, *Annalen*, **241**, 368.

The dihydroxynaphthalene obtained from β-naphthalenedisulphonic acid should be identical with this substance. It crystallizes in thin, lustrous tablets, which become black when heated below 200°; its alkaline solution is stable in the air, and is coloured a splendid red by a small amount of *o*-diazobenzenesulphonic acid.[1] Phosphorus pentachloride converts it into 2 : 3'-dichloronaphthalene.

Diethyl-2 : 3'-*dihydroxynaphthalene* crystallizes from alcohol in silky plates, melting at 162°.

Diaceto-2 : 3'-*dihydroxynaphthalene* forms lustrous plates, melting at 175° (Emmert).

2 : 2'-*Dihydroxynaphthalene* is obtained by fusing α-naphthalenedisulphonic acid with caustic potash or soda. It crystallizes from hot benzene in long needles and from water in fine needles or plates, which melt at 186° (Weber), or 190° (Clausius) and sublime at a higher temperature with partial carbonization. Its alkaline and ethereal solutions gradually become black in the air; bleaching powder produces a fugitive red colouration in the aqueous solution, whilst nitric acid gives a similar but more permanent colour.[2]

Dimethyl-2 : 2'-*hydroxynaphthalene*, $C_{10}H_6(OCH_3)_2$, is formed when dihydroxynaphthalene is heated to 150° with methyl iodide and caustic potash. It forms nacreous plates, melting at 104°.[3]

Diaceto-2 : 2'-*hydroxynaphthalene*, $C_{10}H_6(OCO.CH_3)_2$, was obtained by Weber by the action of acetyl chloride on dihydroxynaphthalene; it crystallizes from alcohol in small plates, melting at 129° (Weber), 136° (Clausius).

2 : 2'-*Dibenzodihydroxynaphthalene*, $C_{10}H_6(OCO.C_6H_5)$, forms small plates, melting at 138—139°.

Dichlorodihydroxynaphthalene (1 : 1'; 2 : 2'), $C_{10}H_4Cl_2(OH)_2$, is formed when chlorine is passed into a cooled solution of 2 : 2'-dihydroxynaphthalene in ten parts of glacial acetic acid. It forms coarse, white needles, melting at 192°. Its *diacetate* forms white needles, melting at 195°.[4]

Dekachloro-2 : 2'-*diketohydronaphthalene*, $C_{10}H_2Cl_{10}O_2$, is obtained by the continued action of chlorine on dihydroxynaphthalene in acetic acid solution. It forms colourless, octo-

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[1] Dusart, *Compt. Rend.* **64**, 859; Wichelhaus and Darmstädter, *Annalen*, **152**, 306; Armstrong and Graham, *Journ. Chem. Soc.* 1881, **1**, 139.

[2] Ebert and Merz, *Ber.* **9**, 609; Weber, *Ber.* **14**, 2006; Clausius, *Ber.* **23**, 517.

[3] Liebermann and Hagen, *Ber.* **15**, 1428.

[4] Clausius, *Ber.* **23**, 525.

hedral crystals, which are sparingly soluble in alcohol and glacial acetic acid, and melt and decompose at 200°.

Tetrachloro-2 : 2′-dihydroxynaphthalene, $C_{10}H_2Cl_4(OH)_2$, is formed on the reduction of the preceding substance by means of stannous chloride. It crystallizes from alcohol in long, slender needles, melting at 176°. The *acetyl* compound forms white needles, melting at 196°. The constitution of these three substances is not yet accurately known.

2 : 2′-*Dithionaphthol*, $C_{10}H_6(SH)_2$, is obtained by reducing *a*-naphthalenedisulphochloride with zinc dust and dilute sulphuric acid [1] or tin and hydrochloric acid.[2] It is very slightly soluble in cold alcohol, ether, light petroleum and toluene, crystallizes from hot alcohol in pearly plates; melts at 180—181° (173—174° according to Ebert and Kleiner), and boils at 210° under a pressure of 15 mm. It is stable in the air but rapidly absorbs oxygen in alkaline solution, a white precipitate being formed. Lead acetate produces a deep yellow precipitate in its alcoholic solution, but no precipitate is formed when hydrochloric acid is present.

2 : 2′-*Diacetodithionaphthol*, $C_{10}H_6(SCOCH_3)_2$, forms colourless crystals melting at about 110°.

2 : 2′-*Dibenzodithionaphthol*, $C_{10}H_6(S.CO.C_6H_5)_2$, forms silky crystals and melts at 152—153°.

2 : 2′-*Dithionaphtholcyanate*, $C_{10}H_6(SCN)_2$, is prepared by the action of cyanogen chloride on the lead salt of dithionaphthol suspended in alcohol. It crystallizes from glacial acetic acid in fascicular groups of needles, melts at 78° and cannot be sublimed.[3]

THE NAPHTHOQUINONES, $C_{10}H_6O_2$.

2616 *a-Naphthoquinone* was first obtained by Groves by oxidizing naphthalene dissolved in glacial acetic acid with chromium trioxide.[4] It can also be easily obtained by gradually adding a 1-2 per cent. solution of chromium trioxide to a boiling solution of 1 : 4-diamidonaphthalene hydrochloride, or by dissolving *a*-naphthylamine hydrochloride in a large quantity of boiling water, adding a little sulphuric acid, and then gradually

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[1] Grosjean, *Ber.* **23**, 2370.

[2] Ebert and Kleiner, *Ber.* **24**, 144.

[3] Ebert and Kleiner, *Ber.* **24**, 146.

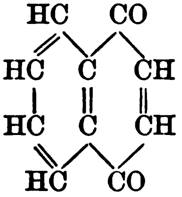
[4] *Annalen*, **167**, 357.

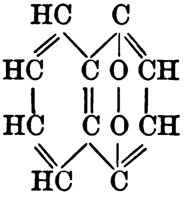
running it into the oxidizing solution.[1] It is also formed by the oxidation of α-naphthol,[2] 1 : 4-amidonaphthol,[3] &c. In order to prepare it, 400 grms. of chromium trioxide are dissolved in 740 grms. of acetic acid of 80 per cent. and well cooled with ice, a solution of 100 grms. of naphthalene in 1,000 grms of glacial acetic acid being then gradually added and the mixture allowed to stand for three days at 15—20°. The solution is then diluted with 8·5 litres of water, and the precipitate washed, dried in the air and finally recrystallized from light petroleum.[4]

α-Naphthoquinone crystallizes in sulphur-yellow, asymmetric needles, which have a penetrating odour, resembling that of benzoquinone, melt at 125°, and readily sublime and volatilize with steam. It is slightly soluble in water and light petroleum, readily in ether and hot alcohol, and forms reddish-brown solutions in the alkalis. Sulphurous acid does not readily act upon it, whilst nitric acid converts it into phthalic acid.

α-Naphthoquinhydrone, $C_{10}H_6O_2 + C_{10}H_6(OH)_2$, is formed by the partial reduction of α-naphthoquinone, and separates out in purple crystals when the solutions of its constituents are mixed (Groves).

α-Naphthoquinone closely resembles benzoquinone, both in its physical and chemical characteristics. Like this it is formed by the oxidation of para-compounds and behaves sometimes like a diketone, sometimes as a peroxide. Its constitution is therefore expressed by the following tautomeric formulæ:





Chlor-α-naphthoquinone, $C_{10}H_5ClO_2$, is formed when 2:4-dichlor-α-naphthol is oxidized in acetic acid solution with chromium trioxide or nitric acid,[5] and by the action of chromium

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[1] Liebermann and Dittler, *Annalen*, **183**, 242 and 248.

[2] Miller, *Ber.* **14**, 1600.

[3] Monnet, Reverdin and Nölting, *Ber.* **12**, 2305; Liebermann and Jacobsen, *Annalen*, **211**, 60.

[4] Miller, *Beilstein's Handb.* **3**, 184; see also Plimpton, *Journ. Chem. Soc.* 1880, **1**, 633; Japp and Miller, *Journ. Chem. Soc.* 1881, **1**, 220.

[5] Cleve, *Ber.* **21**, 891; Zincke, *Ber.* **21**, 1027.

trioxide on 1 : 3-dichloronaphthalene.[1] It crystallizes from alcohol in long, golden-yellow, lustrous needles and melts at 117—118°.

2 : 3-*Dichlor-a-naphthoquinone*, $C_{10}H_4Cl_2O_2$, was obtained by Laurent by boiling chloronaphthalene tetrachloride with nitric acid, and was named by him "Oxide de chloroxénnaphtose,"[2] whereas Gerhardt subsequently termed it "chloroxynaphthalene chloride." Gräbe then pointed out that it resembled the chlorinated benzoquinones in every respect, and must be considered as a derivative of the then unknown naphthoquinone and he afterwards confirmed this view by his researches.[3] Laurent's method does not readily give a pure product, but Gräbe found that it can readily be obtained pure by mixing naphthol yellow, as in the preparation of chloranil from phenol, with 3 to 4 parts of potassium chlorate and bringing the mixture into hydrochloric acid diluted with an equal volume of water. The reaction is aided by gentle heat, and after all the naphthol yellow has been used, potassium chlorate is gradually added until the yellowish-red oily product changes into yellow crystals, which are then washed with hot water and cold alcohol and recrystallized from hot alcohol.

It may be obtained in the same way from α-naphthol,[4] and is also formed by the action of chromyl chloride on an acetic acid solution of naphthalene,[5] or by oxidizing dichlor-α-naphthol[6] or δ-tetrachloronaphthalene[7] with a solution of chromium trioxide in glacial acetic acid and by passing chlorine into a solution of chlor-α-naphthoquinone in acetic acid (Zincke).

It is insoluble in water, sparingly soluble in cold alcohol and ether, and crystallizes from hot alcohol in well developed, golden-yellow needles, which melt at 189°, but sublime in long yellow needles or small plates at a lower temperature. It forms a carmine-red solution in boiling caustic soda solution, chloroxynaphthalenic acid (p. 133), which corresponds to chloranilic acid, being formed. It combines with potassium sulphite to form compounds resembling those formed by chloranil with this substance (Part III. p. 161). On heating with phosphorus

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[1] Cleve, *Ber.* **23**, 955.

[2] *Ann. Chim. Phys.* **74**, 35.

[3] *Annalen*, **149**, 1.

[4] Darmstädter and Wichelhaus, *Annalen*, **152**, 298.

[5] Carstanjen, *Ber.* **2**, 633.

[6] Claus and Knyrim, *Ber.* **18**, 2294.

[7] Claus and Mielke, *Ber.* **19**, 1182.

pentachloride to 180—200°, it is converted into pentachloronaphthalene, and it is slowly oxidized to phthalic acid by boiling nitric acid.

2 : 3-*Dichloronaphthoquinone dichloride*, $C_{10}H_4Cl_4O_2$, is formed when the preceding compound is heated to 230° with manganese dioxide and hydrochloric acid. It crystallizes from ether in large, colourless prisms, which melt at 117° and readily sublime. Stannous chloride converts it first into the dichloroquinone.[1] On treatment with alcoholic potash it yields *o*-trichloracrylbenzoic acid, $CCl_2 : CCl.CO.C_6H_4.COOH$, and Zincke therefore considers it to be *tetrachlor-a-diketohydronaphthalene*.[2]

1′ : 4′-*Dichlor-a-naphthoquinone* is obtained together with dichlorophthalide when 1 : 4-dichloronaphthalene is oxidized with chromium trioxide in acetic acid solution, and crystallizes from alcohol in long, yellow needles, which melt at 174° and readily sublime.[3]

1′ : 2′-*Dichlor-a-naphthoquinone* has been prepared in the same way from 1 : 2-dichloronaphthalene, and sublimes in yellow needles melting at 181°.[4]

2 : 3′-*Dichlor-a-naphthoquinone* is a product of the oxidation of 2 : 3′-dichloronaphthalene, crystallizes in deep-yellow, slender needles, which melt at 148—149°, and forms a dark-red solution in caustic potash.[5]

Trichlor-a-naphthoquinone, $C_{10}H_3Cl_3O_2$, is formed in small quantity, together with phthalic acid, when *o*-dichlor-*a*-naphthoquinone is oxidized with nitric acid. It crystallizes in yellow needles, melting at 250°.[6]

Tetrachlor-a-naphthoquinone, $C_{10}H_2Cl_4O_2$ ($Cl = 1' : 2' : 3' : 4'$) is obtained, accompanied by a little tetrachlorophthalic acid, when pentachloronaphthalene is heated with fuming nitric acid to 110—120°. It crystallizes in long, yellow, lustrous needles, melting at 160°, sublimes without decomposition, and is oxidized when strongly heated with fuming nitric acid to tetrachlorophthalic acid (Claus and von der Lippe).

Pentachlor-a-naphthoquinone, $C_{10}HCl_5O_2$, is formed by the oxidation of heptachloronaphthalene with nitric acid, and crystallizes from chloroform in lustrous, golden-yellow plates,

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[1] Claus, *Ber.* **19**, 1142.

[2] Zincke and Cooksey, *Annalen*, **255**, 356. Cf. Claus, *J. Pr. Chem.* **41**, 285.

[3] Guareschi, *Ber.* **19**, 1154.

[4] Hellström, *Ber.* **21**, 3267.

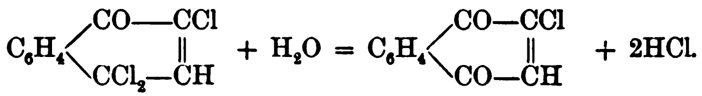
[5] Claus and Müller, *Ber.* **18**, 3073.

[6] Claus and von der Lippe, *Ber.* **16**, 1016.

which melt at 217° and sublime in long needles. It is oxidized to tetrachlorophthalic acid by chromic acid.[1]

Perchlor-a-naphthoquinone, $C_{10}Cl_6O_2$, was obtained by Laurent, who termed it *oxide de chloroxénnaphtalise*, by boiling hexchloronaphthalene with nitric acid. It crystallizes from ether in very lustrous yellow plates, which melt at a high temperature and sublime with slight decomposition.[2]

2617 *Trichlor-a-ketonaphthalene*, $C_{10}H_9Cl_3O$, is formed when chlorine is passed into a well-cooled solution of *a*-naphthol in 10 parts of glacial acetic acid until the dark-coloured liquid becomes light and an excess of chlorine is present. It may also be obtained by the action of chlorine on dichlor-*a*-naphthol, and crystallizes from hot benzene in large, transparent, flat prisms. It is sparingly soluble in alcohol, somewhat more freely in glacial acetic acid. On boiling with dilute alcohol it is converted into chlor-*a*-naphthoquinone:



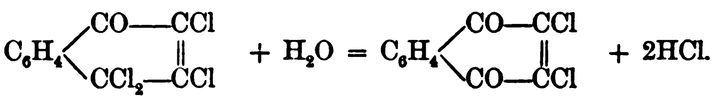
$$C_6H_4\left\langle\begin{array}{l}CO—CCl\\ \qquad\ \ \|\\ CCl_2—CH\end{array}\right. + H_2O = C_6H_4\left\langle\begin{array}{l}CO—CCl\\ \qquad\ \|\\ CO—CH\end{array}\right. + 2HCl.$$

Aniline converts it into naphthoquinonedianilide, and on reduction it yields dichlor-*a*-naphthol.

Tetrachlor-a-ketonaphthalene, $C_{10}H_4Cl_4O$, is formed in two modifications when trichlor-*a*-naphthol is suspended in glacial acetic acid and treated with chlorine, without being cooled. A portion of the *a*-modification crystallizes out on standing in small, transparent rhombohedra, resembling those of calcspar, which become yellow in the air, melt at 104—105°, and are moderately soluble in hot alcohol.

The *β*-modification separates from ether in lustrous, transparent, rhombic crystals, resembling those of topaz, which melt at 93—94° and assume an amethyst colour in the air. On heating with alcohol or acetic acid it is partially converted into the *a*-modification.

Both forms are converted into dichlor-*a*-naphthoquinone by boiling with alcohol:



$$C_6H_4\left\langle\begin{array}{l}CO—CCl\\ \qquad\ \ \|\\ CCl_2—CCl\end{array}\right. + H_2O = C_6H_4\left\langle\begin{array}{l}CO—CCl\\ \qquad\ \|\\ CO—CCl\end{array}\right. + 2HCl.$$

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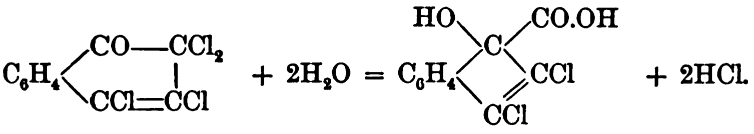
[1] Claus and Wenzlik, *Ber.* **19**, 1165.

[2] *Ann. Chim. Phys.* **74**, 26.

Reducing agents convert both of these substances into trichlor-α-naphthol, and they both yield hydroxychloronaphthoquinone (p. 133) on treatment with dilute alcoholic potash.

When they are treated with concentrated caustic potash and a little alcohol, on the other hand, the dichlorohydroxyindene-carboxylic acid (p. 10) which was first prepared from dichloro-β-naphthoquinone, is formed; the formation of this substance can only be simply explained in the following manner:



$$C_6H_4\left\langle\begin{matrix}CO-CCl_2\\ |\\ CCl=CCl\end{matrix}\right. + 2H_2O = C_6H_4\left\langle\begin{matrix}C\begin{matrix}HO\\ CO.OH\end{matrix}\\ CCl\\ \| \\ CCl\end{matrix}\right. + 2HCl.$$

This compound is therefore tautomeric, but it has not yet been ascertained which of the above formulæ corresponds to the α- and which to the β-modification.

Pentachlor-a-ketohydronaphthalene or *Trichloroketonaphthalene dichloride*, $C_{10}H_5Cl_5O$, is formed when the process employed for the preparation of the trichloroketone is modified by saturating the liquid with chlorine and allowing it to stand. It is sparingly soluble in alcohol, more freely in acetic acid, and readily in benzene, from which it crystallizes in small, almost rectangular, monosymmetric tablets, melting at 156—157°. When acted upon by reagents it in many cases yields the same products as the tetrachloroketone, since it passes into this with loss of hydrochloric acid.

Hexchloroketohydronaphthalene, or *Tetrachloroketonaphthalene dichloride*, $C_6H_4Cl_6O$, is obtained when the tetrachloroketones are heated to 140—150° with manganese dioxide and concentrated hydrochloric acid for six to eight hours. It is readily soluble in benzene and hot alcohol, and separates from glacial acetic acid in hard, apparently monosymmetric crystals, melting at 130°. On reduction it yields trichlor-α-naphthol.[1]

Brom-a-naphthoquinone (Br = 2 or 3) is obtained when brom-α-naphtho-β-quinonoxime is heated with hydrochloric acid, and forms brown crystals, melting at 200—201°.[2]

α-2 : 3-*Dibrom-a-naphthoquinone*, $C_{10}H_4Br_2O_2$, is formed when a solution of α-naphthoquinone is heated with bromine and a little iodine to the boiling-point. It crystallizes from alcohol in slender, yellow needles, and melts at 218·4°.[3]

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[1] Zincke, *Ber.* 21, 1027.

[2] Brömme, *Ber.* 21, 386.

[3] Miller, *Ber.* 17, 355 R.

β-2 : 3-*Dibrom-a-naphthoquinone* was prepared by heating α-naphthoquinone with bromine, iodine, and water, crystallizes from hot alcohol in granular masses of needles, and sublimes in small, well-formed needles, which melt at 151·5°.

Both of these compounds yield phthalic acid on oxidation, and should therefore be identical. In any case, they require further investigation.

1 : 4-*Dibrom-a-naphthoquinone* is formed, together with dibromophthalide, by the oxidation of 1 : 4-dibromonaphthalene in acetic acid solution with chromium trioxide. It is insoluble in water and only slightly soluble in cold alcohol, but crystallizes from hot alcohol in bright, golden-yellow, lustrous needles, which melt at 171—173°, and are volatile with steam. It is readily oxidized by potassium permanganate, but without the formation of phthalic or bromophthalic acid.[1]

Tetrabrom-a-naphthoquinone, $C_{10}H_2Br_4O_2$, has been obtained by the oxidation of pentabrom-α-naphthol with nitric acid, and crystallizes in small plates, melting at 265°.[2]

2618 *ar-Tetrahydro-a-naphthoquinone*, $C_6H_8.C_4H_2O_2$, was obtained by Bamberger and Lingfeld[3] by applying Nietzki's process for preparing benzoquinone from aniline to *ar*-tetrahydro-α-naphthylamine. It is almost precisely similar to benzoquinone in all its physical properties, and melts at 55·5°.

ar-Tetrahydro-a-naphthoquinol, $C_6H_8.C_4H_2(OH)_2$, is formed by reducing the above compound with sulphurous acid or phenylhydrazine. It crystallizes in aggregates of slender, colourless, silky prisms, and sublimes almost without decomposition in well-formed needles, melting at 172—172·5°. The usual solvents dissolve it readily, with the exception of cold water, in which it is only sparingly soluble. Oxidizing agents reconvert it into the quinone, and on partial oxidation with potassium dichromate in the cold, the *quinhydrone* is formed. This substance is also formed when boiling aqueous solutions of the quinone and quinol are mixed, and separates in long, brown, filiform crystals.

2619 β-*Naphthoquinone*, $C_{10}H_6O_2$, is readily formed by the oxidation of amido-β-naphthol with chromic acid solution,[4] and crystallizes from ether in red needles, resembling those of

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[1] Guareschi, *Annalen*, **222**, 279.

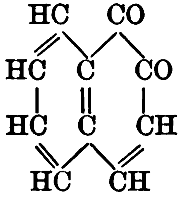
[2] Blümlein, *Ber.* **17**, 2485.

[3] *Ber.* **23** 1121.

[4] Stenhouse and Groves, *Annalen*, **189**, 145; **194**, 202; Liebermann and Jacobsen, *Annalen*, **211**, 36.

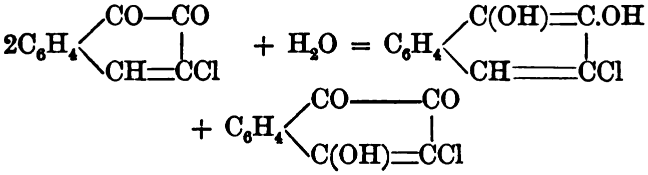
chromium trioxide, and from benzene in small, yellowish-red plates, which are insoluble in water. It differs from the α-compound in being odourless, in not being volatile with steam, and in carbonizing and decomposing at 115—120°. Its yellow alkaline solution readily absorbs oxygen, and it is oxidized to phthalic acid by the continued action of nitric acid or potassium permanganate.

Since the substituted groups in amido-β-naphthol have the position 1 : 2, the constitution of β-naphthoquinone is represented by the formula:

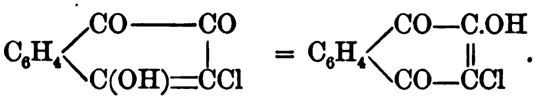


3-*Chloro-β-naphthoquinone*, $C_{10}H_5ClO_2$, is obtained when dry chlorine is passed into acetic acid in which β-naphthoquinone is suspended. It crystallizes from hot alcohol in red needles, which melt with decomposition at 172°. It forms a reddish brown solution in caustic soda, hydroxychlor-α-naphthoquinone being formed by isomeric change from the corresponding β-derivative, which is doubtless the first product.[1]

In the formation of this substance a portion of the chloroquinone must be reduced to chloroquinol:

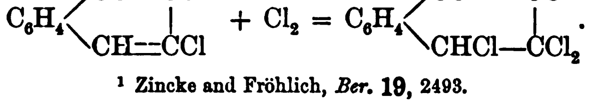


$$2C_6H_4\left\langle\begin{array}{l}CO{-}CO\\ CH{=}CCl\end{array}\right. + H_2O = C_6H_4\left\langle\begin{array}{l}C(OH){=}C.OH\\ CH{=}CCl\end{array}\right. + C_6H_4\left\langle\begin{array}{l}CO{-}CO\\ C(OH){=}CCl\end{array}\right.$$



$$C_6H_4\left\langle\begin{array}{l}CO{-}CO\\ C(OH){=}CCl\end{array}\right. = C_6H_4\left\langle\begin{array}{l}CO{-}C.OH\\ CO{-}CCl\end{array}\right. .$$

Chloro-β-naphthoquinone dichloride, or *Trichlorodiketohydronaphthalene*, $C_{10}H_5Cl_3O_2$, is obtained when the solution of quinone is saturated with chlorine and allowed to stand:



$$C_6H_4\left\langle\begin{array}{l}CO{-}CO\\ CH{=}CCl\end{array}\right. + Cl_2 = C_6H_4\left\langle\begin{array}{l}CO{-}CO\\ CHCl{-}CCl_2\end{array}\right. .$$

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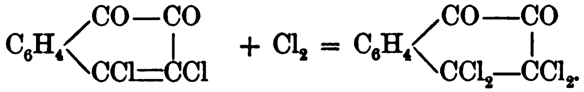
[1] Zincke and Fröhlich, *Ber.* **19**, 2493.

It crystallizes from glacial acetic acid or a mixture of ether and light petroleum in large, lustrous monosymmetric prisms, which contain two molecules of water, and melt at 112° with loss of water.[1] Like other similarly-constituted compounds it probably contains the group $C(OH)_2.C(OH)_2$. When heated to 180°, it decomposes into hydrochloric acid and dichloro-β-naphthoquinone. It is converted by alkalis into trichlorohydroxyhydrindenecarboxylic acid (p. 8).

3:4-*Dichloro-β-naphthoquinone*, $C_{10}H_4Cl_2O_2$, is best prepared by suspending 1-amido-β-naphthol in glacial acetic acid and passing in chlorine until almost complete solution has taken place. It is also formed by the oxidation of trichlor-α-naphthol with nitric acid (p. 92), and crystallizes from hot acetic acid or benzene in red plates or thick, brownish-red tablets, which melt at 184° and sublime without decomposition. It is converted into dichlorohydroxyindenecarboxylic acid (p. 10) by cold dilute caustic soda solution.

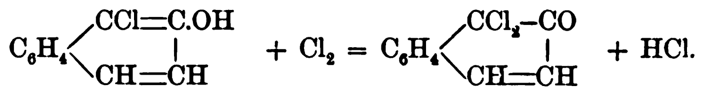
Dichloro-β-naphthoquinone dichloride, or *Tetrachlorodiketohydronaphthalene* is formed when the liquid is saturated with chlorine and allowed to stand:



$$C_6H_4\left\langle\begin{array}{l}CO—CO\\ \quad\ |\\ CCl{=}CCl\end{array}\right. + Cl_2 = C_6H_4\left\langle\begin{array}{l}CO—CO\\ \quad\ |\\ CCl_2—CCl_2.\end{array}\right.$$

On the addition of water it is precipitated in small plates having a satin lustre, and containing three molecules of water, which are lost at 100—105°. The anhydrous compound forms yellow solutions in absolute alcohol and glacial acetic acid, from which it separates in light sulphur-yellow, lustrous crystals, which melt at 90—91°, and decompose at about 180° with formation of dichloro-β-naphthoquinone. It is converted by caustic soda into dichloroketohydroxyhydrindic acid.[2]

Dichloro-β-ketonaphthalene, $C_{10}H_6Cl_2O$, is formed when the calculated amount of chlorine is passed into a solution of α-chloro-β-naphthol in acetic acid solution:



$$C_6H_4\left\langle\begin{array}{l}CCl{=}C.OH\\ \quad\ |\\ CH{=}CH\end{array}\right. + Cl_2 = C_6H_4\left\langle\begin{array}{l}CCl_2-CO\\ \quad\ |\\ CH{=}CH\end{array}\right. + HCl.$$

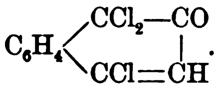
It is a thick liquid, which is converted into anilido-β-naphthoquinone by the action of aniline on its alcoholic solution, whilst

[1] Zincke, *Ber.* **20**, 2890.

[2] Zincke, *Ber* **21**, 491.

it yields naphthoquinonedianilide when acted upon in acetic acid solution.

2620 *a-Trichloro-β-ketonaphthalene*, $C_{10}H_5Cl_3O$, is obtained by the action of chlorine on 1 : 4-dichloro-β-naphthol, and has therefore the following constitution :

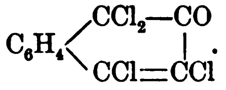


$$C_6H_4\left\langle\begin{array}{l}CCl_2—CO\\ \qquad\quad\;\;|\\ CCl=CH\end{array}\right..$$

It forms thick, white needles, or clear rhombic crystals, and is converted into hydroxy-α-naphthoquinone by alkalis.

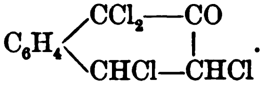
β-Trichloro-β-ketonaphthalene. The formation of this substance has already been described (p. 94). It may be readily obtained by dissolving β-naphthol in ten parts of glacial acetic acid, passing in chlorine until the liquid smells strongly of it, and then pouring it into an equal volume of alcohol. It crystallizes from hot alcohol or glacial acetic acid in thick, yellowish needles, and from ether in large, monosymmetric prisms, which melt at 95—96°. Dilute alkalis convert it into hydroxychlor-α-naphthoquinone, and reducing agents into 1 : 3-dichloro-β-naphthol.

Tetrachloro-β-ketonaphthalene, $C_{10}H_4Cl_4O_4$, is formed when chlorine is passed into acetic acid in which trichloro-β-naphthol is suspended, until complete solution has taken place. It separates out in transparent tablets or small plates, melting at 96—97°. Concentrated caustic potash dissolves it with formation of dichlorohydroxyindenecarboxylic acid. Its constitution is expressed by the formula:



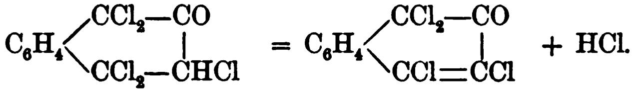
$$C_6H_4\left\langle\begin{array}{l}CCl_2—CO\\ \qquad\quad\;\;|\\ CCl=CCl\end{array}\right..$$

Tetrachloro-β-ketohydronaphthalene, $C_{10}H_6Cl_4O$, is obtained by passing an excess of chlorine into an acetic acid solution of β-naphthol, and separates from the concentrated solution in lustrous white plates, containing one molecule of water of crystallization, whilst it crystallizes from light petroleum in white plates, needles, or transparent monosymmetric prisms, which melt at 102—103°. It decomposes in alcoholic solution with formation of β-trichloroketonaphthalene, and on reduction yields both the dichloronaphthols simultaneously, whilst on treatment with sodium carbonate solution it forms chloro-β-naphthoquinone. Its constitution is therefore:



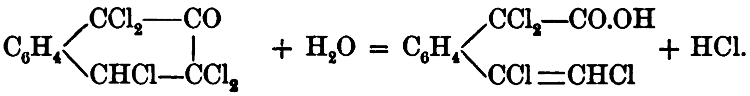
$$C_6H_4\begin{array}{l}\diagup CCl_2-CO \\ \qquad\qquad\quad | \\ \diagdown CHCl-CHCl\end{array}.$$

a-Pentachloro-β-ketohydronaphthalene, $C_{10}H_5Cl_5O$, is formed by the action of chlorine on a solution of α-trichloro-β-keto-naphthalene in carbon disulphide, and separates from the latter in splendid, colourless, monosymmetric crystals, which have a vitreous lustre. It melts at 123°, and is readily decomposed by alcohol or acetic acid with formation of tetrachloro-β-keto-naphthalene; it is for this reason that the pentachloro-compound is not formed in acetic acid solution.[1] Its decomposition proceeds according to the equation:



$$C_6H_4\begin{array}{l}\diagup CCl_2-CO \\ \qquad\qquad\; | \\ \diagdown CCl_2-CHCl\end{array} = C_6H_4\begin{array}{l}\diagup CCl_2-CO \\ \qquad\qquad\; | \\ \diagdown CCl=CCl\end{array} + HCl.$$

β-Pentachloro-β-ketohydronaphthalene, $C_{10}H_5Cl_5O$, is the product of the further action of chlorine on β-trichloro-β-keto-naphthalene, and crystallizes from hot glacial acetic acid or ether in colourless, transparent, monosymmetric prisms,[2] which melt at 116—117°. On reduction it yields trichloro-β-naphthol and is converted by alkalis into *o-dichlorovinyldichlorobenzylcarboxylic acid*:



$$C_6H_4\begin{array}{l}\diagup CCl_2-CO \\ \qquad\qquad\quad | \\ \diagdown CHCl-CCl_2\end{array} + H_2O = C_6H_4\begin{array}{l}\diagup CCl_2-CO.OH \\ \\ \diagdown CCl=CHCl\end{array} + HCl.$$

It forms clear, colourless, lustrous crystals, which melt at 130—131° with decomposition. On further treatment with alkalis it yields *dichlorovinylbenzoylcarboxylic acid*, $C_6H_4(C_2Cl_2H)CO.CO_2H$, which crystallizes in long, thick, yellowish needles, and melts at 106—107° with decomposition.

Hexchloro-β-ketohydronaphthalene, $C_{10}H_4Cl_6O$, is prepared from the tetrachloroketone by heating with manganese dioxide and hydrochloric acid to 140—150°, and crystallizes in prisms or tablets, which melt at 129°. Hot alcoholic potash converts it into

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[1] Zincke, *Ber.* **22**, 1024.

[2] Zincke, *Ber.* **22**, 1034.

trichlorovinyldichlorobenzylcarboxylic acid, $C_6H_4(C_2Cl_3)CCl_2.CO_2H$, which crystallizes in elongated tablets and is converted into trichlorovinylbenzoic acid (p. 13) on oxidation.[1]

Hexchloroketohydronaphthalene combines with tetrachloro-β-ketonaphthalene to form the compound $C_{10}H_4Cl_4O + C_{10}H_4Cl_6O$, which crystallizes from glacial acetic acid in yellow rhombic pyramids, resembling those of sulphur, and separates from ether in larger, lustrous crystals.[2]

Bromo-β-naphthoquinone, $C_{10}H_5BrO_2(O:O:Br = 1:2:3)$, may readily be obtained by the action of bromine on the quinone suspended in glacial acetic acid. It crystallizes in red to brownish-red needles or prisms, which are moderately soluble in hot alcohol, glacial acetic acid, or benzene, melt at 177—178°, and sublime without decomposition.

Dibromo-β-naphthoquinone, $C_{10}H_4Br_2O_2$, is prepared by the addition of bromine to a hot solution of the preceding compound in acetic acid, and is still more readily formed from 1-amido-β-naphthol. It crystallizes from glacial acetic acid in thick plates, melting at 172—174°.[3]

Tribromo-β-naphthoquinone, $C_{10}H_3Br_3O_2$, is obtained by the oxidation of pentabromo-β-naphthol with nitric acid, and forms cinnabar-red granules, which melt at 164°.[4]

Nitro-β-naphthoquinone, $C_{10}H_5(NO_2)O_2$, is formed when the quinone is dissolved in hot dilute nitric acid of sp. gr. 1·38°,[5] and the solution rapidly cooled. It crystallizes from hot glacial acetic acid in splendid tablets, having the colour and lustre of chromium trioxide, which melt at 158° and are oxidized to phthalic acid by potassium permanganate.[6] The quinone combines with one molecule of hydroxylamine to form an addition product, which is a yellow, hygroscopic powder, and melts at 140—141° with vigorous evolution of gas. On boiling with acetic acid, phenol, or alcohol, nitrogen is evolved and nitronaphthoquinol formed.[7]

γ-Naphthoquinone is formed to the extent of 0·5 per cent. by the action of fuming nitric acid on dibrom-α-naphthol. The bromindone (p. 11) formed at the same time is dissolved in alcohol and filtered off, the quinone being then well washed with hot alcohol and purified by recrystallization from glacial acetic acid or

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[1] Zincke, *Ber.* **21**, 3540.
[2] Zincke, *Ber.* **22**, 1032.
[3] Weltner and Zincke, *Ber.* **19**, 2495.
[4] Flessa, *Ber.* **17**, 1479.
[5] Zaertling, *Ber.* **23**, 175.
[6] Groves and Stenhouse, *Annalen*, **194**, 202
[7] Zaertling, *Ber.* **23**, 179.

nitrobenzene. It forms slender, pale-yellow needles, is remarkably insoluble in most solvents, and has no definite melting-point, but blackens and decomposes above 200°. Zinc dust and acetic acid convert it into a *dihydroxynaphthalene*, which is precipitated by water in minute, whitish needles. It is insoluble in hot water, slightly soluble in alcohol, forming a solution which becomes violet in the air. On heating it shrinks and blackens at about 205°. The *diacetyl* derivative forms stellate bundles of whitish flattened needles, melting at 226—227°. On oxidation with hot alkaline permanganate solution the dihydroxynaphthalene is converted into an acid which is probably v-hydroxyphthalic acid. This shows that the dihydroxynaphthalene and therefore the quinone is a 1 : 1′- or peri-compound.[1] The hydroxy-compound, however, differs from that obtained by Erdmann (p. 117).[2]

Nitro-γ-naphthoquinone is obtained, together with nitronaphthalic acid, $C_{10}H_5(NO_2)(CO_2H)_2$, when acenaphthene, $C_{10}H_6.C_2H_4$, is boiled with nitric acid, and crystallizes from alcohol or glacial acetic acid in yellowish-red needles, melting at 208°. It contains the quinone oxygen atoms in the 1 : 1′-position, like the carboxyl-groups in naphthalic acid.[3]

THE TRIHYDROXYNAPHTHALENES, $C_{10}H_5(OH)_3$ AND HYDROXYNAPHTHOQUINONES, $C_{10}H_5(OH)O_2$.

2621 1 : 2 : 4-*Trihydroxynaphthalene* is formed by the action of tin and hydrochloric acid on hydroxy-α-naphthoquinone, and crystallizes from ether in yellow needles, which are sparingly soluble in water. It reduces solutions of silver and mercury, as well as Fehling's solution, and its alkaline solution rapidly becomes red in the air, the original hydroxyquinone being formed.

Hydroxy-a-naphthoquinone, or *Naphthalenic acid*, is obtained by heating hydroxyimidonaphthol, $C_{10}H_5O(NH)OH$, or di-imidonaphthol, $C_{10}H_5(OH)(NH)_2$, with acids or alkalis.[4] It is, however,

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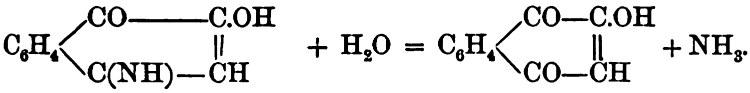
[1] Meldola and Hughes, *Journ. Chem. Soc.* 1890, **1**, 631.

[2] Meldola and Hughes, *Journ. Chem. Soc.* 1890, **1**, 809.

[3] Quincke, *Ber.* **21**, 1460.

[4] Martius and Griess, *Annalen*, **134**, 375 ; Gräbe and Ludwig, *Annalen*, **154**, 303.

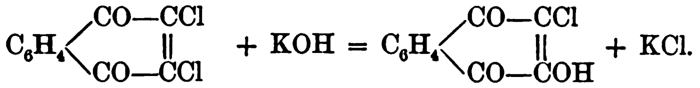
most conveniently prepared by heating the former compound with sodium carbonate solution :[1]



$$\mathrm{C_6H_4}\left\langle\begin{array}{l}\mathrm{CO\text{———}C.OH}\\ \qquad\qquad\ \|\\ \mathrm{C(NH)\text{—}CH}\end{array}\right. + \mathrm{H_2O} = \mathrm{C_6H_4}\left\langle\begin{array}{l}\mathrm{CO\text{—}C.OH}\\ \qquad\ \ \|\\ \mathrm{CO\text{—}CH}\end{array}\right. + \mathrm{NH_3}.$$

When the cold concentrated solution is acidified with hydrochloric acid, it is precipitated as a yellow powder which becomes electrically charged on drying; it crystallizes from a hot dilute solution, on the other hand, in lustrous yellow needles, which melt at 190° with decomposition.[2] It partially sublimes in reddish-yellow needles, resembling those of alizarin, which was formerly thought to be an isomeride of naphthalenic acid. It is scarcely soluble in cold water, but readily soluble in alcohol and ether, decomposes carbonates and forms red salts with the alkalis and alkaline earths. The *silver salt*, $C_{10}H_5O_2(OAg)$, is a reddish-brown precipitate, which crystallizes from hot water in cinnabar-red needles.

Hydroxychlor-α-naphthoquinone, *Chloroxynaphthalenic acid*, or *Chloronaphthalenic acid*, $C_{10}H_4ClO_2(OH)$, was obtained by Laurent by boiling *α*-chloronaphthalene tetrachloride with nitric acid, and by the action of alcoholic potash on 2:3-dichloronaphthoquinone :[3]



$$\mathrm{C_6H_4}\left\langle\begin{array}{l}\mathrm{CO\text{—}CCl}\\ \qquad\ \ \|\\ \mathrm{CO\text{—}CCl}\end{array}\right. + \mathrm{KOH} = \mathrm{C_6H_4}\left\langle\begin{array}{l}\mathrm{CO\text{—}CCl}\\ \qquad\ \ \|\\ \mathrm{CO\text{—}COH}\end{array}\right. + \mathrm{KCl}.$$

It was at one time prepared by Castelhaz, of Paris, according to P. and E. Depouilly's method, by acting with nitric acid on the mixture of naphthalene dichloride and chloronaphthalene dichloride obtained by the action of potassium chlorate and hydrochloric acid on naphthalene; phthalic acid and hydroxychloronaphthoquinone are thus formed and can readily be separated.[4] The latter compound is, however, best prepared by covering dichloronaphthoquinone with alcohol and adding concentrated caustic potash; the potassium salt separates out after a short time.[5]

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[1] Diehl and Merz, *Ber.* **11**, 1314.

[2] Liebermann and Jacobsen, *Annalen*, **211**, 81.

[3] *Annalen*, **35**, 292.

[4] *Annalen*, **137**, 373.

[5] Gräbe, *Annalen*, **149**, 13.

Hydroxychlor-α-naphthoquinone crystallizes in long, yellow, transparent needles, which melt above 200°, are scarcely soluble in water, moderately in alcohol, ether and benzene, and sublime without decomposition. It is oxidized by nitric acid to phthalic and oxalic acids, and is converted by phosphorus pentachloride into pentachloronaphthalene; on heating with soda lime it yields benzene.

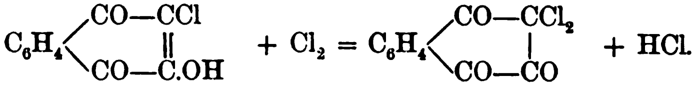
Potassium chloronaphthalenate, $C_{10}H_4ClO_3K$, crystallizes in cherry-red needles, which contain water of crystallization, and are only sparingly soluble in cold water.

Barium chloronaphthalenate, $(C_{10}H_4ClO_3)_2Ba + 3H_2O$, is scarcely soluble in cold water, and crystallizes from hot water in slender, yellow, silky needles.

Chloronaphthalenic acid dyes wool a deep red; if it be treated with water and sodium amalgam a colourless solution is obtained which rapidly becomes red again in the air. The alkaline solution becomes yellow on treatment with zinc dust, and this is changed to green after a little time when ammonia is added.

Hydrochloric acid precipitates from this solution a brown powder, which after washing and drying, takes a green metallic lustre and, according to Köchlin, consists of *trihydroxychloronaphthalene*, $C_{10}H_4Cl(OH)_3$. It dissolves in alcohol, forming a violet solution, which is coloured blue by ammonia, red by acids, and dyes wool direct.[1]

Dichlorotriketohydronaphthalene, $C_{10}H_4Cl_2O_3 + H_2O$, is formed when chlorine is allowed to act upon hydroxychlor-α-naphthoquinone dissolved in glacial acetic acid:



$$\mathrm{C_6H_4}\left\langle\begin{array}{l}\mathrm{CO{-}CCl}\\ \quad\;\,\|\\ \mathrm{CO{-}C.OH}\end{array}\right. + \mathrm{Cl_2} = \mathrm{C_6H_4}\left\langle\begin{array}{l}\mathrm{CO{-}CCl_2}\\ \quad\;\,|\\ \mathrm{CO{-}CO}\end{array}\right. + \mathrm{HCl.}$$

It crystallizes in thick, white needles, which become anhydrous at 100° and melt at 105°. On boiling with water it dissolves, and when potassium iodide is added to this solution the original hydroxychloronaphthoquinone separates out, hypochlorous acid being certainly eliminated. It is converted into dichloroketohydrindenic acid by dilute alkalis.[2]

Hydroxybrom-a-naphthoquinone, or *a-Bromonaphthalenic acid*,

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[1] *Zeitsch. Chem.* **1866**, 223.

[2] Zincke and Gerland, *Ber.* **20**, 3216; **21**, 2379.

$C_{10}H_4Br(OH)O_2$, was obtained by Miller by heating the dibromonaphthoquinone which melts at 218°, with a solution of caustic potash in dilute alcohol. It crystallizes from alcohol in yellow needles, which melt at 201—202°.

Potassium a-bromonaphthalenate, $C_{10}H_4BrO_3K$, crystallizes in long, red, anhydrous needles.

Barium a-bromonaphthalenate, $(C_{10}H_4BrO_3)_2Ba + 3H_2O$, is a yellowish-red precipitate, which is scarcely soluble in cold, sparingly in hot water, and crystallizes from the latter in long, very slender needles.

Hydroxy-β-brom-a-naphthoquinone, or *β-Bromonaphthalenic acid*, is formed when the dibromonaphthoquinone which melts at 151·5° is heated with caustic soda solution, and when a solution of naphthalenic acid in bromine is boiled for several hours.[1] It is also obtained by the action of caustic soda solution on monobromo-β-naphthoquinone, a portion of the latter being simultaneously reduced to the bromoquinol, and is formed in small quantity by the bromination of β-naphthoquinone.[2] It crystallizes from alcohol in golden-yellow scales, and from dilute alcohol in fascicular groups of irregular needles, which are sparingly soluble in ether and benzene, and scarcely soluble in boiling water; it melts at 196·5°, and sublimes, with partial carbonization, in golden-yellow, pointed needles. Its solution has a yellow or red colour according to the concentration. Sodium amalgam converts it into naphthalenic acid (Zincke).

Potassium β-bromonaphthalenate, $C_{10}H_4BrO_3K + 4H_2O$, is readily soluble in water, and crystallizes in aggregates of dark-red needles.

Barium β-bromonaphthalenate, $(C_{10}H_4BrO_3)_2Ba$, is obtained by mixing hot solutions of the potassium salt and barium chloride, and separates out in slender, yellowish-red, matted needles, which are only very slightly soluble in water.

Both of the hydroxybromonaphthoquinones, like the corresponding dibromonaphthoquinones, yield phthalic acid on oxidation, and should therefore be identical. Zincke assumes that in the formation of the second compound from dibromo-β-naphthoquinone an intermolecular change takes place.

Dibromotriketohydronaphthalene, $C_{10}H_4Br_2O_3 + H_2O$, is obtained by the action of bromine on a solution of hydroxybrom-a-naphthoquinone in glacial acetic acid, and crystallizes in dull white needles, which are readily soluble in alcohol and benzene,

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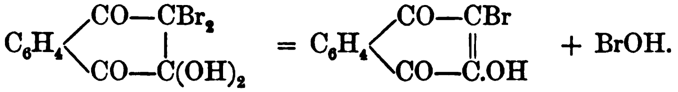
[1] Diehl and Merz, *Ber.* **11**, 1064.

[2] Zincke, *Ber.* **19**, 2493.

and melt at 114—115°, hypobromous acid being evolved; the following formula, therefore, probably represents the constitution of this compound:



$$C_6H_4\left\langle\begin{array}{l}CO-CBr_2\\ \quad\;\;|\\ CO-C(OH)_2\end{array}\right. = C_6H_4\left\langle\begin{array}{l}CO-CBr\\ \quad\;\;\|\\ CO-C.OH\end{array}\right. + BrOH.$$

This decomposition takes place quantitatively on boiling with dilute alcohol. The chlorine compound, mentioned above, has probably a similar constitution (Zincke and Gerland).

Hydroxynitro-a-naphthoquinone or *Nitronaphthalenic acid*, $C_{10}H_4(NO_2)(OH)O_2$, is formed when fuming nitric acid is added to a solution of naphthalenic acid in sulphuric acid,[1] and may also be obtained by heating equal parts of dichlor-*a*-naphthoquinone and sodium nitrite with a sufficient quantity of water, a little alcohol being occasionally added, until complete solution has been effected:

$$C_{10}H_4Cl_2O_2 + 3NaNO_2 + H_2O = \\ C_{10}H_4(NO_2)(ONa)O_2 + 2NaCl + 2NO_2H.$$

On cooling, the sodium salt separates out, and is decomposed with nitric acid.[2]

Nitronaphthalenic acid forms golden-yellow solutions in hot water, alcohol, ether, or benzene, and crystallizes from the latter in yellowish plates or tablets, which melt at 157° with decomposition. It is oxidized by dilute nitric acid to phthalic acid, which is also formed, accompanied by hydrocyanic acid and humus substances, when it is boiled with water for a considerable time.

Sodium nitronaphthalenate, $C_{10}H_4(NO_2)O_3Na + H_2O$, forms flat needles, which have a strong brassy lustre.

Potassium nitronaphthalenate, $C_{10}H_4(NO_2)O_3K + H_2O$, crystallizes from hot water in lustrous golden-yellow needles.

Ammonium nitronaphthalenate, $C_{10}H_4(NO_2)O_3NH_4$, is not very soluble, and forms anhydrous golden-yellow prisms, which are powerfully iridescent.

Barium nitronaphthalenate, $[C_{10}H_4(NO_2)O_3]_2Ba$, forms orange-red scales, sparingly soluble in cold water.

Silver nitronaphthalenate, $C_{10}H_4(NO_2)O_3Ag$, crystallizes from hot water in dark-yellow or reddish-brown, pointed needles.

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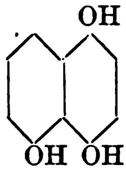
[1] Diehl and Merz, *Ber.* **11**, 1214.

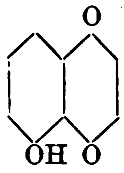
[2] Kehrmann and Weichardt, *J. Pr. Chem.* II. **40** 179.

JUGLONE AND HYDROJUGLONE.

2622 Vogel and Reischauer discovered a substance, which crystallized in reddish-yellow needles, in the green outer shell of the unripe walnut (*Juglans regia*), and gave to it the name of *nucine*, which they afterwards changed to *juglone*. C. Reischauer then pointed out that this substance was probably identical with the *regianine*, which had been prepared from the nutshells by Phipson, and this was confirmed by the latter chemist.[1] Reischauer[2] derived the formula $C_{18}H_{12}O_5$ from his analyses, but Bernthsen[3] showed that the substance is a hydroxynaphthoquinone, $C_{10}H_6O_3$, since on heating with zinc dust it is converted into naphthalene. According to Mylius[4] the juglone does not occur ready formed in the unripe shells, but these and the other green parts of the tree contain during growth two trihydroxynaphthalenes or hydrojuglones, one of which, the *α*-compound, is readily oxidized to juglone. The ripe shells contain no hydrojuglones, but complex substances, perhaps glucosides, which can nevertheless be employed for the preparation of hydrojuglone and juglone. Mylius found that on fusion with caustic potash, *α*-hydrojuglone yields *m*-hydroxybenzoic acid, accompanied by other products, so that the hydroxyl groups must be distributed between the two nuclei. Bernthsen and Semper[5] then showed that juglone is converted by dilute nitric acid into dinitro-v-hydroxyphthalic acid, and by hydrogen dioxide into v-hydroxyphthalic acid, which confirmed the views expressed by Mylius, and further found that the hydroxyl-group in one nucleus is in the *α*-position, the constitution of juglone being thus determined. They then prepared this substance artificially by oxidizing 1 : 4′-dihydroxynaphthalene with chromic acid solution.



α-Hydrojuglone.



Juglone.

Juglone is obtained from the dry, ripe, green outer shell of the walnut by extracting with ether and shaking up the brownish-

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[1] *Ber.* **19**, 28 R.

[2] *Ber.* **10**, 1542.

[3] *Ber.* **17**, 1945.

[4] *Ber.* **17**, 2411; **18**, 2564.

[5] *Ber.* **18**, 203; **19**, 164; **20**, 934.

green solution with a dilute solution of chromic acid, which alters the colour to a fine golden-yellow. The ether is distilled off, and the residue, after repeated extraction with small quantities of boiling ether to remove fat and resinous matter, purified by solution in chloroform and addition of light petroleum, which precipitates a viscid substance; this is filtered off, and the solution evaporated. About 150 grms. of juglone are thus obtained from rather more than 100 kilos. of walnut-shells (Bernthsen and Semper).

It is readily soluble in chloroform, and crystallizes from it or from hot glacial acetic acid in thin, lustrous, yellowish-red to brownish-red needles or prisms; from alcohol, in which it is less soluble, it is obtained in garnet-red needles. It is still less freely soluble in ether and light petroleum, in which it forms yellow solutions, whereas its concentrated solution in chloroform is reddish-brown. It melts at about 150° with decomposition, and sublimes at a higher temperature, a portion being simultaneously carbonized. On boiling with water it is also decomposed, a portion volatilizing with the steam, and imparting to it the characteristic quinone-like smell of the shells as well as the property, which is also possessed by the powdered substance, of causing coughing and sneezing. Its solutions colour the skin a deep yellowish-brown in the same way as walnut-juice. Cold sulphuric acid dissolves it with a blood-red colour, but it is reprecipitated by the addition of water. Reducing agents readily convert it into α-hydrojuglone.

It forms violet solutions in the alkalis, but the colour soon changes to reddish-brown, oxyjuglone, $C_{10}H_6O_4$, and other products being formed. Copper acetate added to the alcoholic solution precipitates the compound $(C_{10}H_5O_3)_2Cu$ in microscopic, obtuse-angled violet prisms.

Acetyljuglone, $C_{10}H_5O_2(O.CO.CH_3)$, is formed by the continued boiling of juglone with acetic anhydride, and by oxidizing 1 : 4′-diacetoxynaphthalene with chromic acid. It crystallizes from hot alcohol in light-yellow plates or tablets, which have a fatty lustre, melt at 154—155° to a red liquid, and sublime in splendid long thin plates. It is also volatile with steam, the vapour having a fainter smell than that of juglone, but irritating the mucous membrane in the same way.

α-Hydrojuglone, $C_{10}H_5(OH)_3$, crystallizes in colourless plates or needles, which melt at 168—170°, and dissolve at 25° in about 200 parts of water. It is readily soluble in alcohol and ether

but is insoluble in chloroform. With alkalis it forms a yellow solution, which becomes violet-coloured in the air owing to the formation of juglone, which is also produced when bromine water or ferric chloride is added to its solution. On fusion with caustic potash it yields *m*-hydroxybenzoic acid, which partially decomposes into carbon dioxide and phenol; salicylic acid, and catechol being then formed from these as secondary products.

α-Hydrojuglone is odourless, but has an unbearable bitter taste, and is poisonous. Rabbits are rapidly killed by a subcutaneous injection of its saturated solution, whilst a dose of 0·5 grms. administered internally kills them within two hours. The green walnut-shells are known to be poisonous, since goats die shortly after eating them.

β-Hydrojuglone occurs in small quantity in the green parts of the tree, and crystallizes from alcohol in silvery, six-sided tablets or flat needles, which melt at 97°, and volatilize with steam, an aromatic vapour being produced. It has a sharp, burning taste, dissolves at 25° in 900—1000 parts of water, and is sparingly soluble in alcohol and ether, but freely in chloroform. Its solution is coloured deep-red by ferric chloride.

It is also formed by the distillation of α-hydrojuglone, and is re-converted by the action of acid chlorides or by boiling with dilute acids into this substance; for this reason, juglone is formed when its alcoholic solution is heated with acid ferric chloride.

The position of its hydroxyl-groups is not known, but since it does not behave as a quinol, they cannot be in the para-position.[1] The following compounds have been obtained from α- and β-hydrojuglones, and yield the latter on hydrolysis:

	Melting-point.
Triacetyl-β-hydrojuglone, $C_{10}H_5(O.CO.CH_3)_3$, colourless prisms	129—130°
Tribenzoyl-β-hydrojuglone, $C_{10}H_5(O.CO.C_6H_5)_3$, needles	228—229°

Trihydroxynaphthalene is formed when naphthalenemetadisulphonic acid is fused with caustic potash at 280—300° for several hours. It crystallizes from water in minute scales, and from light petroleum in small white aggregates, melting at 120—121°. It sublimes in thin lustrous scales, is extremely

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[1] Mylius *loc. cit.*; *Ber.* **18**, 463.

soluble in ether and benzene, and gives no characteristic colouration with ferric chloride.[1]

2623 *2′-Hydroxy-β-naphthoquinone*, is obtained from the amido-compound formed by the reduction of 2′-hydroxy-β-naphthoquinonoxime by treating its hydrochloride in aqueous solution with dilute ferric chloride, and is also probably formed by the direct oxidation of 2 : 2′-dihydroxynaphthalene. It is a reddish-brown amorphous substance which is readily soluble in alcohol and glacial acetic acid, but is insoluble in ether, chloroform, and benzene, and has not been obtained in the crystalline form.[2] It forms a reddish-brown solution in alkalis.

THE DIHYDROXYNAPHTHOQUINONES, $C_{10}H_4O_2(OH)_2$.

2624 *a-Dihydroxynaphthoquinone*, (OH : OH = 2 : 3), is formed when amidonaphthalenic acid, $C_{10}H_4O_2(NH_2)OH$, is heated to 170—180° with dilute hydrochloric acid:

$$C_{10}H_4(NH_2)(OH)O_2 + H_2O + HCl = C_{10}H_4(OH)_2O_2 + NH_4Cl.$$

It crystallizes from hot alcohol in slender reddish-brown needles, and from hot glacial acetic acid in dark-red scales, showing a strong metallic lustre in sunlight. It is sparingly soluble in cold, more freely in hot water, forming a red solution, and imparts a dark violet-blue colour to the alkalis, which becomes blue when more alkali is added and changes to brown on exposure to the air, a black powder being subsequently deposited and the solution left colourless. The red aqueous solution is decolourized by tin and hydrochloric acid, but regains its original tint on exposure to the air. It sublimes when carefully heated in slender, cinnabar-red needles or very lustrous dark-bronze coloured, pointed needles, a portion being simultaneously carbonized. Nitric acid converts it into phthalic acid.

The *barium salt*, $C_{10}H_4O_4Ba$, is a blackish-violet precipitate, the *lead salt* dark-blue and the *silver salt* greyish-blue; the last of these takes a strong brassy lustre on drying. *a*-Dihydroxynaphthoquinone dyes cotton violet on an alumina mordant, and

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[1] Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 136.

[2] Clausius, *Ber.* **23**, 522.

dark-blue on an iron mordant, this colour being fast to soap. Silk is dyed a brownish-violet and takes a strong metallic lustre,

Diacetyl-a-dihydroxynaphthoquinone, $C_{10}H_4(O.CO.CH_3)_2O_2$, crystallizes from hot dilute alcohol in brown scales.[1]

β-Dihydroxynaphthoquinone. In the year 1861 Roussin prepared a colouring matter by the action of zinc on a solution of dinitronaphthalene in hot sulphuric acid, and, looking upon it as identical with the colouring principle of madder, called it artificial alizarin.[2]

Analyses of this substance soon convinced him, however, that it differed from alizarin,[3] and Jacquemain also found that the reactions of the two substances were by no means identical.[4] The new compound was then termed *naphthazarin* by Kopp,[5] and this name soon passed into general use. Its correct formula and constitution were established by Liebermann, who proved it to be a dihydroxynaphthoquinone.[6] Since the dinitronaphthalene employed for its preparation was a mixture, it still remained to be decided from which of the isomerides the naphthazarin was formed, and this question was settled by de Aguiar and Bayer in favour of *a*-dinitronaphthalene.[7]

According to Liebermann, naphthazarin is best prepared in the following manner :—A mixture of 400 grms. of concentrated sulphuric acid with 40 grms. of the fuming acid is heated to 200°, and to this are added 40 grms. of dinitronaphthalene and then granulated zinc, care being taken that the temperature does not rise above 205° or fall below 195°. Five or ten grms. of zinc are required and should be added during about fifteen minutes. A small portion is removed from time to time, boiled with water and filtered; as soon as the colour of the filtrate is a fine red and a gelatinous precipitate is deposited on cooling, the reaction is complete. The product is poured into 10 parts of water, heated to boiling and filtered. The naphthazarin separates out on cooling and is re-crystallized from alcohol. It is thus obtained in elegant brown needles, with a green surface lustre and is further purified by sublimation, small reddish-brown needles being formed, or if it be more strongly heated, aggregates of longer feathery needles, which have a strong green metallic lustre, and resemble small cock's feathers.

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[1] Diehl and Merz, *Ber.* **11**, 1321.

[2] *Compt. Rend.* **52**, 1033.

[3] *Compt. Rend.* **52**, 1177.

[4] *Compt. Rend.* **52**, 1180.

[5] *Repert. Chim. App.* **3**, 411.

[6] *Ber.* **3**, 905; *Annalen*, **162**, 328.

[7] *Ber.* **4**, 251.

It is slightly soluble in hot water and freely in alcohol, forming a red solution. Its alkaline solution, which has a splendid cornflower blue colour is decolourized by sodium amalgam, but regains its colour in the air. Sulphuric acid dissolves it with formation of a magenta-red solution, from which it is precipitated by water. Heated zinc dust reduces it to naphthalene, whilst it is oxidized by nitric acid to oxalic acid, no phthalic acid being formed.

Its alkaline solution gives blue precipitates with the salts of calcium, barium, and lead. The iron lake is bluish-green, and that with alumina carmine-red ; the shades produced on mordanted cotton can however be more cheaply obtained by means of dye-woods. On the other hand it dyes fast shades on a chromium mordant, which can be varied from the most delicate grey to the deepest black. In order to employ it for printing and dyeing, it is converted into the soluble sulphite compound, $C_{10}H_6O_4 + NaHSO_3$, discovered by Bohn, which is known as alizarin black, by mixing it in the form of paste with a strong solution of acid sodium sulphite of 30—40° B, and allowing the whole to stand for several days at 50—70°. On the addition of common salt a black precipitate is obtained which forms a reddish-brown solution in water, and a yellowish-brown solution with a green fluorescence in alcohol.

Alizarin black is fixed on cotton by mixing it with chromium acetate and dilute acetic acid, thickening with starch paste and printing this mixture on the fabric, which is then dried and steamed, a compound of naphthazarin with chromium oxide being thus formed. It is fixed on wool in a similar manner, whilst to dye wool the fabric must first be mordanted with chromium oxide and then brought into a hot solution of the colouring matter.

In the preparation of naphthazarin, a black mass is obtained and, indeed, forms the larger portion of the product. This substance forms dirty-violet coloured solutions in alkalis, from which it is precipitated by acids as a black powder which takes a reddish metallic lustre in drying. This compound, which is considered by de Aguiar and Bayer to be *trihydroxynaphthoquinone*, $C_{10}H_3(OH)_3O_2$, is also obtained by heating naphthazarin with sulphuric acid.[1]

γ-Dihydroxynaphthoquinone, or *Hydroxyjuglone*, (OH:OH=2:5 or 3:5). Mylius observed that juglone combines with dimethyl-

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[1] *Ber.* **4**, 438.

amine to form *dimethylamidojuglone*, $C_{10}H_4O_2(OH)N(CH_3)_2$, which crystallizes from glacial acetic acid in brownish-violet tablets, having a metallic lustre and melting at 149—150°. On heating with hydrochloric acid this substance is converted into hydroxyjuglone:

$$C_{10}H_4O_2(OH)N(CH_3)_2 + H_2O = C_{10}H_4O_2(OH)_2 + NH(CH_3)_2$$

It is also formed by the oxidation of α-hydrojuglone with an alkaline solution of potassium ferricyanide. It crystallizes in golden-yellow needles, or small lemon-yellow tablets, which are scarcely soluble in water, sparingly in alcohol and ether, readily in chloroform and acetone, and are decomposed and blackened at 200°. When carefully heated however it can be sublimed and gives a vapour which smells like that of juglone. It forms a cherry-red solution in concentrated sulphuric acid and a yellowish-red solution in alkalis, which is unaltered in the air.[1] When it is heated in alcoholic solution with stannous chloride, the colourless crystalline quinol, $C_{10}H_4(OH)_4$, is formed, which is rapidly re-converted into hydroxyjuglone in the air.

It dyes mordanted cloth faintly, as does also hydroxynaphthoquinone, whilst juglone produces no colour, because, according to Kostanecki only those quinones which contain an hydroxyl-group in the ortho-position to a quinone oxygen atom are colouring matters.[2]

Sodium hydroxyjuglone, $C_{10}H_4O_2(ONa)_2$, crystallizes in brick-red needles, which are readily soluble in water, but insoluble in alcohol and concentrated caustic soda solution.

The *potassium and ammonium salts* resemble it closely. The *calcium salt* crystallizes in dark-red, difficultly-soluble needles, whilst the *barium salt* is a brownish-black, amorphous precipitate; the *silver* and *copper compounds* are carmine-red coloured.

Benzoylhydroxyjuglone, $C_{10}H_4O_2(O.CO.C_6H_5)_2$, is formed by the action of benzoyl chloride on the sodium salt, and separates from a hot alcoholic solution in small, yellowish white granular crystals.

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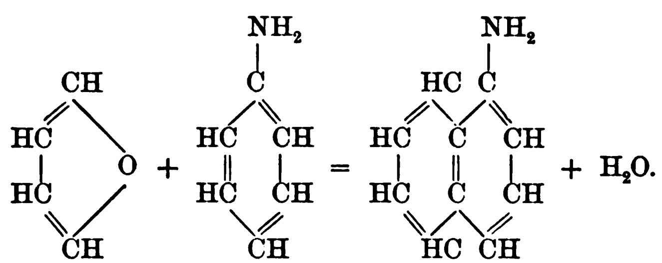
[1] *Ber.* **18**, 463.

[2] *Ber.* **22**, 1347.

THE AMIDO-DERIVATIVES OF NAPHTHALENE.

α-AMIDONAPHTHALENE, OR α-NAPHTHYLAMINE, $C_{10}H_7NH_2$.

2625 This important substance was discovered by Zinin,[1] who obtained it by reducing nitronaphthalene with ammonium sulphide, and named it *naphthalidam* (Pt. III., p. 195). Piria then observed it as a decomposition product of thionaphthamic acid, $C_{10}H_7.NH.SO_3H$, and termed it *naphthalidine*,[2] after which Béchamp showed that it can easily be obtained by heating nitronaphthalene with iron filings and acetic acid.[3] When it was recognized as a compound ammonia it received the name of *naphthylamine*, by which it is still known. It can also be prepared from α-naphthol by heating this to 270° with ammonium acetate; acetonaphthalide is formed, from which the base is obtained by heating with dilute acids or alkalis.[4] A certain amount of dinaphthylamine, $(C_{10}H_7)_2NH$, is also formed in this reaction, and is obtained in small quantity, together with a large amount of α-naphthylamine when α-naphthol is heated with four parts of calcium chloride ammonia, containing water, for eight hours to 270°.[5] α-Naphthylamine is also formed in small quantity when aniline hydrochloride is heated with mannitol to 200—240°,[6] and Canzoneri and Oliveri have obtained it by heating an intimate mixture of pyromucic acid, lime, zinc chloride, and aniline for twelve hours to 300°. The pyromucic acid is decomposed into carbon dioxide and furfuran, which then acts upon the aniline in the following manner:[7]



On the large scale it is manufactured by heating equal parts of α-nitronaphthalene and water to 80°, adding one part of fine iron

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[1] *Annalen*, **44**, 283.
[2] *Annalen*, **78**, 31.
[3] *Annalen*, **92**, 401.
[4] Calm, *Ber.* **15**, 615.
[5] Benz, *Ber.* **16**, 14.
[6] Benz, *Ber.* **18**, 383 R.
[7] *Gazzetta*, **16**, 486.

turnings to the stirred mixture and starting the reaction by the addition of a small quantity of hydrochloric acid. The product is distilled with lime and the crude base rectified from iron cylinders.[1]

α-Naphthylamine is only very slightly soluble in water, readily in alcohol and ether; it crystallizes in flat, silky needles or plates, and from hot aniline in prisms,[2] has a characteristic unpleasant smell, and a sharp, bitter taste. In the air it becomes coloured red to dark-violet; it melts at 50°, boils at 300°, and forms salts which crystallize well and colour pine wood a deeper yellow than those of aniline. Oxidizing agents such as ferric chloride, chromic acid, &c., produce in solutions of its salts an azure-blue precipitate of *naphthameïne* or *oxynaphthamine*, $C_{10}H_9NO$, which soon becomes purple.[3] A small amount of alcohol, containing nitrous acid, produces a yellow colouration in a solution of the base in alcohol or glacial acetic acid. If hydrochloric acid be now added, a magenta or deep violet-red colouration is produced, the hydrochloride of azo-amido-naphthalene being formed; when only a small quantity of naphthylamine is present, the colouration is only a faint red.[4] On boiling with chromic acid, α-naphthoquinone, phthalic acid and a brown insoluble substance are formed.[5] α-Naphthylamine is employed in the manufacture of colouring matters.

α-Naphthylamine hydrochloride, $C_{10}H_7.NH_3Cl$, crystallizes from hot water in long, fibrous needles, resembling asbestos, and from alcohol in lustrous scales, which are readily soluble in ether, but only sparingly in concentrated hydrochloric acid, and sublime at 200°. When platinum chloride is added to its alcoholic solution, a brownish-yellow, crystalline precipitate of $(C_{10}H_{10}N)_2PtCl_6$ is formed, which is slightly soluble in water, and even less readily in alcohol and ether (Zinin).

α-Naphthylamine sulphate, $(C_{10}H_7.NH_3)_2SO_4 + 2H_2O$, is sparingly soluble in cold water and alcohol, readily in hot alcohol, and crystallizes in silvery scales, which become coloured red in the moist state.

α-Naphthylamine nitrate, $C_{10}H_7.NH_3.NO_3$, is obtained by dissolving the base in pure dilute nitric acid, and crystallizes in lustrous scales.

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[1] Schultz, *Steinkohlentheer*, **1**, 362.
[2] Ballo, *Ber.* **3**, 288.
[3] Piria, *Annalen*, **78**, 64; Schiff, *Annalen*, **101**, 92; **129**, 255.
[4] Monet, Reverdin and Nölting, *Ber* **12**, 2305.
[5] Liebermann, *Annalen*, **183**, 265.

a-Naphthylamine oxalate, $(C_{10}H_7.NH_3)_2C_2O_4$, crystallizes in narrow, lustrous plates, whilst the *acid salt*, $C_{10}H_9N.C_2H_2O_4$, forms dull white aggregates.

a-Naphthylamine phenate, $C_{10}H_7.NH_2 + C_6H_5.OH$, crystallizes from light petroleum in needles, melting at 30°.[1]

SECONDARY AND TERTIARY α-NAPHTHYLAMINES.

2626 *Methyl-a-naphthylamine*, $C_{10}H_7.NH.CH_3$, is formed, together with α-dinaphthylamine, when methyl chloride is passed into α-naphthylamine heated to 150—180°. The product is extracted with ether and the ethereal solution shaken with dilute sulphuric acid, which dissolves the methyl base and forms insoluble naphthylamine sulphate with any unattacked base, the dinaphthylamine being left in the ethereal solution. It is a red liquid which boils at 293°, and becomes darker and opaque in the air.[2]

Dimethyl-a-naphthylamine, $C_{10}H_7N(CH_3)_2$, is obtained by heating α-naphthylamine with methyl iodide and wood spirit to 100° (Landshoff), as well as by heating the hydrochloride to 180° with methyl alcohol.[3] It is a colourless liquid, which is very strongly refractive, becomes brown in the air, fluoresces like petroleum, has a faint odour, resembling that of dimethylaniline,[4] and boils at 274·5° (711 mm.). Ferric chloride imparts a purple-red colour to the alcoholic solution, which changes to violet in the air. Its *sulphate* and *hydrochloride* are readily soluble.

Trimethyl-a-naphthylammonium iodide, $NC_{10}H_7(CH_3)_3I$, is formed when the tertiary base is heated to 100° with methyl iodide, and crystallizes in flat, faint yellowish-green needles, which decompose into the constituents at 164°. The *hydroxide* is a strongly alkaline, deliquescent mass.

Ethyl-a-naphthylamine, $C_{10}H_7NH.C_2H_5$. The hydrobromide of this base was obtained by Limpricht, by the action of ethyl bromide on naphthylamine, in reddish nodular aggregates, which yielded naphthylamine on treatment with caustic potash.[5] Schiff

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[1] Dyson, *Journ. Chem. Soc.* 1883, **1**, 466.

[2] Landshoff, *Ber.* **11**, 638.

[3] Hantzsch, *Ber.* **13**, 1348.

[4] Friedländer and Welmans, *Ber.* **21**, 3125; Bamberger and Hellwig, *Ber.* **22**, 1315.

[5] *Annalen*, **99**, 117.

then prepared the hydriodide, which crystallizes in four-sided prisms.[1] He also failed to isolate the base which was, however, prepared by Bernthsen and Trompetter by the action of zinc dust and hydrochloric acid on thio-acetonaphthalide, $C_{10}H_7N(CS.CH_3)H$; these chemists, however, did not further examine it, but converted it into the hydrochloride and platinochloride.[2] According to Bamberger and Hellwig, ethyl-α-naphthylamine is a liquid which rapidly becomes coloured in the air, and appears brownish-red by transmitted light, but steel blue by reflected light; on heating, this dichroism disappears and the colour changes from dark cherry-red to light-orange. It boils at 303° (722·5 mm.).[3]

Diethyl-α-naphthylamine, $C_{10}H_7.N(C_2H_5)_2$, can easily be prepared by heating α-naphthylamine with the calculated quantity of caustic soda, ethyl bromide, and some water to 100—120°. It is a colourless, transparent, oily liquid, which becomes brown in the air, is strongly refractive, and boils at 283—285°. Its *sulphate* is readily soluble, and crystallizes in well-developed, thick prisms.[4]

Triethyl-α-naphthylammonium bromide, $N(C_{10}H_7)(C_2H_5)_3Br$, is formed in small quantity together with the tertiary base, and crystallizes from water in silky plates. When sulphuric acid and potassium ferrocyanide are added to its aqueous solution, a precipitate is formed, from which ammonia separates diethylnaphthylamine.[5]

Triethyl-α-naphthylammonium iodide, $N(C_{10}H_7)(C_2H_5)_3I$, forms well-developed cube-shaped crystals (Friedländer and Welmans).

Ethylene-α-naphthylamine, $(C_{10}H_7NH)_2C_2H_4$, is obtained when naphthylamine is boiled with ethylene bromide and benzene, and forms crystals, which melt at 127° and are sparingly soluble in alcohol, more readily in absolute alcohol, and readily in ether. The *sulphate*, $C_{22}H_{20}N_2SO_4H_2$, is only very slightly soluble and forms microscopic crystals, which have a strong silvery lustre.[6]

Phenyl-α-naphthylamine, $C_{10}H_7.NH.C_6H_5$, is formed when α-naphthylamine is heated to 240° with aniline hydrochloride[7] and when one molecule of α-naphthol is heated to 280° with two molecules of aniline and one molecule of calcium chloride.[8]

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[1] *Annalen*, **101**, 90. [2] *Ber.* **11**, 1761. [3] *Ber.* **22**, 1312.

[4] Friedländer and Welmans, *Ber.* **21**, 3123.

[5] B. E. Smith, *Journ. Chem. Soc.* 1882, **1**, 180. [6] Reuter, *Ber.* **8**, 23.

[7] Girard and Vogt, *Bull. Soc. Chim.* **18**, 68; Streif, *Annalen*, **209**, 151.

[8] Friedländer, *Ber.* **16**, 2075.

It crystallizes from alcohol in colourless needles or prisms, melts at 62°, and boils at 335° under a pressure of 258 mm. Its alcoholic solution shows a blue fluorescence, whilst its solution in sulphuric acid which contains nitric acid is coloured blue, but changes on heating to green and then to brown. It is insoluble in dilute acids, but when hydrochloric acid is passed into its alcoholic solution the hydrochloride separates out in prisms, which are decomposed by water.

Phenyl-a-naphthylnitrosamine, $C_{10}H_7N(C_6H_5)NO$, is formed when an acetic acid solution of phenyl-α-naphthylamine is shaken with powdered sodium nitrite and the mixture allowed to stand in a cool place. It crystallizes from methyl alcohol in faint, yellowish-red tablets or prisms, melting at 92°.[1]

	Melting-point.
o-Tolyl-α-naphthylamine, $C_{10}H_7NH.C_6H_4.CH_3$, long, flat needles	94—95°
p-Tolyl-α-naphthylamine,[2] $C_{10}H_7NH.C_6H_4.CH_3$, short prisms	78°
Benzylnaphthylamine,[3] $C_{10}H_7NH.CH_2.C_6H_5$, brown, lustrous scales	66—67°
Cholesterylnaphthylamine,[4] $C_{10}H_7NH\ C_{26}H_{43}$, crystals	202°

p-Phenylene-a-naphthylamine, $(C_{10}H_7.NH)_2C_6H_4$, is obtained by heating α-naphthol with *p*-diamidobenzene to 200°, and crystallizes from aniline in small white plates, which melt at 235°, and are almost insoluble in boiling alcohol, ether, or benzene. Its solution in concentrated sulphuric acid is coloured greenish violet, and then deep blue by potassium nitrite. It unites with picric acid to form the compound $(C_{10}H_7NH)_2C_6H_4 + 2C_6H_3(NO_2)_2O$, which crystallizes in small, black, lustrous needles, is sparingly soluble in alcohol, but freely in hot benzene, and melts at 217° with evolution of gas. When the base is heated to 140° with methyl iodide and wood spirit, *p-phenylenemethylnaphthylamine*, $(C_{10}H_7.NCH_3)_2C_6H_4$, is formed. This substance crystallizes from hot benzene in small white plates, melting at 180°.[5]

a-Dinaphthylamine, $(C_{10}H_7)_2NH$, was first prepared by Girard

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[1] O. Fischer and Hepp, *Ber.* **20**, 1247.

[2] Friedländer, *Ber.* **16**, 2075.

[3] Froté and Tommasi, *Bull. Soc. Chim.* **20**, 67.

[4] Wallitzky, *Beilstein's Handb.* **2**, 397.

[5] Ruoff, *Ber.* **22**, 1080

and Vogt by heating *a*-naphthylamine with its hydrochloride.[1] As already mentioned, it is also formed when *a*-naphthylamine is heated with methyl chloride. On heating a mixture of 10 parts *a*-naphthol, 13 parts sodium acetate, and 3 parts ammonium chloride for 8 hours to 270°, 31 per cent. of dinaphthylamine and 25 per cent. of naphthylamine are formed.[2] It may also be obtained by heating *a*-naphthol with *a*-naphthylamine and calcium chloride.[3]

It is insoluble in water, moderately soluble in alcohol, and readily in ether, crystallizes in quadratic plates, melting at 111°, and boils at 310—315° (15 mm.). Its alcoholic solution is coloured green by ferric chloride; sulphuric acid dissolves it, forming a yellow solution which becomes green on heating, whilst dilute acids and even concentrated hydrochloric acid only dissolve it to a very slight extent. It forms with picric acid the compound $C_{20}H_{15}N + 2C_6H_3(NO_2)_3O$, which crystallizes in small black needles, melting at 168—169° (Benz).

a-Dinaphthylnitrosamine, $(C_{10}H_7)_2N(NO)$, is a yellow crystalline powder, which melts at 260—262° with decomposition, and is only slightly soluble in water and alcohol (Landshoff).

a-NAPHTHALIDES.

2627 *a-Formylnaphthalide*, $C_{10}H_7.NH.COH$, was obtained by Zinin, together with oxalnaphthalide by heating acid naphthylamine oxalate to 200°.[4] It is also readily formed when *a*-naphthylamine is boiled with aqueous formic acid, and crystallizes from boiling water, in which it is moderately soluble, in silky needles, melting at 138·5°.[5]

a-Acetonaphthalide, or *a-Naphthylacetamide*, $C_{10}H_7NH.CO.CH_3$, is obtained when *a*-naphthylamine is heated for some time with glacial acetic acid,[6] and when *a*-naphthol is heated with ammonium acetate (p. 144). It is insoluble in cold water, somewhat soluble in hot water, and readily in alcohol, and crystallizes in silky needles, which melt at 159°, and sublime in very delicate

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[1] *Bull. Soc. Chim.* **19**, 68.

[2] Calm, *Ber.* **15**, 609.

[3] Benz, *Ber.* **16**, 17.

[4] *Annalen*, **108**, 229.

[5] Tobias, *Ber.* **15**, 2443.

[6] Rother, *Ber.* **4**, 850; Andreoni and Biedermann, *Ber.* **6**, 342; Tommasi, *Bull. Soc. Chim.* **20**, 19; Dittler and Liebermann, *Annalen*, **183**, 229.

thread-like forms, resembling the finest silk fibres. It is not attacked by boiling hydrochloric acid, but is decomposed by continued heating with caustic potash solution.

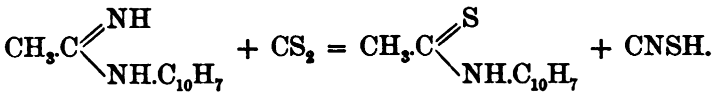
a-Acetomethylnaphthalide, $C_{10}H_7N(CO.CH_3)CH_3$, is formed when *a*-methylnaphthylamine is boiled with acetic anhydride, and crystallizes from hot water in small prisms, melting at 90—91°.[1]

a-Acetophenylnaphthalide, $C_{10}H_7N(CO.CH_3)C_6H_5$, is prepared by heating phenylnaphthylamine with acetic anhydride, and forms indistinct crystals, which melt at 115° (Streiff).

p-Phenylene-a-acetonaphthalide, $(C_{10}H_7N.CO.CH_3)_2C_6H_4$, forms white plates, melting at 210° (Ruoff).

a-Dinaphthylacetamide, $(C_{10}H_7)_2N.CO.CH_3$, crystallizes from alcohol in stellate aggregates of small, yellowish needles, melting at 217° (Benz).

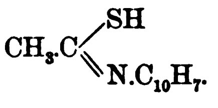
a-Thio-acetonaphthalide is formed when ethenylnaphthylamidine is heated with carbon disulphide:[2]



$$CH_3.C\left\langle\begin{matrix}NH\\NH.C_{10}H_7\end{matrix}\right. + CS_2 = CH_3.C\left\langle\begin{matrix}S\\NH.C_{10}H_7\end{matrix}\right. + CNSH.$$

It may be more simply obtained by melting *a*-acetonaphthalide with phosphorus pentasulphide.[3] It crystallizes from alcohol in well-developed white tablets, which melt at 110—111°.

Like thio-acetanilide, it behaves in many reactions as the tautomeric mercaptan:



$$CH_3.C\left\langle\begin{matrix}SH\\N.C_{10}H_7.\end{matrix}\right.$$

a-Benzonaphthalide, $C_{10}H_7.NH(CO.C_6H_5)$, is obtained by the action of benzoyl chloride on *a*-naphthylamine,[4] and also by heating the latter with benzoic acid.[5] It crystallizes from alcohol in needles, melting at 159—160°.

a-Thiobenzonaphthalide, $C_{10}H_7.NH(CS.C_6H_5)$, is prepared in a similar manner to the thio-acetyl compound, and resembles it in

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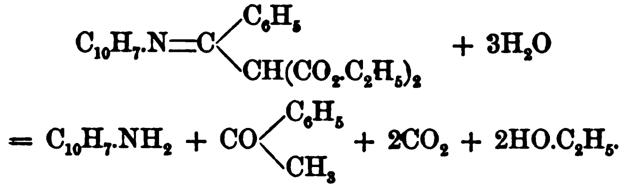
[1] Landshoff, *Ber.* **11**, 634.
[2] Bernthsen and Trompetter, *Ber.* **10**, 1756.
[3] Jacobson, *Ber.* **20**, 1895.
[4] Church, *Chem. News*, **5**, 324; Ebell, *Annalen*, **208**, 324.
[5] Hofmann, *Ber.* **20**, 1798.

properties. It crystallizes from alcohol in yellowish needles, and melts at 147·5—148·5° (Bernthsen and Trompetter; Jacobson).

a-Benzonaphthalidimidochloride, $C_{10}H_7N{=}CCl.C_6H_5$, is formed by the action of phosphorus chloride on a-benzonaphthalide:

$$C_{10}H_7N(CO.C_6H_5)H + PCl_5 = C_{10}H_7N{=}CCl.C_6H_5 + HCl + POCl_3.$$

It crystallizes from light petroleum in large, colourless plates, melts at 60°, and is converted by sodiomalonic ester into *ethyl a-naphthylaminebenzenylmalonate*, $C_{10}H_7.N{=}C(C_6H_5)CH(CO_2.C_2H_5)_2$, which crystallizes from alcohol in large, hard, strongly refractive, obtuse-angled crystals, melting at 145·5°. On heating with dilute hydrochloric acid to 120°, acetophenone and a-naphthylamine are obtained:[1]



$$C_{10}H_7.N{=}C\begin{cases}C_6H_5\\CH(CO_2.C_2H_5)_2\end{cases} + 3H_2O$$
$$= C_{10}H_7.NH_2 + CO\begin{cases}C_6H_5\\CH_3\end{cases} + 2CO_2 + 2HO.C_2H_5.$$

a-Naphthylglycocoll, $C_{10}H_7.NH.CH_2.CO_2H$, is formed on heating a-naphthylamine with chloracetic acid and sodium acetate, and crystallizes from alcohol in needles, which melt at 198—199°.[2] When heated to 230°, it forms the *anhydride*, $(C_{10}H_7.NH.CH_2.CO)_2O$, which crystallizes in lustrous scales, melting at 268—269°, whilst *acetylnaphthylglycocoll*, $C_{10}H_7.N(CO.CH_3)CH_2CO_2H$, is obtained by heating the glycocoll with acetic anhydride, and crystallizes from water in white prisms, which melt at 154°, and have an acid reaction.

a-Naphthylglycocoll is converted by nitrous acid into an exceedingly unstable nitroso-derivative.[3]

a-Naphthylimidodiacetic acid, $C_{10}H_7N(CH_2.CO_2H)_2$, is formed when a-naphthylglycocoll is heated to 140° for two hours with one molecule of chloracetic acid and 1½ molecules of sodium carbonate. It is readily soluble in alcohol and glacial acetic acid, sparingly in light petroleum and benzene, from the last of which it separates in crystals containing one molecule of benzene, which

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[1] Just, *Ber.* **19**, 979.

[2] Bischoff and Nastvogel, *Ber.* **22**, 1807; Forte, *Ber.* **22**, 731 c.

[3] Jolles, *Ber.* **22**, 2372.

is lost at 100°. The pure acid melts at 133—133·5°, with evolution of gas. Ferric chloride colours its solutions red, brown, and on heating green.[1]

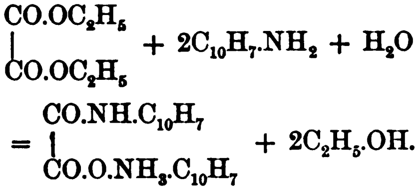
On heating with naphthylamine to 140°, the mono- and dinaphthalides of this acid are obtained.

The *mononaphthalide*, $C_{10}H_7N(CH_2.COOH)CH_2.CO.NH.C_{10}H_7$, is soluble in benzene and alcohol, melts at 197—199°, and dissolves in alkalis.

The *dinaphthalide*, $C_{10}H_7N(CH_2.CO.NC_{10}H_7)_2$, forms colourless crystals, melting at 200—202°.

a-Oxalonaphthalide, $(C_{10}H_7.NH)_2C_2O_2$, is insoluble in water, and crystallizes from boiling alcohol, in which it is only slightly soluble, in small scales, which melt at about 200°, and on further heating decompose into carbonic oxide and dinaphthyl urea. It is scarcely attacked by dilute caustic potash solution, but is decomposed by a concentrated solution on heating (Zinin).

a-Naphthyloxamic acid, $C_{10}H_7.NH.C_2O_2.OH$, is obtained when naphthylamine is heated to 100° with ethyl oxalate and a little alcohol:



$$\begin{array}{l}CO.OC_2H_5\\ |\\ CO.OC_2H_5\end{array} + 2C_{10}H_7.NH_2 + H_2O$$

$$= \begin{array}{l}CO.NH.C_{10}H_7\\ |\\ CO.O.NH_3.C_{10}H_7\end{array} + 2C_2H_5.OH.$$

The *naphthylamine salt* thus obtained crystallizes in white needles, melting at 154°; when its solution in hot, very dilute hydrochloric acid is allowed to cool, the free acid separates in fascicular groups of needles, which decompose and froth up on heating.

Ethyl a-naphthyloxamate, $C_{10}H_7.NH.C_2O_2.OC_2H_5$, is formed when naphthylamine and ethyl oxalate are heated together without alcohol, and crystallizes in fascicular groups of needles, melting at 106°.[2]

a-Succinonaphthalide, $(C_{10}H_7.NH.CO)_2C_2H_4$, is obtained, together with the compound next to be described, by heating naphthylamine to 190° with succinic acid. It is scarcely soluble in alcohol, and crystallizes from glacial acetic acid in delicate needles, melting with decomposition at 285°.[3]

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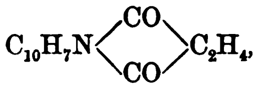
[1] Bischoff, Hausdörfer, Leykin, *Ber.* **23**, 2003.

[2] Ballo, *Ber.* **6**, 247.

[3] Hübner, *Annalen*, **209**, 381.

α-Succinonaphthil or *α-Naphthylsuccinimide*,

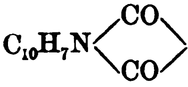


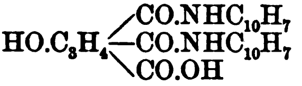
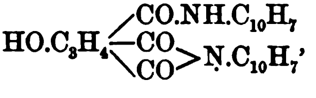
$$C_{10}H_7N\genfrac{}{}{0pt}{}{\diagup CO \diagdown}{\diagdown CO \diagup}C_2H_4,$$

is also formed when succinic acid is heated to 200° with 1 : 4-naphthylaminesulphonic acid,[1] $C_{10}H_6(NH_2)SO_3H$, and crystallizes from boiling water in coarse lustrous needles, which melt at 153°, and are volatile without decomposition.

α-Naphthylsuccinamic acid, $C_{10}H_7.NH.CO.C_2H_4.CO_2H$, is prepared by dissolving succinonaphthil in caustic potash solution, and crystallizes from alcohol in flat needles, which melt at 171°, and on further heating are converted into the preceding compound.

Malo-α-dinaphthalide, $C_{10}H_7NH.CO.CH.CHOH.CONHC_{10}H_7$, is prepared by heating malic acid with naphthylamine. It can be recrystallized from alcohol, and melts at 205°. On treatment with acetic anhydride it yields an *acetyl derivative* melting at 223—224°.[2]

Citracon-α-naphthalide or *α-Naphthylcitraconimide*,  $C_{10}H_7N\genfrac{}{}{0pt}{}{\diagup CO \diagdown}{\diagdown CO \diagup}C_3H_4$, is obtained by heating equal molecules of citraconic acid and α-naphthylamine to 140—150°; it crystallizes in yellow plates or small, honey-yellow, rhombic tablets, melting at 142—143°.[3]

	Melting-point.
α-Citrodinaphthylamic acid,  $HO.C_3H_4\begin{cases}CO.NHC_{10}H_7\\CO.NHC_{10}H_7\\CO.OH\end{cases}$ small needles	149°
α-Citrotrinaphthylamide, $HO.C_3H_4(CO.NH.C_{10}H_7)_3$, microscopic prisms	129°
α-Citrodinaphthylamidimide,  $HO.C_3H_4\begin{cases}CO.NH.C_{10}H_7\\ \genfrac{}{}{0pt}{}{CO}{CO}>N.C_{10}H_7\end{cases}$, six-sided plates[4]	194°

α-Naphthylamido-m-nitrobenzoic acid, $C_{10}H_7NH.C_6H_3(NO_2)CO_2H$, is formed when α-naphthylamine is heated with *p*-bromo-

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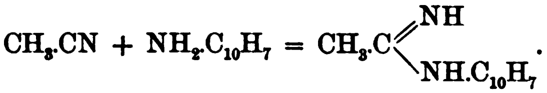
[1] Pellizzari and Matteucci, *Chem. Centralbl.* **59**, 1000.
[2] Bischoff and Nastvogel, *Ber.* **23**, 2046.
[3] Morawski and Gläser, *Monatsh. Chem.* **9**, 284.
[4] Hecht, *Ber.* **19**, 2616.

m-nitrobenzoic acid as a reddish-brown amorphous powder. The *ethyl ester* crystallizes from alcohol in reddish-brown plates, melting at 109° On reduction, the acid yields the corresponding *amido-acid,* which crystallizes from dilute alcohol in white needles, decomposing at 90.[1]

α-NAPHTHYLAMIDINES.

2628 *Ethenylnaphthylamidine,* $CH_3.C(NH)NH(C_{10}H_7)$, is obtained by heating α-naphthylamine hydrochloride to 160—170° with acetonitrile:



$$CH_3.CN + NH_2.C_{10}H_7 = CH_3.C\left\langle\begin{array}{l} NH \\ NH.C_{10}H_7 \end{array}\right. .$$

It is a gummy, elastic mass, which is insoluble in water, but dissolves readily in alcohol, and has an alkaline reaction.

Ethenylnaphthylamidine hydrochloride, $C_{12}H_{12}N_2,HCl$, crystallizes in lustrous, abrupt prisms, which are readily soluble in water.

Benzenylnaphthylamidine, $C_6H_5.C(NH)NH.C_{10}H_7$, is formed when α-naphthylamine is heated to 200° with benzonitrile, and crystallizes from alcohol in tablets which have a satin lustre, melt at 141°, and form a faintly alkaline solution in dilute alcohol.

Benzenylnaphthylamidine hydrochloride, $C_{17}H_{14}N_2,HCl$, crystallizes in white prisms.[2]

α-NAPHTHYLCARBAMIDES.

2629 *a-Naphthyl urea,* $CO(NH_2)NH.C_{10}H_7$, was prepared by Schiff by passing the vapour of cyanic acid into an ethereal solution of α-naphthylamine,[3] whilst Pagliani obtained it, together with dinaphthyl urea, by heating α-naphthylamine hydrochloride to 150—160° with urea.[4] It crystallizes from hot water or alcohol in pliable, flat, lustrous needles, which decompose at 250° without fusing.

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[1] Heidensleben, *Ber.* **23**, 3457.

[2] Bernthsen and Trompetter, *Ber.* **11**, 1756.

[3] *Annalen,* **101**, 90.

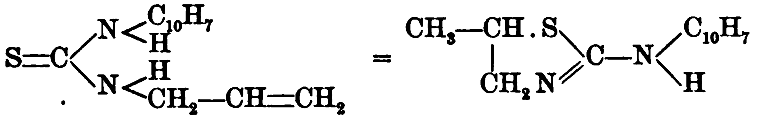
[4] *Ber.* **12**, 385.

a-Dinaphthyl urea, $CO(NH.C_{10}H_7)_2$, was first obtained by Delhos by heating acid naphthylamine oxalate, and was named by him *naphthalidamcarbamide*.[1] Zinin then showed that the same substance, which he called *carbonaphthalide*, is a product of the decomposition of oxalonaphthalide, which is first formed.[2] It is slightly soluble in alcohol, from which it crystallizes in small needles, melting with decomposition at 270° (Pagliani).

a-Ethyl naphthylcarbamate, $CO(OC_2H_5)NH.C_{10}H_7$, is formed by the action of ethyl chloroformate on α-naphthylamine. It is insoluble in water, and crystallizes from alcohol in needles, melting at 79°.[3]

a-Naphthyl thio-urea, $CS(NH_2)NH.C_{10}H_7$, is obtained by heating a solution of naphthylamine hydrochloride with ammonium thiocyanate, and crystallizes from hot alcohol in small, rhombic prisms, which melt at 198°.[4]

a-Naphthyl allyl thio-urea, $CS(NH.C_3H_5)NH.C_{10}H_7$, was prepared by Zinin by the action of mustard oil on α-naphthylamine.[5] It forms small crystals, melting at 145°, and, like other allyl thio-ureas, is converted by heating with hydrochloric acid into the basic *naphthylpropylene pseudothio-urea* :



This substance crystallizes in rhombic tablets melting at 134° and forms a *picrate*, which crystallizes in rectangular needles, and a *platinochloride*, which is an orange coloured crystalline precipitate.[6]

a-Naphthyl phenyl thio-urea, $CS(NH.C_6H_5)NH.C_{10}H_7$, is formed by the action of phenyl mustard oil on α-naphthylamine[7] and of aniline on α-naphthyl mustard oil.[8] It crystallizes in plates, which are only slightly soluble in alcohol and melt at 158—159°. When it is heated to 150—160° with concentrated hydrochloric acid, all four of the substances from which it has been prepared are formed.[9]

a-Dinaphthyl thio-urea, $CS(NH.C_{10}H_7)_2$, was obtained by Delhos by boiling α-naphthylamine with carbon disulphide and

[1] *Annalen*, **64**, 370.
[2] *Annalen*, **108**, 228.
[3] Hofmann, *Ber.* **3**, 657.
[4] Clermont and Wehrlin, *Bull. Soc. Chim.* **26**, 125.
[5] *Annalen*, **84**, 346.
[6] Gabriel, *Ber.* **22**, 3000.
[7] Hofmann, *Jahresb.* **1858**, 350.
[8] Hall, *Jahresb.* **1858**, 350.
[9] Mainzer, *Ber.* **15**, 1414.

absolute alcohol;[1] according to Schiff it may be more conveniently prepared by heating to 100° without the addition of alcohol.[2] It is only slightly soluble in hot alcohol and glacial acetic acid, and crystallizes in strongly lustrous needles, which melt at 203°.[3] On boiling with alcoholic potash it is converted into dinaphthyl urea (Delhos), whilst on heating with benzene and mercuric oxide, *a-carbodinaphthylimide*, $C(NC_{10}H_7)_2$, is formed. This substance crystallizes from a mixture of benzene and ether in large prisms, melting at 93—94°, is converted into α-dinaphthyl urea on heating with dilute alcohol, and combines with sulphuretted hydrogen to form the original dinaphthyl thio-urea.[4]

β-AMIDONAPHTHALENE or β-NAPHTHYLAMINE, $C_{10}H_7.NH_2$.

2630 This base was first obtained by Liebermann by boiling 1 : 2-bromonitronaphthalene with tin and hydrochloric acid.[5] It is also formed, together with β-dinaphthylamine, when β-naphthol is heated to 200—210° with zinc chloride ammonia.[6] The same products are obtained, accompanied by β-acetonaphthalide, by heating β-naphthol with ammonium acetate to 270—280°.[7] Gräbe has found that it can also be prepared by acting on heated β-naphthol with gaseous ammonia,[8] and this reaction is utilized in its manufacture. The apparatus consists of three iron boilers, which will withstand a considerable pressure, and are connected with one another by air-tight joints. The gas is evolved by heating a concentrated solution of ammonia contained in the first vessel, is dried by caustic lime contained in the second, and in the third is brought into contact with β-naphthol heated to 150—160°; the conversion proceeds gradually, and is accompanied by a diminution of the pressure. After 60—70 hours about half of the naphthol has been converted into the base and the operation is then interrupted, the naphthol removed by caustic soda, and the β-naphthylamine extracted from the product by dilute hydrochloric acid, dinaphthyl-

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[1] *Annalen*, **64**, 370.

[2] *Annalen*, **101**, 90; see also Evers, *Ber.* **21**, 962.

[3] Baeyer, *Ber.* **12**, 1860.

[4] Huhn, *Ber.* **19**, 2404.

[5] *Annalen*, **183**, 258.

[6] *Ber.* **13**, 3100.

[7] Merz and Weith, *Ber.* **14**, 2243; Calm, *Ber.* **15**, 613.

[8] Calm, *Ber.* **13**, 1349.

amine which is formed more abundantly on heating longer and more strongly, and which has scarcely basic properties, being left behind. According to a simpler process, 10 kilos. of β-naphthol are heated with 4 kilos. of caustic soda and 4 kilos. of ammonium chloride to 150—160° for 60—70 hours.[1]

It is also abundantly formed when β-naphthol is heated for two hours to 230—250° with calcium chloride ammonia containing water, and the temperature finally raised to 270-280° for six hours; 80 per cent. of β-naphthylamine and 12—13 per cent. of β-dinaphthylamine are thus obtained, and these are then separated from one another and from unattacked β-naphthol as described above.[2]

β-Naphthylamine is slightly soluble in cold, readily in hot water, alcohol and ether, and crystallizes in nacreous plates melting at 112°. It boils at 299·5°,[3] and is distinguished from the α- compound by the facts that it is odourless, gives no characteristic reactions with oxidizing agents or alcohol containing nitrous acid, and does not become coloured in the air. Its aqueous solution shows a blue fluorescence, but not that of its salts.

It is employed for the manufacture of azo-colouring matters.

β-Naphthylamine hydrochloride, $C_{10}H_7.NH_3Cl$, crystallizes in small plates, which are readily soluble in water and alcohol, but only slightly in hydrochloric acid. The *platinochloride*, $(C_{10}H_7.NH_3)_2PtCl_6$, forms yellow plates, which are soluble in cold water.

β-Naphthylamine sulphate, $(C_{10}H_7.NH_3)_2SO_4$, is less soluble than the α-compound, and crystallizes from hot water in fine plates.

β-Naphthylamine picrate, $C_{10}H_7N.C_6H_3(NO_2)_3O$, crystallizes from alcohol in long yellow needles.

β-Naphthylamine silicon chloride, $(C_{10}H_7NH)_2SiCl_2$, is formed when silicon chloride is added to a solution of β-naphthylamine in benzene, naphthylamine hydrochloride separating out as a very voluminous precipitate. On evaporating the filtrate, the compound is obtained as a white powder, which decomposes without fusing when heated.[4]

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[1] Schultz, *Steinkohlentheer*, **1**, 364.

[2] Benz, *Ber.* **16**, 8.

[3] Bamberger, *Ber.* **22**, 772.

[4] Harden, *Journ. Chem. Soc.* 1887. **1**, 45.

SECONDARY AND TERTIARY β-NAPHTHYLAMINES.

2631 *Dimethyl-β-naphthylamine*, $C_{10}H_7.N(CH_3)_2$, was obtained by Hantzsch by heating β-naphthol with commercial trimethylamine, containing methylamine, to 200°, and treating the product with methyl iodide; the hydroxide prepared from the trimethylnaphthylammonium iodide thus obtained decomposes on dry distillation into methyl alcohol and dimethyl-β-naphthylamine.[1] According to Bamberger and Müller, it is better to prepare the ammonium iodide by heating β-naphthylamine to 120° with methyl iodide, caustic soda and water, and to decompose it by distillation with potash.[2] Dimethyl-β-naphthylamine is a crystalline mass, melts at 46°, and boils at 305°. Its salts are readily soluble, with the exception of the platinochloride, which is only slightly soluble even in boiling alcohol.

Trimethyl-β-naphthylammonium iodide, $C_{10}H_7(CH_3)_3NI$, crystallizes in thin plates with a satin lustre or silver-white tablets, which have a bitter taste and are sparingly soluble in cold water and alcohol. Its hydroxide solidifies *in vacuo* to a crystalline, strongly alkaline, but not very caustic mass.

Ethyl-β-naphthylamine, $C_{10}H_7(NH.C_2H_5)$, is an oily liquid, which distils at 305° (716 mm.)[3] and does not solidify in a freezing mixture. Its *hydrochloride* crystallizes from hot water in elegant plates, which melt at 235°, and volatilize on further heating almost without decomposition.

Ethyl-β-naphthylnitrosamine, $C_{10}H_7.N(NO)C_2H_5$, forms colourless crystals, melting at 56°.[4]

Diethyl-β-naphthylamine, $C_{10}H_7N(C_2H_5)_2$, is a viscid, oily liquid which rapidly becomes brown in the air; the colouration disappears on heating but returns on cooling. It boils at 316° under a pressure of 717 mm.

Diethyl-β-naphthylamine hydrochloride, $C_{10}H_7N(C_2H_5)_2HCl$, separates out when hydrochloric acid is passed into a solution of the base in anhydrous ether, in the form of elongated six-sided microscopic tablets, whilst on the evaporation of the aqueous

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[1] *Ber.* **13**, 2053.

[2] *Ber.* **22**, 1306.

[3] Bamberger and Müller, *Ber.* **22**, 1297.

[4] Henriques, *Ber.* **17**, 2668; Fischer and Hepp, *Ber.* **20**, 1247.

solution it is usually left as a viscid syrup, which soon solidifies to groups of needles, resembling wavellite. It is decomposed by heated lime into β-naphthylamine and a combustible gas, which Bamberger and Williamson consider to be butylene,[1] but which is probably ethylene.

Phenyl-β-naphthylamine, $C_{10}H_7NH.C_6H_5$, is formed when β-naphthol is heated with aniline hydrochloride,[2] or zinc chloride aniline.[3] It is, however, best prepared by heating a molecule of β-naphthol with two molecules of aniline and one molecule of calcium chloride for nine hours to 280°.[4] It is freely taken up by the usual solvents at their boiling-points, sparingly in the cold, and crystallizes from hot methyl alcohol in hard, colourless, rhombic needles, which melt at 108°. Its solutions show a blue fluorescence. It boils at 395°, and is decomposed into aniline and β-naphthol when heated to 240° with concentrated hydrochloric acid. If hydrochloric acid be passed into its solution, the *hydrochloride* separates as a snow-white, crystalline powder, which is decomposed by water. Its *picrate* forms brownish needles, which decompose in moist air.

Phenyl-β-naphthylnitrosamine, $C_{10}H_7N(NO)C_6H_5$, is obtained when amyl nitrite is added to a solution of the base in benzene and crystallizes in yellow prisms melting at 93°.[5]

	Melting-point.
o-Tolunaphthylamine, $C_{10}H_7N(C_6H_4.CH_3)H$, small plates	95—96°
p-Tolunaphthylamine, $C_{10}H_7NHC_6H_4.CH_3$, lustrous plates[6]	104°

β-Dinaphthyl-p-diamidobenzene, or *p-Phenylene-β-naphthylamine*, $C_6H_4(NH.C_{10}H_7)_2$, is formed when *p*-diamidobenzene is heated with β-naphthol to 200°, and crystallizes from boiling aniline in plates, melting at 235°, which are insoluble in dilute acids. Its solution in concentrated sulphuric acid is coloured greenish-violet and then deep-blue by sodium nitrite. When it is heated with a solution of picric acid in alcohol the compound $C_6H_4(NH.C_{10}H_7)_2 + 2C_6H_3(NO_2)_3O$ is formed, which crystallizes from a mixture of benzene and light petroleum in lustrous black needles.[7]

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[1] *Ber.* **22**, 1760.

[2] Merz and Weith, *Ber.* **13**, 1298.

[3] Gräbe, *Ber.* **13**, 1849.

[4] Friedländer, *Ber.* **16**, 2075.

[5] Streiff, *Annalen*, **209**, 159.

[6] Merz and Weith, *Ber.* **14**, 2343; Witt, *Ber.* **20**, 578.

[7] Rueff, *Ber.* **22**, 1080.

β-Dinaphthyl-m-diamidobenzene is prepared in a similar manner and forms violet, matted needles, melting at 126°.[1]

β-Dinaphthylamine, $(C_{10}H_7)_2NH$. The preparation of this substance has already been mentioned under β-naphthylamine. It is also formed when hydrochloric acid is passed into β-naphthylamine heated to 170—190°,[2] and crystallizes in silvery plates, melting at 170·5°, which are sparingly soluble in boiling alcohol, readily in boiling glacial acetic acid and benzene; its solutions show a blue fluorescence. On heating to 240° with hydrochloric acid, it decomposes into β-naphthol and β-naphthylamine, whilst much β-naphthylamine is formed when it is heated to 370° with zinc chloride ammonia and ammonium chloride.[3] Its crystalline *hydrochloride* is also decomposed by water, and it forms a *picrate* which crystallizes in hair-like reddish-brown needles, melting at 164—165° (Benz).

β-Dinaphthylnitrosamine, $N(C_{10}H_7)_2NO$, is formed when the base is mixed with alcohol and sulphuric acid and a concentrated solution of sodium nitrite added; it crystallizes from benzene in white fascicular groups of needles, which become brown on heating, and melt at 139—140°.[4]

Ris has also prepared the following compounds:

	Melting-point.
Methyl-β-dinaphthylamine, $(C_{10}H_7)_2NCH_3$, needles	139—140°
Ethyl-β-dinaphthylamine, $(C_{10}H_7)_2NC_2H_5$, needles	231°

α-β-Dinaphthylamine is not obtained when α-naphthol is heated with β-naphthylamine, the product being in this case β-dinaphthylamine; it is, however, formed when β-naphthol is heated to 280° with α-naphthylamine and calcium chloride ammonia containing water. It crystallizes in prisms, which have a vitreous lustre, melt at 110—111°, and dissolve readily in hot alcohol and benzene. Its *picrate* crystallizes in small, brownish-black needles, melting at 172—173°.[5]

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[1] Ruhemann, *Ber.* **14**, 54.

[2] Klopsch, *Ber.* **18**, 1585.

[3] Ris, *Ber.* **19**, 2016.

[4] Ris, *Ber.* **20**, 2618.

[5] Benz, *Ber.* **16**, 17.

β-NAPHTHALIDES.

2632 *β-Formonaphthalide*, $C_{10}H_7NH.CHO$, is formed when β-naphthylamine is heated with ethyl formate[1] or boiled with formic acid;[2] it crystallizes in plates, melting at 129°.

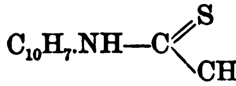
β-Acetonaphthalide, $C_{10}H_7.NH.CO.CH_3$, is obtained together with β-dinaphthylamine by boiling β-naphthylamine with glacial acetic acid,[3] and by heating β-naphthol to 270—280° with ammonium acetate and glacial acetic acid.[4] It crystallizes from a concentrated alcoholic solution in small plates, melting at 132°. It differs from the α-compound in being much more readily decomposed by dilute acids than by alkalis.[5]

β-Dinaphthylacetamide, $(C_{10}H_7)_2N.CO.CH_3$, is formed when β-dinaphthylamine is heated with acetyl chloride, and crystallizes from a mixture of benzene and light petroleum in small needles which melt at 114—115°.

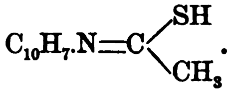
α-β-Dinaphthylacetamide forms stellate groups of thick needles, melting at 125°.[6]

β-Glycolyldinaphthalide, $C_{10}H_7.NH.CO.CH_2NH.C_{10}H_7$, is obtained by heating β-naphthylamine with chloracetic acid; it crystallizes from alcohol in light-yellow, lustrous plates, which melt at 170° (Cosiner).

β-Thio-acetonaphthalide, $C_{10}H_7NH(CS.CH_3)$, is prepared by heating β-acetonaphthalide with phosphorus pentasulphide, and crystallizes from alcohol in needles, which on standing in their mother-liquor change into coarse tablets; both of these modifications melt at 145—146°. It is possible that they are represented by the tautomeric formulæ:[7]



$$C_{10}H_7.NH{-}C\left\langle\begin{matrix}S\\CH_3\end{matrix}\right.$$



$$C_{10}H_7.N{=}C\left\langle\begin{matrix}SH\\CH_3\end{matrix}\right. .$$

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[1] Cosiner, *Ber.* **14**, 58.

[2] Liebermann and Jacobson, *Annalen*, **211**, 42.

[3] Cosiner; Liebermann and Jacobson.

[4] Merz and Weith, *Ber.* **14**, 2343.

[5] Calm, *Ber.* **15**, 612.

[6] Benz, *Ber.* **16**, 19.

[7] Jacobson, *Ber.* **21**, 2627. Jacobson proposes the term "desmotropism" in place of "tautomerism," since the latter implies the view that the compounds belonging to this class are continually being changed by the vibrations of their atoms from one form to the other. He does not share this view, but assumes that each form can exist independently, but that in certain reactions, one form passes into the other, the mode of combination (*δεσμός*, band) changing (*τρέπειν*, to change).

β-Benzonaphthalide, $C_{10}H_7NH(CO.C_6H_5)$, is formed by the action of benzoyl chloride on β-naphthylamine, and crystallizes from alcohol in large white needles, melting at 157°. Hofmann endeavoured to prepare it in a similar manner to the α-compound, by heating β-naphthylamine with benzoic acid, but found that ammonia was evolved, and a large amount of β-dinaphthylamine formed.[1]

β-Benzonaphthalide-imido-chloride, $C_{10}H_7N{=}CCl.C_6H_5$, is obtained in a similar manner to the α-compound by the action of phosphorus pentachloride on β-benzonaphthalide, and crystallizes from light petroleum in large plates, melting at 68°, which become dull and opaque in moist air, β-benzonaphthalide being again formed. It reacts with sodiomalonic ester to form *ethyl β-naphthylaminebenzenylmalonate*, $C_{10}H_7N{=}C(C_6H_5)CH(CO_2.C_2H_5)_2$, which separates from alcohol in large, hard, strongly refractive, obtuse-angled crystals, melting at 140·5°. On heating to 120° with hydrochloric acid it decomposes in a similar manner to the α-compound (p. 151).

β-Naphthylamido-acetic acid, $C_{10}H_7NH.CH_2.COOH$, is obtained in the form of its naphthylamine salt by heating β-naphthylamine with an aqueous solution of chloracetic acid.[2] On decomposition with boiling hydrochloric acid the free acid is obtained, which crystallizes from water in microscopic needles, and melts at 134—135°.

Nitroso-β-naphthylamido-acetic acid, $C_{10}H_7N(NO)CH_2.CO_2H$, crystallizes from dilute alcohol in reddish plates and decomposes at 125—126°.

β-Naphthylimidodiacetic acid $C_{10}H_7N(CH_2.CO_2H)_2$ is prepared by heating sodium β-naphthylamido-acetate with chloracetic acid in aqueous solution to 140°. It is an unstable, amorphous substance, which decomposes at 182°.[3]

Malo-β-dinaphthalide, $C_{10}H_7NH.CO.CH_2.CH(OH)CONHC_{10}H_7$, obtained by heating malic acid with β-naphthylamine, is almost insoluble in the usual solvents, but can be recrystallized from aniline; it melts at 260—263°.[4]

β-Imidobutyrodinaphthalide, is formed, together with the following compound, when β-naphthylamine is heated with acetacetic ester to 150—180°:

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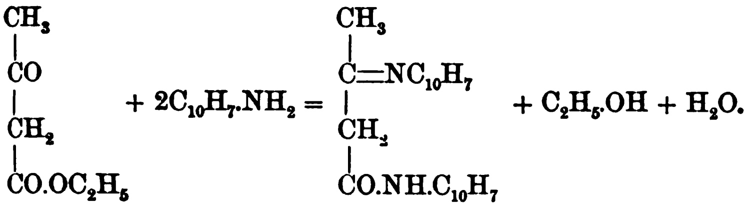
[1] Hofmann, *Ber.* **20**, 1803.
[2] Jolles, *Ber.* **22**, 2372.
[3] Bischoff and Hausdörfer, *Ber.* **23**, 2008.
[4] Bischoff and Nastvogel, *Ber.* **23**, 2046.



$$\begin{array}{l}CH_3\\ |\\ CO\\ |\\ CH_2\\ |\\ CO.OC_2H_5\end{array} + 2C_{10}H_7.NH_2 = \begin{array}{l}CH_3\\ |\\ C{=}NC_{10}H_7\\ |\\ CH_2\\ |\\ CO.NH.C_{10}H_7\end{array} + C_2H_5.OH + H_2O.$$

It is almost insoluble in the usual solvents and crystallizes from a large quantity of benzene in needles, melting at 200°.

β-Naphthylimidobutyric acid, $C_{10}H_7N{=}C(CH_3)CH_2.CO_2H$, is obtained when the preceding compound is boiled with hydrochloric acid of 4 per cent., and crystallizes from hot water in well-developed needles, melting at 92°.[1]

Succino-β-naphthalide, or *β-Naphtylsuccinimide*, $C_{10}H_7N{<}\begin{array}{c}CO\\CO\end{array}{>}C_2H_4$, is prepared by heating β-naphthylaminesulphonic acid with succinic acid to 200°; it crystallizes from alcohol in long, white needles, melting at 180°. When it is dissolved in caustic potash, *β-naphthylsuccinamic acid*, $C_{10}H_7.NH.CO.C_2H_4CO_2H$, is formed. This substance separates in small white crystals and on heating to 190° is reconverted into the imide.[2]

Citracono-β-naphthalide, $C_{10}H_7N{<}\begin{array}{c}CO\\CO\end{array}{>}C_3H_4$, is formed when equal molecules of citraconic acid and β-naphthylamine are fused together at 170—180° and crystallizes from alcohol in faint-yellow needles, which melt at 110°.[3]

	Melting-point.
β-Citrodinaphthylamic acid,[4] $C_3H_4(OH)(CO.NH.C_{10}H_7)_2CO_2H$, microscopic yellow needles	172°
β-Citrotrinaphthylamide, $C_3H_4(OH)(CO.NH.C_{10}H_7)_3$, microscopic prisms	215°
β-Citrodinaphthylamide, $C_3H_4(OH){<}\begin{array}{l}CO.NH.C_{10}H_7\\ CO{>}N.C_{10}H_7\\ CO\end{array}$, six-sided plates	233°

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[1] Knorr, *Ber.* **17**, 540.

[2] Pellizzari and Matteucci, *Chem. Centralbl.* **59**, 1000.

[3] Hecht, *Ber.* **19**, 2116.

[4] Morawski and Gläser, *Monatsh.* **9**, 284.

β-Naphthylamido-m-nitrobenzoic acid, $C_{10}H_7NH.C_6H_3(NO_2)CO_2H$, is obtained by the action of β-naphthylamine on *p*-bromo-*m*-nitrobenzoic acid, dissolved in glycerol, as a brick red amorphous mass. The *ethyl ester* crystallizes from alcohol in splendid light yellow lustrous needles melting at 127·5°.[1]

β-NAPHTHYLCARBAMIDES or β-NAPHTHYLUREAS.

2633 *β-Naphthyl urea*, $CO(NH_2)NH.C_{10}H_7$, is obtained by heating naphthylamine hydrochloride with urea to 150° and crystallizes from hot water or alcohol in matted needles, which soften at 200° but do not completely fuse until 287°.[2]

β-Dinaphthyl urea, $CO(NHC_{10}H_7)_2$, is formed when the corresponding thio-compound is heated with mercuric oxide and alcohol; it crystallizes in slender, interlaced needles, which melt at 293° and are only slightly soluble in alcohol, ether, &c.[3]

β-Dinaphthyl-chloroformamide, $(C_{10}H_7)_2N.COCl$, is obtained by heating β-dinaphthylamine with a solution of phosgene in toluene to 150—160°. It forms a white, cauliflower-like crystalline mass, dissolves readily in boiling benzene or alcohol, and melts at 173°.[4]

as-β-Dinaphthyl urea, $(C_{10}H_7)_2N.CO.NH_2$, is formed when the preceding compound is heated with alcoholic ammonia. It crystallizes in large, pointed needles, dissolves readily in hot benzene and alcohol, and melts at 192—193°.

Phenyl-β-dinaphthyl urea, $(C_{10}H_7)_2N.CO.NH.C_6H_5$, is prepared from the corresponding chloroformamide and aniline, and has also been obtained from β-dinaphthylamine and carbanil. It crystallizes from alcohol in fascicular aggregates of long, white needles, melting at 181—182°.[5]

β-Tetranaphthyl urea is formed when thechloroformamide is treated with β-dinaphthylamine. It crystallizes from alcohol in small lustrous needles, melting at 294—295°.[6]

Ethyl β-naphthylcarbamate, $CO(OC_2H_5)NH.C_{10}H_7$, is prepared by the action of ethyl chloroformate on an ethereal solution of

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[1] Heidensleben, *Ber.* **23**, 3456.

[2] Cosiner, *Ber.* **14**, 58.

[3] Huhn, *Ber.* **19**, 2404.

[4] Kym, *Ber.* **23**, 427.

[5] Gebhardt, *Ber.* **17**, 3039.

[6] Kym, *Ber.* **23**, 1542; Kühn and Landau, *Ber.* **23**, 811, 2161.

β-naphthylamine; it crystallizes from dilute alcohol in pliable needles, melting at 73° (Cosiner).

β-Naphthylphenyl urea, $CO(NH.C_6H_5)NH.C_{10}H_7$, is formed by the action of phenylcarbimide on β-naphthylamine, and crystallizes in short, lustrous white prisms, which melt at 220—221°, and are only sparingly soluble in alcohol.[1]

Phenyl-β-naphthyl chloroformamide, $(C_{10}H_7)(C_6H_5)N.COCl$, is prepared by gently heating phenyl-β-naphthylamine with phosgene dissolved in toluene. It crystallizes from alcohol in small, white lustrous plates, melting at 101—102°.

as-Phenyl-β-naphthyl urea, $(C_{10}H_7)(C_6H_5)N.CO.NH_2$, forms long white needles and melts at 189—190°.

Diphenyl-β-naphthyl urea $(C_{10}H_7)(C_6H_5)N.CO.NHC_6H_5$, is obtained by heating a solution of the chloroformamide in chloroform with aniline. It crystallizes from alcohol in white plates, melting at 132—133°.[2]

β-Naphthyl thio-urea, $CS(NH_2)NH.C_{10}H_7$, is obtained when β-naphthylamine thiocyanate is heated for some time to 100° and crystallizes from hot alcohol, in which it is only slightly soluble, in well-developed rhombic plates, melting at 180° (Cosiner).

β-Dinaphthyl thio-urea, $CS(NH.C_{10}H_7)_2$, is prepared by heating β-naphthylamine with carbon disulphide and some alcoholic potash; it is sparingly soluble in all solvents, and crystallizes in small white plates, melting at 193° (Cosiner). On heating to 100° with alcoholic ammonia it decomposes into β-naphthylamine and naphthyl thio-urea,[3] whilst on boiling with benzene and mercuric oxide it is converted into *β-carbodinaphthylimide*, $C(NC_{10}H_7)_2$, which forms granular crystals, easily soluble in benzene, freely but slowly, in ether, and melts at 145—146°. When it is boiled with dilute alcohol, dinaphthyl urea is obtained, and it combines with sulphuretted hydrogen to form dinaphthyl thio-urea.[4]

Ethyl-β-naphthylthiocarbamate, $CS(OC_2H_5)NH.C_{10}H_7$, is obtained when β-naphthyl thiocarbimide is heated to 130° with alcohol, and crystallizes in yellowish prisms, needles, or rhombic plates, which melt at 96—97° (Cosiner).

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[1] Goldschmidt and Molinari, *Ber.* **21**, 2566; see also Mainzer, *Ber.* **15**, 1417.

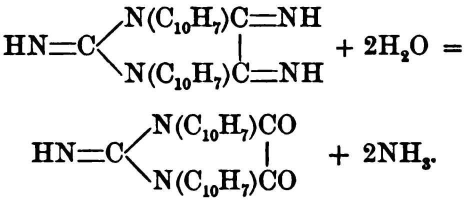
[2] Kym, *Ber.* **23**, 425.

[3] Gebhardt, *Ber* **17**, 3043.

[4] Huhn, *Ber.* **19**, 2404.

NAPHTHYLGUANIDINES.

2634 *a-Dinaphthylguanidine,* $HN{=}C(NH.C_{10}H_7)_2$, was obtained by Perkin by the action of cyanogen chloride on fused naphthylamine and was termed *menaphthylamine* (Pt. III. p. 225). It crystallizes from hot alcohol in small white needles, which melt at 200° and have a bitter taste, and an alkaline reaction to litmus paper. The salts are only sparingly soluble in water. When a current of cyanogen is passed through it suspended in ether, *dicyanmenaphthalidine* is formed as a dark-yellow crystalline mass, which is decomposed by acids into ammonia and *menaphthoximide*:



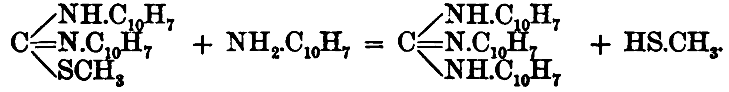
$$HN{=}C\begin{array}{l}\diagup N(C_{10}H_7)C{=}NH\\ \qquad\qquad\quad\;|\\ \diagdown N(C_{10}H_7)C{=}NH\end{array} + 2H_2O =$$

$$HN{=}C\begin{array}{l}\diagup N(C_{10}H_7)CO\\ \qquad\qquad\quad\;|\\ \diagdown N(C_{10}H_7)CO\end{array} + 2NH_3.$$

This crystallizes in small yellow scales, melting at 245°, which are insoluble in water, sparingly soluble in alcohol, and are decomposed by alkalis and strong acids into dinaphthylguanidine and oxalic acid.[1]

a-Naphthyldiphenylguanidine, $C_{10}H_7N{=}C(NH.C_6H_5)_2$, was obtained by Tiemann by acting upon an alcoholic solution of *a*-naphthylamine and diphenyl thio-urea with lead oxide. It forms crystalline crusts, melting at 155°; the *hydrochloride* separates out in indistinct crystals when its hot solution is allowed to cool.[2]

a-Trinaphthylguanidine. When *a*-dinaphthyl thio-urea is heated with methyl iodide, the *methyl a-naphthylimidonaphthylthiocarbamate* is formed, which crystallizes in flat prisms, melting at 136°, and on heating with *a*-naphthylamine and absolute alcohol is converted into trinaphthylguanidine:



$$C\begin{array}{l}\diagup NH.C_{10}H_7\\ {=}N.C_{10}H_7\\ \diagdown SCH_3\end{array} + NH_2.C_{10}H_7 = C\begin{array}{l}\diagup NH.C_{10}H_7\\ {=}N.C_{10}H_7\\ \diagdown NH.C_{10}H_7\end{array} + HS.CH_3.$$

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[1] *Annalen*, **98**, 236.

[2] *Ber.* **3**, 6.

The latter crystallizes in flat needles melting at 178°, which are insoluble in water, and dissolve slowly but freely in hot alcohol.[1]

CYANOGEN COMPOUNDS OF NAPHTHYL.

2635 *α-Naphthylcarbamine*, $C_{10}H_7.NC$, is formed by the action of chloroform and alcoholic potash on α-naphthylamine, and is an almost amorphous mass, which has an adhering but not very powerful smell of the carbamines, and dissolves readily in alcohol, but is insoluble in water.

β-Naphthylcarbamine differs from the α-compound in forming needles, melting at 54°.[2]

α-Naphthylcarbimide, $C_{10}H_7N(CO)$, was obtained by Hofmann by heating ethyl naphthylcarbamate with phosphorus pentoxide as an almost odourless liquid, boiling at 269—270°, the vapour of which has a pungent odour.[3]

α-Naphthylthiocarbimide, or *α-Naphthyl mustard oil*, $C_{10}H_7N(CS)$, was prepared by Hall by the distillation of α-dinaphthyl thio-urea with phosphorus pentoxide. It may be more simply obtained by heating the first-named substance with 2·5 parts of phosphoric acid containing 62—63 per cent. of pentoxide. It crystallizes from alcohol in long, lustrous needles, melting at 58°, and is converted into ethyl α-naphthylcarbamate by continued boiling with alcohol.[4]

β-Naphthyl thiocarbimide is prepared in a similar manner to the α-compound; it crystallizes in yellowish needles, melting at 62—63°, and is very readily converted into ethyl β-naphthylthiocarbamate by boiling alcohol (Cosiner; Mainzer).

β-Naphthyl thiocyanate, $C_{10}H_7S.CN$, is formed when cyanogen chloride is passed into an alcoholic solution of β-thionaphthol, and separates on the addition of water as an oily liquid, which after some time solidifies to a snow-white mass; it melts at 35°, and decomposes at a higher temperature.[5]

Fries[6] has prepared the following compounds by the action of cyanogen chloride on the naphthylamines :

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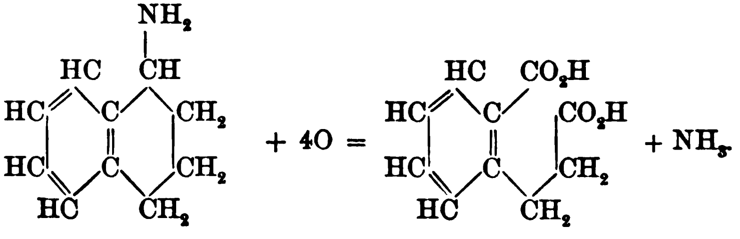
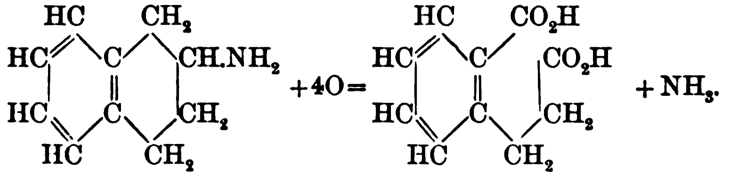
[1] Evers, *Ber.* **21**, 962.
[2] Liebermann, *Ber.* **16**, 1640.
[3] Liebermann, *Ber.* **3**, 657.
[4] Hofmann, *Ber.* **15**, 985. ; Mainzer, *Ber.* **15**, 1412 ; **16**, 2016.
[5] Billeter, *Ber.* **8**, 462.
[6] Billeter, *Ber.* **19**, 242 and 2055.

		Melting-point
Naphthylamidocyanuric chloride,		
$C_{10}H_7.NH.C_3N_3Cl_2$	α- needles	149°
	β- well formed crystals	154°
Dinaphthylamidocyanuric chloride,		
$(C_{10}H_7.NH)_2C_3N_3Cl$	α- needles	215°
	β- needles	178°
Trinaphthylcyanuramide,		
$(C_{10}H_7NH)_3C_3N_3$	α- needles	223°
	β- needles	209°

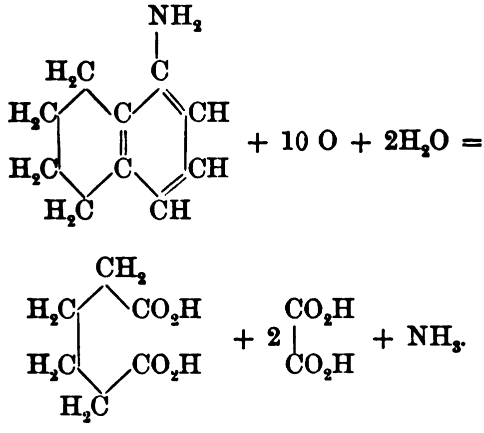
THE TETRAHYDRONAPHTHYLAMINES.

2636 The *alicyclic* compounds of this group, containing the four hydrogen atoms in the nucleus which also contains the amido-group, have lost the character of aromatic amido-compounds and behave like fatty amines. They have a strong alkaline reaction, colour turmeric paper brown, decompose ammonium salts, and have a sharp smell which resembles that of ammonia and of piperidine, and produces irritation in the throat. They form neutral salts, eagerly absorb carbon dioxide from the air, and those of them which are primary compounds combine with carbon disulphide with explosive violence. A very characteristic property is that they are not converted by nitrous acid into diazo-compounds but into stable nitrites. Moreover, they do not combine with diazo-salts to form azo-colouring matters, but form diazo-amines (Pt. III. p. 28). They do not possess any reducing properties, and their solutions are not perceptibly altered by sulphuric acid and potassium dichromate, whilst the solutions of their hydrochlorides are only coloured deep reddish-brown by ferric chloride on heating. Potassium permanganate oxidizes them to *o*-carboxyhydrocinnamic acid :





The *aromatic* tetrahydronaphthylamines on the other hand retain the characteristics of true amido-derivatives. They are without action on vegetable colouring matters, form salts which have an acid reaction, and do not combine with carbon dioxide and carbon disulphide at the ordinary temperature. They have a powerful reducing action and give colour reactions with ferric chloride, and sulphuric acid and potassium dichromate, the shades of which depend on the nature of the base. The primary compounds can be diazotized, the secondary form nitrosamines, and the tertiary *p*-nitroso-compounds; with diazo-salts they form azo-colours. Potassium permanganate oxidizes them to adipic and oxalic acids:



a-Naphthylamine and its alkyl derivatives only yield aromatic hydrobases on reduction, whereas the *β*- compounds form both aromatic and alicyclic reduction products.[1]

2637 *ac-Tetrahydro-a-naphthylamine* is, as just mentioned, not formed by the direct reduction of *a*-naphthylamine. In order to prepare it, Bamberger and Bammann were compelled to start with 1:4′-diamidonaphthalene. This combines with

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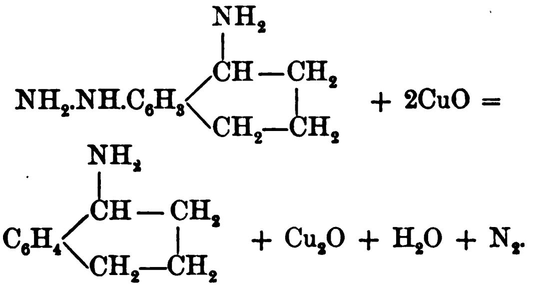
[1] Bamberger, *Ber.* **22**, 767.

hydrogen to form 1 : 4′-tetrahydrodiamidonaphthalene, which is at once an alicyclic and aromatic compound and therefore forms a diazo-chloride. The solution of this on treatment with a hydrochloric acid solution of stannous chloride deposits a crystalline precipitate of tetrahydro-1 : 4′-amidonaphthalenehydrazine hydrochloride. This is decomposed with caustic soda solution, the base dissolved in 15 to 20 parts of hot water, the solution heated on the water-bath, and a 10 per cent. copper sulphate solution added until the liquid is coloured permanently blue:



As soon as the reaction is over, caustic soda is added, and the base distilled off with steam. The distillate is neutralized with hydrochloric acid, the solution concentrated, and the crystallized hydrochloride again decomposed with caustic soda, the base dissolved in ether, dried over caustic potash and caustic baryta, and then separated by distillation.

ac-Tetrahydro-*α*-naphthylamine is a colourless, transparent, viscid oil, which shows no fluorescence, and boils at 246·5° under a pressure of 714 mm. It is moderately soluble in cold water, more freely in hot water, and is precipitated by caustic soda. It possesses the characteristic odour of these bases, and its vapour causes irritation of the throat, especially when its aqueous solution is boiled. It attracts carbon dioxide from the air so vigorously that an incrustation of the carbonate is always formed when it is poured from one vessel into another.

ac-Tetrahydro-a-naphthylamine hydrochloride, $C_{10}H_{11}.NH_3Cl$, crystallizes in splendid silky needles, united into small round masses, and is readily soluble in water, less readily in hydrochloric acid.

The *platinochloride*, $(C_{10}H_{11}NH_3)_2PtCl_6+2H_2O$, forms broad orange-yellow lustrous prisms an inch in length, and is moderately soluble in water.

The *nitrite*, $C_{10}H_{11}.NH_3NO_2$, separates out in white needles when nitrogen trioxide is passed into a cooled ethereal solution of the base. It is very readily soluble in water, and crystallizes on evaporating the solution in splendid silky needles, which melt at 138—139°, and are not decomposed by boiling water.

The *carbonate*, $(C_{10}H_{11}.NH_3)_2CO_3$, forms white lustrous needles, and the *picrate* is a yellow flocculent precipitate, which crystallizes from hot water in lustrous needles.

Acetyl-ac-tetrahydro-a-naphthylamine, $C_{10}H_{11}.NH(CO.CH_3)$, crystallizes from dilute acetic acid in long prisms, and from weak alcohol in hair-like needles, aggregated in forms resembling spiders' webs, which melt at 148—149°.

Diazobenzene-ac-tetrahydro-a-naphthylamine, $C_6H_5.N_2.NH.C_{10}H_{11}$, is formed when the base is suspended in water, cooled with ice, and treated with diazo-benzene nitrate:

$$C_6H_5.N_2.ONO_2 + 2C_{10}H_{11}.NH_2 =$$
$$C_6H_5.N_2.NH.C_{10}H_{11} + C_{10}H_{11}NH_3.ONO_2.$$

It is a thick reddish-yellow oil, which has a sweet and somewhat stupefying odour, and gradually solidifies in cold water to lustrous needles. The *picrate*, $C_6H_5N_2.NH.C_{10}H_{11} + C_6H_3(NO_2)_3O$, crystallizes from hot water in long silky, sulphur-yellow needles.[1]

2638 *ac-Tetrahydro-β-naphthylamine*, $C_6H_4.C_4H_7.NH_2$, was obtained by Bamberger and Müller by allowing a boiling solution of β-naphthylamine in amyl alcohol to flow on to small pieces of sodium,[2] or more conveniently by gradually adding the sodium to the boiling solution.[3] Water is then added and the upper layer removed, acidified with hydrochloric acid, and freed from amyl alcohol by distillation, the base being then liberated from the residue. In order to free it from *ar*-tetrahydro-β-naphthylamine, which is simultaneously formed, and from unaltered β-naphthylamine, the product is dissolved in ether, and a stream of moist carbon dioxide passed through the solution; the carbonate thus obtained is then decomposed by caustic soda.

ac-Tetrahydro-β-naphthylamine is a colourless, transparent liquid, which boils at 249·5° under a pressure of 710mm., and has a sp. gr. of 1·031 at 16°. It possesses all the characteristic properties of the alicyclic bases. On boiling, a small portion of it

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[1] *Ber.* **22**, 951.

[2] Bamberger and Müller, *Ber.* **21**, 847 and 1112.

[3] *Ber.* **22**, 944 (Note).

decomposes into ammonia and dihydronaphthalene, the liquid taking a bluish-violet fluorescence. It is rapidly converted into the crystalline carbonate in the air. When sodium nitrite is added to its solution in very dilute sulphuric acid, a reaction only takes place on heating, nitrogen and naphthalene being formed. Tetrahydro-β-naphthol is probably first formed, and immediately decomposes into water and dihydronaphthalene, the latter being then oxidized by the nitrous acid to naphthalene. When equal molecules of the base and amyl nitrite are heated together, the following reaction occurs:

$$C_{10}H_{11}.NH_2 + C_5H_{11}O.NO = C_{10}H_{10} + C_5H_{11}.OH + N_2 + H_2O.$$

The base is oxidized by potassium chromate and sulphuric acid to α-naphthol and α-naphthoquinone, whereas naphthalene is obtained when nitric acid is employed.[1] Potassium permanganate converts it into a mixture of phthalic and o-carboxyhydrocinnamic acids.[2]

ac-Tetrahydro-β-naphthylamine hydrochloride, $C_{10}H_{11}.NH_3Cl$, crystallizes in nacreous silver-white thin quadratic tablets and is readily soluble in water and alcohol.

The *platinochloride*, $(C_{10}H_{11}.NH_3)_2PtCl_6$, crystallizes from boiling water in splendid flat orange-yellow prisms, which have a satin lustre. The *sulphate*, $(C_{10}H_{11}.NH_3)_2SO_4$, forms flat lustrous white prisms. The *nitrite*, $C_{10}H_{11}.NH_3.NO_2$, separates in the crystalline form when nitrogen trioxide is passed into a cooled ethereal solution of the base, and crystallizes from boiling alcohol in fascicular groups of long silky needles, or when the solution is gradually evaporated, in short, clear, strongly refractive prisms. It decomposes at 180—190° into nitrogen, water, and dihydronaphthalene.

Normal ac-tetrahydro-β-naphthylamine carbonate, $(C_{10}H_{11}.NH_3)_2CO_3$, forms lustrous white needles, which are more soluble in hot water than in cold, and lose carbon dioxide when preserved in a dessicator. The *acid carbonate*, $(C_{10}H_{11}NH_3)HCO_3$, is formed as a granular crystalline precipitate when solutions of the hydrochloride and sodium bicarbonate are mixed. It is sparingly soluble in cold water, and is decomposed by boiling water, the base being liberated.

The *acetate* crystallizes in thick monosymmetric columns, which have a vitreous lustre and melt at 155·5—156°.

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[1] Bamberger and Kitschelt, *Ber.* **23**, 880.

[2] *Ber.* **21**, 1119.

The *nitrate* is only sparingly soluble in cold water, and melts at 210—212°.

The physiological action of this base is very remarkable. When a 1 to 5 per cent. solution is dropped into the eye, enlargement of the pupil is caused in the eye experimented on, whilst if a sufficient quantity be introduced into the system by subcutaneous injection, or other means, a similar effect is produced in both eyes. The enlargement is greater than that which is brought about by atropine, but whilst the latter and other tropeïnes paralyze the motor nerve endings of the sphinctor, tetrahydro-β-naphthylamine when locally applied only acts as an irritant on the nerve endings of the dilator, and when brought into the system by absorption acts to a certain extent in the same manner, but chiefly still as a direct irritant, upon the central nuclei of these nerve endings. Tetrahydro-β-naphthylamine is the first substance which has been observed to exert this action.

The most interesting effect is however undoubtedly the considerable rise of temperature caused by *ac*-tetrahydro-β-naphthylamine in animals, which sometimes amounts to as much as 4·5°. It is due to diminished loss of heat accompanied by increased production. This characteristic effect is produced by all the alicyclic hydro-bases of the β-series, whilst those of the α-series and the aromatic hydro-bases show no signs of it.

The group $CH(NH_2)$ in the β-position seems therefore to actually condition this physiological action, and physiological experiments become of great value in determining the constitution of a hydro-base of the β-series. In such a case the aromatic or alicyclic nature of a base can be determined by an experiment performed on an animal with less substance and in a shorter time than by employing the oxidation method.[1] Traces of an alicyclic β-compound can also be easily detected in an aromatic hydrobase in this way, since the mydriasis produced is a much more delicate test than the reaction with turmeric paper.[2]

ac-Tetrahydroacetyl-β-naphthylamine, $C_{10}H_{11}.NH.CO.CH_3$, is obtained by the action of acetyl chloride or acetic anhydride on the base, and crystallizes in asymmetric prisms with a vitreous lustre, which melt at 107·5°.

ac-Ditetrahydro-β-naphthyl thio-urea, $CS(NH.C_{10}H_{11})_2$. When very dilute ethereal solutions of tetrahydro-β-naphthylamine

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[1] Bamberger and Filehne, *Ber.* **22**, 777.

[2] *Ber.* **22**, 1296 (Footnote).

and carbon disulphide are mixed, a violent reaction takes place, and *tetrahydro-β-naphthylamine tetrahydro-β-naphthylthiocarbamate*, $C_{10}H_{11}.NH.CS.SN(C_{10}H_{11})H_3$, is formed. This substance is only sparingly soluble in cold water, from which it separates on evaporation in long, lustrous needles, melting at 142°. On boiling with alcohol, the thio-urea is formed, which crystallizes in lustrous white needles, united to form rosette-shaped aggregates, and melts at 166·5°.

Diazobenzenetetrahydro-β-naphthylamine, $C_6H_5N_2NH.C_{10}H_{11}$, is a yellowish-red, very viscid oil, which has a faint, sweet odour, and explodes on heating. It combines with picric acid to form the compound $C_{16}H_{17}N_3 + C_6H_3(NO_2)_3O$, which crystallizes in lustrous ruby-red needles. On heating with dilute sulphuric acid, the diazo-compound decomposes into dihydronaphthalene, aniline, and nitrogen.

ac-Benzylidenetetrahydro-β-naphthylamine, $C_6H_5.CH{=}N.C_{10}H_{11}$, is formed by the direct combination of benzaldehyde with the base. It crystallizes from alcohol in colourless asymmetric tablets, melting at 51·5—52°, and is remarkably stable towards alkalis, but is easily decomposed by acids.[1]

2639 *ac-Tetrahydro-ethyl-β-naphthylamine*, $C_{10}H_{11}NH.C_2H_5$, is prepared by adding 24 grms. of sodium cut into small pieces, 3 to 4 grms. at a time, to a solution of 15 grms. of ethyl-β-naphthylamine in 200 grms. of boiling amyl alcohol,[2] the bases being obtained as already described. They are dissolved in light petroleum and treated with moist carbon dioxide, which soon produces a precipitate of the alicyclic carbonate. This may be mixed with a little of the aromatic base, which is best removed by dissolving in very dilute hydrochloric acid and adding a small quantity of sodium nitrite The oily aromatic nitrosamine is thus formed and is removed by ether, the alicyclic base being then liberated from the solution. Its purity is tested by bringing it into a solution of diazobenzenesulphonic acid, which ought not to produce a colouration. If a scarlet colouration appears the purification must be repeated.

ac-Tetrahydroethyl-β-naphthylamine is a colourless, viscid oil, which boils at 267° under a pressure of 724 mm., and has a sp. gr. of 0·998 at 15°. Its remaining properties resemble those of the other bases of the group; it is only sparingly

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[1] *Ber.* **23**, 879.

[2] Bamberger and Müller, *Ber.* **22**, 1293; see also *Ber.* **22**, 944 (Notes).

soluble in water, and its physiological action is like that of the unsubstituted base.

On oxidation it does not yield *o*-carboxyhydrocinnamic acid but a viscid oily acid, which is probably a mixture and, on account of the small quantity obtained, has not been more closely examined.

ac-Tetrahydroethyl-β-naphthylamine hydrochloride, $C_{10}H_{11}.NH_2(C_2H_5)Cl$, crystallizes from water in flat prisms, with a vitreous lustre, and from chloroform on the addition of light petroleum in short lustrous, strongly refractive needles.

The *platinochloride* $(C_{10}H_{11}.NH_2.C_2H_5)_2PtCl_6$, is moderately soluble in hot water, and crystallizes on spontaneous evaporation in orange-yellow, lustrous stellate masses.

ac-Tetrahydroethyl-β-naphthylamine nitrate, $C_{10}H_{11}.NH_3.NO_3$, is precipitated by the addition of nitric acid to the solution of the hydrochloride as a lustrous crystalline mass, which readily dissolves in hot water, and crystallizes when the solution is slowly cooled in long, flat needles, with a vitreous lustre, but when rapidly cooled in silver white plates, with a satin lustre, which melt at 184°.

ac-Tetrahydroethyl-β-naphthylamine nitrite, $C_{10}H_{11}.NH_2(C_2H_5)NO_2$, crystallizes from hot water in long, silky needles, which form masses resembling wavelite, and melt at 180°.

The *picrate*, $C_{10}H_{11}NH_2(C_2H_5)OC_6H_3(NO_2)_3$, separates from hot water in light orange-red, hair-like needles, which resemble spider's web in appearance and have a woolly structure; it melts at 183·5°.

The *carbonate* forms white, lustrous needles, and the *oxalate*, $(C_{10}H_{11}NH_2.C_2H_5)_2C_2O_4$, crystallizes from an aqueous solution on evaporation in flat needles, with a satin lustre, whilst the *acetate* remains as a viscid syrup when its solution is evaporated.

ac-Tetrahydroethyl-β-naphthylnitrosamine, $C_{10}H_{11}.N(NO)C_2H_5$, is formed when sodium nitrite is added to an acid solution of the hydrochloride, and the mixture allowed to stand for some time; if the solution be heated it separates out as a yellowish oily liquid. When it is treated with phenol and sulphuric acid, and caustic soda then added, a light grass-green colouration is produced.

Diazobenzenetetrahydroethyl-β-naphthylamine, $C_{10}H_{11}.NH.N_2C_6H_5$, forms splendid, sulphur-yellow, flat, six-sided tablets, and melts at 58°.

ac-Tetrahydrodimethyl-β-naphthylamine, $C_{10}H_{11}.N(CH_3)_2$, is only formed in small quantity, together with the aromatic base, by the action of sodium on a solution of β-dimethylnaphthylamine in amyl alcohol, and is a liquid which boils at 166·5° under a pressure of 22 mm., and has even a more powerful physiological action than tetrahydro-β-naphthylamine. Its *hydrochloride* crystallizes in long needles with a vitreous lustre, which do not alter in the air, and its *platinochloride* separates out in lustrous orange-yellow needles when the aqueous solution is evaporated.

ac-Tetrahydro-p-tolyl-β-naphthylamine, $C_{10}H_{11}NH(C_6H_4.CH_3)$, is not readily formed, and crystallizes from hot water in silver-white plates, which have a satin lustre and a characteristic odour, in which the perfume of the narcissus can be recognized along with the sharp smell of piperidine. It melts at 44°, boils at 93°, under a pressure of 18 mm., and evaporates at the ordinary temperature as rapidly as camphor (Bamberger and Müller).

2640 *ar-Tetrahydro-a-naphthylamine*, $C_{10}H_{11}.NH_2$, is formed when a boiling solution of α-naphthylamine in amyl alcohol is allowed to flow in a continuous stream on to small pieces of sodium. It is a colourless, oily liquid, which smells like dimethylaniline, has a sp. gr. of 1·0625 at 16°, and boils at 275° under a pressure of 712 mm. It does not act on vegetable colouring matters, reduces silver solution on heating, and gold and platinum chlorides in the cold.

Tetrahydro-a-naphthylamine hydrochloride, $C_{10}H_{11}.NH_3Cl$, crystallizes in nacreous, quadratic tablets. It combines with mercuric chloride to form the *double salt*, $C_{10}H_{11}.NH_3Cl + HgCl_2$, which crystallizes from hot water in silver-white, flat needles, which have a satin lustre.

Tetrahydro-a-naphthylamine sulphate, $2(C_{10}H_{11}.NH_3)_2SO_4 + H_2O$, forms silver-white plates, or flat needles, with a satin lustre.

When a solution of one of the salts is heated with ferric chloride or potassium dichromate and sulphuric acid, naphthameïn separates out after some time. The base is converted into tetrahydro-α-naphthol by the diazo-reaction (p. 81).

ar-Tetrahydro-a-acetonaphthalide, $C_{10}H_{11}.NH.CO.CH_3$, is obtained by heating the hydrochloride with sodium acetate and acetic anhydride, and crystallizes in asbestos-like masses of silky needles, which melt at 158°.[1]

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[1] Bamberger and Althausse, *Ber.* **21**, 1786 and 1892.

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ar-Tetrahydroethyl-a-naphthylamine, $C_{10}H_{11}.NHC_2H_5$, is a colourless, viscid liquid, which boils at 286—287° under a pressure of 717 mm., has a faint odour, resembling that of dimethylaniline, and is slightly soluble in water. It reduces alcoholic silver nitrate solution at the temperature of the hand, and forms an orange-red colouring matter with diazobenzenesulphonic acid. When its solution in hydrochloric acid is heated with ferric chloride, it becomes coloured red and then greenish-yellow; potassium dichromate and sulphuric acid produce in the cold a dirty-yellow precipitate, and on heating a raspberry-red and then a greenish-brown colouration, a bluish-black flocculent precipitate being formed when more dichromate is added.

ar-Tetrahydroethyl-a-naphthylamine hydrochloride, $C_{10}H_{11}.NH_2(C_2H_5)Cl$, crystallizes from water in large, thick prisms, with a vitreous lustre, or when rapidly cooled, in needles, which lose water and fall to powder at 80—90° and melt at 118°.

The *platinochloride*, $(C_{10}H_{11}.NH_2.C_2H_5)_2PtCl_6$, forms lustrous golden-yellow plates, which are moderately soluble in hot water, but are soon decomposed by it.

Tetrahydroethyl-a-naphthylnitrosamine, $C_{10}H_{11}N(NO)C_2H_5$, separates out when sodium nitrite is added to an acid solution of the hydrochloride. It is a yellow, oily liquid, which has a characteristic, somewhat stupefying odour. It gives Liebermann's reaction,[1] and is converted by alcoholic potash into the isomeric ethylamidonitrosotetrahydronaphthalene, which will be subsequently described.

ar-Tetrahydrodimethyl-a-naphthylamine, $C_{10}H_{11}.N(CH_3)_2$, is a colourless, oily, strongly-refractive liquid, which has a peculiar alkaline smell, and boils at 261—262° under a pressure of 721 mm. It reduces alcoholic silver nitrate solution on heating, a metallic mirror being deposited; an acid solution of ferric chloride produces a red colouration on heating, which disappears at a higher temperature, whilst potassium dichromate and sulphuric acid give a dirty-yellow precipitate in the cold, and a brown colouration accompanied by a brown-black flocculent precipitate on heating.

The *hydrochloride* forms a syrup, whilst the *platinochloride* separates out in resinous masses, which break up on rubbing into orange-yellow crystalline flakes.

When the base is heated with methyl iodide, the *ammonium*

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[1] Bamberger and Hellwig, *Ber.* **22**, 1311.

iodide, $C_{10}H_{11}N(CH_3)_3I$, is formed; this substance crystallizes from water in splendid prisms with a vitreous lustre, and melts at 164·5° (Bamberger and Hellwig).

2641 *ar-Tetrahydro-β-naphthylamine*, $C_{10}H_{11}.NH_2$, is a liquid which boils at 276·5°, and like the corresponding *a*-compound is oxidized to adipic acid by potassium permanganate.[1]

ar-Tetrahydroethyl-β-naphthylamine, $C_{10}H_{11}.NHC_2H_5$, is formed in small quantity together with the alicyclic compound, and is a colourless, viscid oil, which has a faint aromatic odour, and is immediately converted by nitrous acid into the oily nitrosamine, which gives Liebermann's reaction.

Its *hydrochloride*, $C_{10}H_{11}.NH_2(C_2H_5)Cl$, forms long bundles of needles, which have a vitreous lustre. It is readily soluble in water, and is precipitated by hydrochloric acid in silver-white, nacreous plates. The hot aqueous solution is coloured deep reddish-brown by ferric chloride.

The *platinochloride*, $(C_{10}H_{11}.NH_2.C_2H_5)_2PtCl_6$, crystallizes in slender glittering needles, which are sparingly soluble in water, and readily decompose with separation of platinum.

ar-Tetrahydrodimethyl-β-naphthylamine, $C_{10}H_{11}.N(CH_3)_2$, forms the chief product of the reduction of dimethyl-β-naphthylamine, and is also a viscid liquid possessing a faint aromatic odour; it boils at 287° under a pressure of 718 mm. When ferric chloride is added to its hot solution in hydrochloric acid, a yellow colouration accompanied by turbidity is produced, whilst gold chloride colours it first yellow, then green, and finally blue, producing a solution which appears violet by reflected light, and when heated deposits gold as a red powder on the sides of the containing vessel. The alcoholic solution is coloured blue by silver nitrate, and then deposits metallic silver. Potassium dichromate and sulphuric acid give a yellow precipitate, a dirty grey-green colouration being produced on heating.

The *hydrochloride* separates out as a white deliquescent crystalline mass when hydrochloric acid is passed into the anhydrous ethereal solution of the base.

The *platinochloride* is a light yellow flocculent precipitate, which becomes crystalline when rubbed with a glass rod.

The *picrate* crystallizes from hot water in woolly, lustrous yellow needles (Bamberger and Müller.)

ar-Tetrahydrodiethyl-β-naphthylamine, $C_{10}H_{11}.N(C_2H_5)_2$, is almost exclusively formed by the reduction of diethyl-β-naph-

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[1] *Ber.* **23**, 883.

thylamine, and is an oily liquid, which boils at 298° under a pressure of 709 mm., rapidly becomes brown in the air, immediately reduces alcoholic silver solution, and forms a ponceau-red colouring matter with diazobenzenesulphonic acid. Potassium dichromate and sulphuric acid produce an oily precipitate which dissolves on heating, forming a brown solution, whilst ferric chloride added to the solution in hydrochloric acid produces a dirty dark-brown colouration on heating.

The *hydrochloride* is a granular crystalline precipitate which is remarkably soluble in water.[1]

HALOGEN SUBSTITUTION PRODUCTS OF α-NAPHTHYLAMINE.

2642 *Chlor-a-naphthylamine*, $C_{10}H_6Cl.NH_2$(2 : 1 or 3 : 1) was obtained by Cleve by the reduction of dichlor-α-acetonaphthalide. It crystallizes in thin white needles, which melt at 56°, and have an unpleasant fæcal odour. Its *hydrochloride* forms silky needles and is decomposed by water.[2]

4-Chlor-a-naphthylamine, was prepared by Otterberg from 4-chlor-α-nitronaphthalene by reduction. It is a crystalline mass which melts at 85—86°, smells like α-naphthylamine and rapidly oxidizes in the air.[3]

2'-Chlor-a-naphthylamine, was obtained by Erdmann and Kirchhoff by heating 2'-chlor-α-naphthol with calcium chloride ammonia. It is a liquid which has an odour resembling that of naphthylamine, and forms an ethereal solution which has a fine bluish-violet fluorescence. Its *hydrochloride* crystallizes from hot water in fine plates, and becomes coloured grey in the light. On heating with ferric chloride, an azure blue precipitate is formed.[4]

1'-Chlor-a-naphthylamine, was prepared by Atterberg from γ-dichloronitronaphthalene by the action of tin and hydrochloric acid. Its *hydrochloride*, $C_{10}H_6Cl.NH_3Cl+H_2O$, crystallizes in long prisms, which become anhydrous at 100° and gradually volatilize: ammonia precipitates the base from solutions of this salt as a flocculent mass which is odourless, and melts at 93—94°. Ferric chloride produces a greyish-green

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[1] Bamberger and Williamson, *Ber.* **22**, 1760.

[2] *Ber.* **20**, 448.

[3] *Ber.* **10**, 547.

[4] *Annalen*, **247**, 375.

colouration followed by a precipitate. It is converted into 1 : 1′-dichloronaphthalene by the diazo-reaction.[1]

a-Dichloronaphthylamine, $C_{10}H_5Cl_2.NH_2(2:4:1)$, is prepared by the action of concentrated caustic potash solution on *dichloracetonaphthalide*, $C_{10}H_5Cl_2NH.CO.CH_3$, which was prepared by Cleve by passing chlorine into a solution of acetonaphthalide in glacial acetic acid and crystallizes in long thin needles, melting at 214°. The free base crystallizes from alcohol in nodular masses, which melt at 82°, and have an unpleasant fæcal odour. It is volatile with steam, and does not form salts; on oxidation it yields phthalic acid and is converted by the diazo-reaction into 1 : 3-dichloronaphthalene.

β-Dichloronaphthylamine, $(Cl:Cl:NH_2=1:4:8)$, is formed by the action of tin and hydrochloric acid on β-dichloronitronaphthalene; it crystallizes from alcohol in soft white needles, which melt at 104°. The *hydrochloride* forms anhydrous needles.[2]

η-Dichloronaphthylamine, was prepared by Cleve from η-dichloronitronaphthalene; it is slightly soluble in water, readily in alcohol, and crystallizes in needles which have an unpleasant odour, and melt at 94°. Its *hydrochloride* forms thin crystals, which are only slightly soluble in water.[3]

4-Brom-a-naphthylamine, $C_{10}H_6Br.NH_2$, was obtained by Rother from brom-*a*-acetonaphthalide by the action of boiling caustic potash solution,[4] and Morawski and Gläser prepared it in a similar manner from bromocitraconobrom-*a*-naphthalide.[5] It volatilizes with steam and condenses in slender, microscopic needles, which melt at 102°, have a faint odour of *a*-naphthylamine, and become coloured reddish-violet in the light. It is converted into 1 : 4-dibromonaphthalene by the diazo-reaction. Its salts crystallize well.

4-Brom-a-acetonaphthalide, $C_{10}H_6Br.NH.CO.CH_3$, is formed when bromine is added to a solution of acetonaphthalide in glacial acetic acid,[6] and when a solution of bromine in caustic soda solution, and then hydrochloric acid are added to acetonaphthalide ground up with water.[7] It crystallizes from hot alcohol in fascicular groups of lustrous needles, and melts at 193° (Rother).

[1] *Ber.* **9**, 1730.

[2] Widman, *Bull. Soc. Chim.* **28**, 505.

[3] *Bull. Soc. Chim.* **29**, 499.

[4] *Ber.* **4**, 850.

[5] *Monatsh.* **9**, 284.

[6] Meldola, *Ber.* **11**, 1904.

[7] Prager, *Ber.* **18**, 2158.

Bromocitraconobromonaphthalide, $C_{10}H_6BrN(CO)_2.C_3H_3Br$, is formed by the action of bromine on citracononaphthalide, and crystallizes in faint-yellow, lustrous prisms, which melt at 199°.

3-*Brom-a-naphthylamine* is obtained by the action of zinc dust and acetic acid on the corresponding bromonitronaphthalene, and crystallizes in needles, which melt at 62° and are insoluble in water but readily soluble in alcohol and hydrochloric acid.[1]

1 : 3-*Brom-a-acetonaphthalide* is formed by the action of acetic anhydride on the preceding compound, and crystallizes in white needles, melting at 187°.

β-Brom-a-naphthylamine, ($Br : NH_2 = 3' : \text{or } 2' : 1$), was prepared by Guareschi from *m*-bromonitronaphthalene, which melts at 122·5°, by boiling with tin and hydrochloric acid. It is readily soluble in alcohol, insoluble in cold water, and only sparingly soluble in hot water, from which it crystallizes in plates, melting at 63—64°. Its *hydrochloride* forms needles or quadratic plates, which are sparingly soluble in cold water; ferric chloride produces a blue colouration in its aqueous solution, and potassium permanganate oxidizes it to a-bromophthalic acid.[2]

Dibrom-a-naphthylamine, $C_{10}H_5Br_2.NH_2(4 : 2 : 1)$, is formed when its acetyl compound is heated with strong caustic soda solution to 140—150°. It crystallizes from dilute alcohol in large needles, which melt at 118—119°, and are readily soluble in alcohol, ether, benzene, etc. It forms no compounds with acids; when it is dissolved in glacial acetic acid and a few drops of an acetic acid solution of chromium trioxide added, a fugitive indigo-blue colouration is produced. It is oxidized by nitric acid to phthalic acid and is converted by the diazo-reaction into 1 : 3-dibromonaphthalene.[3]

Dibrom-a-acetonaphthalide, $C_{10}H_5Br_2NH.CO.CH_3$, (4 : 2 : 1), is obtained by dissolving 4-brom-α-acetonaphthalide in glacial acetic acid, and adding a little iodine and an excess of bromine. It is readily soluble in alcohol and acetic acid, less readily in benzene, from which it crystallizes in silky, fibrous needles, which melt and partially sublime at 225°.[4]

Dibrom-a-naphthylamine, (3 : 1′ : 1 or 3 : 4′ : 1) was obtained by Meldola from the acetyl-compound; it crystallizes from dilute alcohol in needles, which melt at 101—102°. When the

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[1] Meldola, *Journ. Chem. Soc.* 1885, **1**, 510.

[2] *Annalen*, **222**, 296.

[3] Meldola, *Ber.* **12**, 1961.

[4] *Ber.* **11**, 1904.

amido-group is replaced by bromine, ξ-tribromonaphthalene is formed.[1]

Dibrom-α-acetonaphthalide (3 : 1′ : 1 or 3 : 4′ : 1), is formed when bromine is added to a solution of 3-brom-α-acetonaphthalide in glacial acetic acid, and occurs in crystals, melting at 221°.

HALOGEN SUBSTITUTION-PRODUCTS OF β-NAPHTHYLAMINE.

2643 1-*Chloro-β-naphthylamine*, $C_{10}H_6Cl.NH_2$, is obtained by the action of hydrochloric acid on its acetyl derivative. It crystallizes from dilute alcohol in slender, colourless needles which are devoid of any unpleasant odour and melt at 59°. The *hydrochloride* crystallizes with one molecule of water in colourless lustrous needles, which are scarcely soluble in cold water, but somewhat readily in boiling dilute hydrochloric acid.

1-Chloro-β-naphthylamine can be converted into α-chloronaphthalene and 1 : 2-dichloronaphthalene (M.P. 34-35°) by the diazo-reaction, and yields phthalic acid on oxidation with nitric acid.

1-*Chloro-β-acetonaphthalide*, $C_{10}H_6Cl.NHC_2H_3O$, is formed by the action of chlorine on β-acetonaphthalide dissolved in dilute acetic acid. It crystallizes from alcohol in radiating groups of slender, colourless needles, which are readily soluble in alcohol but with difficulty in boiling water, and melt at 147°.[2]

4-*Bromo-β-naphthylamine*, $C_{10}H_6Br.NH_2$, is obtained by adding zinc dust to a cooled solution of 1 : 3-bromonitronaphthalene. It crystallizes in needles, which melt at 71°, are insoluble in water, readily soluble in alcohol and benzene, and have only faintly basic properties. Its *acetyl compound* forms white needles, melting at 186·5°.[3]

1-*Bromo-β-naphthylamine* was prepared by Cosiner from the acetyl compound by boiling with concentrated caustic potash solution,[4] whilst Marawski and Gläser prepared it from bromocitracono-β-bromonaphthalide.[5] It crystallizes from hot

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[1] *Journ. Chem. Soc.* 1885, **1**, 514.

[2] *Cleve, Ber.* **20**, 1989.

[3] *Journ. Chem. Soc.* 1885, **1**, 509.

[4] *Ber.* **14**, 58.

[5] *Monatsh.* **9**, 284.

water in small needles, melts at 79°, and does not combine with acids. When the amido-group is replaced by hydrogen, α-bromonaphthalene is formed, and it is converted by oxidation with nitric acid into phthalic acid.[1]

1-*Bromo-β-acetonaphthalide* is formed when bromine and β-acetonaphthalide are brought together in acetic acid solution. It crystallizes in needles, melting at 134—135°.

Bromocitracono-β-bromonaphthalide, $C_{10}H_6BrN(CO)_2C_3H_3Br$, forms yellow needles and melts at 181°.

α-Dibromo-β-naphthylamine, $C_{10}H_5Br_2.NH_2$ (1 : 3′ : 3 or 1 : 2′ : 3) has been obtained from its acetyl compound, and crystallizes from alcohol in silky needles, melting at 105°. It is oxidized by dilute nitric acid to a-bromophthalic acid.[2]

Dibromo-β-acetonaphthalide, $C_{10}H_5Br_2NH.CO.CH_3$, is formed by the action of bromine on *m*-bromo-β-acetonaphthalide, and crystallizes in needles, which melt at 221—222°.

β-Dibromo-β-naphthylamine was obtained by Lawson by the action of bromine on benzenediazo-β-naphthylamine and similar compounds. It crystallizes in long needles, melting at 121°, and has weak basic properties. Its *acetyl compound* melts at 208°.[3]

Tetrabromo-β-dinaphthylamine, $C_{20}H_{11}Br_4N$, is formed when the calculated quantity of bromine is added to an acetic acid solution of β-dinaphthylamine, and crystallizes from benzene in long white, matted needles, which melt at 245—246°. If an excess of bromine be employed, *octobromo-β-dinaphthylamine*, $C_{20}H_7Br_8N$, is formed, which crystallizes in slender needles, melting above 300°.[4]

NITRO-SUBSTITUTION-PRODUCTS OF α-NAPHTHYLAMINE.

2644 *4-Nitro-a-naphthylamine*, $C_{10}H_6(NO_2)NH_2$, was obtained by Liebermann by gently heating 1 : 4-nitro-α-acetonaphthalide with alcoholic potash. It crystallizes from alcohol in thin, orange-coloured needles, melts at 191°, and dyes wool a fine orange-yellow. It is more soluble in hot acids than in water, but separates out again on cooling. On boiling with

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[1] Meldola, *Journ. Chem. Soc.* 1883, **1**, 6.

[2] *Journ. Chem. Soc.* 1885, **1**, 511.

[3] *Ber.* **18**, 2424.

[4] Ris, *Ber.* **20**, 2618.

caustic soda solution it is converted into *a*-nitro-naphthol, and yields *a*-nitronaphthalene when diazotised.[1]

4-*Nitro-a-acetonaphthalide*, $C_{10}H_6(NO_2)NH.CO.CH_3$. Andreoni and Biedermann obtained a substance melting at 171° as the product of the action of nitric acid on *a*-acetonaphthalide dissolved in glacial acetic acid.[2] Liebermann, however, found that this is a mixture of two isomerides, one of which (1 : 4) can readily be obtained pure, whilst the other, subsequently recognized as the 1 : 2-compound by Lellmann, cannot easily be isolated. In order to prepare these compounds 100 grms. of acetonaphthalide are dissolved in 600 grms. of glacial acetic acid, and a mixture of 45 grms. of nitric acid of sp. gr. 1·54 and 40 grms. of glacial acetic acid added. After about two days the substance melting at 171° is deposited, and then pure 1 : 4-nitro-*a*-acetonaphthalide, which crystallizes in needles melting at 190°. The substance melting at 171° proved to be a compound of equal molecules of 1 : 4- and 1 : 2-nitro-acetonaphthalide, which cannot be separated by crystallization. If, however, it be dissolved in hot alcohol, the calculated amount of concentrated caustic potash added and the liquid heated. the 1 : 4-compound is decomposed, whilst the 1 : 2-compound remains undissolved.

2-*Nitro-a-naphthylamine* is obtained by heating the nitro-acetonaphthalide to 110° with the necessary quantity of alcoholic potash. It crystallizes from alcohol in monosymmetric prisms of the colour of potassium dichromate, which melt at 144°, and are converted into *β*-nitronaphthalene by heating with nitrous acid and alcohol, and into 2-nitro-*a*-naphthol by boiling with caustic soda solution.

2-*Nitro-a-acetonaphthalide* forms yellow needles, melting at 199°. When equal parts of this and of the 1 : 4-compound are dissolved in glacial acetic acid, needles of the double compound already mentioned separate out after some time.[3]

4′-*Nitro-a-naphthylamine* is formed by the action of ammonium sulphide on 1 : 4-dinitronaphthalene, and crystallizes from hot water in small red lustrous needles, which melt at 118—119°, and are converted into *a*-nitronaphthalene by nitrous acid in the presence of alcohol.[4]

2 : 4-*Dinitro-a-naphthylamine*, $C_{10}H_5(NO_2)_2NH_2$, was obtained

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[1] *Annalen*, **183**, 228

[2] *Ber.* **6**, 342.

[3] Lellman, *Ber.* **17**, 109 ; Lellman and Remy, *Ber.* **19**, 796.

[4] Beilstein and Kuhlberg, *Annalen*, **169**, 87.

by Liebermann and Hammerschlag by heating its acetyl compound to 140° with alcoholic ammonia.[1] Witt found that it can be prepared in the same manner from dinitro-α-naphthol if the temperature be maintained for some time at 190–200°.[2] It is, however, best prepared from freshly-precipitated moist dinitro-α-acetonaphthalide by adding sulphuric acid, and, if necessary, aiding the reaction by heat.[3] It is insoluble in cold water, sparingly soluble in boiling water, and crystallizes from alcohol in lemon-yellow needles, which melt at 238–239°. It forms no compounds with acids; caustic potash readily converts it into dinitro-α-naphthol, and it yields γ-dinitronaphthalene when the amido-group is replaced by hydrogen.

Dinitro-α-acetonaphthalide, $C_{10}H_5(NO_2)_2(NH.CO.CH_3)$, is formed when α-acetonaphthalide is nitrated in acetic acid solution with the necessary amount of concentrated nitric acid, and crystallizes in long, yellowish needles, melting at 250·5°.

Trinitro-α-naphthylamine, $C_{10}H_4(NO_2)_3NH_2$, was obtained by Städel by heating ethyl α-trinitronaphthate with alcoholic ammonia. It is scarcely soluble in alcohol, ether, benzene, &c., and slightly soluble in hot toluene, from which it crystallizes in small yellow plates. Nitrous acid and alcohol convert it into β-trinitronaphthalene.[4]

Tetranitro-α-naphthylamine, $C_{10}H_3(NO_2)_4NH_2$, is formed when ammonia is passed into the solution in benzene of the bromotetranitronaphthalene obtained by the action of fuming nitric acid on α-bromonaphthalene. It crystallizes in light-yellow, lustrous needles, and melts at 194°.[5]

4 : 2-*Bromonitro-α-naphthylamine*, $C_{10}H_5Br(NO_2)NH_2(4:2:1)$, was prepared by Liebermann from the acetyl-compound by boiling with alcoholic potash or heating with alcoholic ammonia to 160—170°. It forms long, orange-coloured crystals, which melt at 200°. Dilute nitric acid oxidizes it to phthalic acid; it yields *m*-bromonitronaphthalene when acted upon by nitrous acid and alcohol, and is converted into δ-tribromonaphthalene by heating with hydrobromic acid.

4:2-*Bromonitro-α-acetonaphthalide* is obtained when *p*-bromacetonaphthalide is nitrated in hot acetic acid solution, and crystallizes in long, light-yellow needles, melting at 232°.

2 : 4-*Bromonitro-α-naphthylamine* was prepared by Meldola by

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[1] *Annalen*, **183**, 272.

[2] *Ber.* **19**, 2032.

[3] Meldola, *Ber.* **19**, 2683.

[4] *Annalen*, **217**, 173.

[5] Merz and Weith, *Ber.* **15**, 2708.

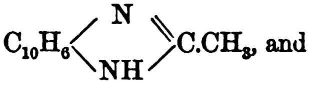
dissolving the acetyl compound in sulphuric acid and gradually adding water, sufficient heat for the decomposition of the compound being thus generated. It crystallizes from toluene in long, orange-red needles, melts at 197°, is soluble in hot alcohol, and yields phthalic acid on oxidation.

2 : 4-*Bromonitro-a-acetonaphthalide* is formed by the bromination of 4-nitro-*a*-acetonaphthalide, and crystallizes from alcohol in long, fibrous ochreous needles, which melt at 225°.[1]

NITRO-SUBSTITUTION-PRODUCTS OF β-NAPHTHYLAMINE.

2645 1-*Nitro-β-naphthylamine*, $C_{10}H_6(NO_2)NH_2(1:2)$, is formed when its acetyl-compound is boiled with alcoholic potash, and crystallizes from alcohol in long, lustrous, orange-yellow needles, which melt at 126—127°. It is converted into *a*-nitronaphthalene by the diazo-reaction.[2]

1-*Nitro-β-acetonaphthalide*, $C_{10}H_6(NO_2)(NH.CO.CH_3)$, is obtained by gradually adding concentrated nitric acid to a well-cooled paste of β-acetonaphthalide and glacial acetic acid. It crystallizes from alcohol in long, yellow needles or rhombic prisms, and melts at 123·5°.[3] On heating with acid stannous chloride it is converted into ethenyl-β-diamidonaphthalene;



$C_{10}H_6\left\langle\begin{matrix}N\\NH\end{matrix}\right\rangle C.CH_3$, and is thus proved to be an ortho-compound. When it is boiled with caustic soda solution, nitro-β-naphthol is formed, whilst cold concentrated caustic potash solution rapidly decomposes it into acetic acid and the foregoing substance.[4]

Dinitro-β-naphthylamine, $C_{10}H_5(NO_2)_2NH_2$, is formed when ethyl dinitro-β-naphthate is heated to 140° with ammonia. It is sparingly soluble in water and alcohol, melts at 238°, and is converted into δ-dinitronaphthalene by the diazo-reaction.[5]

1′ : 4′-*Dinitro-β-naphthylamine* is formed by the action of alcoholic ammonia on the ethyl ether of dinitro-β-naphthol at

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[1] *Journ. Chem. Soc.* 1885, **1**, 499.
[2] Liebermann and Jacobson, *Annalen*, **211**, 64.
[3] *Annalen*, **211**, 45.
[4] Kleemann, *Ber.* **19**, 334.
[5] Graebe and Drews, *Ber.* **17**, 1170.

220—225°. It is only slightly soluble in boiling toluene, from which it separates in thin yellow needles, which blacken at 235° without melting. The crystals are insoluble in dilute acids, and gradually become darker coloured on exposure to the air.[1]

Trinitro-β-naphthylamine, $C_{10}H_4(NO_2)_3NH_2$, is obtained by heating ethyl trinitro-β-naphthate with alcoholic ammonia, and is scarcely soluble in alcohol, ether, glacial acetic acid, or benzene, and is very sparingly soluble in boiling toluene, from which it crystallizes in small lustrous needles, which become black and detonate on heating. Its diazo-nitrate is converted by alcohol into β-trinitronaphthalene.[2]

Tetranitro-β-naphthylamine, $C_{10}H_3(NO_2)_4NH_2$, is prepared by the action of ammonia on β-bromotetranitronaphthalene suspended in benzene, and crystallizes from alcohol in yellow needles, melting at 202°.[3]

Dinitro-β-dinaphthylamine, $C_{20}H_{11}(NO_2)_4N$, is formed by the action of ordinary nitric acid on a cooled solution of β-dinaphthylamine in acetic acid. It is slightly soluble in alcohol, rather more freely in benzene, and readily in coal-tar cumene, from which it crystallizes in yellowish-red needles or slender prisms, which melt at 224—225°.

Tetranitro-β-dinaphthylamine, $C_{20}H_{11}(NO_2)_4N$, is the product when concentrated nitric acid is employed, and separates from boiling nitrobenzene in brownish-red crystalline granules, which melt at 285—286°, and detonate when more strongly heated.

Hexnitro-β-dinaphthylamine, $C_{20}H_9(NO_2)_6N$, is obtained when a large excess of fuming nitric acid is employed, and is precipitated in lemon-yellow flakes by water.[4]

Amidochlorotrinitronaphthalene, $C_{10}H_3(NH_2)Cl(NO_2)_3$, is obtained by the action of alcoholic ammonia on dichlorotrinitronaphthalene (Cl : Cl : 1 : 3), and forms citron-yellow, pliant needles, containing a molecule of alcohol; it melts at 252°. The corresponding phenyl-substituted derivative is obtained by the action of aniline on the dichloro-compound. It forms red scales, and melts at 230°.[5]

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[1] Onufrowicz, *Ber.* **23**, 3362.

[2] Staedel, *Annalen*, **217**, 173.

[3] Merz and Weith, *Ber.* **15**, 2720.

[4] Ris, *Ber.* **20**, 2618.

[5] Cleve, *Ber.* **23**, 957.

THE MONOSULPHONIC ACIDS OF α-NAPHTHYLAMINE

α-Naphthylamine-α-Sulphonic Acids, $C_{10}H_6(NH_2)SO_3H$.

2646 1 : 4-*Naphthylaminesulphonic acid.* Piria obtained the ammonium salt of *thionaphthamic acid*, $C_{10}H_9NSO_3$, by boiling nitronaphthalene for a considerable time with a solution of ammonium sulphite and alcohol, and keeping the liquid neutral by the addition of ammonium carbonate. From this he prepared other salts, all of which crystallize in pearly plates, and have a reddish or amethystine tinge, resembling that of the internal coating of many shells. When it is decomposed by an acid, the free thionaphthamic acid immediately takes up the elements of water and decomposes into naphthylamine and sulphuric acid.

In addition to this substance he obtained an isomeric stable substance, *naphthionic acid*,[1] which he considered to stand in the same relation to thionaphthamic acid as isethionic acid to sulphovinic acid.[2] Kolbe distinguished naphthionic acid as *amidonaphthylsulphuric acid* and thionaphthamic acid as *naphthylamidosulphuric acid*.[3] Employing the modern symbols his formulæ become :

Naphthionic Acid.	Thionaphthamic Acid.
$C_{10}H_6(NH_2)SO_3H$	$C_{10}H_7.NH.SO_3H.$

The latter formula explains in a simple manner the ready decomposition of thionaphthamic acid ; whilst, according to the former, naphthionic acid would be a sulphonic acid of naphthylamine, and this constitution was also considered probable by Butlerow,[4] and was proved by Schmidt and Schaal, who obtained the acid by the action of sulphuric acid on naphthylamine.[5]

Cleve then showed that it is converted by the diazo-reaction into 1 : 4-dichloronaphthalene.[6] Witt afterwards carefully compared naphthionic acid prepared by Piria's method with the acid obtained by the action of an excess of sulphuric acid on α-naph-

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[1] It is first called naphthionic acid in *Gmelin's Handbuch*, and this name has hitherto been universally employed.

[2] *Annalen*, **78**, 31.

[3] *Lehrbuch Organ. Chem.* **2**, 806.

[4] *Lehrbuch Organ. Chem.* p. 693.

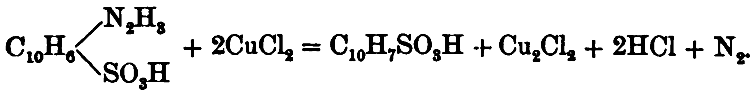
[5] *Ber.* **7**, 1367.

[6] *Ber.* **10**, 1722.

thylamine, and with that prepared by Nevile and Winther by heating equal molecules of sulphuric acid and α-naphthylamine to 180—200°,[1] and found that all three were identical.[2] He proposed that the name naphthionic acid should be retained for these acids, and adduced further proofs of their constitution.[3] It is manufactured either by heating α-naphthylamine with 3-5 parts of sulphuric acid until the mass is completely soluble in alkalis, or by employing the method of Nevile and Winther.

Naphthionic acid crystallizes in small silky needles containing half a molecule of water, which is lost at 100°. It is scarcely soluble in alcohol and dissolves in almost 4,000 parts of cold water. Its solutions and those of its salts show a deep reddish-blue fluorescence, and several of its isomerides are employed for the manufacture of colouring matters. As already mentioned, Erdmann has determined the constitution of many of the disubstitution products of naphthalene, taking the naphthylamine-sulphonic acids as his starting-point, and converting them into other derivatives. The methods employed for this purpose may be here shortly described.

In order to convert naphthionic acid into α-naphthylamine, 180 grms. of distilled sulphuric acid are mixed with 50 grms. of water, and 20 grms. of sodium naphthionate added to the hot mixture; strongly superheated steam is then passed in and the temperature gradually raised to 180—185°, at which point the amido-acid suddenly dissolves. The liquid is maintained at this temperature for a quarter of an hour, and is then diluted with water and the naphthylamine precipitated by a slight excess of ammonia. If it be desired to convert it into α-naphthalenesulphonic acid, naphthylhydrazinesulphonic acid is first prepared and is then suspended in water, hydrochloric acid added, and an acid solution of cupric chloride allowed to drop slowly into the mixture:



$$C_{10}H_6\begin{cases}N_2H_3\\SO_3H\end{cases} + 2CuCl_2 = C_{10}H_7SO_3H + Cu_2Cl_2 + 2HCl + N_2.$$

The conversion of naphthionic acid into 1 : 4-naphtholsulphonic acid can be readily effected by preparing diazonaphthalenesulphonic acid from it and bringing this in the moist state into a

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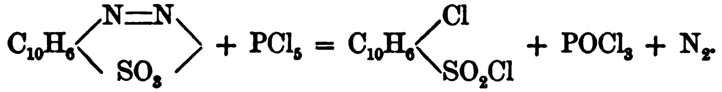
[1] *Ber.* **13**, 1948.
[2] *Ber.* **19**, 55.
[3] *Ber.* **19**, 1719.

boiling mixture of 100 parts of sulphuric acid and 400 parts of water. Naphthionic acid can also be readily converted into 1 : 4-dichloronaphthalene. In order to do this 308 grms. of phosphorus pentachloride are covered with about an equal weight of phosphorus oxychloride, and the mixture heated until the greater part of the former has dissolved; 114 grms. of dry diazonaphthalenesulphonic acid are then gradually added, the operation being occasionally interrupted and the liquid vigorously boiled for a short time to prevent the accumulation of the diazo-compound. As soon as all has been added, the liquid is heated to boiling for six hours in a flask provided with an inverted condenser. Chloronaphthalenesulphonic chloride is the first product of this reaction:



$$C_{10}H_6\left\langle\begin{matrix}N{=}N\\SO_3\end{matrix}\right\rangle + PCl_5 = C_{10}H_6\left\langle\begin{matrix}Cl\\SO_2Cl\end{matrix}\right. + POCl_3 + N_2.$$

This is then converted into dichloronaphthalene according to one of the following equations:

$$C_{10}H_6Cl(SO_2Cl) + PCl_5 = C_{10}H_6Cl_2 + SOCl_2 + POCl_3$$
$$C_{10}H_6Cl(SO_2Cl) + PCl_5 = C_{10}H_6Cl_2 + SO_2Cl_2 + PCl_3.$$

The phosphorus and sulphur compounds are distilled off, and the temperature is then raised until the dichloronaphthalene has come over. The latter is purified by washing with water, caustic soda solution, and acidified water, and is finally recrystallized from alcohol.[1] The salts of naphthionic acid have been examined by Piria and by Witt.

Sodium naphthionate, $C_{10}H_8NSO_3Na+4H_2O$, crystallizes in large transparent monosymmetric tablets, or when its saturated solution is rapidly cooled, in plates which after a few moments change into tablets. It is readily soluble in water but only sparingly in caustic soda or caustic potash solution, the solubility decreasing as the concentration of the caustic solution increases; it is therefore precipitated from solution in water by alkalis. Its taste is at first scarcely perceptible, but then becomes persistently sweet. The concentrated solution shows no fluorescence, but dilute solutions fluoresce with a violet-blue colour.

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[1] *Annalen*, **247**, 350; *Ber.* **20**, 3185.

Calcium naphthionate, $(C_{10}H_8NSO_3)_2Ca+8H_2O$, crystallizes from hot water in white, monosymmetric tablets, with a fatty lustre, which are readily soluble in water, but scarcely soluble in alcohol.

Barium naphthionate, $(C_{10}H_8NSO_3)_2Ba$, crystallizes from a hot concentrated solution in micaceous plates, and from a dilute solution in large transparent plates, which are probably isomorphous with those of the calcium salt, and effloresce so rapidly that Piria was unable to determine the amount of water of crystallization present.

1 : 4′-*Naphthylaminesulphonic acid.* Laurent by the reduction of nitronaphthalenesulphonic acid with ammonium sulphide, obtained *sulphonaphthalidamic acid* (*acide sulphonaphtalidamique*).[1] It remained uncertain whether this substance was identical or isomeric with naphthionic acid[2] until Cleve, who prepared it by the reduction of pure *a*-nitronaphthalenesulphonic acid, examined it more carefully and found it to be different from naphthionic acid, giving it the name of *a-amidonaphthylsulphonic acid.*[3] Witt then obtained by the action of cold fuming sulphuric acid on *a*-naphthylamine hydrochloride, *naphthalidinesulphonic acid,* and although very similar to Cleve's acid, it was considered to be different,[4] until Erdmann[5] and Mauzelius[6] showed that they are identical. The same acid is also formed when *a*-acetonaphthalide is treated with fuming sulphuric acid,[7] and, together with much naphthionic acid, by heating *a*-naphthylamine with the fuming acid. It can be separated from naphthionic acid by the solubility of its sodium salt in alcohol (Erdmann).

1 : 4′-Naphthylaminesulphonic acid crystallizes in very slender needles and requires four times as much cold water to dissolve it as naphthionic acid. Erdmann has converted it by the above-mentioned reactions into *a*-naphthylamine and *a*-naphthalenesulphonic acid; in the formation of the latter, however, a considerable proportion of 1 : 4′-naphtholsulphonic acid is also obtained, which can readily be prepared pure from the diazo-compound, and is converted by phosphorus pentachloride into 1 : 4′-dichloronaphthalene. The salts of 1 : 4′-naphthylamine-

[1] *Compt. Rend.* **31**, 537.

[2] Carius, *Gmelin's Handb. Organ. Chem.* **4**, 105.

[3] *Bull. Soc. Chim.* **24**, 506.

[4] *Ber.* **19**, 578.

[5] *Ber.* **20**, 3185; *Annalen,* **247**, 315.

[6] *Ber.* **20**, 3401.

[7] Lange, *Ber.* **20**, 2940; Schultz, *Ber.* **20**, 3158.

sulphonic acid are more readily soluble than the naphthionates, and their solutions have a greenish fluorescence.

Sodium 1 : 4'-*naphthylaminesulphonate*, $C_{10}H_8NSO_3Na + H_2O$, crystallizes in flat needles or pearly scales, which lose their water of crystallization at 140°.

Calcium 1 : 4'-*naphthylaminesulphonate*, $(C_{10}H_8NSO_3)_2Ca + 9H_2O$, forms large pearly tablets, which are readily soluble in hot water.

Barium 1 : 4' - *naphthylaminesulphonate*, $(C_{10}H_8NSO_3)_2Ba + 6H_2O$, crystallizes readily in soluble plates or small prisms.

1 : 4'-*Amidonaphthalenesulphamide*, $C_{10}H_6(NH_2)SO_2.NH_2$, is formed by the action of hydriodic acid on the corresponding nitro-derivative. It is almost insoluble in cold, more readily in hot alcohol, and crystallizes in lustrous, colourless tablets, melting at 259—260°. It forms a crystalline *hydrochloride* and *sulphate*, and on treatment with acetic anhydride yields the *mono-* and *di-acetyl derivatives*, which melt at 231-232° and 200° respectively.[1]

1 : 1'-*Naphthylaminesulphonic acid.* According to Schoellkopf's patent, two nitronaphthalenesulphonic acids are formed when α-naphthalenesulphonic acid is first treated with concentrated sulphuric acid and then with nitric acid. These are converted by reduction into the amido-acids, one of which forms a readily soluble sodium salt and was shown by Erdmann to be the 1 : 4'- acid, whilst the other, the sodium salt of which is sparingly soluble, is the 1 : 1'- acid.[2] The latter crystallizes in white needles, which dissolve at 21° in 4,800 parts of water. When a few cc. of this solution are treated with a drop of ferric chloride, a fine violet colouration is gradually produced; if more of the reagent be added, turbidity is produced, accompanied by an inky colouration, which disappears when the solution is boiled, a grey or yellowish-brown precipitate being formed. The constitution of the acid has been determined by Erdmann by converting it into α-naphthylamine and α-naphthalenesulphonic acid; only three α-α-naphthylaminesulphonic acids can exist, two of which have already been described, and therefore this compound must be the third possible isomeride. When the 1-1'-diazonaphthalene acid is decomposed by water, the corresponding naphtholsulphonic acid is not obtained, but naphthosultone is formed (p. 103), and similarly chloronaphthosultone is obtained by the action of phosphorus pentachloride.

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[1] Ekbom, *Ber.* **23**, 1119.

[2] *Annalen*, **247**, 318.

Sodium 1 : 1′-*naphthylaminesulphonate*, $C_{10}H_8NSO_3Na$, crystallizes from hot water in somewhat coarse tablets or elegant plates, which dissolve at 24° in 887 and at 100° in 374 parts of water.

α-NAPHTHYLAMINE-β-SULPHONIC ACIDS.

2647 1 : 3′-*Naphthylaminesulphonic acid*, termed by Cleve β-amidonaphthalenesulphonic acid, is formed by the reduction of the corresponding nitrosulphonic acid, and crystallizes in anhydrous rhombic tablets or slender pliant needles, which contain two molecules of water and are very slightly soluble in hot, more readily in boiling water. On heating with phosphorus chloride it is converted into 1 : 3′-dichloronaphthalene. Its salts have a yellow colour.

Sodium 1 : 3′-*naphthylaminesulphonate*, $C_{10}H_8NSO_3Na$, is readily soluble in water, and crystallizes in thin rhombic tablets.

Calcium 1 : 3′-*naphthylaminesulphonate*, $(C_{10}H_8NSO_3)_2Ca + 7H_2O$, forms lustrous rhombohedra.

Barium 1 : 3′-*naphthylaminesulphonate*, $(C_{10}H_8NSO_3)_2Ba + H_2O$, crystallizes in flat needles and is readily soluble in water.[1]

1 : 3′-*Amidonaphthalenesulphamide*, $C_{10}H_6(NH_2)SO_2NH_2$, is formed by the action of hydriodic acid on the corresponding nitro-compound. It is readily soluble in hot alcohol, from which it crystallizes in slender silky needles melting with decomposition at 218—219°. The *monacetyl* derivative forms light red needles, melting at 238—239°.[2]

1 : 2′-*Naphthylaminesulphonic acid*, which was termed γ-amidonaphthalenesulphonic acid by Cleve, was also prepared from the corresponding nitrosulphonic acid, and forms small yellow, sparingly soluble needles.[3]

Sodium 1 : 2′-*naphthylaminesulphonate*, $C_{10}H_8NSO_3Na$, forms readily soluble, anhydrous scales.

Barium 1 : 2′-*naphthylaminesulphonate*, $(C_{10}H_8NSO_3)_2Ba + H_2O$, is also readily soluble and crystallizes in thin plates. The *calcium salt* is very soluble and separates from a syrupy solution in needles.[4]

1 : 3-*Naphthylaminesulphonic acid*, which Cleve named diamidonaphthylaminesulphonic acid, forms crystals, which contain a molecule of water. The solutions of its salts assume a violet colour in the air.

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[1] *Bull. Soc. Chim.* **26**, 444.

[2] Ekbom, *Ber.* **24**, 329.

[3] *Ber.* **19**, 2179.

[4] *Ber.* **21**, 3271.

Sodium 1 : 3-*naphthylaminesulphonate*, $2C_{10}H_8NSO_3Na+H_2O$ crystallizes in thin, very soluble needles.

Barium 1 : 3-*naphthylaminesulphonate*, $(C_{10}H_8NSO_3)_2Ba$, is sparingly soluble and crystallizes in flat tablets.[1]

1 : 2-*Naphthylaminesulphonic acid* is formed when α-naphthylamine is heated with five parts of concentrated sulphuric acid to 125—130° for eight to nine hours, the first formed 1 : 4- and 1 : 4′- acids being converted into this compound, which is termed α-naphthylamine-δ-sulphonic acid by Hirsch. Its constitution follows from the fact that only seven α-monosulphonic acids of naphthalene can exist, and the constitution of the other six is known.

It crystallizes in rhombic tablets, which dissolve in 150 parts of boiling water and 480 parts of cold water. Its *sodium salt* is very readily soluble but is precipitated by common salt.

Barium 1 : 2-*naphthylaminesulphonate*, $(C_{10}H_8NSO_3)_2Ba$, crystallizes in three-sided serrate tablets, which are sparingly soluble in water.[2]

α-NAPHTHYLAMINEDISULPHONIC ACIDS.

2648 Two compounds of this composition are manufactured and employed for the preparation of azo-colouring matters.

α-Naphthylamine-4-2′-disulphonic acid, $C_{10}H_5(NH_2)(SO_3H)_2$ is formed by the action of fuming sulphuric acid on naphthionic acid at a low temperature, and can be separated from the isomeric acids which are formed at the same time by means of its calcium salt, which is insoluble in alcohol. This is then converted into the sodium salt and hydrochloric acid added, which precipitates the disulphonic acid in the form of a white powder.[3] It is converted by the diazo-reaction into 1 : 2′-naphthalenedisulphonic acid.[4]

α-Naphthylamine-3 : 1′-*disulphonic acid* is formed when naphthalene is heated to 90—110° with five parts of ordinary sulphuric acid, the product nitrated, and the nitro-acid precipitated from the solution by common salt and reduced. The pure acid is obtained from the product by converting it into the

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[1] *Ber.* **21**, 3264.

[2] *Ber.* **21**, 2370.

[3] Dahl and Co., *Ber.* **21**, 119 c.

[4] Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 16.

normal sodium salt and adding hydrochloric acid, which precipitates the acid sodium salt. The free acid crystallizes with three molecules of water in scales which have a fatty lustre and are very freely soluble in hot water. The *normal sodium salt* $C_{10}H_5(NH_2)(SO_3Na)_2+6H_2O$, forms very readily soluble needles, or thin prisms; the *acid salt* $C_{10}H_5(NH_2)(SO_3Na)(SO_3H)+2H_2O$ crystallizes in similar forms, but is only very sparingly soluble in cold water. Bernthsen has converted this acid into the corresponding naphtholdisulphonic acid (p. 107) by means of the diazo-reaction.[1]

α-Naphthylamine-4 : 1′-disulphonic acid, (δ) is formed by the sulphonation of α-naphthylamine-α-sulphonic acid,[2] and also by the reduction of the product of the direct nitration of 1 : 4′-naphthalenedisulphonic acid.[3]

The *acid sodium salt,* $C_{10}H_5(NH_2)(SO_3Na)(SO_3H)+H_2O$, crystallizes in long prismatic needles.

α-Naphthylamine-4 : 3′-disulphonic acid is formed, together with the 1 : 4 : 2′-acid and *α-naphthylaminetrisulphonic acid* by the sulphonation of naphthionic acid. It is converted into 1 : 4 : 3′-trichloronaphthalene by the diazo-reaction, followed by distillation with phosphorus pentachloride.[4]

THE SULPHONIC ACIDS OF β-NAPHTHYLAMINE.

2649 *β-Naphthylamine-α-sulphonic acid* (2 : 1′) is obtained, together with its isomerides, when β-naphthylamine is heated to 140° with three to four parts of sulphuric acid,[5] and when a salt of β-naphthol-α-sulphonic acid is heated with ammonia under pressure.[6] Hydrochloric acid precipitates it from solutions of its salts in matted needles, which dissolve in about 1,700 parts of cold water. This solution and those of its salts show a blue fluorescence. It is converted by phosphorus pentachloride into 1 : 2′-dichloronaphthalene.

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[1] *Ber.* **22**, 3327.

[2] Schöllkopf Co., German Patent 40571, *Ber.* **20**, 667 R.

[3] Bernthsen, *Ber.* **22**, 3323. Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 126.

[4] Dahl and Co., German Patent 41957, **1886** Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 125.

[5] Forsling, *Ber.* **20**, 2099 ; **22**, 619.

[6] Bayer and Duisberg, *Ber.* **20**, 1426.

Sodium β-naphthylamine-α-sulphonate, $C_{10}H_8NSO_3Na$, crystallizes in thin, four-sided plates, which are insoluble in alcohol.

The *ammonium salt* forms large, very soluble prisms (Green).

Calcium β-naphthylamine-α-sulphonate, $(C_{10}H_8NSO_3)_2Ca + 6H_2O$, forms large thick tablets, soluble in eleven parts of cold water.

Barium β-naphthylamine-α-sulphonate, $(C_{10}H_8NSO_3)_2Ba+4H_2O$, is very freely soluble in hot water and crystallizes in aggregates of splendid prisms.

β-Naphthylamine-β-sulphonic acid (2 : 3′), always accompanies its isomerides in larger or smaller quantity according to the temperature at which the sulphonation is carried out. It is manufactured by heating ammonium β-naphthol-β-sulphonate with lime or caustic soda and water to 180° in autoclaves.[1] It crystallizes with one molecule of water in silky scales, plates, or flat needles, whilst according to Green, when perfectly pure it forms coarse, prismatic needles, which are sparingly soluble in water, the solution showing a blue fluorescence. It may be converted by the diazo-reaction into 2 : 3′-dichloronaphthalene.

Sodium β-naphthylamine-β-sulphonate, $C_{10}H_8NSO_3Na+2H_2O$, forms silky needles, which are freely soluble in alcohol, but only sparingly in water.

The *ammonium salt* crystallizes in large, thin tablets, which have a blue fluorescence, and is less readily soluble than the ammonium salts of the isomeric acids.

Calcium β-naphthylamine-β-sulphonate, $(C_{10}H_8NSO_3)_2Ca + 6H_2O$, is only very slightly soluble in cold water and crystallizes in splendid silky plates.

Barium β-naphthylamine-β-sulphonate, $(C_{10}H_8NSO_3)_2Ba + 6H_2O$, forms long silky needles, sparingly soluble in cold water.[2]

The *copper salt* is very characteristic, forming lustrous crystals resembling those of mosaic gold, which are scarcely soluble in cold and only sparingly in hot water. The *lead salt* is immediately precipitated when lead acetate is added to a solution of the sodium salt.[3]

On sulphonation the 2 : 3′- acid is converted into the 2 : 1 : 3′-disulphonic acid, accompanied by a smaller quantity of 2 : 1′ : 3′-acid.[4]

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[1] Farbenfabrik, vormals Brönner, *Ber.* **16**, 1517.

[2] Forsling, *Ber.* **20**, 76.

[3] Actiengesellsch. Anilinfabr., *Ber.* **21**, 816 R.

[4] Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 130.

β-Naphthylamine-γ-sulphonic acid (2 : 4′) is obtained, accompanied by the *a*-acid, when β-naphthylamine is mixed with fuming sulphuric acid, containing 20 per cent. of trioxide, and allowed to stand for two or three days, the mixture being occasionally stirred,[1] or when such a mixture is heated for a short time to 70—80°.[2] It crystallizes in small tablets, and may be separated from the *a*-acid by the insolubility of its *sodium salt* in alcohol, and from the other isomerides by means of its *barium salt,* which is readily soluble in cold water, and crystallizes with some difficulty in nodular aggregates; the *ammonium salt,* which is also readily soluble, forms tablets. When the amido-group is replaced by bromine, 2 : 4′-bromonaphthalenesulphonic acid is formed, and this on heating with phosphorus chloride is converted into 1 : 3-dichloronaphthalene.[3] This acid is converted by sulphonation into a mixture of the 2 : 4′ : 2′ and 2 : 1 : 4′-disulphonic acids.[4]

β-Naphthylamine-δ-sulphonic acid (2 : 2′) is formed, together with the β-acid, when one part of β-naphthylamine sulphate is brought into three parts of sulphuric acid heated to 150°, and the mixture kept at this temperature for one or two hours.[5] These two acids can be obtained in the same way from the *a*- and γ-acids.[6] In order to separate them, the mixture is repeatedly crystallized from luke-warm water, in which the δ-acid is much more soluble than the Brönner acid, as the β-compound is usually called. The same end may be much more rapidly attained by preparing a solution of the mixed sodium salts, and adding copper sulphate solution as long as a precipitate is formed; the latter consists of the insoluble copper salt of the β-acid, whilst the sodium salt of the δ-acid, which is not precipitated by copper sulphate remains in solution. The γ-acid prepared from this may be easily purified by conversion into the calcium or barium salt, which is repeatedly re-crystallized and then decomposed by acid. The δ-acid is also formed when a salt of β-naphthol-δ-sulphonic acid is heated under pressure with ammonia. It crystallizes in long, silky needles, containing one molecule of water, which is lost on boiling with water, the crystals falling to a sandy powder, which under

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[1] Dahl and Co., German Patents 29084, 32271, 32276.

[2] Green, *Journ. Chem. Soc.* 1889, **1**, 33; *Ber.* **22**, 721.

[3] Sindall, *Proc. Chem. Soc.* **1889**, 118.

[4] Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 129.

[5] Bayer and Duisberg, *Ber.* **20**, 1426; Weinberg, *Ber.* **20**, 2906; Schultz, *Ber.* **20**, 3158.

[6] Weinberg, *Ber.* **20**, 3353.

the microscope presents the appearance of fragments of prisms, and is scarcely soluble in cold, very sparingly in hot water. It may be converted into 2 : 2′-dichloronaphthalene by the diazo-reaction.[1]

Sodium β-naphthylamine-δ-sulphonate, $C_{10}H_8NSO_3Na + 4H_2O$, is sparingly soluble in cold, readily in hot water, and crystallizes in lustrous plates which have a reddish-blue fluorescence.

The *ammonium salt* is moderately soluble in water, and crystallizes in small tablets.

Calcium β-naphthylamine-δ-sulphonate, $(C_{10}H_8NSO_3)_2Ca + 6H_2O$, forms blue fluorescent plates, which dissolve in 260—270 parts of cold water.

Barium β-naphthylamine-δ-sulphonate, $2(C_{10}H_8NSO_3)_2Ba + 9H_2O$, is readily soluble in hot water, and dissolves in 400 parts of cold water; it crystallizes in fascicular groups of small plates. When lead acetate is added to the solution of the sodium salt, a precipitate is formed after some time, and this property may be made use of in separating the δ-acid from the β-acid.

β-Naphthylaminedisulphonic acid (G), (2 : 1′ : 3′), is obtained from the corresponding naphthol derivative, and is also formed when 2 : 1′-naphthylaminesulphonic acid is sulphonated. It can be converted into 1 : 3 : 2′-trichloronaphthalene.[2]

β-Naphthylaminedisulphonic acid, (δ) (2 : 3 : 2′), is obtained by the action of ammonia on the corresponding β-naphthol derivative.[3]

β-Naphthylaminedisulphonic acid (2 : 4 : 2′), is obtained by the reduction of the corresponding nitro-compound, which is formed in small quantities by the nitration of 1 : 3′-naphthalenedisulphonic acid.[4]

a-Chloro-β-naphthylaminesulphonic acids. When α-chloro-β-naphthylamine is treated with four parts of sulphuric acid containing 2 per cent. of anhydride, three isomeric monosulphonic acids are obtained.

The 1 : 2 : 4′-*acid* is almost exclusively formed when the mixture is heated to 70° for six hours. It is only slightly soluble in water, from which it crystallizes in glistening, flat elongated prisms, and is best purified by conversion into the sodium salt and precipitation by acid. Its salts crystallize well

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[1] Bayer and Duisberg, *loc. cit.*; Erdmann, *Ber.* **21**, 637.

[2] Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 13, 128.

[3] Cassella and Co., German Patent 44079; Armstrong and Wynne, *Proc. Chem. Soc.* **1890**, 127

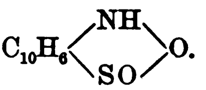
[4] Armstrong and Wynne, *Proc. Chem. Soc.* **1891**, 27.

but are easily soluble. After the elimination of the amido-group, it yields 1 : 4′-dichloronaphthalene on treatment with phosphorus pentachloride.[1]

The 1 : 2 : 3′-*acid* is the chief product when the mass is heated for twelve hours to 100°. It is somewhat more soluble than the preceding acid, and forms a characteristic *sodium salt*, which crystallizes with four and a half molecules of water in lustrous plates. It can be converted after elimination of the amido-group into 1 : 3′-dichloronaphthalene.

The 1 : 2 : 2′-*acid* is chiefly produced if the sulphonation be effected at 160°. It is more readily soluble than either of the others, crystallizes in tufts of needles, and yields very soluble salts which do not crystallize well. On eliminating the amido-group and treating with phosphorus pentachloride, 1 : 2′-dichloronaphthalene is obtained.[2]

SULPHIMIDONAPHTHALENES,



$C_{10}H_6\left\langle\begin{matrix}NH\\SO\end{matrix}\right\rangle O.$

2650 These compounds, which were discovered by Cleve, are formed by the action of hydriodic acid on the chlorides of the nitro-sulphonic acids, whatever be the relative positions of the two side-chains. They cannot be volatilized without decomposition, do not combine with either acids or bases, and are very stable substances.[3]

1 : 4′-*Sulphimidonaphthalene* is sparingly soluble in acetic acid, from which it separates in crystalline plates melting at 167°. These can be boiled for hours with caustic soda solution without undergoing any considerable change, a small quantity being dissolved and colouring the liquid brown.

1 : 3′-*Sulphimidonaphthalene* crystallizes in slender yellow needles, melting at 180°.

1 : 2′-*Sulphimidonaphthalene* forms slender, lustrous, lemon-yellow needles, and melts at 124°.

1 : 3-*Sulphimidonaphthalene* also crystallizes in yellow needles, melting at 173°.

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[1] Armstrong and Wynne, *Proc. Chem. Soc.* **1889,** 34, 48 ; *Chem. News,* **59,** 140, 188.

[2] Armstrong and Wynne, *loc. cit.*

[3] *Ber.* **20,** 1534.

DIAMIDONAPHTHALENES, OR NAPHTHYLENE-DIAMINES, $C_{10}H_6(NH_2)_2$.

α-α-DIAMIDONAPHTHALENES.

2651 1 : 4-*Diamidonaphthalene* was first prepared by Perkin by the reduction of azo-α-naphthylamine.[1] It is also formed by the action of tin and hydrochloric acid on 4-nitro-α-naphthylamine or azo-α-naphthylamine sulphanilic acid,[2] $HSO_3.C_6H_4.N_2.C_{10}H_6.NH_2$, and is best prepared by making up a solution of diazobenzene chloride from 93 grms. of aniline, 245 grms. of hydrochloric acid of 40 per cent., 245 grms. of water, and 71 grms. of sodium nitrite dissolved in a small quantity of water, and adding this gradually to a well-stirred luke-warm solution of 143 grms. of α-naphthylamine in a litre of alcohol of 90 per cent. Phenylazo-α-naphthylamine, $C_6H_5.N_2.C_{10}H_6.NH_2$, separates out as a thick mass of green needles, with a metallic lustre; this is brought in quantities of 6 grms. into contact with zinc dust and boiling water, and the decolourized boiling solution filtered into sulphuric acid. The sulphate separates out in lustrous white needles, and is then decomposed with sodium carbonate solution, and the base, which is deposited on cooling, is finally filtered off, washed with a little water, and rapidly dried on a porous plate.[3]

1 : 4-Diamidonaphthalene is readily soluble in alcohol and ether, somewhat sparingly in hot water, from which it crystallizes in white needles or small prisms, which readily take a greenish tint, have a repulsive, sharp burning taste, and when brought on the tongue in somewhat larger quantity produce very violent pain, which lasts for some days. It melts at 120° to a brown oil, which smells strongly of quinone on evaporation, and can be distilled almost without decomposition in a current of hydrogen. Its aqueous solution soon decomposes, a violet flocculent precipitate being deposited.

1 : 4-*Diamidonaphthalene hydrochloride*, $C_{10}H_6(NH_3Cl)_2$, crystallizes from hot water in lustrous, four-sided plates, which are scarcely soluble in hydrochloric acid. When ferric chloride is added to its dilute solution, the latter becomes green and

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[1] *Annalen*, **137**, 359.

[2] Griess, *Ber.* **15**, 2912.

[3] Bamberger and Schieffelin, *Ber.* **22**, 1381.

then yellow, a brown precipitate containing α-naphthoquinone being formed, whilst in an acid solution the latter compound alone is produced.

Phenyl-1 : 4-*diamidonaphthalene*, $C_{10}H_6(NH_2)NH.C_6H_5$, is formed when α-phenylamido-α-nitrosonaphthalene, $C_{10}H_6(NO).NHC_6H_5$, is reduced with stannous chloride; it crystallizes from benzene in lustrous plates and from alcohol in well-formed lustrous needles, melting at 148°.

Diphenyl-1 : 4-*diamidonaphthalene*, $C_{10}H_6(NHC_6H_5)_2$, is obtained by the action of zinc and glacial acetic acid on an alcoholic solution of α-naphthoquinonedianil (p. 224). It crystallizes from alcohol in colourless prisms, and melts at 144°.[1]

a-Naphthyl-1 : 4-*diamidonaphthalene*, $C_{10}H_6(NH_2)NHC_{10}H_7$, is obtained in a similar manner to the phenyl derivative from α-naphthylamido-α-nitrosonaphthalene, and forms wax-yellow microscopic crystals.[2]

Acetyl-1 : 4-*diamidonaphthalene* $C_{10}H_6(NH_2)(NH.CO.CH_3)$ is prepared by the reduction of 4-nitro-α-acetonaphthalide with tin and hydrochloric acid; its *hydrochloride* crystallizes in long needles,[3] and is converted into *diacetyldiamidonaphthalene*, $C_{10}H_6(NH.CO.CH_3)_2$, by heating with sodium acetate and acetic anhydride.[4] This substance may also be obtained by the action of the anhydride on the base (Bamberger and Schieffelin), and crystallizes in lustrous white needles, melting at 305°.

ar-Tetrahydro-1 : 4-*diamidonaphthalene*, $C_{10}H_{10}(NH_2)_2$, is obtained in a similar manner to the hydronaphthylamines; its *hydrochloride* forms a glittering crystalline powder. Alkalis set free the base as an oil, which can be distilled under diminished pressure without decomposition, and solidifies on cooling to an acicular crystalline mass, which rapidly becomes coloured reddish-brown, green, and violet in the air, and completely decomposes in a short time. It rapidly reduces the salts of silver and platinum with formation of α-naphthoquinone, and is oxidized by potassium permanganate to adipic acid, its constitution being thus shown (p. 169).

Diacetyltetrahydro-1 : 4-*diamidonaphthalene*, $C_{10}H_{10}(NH.CO.CH_3)_2$, is formed when the hydrochloride is heated with sodium acetate and acetic anhydride, and crystallizes from hot water

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[1] Fischer and Hepp, *Annalen*, **256**, 255.

[2] Wacker, *Annalen*, **243**, 300.

[3] Liebermann and Dittler, *Annalen*, **183**, 229.

[4] Kleemann, *Ber.* **19**, 334.

in long, white, silky needles, which melt at 285° (Bamberger and Schieffelin).

1 : 4′-*Diamidonaphthalene* was obtained by Zinin by reducing impure α-dinitronaphthalene with ammonium sulphide, and was termed by him *seminaphthalidine.*[1] De Aguiar then prepared it by the action of phosphorus iodide and a little water on the pure nitro-compound.[2] It is also readily formed when α-dinitronaphthalene is heated with tin, hydrochloric acid and alcohol,[3] as well as when 1 part of 1 : 4′-dihydroxynaphthalene is heated with 10 parts of commercial solution of ammonia or 5 parts of ammonia solution saturated at —10°, the temperature being first kept at 150—180° and then raised to 250—300°.[4]

It crystallizes from hot water or alcohol in needles, and from ether in well-developed prisms, which melt at 189·5° and sublime in feather-like aggregates of fine needles. Its dilute alcoholic solution is coloured a fine but fugitive blue or violet-blue by a drop of amyl nitrite accompanied by one or two drops of hydrochloric acid. When ferric chloride is added to the base suspended in water a bluish-violet colouration, followed by a precipitate of the same colour, is produced. Potassium hypochlorite added to the alcoholic solution gives a red colouration, followed by a precipitate; if a drop of hydrochloric acid be added to the solution, the colour is changed to violet and a blue precipitate, which soon decomposes, is formed. The base may be converted into 1 : 4′-dichloronaphthalene by the diazo-reaction (Erdmann).

1 : 4′-*Diamidonaphthalene hydrochloride*, $C_{10}H_6(NH_3Cl)_2$, forms small white prisms, which are readily soluble in water. It does not separate out when its hot saturated solution is allowed to cool, but is completely precipitated by hydrochloric acid.

1 : 4′-*Diamidonaphthalene sulphate*, $C_{10}H_6(NH_3)_2SO_4$, is precipitated by sulphuric acid from a solution of the hydrochloride in lustrous needles. When sodium nitrite is added to its solution, a violet precipitate of the composition, $C_{20}H_{15}N_3O_3$, is formed.

Tetrahydro-1 : 4′-*diamidonaphthalene*, $C_{10}H_{10}(NH_2)_2$, was prepared by Bamberger and Abrahall by dissolving 14 grms. of 1 : 4′-diamidonaphthalene in 200 grms. of boiling amyl alcohol and adding 18—20 grms. of sodium cut up into small

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[1] *Annalen*, **52**, 362; **85**, 329.

[2] *Ber.* **3**, 27; **7**, 306.

[3] Hollemann, *Zeitsch. Chem.* **1865**, 556; Erdmann, *Annalen*, **247**, 360.

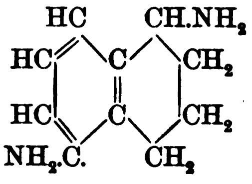
[4] Ewer and Pick, *Annalen*, **247**, 361.

pieces in portions of 4—5 grms. The base was then extracted from the amyl alcohol solution by agitation with dilute hydrochloric acid, the solution concentrated by evaporation, the hydrochloride decomposed, and the base finally taken up with ether. It was then converted into the pure carbonate by a current of carbon dioxide, again liberated by caustic soda and distilled *in vacuo*.

It crystallizes from ether in colourless transparent prisms, with a vitreous lustre, which become coloured yellow and finally brown in the air, melts at 77°, and boils at 264° under a pressure of 60 mm., whereas at a temperature above 360° under the atmospheric pressure it boils and gives off ammonia very vigorously. It has a sharp smell, like that of piperidine, irritates the throat, is alkaline to litmus, decomposes ammonium salts, combines energetically with carbon dioxide and carbon disulphide, and gives no colouration with ferric chloride in the cold but becomes reddish-brown on heating. It corresponds therefore with the alicyclic hydrobases in all these reactions.

On the other hand, however, it behaves in many respects as an aromatic amido-compound, inasmuch as it forms diazo-compounds, combines with diazo-derivatives to form azo-colouring matters, and gives a deep port-wine red colouration when it is boiled with dilute sulphuric acid and potassium dichromate. Its double character is also shown by the fact that when it is dissolved in fuming hydrochloric acid and titrated with a concentrated solution of sodium nitrite in the presence of starch paste and potassium iodide, the blue colouration is produced as soon as exactly one molecule of nitrous acid has been added.

As already mentioned (p. 169) tetrahydro-1 : 4'-diamidonaphthalene is converted into ac-tetrahydro-α-naphthylamine when one of its amido-groups is replaced by hydrogen, and it has therefore the following constitution:



*Tetrahydro-*1 : 4'*-diamidonaphthalene hydrochloride,* $C_{10}H_{10}(NH_3Cl)_2$, forms splendid rhombio crystals, and is readily soluble in water. Concentrated hydrochloric acid precipitates it from solution in colourless, strongly refractive prisms, which have a vitreous lustre.

This salt, like the free base, is optically inactive, but when the latter is converted into the acid tartrate, this can be divided into two portions, one of which is more readily soluble than the other. If the hydrochloride be again prepared from these portions, that from the less soluble rotates the plane of polarization to the left and the other to the right.[1]

The *platinochloride*, $C_{10}H_{10}(NH_3)_2PtCl_6$, separates out in thick orange-yellow prisms, which contain water and have a vitreous lustre, when a strongly acid solution of the hydrochloride is treated with platinum chloride and evaporated. The compound, $[C_{10}H_{10}(NH_2)NH_3]_2PtCl_6$, is, however, formed as an ochre-yellow, crystalline precipitate, when platinum chloride is added to an aqueous solution of the base.

Tetrahydro-1 : 4′-diamidonaphthalene sulphate, $C_{10}H_{16}N_2SO_4 + 2H_2O$, crystallizes in well developed colourless asymmetric prisms when alcohol is added to its hot aqueous solution and the liquid allowed to cool.

The *carbonate* is a white lustrous powder, possessing the odour of the free base, and is a mixture of the normal with the acid salt.

Diacetyltetrahydro-1 : 4′-diamidonaphthalene, $C_{10}H_{10}(NH.CO.CH_3)_2$, crystallizes from alcohol in slender, silky prisms, which melt at 262°.

Diamidotetrahydronaphthyl thiocarbamide, $CS(NH.C_{10}H_{10}NH_2)_2$. When an ethereal solution of the base is added drop by drop to a well-cooled mixture of carbon disulphide and ether, the alicyclic amido-group alone is attacked, and the *thiocarbamate*, $NH_2.C_{10}H_{10}.NH.CS.SH_3N.C_{10}H_{10}.NH_2$, is formed as a lustrous crystalline powder. It is a weak base, can be diazotised, and combines with diazo-compounds to form azo-colouring matters. By boiling with alcohol it is converted into the crystalline thiocarbamide, which becomes resinous on recrystallization and is also an aromatic diamido-compound. When, however, the thiocarbamate is decomposed in presence of litharge, the urea $CO(NH.C_{10}H_{10}.NH_2)$, is formed, which is also a crystalline powder, readily decomposes and resembles the compounds just described.

Ditetrahydronaphthyl dithiocarbamide, $CS(NH.C_{10}H_{10}.NH)_2CS$,

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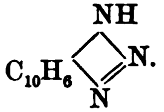
[1] Bamberger, *Ber.* **23**, 291.

is formed when the base is heated with alcohol and an excess of carbon disulphide, and is a white crystalline powder which is insoluble in acids, forms no azo-colours, and cannot be diazotised.[1]

1 : 1′-*Diamidonaphthalene* was obtained by de Aguiar and by Erdmann from 1 : 1′-dinitronaphthalene, and was also prepared by the latter by heating 1 : 1′-dihydroxynaphthalene with ammonia in the manner already described. It crystallizes from dilute alcohol in brittle, white needles melting at 67°, which are more readily soluble in water and less readily in chloroform than the 1 : 4′-compound. When more strongly heated it volatilizes, forming a vapour which smells like α-naphthylamine. Its solutions give a chestnut-brown precipitate with ferric chloride, and a blue precipitate, which becomes red in the air, with potassium hypochlorite. It may be converted into 1 : 1′-dichloronaphthalene by the diazo-reaction.

1 : 1′-*Diamidonaphthalene hydrochloride*, $C_{10}H_6(NH_3Cl)_2$, is readily soluble in water, and is precipitated by hydrochloric acid in crystals.

1 : 1′-*Diamidonaphthalene sulphate*, $C_{10}H_6(NH_3)_2SO_4$, forms small crystals, which are readily soluble in water. Sodium nitrite added to its solution produces a vermilion-coloured precipitate of $C_{10}H_7N_3$, which crystallizes from benzene in needles and forms salts both with acids and bases; this substance is probably *naphthalenediazimide* of the following constitution:



When the hydrochloride of 1 : 1′-diamidonaphthalene is heated to 100° with benzaldehyde, hydrochloric acid is evolved;[2] this base therefore behaves as an ortho-compound (Pt. III. p. 62),[3] the amido-groups being in the peri-position (p. 28).

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[1] Bamberger and Abrahall, *Ber.* **22**, 943; Bamberger and Bammann, *Ber.* **22**, 951.

[2] Ladenburg, *Ber.* **11**, 1650.

[3] Ekstrand, *Ber.* **18**, 2888.

α-β-DIAMIDONAPHTHALENES.

2652 1 : 2-*Diamidonaphthalene* was prepared by Griess by reducing azo-β-naphthylaminesulphanilic acid, $C_6H_4(SO_3)N_2.C_{10}H_6NH_2$, with tin and hydrochloric acid.[1] It may also be obtained in a similar manner from other azo-β-naphthylamine compounds,[2] and is formed when 2-nitro-α- and 1-nitro-β-naphthylamine,[3] or β-naphthoquinonedioxime[4] are boiled with stannous chloride and hydrochloric acid. It is, however, best prepared by making up a solution of diazobenzene chloride (p. 200), and adding an alcoholic solution of 143 grms. of β-naphthylamine, and then 43 grms. of crystallized sodium acetate. Benzene-azo-β-naphthylamine, $C_6H_5.N_2.C_{10}H_6.NH_2$, separates out in red needles, with a green lustre, which are filtered off; 10 grms. of these crystals are dissolved in 300 grms. of acetic acid of 16 per cent., and zinc dust added to the solution until the colour changes from red to light-yellow. The boiling solution is then filtered and allowed to run into dilute sulphuric acid, the precipitated mass of sulphate washed with acidulated water and brought into a hot solution of sodium carbonate, the temperature being raised to the boiling-point and water added if necessary until it has all dissolved. The base separates out, when the filtered liquid is allowed to cool, in small silver-white plates with a satin lustre, which become coloured pink and then brown when exposed to the air in the moist state.[5] It readily dissolves in alcohol and ether, from which it crystallizes in large prisms resembling those of apophyllite, melts at 98·5°, and has a biting bitter taste.

1 : 2-*Diamidonaphthalene hydrochloride*, $C_{10}H_6(NH_3Cl)_2$, is readily soluble in water, from which it is precipitated by hydrochloric acid in white plates, which readily lose some of their hydrochloric acid. Ferric chloride added to its solution produces a green colouration which passes into yellow, an amorphous brown precipitate being finally formed.

1 : 2-*Diamidonaphthalene sulphate*, $C_{10}H_6(NH_3)_2SO_4$, separates in silvery plates when sulphuric acid is added to an alcoholic solution of the hydrochloride.

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[1] Lawson, *Ber.* **15**, 2193.

[2] *Ber.* **18**, 800 and 2422; Sachs, *Ber.* **18**, 3125.

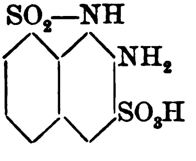
[3] Lawson, Lellmann and Remy, *Ber.* **19**, 796.

[4] Koreff, *Ber.* **19**, 179.

[5] Bamberger and Schieffelin, *Ber.* **22**, 1374.

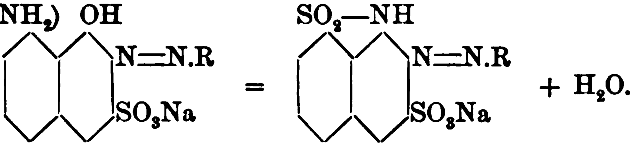
1 : 2 : 3 : 1′-*Diamidonaphthalenedisulphonic acid* is obtained in the form of its *acid sodium salt*, $C_{10}H_4(NH_2)_2(SO_3H)(SO_3Na)+3H_2O$ which crystallizes in small needles, by the reduction of the azo-colour prepared from aniline and 1 : 3 : 1′-naphthylaminedisulphonic acid (ε).[1]

An anhydride of this acid having the formula



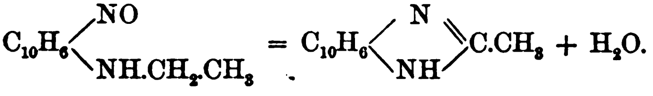
$+ 2H_2O.$

has also been prepared by Bernthsen. When the colouring matter obtained from naphtholsulphamidosulphonic acid (p. 107), and *m*-xylidine is acted on by caustic potash, the colour of the solution changes to a light reddish-yellow, and a new azo-colour is found to be in solution, which on reduction yields the anhydride of the above formula. This remarkable reaction proceeds according to the following equation:



The acid is only slightly soluble in water, crystallizes in long flat needles, and forms yellow solutions in the alkalis.

Ethenyl-1 : 2-*diamidonaphthalene*, $C_{10}H_6N_2(C_2H_3)H$, was first obtained by the reduction of 1-nitro-β-acetonaphthalide (p. 186), and is also formed when β-naphthylethylnitrosamine, $C_{10}H_7N(C_2H_5)NO$, is allowed to stand for some time with alcoholic hydrochloric acid; the isomeric β-ethylamido-α-nitrosonaphthalene is first formed in this reaction, and then, as an ortho-compound, loses water and passes into the anhydro-base:



$$C_{10}H_6\begin{cases} NO \\ NH.CH_2.CH_3 \end{cases} = C_{10}H_6\begin{cases} N \\ NH \end{cases}C.CH_3 + H_2O.$$

The latter is sparingly soluble in hot water, from which it separates in nodular crystals, whilst it crystallizes from wood-spirit

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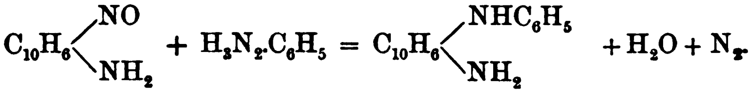
[1] Bernthsen, *Ber.* **23**, 3094.

in short, thick prisms, with a diamond lustre, which contain a molecule of methyl alcohol, melt at 75°, and readily decompose with formation of a crystalline powder, melting at 168°. The *hydrochloride*, $2(C_{12}H_{10}N_2)HCl+3H_2O$, crystallizes in long needles, and the *platinochloride*, $(C_{12}H_{12}N_2)_2PtCl_6+3H_2O$, forms slender, yellow needles, which are sparingly soluble in water, more freely in alcohol.[1]

*a-Phenyl-*1 : 2*-diamidonaphthalene*, $C_{10}H_6(NH_2)NHC_6H_5$, is formed when phenylhydrazine hydrochloride is added to a boiling solution of β-amido-α-nitrosonaphthalene:

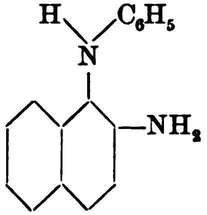


$$C_{10}H_6\left\langle\begin{matrix}NO\\NH_2\end{matrix}\right. + H_3N_2.C_6H_5 = C_{10}H_6\left\langle\begin{matrix}NHC_6H_5\\NH_2\end{matrix}\right. + H_2O + N_2.$$

It crystallizes from benzene in small needles, which melt at 161°, and are moderately soluble in water.[2]

*β-Phenyl-*1 : 2*-diamidonaphthalene* is prepared by the reduction of β-phenylnaphthylamine-azobenzenesulphonic acid, $C_6H_4(SO_3H)N{=}N.C_{10}H_6.NH(C_6H_5)$, with stannous chloride, sulphanilic acid being also formed. It crystallizes from alcohol or benzene in clear, flat prisms, which melt at 136—137°, and become red on exposure to air, especially when moist.[3]

Its *hydrochloride* crystallizes from acetic acid containing hydrochloric acid, in long, lustrous needles, which are sparingly soluble in water and are partially decomposed by it.[4] The isomerism of the two phenyldiamidonaphthalenes is explained by their methods of formation:



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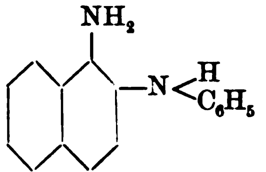

β

*Diacetyl-*1 : 2*-diamidonaphthalene*, $C_{10}H_6(NH.CO.CH_3)_2$, is formed when a solution of 1 : 2-diamidonaphthalene hydro-

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[1] Fischer and Hepp, *Ber.* **20**, 1247 and 2471.
[2] Harden, *Annalen*, **255**, 161.
[3] Witt, *Ber.* **20**, 1184.
[4] Lawson and Zincke, *Ber.* **20**, 1167.

chloride in glacial acetic acid is boiled with sodium acetate and acetic anhydride; it crystallizes from alcohol in white needles, melting at 234°.[1]

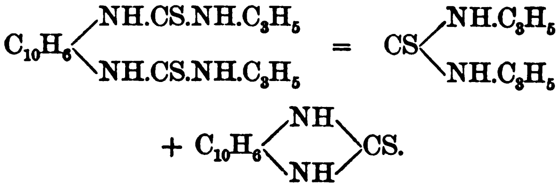
Dibenzoyl-1 : 2-*diamidonaphthalene*, $C_{10}H_6(NH.CO.C_6H_5)_2$, is obtained by agitating the base with benzoyl chloride and caustic soda solution. It crystallizes in faintly-red plates, melts at 291°, and is sparingly soluble in alcohol and glacial acetic acid and almost insoluble in water.[2]

Phenylamidonaphthyl carbamide, $C_6H_5.NH.CO.NH.C_{10}H_6.NH_2$, is formed when a solution of 1 : 2-diamidonaphthalene in benzene is treated with phenyl carbimide; it is a crystalline powder which remains solid even at 335°.

Naphthylenediphenyl carbamide, $C_{10}H_6(NH.CO.NH.C_6H_5)_2$, accompanies the compound just described, and resembles it in its properties, but is almost completely insoluble in alcohol.

Naphthylenediphenyl thiocarbamide, $C_{10}H_6(NH.CS.NH.C_6H_5)$, is prepared in a similar manner from phenyl thiocarbimide, and forms yellowish needles, which melt with decomposition at about 360°.[3]

Naphthylenediallyl thiocarbamide, $C_{10}H_6(NH.CS.NH.C_3H_5)_2$, was obtained by Lellmann from the base and allyl mustard oil; it crystallizes in slender, silky needles, and decomposes at 200° into diallyl thiocarbamide and *naphthylene thiocarbamide*:



$$C_{10}H_6\left\langle\begin{array}{l}NH.CS.NH.C_3H_5\\NH.CS.NH.C_3H_5\end{array}\right. = CS\left\langle\begin{array}{l}NH.C_3H_5\\NH.C_3H_5\end{array}\right. + C_{10}H_6\left\langle\begin{array}{c}NH\\NH\end{array}\right\rangle CS.$$

The latter remains as a powder, which only melts at a very high temperature.[4]

ar-Tetrahydro-1 : 2-*diamidonaphthalene*, $C_{10}H_{10}(NH_2)_2$, crystallizes from hot water in flat needles with a satin lustre, melts at 84°, and boils under a pressure of 81 mm. at 220°. It has strong reducing properties, and is coloured a splendid carmine-red in hydrochloric acid solution by ferric chloride. Potassium permanganate oxidizes it to adipic and oxalic acids.

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[1] Lawson, *Ber.* **18**, 801.

[2] Hinsberg and Udranszky, *Annalen*, **254**, 252.

[3] Schieffelin, *Ber.* **22**, 1377.

[4] *Ber.* **19**, 808.

The *hydrochloride*, $C_{10}H_{10}(NH_3Cl)_2$, crystallizes from hot water in lustrous tablets, whilst the sparingly soluble *nitrate*, $C_{10}H_{10}(NH_3NO_3)_2$, forms silver-white plates, with a satin lustre.

The *diacetyl-compound*, $C_{10}H_{10}(NH.CO.CH_3)_2$, crystallizes in matted silky needles, and melts at 245°.

ac-Tetrahydro-1 : 2-*diamidonaphthalene* is only produced in very small quantity, and has the characteristic smell, &c., of this class of compounds. Its *hydrochloride* crystallizes in lustrous needles, and its *platinochloride* in golden-yellow needles (Bamberger and Schieffelin).

1 : 3-*Diamidonaphthalene* is not known in the free state, but its *hydrochloride* has been prepared by the reduction of 1 : 3-dinitronaphthalene with tin and hydrochloric acid. It is readily soluble in water, less easily in alcohol, gives a yellow colouration with water containing nitrous acid, and reacts with a solution of diazosulphanilic acid to form the corresponding chrysoïdine. These reactions show that the base is a meta-derivative. Its *acetyl* compound crystallizes from a mixture of benzene and light petroleum in transparent prisms, melting at 154—156°.[1]

β-β-DIAMIDONAPHTHALENES.

2 : 2′-*Diamidonaphthalene* is obtained by heating 2 : 2′-dihydroxynaphthalene with ammonia[2] or zinc chloride ammonia[3] to 250°; it is moderately soluble in hot water, from which it crystallizes in silver-white plates with a satin lustre, which become red on exposure to the air, and melt at 161°. It gives no colouration with ferric chloride; most of the salts are readily soluble and the *hydrochloride* is not precipitated from its solution by concentrated hydrochloric acid.

2 : 2′-*Diphenylamidonaphthalene*, $C_{10}H_6(NHC_6H_5)_2$, is obtained by heating the corresponding dihydroxynaphthalene with aniline and calcium chloride to 280—290°.[4] It crystallizes from benzene in colourless, lustrous plates, melting at 168°. The *diacetyl* derivative forms small yellowish crystals, and melts at 197·5°.

2 : 3′-*Diamidonaphthalene* is similarly prepared by heating 2 : 3′-dihydroxynaphthalene to 250° with ammonia; it crystallizes in plates, melting at 216—218°, and its solution is coloured

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[1] Urban, *Ber.* **20**, 973.

[2] Lange, *Chem. Zeitsch.* **12**, 856.

[3] Bamberger and Schieffelin, *Ber.* **22**, 1384.

[4] Clausius, *Ber.* **23**, 528.

green by ferric chloride. The *sulphate* is almost insoluble in cold water, and the *hydrochloride* is precipitated by concentrated hydrochloric acid (Lange).

Diamidonaphthalene. An isomeride, the constitution of which is not known, is formed on the reduction of the dinitronaphthalene obtained from dinitronaphthylamine. Its *hydrochloride* is very readily soluble in water and forms yellow needles.[1]

HIGHER AMIDO-DERIVATIVES OF NAPHTHALENE.

2653 *Diamido-β-naphthylamine*, $C_{10}H_5(NH_2)_3$, is formed by the reduction of dinitro-β-naphthylamine with tin and hydrochloric acid. The free base has not been obtained, but the salts crystallize well.

The *normal hydrochloride*, $C_{10}H_5(NH_2)_3,3HCl$, crystallizes from water in faintly-yellow needles and loses one molecule of hydrochloric acid over soda lime in a vacuum.

The *triacetyl* derivative crystallizes in white needles, and melts with decomposition at 280°; the *tribenzoyl* compound is slightly soluble in alcohol and water, crystallizes in faintly yellow needles, and melts at 277°.[2]

Trianilidonaphthalene, $C_{10}H_5(NHC_6H_5)_3$, is formed together with the tetranilido-derivative, as a by-product in the preparation of rosinduline by heating phenylamido-α-nitrosonaphthalene with aniline and aniline hydrochloride. It is much more soluble in alcohol than the tetranilido-compound and crystallizes in fine needles, melting at 148°. It has faintly basic properties, and is readily oxidized to phenylrosinduline.[3]

Tri-p-toluidonaphthalene, $C_{10}H_5(NHC_7H_7)_3$, is prepared in a similar manner to the preceding compound. It crystallizes from alcohol in white needles, which melt at 159—160°, and gradually become red in the air.

Tetranilidonaphthalene, $C_{10}H_4(NHC_6H_5)_4$, is a white crystalline substance, which is very sparingly soluble in alcohol, and melts at 191°.[4]

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[1] Loewe, *Ber.* **23**, 2546

[2] Loewe, *Ber.* **23**, 2546.

[3] Fischer and Hepp, *Annalen*, **256**, 251.

[4] Fischer and Hepp, *Ber.* **21**, 269; *Annalen*, **256**, 250.

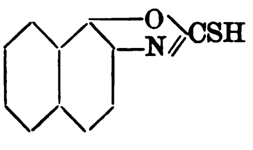
THE AMIDONAPHTHOLS

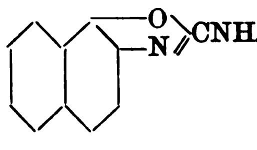
2654 *2-Amido-a-naphthol*, $C_{10}H_6(NH_2)OH$, was obtained by Dittler and Liebermann by the reduction of 2-nitro-α-naphthol with tin and hydrochloric acid;[1] it may also be prepared in this way from α-naphtho-β-quinonoxime, and forms a *hydrochloride*, which crystallizes in broad, white plates. The solution of this salt colours pinewood orange, and on oxidation yields dinaphthyl-β-diquinone, $C_{20}H_{14}O_4$. When the alkaline solution of the hydrochloride is agitated in the air, imidoxynaphthalene (p. 221) separates out as a violet film with a metallic lustre.

2-Thiocarbamido-a-naphthol, $C_{11}H_7NSO$, is formed, together with the compound next described, when β-naphthoquinonephenylhydrazone is heated with carbon disulphide to 250°. It crystallizes from alcohol in long needles, which melt with decomposition at 259—260°.

Carbanilido-a-naphthol, $C_{17}H_{12}N_2O$, separates from chloroform in small needles, which melt at 232—233°, and are readily soluble in alcohol.

These compounds have the following constitution:[2]





4-Amido-a-naphthol is obtained by the reduction of 4-nitronaphthol (Liebermann and Dittler). It is, however, best prepared by boiling five parts of α-naphthol orange, $C_{10}H_6(ONa)N_2.C_6H_4.SO_3Na$, with ten parts of strong hydrochloric acid, and twelve parts of stannous chloride.[3] The *hydrochloride* is thus obtained, which is readily soluble in water, with difficulty in hydrochloric acid, and crystallizes in white needles or elongated plates, which rapidly become coloured violet on exposure to the air in the moist state. It likewise colours pine wood yellow, and on boiling with ferric chloride is quantitatively converted into

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[1] *Annalen*, **183**, 245.

[2] Jacobson and Schenke, *Ber.* **22**, 3241.

[3] Jacobsen and Liebermann, *Annalen*, **211**, 60.

α-naphthoquinone. The free base, separated from the hydrochloride by alkalis, rapidly blackens in the air.

4′-Amido-a-naphthol is formed when three parts of sodium 1 : 4′-naphthylaminesulphonate are heated with three parts of caustic soda, and two parts of water to 240—250° for eight to ten hours. The *hydrochloride* forms a white crystalline mass.[1]

It differs from its isomerides in giving a blue colouring matter with diazonaphthalenesulphonic acid.

2 : 4-*Diamido-a-naphthol*, $C_{10}H_5(NH_2)_2OH$, is not known in the free state; when dinitro-α-naphthol is treated with tin and hydrochloric acid, the compound $C_{10}H_6O(NH_3Cl)_2+SnCl_2+2H_2O$, is obtained, crystallizing in lustrous, monosymmetric prisms.[2] If this be decomposed by sulphuretted hydrogen, the solution evaporated in a vacuum, and hydrochloric acid added to the residue, the *hydrochloride* of diamidonaphthol separates out in microscopic plates, which are moderately stable when dry,[3] but rapidly decompose when moist, the so-called di-imidonaphthol (p. 222) being formed.

Diacetamido-a-naphthyl acetate, $C_{10}H_5(NH.CO.CH_3)_2O.CO.CH_3$, was obtained by Meerson by the action of acetic anhydride and sodium acetate on the hydrochloride. It crystallizes from acetic acid in microscopic needles, which melt at 280° with decomposition. Ferric chloride oxidizes it to acetamido-β-naphthoquinone (p. 220).

Triamido-a-naphthol, $C_{10}H_4(NH_2)_3OH$, has been prepared by the reduction of trinitro-α-naphthol with tin and hydrochloric acid; the compound, $C_{10}H_5O(NH_3Cl)_3 + SnCl_2 + H_2O$, is thus obtained in nodular aggregates of prisms. The free base is not known, and its salts rapidly oxidize in the air to the so-called amidodi-imidonaphthol.[4]

ac-Tetrahydro-1 : 4′-*amidonaphthol*, $C_{10}H_{10}(NH_2)OH$, is formed when one molecule of *ac*-tetrahydro-1 : 4′-diamidonaphthalene is suspended in fuming hydrochloric acid and a concentrated solution of one molecule of sodium nitrite added drop by drop, an equal volume of water being then added and the mixture heated. As soon as the evolution of nitrogen has ceased, the solution is filtered, and the hydrochloride, which crystallizes out

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[1] Actiengesellschaft für Anilinfabr., German Patent 49448, 1889, *Ber.* **23**, 41 c.

[2] Griess and Martius, *Annalen*, **134**, 377; Gräbe and Ludwig, *Annalen*, **154**, 307.

[3] Meerson, *Ber.* **21**, 1195.

[4] Ekstrand, *Ber.* **11**, 164; Diehl and Merz, *Ber.* **11**, 1661.

on cooling, decomposed with caustic soda solution. The amidonaphthol thus obtained is an oily liquid, which possesses the sharp smell and other characteristic properties of the alicyclic hydrobases, and is therefore insoluble in alkalis, in spite of the fact that it is a phenol, although sodium acts upon it in ethereal solution with evolution of hydrogen, and it yields azo-colours with diazo-compounds and a diacetyl compound with acetic anhydride.

Its *hydrochloride*, $C_{10}H_{10}(NH_3Cl)OH$, crystallizes from water in long, vitreous needles, and from hydrochloric acid in silver-white, pearly plates.

Diacetyltetrahydro-amidonaphthol, $C_{10}H_{10}(O.CO.CH_3)NH.CO CH_3$, crystallizes from dilute acetic acid in long, elegant needles resembling wavellite, and melts at 151—151·5°.[1]

1-*Amido-β-naphthol*, $C_{10}H_6(NH_2)OH$, is formed by the action of ammonium sulphide on β-naphthoquinone-α-oxime,[2] as well as by the reduction of nitro-β-naphthol with tin and hydrochloric acid.[3] It is, however, best prepared by heating benzene-azo-β-naphthol, $C_6H_5.N_2.C_{10}H_6.OH$, or the sodium salt of its sulphonic acid, which occurs in commerce as β-naphthol orange, with hydrochloric acid and stannous chloride,[4] or reducing it in alkaline solution with sulphuretted hydrogen (Groves).

It is sparingly soluble in boiling water, and by no means freely in ether, showing a splendid blue fluorescence, and crystallizes from the latter in lustrous plates, which rapidly become coloured dark when moist. Its ammoniacal solution becomes dark-brown when it is shaken up with air, and it is oxidized to β-napthoquinone by chromic acid.

Its *hydrochloride* crystallizes in slender needles, which are sparingly soluble in water.

Amido-β-naphtholdisulphonic acid is obtained as the acid sodium salt by the reduction of the azo-colours prepared from the β-naphtholdisulphonic acids R and G.[5]

1-*Acetamido-β-naphthol*, $C_{10}H_6(NH.CO.CH_3)OH$, is formed by a remarkable reaction when nitro-β-naphthyl acetate is treated with glacial acetic acid and zinc dust, the acetyl group being displaced. It crystallizes from dilute alcohol in plates melting at 225°, which decompose on further heating into

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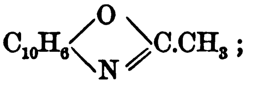
[1] Bamberger and Bammann, *Ber.* **22**, 962.

[2] Stenhouse and Groves, *Annalen*, **189**, 163; Groves, *Journ. Chem. Soc.* 1884, **1**, 291.

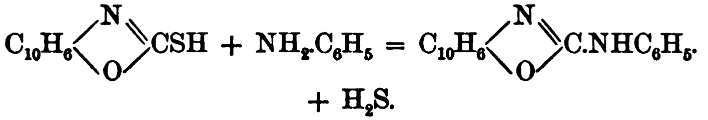
[3] Liebermann and Jacobsen, *loc. cit.*

[4] Liebermann, *Ber.* **16**, 2858.

[5] Witt, German Patent, 49857, 1889, *Ber.* **23**, 128 c.

water and *ethenylamido-β-naphthol*,  $C_{10}H_6\left\langle\begin{matrix}O\\N\end{matrix}\right\rangle C.CH_3$; the latter is an oily liquid, which has a characteristic odour resembling that of aniseed.[1]

1-*Thiocarbamido-β-naphthol*, $C_{11}H_7NSO$, is obtained when β-naphthol is heated to 130—140° with carbon disulphide and alcohol, and crystallizes from alcohol in long needles, which melt at 248—249°. On boiling with aniline, *carbanilido-β-naphthol* is formed:



$$C_{10}H_6\left\langle\begin{matrix}N\\O\end{matrix}\right\rangle CSH + NH_2.C_6H_5 = C_{10}H_6\left\langle\begin{matrix}N\\O\end{matrix}\right\rangle C.NHC_6H_5. + H_2S.$$

This substance is also formed, together with thiocarbamido-β-naphthol, when benzene-azo-β-naphthol is heated with carbon disulphide (p. 210).[2] It crystallizes from alcohol in small needles, melting at 167—168°.

2′-*Amido-β-naphthol* is prepared on the large scale by gradually bringing 1 kilo. of well-dried sodium β-naphthylamine-δ-sulphonate into a mixture of 2 kilos. of caustic soda and 2 litres of water heated to 260°, the temperature being gradually raised to 300° in the course of two or three hours. The melt is dissolved in 7 litres of water, partially neutralized with hydrochloric acid, and the precipitated impurities filtered off. The solution is then concentrated and the amidonaphthol precipitated by hydrochloric acid. It crystallizes from alcohol in concentrically arranged needles, and melts with decomposition at 200°. It is employed in the preparation of azo-colouring matters.[3]

2′-*Phenylamido-β-naphthol* is formed in the preparation of 2 : 2′-diphenylamidonaphthalene (p. 210), and crystallizes from a mixture of benzene and light petroleum in small needles, which are readily soluble in alcohol and melt at 163°.[4]

Diamido-β-naphthol is obtained in the form of its *hydrochloride* by the reduction of dinitronaphthol with tin and hydrochloric acid. It crystallizes in almost colourless needles, which are fairly stable when dry.[5]

Triacetyldiamido-β-naphthol crystallizes in silvery needles, melting at 203°.

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[1] Böttcher, *Ber.* **16**, 1933.

[2] Jacobsen, *Ber.* **21**, 414.

[3] *Ber.* **22**, 463 c.

[4] Clausius, *Ber.* **23**, 529.

[5] Loewe, *Ber.* **23**, 2543.

Tribenzoyldiamido-β-naphthol melts at 265°.

1 : 4′-*Diamidodinaphthyldisulphide*, $(C_{10}H_6(NH_2)S)_2$, is formed by the reduction of nitronaphthalenesulphamide and of dinitrodinaphthyldisulphide. It crystallizes from alcohol in lustrous scales, melting at 192°. The *hydrochloride* forms microscopic, colourless needles, and is decomposed by water.[1]

Diacetodiamidodinaphthyldisulphide forms colourless scales, melting at 274° with carbonization.

Dipropionyldiamidodinaphthyldisulphide melts at 242°.

1 : 3′-*Diamidodinaphthyldisulphide*, $[C_{10}H_6(NH_2)S]_2$, is formed when nitronaphthalenesulphamide is heated with hydriodic acid and amorphous phosphorus. It is readily soluble in alcohol from which it crystallizes in long needles, melting at 166°. The *diacetyl derivative* crystallizes in colourless, microscopic needles and melts at 276° with decomposition.[2]

AMIDODIHYDROXYNAPHTHALENES,
$C_{10}H_5(NH_2)(OH)_2$.

2655 3-*Amido-β-naphthoquinol* is obtained by the action of tin and hydrochloric acid[3] or stannous chloride[4] on nitro-β-naphthoquinone. The *hydrochloride* is thus obtained, and crystallizes in yellow tablets, which rapidly become brown in the air. It can be heated to 140° with hydrochloric acid without undergoing any alteration, reduces silver solution in the cold, and gives a black-blue precipitate with ferric chloride. Ammonia produces a yellow precipitate, which becomes superficially green in the air and gradually changes into a blue powder.

4-*Amido-β-naphthoquinol* has been prepared by the reduction of oximidonaphthol, $C_{10}H_5O(NH)OH$; its *hydrochloride* crystallizes in tablets, which become black when exposed to air in a moist state. When it is heated to 120° with hydrochloric acid, it is converted into hydroxy-α-naphthoquinone; oximidonaphthol is deposited when ammonia is added to its solution.[5]

Triacetyl-4-amido-β-naphthoquinone, $C_{10}H_5(NH.CO.CH_3)(OCO.CH_3)_2$, is formed when oximidonaphthol or amido-β-naphthoquinone is heated with zinc dust, acetic anhydride and sodium

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[1] Ekbom, *Ber.* **23**, 1121.

[2] Ekbom, *Ber.* **24**, 332.

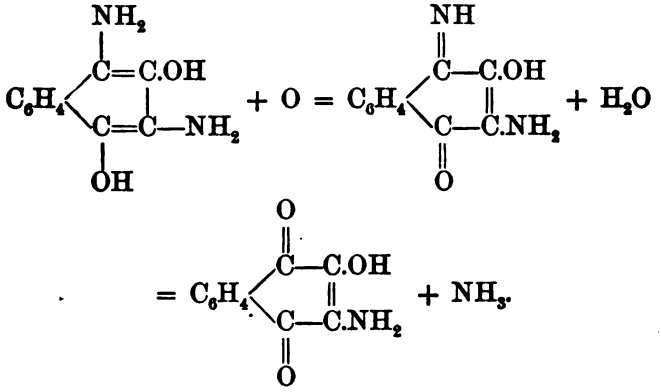
[3] Groves, *Journ. Chem. Soc.* 1884, **1**, 300.

[4] Korn, *Ber.* **17**, 906.

[5] Gräbe and Ludwig, *Annalen*, **154**, 303; Korn, *loc. cit.*

acetate. It crystallizes from acetic acid in lustrous white needles and is converted by cold sulphuric acid into acetamido-β-naphthoquinone.[1]

Diamidonaphthoresorcinol, $C_{10}H_4(OH)_2(NH_2)_2$, is obtained by adding amidohydroxynaphthoquinonoxime (p. 237) to a cold, dilute acid solution of stannous chloride. On the addition of fuming hydrochloric acid, the *hydrochloride* separates out in long, lustrous, snow-white needles, which change on standing into heavy, granular crystals. These oxidize in the air and become red; the alkaline solution absorbs oxygen still more rapidly and assumes a deep carmine-red colour, amidohydroxy-α-naphthoquinone being slowly deposited on the subsequent addition of hydrochloric acid; if, on the other hand, the alkaline solution be boiled, ammonia is evolved and the liquid becomes blue, a salt of the amidohydroxyquinone being formed. The unstable red product is most probably a salt of amidohydroxynaphthoquinonimide, the formation of the amidohydroxyquinone being represented by the following equations:[2]



2:2′-*Dihydroxy-α-naphthylamine* is obtained by reducing 1:2:2′-hydroxynaphthoquinonoxime (p. 237) with stannous chloride. The *hydrochloride* forms small greyish, lustrous needles or plates, and readily becomes coloured blue in the air.[3]

2656 *Amidotrihydroxynaphthalene*, $C_{10}H_4NH_2(OH)_3$. When sodium nitronaphthalenate, $C_{10}H_4(NO_2)(ONa)O_2$, is brought into a strongly acid solution of stannous chloride, and the bluish-

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[1] Meerson, *Ber.* **21**, 2516.

[2] Kehrmann and Weichardt, *J. Pr. Chem.* II. **40**, 179.

[3] Clausius, *Ber.* **23**, 521.

black mass of crystals which is formed heated on the water-bath with a little zinc until the solution is almost colourless, the *hydrochloride*, $C_{10}H_4(OH)_3NH_3Cl$, is formed, which crystallizes in large, long monosymmetric prisms. On the addition of sodium carbonate to the concentrated solution of this salt, the base separates out as a greyish-white crystalline mass, which after a short time oxidizes and becomes blue, amidohydroxyquinone being formed; the latter separates out in long, brownish-violet needles, when the solution of the hydrochloride is allowed to stand in the air.

Tetracetylamidotrihydroxynaphthalene, $C_{10}H_4(NH.CO.CH_3)(O.CO.CH_3)_3$, forms crystals, melting at 145°, which dissolve without change in fuming nitric acid and are not attacked by an acetic acid solution of chromium trioxide in the cold.[1]

AMIDO-DERIVATIVES OF α-NAPHTHOQUINONE

2657 *Methylamido-a-naphthoquinone*, $CH_3.NH.C_{10}H_5O_2$, is formed when an alcoholic solution of the quinone is evaporated with methylamine acetate. The concentrated solution is diluted with water, and the precipitate dissolved in alcohol and boiled with animal charcoal; it is thus obtained in red, lustrous needles, melting at 232°.[2]

Plimpton has also prepared the following compounds, which likewise crystallize in red needles:

	Melting-point.
Dimethylamido-*a*-naphthoquinone, $(CH_3)_2N.C_{10}H_5O_2$.	118°
Ethylamido-*a*-naphthoquinone, $C_2H_5.NH.C_{10}H_5O_2$ . .	140°

Phenylamido-a-naphthoquinone, or *Anilido-a-naphthoquinone*, $C_6H_5.NH.C_{10}H_5O_2$, is formed when aniline is heated with an alcoholic solution of the quinone (Plimpton):

$$C_6H_5.NH_2 + 2C_{10}H_6O_2 = C_6H_5.NH.C_{10}H_5O_2 + C_{10}H_6(OH)_2.$$

It is precipitated by the addition of acetic acid, and the mother liquor deposits a further quantity on standing in the air if an excess of aniline is present, the quinol being reoxidized to the quinone.

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[1] Kehrmann and Weichardt, *J. Pr. Chem.* II. **40**, 179.

[2] Plimpton, *Journ. Chem. Soc.* 1880, **1**, 633.

Anilido-*a*-naphthoquinone is also formed when an acetic acid solution of aniline and hydroxy-*a*-naphthoquinone is boiled:[1]

$$C_6H_5.NH_2 + HO.C_{10}H_5O_2 = C_6H_5.NH.C_{10}H_5O_2 + H_2O.$$

It crystallizes from dilute alcohol in very lustrous red needles, which melt at 190—191°, and sublime with decomposition. It forms a splendid bright-red solution in concentrated sulphuric acid, and dissolves in caustic potash solution with a purple colour. Tin and hydrochloric acid or ammonium sulphide convert it into a colourless, very unstable reduction product; on boiling with dilute caustic soda solution or alcoholic sulphuric acid, it decomposes into aniline and hydroxy-*a*-naphthoquinone.

The following compounds have been investigated by Plimpton and Elsbach:[2]

	Melting-point.
Diphenylamido-*a*-naphthoquinone, $(C_6H_5)_2N.C_{10}H_5O_2$, dark violet needles	164°
o-Toluido-*a*-naphthoquinone, $C_7H_7.NH.C_{10}H_5O_2$, light red needles	141°
p-Toluido-*a*-naphthoquinone, $C_7H_7.NH.C_{10}H_5O_2$, red needles	202°

A number of substitution-products of these compounds are known, some of which are obtained directly, and others by the action of amido-bases and their substitution-products on *a*-naphthoquinone or its substitution-products.[3]

Amido-a-hydroxynaphthoquinone, or *Amidonaphthalenic acid*, $C_{10}H_4(NH_2)(OH)O_2$, was prepared by Diehl and Merz[4] by the reduction of nitronaphthalenic acid, the first product being amidotrihydroxynaphthalene, which then rapidly becomes oxidized to amidohydroxynaphthoquinone. The latter crystallizes from alcohol in long, dark brownish-red needles with a strong bronze lustre, becomes black at about 100°, and melts at a higher temperature, a small portion subliming in slender needles, with a bright metallic lustre, whilst the greater part becomes carbonized. It forms deep-blue solutions in the alkalis, and is converted into 2:3-dihydroxynapthoquinone by hydrochloric acid at 180°.[5]

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[1] Liebermann and Jacobson, *Annalen*, **211**, 82.

[2] *Ber.* **15**, 685.

[3] Baltzer, *Ber.* **14**, 1899; Plagemann, *Ber.* **15**, 484; Cleve, *Ber.* **21**, 891; Knapp and Schultz, *Annalen*, **210**, 189.

[4] *Ber.* **11**, 1341.

[5] Diehl and Merz, *Ber.* **11**, 1341.

Acetamido-a-hydroxynaphthoquinone, $C_{10}H_4O_2(NH.CO.CH_3)OH$, is formed when tetracetylamidotrihydroxynaphthalene is treated with cold concentrated caustic potash solution; the monacetyl compound is the first product, but its colourless solution rapidly absorbs oxygen and becomes coloured blood-red. On the addition of hydrochloric acid, acetamidohydroxynaphthoquinone is precipitated as a golden-yellow crystalline powder, which crystallizes from acetic acid in yellow, zig-zag needles, and melts at 219—220°. It may also be obtained by boiling amidonaphthalenic acid with acetic anhydride. Its salts with the alkalis are of a red colour and are crystalline; when it is boiled with caustic potash the solution becomes blue and deposits *potassium amidonaphthalenate*, $C_{10}H_4(NH_2)(OK)O_2$, on cooling in black-blue needles, with a copper lustre.[1]

AMIDO-DERIVATIVES OF β-NAPHTHOQUINONE

2658 4-*Amido-β-naphthoquinone*, $C_{10}H_5(NH_2)O_2$, is obtained by heating its acetyl compound with concentrated sulphuric acid, and crystallizes from alcohol in brown lustrous plates, which are soluble in ether and melt at 200°. On heating with zinc dust, acetic anhydride and sodium acetate, it is converted into triacetylamido-β-naphthoquinol.

Acetamido-β-naphthoquinone, $C_{10}H_5O_2(NH.CO.CH_3)$, is formed by the action of ferric chloride on an acid solution of diacetodiamido-a-naphthyl acetate (p. 213), or when the acetyl compound of di-imidonaphthol is oxidized with fuming nitric acid (p. 222). It crystallizes from alcohol in lustrous, golden-yellow plates, which melt with decomposition at 198°.[2]

Anilido-β-naphthoquinone, $C_{10}H_5O(NC_6H_5)OH$, is obtained together with β-naphthoquinol by heating β-naphthoquinone with an alcoholic solution of aniline. It crystallizes in red needles or plates, with a splendid golden or green lustre, and melts and sublimes, with partial decomposition, above 240°. It is insoluble in water, sparingly soluble in hot alcohol, and forms a brown solution in sulphuric acid. Sulphurous acid does not reduce it even on heating. It differs from the a-compound in

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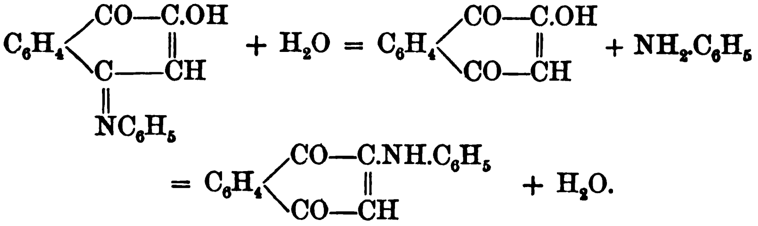
[1] Kehrmann and Weichardt, *J. Pr. Chem.* II. **40**, 179.

[2] Meerson, *Ber.* **21**, 1195 and 2516.

containing an atom of hydrogen which can be replaced by metals and alcohol radicals, but is converted into hydroxy-*a*-naphthoquinone by boiling with hydrochloric acid or alcoholic sulphuric acid, in the same way as anilido-*a*-naphthoquinone, and is in fact converted into the latter by boiling with glacial acetic acid,[1] the change being represented by the following equations:



$$C_6H_4\left<\begin{array}{l}CO-C.OH\\ \|\\ \underset{\underset{NC_6H_5}{\|}}{C}-\!\!-\!\!-CH\end{array}\right. + H_2O = C_6H_4\left<\begin{array}{l}CO-C.OH\\ \|\\ CO-CH\end{array}\right. + NH_2.C_6H_5$$

$$= C_6H_4\left<\begin{array}{l}CO-C.NH.C_6H_5\\ \|\\ CO-CH\end{array}\right. + H_2O.$$

The *alkali salts* are resinous, and readily soluble in water and alcohol, but insoluble in alkalis; the *barium salt* crystallizes in small red needles, and the *silver salt* is a brown precipitate.

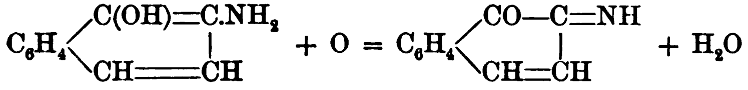
The ethers of this substance are best obtained by heating an alcoholic solution of anilido-*β*-naphthoquinone and sodium with the alkyl bromides.[2] Zincke has prepared the following:

	Melting-point.
$C_{16}H_{10}NO_2.CH_3$, yellow needles	151°
$C_{16}H_{10}NO_2.C_2H_5$, lustrous red monosymmetric prisms	104°
$C_{16}H_{10}NO_2.C_3H_7$, lustrous red monosymmetric prisms	104°
$C_{16}H_{10}NO_2.CH(CH_3)_2$, large yellowish red prisms .	100°

Anilidonitro-γ-naphthoquinone, $C_6H_5.NH.C_{10}H_4(NO_2)O_2$, is readily obtained by bringing together nitro-γ-naphthoquinone and aniline; it crystallizes in dark-violet needles, which melt with decomposition at 128°.

IMIDOKETOHYDRONAPHTHALENES

2659 *Imidoketohydronaphthalene*, $C_{10}H_6O(NH)$. This substance, which is also known as imido-oxynaphthalene, separates out in violet films, with a metallic lustre, when an alkaline solution of 2-amido-*a*-naphthol is agitated with air:



$$C_6H_4\left<\begin{array}{l}C(OH)=C.NH_2\\ |\\ CH=\!=\!=CH\end{array}\right. + O = C_6H_4\left<\begin{array}{l}CO-C=NH\\ |\\ CH=CH\end{array}\right. + H_2O$$

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[1] Zincke, *Ber.* **14**, 1493; Liebermann and Jacobson, *Annalen*, **211**, 95.

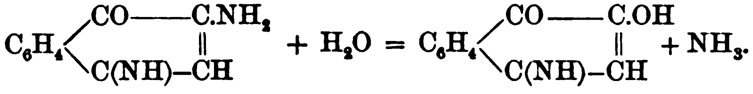
[2] *Ber.* **15**, 279.

It forms a fine violet-coloured solution in alcohol, from which it separates on evaporation as a dark-violet satin-like powder.[1]

Amido-imidoketohydronaphthalene, $C_{10}H_5(NH_2)O(NH)$. This substance, which is usually termed *di-imidonaphthol*, is formed by the addition of ferric chloride to a solution of diamido-α-naphthol hydrochloride. The *hydrochloride*, $C_{10}H_8N_2O,HCl$, is thus obtained, and crystallizes in dark-red, monosymmetric prisms or tablets with a metallic lustre, which are readily soluble in water but only sparingly in hydrochloric acid. Ammonia precipitates the base from solutions of this salt in yellow microscopic needles, which are scarcely soluble in cold water but readily in alcohol. Reducing agents convert it into diamidonaphthol, whilst hydroxy-α-naphthoquinone is formed when it is treated with alkalis or acids. On heating with sodium acetate and acetic anhydride the *acetyl* compound, $C_{10}H_5(NH.CO.CH_3)O(NCO.CH_3)$, is formed; this substance crystallizes from alcohol in thick, dark-yellow prisms and is oxidized to acetamido-β-naphthoquinone by fuming nitric acid.[2]

Diamido-imidoketohydronaphthalene, $C_{10}H_4(NH_2)_2O(NH)$, was prepared by Diehl and Merz, who termed it *amidodi-imidonaphthol*, by adding ferric chloride to a solution of triamidonaphthol, the *hydrochloride*, $C_{10}H_9N_3O,HCl$, being formed; this crystallizes in scales with a green metallic lustre and dissolves in water or alcohol with a dark-red colour. The base liberated from this solution by ammonia separates from alcohol in dark-brown needles, and yields triamidonaphthol on reduction.[3]

Oximidoketohydronaphthalene, or *Oximidonaphthol*, $C_{10}H_5O(NH)OH$, is formed when di-imidonaphthol is boiled with water:[4]



$$C_6H_4\left\langle\begin{matrix}CO\text{——}C.NH_2\\ \qquad\quad\ \| \\ C(NH)\text{—}CH\end{matrix}\right. + H_2O = C_6H_4\left\langle\begin{matrix}CO\text{——}C.OH\\ \qquad\quad\ \| \\ C(NH)\text{—}CH\end{matrix}\right. + NH_3.$$

It is slightly soluble in water, readily in alcohol, but insoluble in ether, and crystallizes in yellowish-red needles, which melt at 195°. On boiling with acids or alkalis it is converted into hydroxy-α-naphthoquinone, whilst it is reduced by tin and hydrochloric acid to amido-β-naphthoquinol, which readily changes into amido-β-naphthoquinone. The latter is isomeric

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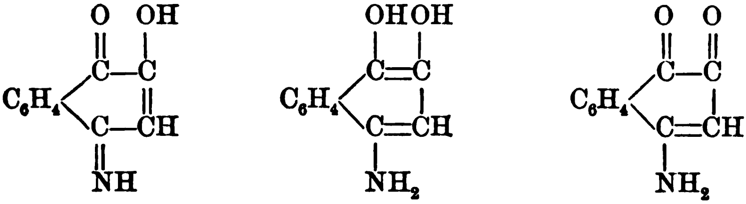
[1] Liebermann, *Ber.* **14**, 1310.

[2] Martius and Griess, *Annalen*, **134**, 377; Gräbe and Liebermann, *Annalen*, **154**, 312; Liebermann, *Ber.* **9**, 1779; Zincke, *Ber.* **15**, 481.

[3] *Ber.* **11**, 1661.

[4] Gräbe and Ludwig, *Annalen*, **154**, 303.

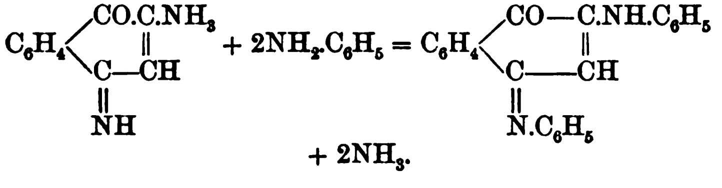
with oximidonaphthol, the constitution of which has not yet been determined with certainty.[1] The formula given above, however, explains in a simple manner its conversion into the isomeric amidoquinone:



Chlorohydroxy-a-naphthoquinonimide, $C_{10}H_5O_2Cl(NH)$, is obtained by heating an acetic acid solution of chloro-β-naphthoquinonoxime (p. 234) with sulphuric acid until a small portion gives a deep brownish-red precipitate on dilution with water. If the heating be continued, chlorohydroxy-α-naphthoquinone is obtained. It forms dirty brownish-red needles, is only sparingly soluble in ether and light petroleum, more freely in benzene, and melts with decomposition at 179—180°.[2]

Naphthoquinonedianilide, or *Anilidonaphthoquinonanil*, $C_6H_5.NH.C_{10}H_5(NC_6H_5)O$, was first obtained by Fuchs by heating β-naphthoquinone-β-oxime with aniline acetate, but was not distinguished by him by any special name.[3] Goës then prepared it by heating di-imidonaphthol hydrochloride with aniline, and termed it *diphenyldi-imidonaphthol*,[4] $C_{10}H_5(OH)(NC_6H_5)_2$.

Its constitution was ascertained by Zincke, who showed that it is formed when an alcoholic solution of β-naphthoquinone is heated with an excess of aniline, and when anilido-β-naphthoquinone, hydroxynaphthoquinone ethyl ether or oxyimidonaphthol is boiled with aniline in acetic acid solution. It is, however, best obtained from the hydrochloride of di-imidonaphthol:[5]



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[1] Meerson, *Ber.* **21**, 1195 and 2516.

[2] Zincke and Schmunk, *Annalen*, **257**, 144.

[3] *Ber.* **8**, 1022.

[4] *Ber.* **13**, 123.

[5] *Ber.* **14**, 1493, 1900; **15**, 281, 481.

The two other naphthoquinonoximes (pp. 227, 230) also yield this substance, whereas the formation of isomerides would be expected.[1] It is also formed when benzene-azo-α-naphthol is heated to 100° with aniline or aniline hydrochloride, and has also been obtained from benzene-azo-α-naphthylamine, phenylamido-α-nitrosonaphthalene, &c.[2]

It crystallizes from hot alcohol in long, deep-red needles, melting at 187°, whilst the crystals deposited from benzene are short and thick, and have a deeper colour and fine metallic lustre. When it is heated with 25 parts of a mixture of equal volumes of sulphuric acid and water for 12 hours, it is decomposed into hydroxynaphthoquinone and aniline. Its alcoholic solution is decolourized by reducing agents, but becomes re-oxidized in the air. Sulphuric acid and zinc dust added to its solution in acetic acid reduce it to aniline and naphthalene. It yields deep violet-coloured solutions in acids, the corresponding salt being formed.

Naphthoquinonedianilide hydrochloride, $C_{22}H_{16}N_2O,HCl$, forms coarse, lustrous, yellowish-green crystals, and is decomposed by water.

		Melting-point.
Bichloranilidonaphthoquinonanil,[3] $C_6H_4Cl.NH.C_{10}H_5(NC_6H_4Cl)O$,	red matted needles	217—218°
Bibromanilidonaphthoquinonanil, $C_6H_4BrNH.C_{10}H_5(NC_6H_4Br)O$,	red matted needles	235°

α-Naphthoquinonedianil, $C_{10}H_6(NC_6H_5)_2$, is formed as a bye-product in the preparation of rosinduline (p. 211) when the operation is carried out at 150°. It is slightly soluble in alcohol, more readily in hot benzene, crystallizes in splendid yellow plates with a golden lustre, and melts at 187°. On reduction it yields diphenyl-1 : 4-diamidonaphthalene.[4]

Toluidonaphthoquinoneditoluide, $C_7H_7NH.C_{10}H_5(NC_7H_7)_2$, is formed by the gentle oxidation of tritoluidonaphthalene; it crystallizes in orange-yellow plates, and melts at 147° (Fischer and Hepp).

α-Naphthol blue, $C_{18}H_{16}N_2O$, which is generally known as *indophenol* comes into the market as a paste, and is prepared by oxidizing a mixture of α-naphthol and dimethyl-*p*-diamidobenzene

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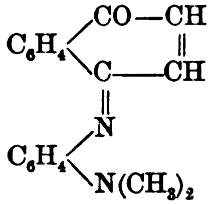
[1] Brömme, *Ber.* **21**, 391.

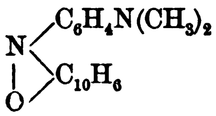
[2] Fischer and Hepp, *Ber.* **21**, 676.

[3] Fischer and Hepp, *Ber.* **21**, 681.

[4] Fischer and Hepp, *Annalen*, **256**, 254.

with potassium dichromate in alkaline solution. It is also formed when an alkaline solution of α-naphthol is heated with nitrosodimethylaniline. It separates from alcohol in irregular crystals, with a bronze lustre, and forms a yellow solution in hydrochloric acid, which soon decomposes with formation of dimethyl-*p*-diamidobenzene and α-naphthoquinone.[1] Its constitution can therefore be represented by one of the following formulæ, according as the diketone or peroxide formula is adopted for the quinones:





Reducing agents convert it into *leucoindophenol* or *indophenol white*, $C_{18}H_{18}N_2O$, which is also sold as a paste, and is obtained by the action of an acid solution of stannous chloride on the blue. It is not oxidized by the oxygen of the air in the presence of small quantities of acid, but undergoes this reaction in the presence of alkalis. Its solution in very dilute acetic acid is employed in dyeing, and is taken up directly by wool and silk, whilst cotton can only be dyed with it after mordanting with Turkey-red oil. To develop the colour, the washed goods are passed through a warm, dilute solution of potassium dichromate. In printing, the blue is usually taken and reduced by stannous acetate before application, the colour being brought out by exposure to the air or in the manner just described. It is also possible to print on a mixture of sodium-α-naphthate and dimethyl-*p*-diamidobenzene and then pass the fabric through a bath of potassium dichromate.[2]

The colour thus produced resembles indigo-blue, and is moderately fast to soap and light. It is also employed in conjunction with indigo, the latter being thus economised and the fastness of the indophenol increased.

β-Naphthol violet, $C_{10}H_{16}N_2O$, was obtained by Meldola by the action of nitrosodimethylaniline hydrochloride on a hot acetic acid solution of β-naphthol:

$$C_{10}H_8O + NO.C_6H_4.N(CH_3)_2 = C_{10}H_6[NC_6H_4N(CH_3)_2]O + H_2O.$$

[1] Möhlau, *Ber.* **16**, 2843; **18**, 2931.

[2] *Ber.* **12**, 2066; *Journ. Chem. Soc.* 1881, **1**, 30.

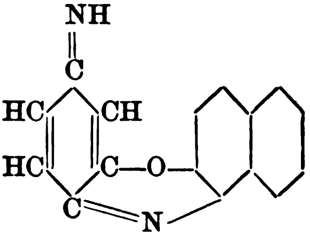
The *hydrochloride* thus obtained crystallizes in needles, with a bronze lustre, resembling those of potassium permanganate, which are readily soluble in hot water and alcohol. Concentrated sulphuric acid changes the dark-violet colour of the solution to deep blue.

Sodium carbonate precipitates the base from solutions of the hydrochloride as a dark flocculent mass, and this yields on reduction in acid solution the hydrochloride of the colourless leuco-base, which rapidly becomes re-oxidized to naphthol violet in the air.[1] The latter is known commercially by the names *fast blue*, *new blue*, and *naphthylene blue.*

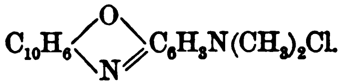
According to Nietzki and Otto it has the formula $C_{18}H_{14}N_2O$, a portion of the nitrosodimethylaniline being reduced in its formation to dimethyl-*p*-diamidobenzene. By the action of quinonedichlorimide on an alcoholic solution of β-naphthol these chemists obtained a reddish-violet colouring matter:

$$C_6H_4(NCl)_2 + C_{10}H_7OH = C_{16}H_9(NH)NO + 2HCl.$$

This substance forms crystalline salts, like Meldola's compound, is very stable towards acids, and forms a green solution in sulphuric acid, which on the addition of water becomes coloured violet-blue and finally red. Ammonia precipitates the yellow base from its salts. According to its reactions this substance cannot be an indophenol, but probably has the following constitution:



Meldola's compound appears to be the dimethyl-derivative,[2] and the chloride would then be:



$$C_{10}H_6\langle{}^{O}_{N}\rangle C_6H_3N(CH_3)_2Cl$$

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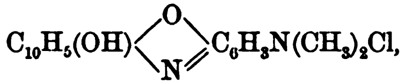
[1] *Ber.* **12**, 2066; *Journ. Chem. Soc.* 1881, **1**, 30.

[2] *Ber.* **21**, 1744.

It is employed to produce indigo-blue shades on cotton mordanted with antimony and tannic acid, and in conjunction with other colours for compound shades.

Cyanamine, $C_{26}H_{28}N_4O_2$, When freshly prepared β-naphthol violet is heated with alcoholic caustic potash solution a base is formed which is almost insoluble in alcohol, ether and benzene, but moderately soluble in chloroform, from which it crystallizes in very slender, black-brown plates. It readily forms blue solutions in dilute acids, salts being formed which can be crystallized from alcohol. The *sulphate* forms green scales, with a metallic lustre, the *hydrochloride* tablets and prisms of the same colour. Solutions of the salts cut off the whole of the spectrum as far as the green, and leave the remaining portion quite unaltered.[1]

A series of greenish-blue colouring matters, which are probably closely related to the above, has also been obtained by the action of aniline, *p*-toluidine and α-naphthylamine on β-naphthol violet.[2]



Muscarine, $C_{10}H_5(OH)<\begin{matrix}O\\N\end{matrix}>C_6H_3N(CH_3)_2Cl$, is formed by the action of nitrosodimethylaniline on 2 : 2′-dihydroxynaphthalene and is a brownish-violet powder, which forms a bluish-violet coloured solution in hot water. It is employed in the same way as Meldola's blue.[3]

Nile blue, $(C_{18}H_{16}N_3O)_2SO_4$, is formed by the action of nitrosodimethyl-*m*-amidophenol hydrochloride on α-naphthylamine. The *hydrochloride* is thus obtained as a green crystalline powder, with a strong bronze lustre, which is only slightly soluble in water, and is therefore converted into the more soluble *sulphate*, which is also a crystalline powder and dyes wool, silk, and mordanted cotton a bright blue.[4]

THE NAPHTHOQUINONOXIMES, $C_{10}H_6O(NOH)$.

2660 *α-Naphthoquinone-α-oxime* or *α-Nitroso-α-naphthol* is formed together with the *α-β*-compound by the addition of dilute sulphuric acid to an alkaline solution of α-naphthol and

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[1] O. Witt, *Ber.* **23**, 2247.

[2] Hirsch and Kalckhoff, *Ber.* **23**, 2992.

[3] Schultz, *Steinkohlentheer*, **2**, 721.

[4] Schultz, *Steinkohlentheer*, **2**, 722.

potassium nitrite,[1] and may also be obtained in a similar manner by means of a solution of nitrosyl sulphate (Pt. III. p. 171).[2] It is also formed when an alcoholic solution of α-naphthoquinone is boiled with hydroxylamine and a little hydrochloric acid.[3] It is best prepared by heating a solution of 2 parts α-naphthol and two parts zinc chloride in 12 parts alcohol to the boiling point, adding a solution of 1 part sodium nitrite, boiling the solution for two or three hours, and allowing the liquid to cool and stand for several hours. A mixture of the free α-naphthoquinone-α-oxime and the zinc salt of the isomeric compound separates out and is filtered off and washed with alcohol. The residue is treated with hot alcoholic potash and allowed to stand for some time, the potassium salt of the β-compound, which separates out completely, being then filtered off and washed with a little alcohol. The filtrate is diluted with water and precipitated with hydrochloric acid, the filtrate from the zinc salt being also diluted with water. One hundred parts of naphthol gave 40 parts of the α- and 50 parts of the β-compound.[4]

α-Naphthoquinone-α-oxime is readily soluble in alcohol and ether, less freely in benzene, and crystallizes, if pure, in colourless needles, which decompose at about 190°. It volatilizes very slowly with steam. It dissolves in the alkaline carbonates, but is precipitated again by carbon dioxide. Concentrated nitric acid converts it into naphthol yellow, whilst it is gradually oxidized to 4-nitro-α-naphthol by an alkaline solution of potassium ferricyanide.

Its salts are unstable ; those of the alkalis and alkaline earths are soluble in water.

Methyl α-naphthoquinone-α-oximate, $C_{10}H_6NO_2(CH_3)$, is obtained by the action of methyl iodide on the brown insoluble silver salt and crystallizes from ether in needles, which melt at 98—100° and form a yellow solution in sulphuric acid.[5]

Carbanilido-α-naphthoquinone-α-oxime, $C_{10}H_6O(NO.CO.NH.C_6H_5)$ is formed when a solution of α-naphthoquinone-α-oxime and phenyl carbimide in benzene is heated. It crystallizes in yellow prisms, which become dark-coloured at about 160°, and

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[1] Fuchs, *Ber.* **8**, 625.

[2] Ilinski, *Ber.* **17**, 2589.

[3] Goldschmidt and Schmid, *Ber.* **17**, 2064.

[4] Henriques and Ilinski, *Ber.* **18**, 706.

[5] Ilinski, *loc. cit.* ; Goldschmidt and Schmid, *Ber.* **18**, 2224.

melt at 170°. It is decomposed by alkalis into carbon dioxide, aniline and the quinonoxime.[1]

2 : 3-*Dibrom-a-naphthoquinone-a-oxime*, $C_{10}H_5Br_2NO_2$, is obtained by the addition of bromine to a solution of the quinonoxime in glacial acetic acid, crystallizes from alcohol in white needles, melts at 174—175°, and on heating with alkalis is converted into bromohydroxynaphthoquinone.[2]

a-Naphthoquinonechlorimide, $C_{10}H_6O(NCl)$, is formed when 1 : 4-amidonaphthol is treated with bleaching powder solution. α-Naphthoquinone is simultaneously formed, and combines with the chlorimide to form the compound $C_{10}H_6O(NCl) + C_{10}H_6O_2$, which crystallizes from dilute acetic acid in brown needles, melting at 85° and exploding at 130°, with separation of carbon and formation of a sharp smelling vapour.[3]

β-Naphthoquinone-β-oxime or *β-Nitroso-a-naphthol*, is also formed when an alcoholic solution of β-naphthoquinone is boiled with hydroxylamine hydrochloride.[4] It crystallizes from hot water in yellow needles, and from benzene in yellowish-green needles, which melt at 152°, and form a dark-yellow solution in alkalis and a deep red solution in sulphuric acid. It is not decomposed by boiling alcoholic potash, and is readily oxidized to 2-nitro-α-naphthol by alkaline potassium ferricyanide, whereas nitric acid converts it into naphthol yellow. Its salts have been examined by Fuchs.

Potassium β-naphthoquinone-β-oximate, $C_{10}H_6NO_2K$, separates out from a mixture of alcoholic solutions of potash and the quinonoxime in green plates with a metallic lustre, which after drying transmit yellow light, but appear to have a colour between that of copper and of brass by reflected light; the salt is readily soluble in water.

Sodium naphthoquinonoximate, $C_{10}H_6NO_2Na$, crystallizes from water in yellowish red prisms, with a strong reddish-brown lustre, and is insoluble in concentrated caustic soda solution. The *ammonium* salt, $C_{10}H_6NO_2(NH_4)$, forms slender, green needles, with a metallic lustre, which readily lose ammonia; the *barium* salt $(C_{10}H_6NO_2)_2Ba + 2H_2O$, crystallizes from hot water in small, dirty yellowish-red plates which have a bronze lustre, and show a strong green and purple-red dichroism.

Methyl β-naphthoquinone-β-oximate, $C_{10}H_6NO_2(CH_3)$, is prepared from the silver salt and methyl iodide, and is also formed

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[1] Goldschmidt and Strauss, *Ber.* **22**, 3105.

[2] Brömme, *Ber.* **21**, 386.

[3] Hirsch, *Ber.* **13**, 1910.

[4] Goldschmidt, *Ber.* **17**, 215.

when an alcoholic solution of β-naphthoquinone is heated with methylhydroxylamine hydrochloride.[1] It crystallizes in yellowish-green needles, melting at 95°, which form a deep red-coloured solution in sulphuric acid, and are reduced to 2-amido-α-naphthol by acid stannous chloride.

Ethyl β-naphthoquinone-β-oximate, $C_{10}H_6NO_2(C_2H_5)$ forms flat, greenish-yellow needles, and melts at 101°.

β-Naphthoquinone-β-oxime benzoate, $C_{10}H_6NO_2C_7H_5O$, is formed by the action of benzoyl chloride on the sodium salt, and separates from glacial acetic acid in small yellow crystals, melting at 162°.[2]

Carbanilido-β-naphthoquinone-β-oxime, $C_{10}H_6O(NO.CO.NH.C_6H_5)$ crystallizes in greenish-yellow, microscopic prisms, which decompose at 119—120°, and behaves towards alkalis like the α-α-compound (Goldschmidt and Strauss).

3-*Bromo-β-naphthoquinone-β-oxime*, $C_{10}H_6BrNO_2$. When bromine is added to a solution of the quinonoxime in chloroform, the *dibromide*, $C_{10}H_7NO_2Br_2$, separates out after some time in small plates, melting at 154—155°. When this substance is heated with alcohol it is converted into bromonaphthoquinone, which separates from alcohol in yellow, and from glacial acetic acid in dark brown crystals, melting at 175°. On heating with hydrochloric acid it yields brom-α-naphthoquinone.[3]

β-Naphthoquinone-α-oxime or *α-Nitroso-β-naphthol* is formed by the action of nitrous acid on β-naphthol.[4] In order to prepare it, 4 parts of the latter and 3 parts of zinc chloride are dissolved in 24 parts of alcohol and a concentrated solution of 2 parts of sodium nitrite added to the boiling liquid. The zinc salt soon separates from the red-coloured boiling solution, and is converted by heating with caustic soda solution into the sodium salt, which is then decomposed by hydrochloric acid. One hundred parts of naphthol yield 110—115 parts of the quinonoxime,[5]

It is thus obtained in yellow needles, and it also separates in this form from hot water, in which it is only slightly soluble. These contain water which they readily lose, simultaneously taking a brown colcur. It crystallizes from alcohol, ether, or benzene in orange-brown plates or short prisms, whilst it

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[1] Goldschmidt and Schmid, *loc. cit.*

[2] Worms, *Ber.* **15**, 1816.

[3] Brömme, *Ber.* **21**, 386.

[4] Fuchs, *Ber.* **8**, 1026; Stenhouse and Groves, *Annalen*, **189**, 145; Ilinski, *Ber.* **17**, 2581; Groves, *Journ. Chem. Soc.* **1884**, I. 295.

[5] Henriques and Ilinski, *Ber.* **18**, 704.

separates from a boiling mixture of light petroleum and benzene in large, lustrous, blackish-brown pointed prisms, melting at 110°. It is readily volatile with steam, and forms a bright red solution in sulphuric acid, from which it is precipitated by water. Dilute nitric acid converts it into 1-nitro-β-naphthol.

This substance and the isomeric β-nitroso-α-naphthol are employed in dyeing under the names of *Gambine Y.* and *Gambine R.*[1]

Potassium β-naphthoquinone-α-oximate, $C_{10}H_6NO_2K$, crystallizes in splendid green plates with a metallic lustre, forms a green solution in water and detonates on heating.

Sodium naphthoquinonoximate, $C_{10}H_6NO_2Na$, is a green crystalline powder, which is somewhat sparingly soluble in water and insoluble in dilute caustic soda.

The *ammonium* salt separates out when hot alcoholic solutions of naphthoquinonoxime and ammonia are mixed; it forms green plates, with a metallic lustre, which lose ammonia in the air. The *barium* salt is a green precipitate whilst the *silver* salt is reddish-brown. When an alcoholic solution of silver nitrate is added to a hot solution of the quinonoxime, a precipitate consisting of microscopic crystals of the composition, $C_{10}H_6NO_2Ag + C_{10}H_7NO_2$, is formed.

A solution of a neutral copper salt is completely precipitated by a solution of the quinonoxime in acetic acid of 50 per cent.; the coffee-brown precipitate has a metallic lustre, dissolves in hot glacial acetic acid and in aniline, and is decomposed by continued heating with caustic potash, cupric oxide being precipitated. Copper can be separated from most of the other metals and determined by this method.[2]

Ferric salts give a black precipitate with the acetic acid solution of the quinonoxime, which is difficultly soluble in hydrochloric acid, but readily in aniline. The salts of aluminium and manganese are not precipitated in this way, and can therefore be readily separated from iron.[3]

When the solution of a cobalt salt is added to that of the sodium salt, a brownish-red precipitate of the composition $(C_{10}H_6NO_2)_2Co$ is formed, whereas if a solution of the quinonoxime in dilute alcohol or acetic acid is employed a

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[1] *Journ. Soc. Chem. Ind.* **1890**, 1126.

[2] v. Knorre, *Ber.* **20**, 283.

[3] Ilinski and v. Knorre, *Ber.* **18**, 2728; v. Knorre, *loc. cit.*

purple-red precipitate of $(C_{10}H_6NO_2)_3Co$ is obtained, which dissolves in concentrated nitric or sulphuric acid and is re-precipitated by water. Boiling caustic potash solution also only attacks it slowly, whilst ammonium sulphide decomposes it. This reaction can be employed for the separation of cobalt from nickel, since the latter gives a brownish-yellow precipitate, $(C_{10}H_6NO_2)_2Ni$, which is readily decomposed by acids.[1]

Methyl β-naphthoquinone-a-oximate, $C_{10}H_6NO_2(CH_3)$, is obtained by heating the silver salt with an ethereal solution of methyl iodide. It is readily soluble in alcohol, moderately in hot water, and crystallizes from hot light petroleum in yellow, prismatic needles, which melt at 75°, and form a deep red coloured solution in sulphuric acid.

Ethyl naphthoquinonoximate, $C_{10}H_6NO_2(C_2H_5)$, forms yellow, silky needles.[2]

Carbanilido-β-naphthoquinone-a-oxime, $C_{10}H_6O(NO.CO.NH.C_6H_5)$ crystallizes in slender, matted needles, melting at 126—128°, and is decomposed by alkalis in a similar manner to its isomerides (Goldschmidt and Strauss).

3-*Bromo-β-naphthoquinone-a-oxime*, $C_{10}H_6BrNO_2$. The *β-a*-compound, like the *β*-*β*-isomeride, forms a *dibromide*, which crystallizes in needles, melting at 130—131°, and is converted by heating with alcohol into the monobromo-compound. The latter crystallizes in long yellow needles, and melts at 172°. (Brömme).

β-Naphthoquinone-a-oximesulphonic acid, $C_{10}H_6NO_2(SO_3H)$, is obtained by covering ammonium *β*-naphthol-*β*-sulphonate with 16—18 parts of water, adding the calculated quantity of sodium nitrite solution, cooling well and adding hydrochloric acid until the salt has dissolved and the liquid has a strongly acid reaction. The deep orange-coloured solution is neutralized with ammonia, and barium chloride added until no further green precipitate is produced. The latter is washed first with cold and afterwards with hot water, and is then treated with hydrochloric acid, which converts it into a heavy orange-coloured crystalline powder consisting of the *normal barium salt*, $(C_{10}H_6NO_2.SO_3)_2Ba+H_2O$. This substance crystallizes from boiling water in fascicular groups of long, flat, golden lustrous needles. When ammonia is added to its hot aqueous solution

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[1] Ilinski and v. Knorre, *Ber.* **18**, 699; Hintz, *Fresenius' Zeitsch.* **28**, 234.

[2] Ilinski, *Ber.* **19**, 340.

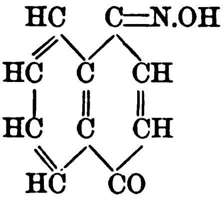
the *basic salt*, $C_{10}H_5O.NOBaSO_3 + 2H_2O$, separates out in microscopic needles.

The free acid is very readily soluble and remains in nodular crystals when its solution is evaporated. If the finely powdered barium salt is added to an acetic acid solution of phenol or resorcinol, and the mixture treated with a little sulphuric acid, the liquid becomes coloured a deep blue, which changes to red on the addition of water; diphenylamine also produces a blue colouration which is not altered by water but is changed to red by alkalis.[1]

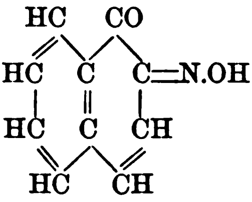
O. Hoffmann found that naphthoquinonoximesulphonic acid forms a green colouring matter with iron,[2] which is manufactured on the large scale and known as *Naphthol green*. In order to prepare it, 5·5 parts of sodium naphthoquinonoximesulphonate are dissolved in 20 parts of water and a solution of 1 part of ferric chloride in 4 parts of water added. The liquid becomes coloured brownish-black on standing, and is then freed from excess of iron by caustic soda and filtered. The colouring matter can be separated from the pure green solution by common salt or by evaporation, and is then recrystallized from alcohol. It occurs in commerce as a dark-green powder, which dissolves in water. When caustic soda is added to the solution, the latter takes a more bluish tinge but no iron is precipitated. It is employed for dyeing wool and silk; its constitution is unknown.[3]

The constitution of the naphthoquinonoximes can be represented by the following formulæ (*cf.*, Pt. III., p. 170):

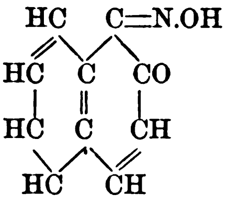
α—α



β—β



β—α



If on the other hand the quinones be looked upon as peroxides, the following alternative formulæ may be employed:

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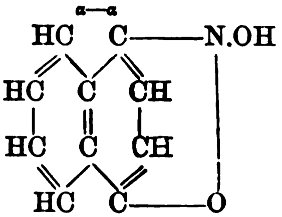
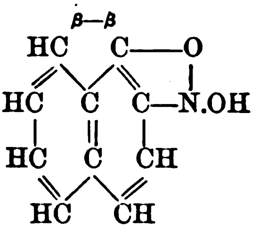
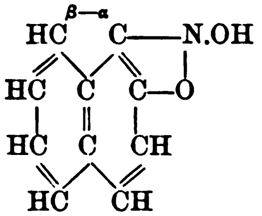
[1] Meldola, *Journ. Chem. Soc.* 1881, **1**, 40.

[2] *Ber.* **18**, 46.

[3] *Ber.* **17**, 393; Schultz, *Steinkohlentheer*, **2**, 39.







Monochloro-β-naphthoquinone-α-oxime, $C_{10}H_5ClO(NOH)$ is formed when the calculated weight of chlorine is passed into a solution of β-naphthoquinone-α-oxime in 8 parts of chloroform.[1]

It crystallizes from alcohol in well-formed yellowish-red needles, is readily soluble in hot alcohol, acetic acid and benzene, and melts and froths up at 167—168°. It forms a red solution in cold concentrated sulphuric acid from which it is precipitated unaltered by water.

The *sodium salt*, $C_{10}H_5ClO(NONa)$, crystallizes in lustrous green plates, and is moderately soluble in water and dilute alcohol.

The oxime is converted by the action of concentrated hydrochloric acid on its acetic acid solution into chlorhydroxy-α-naphthoquinone and by oxidation with nitric acid of sp. gr. 1·4 into chloro-β-naphthoquinone.

Dichloro-β-naphthoquinone-α-oxime, $C_{10}H_4Cl_2O(NOH)$, is obtained by the action of cold caustic potash on a solution of the trichloroxime in methyl alcohol.

It crystallizes in well-formed, lustrous golden-yellow needles, is moderately soluble in hot acetic acid, hot alcohol, benzene and chloroform, and melts with decomposition at 165—166°.

It forms green solutions in the alkali carbonates. Nitric acid converts it into dichloro-β-naphthoquinone (p. 128), whilst on heating with sulphuric acid β-chlorohydroxynaphthoquinone α-oxime is formed.

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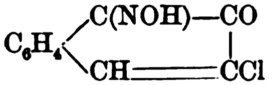
[1] Zincke and Schmunk, *Annalen*, **257**, 141.

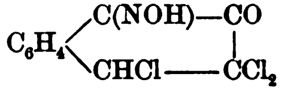
Trichloro-β-ketohydronaphthalene-α-oxime, $C_{10}H_5Cl_3O(NOH)$, is obtained by the action of an excess of chlorine on β-naphthoquinonoxime. It crystallizes from a mixture of benzene and light petroleum in white needles, which become red in the air, and melt at 185—186°, with evolution of gas. It is moderately soluble in alcohol, chloroform, and acetic acid.

This substance readily loses hydrochloric acid on treatment with alkalis, but is stable towards acids.

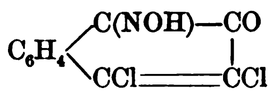
The relations of these three compounds to one another are shown by the following formulæ:



Chloronaphthoquinon-oxime.



Trichloroketohydronaphthalene-α-oxime.



Dichloronaphthoquinonoxime.

Chloronaphthoquinonoxime, $C_{10}H_5Cl.O.NOH$, is obtained by heating the corresponding chloroquinone (p. 121) with alcohol and hydroxylamine hydrochloride. It is readily soluble in alcohol and glacial acetic acid, and melts at 200° with decomposition.[1]

2661 *α-α-Naphthoquinonedioxime*, $C_{10}H_6(NOH)_2$, is formed when α-naphthoquinone-α-oxime is boiled with hydroxylamine hydrochloride and dilute alcohol. It crystallizes in slender, colourless needles, which melt at 207° with decomposition. Tin and hydrochloric acid reduce it to 1 : 4-diamidonaphthalene, and alkaline potassium ferricyanide oxidizes it to α-α-dinitrosonaphthalene (p. 55).[2]

α-α-Naphthoquinonedioxime acetate, $C_{10}H_6(NO.CO.CH_3)_2$, is obtained by the action of acetic anhydride on the dioxime, and crystallizes in matted needles, melting at 160°.

α-α-Naphthoquinonedichlorimide, $C_{10}H_6(NCl)_2$, is formed when a solution of 1 : 4-diamidonaphthalene is treated with bleaching powder solution as long as a precipitate is formed. It crystallizes from alcohol in yellowish needles, which have a strong smell of quinone, and melt at 136—137°; hydrochloric acid converts it into dichloro-α-naphthoquinone,[3] and it is reconverted into diamidonaphthalene by reduction.

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[1] Cleve, *Ber.* **23**, 955.

[2] Nietzki and Guitermann, *Ber.* **21**, 428.

[3] Friedländer and Böckmann, *Ber.* **22**, 590.

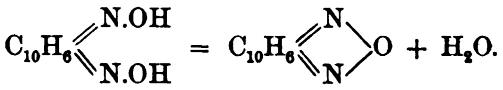
β-Naphthoquinonedioxime is formed when β-β- or β-a-naphthoquinonoxime is heated for some days with hydroxylamine hydrochloride and a little methyl alcohol. It crystallizes from hot water in yellow needles, which melt with decomposition at 149°; it forms a dark red-coloured solution in sulphuric acid, from which it is precipitated by water. It dyes brown on an iron mordant, since it is an ortho-compound, whereas a-a-naphthoquinonedioxime is not a colouring matter (Kostanecki).

When sodium ethylate is added to an ethereal solution of the a-β-dioxime, the *sodium salt* of the latter separates out as a red precipitate, which forms a yellowish red-coloured solution in water.[1] The *silver salt*, $C_{10}H_6(NOAg)NOH$, is a dark red precipitate, and must contain the oximido-group in the a-position, since on treatment with methyl iodide it yields the same *methyl ether*, $C_{10}H_6(NOCH_3)NOH$, as is formed by heating methyl β-naphthoquinone-β-oximate with alcohol and hydroxylamine hydrochloride. It is a light yellow oil, which is soluble in alcohol and takes a brown colour in the air.

The *isomeric ether* is obtained from methyl β-naphthoquinone-a-oximate; it crystallizes in yellow needles, melting at 158—159°, and forms yellow solutions in the alkalis.[2]

When the dioxime is heated with acetic anhydride, the following substance is obtained, no acetyl derivative being formed.

β-Naphthoquinonedioxime anhydride, $C_{10}H_6N_2O$, is also formed by heating an alkaline solution of the dioxime:



$$C_{10}H_6\left\langle\begin{matrix}N.OH\\N.OH\end{matrix}\right. = C_{10}H_6\left\langle\begin{matrix}N\\N\end{matrix}\right\rangle O + H_2O.$$

It may be further obtained, together with diphenyl urea, by heating a solution of the dioxime in benzene with phenyl carbimide (Goldschmidt and Strauss).

It crystallizes from hot water in colourless, monosymmetric needles, which melt at 78°, and are insoluble in alkalis.

On oxidation with alkaline potassium ferricyanide, the dioxime is converted into a-β-dinitrosonaphthalene, and on reduction into the corresponding diamine.

2-*Hydroxy-a-naphthoquinonoxime* or *Nitrosonaphthoresorcinol*, $C_{10}H_6(OH)O(NOH)$, is formed when one molecule of hydroxy-a-naphthoquinone is dissolved in two molecules of dilute caustic

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[1] Goldschmidt and Schmitt, *Ber.* **17**, 2066.

[2] Koroff, *Ber.* **19**, 176.

soda solution and a molecule of hydroxylamine hydrochloride added, and is precipitated by the addition of an acid. After washing and drying it is dissolved in boiling glacial acetic acid, from which it crystallizes on cooling in masses of yellow needles, which melt at 180° with evolution of gas.

It dissolves readily in alkalis and in hot alcohol; the latter solution gives with ferrous salts a green and with ferric salts a dark-brown lake, whilst cobalt salts produce a dark yellow, and nickel salts a scarlet-red precipitate. It dyes fabrics mordanted with iron a fine olive-green, and is therefore employed in dyeing and calico printing. On a nickel mordant it produces red shades which are, however, destroyed by a boiling soap solution.

In order to prepare it on the large scale, potassium hydroxylaminesulphonate from which hydroxylamine is liberated by alkalis, and which is known as *reduction salt*, is employed instead of hydroxylamine hydrochloride.

Nitrosochloronaphthoresorcinol or *β-Chlorohydroxy-a-naphthoquinonoxime*, $C_{10}H_4Cl(OH)O(NOH)$, is obtained in a similar manner from chloronaphthalenic acid, and by the action of hydrochloric acid on dichloro-β-naphthoquinonoxime.[1] It crystallizes from acetic acid in yellow needles, which melt at 187—188° with evolution of gas. It also forms metallic lakes and dyes mordanted fabrics.[2]

2′-Hydroxy-β-naphthoquinone-a-oxime, $C_{10}H_5(OH)O(NOH)$, is formed by the action of sodium nitrite on 2:2′-dihydroxynaphthalene suspended in hydrochloric acid. It crystallizes from alcohol in small, lustrous, brownish-yellow needles, melting at about 235°.[3]

Mononitroso-β-a-dihydroxynaphthalene is obtained as a reddish mass by the action of sodium nitrite on β-a-dihydroxynaphthalene dissolved in caustic soda. It is used for dyeing on mordanted cotton, &c.[4]

Amidohydroxy-a-naphthoquinonoxime or *Amidonitrosonaphthoresorcinol*, $C_{10}H_4(NH_2)(OH)O(NOH)$, is formed when hydroxylamine hydrochloride is added to an alkaline solution of amidonaphthalenic acid, the blue colour of the liquid being changed to deep blood-red. Dilute acetic acid precipitates the oxime as a gelatinous mass, which is purified by solution in

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[1] Kostanecki, *Ber.* **22**, 1342.

[2] Zincke and Schmunk, *Annalen*, **257**, 148.

[3] Clausius, *Ber.* **23**, 521.

[4] German Patent 53915, 1889, *Ber.* **23**, 781 c.

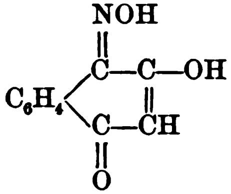
hydrochloric acid, and precipitation as the *hydrochloride* by passing in the acid gas. This salt crystallizes in light yellow needles and yields the free base, which is a greenish-yellow flocculent precipitate. It dissolves in glacial acetic acid and in alcohol on the addition of a little hydrochloric acid with a greenish-yellow colour, and in a small quantity of an alkali with a violet, in larger amounts with a blood-red colour.

Acetamidohydroxynaphthoquinonoxime, $C_{10}H_4(NH.CO.CH_3)(OH)O(NOH)$, is prepared in a similar manner to the preceding compound from acetamidohydroxyquinone, and crystallizes from glacial acetic acid in golden-yellow, very lustrous needles.[1]

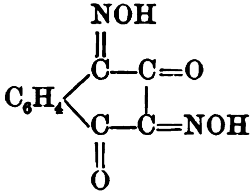
Dinitrosonaphthoresorcinol, $C_{10}H_4O_2(NOH)_2+H_2O$, is formed when the requisite quantity of sodium nitrite is added to an alkaline solution of the monoxime and the solution poured into dilute alcohol. It crystallizes from alcohol in long, faintly-yellow plates, which decompose at 165°. It is also a powerful dye and produces deeper shades than the monoxime. When it is reduced with tin and hydrochloric acid, and air then passed through the liquid, amidonaphthalenic acid is formed, the first product being diamidonaphthoresorcinol.

It follows from this reaction and from the formation and behaviour of these compounds, which correspond exactly to the nitrosoresorcinols, that they have the following constitution (Kostanecki):

Nitrosonaphthoresorcinol.



Dinitrosonaphthoresorcinol.



Mononitroso- and *Dinitroso-* 1 : 1'-*dihydroxynaphthalene* are formed when a solution of the dihydroxynaphthalene in caustic soda is treated with sodium nitrite and hydrochloric acid.[2] They form yellow amorphous precipitates and are employed in calico-printing and in dyeing.

4'-Hydroxy-α-naphthoquinonoxime, or *Juglonoxime*, $C_{10}H_5(OH)O(NOH)$, is obtained by boiling juglone with alcohol and

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[1] Kehrmann and Weichardt, *J. Pr. Chem.* II. **40**, 179.

[2] Erdmann, *Annalen*, **247**, 358 ; German Patent 51478, 1889, *Ber.* **23**, 532 c.

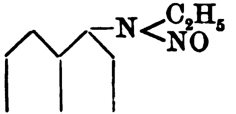
hydroxylamine hydrochloride, and crystallizes from glacial acetic acid in very lustrous-red needles or thin prisms, which melt at about 187° with energetic decomposition, and form deep blood-red coloured solutions in the alkalis and in sulphuric acid. It does not dye mordanted fabrics since the hydroxyl-group is not in the ortho-position to the oximido group (p. 143).

Juglonedioxime, $C_{10}H_5(OH)(NOH)_2$, is formed when the alcoholic solution of juglone and hydroxylamine hydrochloride is heated to 140°. It crystallizes from glacial acetic acid in yellowish needles or prisms, forms yellowish red-coloured solutions in alkalis and sulphuric acid, and detonates vigorously at 225°.[1]

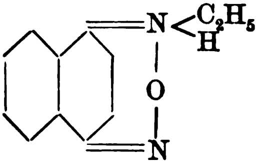
AMIDONITROSONAPHTHALENES OR NITROSO-NAPHTHYLAMINES.

2662 The naphthoquinonoximes behave towards ammonia or ammonium salts like other quinonoximes, and the α-naphthylnitrosamines are, like the corresponding benzene derivatives, converted into *p*-amidonitroso-compounds by the action of alcoholic hydrochloric acid:

Ethyl-α-naphthylnitrosamine.

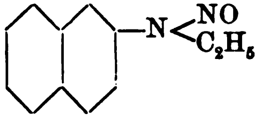


α-Ethylamido-α-nitrosonaphthalene.

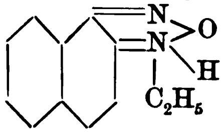


The β-naphthylnitrosamines on the other hand yield ortho-compounds:

Ethyl-β-naphthylnitrosamine.



β-Ethylamido-α-nitrosonaphthalene



α-Ethylamido-α-nitrosonaphthalene, or *p-Nitroso-α-ethylnaphthylamine*, $C_{10}H_6(NO)NH.C_2H_5$, is formed by the addition of

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[1] Bernthsen and Semper, *J. Pr. Chem.* II. **18**, 203; **19**, 164.

alcoholic hydrochloric acid to an ethereal solution of ethyl-α-naphthylnitrosamine.

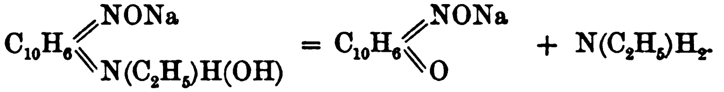
The hydrochloride thus obtained is dissolved in caustic soda solution, and the free base precipitated by a current of carbon dioxide.

It separates from benzene in brown crystals, which melt at 133° with decomposition.

α-Ethylamido-α-nitrosonaphthalene hydrochloride, $C_{10}H_6(NOH)N(C_2H_5)HCl$, forms olive-green, matted needles, which are only sparingly soluble in hydrochloric acid, and form a powder which causes violent sneezing.

When sodium picrate is added to its solution a lemon-yellow precipitate of the *picrate* is obtained, which crystallizes from alcohol in strongly lustrous, light-green plates.

If an excess of caustic soda solution be added to the alkaline solution of the base, the *sodium salt*, $C_{10}H_6(NONa)N(C_2H_5)H(OH)$, separates out in satin-like scales, which become coloured yellow in the air, and form orange-yellow solutions in water and alcohol. On heating with caustic soda, ethylamine and α-naphthoquinonoxime are formed:



$$C_{10}H_6\begin{array}{l}\nearrow NONa\\ \searrow N(C_2H_5)H(OH)\end{array} = C_{10}H_6\begin{array}{l}\nearrow NONa\\ \searrow O\end{array} + N(C_2H_5)H_2.$$

Stannous chloride and hydrochloric acid reduce the base to ethyl-1 : 4-diamidonaphthalene, which on oxidation yields a large proportion of α-naphthoquinone.[1]

Tetrahydro-α-ethylamido-α-nitrosonaphthalene, $C_{10}H_{10}(NO)NHC_2H_5$, is prepared from the corresponding nitrosamine, and crystallizes in brass-yellow silky needles, melting at 119°; its *hydrochloride* forms thick golden-yellow prisms with a splendid lustre.[2]

α-Diethylamido-α-nitrosonaphthalene, or *α-Nitrosodiethylnaphthylamine*, $C_{10}H_6(NO)N(C_2H_5)_2$, is formed by the action of sodium nitrite on a solution of α-diethylnaphthylamine, and crystallizes from alcohol in well-developed, golden-red scales, which melt at 165°, and form a deep blue-coloured solution in sulphuric acid.[3]

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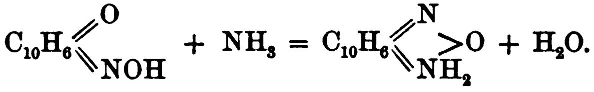
[1] Koch, *Annalen*, **243**, 310.
[2] Bamberger and Helwig, *Ber.* **22**, 1314.
[3] B. E. Smith, *Journ. Chem. Soc.* **1882**, I. 180.

α-Phenylamido-α-nitrosonaphthalene, $C_{10}H_6(NO)NH.C_6H_5$, is obtained by the addition of hydrochloric acid to a solution of phenyl-α-naphthylnitrosamine in a mixture of alcohol and ether. The hydrochloride thus precipitated is partially decomposed by water, and rapidly by ammonia with separation of the base, which crystallizes from dilute wood-spirit in splendid yellowish-brown plates, and melts at 150°.

α-Naphthylamido-α-nitrosonaphthalene, $C_{10}H_6(NO)NH.C_{10}H_7$, crystallizes in thin red plates or brownish-red needles, melting at 169°; its *hydrochloride* forms green needles.[1]

α-Amido-β-nitrosonaphthalene or *β-Nitroso-α-naphthylamine*, $C_{10}H_6(NO)NH_2$, was obtained by Harden by heating a mixture of one part of β-naphthoquinone-β-oxime, 20 parts of ammonium chloride, and 50 parts of ammonium acetate for half an hour on the water bath, the mass being kept alkaline by the addition of ammonium carbonate:



$$C_{10}H_6\begin{matrix}\diagup O \\ \diagdown NOH\end{matrix} + NH_3 = C_{10}H_6\begin{matrix}\diagup N \\ \diagdown NH_2\end{matrix}\!\!>O + H_2O.$$

After washing with cold water, the residue was recrystallized from benzene.

α-Amido-β-nitrosonaphthalene separates out in small hemispherical masses or short prisms, which have a fine beetle green lustre, and form a brown powder. It is slightly soluble in ether, more readily in alcohol with a brown colour. When the calculated amount of caustic soda and then an excess of ether are added to the alcoholic solution the *sodium salt*, $C_{10}H_6(NONa)NH_2.OH$, is precipitated in light brown, very hygroscopic nodular masses.

α-Amido-β-nitrosonaphthalene hydrochloride, $C_{10}H_6(NOH)NH_2Cl$, separates in long, red, matted needles, when ether is added to a solution of the base in alcoholic hydrochloric acid. It can be boiled with alcohol without undergoing decomposition but rapidly decomposes in aqueous solution into the quinonoxime and ammonia. Platinum chloride, added to the alcoholic solution produces a bright red amorphous precipitate having the composition $[C_{10}H_6(NOH)NH_2]_2PtCl_6$.

α-Amido-β-nitrosonaphthalene sulphate, $C_{10}H_6(NOH)NH_2, SO_4H + H_2O$, is obtained in a similar manner to the hydrochloride, and forms light red, matted needles.

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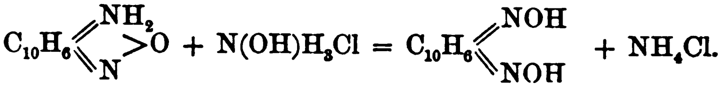
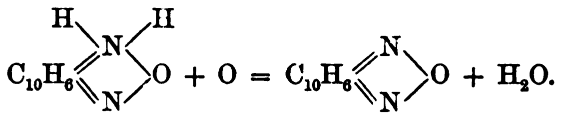
[1] Fischer and Hepp, *Ber.* **20** 1247.

When hydroxylamine hydrochloride is added to an alcoholic solution of the base, β-naphthoquinonedioxime is formed :



Alkaline potassium ferricyanide oxidizes it to the anhydride of the dioxime :



It is reduced by ammonium sulphide to 1 : 2-diamidonaphthalene. When the alcoholic solution of the hydrochloride is boiled with an aqueous solution of an excess of potassium nitrite, a substance of the formula $C_{10}H_6N_4O_4KH$ separates out in white silvery plates, containing water, which on heating become anhydrous and detonate at 250°. Dilute acids added to the aqueous solution of this salt produce a white amorphous, bulky precipitate, probably consisting of the corresponding acid, which detonates violently at 110°, or on continued heating at a lower temperature. When the potassium salt is brought into a small quantity of boiling concentrated hydrochloric acid, deflagration occurs ; if a large excess of acid be employed a vigorous evolution of nitrogen takes place, and β-naphthoquinone-β-oxime is formed.

α-Ethylamido-β-nitrosonaphthalene, $C_{10}H_6(NO)NH.C_2H_5+H_2O$, is formed when β-naphthoquinone-β-oxime is heated on the water bath with ethylamine hydrochloride and acetate, the corresponding carbonate being added from time to time. It crystallizes from dilute alcohol in lustrous green plates, melting at 95°, which lose water and become brown in the air.[1]

β-Amido-α-nitrosonaphthalene was obtained by Ilinski, who named it naphthalene-α-oxime-β-imide, by heating β-naphthoquinone-α-oxime with aqueous ammonia to 100° under pressure. It crystallizes from alcohol in green needles, which melt at 150—152°. Its alcoholic solution is coloured deep purple-red by alcoholic potash ; on the addition of ether the *potassium salt,* $C_{10}H_6(NOK)NH_2.OH$, is precipitated as a crystal-

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[1] Harden, *Inaugural diss.*, Erlangen, 1888 ; *Annalen* **255**, 148.

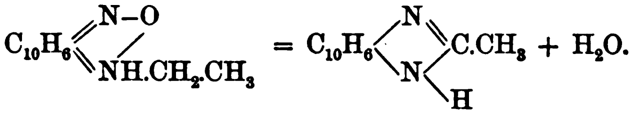
line powder, which is very hygroscopic and readily decomposes, with formation of the nitroso-compound; when its solution is heated, the quinonoxime is regenerated.

The *hydrochloride*, $C_{10}H_6(NOH)NH_2Cl$, crystallizes from alcohol in yellow plates, the aqueous solution of which readily decomposes, instantaneously on boiling, with formation of the quinonoxime, whilst in alcoholic solution it is stable. The *platinochloride* $[C_{10}H_6(NOH)NH_2]_2PtCl_6 + H_2O$, separates from its aqueous solution in orange-yellow needles; ether precipitates it from an alcoholic solution, on the other hand, in anhydrous, red, cross-shaped aggregates of prisms. The *nitrate*, $C_{10}H_6(NOH)NH_2.NO_3$, may be precipitated from a solution of the hydrochloride in slender yellow needles, which soon unite to form large tablets.

The β-α-compound behaves towards oxidizing and reducing agents and hydroxylamine like the α-β-compound. When the alcoholic solution of the hydrochloride is treated with a concentrated solution of excess of potassium nitrite, the red colour changes to green, and on boiling the liquid yellow crystals of $C_{10}H_6N_3O_2K$ separate out;[1] this substance appears to be a diazo-compound.[2]

When phenylhydrazine and acetic acid are added to an alcoholic solution of the base and the mixture allowed to stand, it is reduced to azoxy-β-naphthylamine (Harden).

β-Ethylamido-α-nitrosonaphthalene, $C_{10}H_6(NO)NHC_2H_5$, is formed by the addition of alcoholic hydrochloric acid to a solution of ethyl-β-naphthylnitrosamine cooled with ice,[3] and also when a dilute aqueous solution of β-naphthoquinone-α-oxime is allowed to stand with ethylamine.[4] It crystallizes from benzene in splendid green, flat tablets, melting at 120—121°. Its salts dissolve in water with the colour of potassium dichromate. When it is dissolved in alcoholic hydrochloric acid and allowed to stand at 10—15°, ethenyl-1 : 2-diamidonaphthalene is formed:



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[1] *Ber.* **19**, 340. [2] Fischer and Hepp, *Ber.* **20**, 2471.

[3] Fischer and Hepp, *Ber.* **20**, 1428 and 2471.

[4] Fischer and Hepp, *Ber.* **21**, 686.

THIO-AMIDONAPHTHALENE COMPOUNDS.

2663 *Thio-β-naphthylamine*, $S(C_{10}H_6)_2NH$, is formed when equal molecules of sulphur and β-dinaphthylamine are gradually heated to 250°. until no more sulphuretted hydrogen is evolved. It crystallizes from alcohol or benzene in fascicular groups of faintly yellowish-green needles, which become brown and melt at 236°. On further heating carbonization takes place and sulphuretted hydrogen is evolved. It is insoluble in dilute acids, but forms a violet solution in sulphuric acid, the colour of which is changed to blue by traces of nitric acid. With picric acid it forms the compound $C_{20}H_{13}SN + 2C_6H_2(NO_2)_3OH$, which crystallizes from benzene in almost black, lustrous plates.[1]

Thio-β-naphthylamine is also formed by the action of sulphur dichloride on β-dinaphthylamine; it is accompanied in this case by a much less soluble isomeride, which forms almost white crystalline flakes, melting at 303°.

Acetothio-β-dinaphthylamine, $S(C_{10}H_6)_2N.CO.CH_3$, is obtained by bringing thiodinaphthylamine into warm acetic anhydride and separates on cooling in slender, lustrous needles, which melt at 211° and are readily soluble in hot alcohol[2] (Kym).

Benzothio-β-dinaphthylamine, $S(C_{10}H_6)_2NC_7H_5O$, forms coarse, light yellow needles united in fascicular groups, which melt at 196—197°, and are freely soluble in benzene, very sparingly in cold alcohol or ether, and almost insoluble in light petroleum.[3]

Methylthio-β-dinaphthylamine, $S(C_{10}H_6)_2NCH_3$, is formed when thio-β-dinaphthylamine is heated with methyl iodide and methyl alcohol to 150° and by the action of sulphur or its chlorides on methyl-β-dinaphthylamine. It forms slender, lemon-yellow plates, or when the solution is allowed to cool very slowly, slender needles, which melt at 284—285°, and are almost insoluble in cold alcohol, slightly soluble in cold benzene and toluene, and freely in the last of these on heating.

Ethylthio-β-dinaphthylamine, $S(C_{10}H_6)_2NC_2H_5$, is prepared in a similar manner to the methyl derivative. It forms small, light yellow needles, melting at 212—213°.

Thiophenyl-a-naphthylamine, $S(C_{10}H_6)(C_6H_4)NH$, is obtained by heating phenyl-α-naphthylamine with sulphur to 220—240°. It forms small, lustrous yellow plates, melting at 137—138°,

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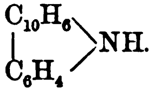
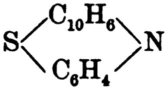
[1] Ris, *Ber.* **19**, 2240.
[2] *Ber.* **21**, 2806.
[3] Kym, *Ber.* **23**, 2458.

and is readily soluble in benzene and hot alcohol. On heating with copper it is converted into phenylnaphthylcarbazol.



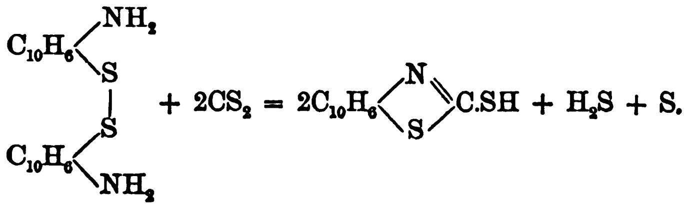
$$\begin{matrix} C_{10}H_6 \\ | \\ C_6H_4 \end{matrix} \!\!> NH.$$

Thiophenyl-β-naphthylamine, forms light yellow, fascicular groups of coarse, lustrous needles, melts at 178°, and dissolves readily in boiling alcohol, very readily in boiling benzene.

Methylthiophenyl-β-naphthylamine,  $S\!\!<\!\!\begin{matrix} C_{10}H_6 \\ C_6H_4 \end{matrix}\!\!>\!NCH_3$, is prepared by heating the foregoing compound with methyl iodide. It forms slender, light yellowish-green needles, melts at 132—133°, and is readily soluble in benzene and hot glacial acetic acid.[1]

Dithio-β-dinaphthylamine, $S_2(C_{10}H_6)_2NH$, is formed in two isomeric modifications when sulphur monochloride, S_2Cl_2, and β-dinaphthylamine are brought together in benzene solution. The product obtained in smaller quantity forms small, reddish-yellow rods, melting at 220°, whilst the isomeric substance crystallizes in lustrous, brass-yellow plates, which melt at 205°, and are scarcely soluble in alcohol, ether and glacial acetic acid. On heating with aniline, sulphuretted hydrogen is evolved and thio-β-dinaphthylamine formed, whilst it is converted by acetic anhydride into acetothio-β-dinaphthylamine (Kym).

α-Amidothionaphthol, $C_{10}H_6(NH_2)SH$, is formed when either of the two compounds next to be described is fused with caustic potash. It is an oily liquid and rapidly oxidizes in the air to *amidonaphthyl disulphide*, $(C_{10}H_6.NH_2)_2S_2$, which crystallizes from alcohol in yellow plates, melting at 131—132°. This substance on heating with alcohol and carbon disulphide is converted into *thiocarbamidothionaphthol*.



$$\begin{matrix} C_{10}H_6\!\!<\!\!\begin{matrix} NH_2 \\ S \end{matrix} \\ | \\ C_{10}H_6\!\!<\!\!\begin{matrix} S \\ NH_2 \end{matrix} \end{matrix} + 2CS_2 = 2C_{10}H_6\!\!<\!\!\begin{matrix} N \\ S \end{matrix}\!\!>\!C.SH + H_2S + S.$$

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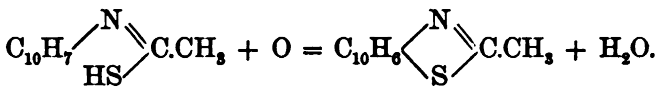
[1] Kym, *Ber.* **23**, 2458.

The latter crystallizes from alcohol in colourless needles, melting above 220°, and is a weak acid which decomposes carbonates.

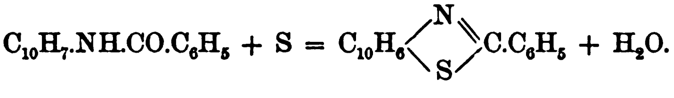
Ethenyl-a-amidothionaphthol is obtained by the oxidation of *a*-thio-acetonaphthalide (p. 150) with an alkaline solution of potassium ferricyanide:



$$C_{10}H_7\left<\begin{matrix}N\\HS\end{matrix}\right>C.CH_3 + O = C_{10}H_6\left<\begin{matrix}N\\S\end{matrix}\right>C.CH_3 + H_2O.$$

It crystallizes from alcohol in splendid prisms, melts at 94·5—95·5°, and has a pleasant aromatic odour. Its *hydrochloride* forms elegant colourless needles. It is not affected by potassium permanganate in alkaline solution but is oxidized by it in presence of sulphuric acid to phthalic acid, a fact which proves that it is not a peri-compound (p. 28), in which case sulphophthalic acid would be formed.[1]

a-Benzenylamidothionaphthol was prepared by Jacobsen from *a*-thiobenzonaphthalide by oxidation, whilst Hofmann obtained it by heating benzonaphthalide with sulphur, water and some sulphuretted hydrogen being also formed:[2]



$$C_{10}H_7.NH.CO.C_6H_5 + S = C_{10}H_6\left<\begin{matrix}N\\S\end{matrix}\right>C.C_6H_5 + H_2O.$$

It crystallizes from hot alcohol in fascicular groups of needles, melting at 102·5—103°.

Oxalamidothionaphthol, $C_{22}H_{12}N_2S_2$, is obtained together with ethenylamidothionaphthol and other products, when acetonaphthalide is heated with sulphur (Part III., p. 374). It forms golden-yellow plates, which melt and sublime above 300° with partial carbonization. It is almost insoluble in boiling alcohol, to which it imparts a bitter taste, and in ether and benzene, but dissolves with moderate ease in hot nitrobenzene, from which it separates in crystals on cooling. It forms a splendid red solution in sulphuric acid from which it is precipitated as a flocculent mass by water. By fusion with caustic potash it is decomposed into oxalic acid and *a*-amidothionaphthol:

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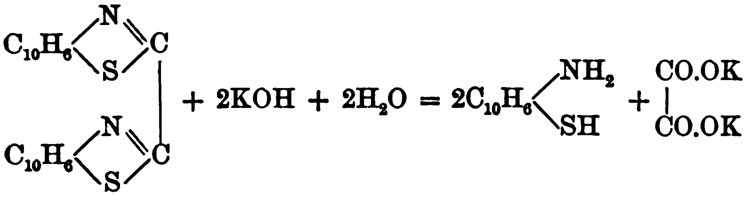
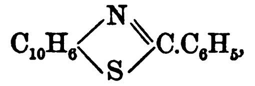
[1] Jacobsen, *Ber.* **20**, 1895; **21**, 2624.

[2] *Ber.* **20**, 1798.



β-Amidothionaphthol, $C_{10}H_6(NH_2)SH$, is prepared in a similar manner to the *α*-compound and is also an oily liquid, which rapidly oxidizes to the disulphide.

β-Ethenylamidothionaphthol, $C_{10}H_6.NS.C.CH_3$, is formed by the oxidation of *β*-thioacetanilide and crystallizes from alcohol in lustrous plates, which melt at 81°, and have a sharp aromatic odour. It dissolves readily in dilute acids.[1]

β-Benzenylamidothionaphthol,  $C_{10}H_6\langle{}^{N}_{S}\rangle C.C_6H_5$, was obtained by Hofmann by heating *β*-benzonaphthalide with sulphur. It crystallizes in matted needles, which melt at 107°, and form an alcoholic solution which shows a green fluorescence.

β-Oxalamidothionaphthol forms small yellow plates and behaves in a similar manner to the *α*-compound.

δ-Amidothionaphthol is formed when 1:3-naphthylamine-sulphamide, $C_{10}H_6(NH_2)SO_2.NH_2$, is heated with hydriodic acid and phosphorus, the *hydriodide* being thus obtained in silvery plates. The free amidothionaphthol is a yellowish oil, and combines with alcohol to form the compound $2C_{10}H_6(NH_2)SH + C_2H_6O$, which crystallizes in colourless needles.[2]

THE DIAZO-COMPOUNDS OF NAPHTHALENE.

2664 These substances are formed by the same reactions as the corresponding benzene derivatives; only few of them have hitherto been prepared pure, although their solutions (Part III. p. 312) are largely employed for the preparation of other compounds, especially azo-colouring matters.

In order to prepare chlorine substitution products by their means, it is best to use a solution of cuprous chloride in hydrochloric acid; this produces a yellow precipitate in solu-

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[1] Jacobsen and Süllwald, *Ber.* **21**, 2627.

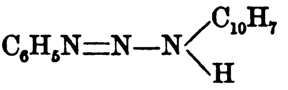
[2] Cleve, *Ber.* **21**, 3264.

tions of diazo-salts, which soon decomposes with evolution of nitrogen.[1] Mathis has analysed the compound obtained in this way from β-diazonaphthalene chloride and found that its composition is $4C_{10}H_7N_2Cl + Cu_2Cl_2$.[2]

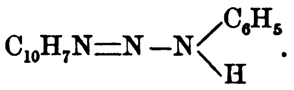
Bromine substitution products are obtained in a similar manner, a solution of cuprous bromide in hydrobromic acid being used. The fiery-red precipitate obtained in this way from β-diazonaphthalene bromide has, according to Lellmann and Remy, the formula $C_{10}H_7N_2Br + Cu_2Br_2$.[3]

Diazo-α-amidonaphthylamine, $C_{10}H_7N = N.NH.C_{10}H_7$, was obtained by Martius by the action of α-naphthylamine sulphate on a faintly alkaline solution of sodium nitrite. It crystallizes from alcohol in yellowish-brown plates, which explode on heating, and are readily decomposed into α-naphthol and α-naphthylamine even by weak acids.[4]

Diazobenzene-β-naphthylamine is formed by the action of a solution of β-diazonaphthalene chloride on aniline suspended in a solution of sodium acetate. It crystallizes from alcohol or benzene in light-yellow needles, which melt with decomposition at 150°. On heating with dilute sulphuric acid it yields aniline, β-naphthylamine, phenol, and β-naphthol. This substance therefore appears, like other similar compounds, to be tautomeric and to react according to the two formulæ:[5]



$$C_6H_5N{=}N{-}N\left\langle\begin{matrix}C_{10}H_7\\ H\end{matrix}\right.$$



$$C_{10}H_7N{=}N{-}N\left\langle\begin{matrix}C_6H_5\\ H\end{matrix}\right. .$$

When it is treated with phenylcarbimide in ethereal solution, *diazobenzene-β-naphthylphenyl carbamide*, $C_6H_5.NH.CO.N(C_{10}H_7.N_2.C_6H_5)$, is formed, which crystallizes in microscopic needles, melting at 123°, and on heating with dilute sulphuric acid yields β-naphthylphenyl carbamide.[6]

1 : 4-*Diazonaphthalenesulphonic acid*, $C_{10}H_6N_2SO_3$, is prepared by running about 700 cc. of a 5 per cent. sodium nitrite solution and a solution of 180 grms. of sodium 1 : 4-naphthylaminesulphonate in 800 cc. of water at the same time in thin

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[1] Sandmeyer, *Ber.* **17**, 1633 and 2650.

[2] *Ber.* **21**, 1097.

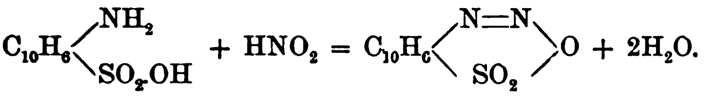
[3] *Ber.* **19**, 810.

[4] *Zeitsch. Chem.* **1886**, 137.

[5] Nölting and Binder, *Ber.* **20**, 3004.

[6] Goldschmidt and Molinari, *Ber.* **21**, 2557.

streams into a mixture of two litres of water with 120 grms. of sulphuric acid well cooled with ice :



$$C_{10}H_6\genfrac{}{}{0pt}{}{\diagup NH_2}{\diagdown SO_2.OH} + HNO_2 = C_{10}H_6\genfrac{}{}{0pt}{}{\diagup N{=}N \diagdown}{\diagdown\ SO_2\ \diagup}O + 2H_2O.$$

If sufficient nitrite solution be added the liquid gives a blue coloration with paper soaked in potassium iodide and starch solutions even after standing for half an hour.

The diazo-acid forms a yellow amorphous or indistinctly crystalline powder which is very stable under friction or percussion, but detonates on heating, a voluminous mass of carbon being left. A small portion of the acid added to a solution of *a*-naphthol in an excess of caustic soda produces a splendid, dark wine-red coloration, whilst it forms a yellow colouring matter with phenol.

1 : 4′-*Diazonaphthalenesulphonic acid* differs from the 1 : 4-compound by its light grey colour, with only a slight shade of yellow.

1 : 1′-*Diazonaphthalenesulphonic acid* is best prepared from the potassium salt, which is the most soluble of its salts, but still requires so much water for solution that a 10 per cent. nitrite solution is employed, and the sulphuric acid diluted with pieces of ice. It crystallizes in small, lustrous prisms, which have a yellow colour slightly inclined to green. It does not explode on heating, but is converted with evolution of nitrogen into naphthosultone (p. 103), a change which also takes place very gradually when it is preserved. If it be suspended in dilute hydrochloric acid, and a solution of sodium *a*-naphthate containing much ammonia added, the *ammonium salt* of *naphtholazonaphthalenesulphonic acid* separates out in red splinters with a metallic lustre, which form a dark red solution in a large quantity of water, the colour being changed to yellow by the addition of caustic soda.[1]

1 : 2′-*Diazonaphthalenesulphonic acid* forms large, wine-yellow crystals.[2]

1 : 3-*Diazonaphthalenesulphonic acid* is obtained as a fawn-coloured powder when nitrogen trioxide is passed into water in which 1 : 3-naphthylaminesulphonic acid is suspended. If,

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[1] Erdmann, *Annalen*, **247**, 328 ; Cleve, *Bull. Soc. Chim.* **24**, 512 ; **26**, 241.

[2] Cleve, *Ber.* **21**, 3271.

however, aqueous alcohol be employed, the azo-colouring matter, $C_{10}H_6(SO_3H)N_2.C_{10}H_5(NH_2)SO_3H$, is obtained, and is left on evaporation of the deep violet-coloured liquid as a beetle-green mass.[1]

1 : 2-*Diazonaphthalenesulphonic acid* crystallizes in elegant, amber-yellow tablets, which explode at 60°.[2]

β-Diazonaphthalene-α-sulphonic acid was obtained by Forsling by passing nitrogen trioxide into alcohol containing β-naphthylamine-α-sulphonic acid in suspension.[3] It is a greenish yellow, scarcely crystalline powder.

β-Diazonaphthalene-β-sulphonic acid was prepared by him in a similar manner from β-naphthylamine-β-sulphonic acid. It is a yellow, microcrystalline powder, which explodes when rubbed.[4]

β-Diazonaphthalene-γ-sulphonic acid is a green or yellowish microcrystalline powder (Forsling).

β-Diazonaphthalene-δ-sulphonic acid is formed when a solution of sodium nitrite is added to one of sodium β-naphthylamine-δ-sulphonate acidified with hydrochloric acid. It separates out after some time in colourless prisms which appear orange red by reflected light.[5]

HYDRAZINE COMPOUNDS OF NAPHTHALENE.

2665 *α-Naphthylhydrazine*, $C_{10}H_7NH—NH_2$, is, according to E. Fischer, best prepared in the following manner. Fifty grms. of α-naphthylamine are very finely ground with an equal weight of strong hydrochloric acid, and washed into a flask with 400 grms. of hydrochloric acid of sp. gr. 1·1, well cooled and treated with the calculated quantity of sodium nitrite, the mixture being thoroughly shaken throughout the addition. The solution of diazonaphthalene chloride is then filtered and run into a cooled well-stirred acid solution of 250 grms. of stannous chloride, the liquid being then heated on the water-bath until it is almost colourless:

$$C_{10}H_7N{=}NCl + 2SnCl_2 + 4HCl = C_{10}H_7NH—NH_3Cl + SnCl_4.$$

On cooling, α-naphthalenehydrazine hydrochloride separates out and is filtered off, well pressed, dissolved in hot water and de-

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[1] Cleve, *Ber.* **21**, 3264.

[2] Hirsch, *Ber.* **21**, 2370.

[3] *Ber.* **20**, 2102.

[4] *Ber.* **20**, 80 ; Weinberg, *Ber.* **20**, 2910.

[5] Baeyer and Duisberg, *Ber.* **20**, 1430 ; Erdmann, *Ber.* **21** 637.

composed with caustic soda solution. The free base is washed with ether and brought into 150 parts of boiling water, a small amount of a dark-coloured resin being left undissolved. On cooling the hydrazine separates out in yellowish plates, which are purified by distillation under diminished pressure, a colourless crystalline mass being finally obtained.

a-Naphthylhydrazine separates from hot alcohol in fine plates, and from benzene in coarse many-faced crystals, melts at 116—117°, and soon becomes yellow and brown coloured in the air. Under the ordinary pressure it boils with considerable decomposition, but distils at about 203° under a pressure of 20 mm. almost without alteration. Like phenylhydrazine it is a powerful reducing agent, and forms stable salts with the mineral acids.

a-Naphthylhydrazine hydrochloride, $C_{10}H_7NH.NH_3Cl$, crystallizes in long thin tablets, which are moderately soluble in water, but sparingly in hydrochloric acid.

The *acetate* is decomposed by water and sodium acetate therefore precipitates the base from solution of its salts.

When sodium nitrite is added to a cold solution of the hydrochloride, *nitrosonaphthylhydrazine*, $C_{10}H_7N(NO)NH_2$, is obtained as a crystalline precipitate, which is even less stable than nitrosophenylhydrazine. If a very dilute solution of the base in an excess of hydrochloric acid be used, an oily liquid separates out on the addition of the nitrite, which has a characteristic, slightly stupefying odour, and decomposes on distillation. This substance is probably *diazonaphthalenimide* or *triazonaphthalene*, $C_{10}H_7N_3$.

Acetone a-naphthylhydrazone, $C_{10}H_7.NH.N{=}C(CH_3)_2$, is formed when the base is dissolved in acetone, or when the latter is added to the solution of one of its salts. It is scarcely soluble in water, readily in alcohol, and separates from hot light petroleum in crystals, which melt at 74°, and become brown and deliquesce in the air.

Pyroracemic acid a-naphthylhydrazone, $C_{10}H_7.NH-N{=}C(CH_3)CO_2H$, crystallizes from hot alcohol in slender lustrous needles, which melt at 159° with evolution of gas.[1] On boiling with alcohol and sulphuric acid the *ethyl ester* is formed, which crystallizes in coarse yellow prisms, melting at 100°.[2]

Glyoxalic acid a-naphthylosazone, $C_{10}H_7N_2H{=}CH.C(N_2H.$

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[1] *Annalen*, **232**, 236.

[2] Schlieper, *Annalen*, **239**, 229.

$C_{10}H_7)CO_2H$, is formed by the action of dibromopyroracemic acid, $CHBr_2.CO.CO_2H$, on a cooled alcoholic solution of α-naphthylhydrazine, and separates from benzene in small cherry-red crystals, melting at 196°. Its alkali salts are sparingly soluble in water, and dye silk and wool yellow.[1]

α-Naphthylsemicarbazide, $C_{10}H_7NH.NH.CO.NH_2$, is obtained by heating α-naphthalenehydrazine with urea. It crystallizes in thin, lustrous, faintly brownish plates, which melt at 231°, and are insoluble in ether, sparingly soluble in hot alcohol.[2]

β-Naphthylhydrazine is prepared in a similar manner to the α-compound. It forms lustrous plates, melts at 124—125°, and cannot be distilled without decomposition even under a pressure of 25 mms., but only becomes slowly coloured red in the air. The *hydrochloride* is very slightly soluble in cold water, and crystallizes from a hot solution in slender lustrous needles, or in plates (Fischer).

Ethyl-β-naphthylhydrazine, $C_{10}H_7N(C_2H_5)NH_2$, is formed when an alcoholic solution of β-naphthylhydrazine is heated with ethyl iodide. It is a yellowish oily liquid, which becomes dark coloured in the air. When mercuric oxide is added to its solution in chloroform reduction takes place, and ethyl-β-naphthylamine is formed, the constitution of the hydrazine being thus shown.[3]

Acetyl-β-naphthylhydrazine, $C_{10}H_7NH.NH.CO.CH_3$, is obtained by boiling the base with glacial acetic acid, and forms colourless needles, melting at 164—165°. It is converted by mercuric oxide into a dark-coloured oil, which probably consists of acetylazonaphthalene, $C_{10}H_7.N_2.CO.CH_3$.

Benzoyl-β-naphthylhydrazine, $C_{10}H_7.NH.NH.CO.C_6H_5$ is prepared by the action of benzoyl chloride on the hydrazine, and crystallizes from hot benzene in needles, melting at 154—155°.

Dibenzoyl-β-naphthylhydrazine, $C_{10}H_7N_2H(CO.C_6H_5)_2$, is only produced when the monobenzoyl compound is heated with benzoyl chloride nearly to the boiling point of the latter. It crystallizes in small needles, melting at 162—163° (Hauff).

Ethidene-β-naphthylhydrazone, $C_{10}H_7N_2H{=}CH.CH_3$, is formed when the base is brought together with acetaldehyde, and crystallizes from alcohol in tablets, which melt at 128—129°, and become coloured yellow and brown in the air.

Acetone-β-naphthylhydrazone crystallizes from hot light petro-

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[1] Nastvogel, *Annalen*, **248**, 90.

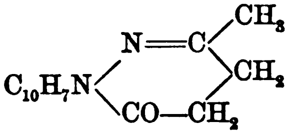
[2] Pinner, *Ber.* **21**, 1222.

[3] Hauff, *Annalen*, **253**, 24.

leum in elegant, light-yellow prisms, melting at 65·5°, is readily soluble in alcohol and ether and rapidly deliquesces in the air, a dark-coloured oil being formed.

Pyroracemic acid β-naphthylhydrazone crystallizes in yellow needles, which melt at 166° with evolution of carbon dioxide. Its *ethyl ester* forms slender yellow needles, melts at 131° and yields β-naphthindolecarboxylic acid and β-naphthindole[1] (substances which will be subsequently described) on heating with zinc chloride.

Levulinic acid β-naphthalenehydrazone is formed when β-naphthylhydrazine and levulinic acid are brought together in alcoholic solution. Water precipitates it in the crystalline condition, but the crystals soon become coloured red and deliquesce on exposure to air. When it is heated to 180° the anhydride, which has the constitution expressed by the following formula, is formed:



The latter crystallizes from hot alcohol in small, white needles, melting at 119°.

The *ethyl ester* is formed by the combination of ethyl levulinate with naphthylhydrazine in alcoholic solution, and is precipitated by water in yellowish crystals, which melt at 129—130°.[2]

β-Naphthylsemicarbazide, $C_{10}H_7NH.NH.CO.NH_2$, is formed when urea is heated with β-naphthylhydrazine hydrochloride,[3] and is obtained as a crystalline mass when equivalent amounts of potassium cyanate and β-naphthylhydrazine hydrochloride are brought together in hot aqueous solution. It is sparingly soluble in water, more freely in hot alcohol, from which it crystallizes in plates, melting at 225°.[4] When it is heated to 140° for ten hours with dilute hydrochloric acid, naphthazine, $C_{20}H_{12}N_2$, is formed.

β-Naphthylsemithiocarbazide, $C_{10}H_7.NH.NH.CS.NH_2$, is prepared by heating an alcoholic solution of β-naphthylhydrazine hydrochloride and ammonium thiocyanate. It forms crystals,

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[1] Schlieper, *Annalen*, **236**, 174.

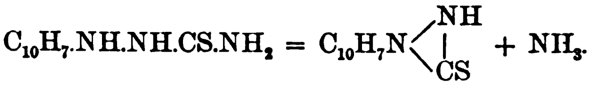
[2] Steche, *Annalen*, **242**, 367.

[3] Pinner, *Ber.* **21**, 1222.

[4] Hauff, *loc. cit.* See also Hillringhaus, *Ber.* **21**, 2656.

melting at 201—202°, and is insoluble in water, slightly soluble in cold alcohol, and readily soluble in aniline.

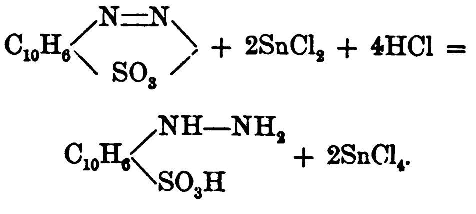
Naphthylthiocarbizine, $C_{10}H_8N_2CS$, is formed when the thiosemicarbazide is heated with hydrochloric acid to 130—140°:



$$C_{10}H_7.NH.NH.CS.NH_2 = C_{10}H_7N\left\langle\begin{matrix} NH \\ | \\ CS \end{matrix}\right. + NH_3.$$

It crystallizes from dilute alcohol in pearly plates, melts at 253—254°, and differs from the preceding compound in not reducing either Fehling's solution or mercuric oxide. When its alcoholic solution is treated with bleaching powder solution, it behaves in a similar manner to phenylthiocarbizine, a violet precipitate being produced, which dissolves in sulphuric acid, forming a dark blue, slightly greenish-coloured liquid, which is decolourized by water (Hauff).

1 : 4-*Naphthylhydrazinesulphonic acid*, $C_{10}H_6(SO_3H)N_2H_3$, is formed by the action of stannous chloride on a solution of 1 : 4-diazonaphthalenesulphonic acid:



$$C_{10}H_6\left\langle\begin{matrix} N{=}N \\ SO_3 \end{matrix}\right\rangle + 2SnCl_2 + 4HCl =$$

$$C_{10}H_6\left\langle\begin{matrix} NH{-}NH_2 \\ SO_3H \end{matrix}\right. + 2SnCl_4.$$

It forms fascicular groups of small white needles, which are slightly soluble in hot water, more readily in hot hydrochloric acid. Fehling's solution is immediately reduced by it on warming. The *sodium salt*, $C_{10}H_6(N_2H_3)SO_3Na + 4H_2O$, crystallizes from hot water in well-developed, compact plates.

1 : 4'-*Naphthalenehydrazinesulphonic acid* forms glittering plates or groups of needles, and is somewhat more freely soluble in water and hydrochloric acid than the 1 : 4-compound. It also reduces Fehling's solution and forms a *sodium salt*, $2C_{10}H_6(N_2H_3)SO_3Na + 7H_2O$, which crystallizes in white, lustrous needles.

1 : 1'-*Naphthalenehydrazinesulphonic acid* is only slightly soluble in hot water, and separates on cooling in slender, silky plates, which show a play of colours under the microscope.

The *sodium salt*, $C_{10}H_6(N_2H_3)SO_3Na$, forms yellow, lustrous microscopic tablets, and is almost insoluble in water, whilst the potassium salt is moderately soluble and the ammonium salt very readily soluble, so that the last two can be used to detect the presence of sodium salts in neutral solutions. A cold saturated solution of the potassium salt, for example, produces a precipitate even in a solution of common salt diluted with 20 parts of water.[1]

THE AZOCOMPOUNDS OF NAPHTHALENE.

2666 *a-a-Azonaphthalene*, $C_{10}H_7N{=}NC_{10}H_7$, is formed when 1 part of *a*-amidoazonaphthalene is dissolved in 100 parts of alcohol of 95 per cent., and 5 parts of sulphuric acid and the calculated amount of sodium nitrite solution gradually added to the hot liquid. The mixture is then boiled for some time, and the azonaphthalene precipitated with water. It is then dissolved in aniline, from which it separates on the careful addition of alcohol in steel-blue crystals, whilst it crystallizes from glacial acetic acid in alizarin-red needles with a bluish dichroism. It melts at 190°, and readily sublimes in yellow plates, which become cinnabar-red when rubbed. It dissolves in alcohol, &c., with a deep orange-red colour, and forms a pure blue solution in sulphuric acid, from which it is precipitated by water. If the sulphuric acid solution be heated to about 180° it becomes coloured violet and takes a splendid brick-red fluorescence.

a-a-Hydrazonapththalene, $C_{10}H_7NH = NHC_{10}H_7$, is obtained by adding zinc dust to a boiling alcoholic caustic soda solution in which finely divided azonaphthalene is suspended, until the mixture becomes colourless. It crystallizes from hot benzene in colourless, lustrous plates, melts at 275°, and does not alter in the air after drying, but is reoxidized to azonaphthalene in alcoholic solution.[2] Acids convert it into two diamidodinaphthyls, $C_{20}H_{12}(NH_2)_2$, in the same manner as hydrazobenzene is converted into two diamido-diphenyls (Part III., p. 357). It is partially converted into *a*-naphthylamine when heated to 130° with alcoholic ammonium sulphide.

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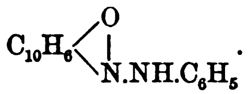
[1] Erdmann, *Annalen*, **247**, 333.

[2] Nietzki and Goll, *Ber.* **18**, 297 and 3252.

α-β-Azonaphthalene was obtained by Nietzki and Göttig from α-β-amidoazonaphthalene. It crystallizes from glacial acetic acid in dark brown plates with a steel-blue reflection, melts at 136°, and forms a violet-coloured solution in sulphuric acid.[1]

Benzeneazo-α-naphthol, $C_6H_5N{=}NC_{10}H_6.OH$, was prepared by Typke by mixing an aqueous solution of diazobenzene nitrate with an alkaline solution of α-naphthol.[2] According to Liebermann, 144 grms. of α-naphthol and 40 grms. of caustic soda are dissolved in 10—15 litres of water and hydrochloric acid added to the well-stirred liquid to precipitate the naphthol as a finely-divided flocculent mass. A tolerably concentrated solution of 129 grms. of aniline hydrochloride is then added to the neutral liquid, the whole cooled with ice, and a solution of 70 grms. of sodium nitrite in 280 cc. of water added, the liquid being stirred for 15—30 minutes after the addition of the nitrite.[3] The same compound is also formed when an aqueous solution of phenylhydrazine hydrochloride is added to α-naphthoquinone suspended in glacial acetic acid, whereas the formation of *α-naphthoquinone hydrazide* would have been expected, the constitution of which is represented by one of the following formulæ :

$$C_6H_5NH.N{=}C_{10}H_6O$$



$$C_{10}H_6\left\langle\begin{array}{l}O\\ |\\ N.NH.C_6H_5\end{array}\right. .$$

This substance must either undergo molecular change into benzeneazo-α-naphthol, or else be tautomeric, as indeed its reactions seem to indicate.[4]

Benzeneazo-α-naphthol is freely soluble in hot glacial acetic acid, sparingly in hot alcohol, from which it crystallizes in small dark needles with a bluish metallic lustre, whereas it separates from hot benzene, in which it is also only sparingly soluble, in flat needles or plates with a fine metallic lustre, which transmit red light. It melts and froths up at 206°, and forms reddish-brown solutions in caustic soda, ammonia, and baryta water. Its alkali salts separate out on the evaporation of solutions containing an excess of alkali as resinous masses, which gradually become crystalline.

Benzeneazo-α-naphthol methyl ether, $C_6H_5N_2C_{10}H_6.OCH_3$, is obtained by heating the sodium salt with methyl iodide. It

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[1] Nietzki and Göttig, *Ber* **20**, 612.

[2] *Ber.* **10**, 1576.

[3] *Ber.* **16**, 2858.

[4] Zincke and Bindewald, *Ber.* **17**, 3026.

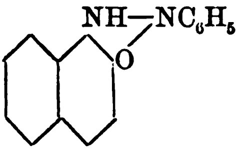
forms granular aggregates of small crystals, whilst the *ethyl ether* crystallizes in brownish-yellow, long, lustrous needles.

Benzeneazo-α-naphthol forms a violet-blue solution in sulphuric acid and combines with acids to form unstable salts, in which it is probably present as the phenylhydrazone group. The *hydrochloride*, $C_6H_5(NH_2Cl)NC_{10}H_6O + 6H_2O$, crystallizes from alcohol in small, bluish needles with a metallic lustre, and from glacial acetic acid in long matted needles with a golden-green surface lustre.

Benzeneazo-ar-tetrahydro-α-naphthol, $C_6H_5.N_2.C_{10}H_{10}(OH)$, is prepared from diazobenzene chloride and an alkaline solution of the naphthol; it crystallizes from dilute alcohol in beetle-green tablets with a metallic lustre. The *sodium salt* of its *sulphonic acid*, prepared from sulphanilic acid, is soluble in water, from which it crystallizes in small plates with a bronze lustre.[1]

Benzeneazo-β-naphthol was prepared by Liebermann in a similar manner to the α-compound; it crystallizes from hot alcohol when the solution is rapidly cooled in long plates with a golden-red lustre, and on gradually cooling in long needles with a dark beetle-green lustre. It melts at 134°, and can be distilled and sublimed in small quantities. It differs from the α-compound in being insoluble in aqueous alkalis, but dissolves in strong acids; the solution in hot hydrochloric acid deposits beetle-green needles on cooling, which lose acid and become red on exposure to the air. It forms a magenta-coloured solution in sulphuric acid. Stannous chloride and hydrochloric acid reduce it to aniline and amido-β-naphthol.

As it does not possess the properties of a phenol, Liebermann assigns to it the following constitution:



It was proved not to be identical with *β-naphthoquinonephenylhydrazone* by Zincke and Bindewald, as the latter substance crystallizes from hot alcohol in long, deep red, golden lustrous needles, melts at 138°, and forms a violet-red solution in sul-

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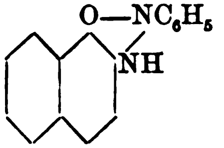
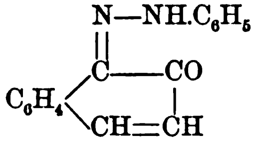
[1] Bamberger and Bordt, *Ber.* **23**, 216.

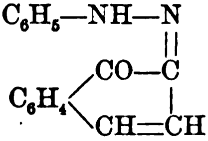
phuric acid. They therefore assume that this compound has the constitution:



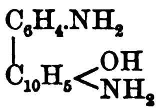
According to this view the isomerism is due to the different positions of the substituted groups, and this was proved by Zincke and Rathgen, who showed that whereas benzeneazo-β-naphthol is converted by reduction into α-amido-β-naphthol, β-naphthoquinonephenylhydrazone passes into β-amido-α-naphthol, whilst nitric acid converts the former into dinitro-β-naphthol and the latter into dinitro-α-naphthol.[1]

If the quinones are looked upon as ketones the isomerism of these two compounds will be expressed by the following formulæ:





Weinberg, however, found that benzeneazo-β-naphthol yields an ethyl ether on heating with ethyl bromide and caustic potash,[2] and it has also been found that when it is boiled for a considerable time with acetic anhydride the *acetate*, $CH_3.CO.OC_{10}H_6N_2C_6H_5$, is formed, which crystallizes from alcohol in deep orange-coloured scales and melts at 117°.[3] The acetyl group is proved not to be combined with nitrogen by the fact that no acetanilide is formed on reduction, but the acetyl group is removed, and aniline accompanied by amido-β-naphthol obtained. A portion of the benzenehydrazo-β-naphthol, $HO.C_{10}H_6.NH.NH.C_6H_5$, which is first formed, is simultaneously converted into the isomeric diamidophenylnaphthol, which has the following constitution:



$$\begin{array}{l} C_6H_4.NH_2 \\ | \\ C_{10}H_5{<}\begin{smallmatrix}OH\\ NH_2\end{smallmatrix} \end{array}$$

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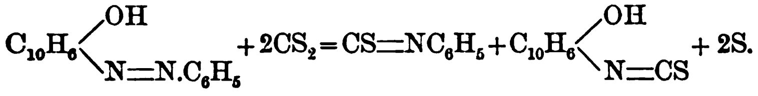
[1] *Ber.* **19**, 2482.

[2] *Ber.* **20**, 3171.

[3] Meldola and East, *Journ. Chem. Soc.* 1888, **1**, 466; Meldola and Morgan, *Journ. Chem. Soc.* 1889, **1**, 114 and 603.

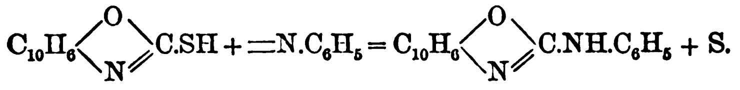
Benzeneazo-β-naphthol can therefore also react as a hydroxyl compound.

It has already been mentioned that 1-thiocarbamido-β-naphthol is obtained together with carbanilido-β-naphthol when benzeneazo-β-naphthol is heated with carbon disulphide. This reaction is most simply explained by assuming that the benzeneazonaphthol also reacts in this case as a hydroxyl derivative:



$$C_{10}H_6\begin{cases}OH\\N{=}N.C_6H_5\end{cases} + 2CS_2 = CS{=}NC_6H_5 + C_{10}H_6\begin{cases}OH\\N{=}CS\end{cases} + 2S.$$

The latter compound is then converted into thiocarbamidonaphthol, which reacts with the aniline residue, carbanilidonaphthol being formed:



2-Thiocarbamido-α-naphthol and carbanilido-α-naphthol can moreover be obtained by this method from β-naphthoquinonephenylhydrazone, so that this substance can also react as a naphthol.

Benzeneazo-2 : 2′-dihydroxynaphthalene, $C_6H_5.N_2.C_{10}H_5(OH)_2$, is prepared by the action of diazobenzene chloride on a solution of the dihydroxynaphthalene in caustic soda. It forms splendid, thick, blackish-green needles, with a strong metallic lustre, is readily soluble in hot alcohol and benzene, and melts at 220°. Its *acetate* forms steel-blue needles, melting at 181°, and its *ethyl ether* dark green cubical crystals with a strong metallic lustre, which melt at 137°.[1]

Benzeneazodihydroxynaphthalene or *Phenylazonaphthoresorcinol*, $C_6H_5.N_2.C_{10}H_5(OH)_2$, is formed when phenylhydrazine is added to a solution of hydroxynaphthoquinone in dilute alcohol. It crystallizes in yellowish-red, lustrous needles, which melt and decompose with considerable frothing at 218—220°.[2] Zincke and Thelen consider that this substance is *hydroxynaphthoquinonephenylhydrazone*, $C_6H_5NH.N = C_{10}H_5(OH)$, since dilute alkalis precipitate salts from its solution which only contain one atom of metal. These salts crystallize from alcohol in slender red

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[1] Clausius, *Ber.* **23**, 523.

[2] Zincke and Thelen, *Ber.* **17**, 1809; **21**, 2200; Kostanecki, *Ber.* **22**, 3163.

needles; the *barium* salt, $(C_{16}H_{12}N_2O_2)_2Ba + 10H_2O$, separates from a large amount of hot water in yellowish-brown transparent plates with a golden lustre or long flat red plates, which become almost black on heating without losing their lustre.

The *ethyl ether*, $C_{10}H_{11}N_2O(OC_2H_5)$, is formed by heating the potassium salt with ethyl bromide and alcohol, and crystallizes in yellowish-red needles, melting at 172—173°.

Zincke and Thelen, by boiling benzeneazodihydroxynaphthalene with acetic anhydride obtained the *monacetate*, $C_6H_5.N_2.C_{10}H_5(O.CO.CH_3)OH$, which crystallizes in red, lustrous needles, and melts at 178—179°; whereas Kostanecki found that when sodium acetate is also added the *diacetate*, $C_6H_5.N_2.C_{10}H_5(OCO.CH_3)_2$, is formed. This substance crystallizes from alcohol in rosette-shaped aggregates of needles, melting at 122—123°.

Nitrosophenylazonaphthoresorcinol, $C_6H_5.N_2.C_{10}H_4O(NOH)OH$, was obtained by Kostanecki by pouring a faintly alkaline solution of phenylazonaphthoresorcinol and sodium nitrite into dilute hydrochloric acid. It crystallizes from dilute acetic acid in lustrous brownish-red plates, which are almost insoluble in water and alkalis, and, probably for this reason, dye mordanted fabrics only very faintly. On reduction with tin and hydrochloric acid it is split up into aniline and amidotrihydroxynaphthalene, which is rapidly oxidized to naphthalenic acid.

β-Naphthaleneazo-β-naphthol, $C_{10}H_7.N_2.C_{10}H_6.OH$, has been obtained by the diazo-reaction from β-amidoazonaphthalene, and is also formed by the action of β-diazonaphthalene chloride on β-naphthol. It dissolves readily in warm aniline, and separates on the addition of alcohol in elegant reddish-brown needles, which melt at 176°, and sublime in golden lustrous needles. Its solution in sulphuric acid is coloured reddish-violet.[1]

2667 *Benzeneazo-a-naphthylamine*, $C_6H_5.N_2.C_{10}H_6.NH_2$, was obtained by Griess, who termed it diazobenzene-amidonaphthol, by adding a solution of diazobenzene nitrate to an alcoholic solution of α-naphthylamine.[2] The free base, liberated by caustic potash, crystallizes in ruby-red, lustrous prisms, and forms a yellow solution in alcohol, which is coloured a bright violet by acids.

Benzeneazo-a-naphthylamine hydrochloride, $C_{16}H_{13}N_3$, HCl, forms lustrous steel-blue needles, and imparts a port wine colour to water.

Benzeneazo-a-naphthylamine nitrate, $C_{16}H_{13}N_3$, NO_3H, crystallizes from hot alcohol in splendid grass-green prisms, which

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[1] Nietzki and Goll, *Ber.* **19**, 1281.

[2] *Annalen*, **137**, 60.

appear ruby-red by transmitted light and are scarcely soluble in water.

Benzeneazo-a-naphthylamine sulphate, $(C_{16}H_{13}N_3)_2SO_4H_2 + 4H_2O$, forms black, microscopic needles, which are only very slightly soluble in water, and form a carmine-red coloured solution in alcohol.[1]

Benzeneazotetrahydro-a-naphthylamine, $C_6H_5.N_2.C_{10}H_{10}.NH_2$, is obtained by adding *ar*-tetrahydro-*a*-naphthylamine hydrochloride to a solution of diazobenzene chloride. The *hydrochloride* crystallizes from alcohol in steel-blue needles, which form a port wine coloured solution in alcohol.[2]

a-Naphthylamineazobenzenesulphonic acid, $C_6H_4(SO_3H)N_2.C_{10}H_6.NH_2$, is formed when equivalent amounts of *p*-diazobenzenesulphonic acid and *a*-naphthylamine hydrochloride are dissolved in water and the solution heated to boiling after standing for some time. It crystallizes in brownish-violet microscopic needles, only slightly soluble even in boiling water. Its salts crystallize well, and form aqueous solutions which even when dilute are coloured orange-red by caustic potash, and magenta by mineral acids.

The formation of this acid serves as a reaction for nitrous acid, which is even more delicate than that given by *m*-diamidobenzene. When a solution which contains only a mere trace of a nitrite is treated with a little sulphuric acid and sulphanilic acid, and after about ten minutes a few drops of a colourless solution of naphthylamine sulphate added, the liquid soon becomes coloured a fine red.

"It forms a very striking experiment to detect the presence of nitrous acid in saliva in this way, and is well fitted by its simplicity to serve as a lecture demonstration. The test should be carried out in a tall glass cylinder placed on a sheet of white paper near a window, and the saliva should be previously diluted with 5—10 volumes of water. If the reagents mentioned above are then added to it, it soon becomes coloured a deep magenta red."[3]

Tetrahydro-a-naphthylamineazobenzenesulphonic acid has been obtained from *ar*-tetrahydro-*a*-naphthylamine, and forms reddish-brown flakes, with a green metallic lustre, soluble in water with a dark orange-red colour. The *sodium salt* crystallizes in light orange-red tablets, with a diamond lustre (Bamberger and Bordt).

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[1] Weselsky and Benedikt, *Ber.* **12**, 226.

[2] Bamberger and Bordt, *Ber.* **22**, 627.

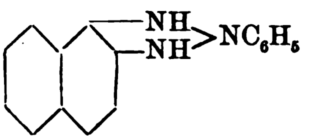
[3] Griess, *Ber.* **12**, 426.

Hydroxybenzeneazo-a-naphthylamine, $C_6H_4(OH)N_2.C_{10}H_6NH_2 + 3H_2O$, is formed when very dilute solutions of phenol, *a*-naphthylamine and potassium nitrite are mixed. It crystallizes in orange-coloured fascicular groups of needles, which lose water on heating, and melt at 170°. Its *sulphate,* $(C_{16}H_{13}N_3O)_2SO_4H_2 + 6H_2O$, forms green needles, and yields a blue solution in alcohol (Weselsky and Benedikt).

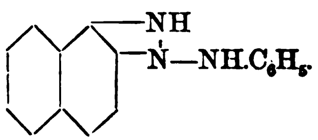
Benzeneazo-β-naphthylamine, $C_6H_5.N_2.C_{10}H_6.NH_2$, is formed when diazobenzene sulphate is brought together with β-naphthylamine in alcoholic solution, and crystallizes from dilute alcohol in light red, long, slender needles, but from absolute alcohol in bright red, rhombic tablets. It melts at 102—104°, and forms a blue solution in sulphuric acid, from which it is precipitated by water. Alcoholic hydrochloric acid dissolves it with production of a dark bluish-red solution. These colourations are probably due to the formation of unstable acid salts. On boiling with dilute sulphuric acid it decomposes into phenol and β-naphthylamine, and is reduced in alcoholic solution by zinc dust and acetic acid, with formation of 1 : 2-diamidonaphthalene and aniline.[1] It is a weak base, the salts of which are decomposed by water and alcohol, and form violet solutions in an excess of acid. The *hydrochloride,* $C_{16}H_{13}N_3$, HCl, separates out in yellowish needles on the addition of hydrochloric acid to a solution of the base in acetic acid.[2]

When an acetic acid solution of the base is heated with acetic anhydride, *benzeneazo-β-acetonaphthalide,* $C_6H_5.N_2.C_{10}H_6NH(CO.CH_3)$, is formed; it crystallizes from alcohol in small red needles, melting at 152—153°, and is reconverted into benzeneazo-β-naphthylamine by boiling with alcoholic potash.

This compound was formerly termed benzenediazo-β-naphthylamine, because it so easily decomposes into phenol and β-naphthylamine. It is, however, much too stable for a diazo-compound, and, as is shown by its oxidation product, which is described below, can be most easily looked upon as *benzenehydrazimidonaphthalene,* with the following constitution, which readily explains the formation of 1 : 2-diamidonaphthalene :



or



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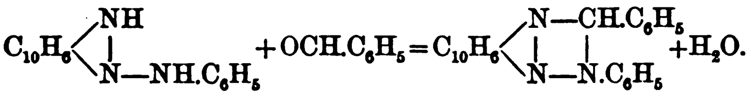
[1] Lawson, *Ber.* **18**, 796.

[2] Zincke and Lawson, *Ber.* **20**, 2896.

The fact that it forms diazo-compounds, and must therefore contain the amido-group, speaks against this view, and it is probable that this substance presents another instance of tautomerism.

On oxidation with chromic acid, benzeneazo-β-phenylnaphthylamine is converted into an ammonium base of the formula $C_{22}H_{16}N_3OH$, the constitution of which is not known. When the chloride of this base is heated with caustic potash, benzeneazo-β-phenylnaphthylamine is regenerated, and a base of the formula $C_{22}H_{15}N_3O$ formed.[1]

When benzeneazo-β-naphthylamine is heated to 140° with benzaldehyde, combination takes place, and a *triazine derivative* is formed:



This substance separates from alcohol as a snow-white microcrystalline mass, melting at 193°.[2]

It is also formed when a solution of diazobenzene chloride is mixed with a cold alcoholic solution of benzylidene-β-naphthylamine, water and ammonia then added, and the precipitated substance heated with acetic acid for a few minutes.[3]

Benzeneazobiazonaphthalene sulphate, $C_6H_5.N_2.C_{10}H_6.N_2.SO_4H$, is formed when the azo-compound is dissolved in glacial acetic acid, sulphuric acid added, and nitrogen trioxide passed through the liquid. On the addition of ether and absolute alcohol it is precipitated in brown needles.

The *chloride* is obtained in a similar manner; when bromine water is added to its solution, the *perbromide*, $C_6H_5.N_2.C_{10}H_6.NBr.NBr_2$, is formed in small, light-red needles.

If water be added to the acetic acid solution of the chloride, nitrogen is evolved and benzeneazo-β-naphthol separates out.

Benzeneazobiazonaphthalene hydride, $C_6H_5.N_2.C_{10}H_6N_2H$, is obtained by the addition of stannous chloride to the cooled solution of the chloride, and crystallizes from alcohol in colourless lustrous needles, melting at 204—205°. It is converted by bromine into the *perbromide*, and by nitric acid into the *diazo-*

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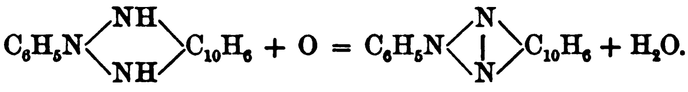
[1] Zincke and Lawson, *Ber.* **20**, 1172; Zincke, *Ber.* **23**, 1315.

[2] Goldschmidt and Rosell, *Ber.* **23**, 506.

[3] Meldola, *Journ. Chem. Soc.* 1890, **1**, 328.

nitrate; on heating with acetyl chloride the compound $C_6H_5.N_2.C_{10}H_6.N_2.CO.CH_3$ is formed, which crystallizes from alcohol in very lustrous needles, melting at 137—139° (Zincke and Lawson).

Pseudo-phenylazimidonaphthalene, $C_6H_5N_3C_{10}H_6$, is prepared by dissolving benzeneazo-β-naphthylamine in hot acetic acid, and gradually adding a concentrated aqueous solution of chromium trioxide:

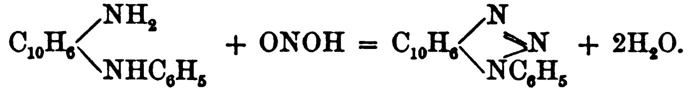


$$C_6H_5N{<}\begin{matrix}NH\\NH\end{matrix}{>}C_{10}H_6 + O = C_6H_5N{<}\begin{matrix}N\\|\\N\end{matrix}{>}C_{10}H_6 + H_2O.$$

It crystallizes from hot glacial acetic acid in slender white needles united in nodular masses, and melts at 107—108°. Concentrated sulphuric acid dissolves it without decomposition, and reducing agents are also without action upon it even on heating.[1]

Benzeneazo-β-phenylnaphthylamine, $C_6H_5.N_2.C_{10}H_6.NH(C_6H_5)$, is obtained by the action of diazobenzene chloride on phenyl-β-naphthylamine and by that of aniline on phenyl-β-naphthylnitrosamine.[2] It crystallizes from hot acetic acid in small lustrous deep-red needles, melting at 141—142°. Stannous chloride reduces it to aniline and 1 : 2-phenyldiamidonaphthalene.

Phenylazimidonaphthalene, $C_{10}H_6.N_3C_6H_5$, is obtained by the action of sodium nitrite on α-amido-β-phenylnaphthylamine suspended in glacial acetic acid:[3]



$$C_{10}H_6{<}\begin{matrix}NH_2\\NHC_6H_5\end{matrix} + ONOH = C_{10}H_6{<}\begin{matrix}N\\ \quad{>}N\\NC_6H_5\end{matrix} + 2H_2O.$$

It crystallizes from hot alcohol in thick white needles, and from glacial acetic acid in prisms, with a vitreous lustre, is almost insoluble in water, and melts at 149—150°. It dissolves with difficulty in concentrated hydrochloric acid, but is at once reprecipitated by the addition of water. This substance readily forms addition products with the alcoholic iodides, yielding ammonium bases which possess the characteristic properties

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[1] Zincke, *Ber.* **18**, 3132.

[2] Zincke and Lawson, *Ber.* **20**, 1167; Henriques, *Ber.* **17**, 2671.

[3] Zincke and Campbell, *Annalen*, **255**, 343.

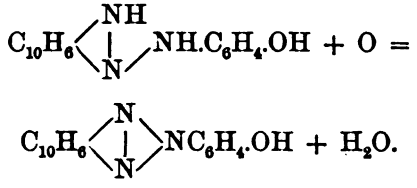
of this class of compounds. The following have been prepared, together with several of their derivatives:

	Melting-point.
Methylphenylnaphthaleneazammonium iodide, $C_{10}H_6.N_3(C_6H_5)(CH_3)I$, colourless needles	196°
Ethylphenylnaphthaleneazammonium iodide, $C_{10}H_6.N_3(C_6H_5)(C_2H_5)I$, almost colourless needles .	192°

o-Hydroxybenzeneazo-β-naphthylamine, $C_6H_4(OH)N_2.C_{10}H_6.NH_2$ is formed when a concentrated aqueous solution of *o*-diazophenol is mixed with an alcoholic solution of β-naphthylamine. It crystallizes from alcohol in slender red needles, and from benzene in well developed dark-red plates with a green metallic lustre, which melt at 192—193°, and are insoluble in water but dissolve in alkalis. When its solution in acetic acid is heated with acetic anhydride, the compound $C_6H_4(OH)N_2C_{10}H_6.NH(CO.CH_3)$ is formed, which crystallizes on cooling in small red needles, melting at 198°. A second acetyl group could not be introduced. The behaviour of the oxidation product which is described below shows that the acetyl group is combined with the nitrogen atom of the amido-group.

When *o*-hydroxybenzeneazo-β-naphthylamine is heated to 150—160° with concentrated hydrochloric acid, it decomposes into nitrogen, catechol and β-naphthylamine, and it is converted into 1:2-diamidonaphthalene by reduction with zinc dust and acetic acid.[1]

Pseudo-o-hydroxyphenylazimidonaphthalene, $C_6H_4(OH)N_3C_{10}H_6$, is prepared by the addition of lead dioxide to a hot alkaline solution of the foregoing compound, which must therefore be looked upon as *o-hydroxyhydrazimidonaphthalene*:



It crystallizes from alcohol in white silky needles, soluble in caustic soda solution, and is not attacked by acetic anhydride or acetyl chloride even on heating.

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[1] Sachs, *Ber.* **18**, 3125.

p-Hydroxybenzeneazo-β-naphthylamine crystallizes from glacial acetic acid or benzene in flat red prisms, melting at 192—193°. Its *acetyl compound* forms red lustrous needles, which melt at 218°. On decomposition with hydrochloric acid it yields quinol and β-naphthylamine.

p-Methoxybenzeneazo-β-naphthylamine, $C_6H_4(OCH_3)N_2.C_{10}H_6.NH_2$, is prepared from diazo-anisoïl, and crystallizes from alcohol in dark red monosymmetric prisms, with a metallic lustre, which melt at 133°. Its *acetyl compound* forms red, strongly lustrous needles, melting at 198—199°.

Pseudo-p-hydroxyphenylazimidonaphthalene crystallizes from glacial acetic acid either in slender asbestos-like needles, hard opaque nodular masses, or thick clear pointed needles. On recrystallization the needles are converted into nodular masses and these finally into the pointed needles. All three forms melt at 198—199°. On boiling with acetic anhydride, the compound $C_6H_4(OC_2H_3O)N_3C_{10}H_6$ is formed, which crystallizes in long silky needles or thin plates, and melts at 164—165°.

The following azo-compounds have been prepared by the action of the diazo-chlorides on the respective bases. Like benzeneazo-β-phenylnaphthylamine they are all converted by oxidation with chromic acid into ammonium bases.[1]

	Melting-point.
p-Tolueneazo-β-phenylnaphthylamine, $C_{10}H_6(NHC_6H_5)N_2C_7H_7$, coarse, deep-red, lustrous needles	120°
Benzeneazo-β-tolylnaphthylamine, $C_{10}H_6(NHC_7H_7)N_2C_6H_5$, long, deep-red, lustrous needles	152°
Benzeneazo-αβ-dinaphthylamine, $C_{10}H_6[NH.C_{10}H_7(\alpha)]N_2C_6H_5$, woolly red needles	167°
α-Naphthaleneazo-β-phenylnaphthylamine, $C_{10}H_6(NHC_6H_5)N_2C_{10}H_7$, dark-red, lustrous needles	140°
β-Naphthaleneazo-β-phenylnaphthylamine, $C_{10}H_6(NHC_6H_5)N_2C_{10}H_7$, long, slender, brick-red needles	154—155°
Benzeneazo-ββ-dinaphthylamine, $C_{10}H_6(NHC_{10}H_7)N_2C_{10}H_7$, red needles and plates	139°

In addition to these the following have been described by Fischer and Hepp:[2]

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[1] Matthes, *Ber.* **23**, 1325.

[2] *Annalen*, **256**, 256.

	Melting-point.
Benzeneazo-ethyl-α-naphthylamine, $C_{10}H_6(NHC_2H_5)N_2C_6H_5$, red tablets or columns .	76°
Benzeneazophenyl-α-naphthylamine, $C_{10}H_6(NHC_6H_5)N_2C_6H_5$, flat scarlet red plates . .	151°
Benzeneazo-*p*-tolyl-α-naphthylamine, $C_{10}H_6(NHC_7H_7)N_2C_6H_5$, red plates with blue surface lustre	144°
Benzeneazo-α-dinaphthylamine, $C_{10}H_6(NHC_{10}H_7)N_2C_6H_5$, short orange-red columns	128°

2668 *α-Amidoazonaphthalene*, $C_{10}H_7.N_2.C_{10}H_6.NH_2$, was obtained by Church and Perkin, who named it azodinaphthylamine, by adding a solution of 1 molecule of caustic potash and 1 molecule of sodium nitrite to a solution of 2 molecules of α-naphthylamine hydrochloride.[1] It is also formed when nitrogen trioxide is passed into a hot alcoholic solution of α-naphthylamine, or when the latter is heated with sodium stannate.[2] In order to prepare it, a molecule of potassium nitrite is added to a moderately dilute solution of α-naphthylamine hydrochloride, and the solution then made faintly alkaline by sodium carbonate;[3] or solutions of equal molecules of α-diazonaphthalene chloride and α-naphthylamine hydrochloride are mixed, and the liquid neutralized with sodium carbonate.[4]

α-Amidoazonaphthalene is insoluble in cold, slightly soluble in hot water, crystallizes from hot alcohol in well developed reddish-brown needles with a green metallic lustre, melts at 180°, and can be volatilized almost without decomposition. It dyes silk and wool a fine orange-red, and is converted by the action of tin and hydrochloric acid into α-naphthylamine and 1 : 4-diamidonaphthalene. It forms a dark green solution, the colour of which is changed to deep blue by the addition of a trace of water, and into a rich, deep violet, by a further quantity. This last colouration is also produced when hydrochloric acid or any other strong acid is added to the orange-red alcoholic solution of the base; alkalis or a large excess of water restore the original colour. This behaviour depends upon the formation of different salts, and is best shown by dipping silk which has been

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[1] *Annalen*, **129**, 104; see also Chapman, *Annalen*, **140**, 326; Lecco, *Ber.* **7**, 1290.

[2] Martius, *Zeitsch.* **1866**, 188.

[3] Nietzki, *Ber.* **18**, 297.

[4] Friedländer, *Ber.* **22**, 589.

dyed with the base into hydrochloric acid, and then washing for a considerable time with water. When a small quantity of hydrochloric acid is added to a cold alcoholic solution of the base, the latter retains its orange-red colour, and on standing deposits flat, golden-brown lustrous prisms of $(C_{20}H_{15}N_3)_4HCl$. If, however, a tenth of a volume of strong hydrochloric acid diluted with an equal volume of alcohol be added to a hot alcoholic solution of the base, the liquid becomes carmine-red coloured, and dark purple-red crystals of $C_{20}H_{15}N_3HCl$ separate out on cooling; finally, when hydrochloric acid is used in excess yellowish-brown crystals, with a greenish lustre, having the composition $C_{20}H_{15}N_3.2HCl$, are deposited. The last two salts are partially converted into the one first described by recrystallization from alcohol.

When sulphuric acid is added to either a cold or a hot solution of the base, the *sulphate*, $(C_{20}H_{15}N_3)_2SO_4H_2$, separates from the violet liquid in greenish-brown crystals, with a golden lustre, which form a red solution in alcohol. The acid salt could not be obtained in crystals.

Tetrahydro-a-amidoazonaphthalene, $C_{10}H_{11}.N_2.C_{10}H_6.NH_2$, was obtained by the action of *a*-naphthylamine on diazotized tetrahydro-*a*-naphthylamine, and crystallizes from alcohol in slender, brick-red needles, which melt at 135°, and form a red solution in alcohol (Bamberger and Bordt).

a-β-Amidoazonaphthalene is formed when *β*-naphthylamine hydrochloride is triturated with the necessary amount of hydrochloric acid and 30 parts of water, sodium nitrite added until everything has dissolved, and a solution of *a*-naphthylamine hydrochloride then poured in; on standing for twelve hours the hydrochloride separates out in brownish-violet needles. The free base crystallizes from alcohol in yellowish-brown needles, which melt at 152°, have no metallic lustre, and are more soluble than the *a*-compound. It forms a violet-coloured solution in sulphuric acid, and its salts have a redder shade than those of the *a*-compound.[1]

β-Amidoazonaphthalene is formed by the action of *β*-diazonaphthalene chloride on *β*-naphthylamine, and crystallizes from aniline or xylene in red needles, melting at 156°, which form violet-coloured solutions in strong acids. It is a much weaker base than the *a*-compound, and is decomposed by the action of stannous chloride into *β*-naphthylamine and 1:2-diamido-

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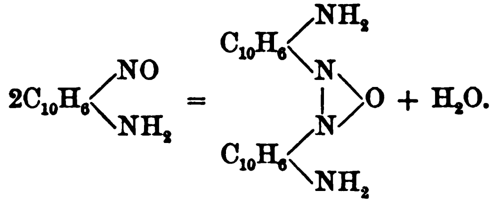
[1] Nietzki and Göttig, *Ber.* **20**, 612.

naphthalene. Its *acetyl compound* crystallizes from benzene in prisms melting at 218°.[1]

Its diazo-chloride is only stable in acetic acid solution, and is converted by the addition of water into β-naphthaleneazo-β-naphthol. Stannous chloride reduces the diazo-chloride to *diazonaphthyl hydride*, $C_{10}H_7.N_2C_{10}H_6N_2H$, which crystallizes in needles melting at 202—204°, and is converted by nitric acid into the diazo-nitrate, and by bromine into the perbromide (Zincke and Lawson).

β-Amidoazoxynaphthalene, $(C_{10}H_6.NH_2)_2N_2O$, is formed when an alcoholic solution of β-amido-α-nitrosonaphthalene (p. 243), acidified with acetic acid, is allowed to stand with phenylhydrazine:



It crystallizes from dilute alcohol in matted red needles, melts at 121—122°, and readily dissolves in concentrated sulphuric acid, from which it is reprecipitated by water.[2]

AZO-COLOURING MATTERS.

2669 The history of these substances has already been briefly sketched (Part III., p. 359). Their preparation received a new impetus when Caro in 1877, by the application of naphthionic acid in place of sulphanilic acid, which had up to that time been employed, prepared the first commercially valuable red dye—known by the name of *fast red.* The use of other sulphonic acids of the naphthols and naphthylamines, especially of the β-compounds, soon led to the preparation of a great number of azo-dyes, whose shades run over the whole gamut of colour between scarlet and the deep shade of port wine.

In the same year Caro and Schraube showed that the diamidoazo-compounds can be converted into diazo-compounds

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[1] Lawson, *Ber.* **18**, 2422; Nietzki and Goll, *Ber.* **19**, 1281.

[2] Harden, *Annalen*, **255**, 160.

which in their turn combine with phenols, &c., to form disazo-compounds *i.e.* containing the group —N=N— twice over; and such disazo-colours, on account of their great dyeing power, soon received technical application. The first example is Biebrich scarlet, discovered by Nietzki, and many others are now known, varying in colour from light-red to bluish-black.

Only the most important colouring matters derived from naphthalene will here be described. For further information reference may be had to the works cited below.[1]

a-Naphtholazobenzene-m-sulphonic acid, $C_{10}H_6(OH).N_2.C_6H_4.SO_3H$, was obtained by Griess by mixing alcoholic solutions of *a*-naphthol and *m*-diazobenzenesulphonic acid, and adding hydrochloric acid to the orange-red solution. It crystallizes in very small, blackish-green plates, which, when rubbed to powder on a watch-glass, appear golden-yellow by reflected and violet by transmitted light; it is moderately soluble in hot alcohol and water.[2] Its *sodium salt* is known as *Metanil-orange I.*

The isomeric substance prepared from *β*-naphthol forms small needles, which show a golden lustre when powdered, and appear red by transmitted light. Its *sodium salt* is known as *Metanil-orange II.*

a-Naphtholazobenzene-p-sulphonic acid is precipitated by hydrochloric acid from its sodium salt in black plates.[3] This salt, which was discovered by Roussin and Witt, is known by the names of *a-Naphthol orange*, *Orange I.*, and *Tropæolin* 000, No. 1.[4] It dyes wool and silk in an acid bath a red shade of orange, but has little value as a dye since its colour is changed to carmine-red by alkalis. It is, however, employed for the preparation of *a*-amidonaphthol and *a*-naphthoquinone. On the small scale it can be easily prepared by dissolving 33 grams of *a*-naphthol and 26 grams of caustic potash (fused sticks) in 2·5 litres of water free from lime, and running this in a thin stream into a second solution made up by mixing a solution of 20 grams of potassium nitrite in 800 grams of water with one of 40 grams. of sulphanilic acid and 12 grams of sodium carbonate in 3 litres of water and adding 24 grams of sulphuric acid. On the addition of common salt to the dark-red liquid, the sodium salt

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[1] Schultz, *Chemie des Steinkohlentheers*; Friedländer, *Theerfarbenfabrikation.*

[2] *Ber.* **11**, 2197.

[3] Schultz, *Chemie des Steinkohlentheers*, 2 ed. **2**, 221.

[4] Schultz, *Chemie des Steinkohlentheers*, 2 ed. **2**, 66.

crystallizes out, and can be obtained from boiling water in long red needles.

β-Naphtholazobenzene-p-sulphonic acid occurs in commerce as the sodium salt, under the names of *β-Naphthol orange, Orange II., Tropæolin* 000, *No.* 2; *Mandarin G, Chrysaureïn*, &c., and is prepared in a similar manner to the preceding compound from β-naphthol and sulphonic acid.[1] It crystallizes from hot water in orange-yellow plates, which lose their water of crystallization on drying, and fall to a scarlet-red powder. When concentrated hydrochloric acid is added to the alcoholic solution, the sulphonic acid separates out in hair-like red needles.[2] The commercial product is used for dyeing orange on wool, silk, and cotton, mordanted with aluminium stannate, and it is also employed in conjunction with red colouring matters for scarlet, &c., as well as with indigo-carmine for different shades of brown, olive, &c.

When β-naphthol orange is made into a paste with hot water, a solution of acid sodium sulphite added, and the mixture heated on the water-bath, the colour of the solution changes from brownish-red to yellow, and on the addition of salt a new dye, known as *Narceïn*, $C_{10}H_6(OH)NH—N(SO_3Na)C_6H_4.SO_3Na$, is precipitated in yellow crystals.[3]

Mandarin G R, $C_6H_3(CH_3)(SO_3Na)N_2.C_{10}H_6.OH$, is obtained by the action of *o*-diazotoluenesulphonic acid on an alkaline solution of β-naphthol, and forms a brick-red powder, which dissolves in water with a reddish-yellow colour. It forms a magenta-red solution in sulphuric acid, from which it is separated by water as a yellowish-brown flocculent precipitate.

β-Naphtholazophenolsulphonic acid, $C_{10}H_6(OH)N_2.C_6H_3(OH)SO_3H$, is the first red azo-dye which was brought into the market, and was obtained by Griess by converting *o*-amidophenol-*p*-sulphonic acid into the diazo-compound, and bringing this into a solution of β-naphthol in caustic soda.[4] Hydrochloric acid added to the carmine-red solution precipitates the colouring matter. The sodium salt produces pink or red shades on alumina or tin mordants, which are fast towards light.

Ponceau 4 G B, $C_6H_5.N_2.C_{10}H_5.(OH)SO_3Na$, which is also called *Brilliant orange* or *Croceïn orange*, was first prepared by Griess by the action of diazobenzene nitrate on an alkaline

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[1] For the manufacture see Mühlhäuser, *Dingl. Polytech. Jour.* **264**, 187.

[2] Hofmann, *Ber.* **10**, 1378; Griess, *Ber.* **11**, 2198; Miller, *Ber.* **13**, 268.

[3] Cf. Spiegel, *Ber.* **18**, 1479; Nölting, *Monit. Scient.* **1886**, 319, &c.

[4] German Patent, No. 3224, March 12th, 1878.

solution of β-naphthol-β-sulphonic acid. The free acid crystallizes in reddish-brown needles with a metallic green surface lustre.[1] The commercial *sodium salt* is a fiery red powder, which forms an orange-coloured solution in water.

Azococcin, $C_6H_3(CH_3)_2.N_2.C_{10}H_5(OH)SO_3Na$, is obtained by the action of diazo-xylene on 1 : 4-naphtholsulphonic acid, and is a reddish-brown powder, only sparingly soluble in water, which forms a magenta-red solution in sulphuric acid. It is employed for dyeing silk red, and produces a red on wool which withstands milling.

Scarlet R is formed in a similar manner from β-naphthol-β-sulphonic acid, and occurs in commerce as a cinnabar-red powder which dissolves in water with a yellowish-red and in sulphuric acid with a magenta-red colour. It is employed for dyeing wool, and for the preparation of lacquer colours.

Ponceau 2 R, $C_6H_3(CH_3)_2.N_2.C_{10}H_4(OH)(SO_3Na)_2$, is largely used as a substitute for cochineal, and is prepared from commercial xylidine, which is diazotized with sodium nitrite in hydrochloric acid solution, an ammoniacal solution of sodium β-naphthol-α-disulphonate being then added. It is a red powder, freely soluble in water; concentrated sulphuric acid dissolves it to a red solution which becomes reddish-yellow on dilution with water.

Fast red or *Roccellin*, $C_{10}H_6(OH)N_2.C_{10}H_6SO_3Na$, was discovered in 1877 by Caro and Roussin, and is formed by the action of 1 : 4-diazonaphthalenesulphonic acid on an alkaline solution of β-naphthol. It occurs in commerce as a brownish-red powder, which is sparingly soluble in cold, readily in hot water with a poppy-red colour. It forms a violet-coloured solution in sulphuric acid, which changes to yellowish-brown on dilution. In acid solution it dyes wool and silk very full shades. Cotton must first be mordanted by being passed through sodium stannate and then through alum solution. Fast red can be applied in conjunction with magenta, orange II., naphthol yellow or indigo-carmine, and is used in most cases as a substitute for the red dye-woods and archil.

The free acid is slightly soluble in cold, more readily in hot water, very readily in alcohol, with a blood-red colour, and is precipitated from the boiling solution by hydrochloric acid in reddish-brown needles, which form a blood-red powder.[2] The pure *sodium salt* crystallizes from water in brown needles. The *calcium* and *barium salts* are scarcely soluble in water.

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[1] *Ber.* **11**, 2197

[2] Griess, *Ber.* **11**, 2199.

DISAZO-COLOURING MATTERS.

2670 *Disazobenzene-a-naphthol*, $(C_6H_5N_2)_2C_{10}H_5.OH$, is readily formed when a solution of two molecules of diazobenzene chloride is allowed to run into a solution of one molecule of α-naphthol, which must be kept faintly alkaline; it is deposited after twelve hours as a brown powder. When its solution in aniline is allowed to cool, it separates out as a mass of slender dark-green needles, which are readily soluble in ether and benzene, with difficulty in alcohol, and melt at 183°. It forms a dark-green coloured solution in sulphuric acid. Its constitution is shown by the fact that it is decomposed into aniline and 2 : 4-diamido-α-naphthol by treatment with tin and hydrochloric acid.[1]

Its *sulphonic acid*, $[C_6H_4(SO_3H)N_2]_2C_{10}H_5.OH$, is manufactured in a similar manner from *p*-diazobenzenesulphonic acid and α-naphthol. The *sodium salt* is sold as *Fast brown G*, and is a brown powder which forms a brownish-red solution in water; in which hydrochloric acid produces a bluish-violet precipitate, and caustic soda a cherry-red colouration. The sodium salt forms a violet coloured solution in sulphuric acid, and is decomposed by reduction into sulphanilic acid and 2 : 4-diamido-α-naphthol (Krohn). It is employed for dyeing wool brown, whilst α-naphthol orange, which is obtained from equal molecules of the above compounds, is an orange-yellow colouring matter. The *Fast brown* which is obtained from α-naphthol and diazoxylylsulphonic acid is very similar to *fast brown G*.

Toluene-azodiamidobenzene-azonaphthalene, $C_7H_7.N_2.C_6H_2(NH_2)_2N_2.C_{10}H_7$. When β-diazonaphthalene chloride is allowed to act upon *m*-diamidobenzene, *naphthalene-azodiamidobenzene*, $C_{10}H_7.N_2.C_6H_3(NH_2)_2$, is formed. This substance crystallizes in elongated, light-yellow plates, and is converted by the action of *p*-diazotoluene into the above compound. The latter crystallizes in small, lustrous, copper-red plates, readily soluble in chloroform, from which they are reprecipitated by alcohol. It is not a colouring matter, but yields one on treatment with fuming sulphuric acid;[2] this substance is closely related to *Acid brown R*, which is obtained by the action of

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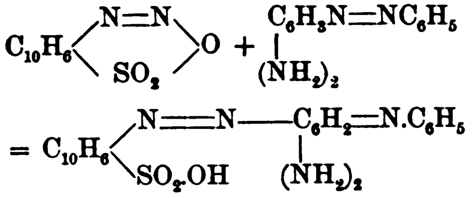
[1] Krohn, *Ber.* **21**, 3240.

[2] Griess, *Ber.* **16**, 2028.

1 : 4-diazonaphthalenesulphonic acid on chrysoïdin (Pt. III., p. 370):



The *sodium salt* comes into the market as a brown powder, the aqueous solution of which gives a brown precipitate with hydrochloric acid. It forms an olive-green coloured solution in sulphuric acid.

Azobenzeneazo-β-naphthol is formed when an alkaline solution of β-naphthol is brought together with one of diazo-azobenzene chloride prepared from amido-azobenzene, sodium nitrite, and hydrochloric acid:

$$C_6H_5N{=}NC_6H_4N{=}NCl + C_{10}H_7.OH = C_6H_5N{=}NC_6H_4N{=}NC_{10}H_6.OH + HCl.$$

In this way a brick-red powder is obtained, which is insoluble in alkalis and crystallizes from acetic acid in brown plates with a green metallic lustre, melting at 195°. It is slightly soluble in alcohol and cold turpentine, readily on heating. It forms a dark-green coloured solution in sulphuric acid, from which it is precipitated by water. Tin and hydrochloric acid decompose it into aniline, *p*-diamidobenzene and amido-β-naphthol.[1]

It is used under the name of *Soudan III.* for colouring lacquers, oils, fats, &c. The sodium salts of several of its sulphonic acids are also sold as dyes.

Disazobenzenedihydroxynaphthalene, or *Phenyldisazonaphthoresorcinol*, $(C_6H_5N_2)_2C_{10}H_4(OH)_2$, is obtained when an alkaline solution of phenylazonaphthoresorcinol is treated with an excess of caustic soda solution, and the brick-red sodium compound thus formed brought together with diazobenzene chloride, the mass becoming coloured dark-red. It crystallizes from a mixture of alcohol and chloroform in long red needles, and on reduction yields the same products as nitrosophenylazonaphthoresorcinol, so that it must have the following constitution (Kostanecki):

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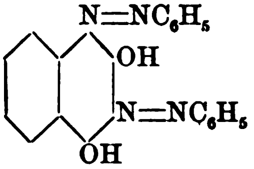
[1] Nietzki, *Ber.* **13**, 1838.



Disazobenzene-a-naphthylamine, $(C_6H_5N_2)_2C_{10}H_5NH_2$, is formed when a solution of one molecule of diazobenzene chloride is allowed to run into an alcoholic solution of one molecule of benzene-azo-α-naphthylamine to which sodium acetate has been added. It crystallizes from aniline in well-developed red needles, melting at 189°. Its salts dissolve in alcohol, forming blue solutions, and are decomposed by water.[1]

Fast scarlet or *Double scarlet*, $C_6H_4(SO_3Na)N_2.C_6H_4N_2.C_{10}H_6.OH$, is obtained from fast yellow or amido-azobenzene-sulphonic acid by diazotizing and running the product into an alkaline solution of β-naphthol. It is a brownish-red powder, forms a poppy-red solution in water, and imparts a green colour to sulphuric acid, which is converted by water into blue, bluish-red, and finally scarlet.

This compound is a constituent of *Biebrich scarlet*, which is obtained by treating amido-azobenzene sulphate with fuming sulphuric acid. The disulphonic acid is the chief product, but is accompanied by a smaller amount of the monosulphonic acid. The mass is neutralized with caustic soda solution and then diazotized at a low temperature with sodium nitrite and hydrochloric acid, the liquid thus obtained being finally run into a solution of β-naphthol in caustic soda solution at a temperature of about 5°.

The commercial product, which is also called *Ponceau 3R*, is a reddish-brown powder, which forms a yellowish-red solution in water. Its green solution in sulphuric acid is coloured blue by water, a flocculent brown precipitate being then produced.

Biebrich scarlet dyes wool and silk the same shade as cochineal. Nietzki has prepared its constituents in the pure state. The *sodium salt* of the monosulphonic acid crystallizes from alcohol in elegant red needles; that of the disulphonic acid, $C_6H_4(SO_3Na)_2N_2.C_6H_3(SO_3Na)N_2.C_{10}H_6.OH$, separates out on cooling as a gelatinous mass, changing to long matted needles when common salt is carefully added to a hot aqueous

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[1] Krohn, *Ber.* **21**, 2346.

solution, which must not be too concentrated. It crystallizes from dilute alcohol in light-red, hair-like needles, which lose water on drying and become brownish-red. Concentrated hydrochloric acid separates the sulphonic acids from their salts in brown needles. When they are treated with zinc dust in alkaline solution they decompose into amido-β-naphthol and the sulphonic acids of amidoazobenzene, whilst when stannous chloride is used the latter decompose into sulphanilic acid and *p*-diamidobenzene or its sulphonic acid.[1]

By the action of diazo-azobenzene on β-naphthol-α-disulphonic acid *Ponceau SS extra* is formed, whilst β-naphthol-β-disulphonic acid yields *Brilliant croceïn.* These colouring matters are, however, at present only of inferior value.[2]

Cloth red G, $C_6H_4(CH_3)N_2.C_6H_3(CH_3)N_2.C_{10}H_5(OH)SO_3Na$, is prepared by the action of diazo-azotoluene chloride on β-naphthol-β-sulphonic acid, and is a powder which is only slightly soluble in water with a brownish-red colour, and forms a blue solution in sulphuric acid; on the addition of water to this a brownish-red precipitate is produced.

Cloth red B, $C_6H_4(CH_3)N_2.C_6H_3(CH_3)N_2C_{10}H_4(OH)(SO_3Na)_2$, is obtained in a similar manner from β-naphthol-α-disulphonic acid. The brownish-red powder dissolves in water, forming a magenta-red solution, and behaves towards sulphuric acid in the same manner as cloth red G.

Both these substances dye shades which are fast to light and milling and can also be used in conjunction with the natural colouring matters, such as the dyewoods, for dyeing wool.

Another *Cloth red B* is prepared in a similar manner from α-naphthol-β-sulphonic acid, and a *Cloth red B extra* from β-naphthol-α-sulphonic acid, whilst *Archil red A* is obtained by the action of diazo-xylene chloride on β-naphthol-α-disulphonic acid.

Other red colouring matters, which are termed *Ponceau*, *Bordeaux*, &c., are obtained from the diazobenzene-, diazotoluene- and diazo-xylene-sulphonic acids by reaction with the various naphtholsulphonic acids.

Fast violet, $C_6H_4(SO_3Na)N_2.C_{10}H_6.N_2.C_{10}H_5(OH)SO_3Na$, which produces a reddish-violet shade on wool, is obtained by diazotizing sulphanilic acid and converting the product by means of α-naphthylamine into naphthylamine-azobenzenesulphonic acid,

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[1] Nietzki, *Ber.* **13**, 800 and 1838.

[2] Friedländer, *Theerfarbenfabr.* 445

which is then again diazotized and caused to combine with β-naphthol-β-sulphonic acid.

Azo-black, $C_{10}H_6(SO_3Na)N_2.C_{10}H_6.N_2.C_{10}H_4(OH)(SO_3Na)_2$, is prepared by sulphonating β-naphthylamine and converting the mixture of sulphonic acids by means of α-naphthylamine into α-naphthylamine-azonaphthalenesulphonic acids, which are then diazotized and combined with β-naphthol-α-disulphonic acid. It is a blue-black powder, which dyes wool bluish-violet, forms a solution of the same colour in water, and imparts a bluish-green colour to sulphuric acid, which on dilution with water becomes blue, a precipitate of the same colour being subsequently formed.

Naphthol black B, $C_{10}H_5(SO_3Na)_2N_2.C_{10}H_6.N_2.C_{10}H_4(OH)(SO_3Na)_2$, is obtained by converting β-naphthol-β-disulphonic acid into the corresponding naphthylaminedisulphonic acid by heating with ammonia and then preparing from this α-naphthylamine-azonaphthyldisulphonic acid, which is finally combined with β-naphthol-α-disulphonic acid. It is a blue-black powder which forms a violet-coloured solution in water, and dyes wool blue-black in an acid bath. It dissolves in sulphuric acid, forming a green solution which is changed to blue by the addition of water, a reddish-violet precipitate being then formed.

Wool black, $CH_3.C_6H_4.NH.C_{10}H_6.N_2.C_6H_3(SO_3Na).N_2.C_6H_4.SO_3Na$, was discovered by L. Schad. In order to prepare it, *p*-tolyl-β-naphthylamine is dissolved in alcohol, the equivalent amount of hydrochloric acid added and diazo-azobenzenedisulphonic acid brought into the solution. The acid of the dye which is thus formed is precipitated by the addition of common salt, washed with water and dissolved in sodium carbonate solution. On the addition of salt to this liquid the wool-black separates out in fine crystalline plates which form a blue-black powder after drying. This dissolves in water with a violet colour, whilst its solution in sulphuric acid is blue. It dyes wool a fast dark bluish-violet to deep black-blue, a fine black being produced when naphthol-yellow and ethyl-green are added.

Other good black dyes for wool are obtained by employing the diazonaphthalenedisulphonic acids instead of the diazobenzenedisulphonic acids.

Violet-black, $NH_2.C_{10}H_6.N_2.C_6H_4.N_2.C_{10}H_5(OH)SO_3Na$. In order to prepare this substance, monacetyl-*p*-diamidobenzene is diazotized and the product treated with an alkaline solution of α-naphthol-α-sulphonic acid. The azo-compound thus formed is boiled with caustic soda solution to replace the acetyl group by hydrogen and the *p-amidobenzeneazonaphtholsulphonic acid,* $C_6H_4(NH_2)N_2.C_{10}H_5(OH)SO_3H$, again diazotized. The product is then brought into a hot solution of *a*-naphthylamine hydrochloride, and the liquid after standing for a considerable time heated to boiling. The filtered and washed colouring matter is then dissolved in hot sodium carbonate solution, and the sodium salt precipitated by common salt.

Violet-black is a powder with a bronze lustre and forms a brownish-red solution in water, which is changed to reddish-violet by caustic soda, whilst hydrochloric acid produces a violet precipitate. It dissolves in concentrated sulphuric acid to form a blue coloured solution in which water produces a violet precipitate.

Violet-black not only dyes silk and wool but also unmordanted cotton a fine dark violet-black in a faintly alkaline soap-bath. It is employed as a ground for aniline colours, since it also acts as a mordant for these.

As already mentioned, only the water-soluble sulphonic acids were at first used for dyeing, as considerable difficulty was experienced in applying the spirit-soluble colouring matters. These were however overcome by the discovery that the dyes in question combine with acid sodium sulphite or ammonium sulphite to form soluble compounds, which can again be decomposed by steaming or by alkalis, the colouring matter being thus fixed on the fibre (Pt. III. p. 360).

Azarin, $C_6H_2Cl_2(OH)NH.N(SO_3NH_4)C_{10}H_6(OH)$, is a substance of this class which was for a time brought into the market and is obtained by heating the compound formed by the action of diazodichlorophenol on *β*-naphthol with a solution of acid ammonium sulphite. It can be employed in calico printing since the *dichlorophenolazo-β-naphthol,* $C_6H_2Cl_2(OH)N_2.C_{10}H_6.OH$, which is set free by steaming, combines with the alumina with which the fabric is simultaneously mordanted to form a fine red compound. Other azarins were also prepared but the process proved to be too dear.

Holliday and Grässler had even before this proposed to produce the insoluble azo-dyes on the fibre itself, and in this way to fix them, especially upon cotton. Difficulties were met with but these have now been overcome.

The material is first passed through an alkaline solution of *a*-naphthol, *β*-naphthol, or some other phenol, hung up in a cold drying room until dry and then taken through a solution of a diazo-salt. The colour has a better appearance when no free mineral acid is present, and it is therefore usual to add sodium acetate to the diazo-solution before employing it. Yarn does not require to be dried but is simply wrung out and then passed through the diazo-bath; the colour rapidly develops and the material is then well washed with water. An essential condition is that the temperature must not rise above 5°, so that ice must usually be added. The azo-colours can be fixed in a similar way in calico printing, the cloth being first passed through an alkaline naphthol solution, then dried, and finally printed with a thickened diazo-solution; or the cloth can be first printed with the naphthol solution and then brought into the diazo-bath.[1]

According to another process a thickened concentrated solution of the diazo-salt is printed on to the cloth, which is then dried in the cold and passed through the alkaline naphthol solution, after which it is well washed and boiled in soap solution. Any required combination of colours can be obtained by the use of mixtures of phenol- or diazo-compounds.[2]

Wool is well known to have the power of absorbing many colouring matters and other chemical compounds, and a further account of this property will be given in discussing the rosaniline dyes. It may here be mentioned that the sulphonic acids of the naphthols are fixed by wool both in acid and in neutral solution in such a way that they cannot be washed out. If the wool is subsequently brought into the solution of a diazo-salt and ammonia added, the colouring matter is developed in the fibre. The sulphonic acids of the naphthylamines are also fixed by wool. When naphthionic acid is used and is then diazotized in an acidified sodium nitrite solution, the wool on treatment with an alkaline β-naphthol solution takes the shade of fast red.

This new process of dyeing however does not appear to be of any technical importance.[3]

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[1] Farbw. vorm. Meister, Lucius and Brüning, *Chem. Zeit. Rep.* 1889, **13**, 212 and 274.

[2] Schultz, *Steinkohlentheer*, **2**, 1038.

[3] Hirsch, *Chem. Zeit.* 1889, **13**, 432 and 449.

PHOSPHORUS DERIVATIVES OF NAPHTHALENE.

2671 *Naphthyl phosphorus chloride*, $C_{10}H_7PCl_2$, was obtained by Kelbe by the action of phosphorus trichloride on mercury-naphthyl as an oily liquid which boils with decomposition above 360°.

Naphthyl hypophosphinic acid, $C_{10}H_7P(OH)_2$, is formed by the decomposition of the chloride with water, and crystallizes in small needles, which melt at 125—126°, and are slightly soluble in cold, more readily in hot water. On boiling with silver nitrate solution, silver is precipitated.

Naphthylphosphinic acid, $C_{10}H_7PO(OH)_2$, is prepared by combining the chloride with chlorine and decomposing the product with water. It is sparingly soluble in cold, more freely in hot water, crystallizes in long needles, melts at 190°, and when strongly heated becomes partially carbonized and decomposes into naphthalene and metaphosphoric acid. The *silver salt*, $C_{10}H_7PO(OAg)_2$, is a white precipitate which becomes dark coloured in the light.

Dinaphthylphosphinic acid, $(C_{10}H_7)_2PO(OH)$, is formed, together with naphthylhypophosphinic acid, when the crude chloride is decomposed with water. It is insoluble in water and crystallizes from alcohol in nodular aggregates of needles, which melt at 202—204° and solidify on cooling to a crystalline mass. It decomposes the alkali carbonates and is reprecipitated by acids as a curdy mass.

Diethylnaphthylphosphine, $C_{10}H_7P(C_2H_5)_2$, is formed by the action of zinc ethyl on the chloride. It is an oily liquid, which has a repulsive odour, resembling that of phenylphosphine, and boils with decomposition above 360°. It unites with ethyl iodide to form *triethylnaphthylphosphonium iodide*, $C_{10}H_7P(C_2H_5)_3I$, which crystallizes from water in well-formed plates, melting at 209°.[1]

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[1] *Ber.* **9**, 1051; **11**, 1499.

ARSENIC DERIVATIVES OF NAPHTHYL.

2672 *Naphthylarsenious chloride*, $C_{10}H_7AsCl_2$, is obtained by the action of arsenic trichloride on mercurynaphthyl. It is a white crystalline powder, melts at 63°, and is readily soluble in alcohol, but insoluble in water, and is not decomposed by the latter even on heating.

Naphthylarsenious oxide, $C_{10}H_7AsO$, is formed by the decomposition of the chloride by alkalis as a white powder, which melts at 245°, and is insoluble in water, slightly soluble in alcohol.[1]

Naphthylarsinic acid, $C_{10}H_7AsO(OH)_2$, is obtained by the action of chlorine and water on the chloride, and crystallizes in well-formed needles, melting at 197° (Kelbe).

Arsenonaphthalene, $(C_{10}H_7)_2As_2$, is prepared by heating the oxide with alcohol and solid phosphorous acid:

$$2C_{10}H_7AsO + 2PO_3H_3 = \begin{array}{c} C_{10}H_7As \\ \| \\ C_{10}H_7As \end{array} + 2\,PO_4H_3.$$

It is a powder which consists of slender yellow needles, melts at 221°, is sparingly soluble in alcohol, insoluble in water, and combines with chlorine to form naphthylarsenious chloride.

MERCURY DERIVATIVES OF NAPHTHALENE.

2673 *Mercurynaphthyl*, $Hg(C_{10}H_7)_2$, is obtained by heating *a*-bromonaphthalene with pasty sodium amalgam, coal-tar naphtha boiling at 120—140° and a little ethyl acetate. It crystallizes in small, lustrous rhombic prisms, which melt at 243° and are odourless. It is only slightly soluble in boiling alcohol, more freely in boiling benzene, and readily in hot chloroform and carbon disulphide. On heating with concentrated hydrochloric acid, naphthalene and mercuric chloride are formed; hydrobromic and hydriodic acids act in a similar manner.

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[1] Michaelis and Schulte, *Ber.* **15**, 1952.

Naphthylmercuric bromide, $C_{10}H_7HgBr$, is formed by the action of bromine on mercurynaphthyl, or by heating the latter with mercuric bromide to 120—130°. It crystallizes in pliable needles, with a velvet lustre, and melts at 195—196°.

Naphthylmercuric iodide, $C_{10}H_7HgI$, is obtained when the calculated amount of iodine is added to a solution of mercurynaphthyl in carbon disulphide. It crystallizes in velvety, pliable needles, which melt at 185°, and are sparingly soluble in cold, more freely in hot water. By the further action of iodine it is converted into *a*-iodonaphthalene, and on treatment with sodium amalgam yields mercurynaphthyl.

Naphthylmercuric acetate, $C_{10}H_7HgO.CO.CH_3$, is formed when mercurynaphthyl is heated with glacial acetic acid:

$$(C_{10}H_7)_2Hg + HO.CO.CH_3 = C_{10}H_7Hg.O.CO.CH_3 + C_{10}H_8.$$

It crystallizes from hot alcohol in small needles with a velvet lustre, melts at 154°, and decomposes into mercuric iodide, naphthalene and acetic acid on heating with hydrochloric acid. The *formate* is an oily liquid, whilst the *butyrate* crystallizes in elegant silky needles, melting at 200°.[1]

[1] Otto, *Annalen*, **147**, 164; **154**, 188.

METHYLNAPHTHALENE GROUP.

METHYLNAPHTHALENE, $C_{10}H_7.CH_3$

2674 The two isomeric methylnaphthalenes occur in coal-tar,[1] and in the products which are obtained when colophonium, benzoïn, or aldehyde resin are heated with zinc dust.[2] They are also formed, together with other hydrocarbons, when naphthalene is heated with ethylene bromide and aluminium chloride.[3]

a-Methylnaphthalene was first prepared by Fittig and Remsen by acting with sodium on a mixture of α-bromonaphthalene and methyl iodide, other products being also formed and much naphthalene regenerated.[4] A much better yield is obtained by distilling naphthylacetic acid, $C_{10}H_7.CH_2.CO_2H$, with lime.[5] In order to extract this hydrocarbon from purified coal-tar oil, the portion boiling between 200° and 300° is submitted to fractional distillation. The fraction boiling at 239—242° is then cooled to 0°, at which temperature the greater portion of the β-methylnaphthalene crystallizes out, the liquid portion being drained off on the filter pump and cooled to $-15°$. A further crystallization is thus obtained, and by a repetition of this process all the β-methylnaphthalene can be removed. As soon as this has been done the liquid is rectified over sodium (Schulze). The methylnaphthalenes obtained by the aluminium chloride reaction can also be separated in this manner.

α-Methylnaphthalene is a liquid which has an aromatic odour, does not solidify at $-18°$, and boils at 240—242°. It combines with picric acid to form the compound $C_{11}H_{10} + C_6H_3(NO_2)_3O$, which crystallizes from alcohol in orange-yellow slender needles, united in fascicular aggregates, and melts at 116°.

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[1] Reingruber, *Annalen*, **206**, 375; Schulze, *Ber.* **17**, 842 and 1527.

[2] Ciamician, *Ber.* **11**, 269; **13**, 1865.

[3] Roux, *Ann. Chim. Phys.* VI. **12**, 289.

[4] *Annalen*, **155**, 112.

[5] Boessneck, *Ber.* **16**, 1546.

Brom-a-methylnaphthalene, $C_{10}H_6Br.CH_3$, is formed when molecular proportions of α-methylnaphthalene and bromine are mixed in solution in carbon disulphide and the liquid exposed to sunlight. It is a liquid which has a faint smell resembling that of bromotoluene, and boils with slight decomposition at 298°. With picric acid it forms the compound $C_{11}H_7Br + C_6H_3(NO_2)_3O$, which crystallizes from alcohol in deep yellow needles, melting at 105° (Schulze).

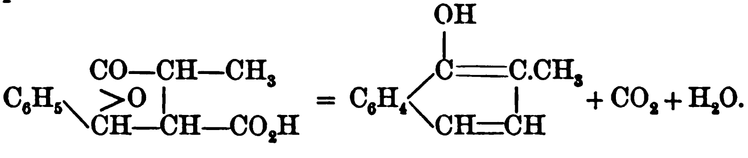
β-Methylnaphthalene is also formed when the β-methylnaphthols are distilled over heated zinc dust, and crystallizes from alcohol in large plates with a fatty lustre, or in pearly needles. It has an aromatic, somewhat irritating odour, and a burning taste, melts at 37—38°,[1] and boils at 241—242°. With picric acid it forms the compound $C_{11}H_{10} + C_6H_3(NO_2)_3O$, which crystallizes in well-developed deep-yellow needles, melting at 115°.[2]

Bromo-β-methylnaphthalene, $C_{10}H_6Br.CH_3$, is obtained in a similar manner to the α-compound which it closely resembles. It boils at 296°, and forms a *picric acid compound* which crystallizes in deep canary-yellow coloured needles, melting at 113° (Schulze).

Nitro-β-methylnaphthalene, $C_{10}H_6(NO_2)CH_3$, is formed when β-methylnaphthalene is agitated with nitric acid of sp. gr. 1·36. As soon as the mixture has cooled, a volume of sulphuric acid equal to that of the nitric acid is added to the well-stirred liquid, which is then heated nearly to boiling. The product which crystallizes out on cooling is separated by recrystallization from alcohol from the difficultly soluble dinitro-compounds, which are also formed. Nitro-β-methylnaphthalene crystallizes in thin, light-yellow needles, melts at 81°, and can only be distilled without decomposition under a pressure of 40 mm. (Schulze).

Dinitro-β-methylnaphthalene, $C_{10}H_5(NO_2)_2CH_3$, forms slender needles, which are strongly refractive, and melt at 206°.

1-*Hydroxy-β-methylnaphthalene*, or 2 : 1-*Methylnaphthol*, $C_{10}H_6(OH)CH_3$, is obtained by the distillation of phenylhomoparaconic acid :



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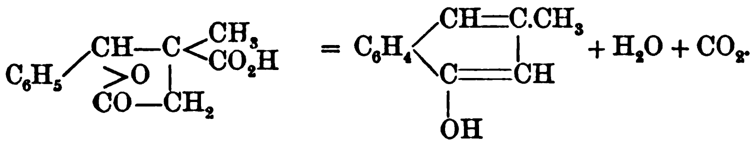
[1] Liebermann, *Ber.* **20**, 3182 ; *Annalen*, **255**, 261 and 273.

[2] Schulze, *loc. cit.*

It crystallizes in yellow needles, which melt at 89°, and forms a colourless solution in hot water from which it always separates even in the dark, as a coloured substance.

4-Hydroxy-β-methylnaphthalene, or 2 : *4-Methylnaphthol,* is obtained from phenylisohomoparaconic acid :



It forms colourless needles and melts at 92°. Both these compounds give a characteristic green precipitate with bleaching powder, which becomes yellow after some time (Liebermann).

NAPHTHOMETHYL COMPOUNDS.

2675 These substances stand in the same relation to naphthalene as the benzyl-compounds to benzene, and have, therefore, also been called the naphthobenzyl-compounds.

α-Naphthomethyl alcohol, $C_{10}H_7.CH_2.OH$, is obtained by heating a solution of α-naphthomethylamine hydrochloride with sodium nitrite. It is readily soluble in alcohol, less freely in hot, and sparingly in cold water, from which it crystallizes on evaporation in long, lustrous needles. It melts at 59·5—60°, and boils at 301° under a pressure of 715 mm.

α-Naphthomethylamine, $C_{10}H_7.CH_2.NH_2$, was prepared by Hofmann, who termed it *menaphthylamine,* by the action of zinc and hydrochloric acid on an alcoholic solution of α-naphthothiamide,[1] $C_{10}H_7.CS.NH_2$, α-α-dinaphthylethane, $C_{10}H_7C_2H_4.C_{10}H_7$, being simultaneously formed.[2]

α-Naphthomethylamine is a very caustic liquid, which boils at 290—293° and absorbs carbon dioxide so eagerly that it cannot be poured from one vessel into another without a film of the difficultly-soluble carbonate being formed upon the surface. When it is heated with chloroform and alcoholic caustic soda solution, *naphthomethylcarbamine,* $C_{10}H_7.CH_2.NC$, a substance distinguished by its abominable odour, is formed.

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[1] *Ber.* **1**, 100.

[2] Bamberger and Lodter, *Ber.* **21**, 51 and 256.

a-Naphthomethylamine hydrochloride, $C_{10}H_7.CH_2.NH_3Cl$, crystallizes readily in long, sparingly-soluble needles, and forms a *platinochloride*, which is a yellow crystalline precipitate.

a-Naphthomethylamine nitrite, $C_{10}H_7.CH_2.NH_3.NO_2$, is formed in a remarkable manner when aqueous solutions of the hydrochloride and of sodium nitrite are mixed. It soon separates out as a mass of lustrous needles, and is sparingly soluble in cold water, from which it crystallizes on evaporation in long, slender prisms. When it is heated in a capillary tube it remains unaltered until the temperature reaches 148·5°, and then suddenly melts and froths up, the same decomposition taking place as is caused by water at 50—60° (Bamberger and Lodter):

$$C_{10}H_7.CH_2.NH_3.O.NO = C_{10}H_7.CH_2.OH + H_2O + N_2.$$

It therefore resembles *ac*-tetrahydro-β-naphthylamine in its properties (p. 172).

a-Naphthomethylamine nitrate, $C_{10}H_7.CH_2NH_3.NO_3$, is also sparingly soluble, and crystallizes in elegant prisms resembling those of saltpetre (Hofmann).

Tetrahydro-a-naphthomethylamine, $C_{10}H_{11}.CH_2.NH_2$, is formed, together with dihydronaphthalene (p. 34) by the action of sodium on a boiling alcoholic solution of α-naphthonitrile, $C_{10}H_7.CN$. It is a viscid, oily, strongly refractive liquid, which has a somewhat sweet ammoniacal odour, distinctly resembling that of piperidine, boils at 269—270°, and absorbs carbon dioxide very energetically.

Tetrahydro-a-naphthomethylamine hydrochloride, $C_{10}H_{11}.CH_2.NH_3Cl$, crystallizes from hot water in fascicular groups of lustrous needles, and is precipitated by hydrochloric acid from aqueous solution in silver-white plates. The *platinochloride*, $(C_{11}H_{16}N)_2PtCl_6$, is a chamois-yellow, crystalline precipitate, which crystallizes from hot water in rosettes of lustrous needles. When ammonium picrate is added to a solution of the hydrochloride, a yellow turbidity is produced, and on agitation a precipitate of yellow lustrous needles, readily soluble in hot water, is formed.[1]

If potassium permanganate be added to a solution of the hydrochloride made alkaline with caustic potash and cooled by ice, phthalic and oxalic acids are formed. This fact shows that the base has the following constitution:[2]

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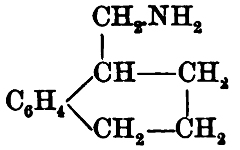
[1] Bamberger and Lodter, *Ber.* **20**, 1703.

[2] Bamberger and Helwig, *Ber.* **22**, 1912.



Acetotetrahydro-a-naphthomethylamine, $C_{10}H_{11}.CH_2.NH.CO.CH_3$, is obtained by heating the base with acetic anhydride and sodium acetate. It crystallizes in pearly scales, melting at 88·5°.

Phenyl-a-tetrahydronaphthomethyl carbamide, $C_6H_5.NH.CO.NH.CH_2.C_{10}H_{11}$, is formed by the action of phenyl isocyanate on the base. It crystallizes from warm alcohol in white, lustrous plates, melting at 126·5°.

2676 *β-Naphthomethyl alcohol*, $C_{10}H_7.CH_2.OH$, is prepared by heating an aqueous solution of β-naphthomethylamine hydrochloride with sodium nitrite. It crystallizes in lustrous plates, melts at 80—80·5° and is sparingly soluble in cold, more freely in hot water and readily soluble in alcohol.[1]

β-Naphthomethyl chloride, $C_{10}H_7.CH_2Cl$, is formed when chlorine is passed into boiling β-methylnaphthalene; it crystallizes in micaceous plates, melting at 47°. On distillation under the ordinary pressure a slight evolution of hydrochloric acid takes place; under a pressure of 20 mm., it boils at 168°.

β-Naphthomethyl bromide, $C_{10}H_7.CH_2Br$, is obtained in a similar manner, and crystallizes from alcohol in plates with a fatty lustre, which melt at 56°. It boils at 213° (100 mm.) forming a vapour which, like that of the chloride, has an odour resembling that of the vapour of the corresponding benzyl compound and attacks the mucous membrane, especially of the eyes, in a similar manner.[2]

β-Naphthomethylamine, $C_{10}H_7.CH_2.NH_2$, is formed, together with β-β-dinaphthylethane, $C_2H_4(C_{10}H_7)$, (Bamberger and Lodter), when zinc dust and alcoholic hydrochloric acid are gradually added to a solution of β-naphthothiamide in alcohol. It is slightly soluble in cold, more readily in hot water and readily in alcohol, from which it crystallizes on evaporation in thick, lustrous, colourless prisms, melting at 59—60°. It absorbs carbon dioxide so vigorously that it rapidly becomes covered with a white efflorescence in the air. It precipitates the hydroxides from solutions of salts of copper, zinc, and lead.

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[1] Bamberger and Boekmann, *Ber.* **20**, 1115.

[2] Schulze, *Ber.* **17**, 1527.

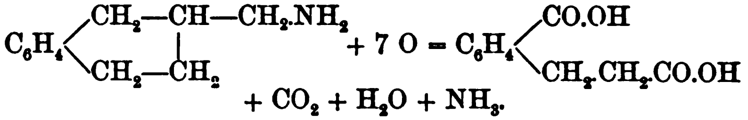
β-Naphthomethylamine hydrochloride, $C_{10}H_7.CH_2.NH_3Cl$, crystallizes in broad, satin-lustrous prisms, which are readily soluble in water and alcohol, only slightly in concentrated hydrochloric acid. The *platinochloride* is an egg-yellow, flaky crystalline precipitate, and separates from hot water in dendritic aggregates of slender needles. When ammonium picrate is added to a solution of the hydrochloride, *naphthomethylamine picrate* separates out in crystalline flakes. It crystallizes from hot water in long, golden-yellow, lustrous needles (Bamberger and Boekmann).

Tetrahydro-β-naphthomethylamine, $C_{10}H_{11}.CH_2.NH_2$, is formed when sodium is added to a hot alcoholic solution of β-naphthonitrile. It is a colourless, transparent oily liquid, which smells like the α-compound and boils at 270°. On exposure to the air it rapidly becomes converted into the lustrous needles of the carbonate.

Tetrahydro-β-naphthomethylamine hydrochloride, $C_{10}H_{11}.CH_2.NH_3Cl$, crystallizes in fascicular groups of lustrous needles, which are readily soluble in water. The *platinochloride* is an egg-yellow precipitate, which crystallizes from hot water in lustrous needles.

Tetrahydro-β-naphthomethylamine sulphate, $(C_{10}H_{11}.CH_2.NH_3)_2SO_4$, forms long, thin prisms with a vitreous lustre, which are readily soluble in water. The *picrate* is precipitated as an oil, which is converted by agitation into yellow, lustrous needles.[1]

The base is oxidized by potassium permanganate to *o*-carboxyhydrocinnamic acid and phthalic acid:



$$C_6H_4\left\langle\begin{array}{l}CH_2—CH—CH_2.NH_2\\ \quad\;\; | \\ CH_2—CH_2\end{array}\right. + 7\,O = C_6H_4\left\langle\begin{array}{l}CO.OH\\ \\ CH_2.CH_2.CO.OH\end{array}\right.$$
$$+ CO_2 + H_2O + NH_3.$$

Acetotetrahydro-β-naphthomethylamine, $C_{10}H_{11}.CH_2.NH.CO.CH_3$, is obtained by heating the hydrochloride with acetic anhydride and sodium acetate, and crystallizes in long, lustrous needles, melting at 64—65°.

Tetrahydro-β-naphthomethyl carbamide, $C_{10}H_{11}.CH_2.NH.CO.NH_2$, is obtained by evaporating the solution of the hydrochloride with potassium cyanate. It crystallizes from hot water in tablets, which have a satin lustre and melt at 135—135·5°.

[1] Bamberger and Boekmann, *Ber.* **20**, 1711.

If the solution contains free acid, *ditetrahydro-naphthomethyl carbamide*, $CO(NH.CH_2.C_{10}H_{11})_2$, is formed, together with the preceding compound. It is more readily soluble than the latter, and forms satin-lustrous plates, which melt at 225·5—226°.

Ditetrahydronaphthomethyl thiocarbamide, $CS(NH.CH_2.C_{10}H_{11})_2$. When solutions of the base and carbon disulphide in absolute ether are mixed, the *thiocarbamate*, $C_{10}H_{11}.CH_2.NH.CS.SNH_3.CH_2.C_{10}H_{11}$, separates out, which crystallizes from alcohol in vitreous needles, and is converted by boiling with alcohol into the thiocarbamide. The latter forms pearly plates, and melts at 142·5—143°.

Phenyl-β-tetrahydronaphthomethyl carbamide, $C_6H_5.NH.CO.NH.CH_2C_{10}H_{11}$, forms slender needles with a vitreous lustre, melting at 141°.

Phenyl-β-tetrahydronaphthomethyl thiocarbamide has been prepared from the base, and phenyl thiocarbimide; it crystallizes from alcohol in rosettes with a vitreous lustre, and melts at 139·5—140°.[1]

THE NAPHTHOIC ACIDS, $C_{10}H_7.CO_2H$.

2677 These substances correspond to benzoic acid in the benzene series, and behave in a similar manner, since they are decomposed by heating with lime into carbon dioxide and naphthalene, and can be again obtained from the latter by the same reactions by which benzoic acid is obtained from benzene.

a-Naphthaldehyde, or *a-Naphthomethyl aldehyde*, $C_{10}H_7.CHO$, is readily formed when potassium dichromate is added to a-naphthomethyl alcohol suspended in dilute sulphuric acid. It is a viscid, oily liquid, which has a faint aromatic odour, and boils at 291·6°. Like benzaldehyde it restores the colour to a solution of magenta in sulphurous acid, reduces an ammoniacal silver solution, and readily oxidizes in the air. It combines with acid sodium sulphite to form the difficultly-soluble compound, $C_{10}H_7.CH(OH)SO_3Na$, which crystallizes in lustrous plates.[2]

Naphthomethyleneoxime, $C_{10}H_7.CH{=}NOH$, is formed when the aldehyde is mixed with aqueous hydroxylamine hydrochloride,

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[1] Bamberger and Helwig, *Ber.* **22**, 1912.

[2] Bamberger and Lodter, *Ber.* **21**, 256.

sodium carbonate and sufficient alcohol to produce a clear solution. The mixture is allowed to stand for a few days, and the oxime then extracted with ether. It crystallizes from alcohol in colourless needles, is only slightly soluble in hot water, and separates from the latter in splendid long needles, which melt at 98°.

Naphthomethylene aniline, $C_{10}H_7.CH{=}N.C_6H_5$, is formed when the aldehyde is brought together with aniline in alcoholic solution and the mixture heated. It crystallizes from alcohol in light-yellow needles, melting at 71°.[1]

	Melting-point.
Naphthomethylene-*o*-toluidine, $C_{10}H_7.CH{=}N.C_6H_4.CH_3$, plates or yellow transparent crystals	59°
Naphthomethylene-*p*-toluidine, long yellow needles.	93°
Naphthomethylene-*a*-naphthylamine, $C_{10}H_7.CH{=}N.C_{10}H_7$, nodular masses of prisms .	117°

Naphthomethylenephenylhydrazone, $C_{10}H_7.CH{=}N.NH.C_6H_5$, crystallizes from alcohol in light yellow, lustrous lates, which melt at 185°, and become coloured red in the light (Bamberger and Lodter).

a-Naphthoic acid was discovered by Hofmann, and termed *menaphthoxylic acid.* He obtained it by converting *a*-formonaphthalide into naphthonitrile by heating with hydrochloric acid, and then decomposing this with alcoholic caustic soda.[2] It was prepared almost simultaneously by Merz, who gave to it, as the benzoic acid of the naphthalene group, the name by which it is still known. He obtained it and also *β*-naphthoic acid by heating the corresponding potassium naphthalenesulphonate with potassium cyanide and hydrolysing the nitrile thus formed.[3] *a*-Naphthoic acid is also formed when potassium *a*-naphthalenesulphonate is heated with sodium formate.[4] In order to prepare it a well-dried intimate mixture of 3 parts of sodium *a*-naphthalenesulphonate with anhydrous ferrocyanide of potassium is submitted to dry distillation in a wrought-iron tube or a flat iron retort provided with a lid. The crude nitrile is purified by rectification, and is then decomposed by heating with alcoholic caustic soda to 130—140°,

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[1] Brandis, *Ber.* **22**, 2148.

[2] *Ber.* **1**, 38.

[3] *Zeitschr. Chem.* **1868**, 34 ; Merz and Mühlhäuser, *Ber.* **3**, 709.

[4] V. Meyer, *Annalen*, **156**, 274.

or with concentrated hydrochloric acid to 150—160°.[1] It is, moreover, unnecessary to separate the two naphthalenesulphonic acids before employing them, as the mixture of naphthoic acids obtained can easily be separated by boiling with lime water, which dissolves the *a*-acid, whilst the calcium salt of the *β*-acid remains for the most part undissolved (Ekstrand).

a-Naphthoic acid is very slightly soluble in cold and only slightly soluble in boiling water, but dissolves readily in hot alcohol, from which it crystallizes in needles, melting at 160°.

The naphthoates of the alkali metals are readily soluble in water.

Calcium a-naphthoate, $(C_{10}H_7.CO_2)_2Ca + 2H_2O$, crystallizes in white needles, which are sparingly soluble in water.

Barium a-naphthoate, $(C_{10}H_7.CO_2)_2Ba + 4H_2O$, also forms sparingly soluble needles.

Silver a-naphthoate, $C_{10}H_7.CO_2Ag$, is a white, scarcely crystalline precipitate.

Ethyl a-naphthoate, $C_{10}H_7.CO_2C_2H_5$, was obtained by Hofmann by the action of absolute alcohol on naphthoyl chloride; it is also formed by the action of sodium amalgam on a mixture of ethyl chloroformate and *a*-bromonaphthalene.[2] It is a liquid which has an aromatic odour and boils at 309°.

a-Naphthoyl oxide, or *a-Naphthoic anhydride*, $(C_{10}H_7.CO)_2O$ was prepared by Hofmann by heating the anhydrous calcium salt with naphthoyl chloride. It is sparingly soluble in alcohol, more readily in ether and benzene, from which it crystallizes in prisms, melting at 145°.

a-Naphthoyl chloride, $C_{10}H_7.COCl$, is formed when the acid is heated with phosphorus pentachloride. It is a heavy liquid, which boils at 296—298°, and solidifies at a low temperature.

a-Naphthamide, $C_{10}H_7.CO.NH_2$, is obtained by the action of ammonia on the chloride as well as, together with *a*-naphthoic acid, when the nitrile is heated with dilute sulphuric acid (Bamberger and Philip), or boiled for a considerable time with alcoholic potash.[3] It is also formed when aluminium chloride is added

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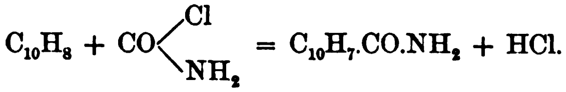
[1] Witt, *Ber.* **6**, 448; Hausamann, *Ber.* **9**, 1513; Boessneck, *Ber.* **16**, 639; Bamberger and Philip, *Ber.* **20**, 241; Ekstrand, *J. Pr. Chem.* II. **38**, 139.

[2] Ekstrand, *J. Pr. Chem.* II. **38**, 146.

[3] Ekstrand, *J. Pr. Chem.* II. **38**, 146.

to a mixture of naphthalene, carbon disulphide and chloroformamide, $CO(NH_2)Cl$, and the whole heated :[1]



$$C_{10}H_8 + CO\begin{matrix}\nearrow Cl \\ \searrow NH_2\end{matrix} = C_{10}H_7.CO.NH_2 + HCl.$$

The chloroformamide employed in this reaction is obtained by heating carbonyl chloride with ammonium chloride.

The amide crystallizes from alcohol in needles with a satin lustre, plates, or tablets, which melt at 202°.

a-Naphthanilide, $C_{10}H_7.CO.NH(C_6H_5)$, was prepared by Hofmann by acting on an alcoholic solution of aniline with the chloride. It forms a silky crystalline mass, and melts at 160°.

a-Naphtho-a-naphthalide, $C_{10}H_7.CO.NH(C_{10}H_7)$, is a crystalline powder, melts at 244°, and is sparingly soluble in alcohol.

2678 *a-Naphthonitrile*, $C_{10}H_7.CN$, is obtained, in addition to the methods already described, when the vapour of *a*-bromonaphthalene is passed over heated ferrocyanide of potassium, and also when a mixture of cyanogen and naphthalene vapour is slowly passed through a tube heated to faint redness.[2] It is further formed when *a*-dinaphthyl thiocarbamide is heated with copper powder :[3]

$$CS(NH.C_{10}H_7)_2 + 2Cu = CN.C_{10}H_7 + C_{10}H_7.NH_2 + Cu_2S.$$

Heim obtained it by heating a mixture of *a*-naphthyl phosphate and potassium cyanide to 200—300° in a current of hydrogen,[4] whilst Gasiorowski and Merz found that it is formed when *a*-formonaphthalide is boiled with zinc dust in a current of hydrogen.[5] Finally, it can be prepared by diazotizing *a*-naphthylamine and pouring the liquid into a hot solution of potassium copper cyanide. In order to remove any unaltered naphthylamine and any naphthol formed by the reaction the product is treated successively with caustic soda solution and hydrochloric acid, and is then distilled with steam, a yield of about 30—35 per cent. of the calculated amount being obtained.[6]

a-Naphthonitrile is insoluble in water, readily soluble in alcohol, and crystallizes from light petroleum in broad needles,

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[1] Gattermann and Schmidt, *Ber.* **20**, 858.

[2] Merz and Weith, *Ber.* **10**, 746.

[3] Weith, *Ber.* **6**, 967.

[4] *Ber.* **16**, 1779.

[5] *Ber.* **18**, 1006.

[6] E. Richter, *Ber.* **22**, 2449.

with a satin lustre, which melt at 37·5°. It has a great tendency to remain liquid below its freezing-point, and boils without decomposition at 297—298°.

When sodium is added to its hot alcoholic solution, α-tetrahydronaphthomethylamine is formed, accompanied by dihydronaphthalene and hydrocyanic acid :

$$C_{10}H_7.CN + 4H = C_{10}H_{10} + HCN.$$

A small quantity is always converted into α-napthoic acid by sodium ethylate.[1]

α-Naphthothiamide, $C_{10}H_7.CS.NH_2$, was obtained by Hofmann by the action of sulphuretted hydrogen on the base; it forms crystals, melting at 126°.

α-Naphthohydroxamic acid, $C_{10}H_7C(OH)N.OH$, is formed when hydroxylamine hydrochloride is dissolved in 8—10 parts of water and the equivalent amount of carbonate of sodium, and α-naphthoyl chloride then added. The precipitated crystalline powder is washed with ether to remove the naphthoic acid which is formed, and the residue recrystallized from alcohol. It forms lustrous plates, which melt at 186—187° with evolution of gas, and are only sparingly soluble in hot water. The aqueous solution is coloured deep wine-red by ferric chloride. On heating with alkalis, naphthohydroxamic acid is decomposed with formation of α-naphthylamine and carbon dioxide.

α-Dinaphthohydroxamic acid, $C_{10}H_7.C(OH)NO.CO.C_{10}H_7$, is obtained, together with α-dinaphthyl carbamide, by the action of α-naphthoyl chloride on the preceding compound, and also in the same manner by adding two molecules of the chloride to one molecule of hydroxylamine. It crystallizes from alcohol in long white needles, which melt at 150°, are slightly soluble in hot water, and give no colouration with ferric chloride.[2]

α-Naphthamidoxime, $C_{10}H_7.C.(NOH)NH_2$, is prepared by heating an alcoholic solution of α-naphthonitrile and hydroxylamine. It crystallizes from dilute alcohol in large plates, melting at 148—149°. When its solution in hydrochloric acid is allowed to evaporate, the *hydrochloride*, $C_{10}H_7C(NOH)NH_3Cl$, remains as a syrupy mass, which solidifies on long-continued standing to stellate groups of needles. The *platino-*

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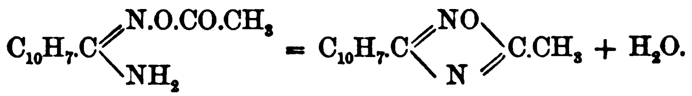
[1] Bamberger and Lodter, *Ber.* **20**, 1703.

[2] Ekstrand, *Ber.* **20**, 1353.

chloride, $[C_{10}H_7.C(NOH)NH_3]_2PtCl_6$, is also readily soluble, and crystallizes on the gradual evaporation of its solution in long yellow needles.[1]

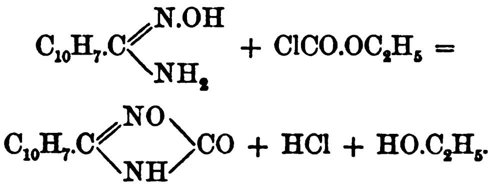
Acetyl-a-naphthamidoxime, $C_{10}H_7C(NO.CO.CH_3)NH_2$, is obtained by the action of acetic anhydride on the amidoxime, and crystallizes from alcohol in white, lustrous needles, which melt at 129°, and are insoluble in alkalis.[2] When it is boiled with water, *ethenyl-a-naphthamidoxime* is formed, which may also be obtained by heating the amidoxime with acetic anhydride (Ekstrand):



This substance crystallizes from alcohol in long needles melting at 36°.

a-Naphthoyl-a-naphthamidoxime, $C_{10}H_7.C(NO.CO.C_{10}H_7)NH_2$, is obtained by heating the amidoxime with *a*-naphthoyl chloride, and crystallizes in slender needles, melting at 228° (Ekstrand).

Carbonyl-a-naphthimidoxime, $C_{11}H_8N_2O_2$, is formed when the amidoxime is heated with ethyl chloroformate:



It crystallizes from alcohol in white needles, melting at 189°, and is insoluble in acids, but dissolves in alkalis (Richter).

a-Tetrahydronaphthoic acid, $C_{10}H_{11}.CO_2H$, is obtained, together with the amide, by heating the corresponding nitrile to 160—170° with alcoholic potash. It crystallizes in dendritic groups of slender prisms with a vitreous lustre, melts at 128°, and is sparingly soluble in cold, more freely in hot water, and very readily in alcohol.

a-Tetrahydronaphthamide, $C_{10}H_{11}.CO.NH_2$, crystallizes from hot water in tablets, which have a satin lustre, and melt at 182°.

a-Tetrahydronaphthonitrile, $C_{10}H_{11}.CN$, is formed when a solution of *a*-tetrahydrodiazonaphthalene chloride is allowed

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[1] Ekstrand, *Ber.* **20**, 223.

[2] E. Richter, *Ber.* **22**, 2449.

to drop into a boiling solution of copper sulphate and potassium cyanide. It is a viscid, colourless, transparent liquid, which has a faint odour resembling that of the nitriles, and boils at 277—279°. When its solution in alcoholic ammonia is saturated with sulphuretted hydrogen, *a-tetrahydrothionaphthamide*, $C_{10}H_{11}.CS.NH_2$, is formed. This substance is a dark yellow, oily liquid, and is decomposed by a gentle heat into the nitrile and sulphuretted hydrogen.[1]

2679 *β-Naphthaldehyde*, $C_{10}H_7.CHO$, was first obtained by Battershall by distilling a mixture of calcium β-naphthoate and calcium formate.[2]

Schulze prepared it by heating naphthomethyl chloride or bromide with water and lead nitrate;[3] and Bamberger and Boekmann by the oxidation of naphthomethyl alcohol with chromic acid solution.[4]

It crystallizes in silvery plates, melts at 60·5—61°, is freely soluble in alcohol, less freely in hot water, and readily volatilizes with steam. Like other aldehydes it reduces ammoniacal silver solution and restores the colour to a solution of magenta in sulphurous acid.

Alcoholic ammonia converts it into *hydronaphthamide* or *naphthomethinetriamine*, $(C_{10}H_7.CH)_3N_2$, which forms nodular masses insoluble in water, alcohol, and ether, and decomposes again into ammonia and the aldehyde on heating with dilute hydrochloric acid.

β-Naphthoic acid is also prepared from its nitrile, which is obtained by the distillation of potassium ferrocyanide with sodium β-naphthalenesulphonate.[5] The latter salt, which is now manufactured, always contains a little sodium naphthalenedisulphonate, which brings about the formation of the dinitrile, $C_{10}H_6(CN)_2$.

The β-naphthonitrile is freed from this by distillation,[6] and is then decomposed by boiling with alcoholic potash or soda, or by heating with acid under pressure. Schulze also obtained it by the oxidation of naphthomethyl chloride with potassium permanganate.[7]

It is scarcely soluble in cold, and sparingly in hot water, but

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[1] Bamberger and Bordt, *Ber.* **22**, 625.

[2] *Annalen*, **168**, 116.

[3] *Ber.* **17**, 1527.

[4] *Ber.* **20**, 1115.

[5] Merz and Mühlhäuser, *Zeitsch.* **1869**, 70; Hausamann, *Ber.* **9**, 1513; Vieth, *Annalen*, **180**, 305.

[6] Ekstrand *J. Pr. Chem.* II. **38**, 139.

[7] *Ber.* **17**, 1530.

readily in alcohol, crystallizes from light petroleum in long needles, melting at 182° and boils above 300°.

The β-naphthoates of the alkali metals are readily soluble in water.

Calcium β-naphthoate, $(C_{10}H_7.CO_2)_2Ca + 3H_2O$, crystallizes from boiling water in long needles, and dissolves in 1800 parts of water at 15°.

Barium β-naphthoate, $(C_{10}H_7.CO_2)_2Ba + 4H_2O$, also forms needles, and dissolves in 1400 parts of water at 15°.

Silver β-naphthoate, $C_{10}H_7CO_2Ag$, is a white flocculent precipitate, which is somewhat soluble in hot water.

Methyl β-naphthoate, $C_{10}H_7.CO_2CH_3$, was prepared by Vieth by heating the chloride with methyl alcohol. It crystallizes in white lustrous plates, melts at 77°, boils at 290°, and has a pleasant smell resembling that of strawberries.

Ethyl β-naphthoate, $C_{10}H_7.CO_2C_2H_5$, is an oily, faintly odorous liquid, which boils at 308—309°, and solidifies in the cold to crystalline scales, which melt with the heat of the hand.

β-Naphthoic anhydride, $(C_{10}H_7.CO)_2O$, was obtained by Hausamann by heating the chloride with calcium β-naphthoate; it crystallizes from ether in tabular aggregates of silky needles, melting at 134°.

a-β-Naphthoic anhydride is prepared in the same manner from α-naphthoyl chloride and potassium β-naphthoate, and crystallizes in slender needles, melting at 126°.[1]

β-Naphthoyl chloride is formed when the acid is heated with phosphorus pentachloride, and is a crystalline mass, melts at 43°, and boils at 304—306°.

β-Naphthamide, $C_{10}H_7.CO.NH_2$, was prepared by Vieth by the action of ammonium carbonate on the chloride. It crystallizes from alcohol in tablets, melts at 92°, and is volatile without decomposition.

β-Naphthanilide, $C_{10}H_7.CO.NH(C_6H_5)$, is obtained by the action of the chloride on aniline and also when the acid is heated to 120° with aniline. It crystallizes from alcohol in lustrous plates, melting at 170°, and sublimes at a higher temperature in large, lustrous plates.

β-Naphthoyl-a-naphthalide, $C_{10}H_7.CO.NH(C_{10}H_7)$, crystallizes in very small needles and melts at 157°.

2680 *β-Naphthonitrile*, $C_{10}H_7.CN$, is formed, in addition to the method already mentioned, when β-naphthyl phosphate is

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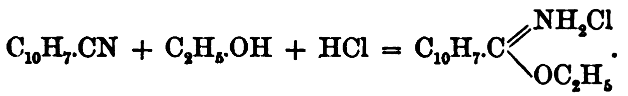
[1] *Ber.* **9**, 1513.

heated with potassium cyanide,[1] and when β-formonaphthalide is heated with zinc dust in a current of hydrogen.[2] It may be prepared by means of the diazo-compound from β-naphthylamine in the same way as the α-compound from α-naphthylamine (Richter). It is less soluble than the α-compound in alcohol, but is fairly easily soluble in hot light petroleum, from which it crystallizes in small plates; it melts at 66·5°, and boils at 304—305°. When its solution in fuming sulphuric acid is poured into water β-naphthamide is formed.[3] Sodium added to its hot alcoholic solution reduces it with formation of tetrahydronaphthomethylamine, dihydronaphthalene, and hydrocyanic acid.

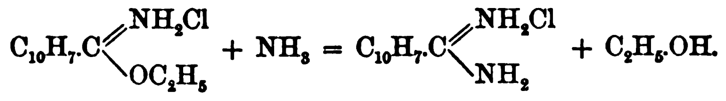
β-Naphthothiamide, $C_{10}H_7.CS.NH_2$, is formed when the nitrile is heated with ammonium sulphide. It crystallizes in long golden-yellow silky needles, melts at 149°, and on boiling with water is decomposed, like all the aromatic thiamides, into the nitrile and sulphuretted hydrogen.[4]

β-Naphthimide ethyl ether is obtained by passing hydrogen chloride into an alcoholic solution of β-naphthonitrile:



$$C_{10}H_7.CN + C_2H_5.OH + HCl = C_{10}H_7.C\begin{cases} NH_2Cl \\ OC_2H_5 \end{cases}.$$

The *hydrochloride* thus obtained crystallizes in needles; ammonia liberates the ether as a thick oil, which only commences to crystallize after being preserved for months. If, however, the salt be heated with alcoholic ammonia, *β-naphthenylamidine hydrochloride* is formed:



$$C_{10}H_7.C\begin{cases} NH_2Cl \\ OC_2H_5 \end{cases} + NH_3 = C_{10}H_7.C\begin{cases} NH_2Cl \\ NH_2 \end{cases} + C_2H_5.OH.$$

The latter crystallizes in stellate groups of pearly needles, while the free base, $C_{10}H_7.C(NH)NH_2$, liberated by caustic soda solution, separates as an oil, which solidifies in a vacuum to a white, nodular mass.

β-Naphthohydroxamic acid, $C_{10}H_7.C(OH)N.OH$, is obtained in

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[1] Heim, *Ber.* **16**, 1771.

[2] Gasiorowski and Merz, *Ber.* **18**, 1008.

[3] Armstrong and Houlding, *Proc. Chem. Soc.* **1889**, 122.

[4] Pinner and Klein, *Ber.* **11**, 1475; Bamberger and Boekmann, *Ber.* **20**, 1115.

a similar manner to the *a*-compound, and crystallizes from alcohol in hard, nodular aggregates of four-sided plates. It melts at 168°, and is only slightly soluble in boiling water, giving a solution in which ferric chloride produces a wine-red colouration.

β-Dinaphthohydroxamic acid, $C_{10}H_7.C(OH)NO.CO.C_{10}H_7$, crystallizes from alcohol in needles, which melt at 171°. Its potassium salt, which forms lustrous scales, decomposes on boiling with water with formation of *β*-dinaphthyl carbamide :

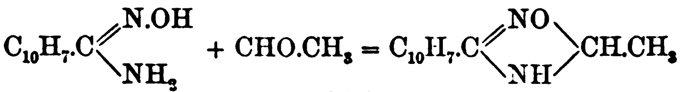
$$2C_{10}H_7.C\begin{matrix}\nearrow N.O.CO.C_{10}H_7\\ \searrow OK\end{matrix} + H_2O =$$
$$CO(C_{10}H_7.NH)_2 + 2C_{10}H_7CO_2K + CO_2.$$

a-β-Dinaphthohydroxamic acid is formed when *β*-naphthohydroxamic acid is heated with *a*-naphthoyl chloride, and crystallizes from alcohol in needles, melting at 160°.[1]

β-Naphthamidoxime, $C_{10}H_7.C(NOH)NH_2$, is prepared from *β*-naphthonitrile in a similar manner to the *a*-compound, and crystallizes from alcohol in lustrous scales, melting at 150°. Its *hydrochloride* forms long needles.[2]

Ethyl β-naphthamidoxime, $C_{10}H_7C(NOC_2H_5)NH_2$, is formed when the amidoxime is heated with sodium ethylate and ethyl iodide ; it crystallizes in white needles, melting at 74—75°.

Ethidene β-naphthamidoxime, $C_{10}H_7C(N_2HO)CH.CH_3$, is obtained by the action of aldehyde on the amidoxime :



$$C_{10}H_7.C\begin{matrix}\nearrow N.OH\\ \searrow NH_2\end{matrix} + CHO.CH_3 = C_{10}H_7.C\begin{matrix}\nearrow NO\searrow\\ \searrow NH\nearrow\end{matrix}CH.CH_3$$
$$+ H_2O.$$

It forms white needles, and melts at 121—122°.[3]

Acetyl-β-naphthamidoxime, $C_{10}H_7C(NO.CO.CH_3)NH_2$, is formed by the action of acetic anhydride, and crystallizes from absolute alcohol in aggregates of brown needles, which melt at 154°. When this substance is boiled with water, or when the amidoxime is heated with acetic anhydride, *ethenyl-β-naphthamidoxime* is formed, which crystallizes in large scales, and melts at 87° (Ekstrand).

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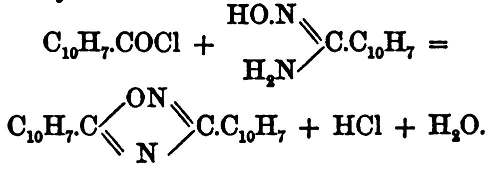
[1] Ekstrand, *Ber.* **20**, 1353.

[2] Ekstrand, *Ber.* **20**, 223.

[3] E. Richter, *Ber.* **22**, 2449.

Benzoyl-β-naphthamidoxime, $C_{10}H_7.C(NO.CO.C_6H_5)NH_2$, is obtained by heating the amidoxime with benzoyl chloride, and crystallizes from alcohol in matted, silky needles, which melt at 179°. On boiling with water it is converted into *benzenyl-a-naphthamidoxime*, $C_{10}H_7.CN_2OC.C_6H_5$, which forms white plates, melting at 116° (Richter).

β-Naphthazoxime is formed when the amidoxime is heated with β-naphthoyl chloride:



$$C_{10}H_7.COCl + \begin{matrix}HO.N \\ H_2N\end{matrix}\!\!>C.C_{10}H_7 = C_{10}H_7.C\!\!<\!\begin{matrix}ON \\ N\end{matrix}\!\!>C.C_{10}H_7 + HCl + H_2O.$$

It crystallizes from glacial acetic acid in plates or broad needles, and melts at 175° (Ekstrand).

Carbonyl-β-naphthimidoxime crystallizes from benzene in lustrous matted needles, and melts at 216°.

HALOGEN SUBSTITUTION PRODUCTS OF a-NAPHTHOIC ACID.

2681 *2-Chlor-a-naphthoic acid*, $C_{10}H_6Cl.CO_2H$. When one molecule of 2-hydroxy-a-naphthoic acid is heated to 180—190° with three molecules of phosphorus pentachloride, the product consists of a dark brown oily liquid, with an olive-green fluorescence, which is probably *chloronaphthotrichloride*, $C_{10}H_6Cl.CCl_3$, and which changes in moist air into crystals of chloronaphthoic acid. The latter is readily soluble in alcohol, with difficulty in water, and melts at 152—153°. It is converted into a-naphthoic acid by sodium amalgam and water.

Calcium 2-chlor-a-naphthoate, $(C_{10}H_6Cl.CO_2)_2Ca + 2H_2O$, dissolves in 150 parts of cold water.

Methyl 2-chlor-a-naphthoate, $C_{10}H_6Cl.CO_2CH_3$, crystallizes in white, broad, brittle prisms, and melts at 50°.[1]

4'-Chlor-a-naphthoic acid, $C_{10}H_6Cl.CO_2H$, is formed when chlorine is passed into a solution of a-naphthoic acid in glacial acetic acid containing iodine, and when its nitrile is heated with hydrochloric acid under pressure. It has also been ob-

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[1] Rabe, *Ber.* **22**, 392.

tained from 4′-amido-a-naphthoic acid by means of the diazo-reaction. It forms colourless needles, is readily soluble in alcohol, slightly in glacial acetic acid, and melts at 245°, but sublimes in elegant needles at a lower temperature than this. It cannot be further chlorinated.[1]

Calcium 4′-chlor-a-naphthoate, $(C_{10}H_6Cl.CO_2)_2Ca + 2H_2O$, crystallizes in needles, and dissolves at the ordinary temperature in 118 parts of water.

Ethyl 4′-chlor-a-naphthoate, $C_{10}H_6Cl.CO_2C_2H_5$, crystallizes from alcohol in quadratic tablets, melting at 42°.

4′-Chloronaphthamide, $C_{10}H_6Cl.CO.NH_2$, is formed when the nitrile is boiled with alcoholic potash and forms plates or tablets, which melt at 239°.

4′-Chloronaphthonitrile, $C_{10}H_6Cl.CN$, is obtained by passing chlorine into a solution of a-naphthonitrile in carbon disulphide containing a little iodine. It crystallizes in large needles, melting at 145°.

1′-Chlor-a-naphthoic acid has been prepared from the corresponding amido-acid by allowing an alkaline solution of the acid and the calculated amount of potassium nitrite to drop into hydrochloric acid cooled by snow, and running the liquid thus obtained into a boiling solution of cuprous chloride in hydrochloric acid. It is also formed in small quantity in the chlorination of a-naphthoic acid. It crystallizes from weak alcohol in scales, melts at 167°, and readily sublimes in tablets.

Calcium 1′-chlor-a-naphthoate, $(C_{10}H_6Cl.CO_2)_2Ca + 2H_2O$, forms tabular aggregates of long hard needles, which dissolve in 42 parts of water, and do not appear to be more soluble in hot than in cold water.

Ethyl 1′-chlor-a-naphthoate, $C_{10}H_6Cl.CO_2C_2H_5$, crystallizes in long hard needles, and melts at 50°.

4′ : 1′-Dichlor-a-naphthoic acid, $C_{10}H_5Cl_2.CO_2H$, is obtained by chlorinating the preceding compound, and has also been obtained from 4′-chloro-1′-amidonaphthoic acid by the diazo-reaction. It crystallizes in scales, which are readily soluble in alcohol, and melt at 186—187°.

Its *calcium salt*, $(C_{10}H_5Cl_2.CO_2)_2Ca + 2H_2O$, crystallizes in long needles, which are moderately soluble in water. The *ethyl ester* forms slender needles, melting at 61°.

Trichlor-a-naphthoic acid, $C_{10}H_4Cl_3.CO_2H$, is formed by the further action of chlorine; it crystallizes from hot water in

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[1] *J. Pr. Chem.* II. **38**, 139.

small needles, melting at 163—164°. It is accompanied by an isomeride, which is only sparingly soluble in alcohol, also crystallizes in needles and melts at 282° (Ekstrand).

4′-Brom-α-naphthoic acid, $C_{10}H_6Br.CO_2H$, is formed when a solution of α-naphthoic acid is heated with bromine in the presence of iodine. It crystallizes from alcohol in slender white needles, which melt at 246°. Its salts have been investigated by Hausamann.[1]

Calcium 4′-brom-α-naphthoate, $2(C_{10}H_6Br.CO_2)_2Ca + 3H_2O$, forms slender, granular crystals, and dissolves at 20° in 66·5 parts of water.

The *ethyl ester* crystallizes in tablets melting at 48—49° (Ekstrand).

4′-Brom-α-naphthonitrile, $C_{10}H_6Br.CN$, is obtained by the action of bromine on a solution of α-naphthonitrile in carbon disulphide. It crystallizes from ether or chloroform in needles, which melt at 147° and readily sublime. On heating with alcoholic caustic soda to 140—150°, it is converted into the acid (Hausamann).

Tetrabrom-α-naphthoic acid, $C_{10}H_3Br_4.CO_2H$, was prepared by Hausamann from α-naphthoic acid by gradually heating it to 350° with bromine and a little iodine. It sublimes in slender needles and melts at 239°.

HALOGEN SUBSTITUTION PRODUCTS OF β-NAPHTHOIC ACID.

2682 *Chloro-β-naphthoic acid*, $C_{10}H_6Cl.CO_2H$. By passing chlorine into a solution of β-naphthonitrile in glacial acetic acid containing a little iodine, Ekstrand obtained *β-chloronaphthonitrile*, which crystallizes from alcohol in needles, melting at 138°. On heating with fuming hydrochloric acid to 150°, this is converted into the acid, which also forms needles, and melts at 261°.[2]

α-Chloro-β-naphthoic acid has been obtained from the corresponding hydroxynaphthoic acid, which is first converted into α-chloro-β-naphthenyl chloride, $C_{10}H_6Cl.CCl_3$, by the action of phosphorus pentachloride, and this substance then decomposed by boiling with acetic acid and a little water. It

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[1] *Ber.* **9**, 1518.

[2] *Beilstein's Handb.* **2**, 931.

crystallizes from benzene in slender needles, melting at 176°, which are scarcely soluble in cold water.

The *calcium salt*, $(C_{10}H_6Cl.CO_2)_2Ca + 2H_2O$, separates from the aqueous solution in clear crystals.[1]

Dichloro-β-naphthoic acid, $C_{10}H_5Cl_2.CO_2H$, is formed when chlorine is passed into a hot solution of β-naphthoic acid in acetic acid containing a little iodine. It crystallizes from alcohol, in which it is only sparingly soluble in needles, melts at 291°, and readily sublimes.

The *calcium salt*, $2(C_{10}H_5Cl_2.CO_2)_2Ca + 5H_2O$, crystallizes in small prisms, and dissolves at the ordinary temperature in 3018 parts of water. The *ethyl ester* crystallizes from alcohol in long needles, melting at 66°.[2]

Monobromo-β-naphthoic acid, $C_{10}H_6Br.CO_2H$, was prepared by Hausamann in a similar manner to the α-compound. It crystallizes from alcohol in granules, melts at 256°, and sublimes in slender white needles.

Calcium bromo-β-naphthoate, $(C_{10}H_6Br.CO_2)_2Ca + 3H_2O$, forms nodular crystals, which require 5000 parts of water for solution at 20°.

Bromo-β-naphthonitrile, $C_{10}H_6Br.CN$, melts at 148—149°, and sublimes when carefully heated in broad white needles, which are extremely like those of benzoic acid.

Hausamann has also prepared the following compounds, which likewise form granular crystals or needles, and sublime in needles:

	Melting-point.
Tribromo-β-naphthoic acid, $C_{10}H_4Br_3.CO_2H$ . . .	269—270°
Tetrabromo-β-naphthoic acid, $C_{10}H_3Br_4.CO_2H$ . .	259—260°

NITRO-SUBSTITUTION PRODUCTS OF α-NAPHTHOIC ACID.

2683 *4′-Nitro-α-naphthoic acid*, $C_{10}H_6(NO_2)CO_2H$, is formed, together with 1′-nitro-α-naphthoic acid, when α-naphthoic acid is thoroughly moistened with twice its weight of nitric acid of sp. gr. 1·41, and gently heated until the evolution of red fumes ceases. The product is washed with water and heated with sodium carbonate solution, a little nitronaphthalene being left

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[1] Wolffenstein, *Ber.* **21**, 1186.

[2] Ekstrand, *Ber.* **17**, 1605.

undissolved. The acids are precipitated by hydrochloric acid, and are then separated by the action of hydrogen chloride on their alcoholic solution, which converts the 4′-nitro-acid alone into the ethyl ester. The latter is separated from the unaltered 1′-nitro-acid, after the removal of the alcohol by evaporation, by treatment with sodium carbonate solution, and is then hydrolysed by heating with concentrated sulphuric acid on the water-bath.[1]

4′-Nitro-α-naphthoic acid has also been obtained by heating its nitrile with hydrochloric acid.[2] It crystallizes from hot alcohol in slender, yellowish-white needles, and melts at 239°; it dissolves in 187 parts of cold commercial alcohol and in 4820 parts of cold water, freely in hot alcohol, and moderately in hot water. When heated it readily sublimes in needles.

Calcium 4′-nitro-a-naphthoate, $[C_{10}H_6(NO_2)CO_2]_2Ca + 2H_2O$, crystallizes in yellow needles, which are somewhat sparingly soluble in water.

The *methyl ester*, $C_{10}H_6(NO_2)CO_2CH_3$, forms small needles, melting at 109—110°, and the *ethyl ester*, $C_{10}H_6(NO_2)CO_2C_2H_5$, crystallizes in long, matted, almost colourless needles, which melt at 92—93°.

4′-Nitro-α-naphthoic acid is oxidized by alkaline potassium permanganate solution and by dilute nitric acid to v-nitrophthalic acid;[3] when it is heated for some time with an excess of nitric acid of sp. gr. 1·3, 1 : 4′-dinitronaphthalene is formed (Ekstrand).

4′-Nitro-a-naphthonitrile, $C_{10}H_6(NO_2)CN$, is formed together with isomeric compounds by the nitration of α-naphthonitrile; it crystallizes in fine needles, melts at 205°, and is readily soluble in hot alcohol.[4]

1′-Nitro-a-naphthoic acid crystallizes from alcohol in yellowish-white, hard prisms, which melt at 215°, and do not sublime even when heated above the melting-point for a considerable time. It dissolves at the ordinary temperature in 21·5 parts of commercial alcohol and in 2590 parts of water; it is readily soluble in hot alcohol and glacial acetic acid, somewhat less freely in boiling water.

Calcium 1′-nitro-a-naphthoate, $[C_{10}H_6(NO_2)CO_2]_2Ca + 3H_2O$,

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[1] Ekstrand, *J. Pr. Chem.* II. **38**, 155 and 241.

[2] Graeff, *Ber.* **16**, 2246.

[3] Graeff, *Ber.* **15**, 1125.

[4] Graeff, *Ber.* **14**, 1063; **16**, 2246.

crystallizes in long yellow tablets, which dissolve in 159 parts of cold water.

The *ethyl ester*, $C_{10}H_6(NO_2)CO_2C_2H_5$, is not formed by the action of hydrogen chloride on the alcoholic solution of the acid, but was prepared by Ekstrand from the silver salt and ethyl iodide; it forms hard, yellow, octohedral crystals, and melts at 68—69°. On continued heating with nitric acid of sp. gr. 1·3, the acid is converted into 1 : 1′-dinitronaphthalene.

4 : 4′-*Dinitro-a-naphthoic acid*, $C_{10}H_5(NO_2)_2CO_2H$, is obtained, accompanied by isomerides, by the action of red, fuming nitric acid on *a*-naphthoic acid, and is the chief product of this reaction, but cannot be completely separated from the other products by crystallization. The pure acid can, however, be obtained by converting the crude substance into the ethyl ester and then decomposing the latter. It can be prepared more readily and purer by heating 4-nitro-*a*-naphthoic acid with fuming nitric acid. It crystallizes from hot alcohol in yellowish-white needles, which melt at 265°.

The *calcium salt*, $[C_{10}H_5(NO_2)_2CO_2]_2Ca + 3H_2O$, crystallizes in needles, which are moderately soluble in hot water.

The *ethyl ester*, $C_{10}H_5(NO_2)_2CO_2.C_2H_5$, forms slender needles, melting at 143°.

When the acid is heated with tin and hydrochloric acid, 1 : 1′-diamidonaphthalene is formed.

4′ : 1′-*Dinitro-a-naphthoic acid* is obtained, together with the preceding compound and with that next to be described, from 4′-nitro-naphthoic acid; it separates from hot alcohol in rhombic crystals, which melt at 218°.

The *calcium salt*, $[C_{10}H_5(NO_2)_2CO_2]_2 + 7H_2O$, is readily soluble in water, and crystallizes in broad, lustrous-yellow needles.

The *ethyl ester* is not formed by the action of hydrogen chloride on the alcoholic solution of the acid, but has been prepared from the silver salt and ethyl iodide; it forms long, hard yellow needles, melting at 129.°

On reduction the acid is converted into amidonaphthostyril.

4′ : 2-*Dinitro-a-naphthoic acid* crystallizes from alcohol in small, broad, colourless, silky plates or broad needles, which melt at 215°.

The *ethyl ester* is readily formed when hydrogen chloride is passed into the alcoholic solution of the acid, and crystallizes in slender matted needles, melting at 137° (Ekstrand).

α-Trinitro-α-naphthoic acid, $C_{10}H_4(NO_2)_3CO_2H$, is formed, together with β-trinitronaphthalene, by the action of a mixture of concentrated sulphuric acid and fuming nitric acid on 1′-nitro-α-naphthoic acid. It crystallizes from alcohol in large broad, brown needles, melts at 283°, and has such an intensely bitter taste that the least trace produces a very persistent loathing. This is in so far remarkable as among all the other derivatives of α-naphthoic acid investigated by Ekstrand, the only one which possesses a similar property is dichloronitronaphthoic acid, a substance described below. This fact may perhaps point to a similar constitution of the two compounds.

β-Trinitro-α-naphthoic acid is obtained, together with the following compounds, when 4 : 4′-dinitronaphthoic acid is heated with sulphuric acid and fuming nitric acid; it is readily soluble in alcohol, and crystallizes in hard, light yellow needles, melting at 236°.

γ-Trinitro-α-naphthoic acid is only sparingly soluble in alcohol, and forms small, light yellow, hard, cubical crystals, melting at 293°.

4′-Chloro-1′-nitro-α-naphthoic acid, $C_{10}H_5Cl(NO_2)CO_2H$, is formed when 4′-chlor-α-naphthoic acid is dissolved in fuming nitric acid. It crystallizes in prismatic needles, which melt with decomposition at 224—225°. On further heating with nitric acid it is converted into β-dinitrochloronaphthalene.

Its *ethyl ester* forms hard tablets, melting at 121°, which are readily soluble in alcohol.

1′-Chloronitro-α-naphthoic acid has been prepared from 1′-chlor-α-naphthoic acid, and crystallizes in plates or hard prisms, melts at 227°, and is also readily soluble in alcohol. The *ethyl ester* forms light yellow scales, melting at 84°.

Dichloronitro-α-naphthoic acid, $C_{10}H_4Cl_2(NO_2)CO_2H$, is obtained from 4′ : 1′-dichloronaphthoic acid and forms a light yellow crystalline mass, melts at 165°, is very readily soluble in alcohol and glacial acetic acid, and has an intensely bitter, repulsive taste.

4′-Bromo-1′-nitro-α-naphthoic acid, $C_{10}H_5Br(NO_2)CO_2H$, was prepared by Ekstrand from 4′-brom-α-naphthoic acid; it crystallizes from alcohol in small, yellowish prisms, melting at 260°.

NITRO-SUBSTITUTION PRODUCTS OF β-NAPHTHOIC ACID.

2684 *α-Nitro-β-naphthoic acid*, $C_{10}H_6(NO_2)CO_2H$, was first obtained by Graeff from its nitrile.[1] It is also formed, together with isomerides, when β-naphthoic acid is dissolved in boiling glacial acetic acid, an excess of fuming nitric acid added and the solution allowed to boil gently for some time. The product is converted into the sodium salts and the solution concentrated. The salt of the α-acid soon separates out on cooling in thin, rhombic tablets, with a golden lustre, which are then decomposed with hydrochloric acid.[2]

α-Nitro-β-naphthoic acid crystallizes from boiling alcohol in long, yellowish hair-like needles, which melt at 293°, and readily sublime in small, almost colourless needles.

Calcium α-nitro-β-naphthoate, $2[C_{10}H_6(NO_2)CO_2]_2Ca + 7H_2O$, crystallizes in small, coarse needles, united in stellate groups.

The *methyl ester*, $C_{10}H_6(NO_2)CO_2.CH_3$, forms large, light yellow needles, melting at 112°.

The *ethyl ester*, $C_{10}H_6(NO_2)CO_2.C_2H_5$, crystallizes from alcohol in long, slender, yellow needles, and melts at 110—111°.

α-Nitro-β-naphthonitrile, $C_{10}H_6(NO_2)CN$, is formed, together with other products, by the nitration of β-naphthonitrile, and separates from hot alcohol or glacial acetic acid, according to the concentration of the solution, in simple or arborescent crystals, with a splendid golden lustre, which melt at 172—173°.

β-Nitro-β-naphthoic acid is readily soluble in alcohol, and crystallizes in slender, colourless needles, melting at 269°.

Its *ethyl ester* forms small yellow tablets or plates, which frequently form needle-shaped aggregates, and melts at 93°.

γ-Nitro-β-naphthoic acid, which is separated from the β- and δ-acids by means of its ethyl ester, crystallizes in small, almost colourless needles, which are sparingly soluble in alcohol, and melt at 288—289°.

The *ammonium salt* crystallizes in long yellow needles, which are very sparingly soluble in water at the ordinary temperature.

The *ethyl ester* forms elongated rhombic tablets, melting at 121°.

On oxidation with potassium permanganate it yields a mixture

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[1] *Ber.* **16**, 2246.

[2] Ekstrand, *Ber.* **18**, 1204.

of nitrophthalic and trimellitic acids. Both this acid and the α-acid yield α-naphthylamine on reduction and elimination of the carboxyl group, so that they are probably the 1′-β and 4′-β isomerides.[1]

δ-Nitro-β-naphthoic acid forms stellate groups of small needles, melting at 285°. The *ethyl ester* crystallizes in small needles and melts at 75°.[2]

α-Dinitro-β-naphthoic acid, $C_{10}H_5(NO_2)_2CO_2H$, is formed, together with the following compound, when β-naphthoic acid is dissolved in fuming nitric acid. On the gradual evaporation of the alcoholic solution, the α-acid separates out in woolly needles, whereas the β-acid crystallizes in small prisms. It is best prepared by heating γ-nitro-β-naphthoic acid with 5 parts of fuming nitric acid,[3] and is purified by recrystallization.

α-Dinitro-β-naphthoic acid forms long, slender, silky needles, or hard yellow crystals, and melts at 226°. Its *ethyl ester* is very soluble in hot alcohol, and crystallizes in matted, silky needles.

β-Dinitro-β-naphthoic acid, which is best prepared by heating α-nitro-β-naphthoic acid with fuming nitric acid, forms small, hard, rectangular prisms, melting at 248°.[4]

The *calcium salt* crystallizes in prismatic needles, and is moderately soluble in hot water; the *ethyl ester* separates from hot alcohol, in which it is not very readily soluble, in small, hard, wedge-shaped crystals, melting at 165°.[5]

AMIDO-α-NAPHTHOIC ACIDS.

2685 *4-Dimethylamido-α-naphthoic acid*, $C_{10}H_6N(CH_3)_2CO_2H$, is obtained by heating dimethyl-α-naphthylamine with carbonyl chloride to 60—70°, and treating the product with sodium amalgam. It crystallizes from alcohol in white pointed needles, melts at 163—165°, and combines both with bases and acids.[6]

4′-Amido-α-naphthoic acid, $C_{10}H_6(NH_2)CO_2H$, is formed when

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[1] Ekstrand, *J. Pr. Chem.* II. **42**, 295.

[2] Ekstrand, *J. Pr. Chem.* II. **42**, 304.

[3] Ekstrand, *J. Pr. Chem.* II. **42**, 300.

[4] Ekstrand, *J. Pr. Chem.* II. **42**, 286.

[5] Ekstrand, *Ber.* **17**, 1600.

[6] Friedländer and Welmans, *Ber.* **21**, 3126.

the corresponding nitro-acid is dissolved in ammonia and ferrous sulphate added. On the addition of acetic acid to the filtrate it separates out in slender needles, which soon become coloured violet. It melts at 211—212°, is sparingly soluble in ether, somewhat more freely in alcohol and acetic acid, and combines both with acids and bases.

Calcium 4'-amido-a-naphthoate, $[C_{10}H_6(NH_2)CO_2]_2Ca + 3H_2O$, crystallizes in hard, faintly violet coloured needles, which are very soluble in water.

Amido-a-naphthoic acid hydrochloride, $C_{10}H_6(NH_3Cl)CO_2H$, crystallizes from hot water in long, faintly violet coloured needles, which are only sparingly soluble in cold water.

The *nitrate* $C_{10}H_6(NH_3NO_3)CO_2H$, forms long, violet needles, and the *sulphate* $[C_{10}H_6(CO_2H)NH_3]_2SO_4$, crystallizes in reddish needles, and is even less soluble in water than the hydrochloride.

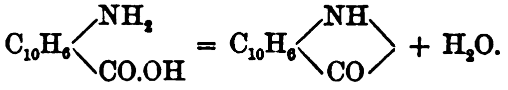
4'-Acetamido-a-naphthoic acid, $C_{10}H_6(NH.CO.CH_3)CO_2H$, is obtained by boiling the amido-acid with acetic anhydride, and crystallizes from hot alcohol in microscopic needles, melting above 280°.[1]

1'-*Chloramido-a-naphthoic acid,* $C_{10}H_5Cl(NH_2)CO_2H$, was prepared by Ekstrand by the reduction of the corresponding nitro-acid; it forms colourless needles, and its *hydrochloride* crystallizes in long hard needles.

1'-*Amido-a-naphthoic acid* is obtained from the corresponding nitro-acid in a similar manner to the 4'-*α*-compound. It separates from the ammoniacal solution on the addition of acetic acid in small needles. The *calcium salt,* $[C_{10}H_6(NH_2)CO_2]_2Ca + 9H_2O$, is very readily soluble, and forms indistinct crystalline aggregates, consisting of slender needles.

When hydrochloric acid is added to a solution of the sodium salt, the *hydrochloride* is precipitated in slender needles, but rapidly changes to the following compound.

Naphthostyril is also formed when the amido-acid is heated with water or alcohol:



$$C_{10}H_6\left\langle\begin{matrix}NH_2\\CO.OH\end{matrix}\right. = C_{10}H_6\left\langle\begin{matrix}NH\\CO\end{matrix}\right\rangle + H_2O.$$

Its formation can readily be understood, since the amido-acid is

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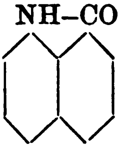
[1] Ekstrand, *J. Pr. Chem.* II. **38**, 244.

a peri-compound; the constitution of naphthostyril is therefore expressed by the formula:



It crystallizes from alcohol in slender, greenish needles, melts at 180—181°, and readily sublimes in small, yellow needles. It dissolves in alkalis, the corresponding salts of the amido-acid being formed, whereas hot hydrochloric acid dissolves it without change, forming a solution from which it separates out again on cooling.

Acetonaphthostyril, $C_{10}H_6CO(N.CO.CH_3)$, is obtained by heating the amido-acid with acetic anhydride on the water-bath. It separates out on cooling in stellate groups of needles, and crystallizes from alcohol in long, white, hair-like needles, melting at 125°.

Benzonaphthostyril, $C_{10}H_6CO(N.CO.C_6H_5)$, is formed when naphthostyril is heated with benzoyl chloride. It crystallizes from alcohol in slender needles, and melts at 170°.

Ekstrand has also prepared the following compounds:[1]

	Melting-point.
α-Naphthoylnaphthostyril, needles	152°
β-Naphthoylnaphthostyril, needles	197—198°

Chloronaphthostyril, $C_{10}H_5Cl(CO.NH)$, is formed by the reduction of 4′-chloro-1′-nitronaphthoic acid, and crystallizes from alcohol in golden-yellow needles, which melt at 270°.

Dichloronaphthostyril, $C_{10}H_4Cl_2(CO.NH)$, is produced by a remarkable reaction, together with carbon dioxide and chloronaphthalene, when 1′-nitro-α-naphthoic acid is heated with an excess of fuming hydrochloric acid to 140—150°:

$$C_{10}H_6(NO_2)CO.OH + 4HCl =$$
$$C_{10}H_4Cl_2(CO.NH) + 3H_2O + Cl_2.$$

It is also formed by the action of chlorine on naphthostyril, and crystallizes from glacial acetic acid in golden-yellow needles, which melt at 264—265°.

Bromonaphthostyril, $C_{10}H_5Br(CO.NH)$, is prepared by the

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[1] *J. Pr. Chem.* II. **38**, 159.

reduction of 4′-bromo-1′-nitronaphthoic acid, and crystallizes from alcohol in brown needles, melting at 257°.

Dibromonaphthostyril, $C_{10}H_4Br_2(CO.NH)$, is formed when 1′-nitro-α-naphthoic acid is heated with hydrobromic acid to 160—170°, and also when a solution of naphthostyril in glacial acetic acid is heated with bromine and a little iodine. It crystallizes from alcohol or acetic acid in golden-yellow needles, and melts at 268—270°. When it is boiled for a considerable time with acetic anhydride, *acetodibromonaphthostyril*, $C_{10}H_4Br_2(CO.N.CO.CH_3)$, is formed. This substance crystallizes in small yellow needles, melts at 185°, and only dissolves in alkalis with difficulty.

4′-*Nitronaphthostyril*, $C_{10}H_5(NO_2)(CO.NH)$, may be obtained either by the nitration of naphthostyril or by heating 4′ : 1′-dinitro-α-naphthoic acid with tin or hydrochloric acid. It crystallizes from glacial acetic acid in orange-yellow needles, which melt at about 300°.

4′-*Amidonaphthostyril*, $C_{10}H_5(NH_2)(CO.NH)$, is formed when the preceding compound is submitted to the further action of tin and hydrochloric acid. It crystallizes from alcohol in broad red needles, and melts at 239—240°. If the amido-group be replaced by chlorine the chloronaphthostyril described above is obtained. The *hydrochloride*, $C_{10}H_5(NH_3Cl)(CO.NH)$, forms yellow needles.

Dinitronaphthostyril, $C_{10}H_4(NO_2)_2(CO.NH)$, is obtained by the action of fuming nitric acid on dibromonaphthostyril and on nitronaphthostyril. It crystallizes in yellow prisms or tablets, which melt above 290°.

Naphthostyrilquinone, $C_{10}H_4O_2(CO.NH)$, is formed by the action of chromium trioxide on an acetic acid solution of naphthostyril, and crystallizes from glacial acetic acid in long red needles, which melt at about 278°. It is a derivative of β-naphthoquinone, since it is converted by o-diamidotoluene into *naphthostyriltoluquinoxaline*, $C_{10}H_4(N_2C_6H_3.CH_3)(CO.NH)$, which forms a yellow crystalline powder.[1]

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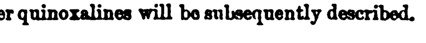
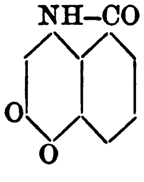
[1] The quinoxalines are feeble bases, which are formed by the action of ortho-diketones on ortho-diamines. The simplest member of the group is obtained from o-diamidobenzene and glyoxal:

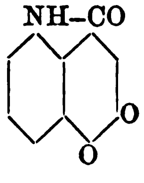


$$C_6H_4\begin{matrix}\diagup NH_2\\ \diagdown NH_2\end{matrix} + \begin{matrix}CHO\\ |\\ CHO\end{matrix} = C_6H_4\begin{matrix}\diagup N-CH\\ \quad\ \ |\\ \diagdown N=CH\end{matrix} + 2H_2O.$$

This and the other quinoxalines will be subsequently described. (See also Part III. p. 73).

The constitution of naphthostyrilquinone must therefore be expressed by one of the following formulæ:





AMIDO-β-NAPHTHOIC ACIDS.

2686 These compounds have been obtained by Ekstrand by the reduction of the nitro-acids with ammonia and ferrous sulphate.[1]

a-Amido-β-naphthoic acid, $C_{10}H_6(NH_2)CO_2H$, crystallizes in microscopic lustrous rhombic tablets, which soon become coloured violet, and melt at 232°. The *hydrochloride*, $C_{10}H_6(NH_3Cl)CO_2H$, forms long violet needles, the *nitrate*, $C_{10}H_6(NH_3NO_3)CO_2H$, large brown needles, and the *sulphate* well developed almost colourless needles.

Acetylamido-β-naphthoic acid, $C_{10}H_6(CO_2H)NH.C_2H_3O$, is obtained by heating the acid with acetic anhydride. It is very sparingly soluble in alcohol, and crystallizes from acetic acid in small tablets, melting at 291°.

Calcium a-amido-β-naphthoate, $[C_{10}H_6(NH_2)CO_2]_2Ca + 4H_2O$, is readily soluble in water, and crystallizes in short, lilac-coloured needles or prisms.

β-Amido-β-naphthoic acid crystallizes from dilute alcohol in small needles, melts at 211°, and soon becomes coloured violet.

γ-Amido-β-naphthoic acid is precipitated from its solution in acetic acid in small yellow needles. It crystallizes from weak alcohol in hair-like colourless needles, which on drying take a violet colour, and melt at 219°.

The *hydrochloride* and *sulphate* form small prisms, whilst the *nitrate* crystallizes in large thin plates. The salts are readily soluble in water, forming cherry-red solutions.

Acetyl-γ-amido-β-naphthoic acid is very readily formed by the action of acetic anhydride on the acid. It crystallizes from

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[1] *Ber.* **18**, 1204.

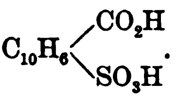
alcohol in slender needles, melting at 258°. The *diacetyl* derivative forms thick, hard crystals, and melts at 181°. The monacetyl derivative is converted by nitric acid into *nitro-acetamido-β-naphthoic acid*, $C_{10}H_5(NO_2)(NHC_2H_3O)CO_2H$, which crystallizes from alcohol in slender needles, and melts at 270°.[1]

a-Nitro-amido-β-naphthoic acid, $C_{10}H_5(NO_2)(NH_2)CO_2H$, is prepared by the action of alcoholic ammonium sulphide on the *a*-dinitro-acid. It is precipitated by acetic acid in stellate groups of small needles, melting at 235°. Its *hydrochloride* forms slender reddish needles.

a-Diamido-β-naphthoic acid forms slender colourless needles, melting at 130°. The *di-hydrochloride* crystallizes in long needles and is moderately soluble in pure water.[2]

β-Diamido-β-naphthoic acid, $C_{10}H_5(NH_2)_2CO_2H$, is obtained by reducing the corresponding dinitro-acid with ferrous sulphate in ammoniacal solution. It forms greenish-yellow needles, melts at 202°, and partially sublimes on heating. The *monohydrochloride* forms glimmering plates, melting at above 285°.

SULPHONAPHTHOIC ACIDS,



$C_{10}H_6\begin{cases}CO_2H\\SO_3H\end{cases}$.

2687 *a-Sulpho-a-naphthoic acid* is formed, together with the compounds next to be described, by the action of slightly fuming sulphuric acid on *a*-naphthoic acid, and is separated from its isomerides by means of the barium salt.[3] It is readily soluble in water, and crystallizes when the solution is allowed to evaporate in a desiccator in well developed prisms which are not deliquescent, and melt at 235° with decomposition.

Normal barium a-sulpho-a-naphthoate, $C_{10}H_6.SO_3BaCO_2 + 4H_2O$, crystallizes in transparent, lustrous, monosymmetric prisms, which are slightly soluble in cold, moderately in boiling water.

Acid barium a-sulpho-a-naphthoate, $[C_{10}H_6(SO_3H)CO_2]_2Ba + 2H_2O$, is much more readily soluble, and crystallizes in lustrous prisms.

β-Sulpho-a-naphthoic acid forms a crystalline, very freely soluble mass, which melts at 218—222° with decomposition.

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[1] Ekstrand, *J. Pr. Chem.* II. **42**, 396.

[2] Ekstrand, *loc. cit.*

[3] Battershall, *Annalen*, **168**, 114; Stumpf, *Annalen*, **188**, 1.

Normal barium β-sulpho-a-naphthoate, $2C_{10}H_6SO_3BaCO_2 + 7H_2O$, forms fascicular groups of thick, colourless, lustrous needles, which are only sparingly soluble in water, but more readily than the salt of the α-sulpho-acid.

Acid barium β-sulpho-a-naphthoate, $[C_{10}H_6(SO_3H)CO_2]_2Ba + 4H_2O$, is more readily soluble than the normal salt, and forms soft nodular aggregates.

γ-Sulpho-a-naphthoate is readily soluble, and crystallizes in small matted needles, melts at 182—185°, and froths up and decomposes at 187°.

Normal barium γ-sulpho-a-naphthoate, $2C_{10}H_6SO_3BaCO_2 + 3H_2O$, is moderately soluble in water, and separates when the hot solution is cooled as a lustrous, hard, crystalline mass.

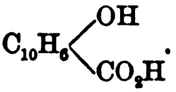
Acid barium γ-sulpho-a-naphthoate, $[C_{10}H_6(SO_3H)CO_2]_2Ba + H_2O$, is precipitated as a crystalline mass when barium chloride is added to a solution of the free acid or hydrochloric acid added to a solution of the normal salt. It is only very slightly soluble even in hot water, from which it separates in small hard nodules.

δ-Sulpho-β-naphthoic acid is readily formed, together with a very small amount of an isomeric acid, when β-naphthoic acid is dissolved in fuming sulphuric acid. It is readily soluble in water, and forms a crystalline mass, melting with slight decomposition at 229—230°.

Normal barium δ-sulpho-β-naphthoate, $2C_{10}H_6SO_3BaCO_2 + 13H_2O$, is readily soluble and crystallizes in fascicular groups of long, silky needles. Battershall obtained it in monosymmetric crystals, containing one molecule of water.

Acid barium δ-sulpho-β-naphthoate, $2[C_{10}H_6(SO_3H)CO_2]_2Ba + 13H_2O$, is almost insoluble in cold water, but dissolves to a moderate extent in hot water, from which it crystallizes in large lustrous plates, or long silky needles.

HYDROXYNAPHTHOIC ACIDS,



$$C_{10}H_6\left\langle\begin{matrix}OH\\CO_2H\end{matrix}\right..$$

2688 Eight of these compounds are at present known; the first four have been prepared by fusing the sulphonaphthoic acids with caustic potash (Battershall, Stumpf).

a-Hydroxynaphthoic acid crystallizes from boiling water in long, thin, matted needles, is readily soluble in alcohol, melts at

234—237°, and when carefully heated sublimes without much decomposition. Its aqueous solution gives a dirty-violet precipitate with ferric chloride. On heating with lime it decomposes into α-naphthol and carbon dioxide.

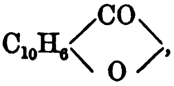
β-Hydroxynaphthoic acid is readily soluble in alcohol, from which it separates in white druses covered with fine hair-like forms, whilst it crystallizes from hot water in voluminous masses, consisting of slender needles. It melts with slight decomposition at 245—247°. The solution is not coloured by ferric chloride, but a reddish-brown precipitate is formed on heating. When it is distilled with lime, β-naphthol is formed.

γ-Hydroxynaphthoic acid separates from hot water in small, branched needles, melts at 186—187°, is very readily soluble in alcohol, and also yields β-naphthol on heating with lime. Ferric chloride produces a chocolate-coloured precipitate in its aqueous solution.

δ-Hydroxynaphthoic acid crystallizes from hot water in long needles, melting at 212—213°, and separates from alcohol in fascicular groups of lustrous needles. Its solution gives a dirty carmine-red precipitate with ferric chloride; on heating with lime it yields α-naphthol.

Perihydroxynaphthoic acid was obtained by Ekstrand by dissolving the corresponding amido-acid in dilute caustic potash solution, adding potassium nitrite, and pouring the solution, after cooling with ice, into cooled dilute sulphuric acid. On heating on the water-bath nitrogen is evolved, and the lactone separates out in small needles, which are boiled with caustic potash solution to obtain a salt of the acid. The latter is then precipitated in small lustrous needles by the addition of hydrochloric acid. It is readily soluble in hot water, alcohol, and ether, from which it crystallizes in nodular aggregates of minute needles, melting at 169°.

Calcium perihydroxynaphthoate, $2[C_{10}H_6(OH)CO_2]_2Ca + 7H_2O$, crystallizes in tabular aggregates of needles; the *basic salt*, $C_{10}H_6OCaCO_2$, separates out when the solution is boiled. Ferric chloride produces a violet precipitate.

Naphtholactone,  $C_{10}H_6\left\langle\begin{matrix}CO\\O\end{matrix}\right\rangle$, crystallizes from alcohol in long needles, and from ether in thick hard tablets, melts at 108°, and sublimes in slender needles. It is insoluble in cold alkalis.

Chloronaphtholactone, $C_{10}H_5Cl(O.CO)$, is formed when chlorine is passed into a solution of the lactone in carbon disulphide containing iodine. It crystallizes from alcohol in needles, melting at 184—185°. On boiling with caustic soda it is converted into *chloroperihydroxynaphthoic acid*, $C_{10}H_5Cl(OH)CO_2H$, which is precipitated by hydrochloric acid as a crystalline powder, consisting of slender needles, and melts and froths up at 190—191°.

Bromonaphtholactone, $C_{10}H_5Br(O.CO)$, forms slender white needles, melting at 192°.

Nitronaphtholactone, $C_{10}H_5NO_2(O.CO)$, is only sparingly soluble in alcohol, and crystallizes from glacial acetic acid in slender yellow needles, which melt at 242°, and readily dissolve in warm caustic soda solution. Hydrochloric acid added to this solution precipitates *nitroperihydroxynaphthoic acid*, $C_{10}H_5NO_2(OH)CO_2H$, as a yellow powder, consisting of small rhombic tablets, which also melt at 242°, the lactone being probably formed.[1]

α-Hydroxy-β-naphthoic acid, or *α-Naphthol-β-carboxylic acid*, is obtained by the action of carbon dioxide on a mixture of α-naphthol and sodium.[2] It is prepared on the large scale by heating sodium α-naphthate with liquid carbon dioxide to 130°[3] (Pt. IV. p. 299). It is sparingly soluble in water, crystallizes from alcohol or ether in stellate groups of needles, and melts at 185—186°, with partial decomposition into α-naphthol and carbon dioxide, which also takes place on continued boiling with water. Its aqueous solution is coloured blue by ferric chloride.

It is employed instead of salicylic acid, since it is a still more powerful antiseptic than this.

Sodium α-hydroxy-β-naphthoate, $C_{10}H_6(OH)CO_2Na+3H_2O$, crystallizes from hot water in large, thin, pearly plates, and from alcohol in well developed rhombic plates. With concentrated nitric acid it gives a characteristic violet or blue colouration, which gradually changes to red.[4]

Calcium α-hydroxy-β-naphthoate, $(C_{11}H_7O_3)_2Ca$, crystallizes in long needles, sparingly soluble in water.

Schmitt and Burkhard have prepared a number of esters and substitution-products, but merely mention their melting-points.

α-Hydroxy-β-naphthophosphoric acid, $PO(OH)_2.O.C_{10}H_6.CO_2H$.

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[1] *J. Pr. Chem.* II. **38**, 278.

[2] Eller, *Annalen*, **152**, 275; Schaffer, *Annalen*, **152**, 279.

[3] Schmitt and Burkhard, *Ber.* **20**, 2699; Schultz, *Steinkohlentheer*, **2**, 976.

[4] Ellenberger and Hofmeister, *Archiv Pathol. Pharmakol.* 1888.

When the α-hydroxy-acid is treated with phosphorus pentachloride it yields the compound $POCl_2(O.C_{10}H_6.CCl_3)$, which crystallizes from light petroleum in transparent prisms melting at 115°. On exposure to moist air this passes into the above acid, which separates from acetone in slender needles, and is quickly resolved by water into phosphoric and α-hydroxynaphthoic acids. If the chloride be further heated with phosphorus pentachloride at 180°, it is converted into *chloronaphthomethine chloride*, $C_{10}H_6Cl.CCl_3$, crystallizing from light petroleum in rhombohedra, which melt at 73° and are converted by boiling aqueous acetic acid into α-chloro-β-naphthoic acid.[1]

α-Hydroxy-4-sulpho-β-naphthoic acid, $C_{10}H_5(OH)(SO_3H)CO_2H + 5H_2O$, is formed when the hydroxy-acid is added to a mixture of 2 parts of fuming sulphuric acid containing 20 per cent. of trioxide, and 3 parts of concentrated sulphuric acid, cooling well with ice-water. The sulphonic acid separates out on warming to 60°, and crystallizes from hot water in small glistering needles. On boiling with dilute sulphuric acid it readily loses not only carbon dioxide but also the sulpho-group with formation of considerable quantities of α-naphthol, whilst with dilute nitric acid it yields ordinary dinitronaphthol or naphthol yellow. When treated with cold nitric acid of sp. gr. 1·48 in acetic acid solution it is converted into α-hydroxy-4-nitro-β-naphthoic acid, which is also obtained by the nitration of α-hydroxy-β-naphthoic acid; with diazobenzene chloride it yields benzeneazo-α-naphtholsulphonic acid.

The salts are more stable than the free acid. The *acid sodium salt*, $C_{10}H_5(OH)(SO_3Na)CO_2H$, separates out in thin elastic lustrous needles when sodium chloride is added to a warm solution of the acid. The *normal salt*, $C_{10}H_5(OH)(SO_3Na)CO_2Na$, is obtained by neutralizing the acid with sodium carbonate, whereas by warming it with an excess of caustic soda it yields the *basic salt*, $C_{10}H_5(ONa)(SO_3Na)CO_2Na$, crystallizing in long glassy needles which become opaque in the air.

On warming the hydroxy-acid with 4 parts of fuming sulphuric acid it forms the *disulphonic acid*, $C_{10}H_4(OH)(SO_3H)_2CO_2H + 4H_2O$, which crystallizes in beautiful stellate groups of needles.[2]

4-*Amido-α-hydroxy-β-naphthoic acid*, $C_{10}H_5(NH_2)(OH)CO_2H$. When an alkaline solution of hydroxynaphthoic acid is mixed with diazobenzene chloride it forms *benzeneazohydroxynaphthoic*

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[1] Wolffenstein, *Ber.* **20**, 1966.

[2] König, *Ber.* **22**, 787; **23**, 806.

acid, $C_6H_5.N : N.C_{10}H_5(OH)CO_2H$, which crystallizes from acetic acid in lustrous green needles, melts at 192°, and is converted by stannous chloride and hydrochloric acid into aniline and the *amido-acid*. The latter forms a crystalline powder scarcely soluble in water, alcohol, or acetic acid, and decomposes on heating in a current of hydrogen chloride at 230° into carbon dioxide and 1 : 4-amido-naphthol.[1]

α-Hydroxy-β-naphthohydroxamic acid, $C_{10}H_6(OH)(O.NH.OH)$, is formed by allowing the methyl ester of the hydroxy-acid, which melts at 78°, to remain with an alkaline solution of hydroxylamine, and crystallizes from ether in microscopic octohedra, soluble in alkalis with formation of green salts. Ferric chloride colours the aqueous solution of the acid violet.[2]

β-Hydroxy-α-naphthaldehyde, $C_{10}H_6(OH)CHO$, is prepared by warming an alkaline solution of β-naphthol with chloroform, and crystallizes from alcohol in beautiful prisms, which melt at 76° and are volatile with steam. On careful fusion with potash it is converted into the acid.[3]

β-Hydroxy-α-naphthoic acid, or *β-Naphthol-α-carboxylic acid*, $C_{10}H_6(OH)CO_2H$, is prepared on the large scale from β-naphthol in a manner corresponding to that employed for the manufacture of the α-β-acid, and is used for the same purposes. It is very sparingly soluble in water, readily in alcohol, and crystallizes from dilute alcohol in slender needles which melt at 156—157° if quickly heated; on slowly heating they decompose at 124—128° with evolution of carbon dioxide, and they are converted into β-naphthol and carbon dioxide on boiling with water. Its aqueous solution is coloured blue by ferric chloride. The salts are somewhat more stable than the free acid, the sodium salt being only coloured greenish-yellow by fuming nitric acid.

Schmitt and Burkhard have prepared esters and other derivatives of this acid, but have given no details. The *methyl* ester melts at 69°, and is converted by hydroxylamine into β-hydroxy-α-naphthohydroxamic acid, which is a yellow amorphous compound, and gives a violet colouration with ferric chloride.

β-Hydroxy-α-naphthophosphoric acid, $PO(OH)_2OC_{10}H_6.CO_2H$, is prepared in the same manner as the α-β-compound. The first product is the *chloride*, $POCl_2O.C_{10}H_6.CCl_3$, crystallizing in

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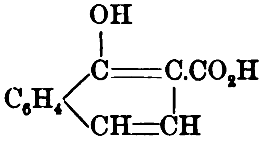
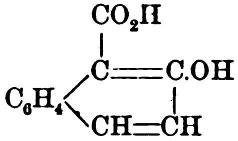
[1] Nietzki and Guitermann, *Ber.* **20**, 1274.
[2] Jeanrenaud, *Ber.* **22**, 1275.
[3] Kaufmann, *Ber.* **15**, 804.

lustrous needles, which melt at 38° and pass into the acid on exposure to moist air. The latter forms fascicular groups of needles, melts at 156°, and is quickly decomposed by boiling water with formation of phosphoric acid, carbon dioxide and β-naphthol.[1]

These two naphtholcarboxylic acids correspond to salicylic acid, their constitutions being represented by the formulæ



α-β-acid.



β-α-acid.

β-Hydroxy-β-naphthoic acid, or *β-Naphthol-β-carboxylic acid,* is obtained by heating sodium β-naphthate in a current of carbon dioxide, the reaction taking place at 280—290°. It crystallizes from water in beautiful, lustrous, yellow rhombic plates, which are sparingly soluble in water, readily in alcohol, and melt at 216° without decomposition. Its aqueous solution gives a blue colouration with ferric chloride. (Schmitt and Burkhard).

Its *methyl* ester melts at 73—76°, and is readily dissolved by an alkaline hydroxylamine solution, but undergoes no alteration.

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[1] Rabe, *Ber.* **22**, 392.

DIMETHYLNAPHTHALENE GROUP

2639 1 : 4-*Dimethylnaphthalene*, $C_{10}H_6(CH_3)_2$, was first obtained by heating santonin and its derivatives with zinc dust.[1] It is also obtained by the action of sodium and methyl iodide on a toluene solution of 1 : 4-dibromonaphthalene, and is an oily, strongly refractive liquid, having a slight naphthalene odour. It does not solidify at – 18°, and boils at 262—264°. Its *picrate* crystallizes in orange needles which melt at 139° and are fairly soluble in hot alcohol.[2]

Dimethylnaphthalenes also occur in the coal-tar oils boiling at 250—270°, but have not yet been obtained pure.[3]

Hydroxydimethylnaphthalene, or *Dimethylnaphthol*, $C_{10}H_5(CH_3)_2OH$, is prepared by heating santonious or isosantonious acid above 360° with caustic baryta, and is also formed, together with dimethylnaphthalene, propylene, and probably xylene when santonic acid is distilled with zinc dust. It crystallizes in lustrous needles, melts at 135—136°, and commences to sublime at 100°. Under reduced pressure it may be distilled without decomposition. It is very sparingly soluble in water, more readily in alcohol, and still more easily in ether and in alkalis, from which latter solution it is reprecipitated by carbon dioxide. When heated with an excess of zinc dust it is converted into dimethylnaphthalene.

Dimethylnaphthol methyl ether, $C_{10}H_5(CH_3)_2OCH_3$, is formed by heating dimethylnaphthol with methyl iodide, methyl alcohol, and caustic soda, and crystallizes in hard prisms, melting at 68°. The corresponding *ethyl ether* is a viscous liquid which does not solidify in a freezing mixture.

Dimethylnaphthyl acetate, $C_{10}H_5(CH_3)_2O.C_2H_3O$, is prepared

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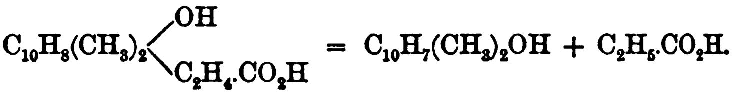
[1] Cannizzaro and Carnelluti, *Gazzetta*, **12**, 293; *Ber.* **12**, 1547; **13**, 1516; **15**, 426.

[2] Giovanozzi, *Gazzetta*, **12**, 147.

[3] Emmert and Reingruber, *Annalen*, **211**, 365.

by boiling dimethylnaphthol and acetic anhydride in presence of sodium acetate, and crystallizes in small plates which melt at 77—78°.

Dimethyldihydronaphthol, $C_{10}H_7(CH_3)_2OH$, is obtained, together with propionic acid, when santonious acid is heated above 320° in a stream of carbon dioxide:



$$C_{10}H_8(CH_3)_2\begin{matrix}\diagup OH \\ \diagdown C_2H_4.CO_2H\end{matrix} = C_{10}H_7(CH_3)_2OH + C_2H_5.CO_2H.$$

At the same time ethyl propionate, dimethylnaphthol, and dimethylnaphthalene are formed. Dimethyldihydronaphthol crystallizes from alcohol in silky needles, which melt at 113° and are volatile with steam. On heating with sulphur it is converted into sulphuretted hydrogen and dimethylnaphthol, whilst with phosphorus pentasulphide it yields water and dimethylnaphthalene.[1]

NAPHTHALENEDICARBOXYLIC ACIDS, $C_{10}H_6(CO_2H)_2$.

2690 1 : 1′-*Naphthalenedicarboxylic acid*, $C_{10}H_6(CO_2H)_2$. By the oxidation of acenaphthene with chromic acid, Behr and van Dorp obtained a dibasic acid of the composition $C_{12}H_8O_4$ which like phthalic acid readily yields an anhydride; on distillation with lime it was found to yield carbon dioxide and naphthalene, showing that it is a naphthalenedicarboxylic acid, whence they gave to it the name *naphthalic acid*.[2] It is also formed by the oxidation of pyreneketone[3] (p. 362).

Bamberger and Philip showed that the carboxyl-groups occupy the peri-position, by preparing it synthetically from 1 : 1′-nitronapthoic acid. For this purpose the latter was converted by reduction into the hydrochloride of 1 : 1′-amido-naphthoic acid, the requisite quantity of sodium carbonate and sodium nitrite added and the mixture allowed to drop into dilute sulphuric acid, cooling well with ice. The resulting solution of diazo-

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[1] Cannizzaro, *Gazzetta*, **13**, 385; *Ber.* **16**, 2604.

[2] *Annalen*, **172**, 263.

[3] Bamberger and Philip, *Annalen*, **240**, 180.

naphthoic acid was slowly poured into a boiling solution of cupric sulphate and potassium cyanide, the cyanonaphthoic acid thus formed being at once converted into the acid by boiling with caustic potash solution.[1]

It separates on addition of acids to solutions of its salts as a voluminous precipitate, consisting of microscopic needles. It is scarcely soluble in water, sparingly in ether, but easily in slightly-warmed alcohol, from which it may be readily crystallized if the latter is not too strongly heated; if the temperature be raised too high the acid passes into the anhydride.

Potassium naphthalate, $C_{10}H_6(CO_2K)_2$, is very soluble in water, and separates on evaporating the solution in vacuo, partly in needles, and partly as an efflorescence at the side of the dish. If alcohol be added to its concentrated solution, lustrous plates of the composition $C_{10}H_6(CO_2K)_2 + C_2H_6O$ are obtained. The *ammonium* salt is very similar, but the *sodium* salt is precipitated as a white powder free from water or alcohol.

Barium naphthalate, $C_{10}H_6(CO_2)_2Ba + H_2O$, separates in small lustrous plates when barium chloride is added to a moderately dilute solution of an alkali salt; in dilute solution it separates only on standing, unless the solution be warmed, when immediate separation takes place.

Calcium naphthalate, $C_{10}H_6(CO_2)_2Ca$, is obtained in a similar manner as spherical crystalline aggregates.

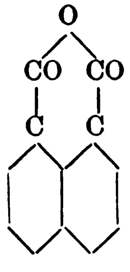
Silver naphthalate, $C_{10}H_6(CO_2Ag)_2$, is a heavy white floccular precipitate, and is not acted upon by light.

Methyl naphthalate, $C_{10}H_6(CO_2CH_3)_2$, is prepared by heating the silver salt with methyl iodide, and crystallizes from alcohol in well-developed prisms, which melt at 102—103°.

Naphthalic anhydride, $C_{10}H_6(CO)_2O$, is formed when the acid is heated at 100—150°, and sublimes on more strongly heating in broad zig-zag plates; it is also obtained by boiling an alcoholic solution of the acid, and crystallizes out on cooling in long flat needles, which melt at 266°, and readily dissolve in alkalis, forming salts of the acid. It is unattacked by bromine and concentrated nitric acid even on heating, but dissolves in cold sulphuric acid, forming a yellow solution with a blue fluorescence, and on warming is converted to a certain extent into a sulphonic acid; the greater portion, however, separates out unaltered on addition of water. The constitution of the

[1] *Ber.* **20**, 237.

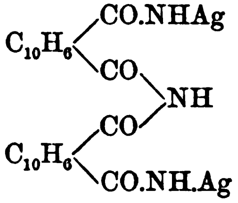
anhydride is represented by the formula below, which accounts well for this extreme stability:



Naphthalimide, $C_{10}H_6(CO)_2NH$, is formed when the powdered anhydride is boiled with concentrated ammonia. It is thus obtained in slender, well-developed prisms, which melt over 280°, and sublime on further heating; it is sparingly soluble in hot alcohol, and crystallizes from it in long needles and from dilute caustic potash in thin lustrous prisms. If an alcoholic solution of silver nitrate be added to a similar solution of naphthalimide containing ammonia the following reaction takes place:

$$2C_{12}H_7NO_2 + Ag_2O + NH_3 = C_{24}H_{15}Ag_2N_3O_4 + H_2O.$$

The constitution of the compound formed is represented by the formula:



$$\begin{array}{l} C_{10}H_6\left\langle\begin{array}{l}CO.NHAg\\ CO\diagdown\end{array}\right. \\ \qquad\qquad\qquad NH \\ C_{10}H_6\left\langle\begin{array}{l}CO\diagup\\ CO.NH.Ag\end{array}\right. \end{array}$$

Bromonaphthalic acid, $C_{10}H_5Br(CO_2H)_2$, is obtained by the oxidation of bromacenaphthene, and crystallizes from benzene in beautiful white needles, which melt at 210°, and readily pass into the anhydride. On boiling with ammonia it is converted into the *imide*, $C_{10}H_5Br(CO)_2NH$, which sublimes in yellow prisms, melting above 265°.

Nitronaphthalic acid, $C_{10}H_5(NO_2)(CO_2H)_2$, is formed, together with nitro-γ-naphthoquinone, by the oxidation of nitroacenaphthene, but is prepared more readily and with a larger yield by boiling acenaphthene with nitric acid of sp. gr. 1·2. Nitronaphthalic acid crystallizes in slender yellow needles, which are scarcely soluble in alcohol and ether; it dissolves more readily in acetic acid, but passes then into the *anhydride*, melting at 220°.

Dihydronaphthalic acid, $C_{10}H_8(CO_2H)_2$, is prepared by acting with sodium amalgam on a boiling solution of naphthalic acid. The product is extracted with ether, which removes certain by-products and leaves a mixture of hydronaphthalic and naphthalic acids. This is boiled with acetic acid, which converts naphthalic acid into the anhydride, and a mixture of the latter and hydronaphthalic acid separates out on cooling. A very short treatment with sodium carbonate solution dissolves out only the hydronaphthalic acid, which may then be precipitated with hydrochloric acid. It forms a crystalline powder which becomes yellow at 150—160°, melts with frothing at 199°, but immediately resolidifies and does not melt again even at 275°, the anhydride and other products being formed. It differs from naphthalic acid inasmuch as its cold alkaline solution instantaneously reduces potassium permanganate.[1]

2691 1 : 4-*Naphthalenedicarboxylic acid* is prepared from 1 : 4-bromonaphthalenesulphonic acid, the potassium salt of which on distillation with potassium cyanide yields the 1 : 4-*nitrile*; this crystallizes in yellow needles, melting at 204°. The acid obtained by boiling it with caustic potash is practically insoluble in water, and is precipitated by hydrochloric acid as a white scarcely crystalline mass. If it is dissolved in alcohol and the solution after dilution with water evaporated, it is obtained in microscopic needles, which do not melt at 240°.

Barium 1 : 4-*naphthalenedicarboxylate*, $C_{10}H_6(CO_2)_2Ba + 2H_2O$, forms granular crystals readily soluble in water.[2]

2 : 2′-*Naphthalenedicarboxylic acid* is prepared from the corresponding disulphonic acid in a similar manner to the 1 : 4-acid. The intermediate *nitrile*, $C_{10}H_6(CN)_2$, sublimes in long needles, and melts at 267—268°. The acid is most readily obtained from it by boiling with caustic potash in amyl alcoholic solution, which, as it boils at a higher temperature than alcoholic potash, causes the reaction to take place more quickly. The nitrile may also be decomposed with hydrochloric acid at 200—210°, and separates on cooling in long, spear-shaped, transparent needles, whilst from boiling alcohol, in which it is sparingly soluble, it crystallizes in slender needles. On adding

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[1] Anselm, *Ber.* **22**, 859.

[2] Darmstädter and Wichelhaus, *Annalen*, **172**, 309.

acids to solutions of its salts it separates as a jelly-like precipitate, which on drying falls to a white apparently amorphous powder. It melts considerably above 300° with decomposition and formation of naphthalene, but may be sublimed by careful heating in small lustrous cauliflower-shaped masses. Its *calcium* salt, $C_{10}H_6(CO_2)_2Ca + 4H_2O$, is precipitated by calcium chloride from a solution of the ammonium salt in small needles, only slightly soluble in water.

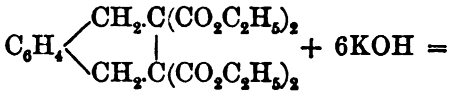
2 : 3′-*Naphthalenedicarboxylic acid* is obtained by the usual reactions from β-naphthalenedisulphonic acid. Its *nitrile* differs only from the α-compound in melting at 296—297°. The acid crystallizes in short needles, and otherwise closely resembles the α-acid. The *calcium* salt, $2C_{10}H_6(CO_2)_2Ca + 7H_2O$, is an almost insoluble precipitate consisting of microscopic needles.[1]

Narceic acid, $C_{15}H_{15}NO_3 + 3H_2O$, is formed when narceïne, one of the opium alkaloids, is dissolved in sulphuric acid, and carefully oxidized with potassium permanganate. It separates from hot water in small lustrous crystals which become anhydrous at 110°, is a tribasic acid and decomposes on heating at 180—200° into carbon dioxide, dimethylamine, and dihydroxynaphthalenedicarboxylic acid.

Dihydroxynaphthalenedicarboxylic acid, $C_{10}H_4(OH)_2(CO_2H)_2$, sublimes in snow-white feathery aggregates of needles, and melts at 162°. The *barium* salt, $C_{10}H_4(OH)_2(CO_2)_2Ba + 2H_2O$, is readily soluble in water, and crystallizes in stellate aggregates of small needles.

When the acid is heated for a long time with hydriodic acid and amorphous phosphorus, it is converted into a naphthalenedicarboxylic acid, which separates from its alkaline solution on addition of hydrochloric acid as a flocculent precipitate, melting at 250—253°. On heating with quicklime it is converted into carbon dioxide and naphthalene.[2]

Tetrahydronaphthalenedicarboxylic acid, $C_{10}H_{10}(CO_2H)_2$. To obtain this acid an alcoholic solution of *o*-xylylene bromide, ethyl acetylenetetracarboxylate (Pt. II., p. 554) and sodium is heated to 130°, and the resulting ester boiled with alcoholic potash:



$$C_6H_4\left\langle\begin{array}{l}CH_2.C(CO_2C_2H_5)_2\\ \qquad\ \,|\\ CH_2.C(CO_2C_2H_5)_2\end{array}\right. + 6KOH =$$

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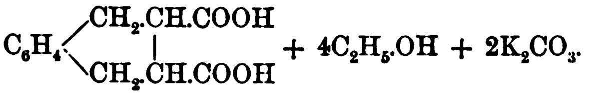
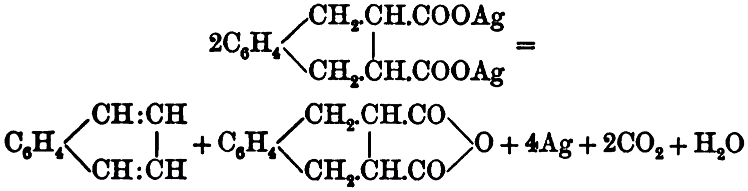
[1] Ebert and Merz, *Ber.* **9**, 604.

[2] Claus and Meixner, *J. Pr. Chem.* II. **37**, 1.



$$C_6H_4\left\langle\begin{array}{l}CH_2.CH.COOH\\ \qquad\ \ |\\ CH_2.CH.COOH\end{array}\right. + 4C_2H_5.OH + 2K_2CO_3.$$

The acid is precipitated from solutions of its salts as a crystalline precipitate consisting of rhomboidal tablets, which are very sparingly soluble in cold water, but readily in hot water and alcohol. The *silver* salt when first prepared is amorphous, but quickly becomes crystalline, and decomposes on heating with formation of the anhydride and naphthalene:



$$2C_6H_4\left\langle\begin{array}{l}CH_2.CH.COOAg\\ \qquad\ \ |\\ CH_2.CH.COOAg\end{array}\right. =$$

$$C_6H_4\left\langle\begin{array}{l}CH:CH\\ \qquad |\\ CH:CH\end{array}\right. + C_6H_4\left\langle\begin{array}{l}CH_2.CH.CO\\ \qquad\ \ |\\ CH_2.CH.CO\end{array}\right\rangle O + 4Ag + 2CO_2 + H_2O$$

The *anhydride* may also be readily obtained by heating the acid to 199°, and is readily soluble in alcohol, sparingly in ether, but crystallizes from the latter in exceptionally large prisms. It melts at 184°, sublimes on stronger heating, and is readily soluble in hot caustic soda solution, with re-formation of the acid. When its vapour is passed through a red-hot tube, naphthalene is formed in considerable quantity.[1]

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[1] Baeyer and Perkin, *Ber.* **17**, 448.

ETHYLNAPHTHALENE GROUP.

2692 *a-Ethylnaphthalene*, $C_{10}H_7.C_2H_5$, is formed by the action of sodium on a mixture of *a*-bromonaphthalene and ethyl bromide, and is a strongly refractive liquid boiling at 256—259°. Its *picrate* crystallizes in orange-yellow needles, melting at 139°. It is converted by bromine into *trilromethylnaphthalene*, $C_{10}H_4Br_3.C_2H_5$, which crystallizes from ether in slender needles, melting at 127°.[1]

β-Ethylnaphthalene is obtained in a similar manner from *β*-bromonaphthalene, or by the action of aluminium chloride or bromide on a mixture of ethyl chloride or bromide and naphthalene.[2] It is a liquid which boils at 250—251° and solidifies at – 19° (Brunel). Its *picrate* forms slender yellow needles, melting at 69°.

β-Ethylnaphthol, $C_{10}H_6(C_2H_5)OH$, was obtained by Marchetti by warming *β*-ethylnaphthalene with sulphuric acid and fusing the resulting sulphonic acid with potash. It is scarcely soluble in water, but crystallizes from alcohol in small silvery plates, which melt at 98°.

NAPHTHYLACETYL-COMPOUNDS.

2693 *a-Naphthylacetic acid*, $C_{10}H_7.CH_2.CO_2H$, is prepared by heating naphthylformic acid, $C_{10}H_7.CO.CO_2H$, with hydriodic acid and a little amorphous phosphorus at 160°. It is sparingly soluble in cold, readily in hot water, from which it crystallizes in long silky needles, melting at 131°.

a-Naphthylacetamide, $C_{10}H_7.CH_2.CO.NH_2$. To prepare this compound, naphthylacetic acid is treated with phosphorus

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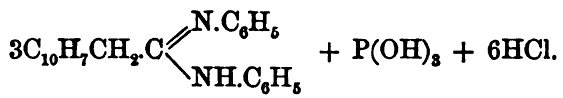
[1] Fittig and Remsen, *Annalen*, **155**, 112; Carnelutti, *Ber.* **13**, 1671.

[2] Marchetti, *Gazzetta*, **11**, 265, 439; Brunel, *Ber.* **17**, 1179; Roux, *Ann. Chim. Phys.* VI. **12**, 289.

pentachloride, which converts it into *naphthylacetyl chloride*, and the latter, after removing the phosphorus oxychloride by distillation, treated with ammonium carbonate. It crystallizes from boiling alcohol in beautiful rosette-shaped aggregates of needles, melting at 180—181°. On heating it with phosphoric anhydride it yields *naphthylacetonitrile*, $C_{10}H_7.CH_2CN$, as an oily liquid, which boils above 300°.

a-Naphthylethenyldiphenyldiamine, $C_{10}H_7.CH_2.C(N.C_6H_5)NH.C_6H_5$, is formed by the action of phosphorus trichloride on a mixture of naphthylacetic acid and aniline:[1]

$$3C_{10}H_7.CH_2.CO_2H + 6C_6H_5.NH_2 + 2\ PCl_3 =$$



$$3C_{10}H_7CH_2.C\begin{matrix}\diagup\!\!\diagup N.C_6H_5\\ \diagdown NH.C_6H_5\end{matrix} + P(OH)_3 + 6HCl.$$

It crystallizes from dilute alcohol in beautiful needles, melting at 130·5°.

a-Naphthylglycollic acid, $C_{10}H_7.CH(OH).CO_2H$, is prepared by triturating a-naphthoic aldehyde with potassium cyanide and a little water, cooling the paste with ice and adding concentrated hydrochloric acid drop by drop with constant stirring. The *nitrile* thus obtained is an oily liquid, and is converted into the acid by allowing it first to stand with hydrochloric acid at the ordinary temperature and finally heating to the boiling-point. a-Naphthylglycollic acid crystallizes from concentrated aqueous solution in colourless rosette-shaped aggregates of needles, melting at 80—81°.[2]

NAPHTHYLMETHYL-COMPOUNDS.

2694 *a-Naphthylmethylketone* or *Acetonaphthone*, $C_{10}H_7.CO.CH_3$, is formed by adding acetyl chloride to a light petroleum solution of naphthalene, and then, gradually, aluminium chloride with frequent agitation;[3] or the latter may be covered with carbon bisulphide, and the calculated quantity of acetyl chloride and naphthalene gradually added.[4] It is a yellowish, almost colour-

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[1] Boessneck, *Ber.* **16**, 639.

[2] Brandis, *Ber.* **22**, 2151.

[3] Pampel and Schmidt, *Ber.* **19**, 2896.

[4] Claus and Feist, *Ber.* **19**, 3180.

less liquid, which boils at 295—297°, and solidifies when strongly cooled to a crystalline mass, and after being well pressed melts at 34°. The *oxime*, $C_{10}H_7.C(NOH).CH_3$, melts at 145°, and the *hydrazone*, $C_{10}H_7(C:N_2H.C_6H_5)CH_3$, crystallizes from carbon bisulphide in slightly yellowish-red needles, melting at 137°.

On oxidation with potassium permanganate in the cold, the ketone is converted into *a*-naphtoylformic acid, but at a higher temperature it yields *a*-naphthoic acid.

a-Naphtoylmethyl bromide, $C_{10}H_7.CO.CH_2Br$, is obtained by acting with bromine on a solution of the ketone in carbon bisulphide, and is a liquid with a slightly pungent smell.

a-Naphtoylmethyl thiocyanate, $C_{10}H_7.CO.CH_2.SCN$, is formed by the addition of an alcoholic solution of potassium thiocyanate to the bromide, and separates on addition of water in iridescent crystals.

a-Hydroxynaphthyl-a-methylketone, or *4-Aceto-1-naphthol*, $C_{10}H_6(OH)CO.CH_3$, is prepared by the action of sulphuric acid on an acetic acid solution of *a*-naphthol. It crystallizes from alcohol in needles, and from benzene in beautiful, pale-green, six-sided prisms, which melt at 103°, and dissolve in sulphuric acid, forming an orange-yellow coloured solution, which is reprecipitated by the addition of water. It gives colouring matters with diazo-compounds resembling those obtained from *a*-naphthol, but which have a yellower tinge. When the warm alkaline solution is mixed with *o*-nitrobenzaldehyde it assumes a deep reddish-brown colour, and acids then precipitate beautiful orange-yellow flakes.

On cooling the yellow alkaline solutions of acetonaphthol, or on addition of sodium chloride, the salts separate in large citron-yellow needles, which are decomposed by carbon dioxide.

a-Hydroxynaphthyl-a-methylketoxime, $C_{10}H_6(OH)C(NOH).CH_3$, is obtained by adding hydroxylamine to an alkaline solution of the ketone, and crystallizes from dilute alcohol in long yellowish needles, which melt with decomposition at 168—170°.

a-Hydroxynaphthyl a-methylketonimide, $C_{10}H_6(OH)C(NH)CH_3$, is formed when acetonaphthol is heated with alcoholic ammonia at 180—200°, and crystallizes from alcohol in long golden-yellow spear-shaped crystals; it is readily reconverted by acids and alkalis into the ketone.[1]

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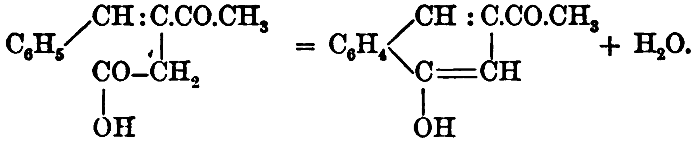
[1] Witt, *Ber.* **21**, 231.

α-Hydroxynaphthyl-β-methylketone, or 3-*Aceto*-1-*naphthol*, is prepared by the distillation of benzylidenelevulinic acid:



It crystallizes from acetic acid in long yellowish-brown needles, melts at 168°, and dissolves with difficulty in water, forming a yellowish-coloured solution. Its hot benzene solution is golden-yellow, and on cooling becomes yellowish-green or pale-green. *o*-Nitrobenzaldehyde gives no colouration with its alkaline solution, and towards alkalis it behaves in the same manner as the 4 : 1 compound. Its *oxime*, obtained by boiling a solution of the sodium salt with hydroxylamine hydrochloride, crystallizes from dilute alcohol in colourless prisms, which melt at 174—175°.[1]

Sodium 3-*aceto*-1-*naphthate*, $C_{10}H_6(ONa)CO.CH_3$, crystallizes from its deep golden-yellow solution in yellow plates on addition of sodium chloride. Its aqueous solution gives the α-naphthol reaction with 1 : 4-diazonaphthalenesulphonic acid, and forms deep-blue indophenols with quinone chlorimide.

3-*Aceto*-1-*naphthyl acetate*, $C_{10}H_6(OC_2H_3O)CO.CH_3$, is formed by boiling 3-aceto-1-naphthol with acetic anhydride, and crystallizes in compact colourless needles, melting at 108—109°.

NAPHTHOYLFORMYL COMPOUNDS.

2695 *α-Naphthoylformonitrile*, $C_{10}H_7.CO.CN$, is prepared by heating α-naphthoyl chloride with mercuric cyanide for ten hours on the water-bath. The product is extracted with water and then with ether, and the latter extract, after evaporating off the ether, fractionated under diminished pressure. The nitrile thus obtained crystallizes from ether in beautiful yellow needles, melts at 101°, and boils at 230° under 85 mm. pressure. On boiling with water or alkalis it decomposes into α-naphthoic acid and hydrocyanic acid, but when allowed to remain with an acetic acid solution of hydrogen chloride it is converted into naphthylformamide.[2]

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[1] Erdmann, *Ber.* **21**, 635; *Annalen*, **254**, 197.

[2] Boessneck, *Ber.* **15**, 3064.

a-Naphthoylformic acid, or *Naphthylglyoxylic acid*, $C_{10}H_7.CO.COOH$, is obtained by boiling the amide with hydrochloric acid, and also, as already mentioned (p. 328), by the oxidation of *a*-naphthylmethylketone with a cold solution of potassium permanganate.[1] It is readily soluble in water and alcohol, sparingly in light petroleum, and crystallizes in slender needles, melting at 113·5°. When its solution is shaken with sulphuric acid and benzene containing thiophen, a brown colouration is formed, and on addition of water the benzene assumes a beautiful crimson colour. When a solution of the acid is made slightly alkaline and reduced with sodium amalgam naphthylglycollic acid is formed.

Calcium naphthoylformate, $2(C_{12}H_7O_3)_2Ca+9H_2O$, forms crystalline crusts, and is much more soluble in hot than in cold water.

a-Naphthoylformamide, $C_{10}H_7.CO.CONH_2$, crystallizes from alcohol in long white needles, melting at 151°.

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[1] Claus and Feist, *Ber.* **19**, 3180.

DERIVATIVES OF NAPHTHALENE CONTAINING MORE THAN TWELVE CARBON ATOMS.

2696 *β-Isopropylnaphthalene*, $C_{10}H_7.C_3H_7$, is formed when aluminium chloride is gradually added to a heated mixture of naphthalene and propyl bromide. It is a strongly refractive liquid, which has an aromatic smell, boils at 265°, and is oxidized by boiling dilute nitric acid to β-naphthoic acid. Its *picrate* crystallizes in slender yellow needles, and melts at 89—90°.[1] (Cf. Pt. V., p. 288).

β-Isobutylnaphthalene, $C_{10}H_7.C_2H_3(CH_3)_2$, is obtained in a similar manner from isobutyl chloride, and forms a colourless liquid boiling at 280°, whose *picrate* crystallizes in yellow needles, melting at 96°.[2]

α-Amylnaphthalene, $C_{10}H_7.C_3H_5(CH_3)_2$. Leone obtained this hydrocarbon by acting on a mixture of amyl bromide and α-bromonaphthalene with sodium. It boils at 303°, and forms a *picrate* crystallizing in slender citron-yellow needles, which melt at 85—90°.[3]

β-Amylnaphthalene was prepared by Roux by the aluminium chloride method from naphthalene and amyl chloride. It is an aromatic smelling liquid, which boils at 288—292°, and yields β-naphthoic acid on boiling with dilute nitric acid. Its *picrate*, like that of the α-compound, crystallizes in citron-yellow needles, and melts at 110°.

Lapachoic acid, $C_{15}H_{14}O_3$. This name was given to the colouring matter of the South American lapacho wood by Paternò, who also showed its identity with *taiguic acid*, obtained by Arnaudou from the taigu wood of Paraguay.[4] The

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[1] Roux, *Ann. Chim. Phys.* VI. **12**, 289.

[2] Wegscheider, *Monatsh.* **5**, 236.

[3] *Gazzetta*, **12**, 209; *Ber.* **15**, 2236.

[4] *Compt. Rend.* **46**, 1154.

latter, like the lapacho wood, is derived from a species of Tecoma, belonging to the family of the Bignoniacæ. It is very hard, resists the action of moisture very well, and takes a very high polish. It is used for the purpose of dyeing cotton wool an orange colour, the wool being boiled with a solution of potassium carbonate, dipped into a bath of the colouring matter, and fixed in a dilute acid bath. According to Stein, taiguic acid is also identical with Groenhartin, which was obtained by de Vry in an attempt to prepare bebireene. The latter alkaloid is chiefly found in the wood known as Greenheart (*Nectandra Rodiaei*), whilst the wood from Surinam, known in Holland by the similar term, Groenhart, contains the above colouring matter in place of bebireene.[1] The latter is probably the wood of *Bignonia leukoxylon*, which also occurs in commerce under the name Greenheart.[2] Lapachoic acid has also been found by Greene and Hooker[3] in Bethabarra wood, which is obtained on the West Coast of Africa, and shipped to America for the manufacture of bows and fishing-rods.

For the preparation of lapachoic acid the wood is boiled with soda, the extracts precipitated with hydrochloric acid and taken up with ether, which leaves behind resinous matter. After evaporating off the ether the residue is recrystallized from benzene. It crystallizes in small, well developed yellow monosymmetric prisms, which are readily soluble in hot alcohol, and crystallize out on cooling in thin tablets, melting at 138°. It dissolves in alkalis and alkaline carbonate solutions with a beautiful red colour, whilst with sulphuric acid it gives a blood-red colouration.

Ammonium lapachoate, $C_{15}H_{13}O_3.NH_4$, crystallizes in brick-red needles, which readily lose ammonia.

Sodium lapachoate, $C_{15}H_{13}O_3Na+5H_2O$, is a deep-red radial crystalline mass, which is readily soluble in water, more sparingly in alcohol.

Calcium lapachoate, $2(C_{15}H_{13}O_3)_2Ca+3H_2O$, is a brick-red precipitate, which on boiling becomes a brown granular powder.

Barium lapachoate, $(C_{15}H_{13}O_3)_2Ba+7H_2O$, is very sparingly soluble in boiling water, and crystallizes out on cooling in long, very slender blood-red needles.

Lead lapachoate, $(C_{15}H_{13}O_3)_2Pb$, is an orange-red precipitate,

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[1] *J. Pr. Chem.* **99**, 1.

[2] Wiesner, *Rohstoffe des Pflanzenreiches*, 589.

[3] *Am. Chem. Journ.* **11**, 267.

which is somewhat soluble in boiling alcohol, and crystallizes from it in small brown needles.

Silver lapachoate, $C_{15}H_{13}O_3Ag$, is a scarlet precipitate.

Aniline lapachoate, $C_{15}H_{10}O_3.C_6H_5.NH_2$, crystallizes from water in small orange-yellow prismatic needles, which melt at 121—122°.

Acetyllapachoic acid, $C_{15}H_{13}(O.C_2H_3O)O_3$, is formed by heating the acid with acetic anhydride, and crystallizes from alcohol in short sulphur-yellow prisms, melting at 82—83°.

If lapachoic acid be treated with zinc dust in alkaline solution, it is converted into *hydrolapachoic acid*. The latter separates on addition of hydrochloric acid in colourless crystals, which are quickly oxidized in the air, lapachoic acid being re-formed.

On warming lapachoic acid with nitric acid of sp. gr. 1·38 a vigorous reaction takes place, and a large quantity of phthalic acid is formed. When heated with zinc dust it yields naphthalene and a hydrocarbon boiling at 250°, and melting at a lower temperature than naphthalene; volatile hydrocarbons which are absorbed by bromine are also formed, dibromides boiling at 149—152°, and at 217—222° being obtained. The former has the composition $C_4H_8Br_2$, and is probably isobutylene bromide.

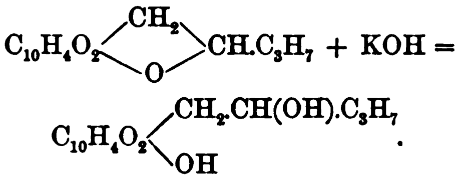
When lapachoic acid is heated with hydriodic acid and amorphous phosphorus it yields large quantities of a hydrocarbon, $C_{15}H_{18}$, which boils at 304—306°, and forms a picrate crystallizing in large orange-red needles, and melting at 140—141°. Paternò regarded this as an amylnaphthalene and concluded therefore that lapachoic acid is *amylenehydroxynaphthoquinone*, $(CH_3)_2.CH.CH:CH.C_{10}H_4O_2(OH)$. This hydrocarbon is not identical with either of the amylnaphthalenes described above, but may contain normal amyl or pentyl.

Lapachon, $C_{15}H_{14}O_3$, is isomeric with lapachoic acid, and is formed by dissolving the latter in sulphuric acid and reprecipitating with water. It crystallizes from alcohol in flat, orange-red, silky needles, melts at 155—156°, and is insoluble in cold caustic potash solution. When heated with acetic anhydride and sodium acetate a green solution is formed from which brown tablets with a blue surface lustre separate. These appear golden-yellow in transmitted light, and yield an indigo-blue powder with a cupreous lustre, and though scarcely soluble in alcohol and ether impart to both liquids a sky-blue colour.

Paternò gave to lapachon the formula $C_{30}H_{28}O_6$, but Greene and Hooker found that the molecular weight as determined by

Raoult's method agrees with the simpler formula. It likewise behaves as a quinone, and its constitution is derived from that of the following compound.[1]

Hydroxyhydrolapachoic acid, $C_{15}H_{16}O_4$, is obtained by dissolving lapachon in hot caustic potash solution :



$$C_{10}H_4O_2\left\langle\begin{matrix}CH_2 \\ O\end{matrix}\right\rangle CH.C_3H_7 + KOH = C_{10}H_4O_2\left\langle\begin{matrix}CH_2.CH(OH).C_3H_7 \\ OH\end{matrix}\right. .$$

Acetic acid precipitates it from the deep-red solution as a reddish oil, which solidifies to a yellow crystalline mass. It is readily soluble in alcohol and acetic acid, and separates on concentrating the solution in large crystals, melting at 125°.

The *barium* salt crystallizes with one molecule of water in orange-red needles, and the *silver* salt in dark-brown needles, which likewise contain one molecule of water of crystallization.

When the salts are treated with hydrochloric acid the hydroxy-acid first formed splits up more or less completely into water and lapachon. The latter is also formed in all probability in a similar manner from lapachoic acid, the elements of water being first added and then again eliminated.

Lapachoic acid and lapachon appear to be derivatives of β-naphthoquinone, as the aqueous solution of the latter gives with a few drops of caustic soda solution a dark-red colouration which disappears when the liquid is shaken in presence of air.

2697 *a-Naphthylpropionic acid*, $C_{10}H_7.C_2H_4.CO_2H$, is formed by the action of sodium amalgam and water on naphthylacrylic acid, and crystallizes from alcohol in small needles, melting at 148°, and fairly soluble in water.

a-Naphthyl-β-bromopropionic acid, $C_{10}H_7.CHBr.CH_2.CO_2H$, is formed by heating naphthylacrylic acid to 100° with a saturated acetic acid solution of hydrogen bromide, and crystallizes from chloroform in needles, which melt at 216°. It is decomposed by sodium carbonate solution with formation of *a-naphthylethylene*, or *naphthalenestyrolene*, $C_{10}H_7.CH{=}CH_2$, which strongly resembles styrolene but has a fainter smell. It yields a *dibromide* which crystallizes from chloroform in small tablets, and melts at 168°.

a - Naphthyldibromopropionic acid, $C_{10}H_7.C_2H_2Br_2.CO_2H$, is

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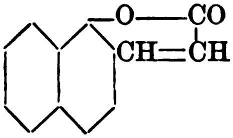
[1] *Ber.* **22**, 1721.

formed by the combination of bromine and naphthylacrylic acid, and crystallizes from chloroform in colourless transparent plates, melting at 189° (Brandis).

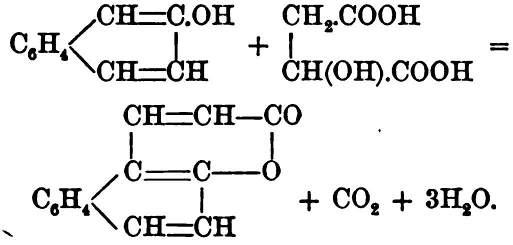
α-Naphthylacrylic acid, or *Naphthocinnamic acid*, $C_{10}H_7.CH{=}CH.CO_2H$, is prepared by heating α-naphthoic aldehyde with acetic anhydride and sodium acetate at 160—180°. It crystallizes from alcohol in needles which dissolve with difficulty in water, but readily in ether, melt at 211—212°, and are not easily volatilized.[1] Its *calcium* salt crystallizes from hot water in lustrous transparent plates, very sparingly soluble in cold water.

α-Hydroxynaphthylacrylic acid, or *α-Naphthocoumaric acid*, $C_{10}H_6(OH)C_2H_2.CO_2H$. When hydroxynaphthoic aldehyde is heated with acetic anhydride and sodium acetate at 180°, it is converted into *α-naphthocoumarin*, $C_{13}H_8O_2$, which has the following constitution:



It crystallizes in felt-like aggregates of needles, which have a vitreous lustre, melt at 118°, and are very sparingly soluble in hot water, but readily in alcohol. Its aqueous solution shows a bluish fluorescence, and evolves a slight odour on warming resembling that of coumarin. It dissolves in hot dilute caustic potash forming a yellow solution, but is reprecipitated by acids. If however it be heated with concentrated potash at 170°, it is converted into α-naphthocoumaric acid, which is precipitated by acids as a crystalline powder, melting at 170°, scarcely soluble in water, but readily in alcohol.[2]

β-Napthocoumarin is prepared by heating β-naphthol with malic and sulphuric acids:



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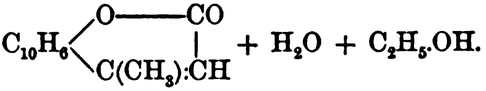
[1] Lugli, *Gazzetta*, **11**, 393; Brandis, *Ber.* **22**, 2153.

[2] Kauffmann, *Ber.* **16**, 683.

It crystallizes from dilute alcohol in needles, melting at 141°.[1]

β-Naphthomethylcoumarin, $C_{14}H_{10}O_2$, is obtained by the action of sulphuric acid on a mixture of β-naphthol and ethyl acetoacetate:

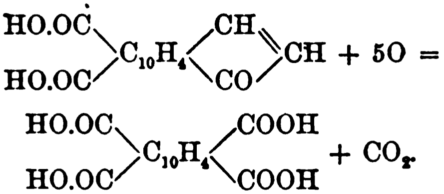
$$C_{10}H_7OH + CH_3.CO.CH_2.CO_2C_2H_5 =$$



$$C_{10}H_6\begin{cases}O\text{———}CO \\ C(CH_3){:}CH\end{cases} + H_2O + C_2H_5.OH.$$

It crystallizes from dilute alcohol in lustrous white needles, melts at 161—162°, and dissolves in sulphuric acid with a uranium-green fluorescence.[2]

Naphthalenetetracarboxylic acid, $C_{10}H_4(CO_2H)_4$, is formed by oxidizing pyrenic acid (p. 362) with an alkaline solution of potassium permanganate.



$$\begin{matrix}HO.OC \\ HO.OC\end{matrix}{>}C_{10}H_4{<}\begin{matrix}CH \\ CO\end{matrix}{>}CH + 5O =$$
$$\begin{matrix}HO.OC \\ HO.OC\end{matrix}{>}C_{10}H_4{<}\begin{matrix}COOH \\ COOH\end{matrix} + CO_2.$$

It is precipitated by hydrochloric acid from solutions of its salts in broad-pointed lustrous plates or spear-shaped needles, resembling the crystals of benzoic acid, and is moderately soluble in hot water, very sparingly in alcohol. It is not attacked by bromine or hot sulphuric acid, and nitric acid even on heating neither oxidizes it nor converts it into a nitro-compound. On heating with quicklime it is resolved into carbon dioxide and naphthalene.

Ammonium naphthalenetetracarboxylate, $C_{10}H_4(CO_2NH_4)_4$, crystallizes in beautiful silky needles, readily soluble in water.

Barium naphthalenetetracarboxylate, $C_{10}H_4(CO_2)_4Ba_2$, is a heavy crystalline precipitate, which is very hygroscopic and becomes electrified when rubbed.

Naphthalenetetracarboxylic anhydride, $O(CO)_2.C_{10}H_4(CO)_2O$, is formed when the acid is gradually heated; if the heating be

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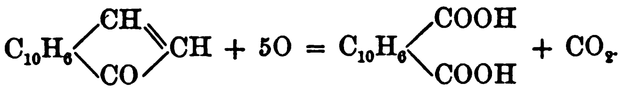
[1] Pechmann and Welsh, *Ber.* **17**, 1646.

[2] Pechmann and Cohen, *Ber.* **17**, 2190.

carried out too quickly lower carboxylic acids of naphthalene are formed. It is also obtained by recrystallizing the acid from acetic acid, or by heating the latter with concentrated nitric acid at 160°, and crystallizes out on cooling in beautiful glassy prisms, whilst from acetic acid it separates in small white needles. When heated above 300° it sublimes in long lustrous needles.

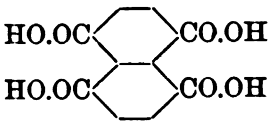
Naphthalenetetracarboxylic imide, $NH(CO)_2C_{10}H_4(CO)_2NH$, is prepared by dissolving the anhydride in warm ammonia, and quickly separates either in fascicular aggregates of microscopic straw-yellow needles, or in aggregates of cross-shaped prisms. It sublimes on heating above 270° in small yellow needles, and dissolves in caustic soda with a lemon-yellow colour, the sodium compound being formed. This is insoluble in concentrated alkali, but dissolves on addition of boiling water, and crystallizes out on cooling in lemon-yellow needles. In moist air, or on boiling with water it is reconverted into the imide, which is attacked with great difficulty by boiling caustic soda solution, reforming a very small quantity of the acid.

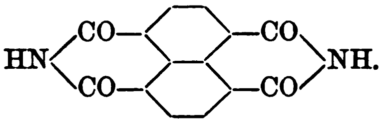
Naphthalenetetracarboxylic acid contains at least two carboxyl-groups in the peri-position, for pyrenic acid is converted on heating into pyreneketone, and this is oxidized by potassium permanganate to naphthalic acid (p. 320).



$$C_{10}H_6\left\langle\begin{matrix}CH\\CO\end{matrix}\right\rangle CH + 5O = C_{10}H_6\left\langle\begin{matrix}COOH\\COOH\end{matrix}\right. + CO_2.$$

It is extremely probable that the second pair also occupies the peri-position, as both pairs behave exactly alike in every respect, no reaction having as yet been found which is confined to one pair. The stability of the imide towards alkalis also agrees with this supposition, as other compounds containing a ring of four carbon atoms and one nitrogen atom behave in a similar manner.[1] The constitutions of naphthalenetetracarboxylic acid and its imide are therefore represented by the following formulæ :





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[1] Bamberger and Philip, *Annalen*, **240**, 147 *Ber.* **20**, 365.

SANTONIN, $C_{15}H_{18}O_3$.

2698 The anthelmintic properties of certain varieties of *Artemisia* have been known for many ages. Thus Dioscorides mentions *῎Αψίνθιον θαλάσσιον* or *σέριφον*, which grew in Asia Minor, and whose seeds, taken in honey, were employed as a remedy for Ascarides and intestinal worms. The kind found in the country of the Santones, in Gaul, and termed therefore *῎Αψίνθιον σαντόνιον* was found to possess similar properties. Pliny mentions also various kinds of *absinthium*, such as *Santonicum* and *Absinthium marinum*.[1] Alexander Trallianus, a physician who lived in Rome in the sixth century, likewise recommends a decoction of *θαλασσία ἀψσινθία* as a vermifuge, whilst Serapion Damascenus, of Baalbek, who lived in the ninth or tenth century, states that the seeds of the herb Sandonica are more active towards worms than wormwood.

The worm seeds, *semen contra vermes, lumbricorum semen*, are frequently mentioned in later times; the Italians termed them *semenzina*, the diminutive of *semenza*, from which was derived the officinal name *semen cinæ*. It was usually reckoned as an Indian product, but probably came to the latter from Central Asia. At the end of the seventeenth century, it was shown by Paul Hermami, of Leyden, that it does not really consist of seeds, but of the unexpanded flower-heads.

The worm seeds (Flores cinæ) now occurring in commerce, are the unopened blossoms of *Artemisia maritima* or its varieties. The product is collected in the Kirgisen steppe, and brought thence in large quantities to Nijni-Novgorod, from which it is brought through Moscow, St. Petersburg or Revel, to Western Europe, where the greater portion is worked up in the manufacture of santonin. *Artemisia maritima* is also found in Europe on the sea-coast, and in inland places where salt is abundant.

Santonin was discovered in 1830 almost simultaneously by the pharmacist Kahler in Düsseldorf, and by Alms, a pharmacist's assistant in Penzlin; the latter also showed that it is the active constituent of worm seeds and recommended its employment in medicine. In the same year another pharmacist, Oberdörffer, observed that it is soluble in alkalis, and Trommsdorf[2] and Heldt,[3] who examined it more closely, found that although

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[1] *Nat. Hist.* **26**, 28, 29.

[2] *Annalen*, **11**, 190.

[3] *Annalen*, **63**, 10.

perfectly neutral it combines with bases and is precipitated by acids, and they also stated that in combining with bases it did not take up the elements of water. Gerhardt therefore believed it to be an acid, which view was generally adopted until Hesse[1] showed that, contrary to the previous supposition, santonin does take up the elements of water when acted on by bases, yielding salts of *santoninic* acid, of which santonin is therefore the anhydride or lactone; its constitution and that of its derivatives was determined by Cannizzaro.[2]

To prepare it from worm seeds, which contain 1·5—2 per cent., these are first freed from the ethereal oil (Pt. V. p. 458), and 20 parts then boiled with 7 parts of freshly-slaked lime, 40 parts of water, and 40 parts of alcohol of sp. gr. 0·830, and this treatment subsequently twice repeated. The alcohol is then distilled off from the filtered liquid, and the latter evaporated till it occupies 50 parts. On addition of a little hydrochloric acid a greenish resin separates out, which is removed and the filtrate treated with a slight excess of hydrochloric acid. The free santoninic acid thus formed speedily splits up into water and santonin, the latter crystallizing out. The crude product is extracted with a little warm water, filtered, the residue warmed with 10 parts of alcohol and a little animal charcoal, finally heated to boiling, and filtered. On cooling, pure santonin crystallizes out.

It forms very lustrous rhombic prisms or tablets, which have a slightly bitter taste, melt at 170°, and sublime on carefully heating in small quantities. At the ordinary temperature it dissolves in 5,000 parts, at the boiling point in 250 parts of water; it is more readily soluble in alcohol, being dissolved in 40 parts of cold and 8 parts of boiling alcohol of sp. gr. 0·830; the alcoholic solution is lævo-rotatory and has an intensely bitter taste. It also dissolves in 4 parts of chloroform and in acetic acid, fatty, and ethereal oils. On exposure to light, especially to direct sunlight, it is coloured yellow, the crystals frequently cracking; it then dissolves in alcohol with a pale yellow colour, from which solution however colourless santonin crystallizes out on cooling.

Taken internally it has not infrequently a remarkable action upon the sight, all objects appearing at first to have a bluish tinge, which afterwards becomes yellow or greenish-yellow. In larger doses it causes headache, dizziness, and sickness, and often, especially with children, convulsions which end in death.

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[1] *Ber.* **6**, 1280.

[2] *Ber.* **18**, 2746; **19**, 2260; *Gazzetta*, **12**, 393.

When santonin is distilled with zinc dust in a current of hydrogen it yields dimethylnaphthalene, dimethylnaphthol, and propylene.

Santoninoxime, $C_{15}H_{18}(NOH)O_2$, was discovered by Cannizzaro.[1] It is best prepared by boiling 4 parts of hydroxylamine hydrochloride, 5 parts of santonin, 50 parts of 90 per cent. alcohol, and 4 parts of precipitated calcium carbonate for 6—7 hours, or preferably by heating the mixture to 70—80° for 3—4 days. It is insoluble in cold, very sparingly in hot water, and crystallizes in white, silky needles, which melt at 216—218°, and are lævo-rotatory.[2] It is also used as a remedy for worms, as it is non-poisonous, but 3—5 times the dose usually given of santonin is necessary.[3]

Santoninphenylhydrazone, $C_{15}H_{18}(N_2HC_6H_5)O_2$, is formed when an acetic acid solution of santonin is boiled with phenylhydrazine, and crystallizes from alcohol in lustrous straw-yellow needles, melting at 220—221° with decomposition. It is dextrorotatory, and forms a red, unstable hydrochloride.[4]

Santoninic acid, $C_{15}H_{20}O_4$, was obtained by Hesse by saturating a cold solution of the sodium salt with dilute hydrochloric acid, and at once extracting the milky liquid with ether. The acid quickly separates from the ethereal solution in crystalline granules, which on recrystallization from alcohol are obtained in beautiful rhombic crystals. These do not become yellow on exposure to light, are very sparingly soluble in cold, more readily in hot water, the solution having an acid reaction. When heated for a long time at 120° it decomposes into water and santonin, which also takes place on addition of sulphuric or hydrochloric acid to its solution, especially on warming. Like santonin it is lævo-rotatory.

Sodium santoninate, $2C_{15}H_{19}O_4Na + 7H_2O$, is likewise employed as a remedy for intestinal worms, and is obtained by boiling santonin with soda crystals and dilute alcohol. It crystallizes in transparent rhombic prisms, which have a bitter saline taste, and an alkaline reaction. They are readily soluble in water, and somewhat less easily in alcohol.

Calcium santoninate, $(C_{15}H_{19}O_4)_2Ca$, is prepared by warming an alcoholic solution of santonin with slaked lime, and separates

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[1] *Ber.* **18**, 2746.

[2] Gucci, *Ber.* **22**, 731 c.

[3] *Chem. Zeit. Rep.* **1889**, 185.

[4] Cristaldi, *Ber.* **20**, 708 c.; **22**, 732 c.

out on evaporating the solution in crystalline crusts, which after drying form a plastic silky mass, readily soluble in water, and have an alkaline reaction.

Santonious acid, $C_{15}H_{20}O_3$, is formed by the long-continued boiling of santonin with hydriodic acid and amorphous phosphorus. It is scarcely soluble in cold, more easily in boiling water, and very readily in alcohol or ether, from which it crystallizes in long, lustrous needles, melting at 178—179°. Its solutions are dextro-rotatory, and its alkaline salts dissolve readily in water and alcohol. The *sodium* salt, $C_{15}H_{19}O_3Na$, crystallizes in very small needles, and the *barium* salt forms readily soluble crystals containing water of crystallization.

Ethyl santonite, $C_{15}H_{19}O_3.C_2H_5$, is obtained by the action of hydrogen chloride on an alcoholic solution of the acid, and separates from ether in white crystals, melting at 116—117°. If its ethereal solution be heated with sodium under pressure it yields *ethyl sodiosantonite*, $C_{15}H_{18}NaO_3.C_2H_5$, as a white powder, which on treatment with ethyl iodide forms *diethyl santonite*, $C_{15}H_{18}O_3(C_2H_5)_2$. The latter crystallizes in long needles, melting at 31—32°, and on hydrolysis yields *ethylsantonious acid*, $C_{15}H_{18}(C_2H_5)O_3$, which also crystallizes in long needles melting at 115·5—116°.

Isosantonious acid, $C_{15}H_{20}O_3$, is obtained by heating santonious acid and dissolving the resinous product in warm alcoholic potash. The acid separates on addition of hydrochloric acid in small plates, melting at 155°. It is a strong monobasic acid and optically inactive.

Ethyl isosantonite forms white crystals, melting at 123°, and is converted by sodium and ethyl iodide into *diethyl isosantonite*, which melts at 54°. From the latter *ethylisosantonious acid*, melting at 143°, may be prepared.[1]

As already mentioned (p. 319) santonious and isosantonious acids decompose on heating with caustic baryta with formation of dimethylnaphthol, which is also obtained mixed with dimethylnaphthalene and propylene by heating them with zinc dust.[2]

When santonious acid is heated in a current of carbon dioxide at 320°, it splits up into dimethyldihydronaphthol and propionic acid; it is therefore dimethylhydroxytetrahydronaphthylpropionic acid. It contains two hydrogen atoms more than

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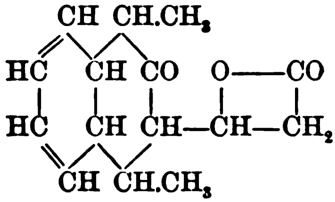
[1] Cannizzaro and Carnelutti, *Gazzetta*, **12**, 393; Cannizzaro, *Gazzetta*, **13**, 385.

[2] *Ber.* **13**, 1516.

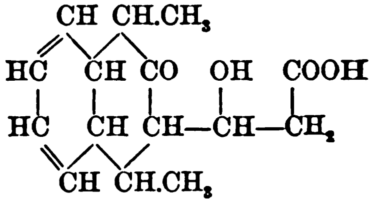
santonin, which is a lactone, and the action of hydroxylamine and phenylhydrazine shows that it is also a ketone.

The constitution of these compounds is explained by the following formulæ:

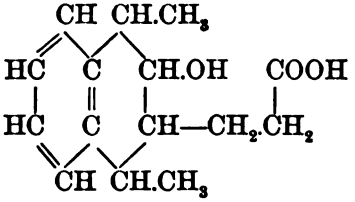
Santonin.



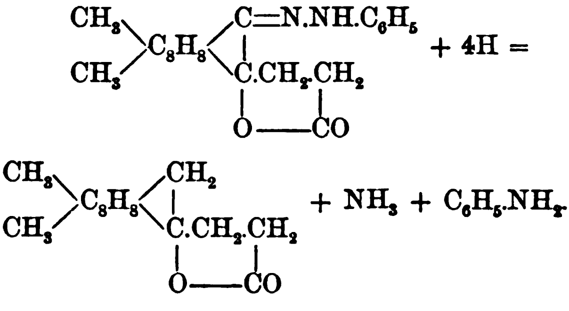
Santoninic Acid.



Santonious Acid.



Hyposantonin, $C_{15}H_{20}O_2$, is obtained by the action of sodium amalgam on an acetic acid solution of santoninoxime or santonin-phenylhydrazone:



It forms rhombic dextro-rotatory crystals, melts at 152° and dissolves in solutions of the alkalis or alkaline carbonates only on warming. When dissolved in a mixture of equal volumes of concentrated sulphuric acid and a very dilute ferric chloride solution, the liquid first assumes the colour of peach blossoms, and then becomes malachite green. On warming with dilute acids it is converted into isohyposantonine, which forms rhombic crystals, melts at 168·5°, is lævo-rotatory, dissolves in alcohol and benzene less readily than hyposantonine, and may be sublimed in a current of carbon dioxide (Cristaldi and Cucci).

2699 *Photosantonic acid*, $C_{15}H_{22}O_5$, was first obtained by Sestini, who exposed an acetic acid solution of santonin for a long time to direct sunlight. Cannizzaro and Fabris found that the isomeric isophotosantonic acid is formed at the same time. To prepare the acids 1 kilo of santonin is dissolved in 52 litres of acetic acid of sp. gr. 1·054, and exposed in a number of flasks to the light for several months, after which $\frac{1}{9}$th of the acetic acid is evaporated off under diminished pressure. On cooling, photosantonic acid crystallizes out, and is washed first with dilute acetic acid, and then with water, the filtrates being added to the mother liquor. On addition of water to the latter a less pure photosantonic acid evaporates out, whilst the isophotosantonic acid and a little photosantonic acid remain in solution.[1]

The latter crystallizes in hexagonal prisms, which are scarcely soluble in cold, with difficulty in hot water, but readily in alcohol and ether, the solutions being lævo-rotatory. It is a dibasic acid, melting at 125—130°, and when quickly heated undergoes conversion into *photosantolactone*, $C_{15}H_{20}O_4$, which is more sparingly soluble in alcohol and ether than the acid, and melts at 153°.

Ethylphotosantolactone, or *Photosantonine*, $C_{15}H_{19}(C_2H_5)O_4$, is formed by the prolonged exposure to sunlight of a solution of santonin in 65 per cent. alcohol, and crystallizes in colourless plates, melting at 68—69°.

When photosantonic acid is heated in a stream of carbon dioxide at the melting-point of lead, it loses carbon dioxide, yielding the monobasic *pyrophotosantonic acid*, $C_{14}H_{20}O_2$, which forms crystals soluble in alcohol and ether, melting at 94·3°.[2] It is also formed by warming photosantonic acid with hydriodic acid (Cannizzaro and Fabris). On distillation with caustic baryta it yields a liquid hydrocarbon, $C_{13}H_{20}$, boiling at 221·5—223°, which is probably an ethylamylbenzene.

Isophotosantonic acid, $C_{15}H_{22}O_5$, is scarcely soluble in water, but readily in alcohol, and separates, on evaporating the latter solution, in thick rhombic crystals. These lose water at 100°, forming *isophotosantolactone*, $C_{15}H_{20}O_4$, which is monobasic and dextro-rotatory.

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[1] *Ber.* **19**, 2260.

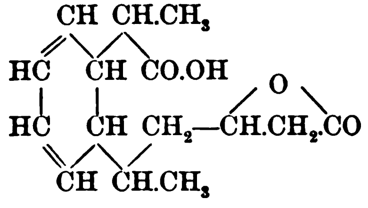
[2] Sestini and Danesi, *Ber.* **15**, 1200 ; *Gazzetta*, **12**, 83.

Acetylisophotosantolactone, $C_{15}H_{19}(CO.CH_3)O_4$, is formed, together with the following compound, in the preparation of the acid, and crystallizes from alcohol in transparent needles, melting at 183°. It is also formed by heating the acid with sodium acetate and acetic acid.

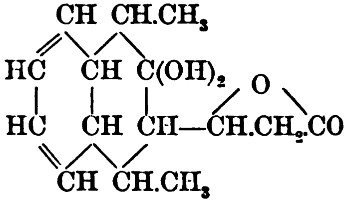
Diacetylisophotosantolactone, $C_{15}H_{18}(CO.CH_3)_2$, forms crystals melting at 163—166°, which readily pass into the monacetyl compound on recrystallization from alcohol or more quickly on heating at 120°.

Cannizzaro assumes that in the formation of photosantonic acid one ring of the dimethylnaphthalene is split, and the carbonyl converted to carboxyl, whilst in isophotosantonic acid the ring remains closed, and the carbonyl forms the group $C(OH)_2$. For the lactones he gives the following formulæ:

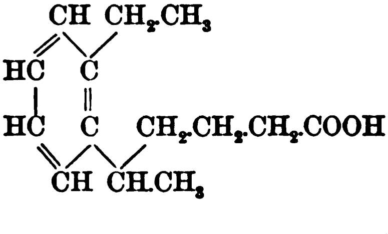
Photosantolactone.



Isophotosantolactone.



Pyrophotosantonic acid is probably an ethylphenylcaproic acid:



2700 *Santonic acid*, $C_{15}H_{20}O_4$, is prepared by boiling santonin for twelve hours with saturated baryta water, and after saturating the product with hydrochloric acid, is extracted with ether. It forms rhombic crystals which melt at 161—163°, and are unacted upon by light. It dissolves with difficulty in cold water, readily in alcohol, forming solutions which are more strongly lævo-rotatory, and much more stable than those of santoninic acid.[1] When santonic acid is boiled with hydriodic acid it yields the hydrocarbon *santone*, $C_{15}H_{26}$, boiling at 235—240°,

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[1] Cannizzaro and Sestini, *Ber.* **6**, 120.

and *iodosantone*, $C_{15}H_{25}I$, which decomposes on distillation.[1] The salts of santonic acid are for the most part obtained crystalline with difficulty, but its esters crystallize well.[2]

Ethyl santonate, $C_{15}H_{19}O_4.C_2H_5$, obtained by passing hydrogen chloride into an alcoholic solution of the acid, forms rhombic crystals melting at 94—95°.

Acetylsantonic acid, $C_{15}H_{19}(CO.CH_3)O_3$, is prepared by heating santonic acid with acetyl chloride, and crystallizes from chloroform in large prisms, which melt at 139—140°. On long-continued boiling with water it decomposes into santonic and acetic acids; if, however, it be heated at 180—200°, santonin and acetic acid are formed.[3]

Santonyl chloride, $C_{15}H_{19}O_3Cl$, forms rhombic crystals, which melt at 170—171°, are dextro-rotatory and are decomposed by alcohol with formation of ethyl santonate.

The constitution of santonic acid and also of the compounds about to be described has not yet been ascertained.

Hydrosantonic acid, $C_{15}H_{22}O_4$, is obtained by the action of sodium amalgam and water on santonic acid, and separates from ethereal solution in rhombic crystals, which melt at 170° with decomposition.[4] It is monobasic, and on heating with acetic acid at 150° is converted into *hydrosantonide* $C_{15}H_{20}O_3$, which likewise forms rhombic crystals melting at 155—156°,[5] and is converted by heating with alcoholic potash into the acid, of which it is therefore the lactone.

Acetylhydrosantonide, $C_{15}H_{19}(CO.CH_3)O_3$, is formed by the action of acetyl chloride on hydrosantonic acid, and crystallizes from ether in needles melting at 204—204·5°. On heating with alcoholic ammonia it yields acetamide and *hydrosantonamide* $C_{15}H_{21}(NH_2)O_3$, which forms crystalline flakes melting at 190° with decomposition.

Metasantonic acid, $C_{15}H_{20}O_4$, was first obtained by Cannizzaro, by heating silver hydrosantonate with water. It is more readily obtained by distilling santonic acid under diminished pressure. If the latter be boiled with acetic acid, and the residue heated, *santonide*, $C_{15}H_{18}O_3$, and the isomeric *parasantonide* are obtained. Santonide forms rhombic crystals melting

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[1] Cannizzaro and Amato, *Ber.* **7**, 1103.

[2] Cannizzaro and Valente, *Gazzetta*, **8**, 309.

[3] Sestini, *Jahresb.* **1875**, 608.

[4] Cannizzaro, *Gazzetta*, **6**, 341.

[5] Cannizzaro and Valente, *Gazzetta*, **8**, 309.

at 127°, and is converted into metasantonic acid when boiled with aqueous caustic potash. On warming santonin with sulphuric acid it is converted into *isosantonin*; the latter melts at 137—138°, and on treatment with sodium carbonate solution yields metasantonic acid. This forms rhombic crystals melting at 161—167°.

	Melting-point.
Methyl metasantonate, $C_{15}H_{19}(CH_3)O_4$, monosymmetric tablets	101·5—102·5°
Metasantonyl chloride, $C_{15}H_{19}O_3Cl$, rhombic crystals	139°

Parasantonic acid, $C_{15}H_{20}O_4$. The *parasantonide* mentioned above likewise crystallizes in the rhombic system, and melts at 110°. On solution in warm dilute hydrochloric acid, or on boiling with caustic soda it is converted into *parasantonic acid*, which forms large rhombic crystals. It is a monobasic acid, fairly soluble in water, and by the action of phosphorus chloride, acetyl chloride, or acetic anhydride re-forms parasantonide.

The *methyl ester* crystallizes in rhombic prisms and melts at 183—184°.

When parasantonide is heated for a long time with hydriodic acid and amorphous phosphorus the following compounds are formed.[1]

a-Metasantonin, $C_{15}H_{18}O_3$. This compound crystallizes from ether in thin elastic rhombic tablets, which are soluble in alcohol and boiling water, and melt at 160·5°. It boils at 238—240°, is unattacked by phosphorus chloride, acetyl chloride, and acetic anhydride, and may be crystallized unaltered from caustic potash solution.

β-Metasantonin crystallizes in long monosymmetric prisms, melts at 136°, and in other respects closely resembles the *a*-compound.

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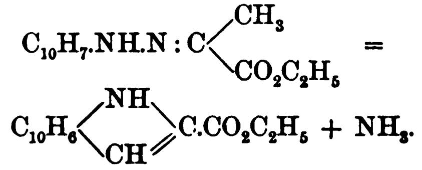
[1] Cannizzaro and Carnellutti, *Gazzetta*, **10**, 461.

INDOLE DERIVATIVES OF NAPHTHALENE.

2701 *α-Naphthindole*, $C_{12}H_9N$. When the *ethyl ester* of α-naphthylhydrazonepyroracemic acid is heated with zinc chloride at 195°, it yields *ethyl α-naphthindolecarboxylate:*

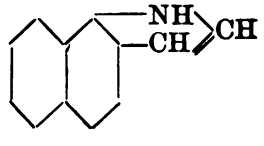


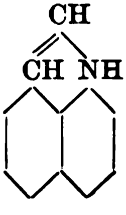
$$C_{10}H_7.NH.N:C\left\langle\begin{matrix}CH_3\\CO_2C_2H_5\end{matrix}\right. = C_{10}H_6\left\langle\begin{matrix}NH\\CH\end{matrix}\right\rangle C.CO_2C_2H_5 + NH_3.$$

It forms clear transparent needles which are volatile with steam, and on hydrolysis yield the acid. This crystallizes in small needles, melting at 202°, readily soluble in alcohol but sparingly in water, and decomposes on distillation into carbon dioxide and α-naphthindole. The latter is very sparingly soluble in hot water, somewhat more readily in dilute acetic acid, from which it crystallizes in beautiful plates, melting at 174—175°, and readily soluble in alcohol. It is slightly volatile with steam, and has only a faint odour.

A piece of pine-wood saturated with its alcoholic solution is coloured red by hydrochloric acid, and when its hot solution is mixed with a similar solution of picric acid a cherry-red coloured solution is obtained, from which the *picrate* crystallizes out on cooling in beautiful red needles. When the dilute acetic acid solution of α-naphthindole is boiled with hydrogen dioxide it becomes bluish-green, and a precipitate of the same colour separates out. The latter contains traces of a colouring matter which is probably the indigo of the naphthalene series, and dissolves in chloroform with a bluish-green colouration; on heating the residue it volatilizes, forming a reddish-violet vapour.

The constitution of α-naphthindole is represented by one of the following formulæ:





α-Hydronaphthindole, $C_{12}H_{11}N$, is formed by gradually adding zinc dust and hydrochloric acid to an alcoholic solution of α-naphthindole, and forms a crystalline mass which does not give the pine-wood reaction. It readily forms salts, and its alcoholic solution is coloured reddish-violet by ferric chloride.

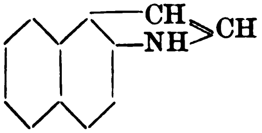
Pr : 2-*Methyl-α-naphthindole*, $C_{10}H_6.NH(C_2H.CH_3)$, is obtained by heating acetone-α-naphthylhydrazone with zinc chloride. It is readily soluble in alcohol, moderately in hot water, and crystallizes out in slender needles, which have a faint characteristic odour, melt at 132°, and colour pine-wood moistened with hydrochloric acid bluish-violet. Its acetic acid solution is coloured cherry-red by ferric chloride, and yields on addition of water a precipitate of the same colour. Its *picrate* crystallizes from benzene in dark-red needles, melting at 167—168°.[1]

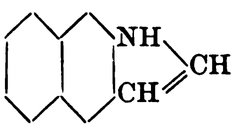
Pr : 2 : 3-*Dimethyl-α-naphthindole*, $C_{10}H_6.NH.C_2(CH_3)_2$, is prepared by heating β-bromolevulinic acid, $CH_3.CO.CHBr.CH_2.COOH$, with α-naphthylamine, and separates out from alcoholic solution in white granules or small prisms which melt at 150°. Its hot acetic acid solution is coloured cherry-red by a trace of ferric chloride, and deep-blue by potassium dichromate.[2]

β-Naphthylindole is formed by heating the ethyl ester of β-naphthylhydrazonepyroracemic acid with zinc chloride; the greater part of the *β-naphthindolecarboxylic acid* first formed decomposes at once, and is therefore only obtained as a by-product, which crystallizes in slender lustrous plates, melting at 226° with evolution of carbon dioxide.

β-Naphthindole is a liquid the faint smell of which has none of the indole characteristics; it boils above 360° under atmospheric pressure and at 220° under 18 mm., and colours pine-wood bluish-violet after moistening with hydrochloric acid. It is converted by ferric chloride into complicated solid oxidation products. Its *picrate* crystallizes from benzene in slender dark-red needles.

Its constitution is represented by one of the following formulæ:





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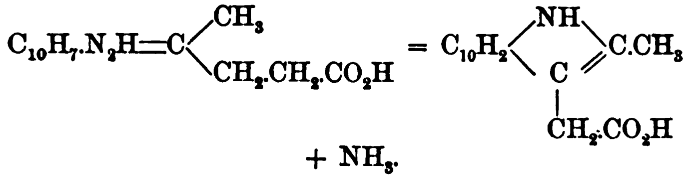
[1] Schlieper, *Annalen*, **239**, 229.

[2] Wolff, *Ber.* **21**, 3360.

Pr: 2-*Methyl-β-naphthindole* has been prepared from acetone-β-naphthylhydrazone, and is a thick yellowish oily liquid which has no fæcal smell, boils at 314—320° under 223 mm. pressure, and gives the same colouration with pine-wood as the foregoing compound. Its *picrate* crystallizes in reddish-brown needles, and melts at 176°.

Hydromethyl-β-naphthindole, $C_{12}H_{10}(CH_3)N$, is a golden-yellow oily liquid, which has a scarcely perceptible odour and boils at 190—200° under 20 mm. pressure.[1]

a-Pr: 2:3-*Dimethyl-β-naphthindole*, $C_{10}H_6.NH.C_2(CH_3)_2$. When β-naphthylhydrazonelevulinic acid is heated with zinc chloride it yields *methyl-β-naphthindoleacetic acid*:



It separates from hot acetone in small crystals showing a large number of surfaces, which have the composition $2C_{15}H_{13}NO_2 + C_3H_6O$, and lose acetone on heating. They are readily soluble in alcohol, sparingly in water, and melt at 210° with evolution of carbon dioxide and formation of a light brown oil, which distils unchanged, and then solidifies to a crystalline mass of dimethyl-β-naphthindole. This separates from alcoholic solution on addition of water in lustrous six-sided tablets, melts at 126°, does not colour pine wood, and forms a dark-red *picrate*. Its acetic acid solution is coloured blue by ferric chloride.

Hydrodimethyl-β-naphthindole, $C_{12}H_9(CH_3)_2N$, is a light yellow thick oil, which gives a red colouration with ferric chloride, and is readily soluble in acids.[2]

β-Pr: 2:3-*Dimethyl-β-naphthindole* is formed by heating β-bromolevulinic acid, $CH_3.CO.CHBr.CH_2.CO_2H$, with β-naphthylamine,[3] and crystallizes from alcohol in small strongly refractive brittle tablets, which melt at 132°, and become violet in the air. It has only a faint odour, and does not readily volatilize with steam. Its concentrated alcoholic solution shows a violet fluorescence, and its acetic acid solution, on boil-

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[1] Schlieper, *Annalen*, **236**, 174.

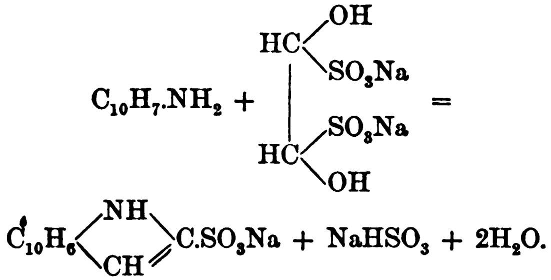
[2] Steche, *Annalen*, **242**, 367.

[3] Wolff, *Ber.* **20**, 425.

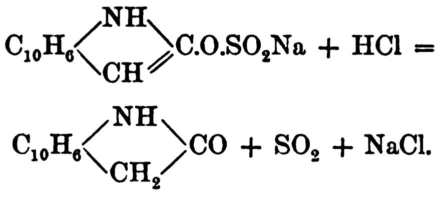
ing with ferric chloride, or hydrochloric acid and potassium dichromate, assumes a beautiful green colour. Its *picrate* crystallizes in dark-brown lustrous needles, melting at 175°.[1]

The existence of two dimethyl-β-naphthindoles is readily understood, but it is not yet known which is the 1 : 2 and which the 2 : 3 compound.

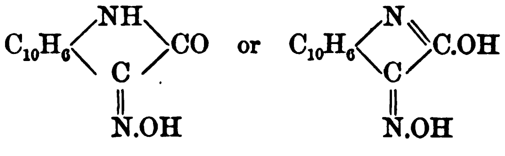
2702 *a-Naphthoxindole*, $C_{12}H_9NO$. When an alcoholic solution of glyoxal sodium sulphite and α-naphthylamine is heated on the water-bath, the following reaction takes place:



The *sodium a-naphthindolesulphite* thus obtained forms crystals which are soluble in water, and have a sweet taste. On warming the aqueous solution with concentrated hydrochloric acid it yields α-naphthoxindole:



The latter crystallizes in colourless needles, melting at 245°, which are insoluble in boiling caustic soda solution. When sodium nitrite is gradually added to its warm solution in alcohol and acetic acid, it is converted into *isonitroso-a-naphthoxindole* or *a-naphthisatinoxime* (compare Pt. V. p. 91).



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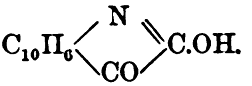
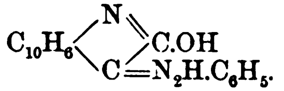
[1] *Ber.* **21**, 3360.

This compound forms pale-red needles, soluble in alcohol. On reduction with tin and hydrochloric acid it yields *amido-α-naphthoxindole*, which has not been closely investigated, but on oxidation with ferric chloride yields *α-naphthisatin*,



$C_{10}H_6\left\langle\begin{matrix}N\\CO\end{matrix}\right\rangle C.OH.$ The latter crystallizes in small red needles, and like isatin combines with acid alkaline sulphites, and dissolves in alcoholic potash with a deep-violet colouration, which changes to yellow on warming. It is distinguished from isatin by the fact that it does not give a blue colouration with sulphuric acid and benzene containing thiophen (Part IV., p. 75).

Its *phenylhydrazone* crystallizes in small, lustrous, yellowish-red plates, which melt at 268—270°, and have the following constitution:



$$C_{10}H_6\left\langle\begin{matrix}N\\C\end{matrix}\right\rangle\begin{matrix}C.OH\\=N_2H.C_6H_5.\end{matrix}$$

β-Naphthoxindole. The *sodium* salt obtained by warming an alcoholic solution of glyoxal sodium sulphite and β-naphthylamine is a sandy powder, almost insoluble in hot water. Boiling caustic potash converts it into *potassium β-naphthindolesulphonate*, $C_{12}H_8N.SO_3K$, which crystallizes from hot water in beautiful white plates having a sweet taste. The *β-naphthoxindole* obtained from it crystallizes from alcohol in greenish needles, melting at 234°. On heating with baryta-water at 140—150° it yields the barium salt of amidonaphthylacetic acid, $C_{10}H_6(NH_2)CH_2.COOH$; the solution of the free acid has a strongly acid reaction, and is reconverted into β-naphthoxindole on gentle warming.

β-Naphthisatinoxime crystallizes from alcohol in slender yellowish-red needles, melts at about 240° with decomposition, and is soluble in alkalis.

β-Naphthisatin forms slender red needles, melting at 248°, and behaves in an analogous manner to the α-compound. Its *phenylhydrazone* crystallizes in beautiful yellowish-red plates.[1]

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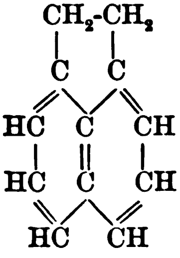
[1] Hinsberg, *Ber.* **21**, 110.

ACENAPHTHENE GROUP.

2703 *Acenaphthene*, or *Peri-ethylenenaphthalene*, $C_{10}H_6.C_2H_4$, was first obtained by Berthelot together with other products by passing a mixture of naphthalene vapour and acetylene through a red hot tube.[1] Later on he found that it occurs in coal-tar.[2] It is also formed, together with a large quantity of naphthalene, when the vapour of ethylnaphthalene is passed through a porcelain tube heated to bright redness, or when it is heated with 1 molecule of bromine at 180°, and the product boiled with alcoholic potash.[3]

$$C_{10}H_7.C_2H_4Br = C_{10}H_6.C_2H_4 + HBr.$$

Behr and van Dorp found that it yields naphthalic acid on oxidation, the exact constitution of which was ascertained by Bamberger and Philip (p. 320). Hence the constitution of acenaphthene is represented by the following formula:



In order to prepare it, the liquid products remaining after the separation of anthracene from coal-tar oil are subjected to fractional distillation. From the combined fractions boiling at

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[1] *Bull. Soc. Chim.* **7**, 275; Ferks, *Ber.* **20**, 661.

[2] *Bull. Soc. Chim.* **8**, 245.

[3] Berthelot and Bardy, *Annalen*, **166**, 135.

265—275°, acenaphthene separates after some time in flat prisms, which are washed with cold alcohol, and recrystallized from the hot liquid. It is thus obtained in needles often over 2 cm. in length, and occasionally in small plates.[1]

It melts at 103°,[2] and boils at 277·5°, its vapour having a sp. gr. of 5·35°.[3] Its *picrate*, $C_{12}H_{10} + C_6H_3(NO_2)_3O$, crystallizes in orange-red prisms, which melt at 161—162°, and are sparingly soluble in alcohol.

Tetrahydroacenaphthene, $C_{12}H_{14}$, is obtained by adding thin slices of sodium to a boiling amyl alcohol solution of acenaphthene, and forms a colourless thick oily liquid which has a faintly aromatic odour, and boils at 249·5°.[4]

Perhydroacenaphthene, $C_{12}H_{20}$, is prepared by heating 1 part of acenaphthene, 1·25 parts of amorphous phosphorus, and 5—6 parts of hydriodic acid (sp. gr. 1·7) for 12—16 hours at 250—260°. It is a liquid boiling at 235—236°, and has a remarkable sweetish mouldering smell.[5]

Bromacenaphthene, $C_{10}H_5Br.C_2H_4$, is formed when bromine is added to an ethereal solution of acenaphthene; it crystallizes from alcohol in beautiful tablets, melting at 52—53°, and yields bromonaphthalic acid on oxidation with chromic acid.

Dibromotetrahydroacenaphthene, or *Dihydroacenaphthene dibromide*, $C_{12}H_{12}Br_2$, is obtained by mixing chloroform solutions of tetrahydroacenaphthene and bromine in a freezing mixture. It crystallizes from boiling benzene in thick glassy rhombic tablets, or short strongly refractive prisms, which are sparingly soluble in cold, readily in hot alcohol, and melt at 138°. On heating with alcoholic potash it is converted into potassium bromide and acenaphthene. In addition to the dibromide, a liquid bromacenaphthene, boiling at 302—307°, is also formed by the action of bromine on tetrahydroacenaphthene.[6]

Dibromacenaphthene tetrabromide, $C_{12}Br_2H_8.Br_4$, is obtained in white crystals when bromine is added to a solution of acenaphthene in carbon bisulphide.[7]

Nitro-acenaphthene, $C_{10}H_5(NO_2)C_2H_4$, is formed, together with the following compound, when nitric acid is added to an acetic

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[1] Behr and van Dorp, *Annalen*, **172**, 263.
[2] Schiff, *Annalen*, **223**, 262.
[3] Graebe, *Annalen*, **163**, 364.
[4] Bamberger and Lodter, *Ber.* **20**, 3073.
[5] Liebermann and Spiegel, *Ber.* **22**, 779.
[6] Bamberger and Lodter, *Ber.* **21**, 840.
[7] Blumenthal, *Ber.* **7**, 1092.

acid solution of acenaphthene, and forms large yellow crystals melting at 101—102°, which are soluble in light petroleum, and are converted, on heating with dilute nitric acid, into nitro-γ-naphthoquinone and nitronaphthalic acid.

Dinitro-acenaphthene, $C_{10}H_4(NO_2)_2C_2H_4$, was first obtained by Berthelot;[1] it is insoluble in light petroleum, but crystallizes from alcohol or acetic acid in small yellow needles, which melt at 206° with carbonization.[2]

Amidoacenaphthene, $C_{10}H_5(NH_2)C_2H_4$, was obtained by Quincke by the reduction of nitroacenaphthene with tin and hydrochloric acid or ammonium sulphide, the nascent hydrogen causing a further reduction to ammonia and acenaphthene. It crystallizes in white needles, melting at 108°, which become discoloured in the air. Its *hydrochloride* is precipitated from aqueous solution by concentrated hydrochloric acid in slender needles, and the *picrate* separates from dilute aqueous solution in yellow crystals.

Acetylamidoacenaphthene, $C_{12}H_9.NH.C_2H_3O$, is formed when the base is boiled with an excess of acetyl chloride, and crystallizes from alcohol in dark-yellow plates, melting at 176°.

Diacetylamidoacenaphthene, $C_{12}H_9N(C_2H_3O)_2$, is obtained in an unusual manner by substituting acetic anhydride for acetyl chloride, and crystallizes from alcohol in pale-brown spangles, melting at 122°.

Acenaphthylthiocarbamide, $CS(NH.C_{12}H_9)_2$, is obtained by boiling the amido-base with carbon bisulphide, and crystallizes from toluene in yellowish or violet asbestos-like needles, which melt at 192°.

Acenaphthylthiocarbimide, $CS:N.C_{12}H_9$, is prepared by boiling the mixture of amidoacenaphthene and carbon bisulphide with alcoholic potash, and crystallizes in lustrous brown plates which melt at 96°.

Diamidoacenaphthene, $C_{10}H_4(NH_2)_2C_2H_4$, crystallizes in small white needles, which quickly undergo decomposition with blackening; its salts are also very unstable.

2704 *Acenaphthylene* or *Periacetylenenaphthalene*, $C_{10}H_6.C_2H_2$, was prepared by Behr and van Dorp by passing the vapour of acenaphthene over lead oxide heated to redness:[3]

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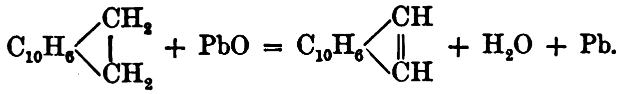
[1] *Bull. Soc. Chim.* **8**, 250.

[2] Quincke, *Ber.* **21**, 1454.

[3] *Loc. cit.*; Blumenthal, *Ber.* **7**, 1092.



$$C_{10}H_6\left<\begin{matrix}CH_2\\ | \\ CH_2\end{matrix}\right. + PbO = C_{10}H_6\left<\begin{matrix}CH\\ \| \\ CH\end{matrix}\right. + H_2O + Pb.$$

It is readily soluble in alcohol and crystallizes in yellow plates or tablets, which do not lose their colour after repeated recrystallization. It melts at 92—93°, volatilizes somewhat at the ordinary temperature, boils with decomposition at 265—275°, and the vapour when more strongly heated carbonizes with re-formation of acenaphthene, on which account the vapour density could not be determined. On oxidation with chromic acid it yields naphthalic acid, and is reconverted into acenaphthene by the action of sodium amalgam on its alcoholic solution. Its *picrate*, $C_{12}H_8 + C_6H_3(NO_2)_3O$, crystallizes in dark-yellow needles, which are sparingly soluble in alcohol, and melt at 201—202°.

Acenaphthylene bromide, $C_{10}H_6.C_2H_2Br_2$, crystallizes from absolute alcohol or benzene in needles, melting at 121—123°, and is also oxidized by chromic acid to naphthalic acid. It readily loses hydrogen bromide, passing into the following compound.

Bromacenaphthylene, $C_{10}H_6.C_2HBr$, is best prepared by warming the dibromide with alcoholic potash; it is an oily liquid, which decomposes on distillation, but yields a *picrate*, $C_{12}H_7Br + C_6H_3(NO_2)_3O$, crystallizing in beautiful yellow needles.

It is not possible to remove a second molecule of hydrogen bromide; on heating it with alcoholic potash at 140°, acenaphthylene is re-formed, the alcohol being oxidized to aldehyde.

$$C_{10}H_6.C_2HBr + C_2H_6O + KOH =$$
$$C_{10}H_6.C_2H_2 + C_2H_4O + KBr + H_2O.$$

Dibromacenaphthylene, $C_{10}H_5Br.C_2HBr$, is obtained by acting on the previous compound with bromine, and crystallizes in beautiful orange-red plates, which do not yield naphthalic acid, but probably bromonaphthalic acid on oxidation.

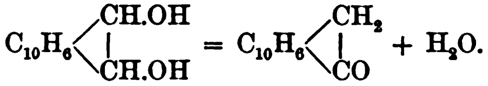
Dibromacenaphthylene bromide, $C_{12}H_6Br_4$, is formed by adding bromine to a carbon bisulphide solution of the dibromide, and separates out in rosette-shaped aggregates of crystals, which are insoluble in alcohol, and melt with decomposition at 161—162°.

Acenaphthylene glycol, $C_{10}H_6.C_2H_2(OH)_2$, is prepared by boiling the monacetate with caustic potash and methyl alcohol, and separates out on cooling in long needles, melting at 204—205°, and sparingly soluble in cold alcohol and hot water, Alkaline potassium permanganate oxidizes it to naphthalic acid.

The *monacetate*, $C_{10}H_6.C_2H_2(OH)(OC_2H_3O)$, is obtained by boiling the bromide with acetic acid and potassium acetate; it crystallizes from alcohol in long slender needles, melting at 122—122·5°, and passes on heating with acetic anhydride into the *diacetate*, $C_{10}H_6.C_2H_2(OC_2H_3O)_2$, melting at 130°.

Acenaphthyl benzoate, $C_{10}H_6.C_2H_2(OH)(OC_7H_6O)$, is formed by the action of silver benzoate on an ethereal solution of the bromide, and crystallizes in small colourless needles, melting at 189—190°.

Acenaphthylene ketone, $C_{12}H_8O$, is prepared by heating the glycol with sodium ethylate:



$$C_{10}H_6\left<\begin{array}{l}CH.OH\\ |\\ CH.OH\end{array}\right. = C_{10}H_6\left<\begin{array}{l}CH_2\\ |\\ CO\end{array}\right. + H_2O.$$

It crystallizes from alcohol in pale-yellow needles, melts at 119—119·5°, and forms a phenylhydrazone.[1]

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[1] Ewan and Cohen, *Journ. Chem. Soc.* **1889**, I. 578.

PYRENE GROUP.

2705 *Pyrene*, $C_{10}H_4(C_3H_3)_2$. In 1837, Laurent found that when the tar obtained in the destructive distillation of coal or fatty substances, is fractionated, a reddish-yellow product is obtained towards the end of the operation. This is more or less solid, and he was able to isolate from it two new hydrocarbons, one of which he termed *Chrysene*, from its yellow colour, whilst to the other he gave the name *Pyrene*, believing that it is frequently obtained by the action of fire on organic substances. He gave to pyrene the formula $C_{15}H_{12}$;[1] Graebe showed however later on that Laurent's compound is a mixture, the chief constituent of which is a hydrocarbon, $C_{16}H_{10}$, for which he retained the name pyrene.[2]

In order to prepare pyrene, the portions which pass over in the distillation of coal tar just previous to the coking of the residue are extracted with carbon disulphide, which dissolves out pyrene and fluoranthene, $C_{15}H_{10}$, whilst chrysene remains behind. After evaporating off the carbon bisulphide the residue is dissolved in alcohol and mixed with an alcoholic solution of picric acid; the picrates of pyrene and fluoranthene crystallize out, and are separated as far as possible by repeated fractional crystallization from alcohol, and reconverted into the hydrocarbons by ammonia. The latter are also recrystallized, again converted into the picrates, and the same treatment repeated, until at length both compounds are obtained pure.[3]

Pyrene also forms a constituent of a by-product obtained in smelting the ores of mercury at Idria, known as "Stuppfett." In the distillation of the ores, besides mercury a black plastic mass is obtained in the condensation chambers. This product, termed "Stupp," contains large quantities of mercury, which can

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[1] *Ann. Chim. Phys*, **66**, 136.

[2] *Annalen*, **158**, 285.

[3] Fittig, Gebhard and Hintz, *Ber.* **10**, 2141.

only be partially separated by mechanical means, 15—20 per cent. remaining behind. To obtain the last portions of the mercury the "stupp" is redistilled; in the condensation chambers are then found mercury and finely divided "stupp," together with a partially crystalline mass saturated with oil, to which the name "stuppfett" is given. It is a mixture of various substances, and its colour likewise varies from yellow to greyish-green and brown. Goldschmiedt and Schmidt found in 100 parts of "stuppfett," 3 parts of naphthalene, $C_{10}H_8$; 45 parts of phenanthrene, $C_{14}H_{10}$; 12 parts of fluoranthene, $C_{15}H_{10}$; and 20 parts of pyrene, $C_{16}H_{10}$. In addition to these, small quantities of the following compounds were obtained: chrysene, $C_{18}H_{12}$; anthracene, $C_{14}H_{10}$; methylnaphthalene, $C_{10}H_7.CH_3$; ethylnaphthalene, $C_{10}H_7.C_2H_5$; acenaphthene, $C_{10}H_6.C_2H_4$; diphenyl, $C_{12}H_{10}$; diphenylene oxide, $C_{12}H_8O$; and quinoline C_9H_7N.[1]

Its composition naturally varies considerably; thus Bamberger and Philip obtained from 10 kilos of "stuppfett" only 550 grams of pyrene. In order to separate the latter the "stuppfett" was warmed with 6 kilos of alcohol on the water-bath till it had melted to a dark oil, and the mixture after repeatedly shaking allowed to cool. After separating off the alcoholic solution, the residue is well pressed, and extracted with 30 kilos of boiling alcohol, and the impure pyrene which separates out again well pressed and purified by conversion into the picrate.[2]

"Stuppfett" is no longer obtained in Idria, the muffle-process in which it is obtained having been given up in 1882.[3]

Pyrene crystallizes from benzene in beautiful lustrous monosymmetric prisms or tablets, and melts at 148—149°. It boils considerably above 360°, is readily soluble in ether and carbon disulphide, but sparingly in absolute alcohol, 100 parts of the latter dissolving 1·37 parts of pyrene at 16°, and 3·08 parts at the boiling-point.[4] Its characteristic *picrate*, $C_{16}H_{10} + C_6H_3(NO_2)_3O$, crystallizes in long lustrous red needles, melting

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[1] *Monatsh.* **2**, 1; Goldschmiedt, *Ber.* **10**, 2022.

[2] *Annalen*, **240**, 147.

[3] This substance appears to have been known to Paracelsus, for he says, "Nimm das Ertz, darauss *Mercurius* wechsst, wie du es in der ersten Coagulation findest, das noch nit erhärtet, oder in ein *Corpus* gangen ist, auff 20. Pfundt, zerstoss, sieds in Regenwasser auff ein Stund, so zerfällt der Wust davon, als dann schleim es. Den kyss behalt, setz jn in ein Viol, distillier jhn mit grossem Fewr, so geht ein weisser blawer Safft vber sich, den behalt. Demnach so distillier die Feuchte von jm durch *Balneum Mariae*, so bleibt am Boden eine schwere öligkeit, nahendt so schwer als *Mercurius*."

[4] Bechi, *Ber.* **12**, 1976.

at 222°, which are sparingly soluble in alcohol, readily in ether and carbon disulphide, and still more easily in benzene.

Hexhydropyrene, $C_{16}H_{16}$, is formed by heating pyrene with an excess of phosphorus and hydriodic acid at 200°, and crystallizes in prisms or needles, melts at 127°, and is readily soluble in ether, benzene, and boiling alcohol. When its vapour is passed through a red-hot tube it is reconverted into pyrene (Graebe).

2706 *Chloropyrene*, $C_{16}H_9Cl$, is obtained, together with the following substitution products, when chlorine is passed into a chloroform solution of pyrene, and crystallizes in long slender lustrous, golden-yellow needles, which melt at 118—119°, and are readily soluble in most of the ordinary solvents. Its solution in sulphuric acid has a beautiful violet-blue fluorescence.[1] With picric acid it yields the compound $C_{16}H_9Cl + C_6H_3(NO_2)_3O$, crystallizing in beautiful red needles, and melting at 177—178°.

a-Dichloropyrene, $C_{16}H_8Cl_2$, crystallizes in flat lustrous sulphur-yellow needles, melts at 154—156°, and readily dissolves in ether, chloroform, and benzene, the solutions showing a greenish fluorescence. It is sparingly soluble in cold alcohol, but dissolves in the hot liquid with a blue fluorescence, and on strongly warming with concentrated sulphuric acid yields an intensely violet-blue fluorescent solution. It does not yield a picrate.

β-Dichloropyrene is sparingly soluble in alcohol, somewhat more readily in chloroform, and melts at 194—196°.

Trichloropyrene, $C_{16}H_7Cl_3$, forms thin plastic matted aggregates of needles, which have a slightly yellowish-tinge, and melt at 256—257°.

Tetrachloropyrene, $C_{16}H_6Cl_4$, crystallizes in long slender elastic needles, which have a pale-yellow colour and a beautiful silky lustre, and melt above 330°.

Dibromopyrene dibromide, $C_{16}H_8Br_4$, is obtained by the action of bromine vapour on pyrene, and crystallizes from boiling nitrobenzene in yellowish needles, which are almost insoluble in alcohol and benzene (Graebe).

Tribromopyrene, $C_{16}H_7Br_3$, was prepared by Graebe by allowing bromine to drop into a carbon disulphide solution of pyrene. It crystallizes from nitrobenzene in colourless needles, which are scarcely soluble in alcohol and carbon disulphide, and very sparingly in boiling benzene.

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[1] Goldschmiedt and Wegscheider, *Monatsh.* **4**, 237.

Nitropyrene, $C_{16}H_9NO_2$, is formed when pyrene is treated with a mixture of equal volumes of nitric acid (sp. gr. 1·2) and water, and when an aqueous solution of potassium nitrite is covered with an ethereal solution of pyrene, and very dilute sulphuric acid gradually added.[1] It is sparingly soluble in cold, readily in hot alcohol, from which it crystallizes in needles or prisms, melting at 149·5—150·5°.[2]

Dinitropyrene, $C_{16}H_8(NO_2)_2$, is prepared by boiling pyrene with nitric acid of sp. gr. 1·45, and crystallizes from acetic acid in slender yellow needles, which are sparingly soluble in alcohol (Graebe).

Tetranitropyrene, $C_{16}H_6(NO_2)_4$, was obtained by Graebe by the long continued boiling of pyrene with concentrated nitric acid. It is scarcely soluble in alcohol, sparingly in boiling acetic acid, from which it crystallizes in lustrous yellow plates or broad needles.

Amidopyrene, $C_{16}H_9NH_2$, is formed by reducing nitropyrene with tin and hydrochloric acid, and crystallizes from dilute alcohol in lustrous quadratic plates, which form bronze-coloured films with a metallic lustre on filter-paper. It melts at 116°, and its alcoholic or acid solution shows a beautiful blue fluorescence which is intensified by dilution. Thus if just sufficient of the solution to wet the sides be placed in a flask it appears as though the whole flask were of blue glass. The alcoholic solution of the *hydrochloride*, which crystallizes in beautiful needles, colours pine-wood deep-red (Goldschmiedt).

Diamidopyrene, $C_{16}H_8(NH_2)_2$, is prepared by the reduction of dinitropyrene with tin and hydrochloric acid. Its *hydrochloride* forms slender yellow needles, and readily undergoes decomposition; the free base is also very unstable, but its solution has even a more intense blue fluorescence than that of amidopyrene.[3]

Pyrenesulphonic acid, $C_{16}H_9.SO_3H$, is obtained by heating pyrenedisulphonic acid. After the melt has assumed a red colour, the heating is continued for a few minutes, and the mass then added to dilute sulphuric acid. *Potassium pyrenesulphonate*, $C_{16}H_9.SO_3H + H_2O$, separates out, and crystallizes from alcohol in microscopic needles.

Pyrenedisulphonic acid, $C_{16}H_8(SO_3H)_2$, is formed by warming pyrene with concentrated sulphuric acid. From the product the lead salt is prepared, and its solution decomposed with

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[1] Goldschmiedt, *Monatsh.* **2**, 580.

[2] Hintz, *Ber.* **10**, 2143.

[3] Jahoda, *Monatsh.* **8**, 449.

sulphuretted hydrogen. On evaporating the filtrate a green pasty mass is obtained, which dissolves in water with a green colour, the solution showing a green fluorescence. The *potassium* salt, $C_{16}H_8(SO_3K)_2$, is precipitated from its aqueous solution by alcohol as a pale yellow powder containing water, and consisting of microscopic prisms (Goldschmiedt and Wegscheider).

2707 *Pyrenequinone*, $C_{16}H_8O_2$, was obtained by Graebe by the action of chromium trioxide on a hot acetic acid solution of pyrene. It is best prepared in the following manner: 10 grams of finely-powdered pyrene are carefully warmed with 15 grams of potassium dichromate and 110 grams of sulphuric acid diluted with four times its volume of water, the heating being continued for an hour after the somewhat vigorous evolution of carbon dioxide has moderated. The red powder which separates out is well washed, and repeatedly digested with sodium carbonate solution at 50° to remove the anhydride of pyrenic acid, which is also formed in the reaction. The residue is then repeatedly crystallized from boiling acetic acid, with addition of animal charcoal, until it is found on microscopic examination to be free from pyrene.[1]

Pyrenequinone forms pale brick-red lustrous needles, which are scarcely soluble in alcohol, ether, chloroform, and benzene, but readily in hot acetic acid and nitrobenzene, and also in solutions of acid sodium sulphite. It melts at 282°, becoming black at the same time, and sublimes on careful heating in dark-brown needles with a green metallic lustre, or in purple-red matted needles. When a drop of aqueous caustic soda is added to its alcoholic solution, the latter assumes a beautiful bordeaux-red colour, which does not disappear on shaking in the air; it is therefore not an ortho-diketone, as the colouration given by members of the latter group is not permanent in the presence of air.[2] A further proof of this is that it yields no quinoxaline with *o*-diamidotoluene (Part III., p. 73). On heating with zinc dust in a current of hydrogen it is again reduced to pyrene.

Pyrenequinol, $C_{16}H_8(OH)_2$ is formed by warming the quinone with ammonia and zinc dust, a yellow solution being thus obtained, which quickly becomes red in the air. When the solution is filtered in absence of air and allowed to drop into dilute hydrochloric acid, pyrenequinol separates as a yellow crystalline precipitate, which dissolves in alcohol with a dark-blue fluorescence, and rapidly oxidizes in the air.

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[1] Goldschmiedt, *Monatsh.* **4**, 309; Bamberger and Philip, *Annalen*, **240**, 165.

[2] Bamberger, *Ber.* **18**, 865.

Diacetylpyrenequinol, $C_{16}H_8(O.C_2H_8O)_2$, is formed by boiling pyrenequinol with acetic anhydride and sodium acetate, and separates on evaporating its benzene solution as a glittering crystalline powder, melting at 166—167° (Goldschmiedt).

Pyrenic acid, $C_{13}H_6O(CO_2H)_2$, is formed by the further oxidation of pyrenequinone with potassium dichromate and sulphuric acid.

$$C_{16}H_8O_2 + 5O = C_{15}H_8O_5 + CO_2.$$

It is precipitated from its alkaline solutions by hydrochloric acid in beautiful pale-yellow plates, which blacken above 250°, part of the compound subliming as anhydride. It is sparingly soluble in alcohol, more readily in boiling acetic acid and acetone; it is also dissolved by sulphuric acid, forming an orange-red solution, and separates on addition of water in pale-yellow flakes. When dissolved in dilute caustic soda, and then mixed with a concentrated solution of the latter, *sodium pyrenate* is precipitated in beautiful golden-yellow plates.

Barium pyrenate, $C_{13}H_6O(CO_2)_2Ba + H_2O$, is a voluminous ochre-yellow precipitate, which becomes anhydrous at 130°.

Pyrenic anhydride, $C_{13}H_8O(CO)_2O$, is best prepared by boiling the acid with acetic acid, and crystallizes out on cooling in short, lustrous golden-yellow prisms. On oxidation with alkaline potassium permanganate it yields naphthalenetetracarboxylic acid, $C_{10}H_4(CO_2H)_4$ (p. 336).

Pyrenimide, $C_{13}H_6O(CO)_2NH$, is formed by dissolving the acid in ammonia, and quickly separates out in beautiful glistening yellow plates.

Phenylhydrazonepyrenic acid, $C_{12}H_6(C:N.NHC_6H_5)(CO_2H)_2 + 2H_2O$, separates out when solutions of sodium pyrenate and phenylhydrazine hydrochloride are mixed. It crystallizes in brass-yellow lustrous plates, which on drying assume a beautiful bronze lustre.

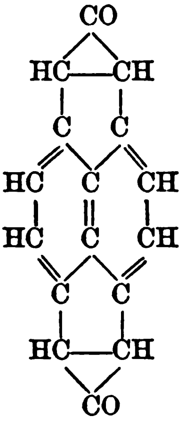
The formation of this compound shows that in addition to two carboxyl groups, pyrenic acid contains a carbonyl group, which is further confirmed by the fact that hydroxylamine hydrochloride also forms an *oxime* when mixed with a solution of sodium pyrenate. *Oximidopyrenic acid*, $C_{12}H_6(C:N.OH)(CO_2H)_2$, crystallizes in yellow, glistening plates.

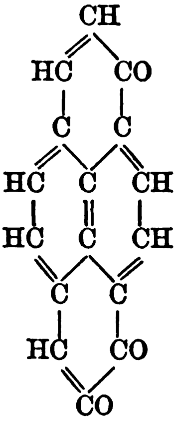
Pyreneketone, $C_{12}H_8(CO)$, is formed when barium pyrenate is heated with a little slaked lime:

$$C_{12}H_6(CO)(CO_2H)_2 = C_{12}H_8(CO) + 2CO_2.$$

It crystallizes from alcohol in large yellow lustrous needles, melts at 142°, is sparingly soluble in water, and only volatile with difficulty in steam. When it is dissolved in a freshly-prepared solution of acid sodium sulphite, thick, white lustrous prisms separate after a time, which are decomposed by acids with separation of the ketone. It does not reduce ammoniacal silver solution, or redden fuchsine-sulphurous acid, and is therefore not an aldehyde. It dissolves in fuming hydrochloric acid, forming a purple-red solution, from which the ketone is reprecipitated by the addition of water.

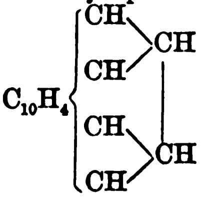
On oxidation with potassium permanganate it yields naphthalic acid or naphthaleneperidicarboxylic acid (p. 320); the formation of the latter compound, as well as that of naphthalenetetracarboxylic acid from pyrenic acid, proves that pyrene is a derivative of naphthalene. The latter acid is probably a di-peri-derivative, the carboxyl groups occupying the positions 1 : 4 : 4′ : 1′, whence it follows that pyrene and pyrenequinone must contains four carbon atoms in these positions. As pyrenequinone is not an *o*-diketone, its constitution must be represented by one of the following formulæ:



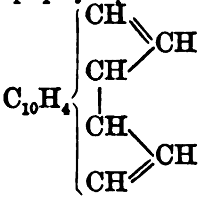


If this be correct, pyrene will then be represented by one of the following:

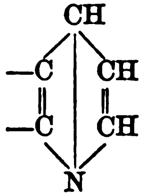
Ditrimethenylnaphthalene.



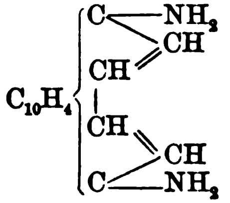
Dipropenylnaphthalene.

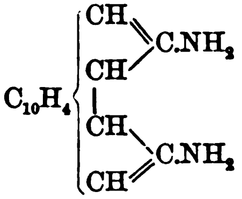


The facts above-mentioned do not suffice to decide between these formulæ, but Jahoda[1] has since found that when amidopyrene is heated with glycerol, sulphuric acid, and nitrobenzene, it is converted into *pyrenoline*, $C_{19}H_{11}N$, which contains the following group:



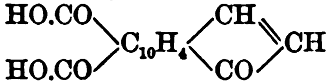
This can only be formed if amidopyrene contains the group $-HC{=}C.NH_2$, *i.e.* if pyrene contains the group $-HC{=}CH-$; hence the constitution of the latter is represented by the second of the formulæ given above, and that of amidopyrene by one of the following:



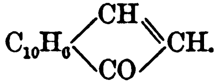


The other derivatives have therefore the following constitution:

Pyrenic Acid.



Pyreneketone.



Pyrenecarboxylic acid, $C_{16}H_9.CO_2H$, is formed when the nitrile is fused with caustic potash and a little water, and separates on addition of dilute sulphuric acid to the alkaline solution as an opalescent gelatinous precipitate. When its solution in a mixture of alcohol and ether is allowed to evaporate it separates in yellow nodules, which melt at 267°, and are readily soluble in absolute alcohol. On carefully warming it sublimes in long needles, but when quickly heated partially decomposes into carbon dioxide and pyrene, a reaction which becomes complete in presence of lime.

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[1] *Monatsh.* 9, 442.

Pyrenecarbonitrile or *Pyrene cyanide*, $C_{16}H_9.CN$, is prepared by heating potassium pyrenedisulphonate with anhydrous potassium ferrocyanide and iron filings. It crystallizes from alcohol, acetic acid, and benzene in white or more or less greenish-coloured needles, which melt at 149—150°. All its solutions show a green fluorescence.

Its *picrate*, $2C_{16}H_9.CN + C_6H_3(NO_2)_3O$, crystallizes in brick-red needles, melting at 133—134°, which are resolved into their constituents by hot water and cold alcohol.

In the preparation of this nitrile, that of pyrenedicarboxylic acid is also obtained in small quantity; it is a yellow granular powder, which, like the corresponding acid, melts above 300°.[1]

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[1] Goldschmiedt and Wegscheider, *Monatsh.* **4**, 252.

DIPHENYL GROUP.

2708 *Diphenyl*, $C_{12}H_{10}$, was first obtained by Fittig by acting with sodium on bromobenzene diluted with an equal volume of ether.[1] He then found that it is not necessary to prepare pure bromobenzene, and proceeded as follows: a mixture of equal molecular proportions of bromine and benzene was allowed to remain in diffused daylight, as long as hydrogen bromide was evolved, the latter being collected in water. After eight to fourteen days, the free bromine was removed by caustic soda, and the mixture of bromobenzene and benzene washed with water, dried by calcium chloride, fractionated, and then heated with sodium.[2]

Berthelot then found that it is also formed when benzene vapour is passed through a red-hot iron tube filled with broken glass.[3]

$$2C_6H_6 = C_6H_5.C_6H_5 + H_2.$$

Brönner observed its formation in small quantity when benzoic acid is distilled with lime, and pointed out that it was probably frequently formed as a decomposition product together with benzene.[4] Thus Laurent and Chancel, in passing ammonium benzoate over heated baryta, obtained besides benzonitrile a crystalline hydrocarbon, which was also formed, together with benzophenone, by the distillation of calcium benzoate.[5] This hydrocarbon was doubtless diphenyl, as was also the "metanaphthalene" obtained by Pelletier and Walter, together with benzene and other hydrocarbons, by the distillation of the resin from *Pinus maritima*[6] (Pt. IV., p. 3). Brönner therefore con-

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[1] *Annalen*, **121**, 361.

[2] *Annalen*, **132**, 201.

[3] *Annalen*, **142**, 252.

[4] *Annalen*, **151**, 50.

[5] *Annalen*, **72**, 279; **80**, 285; *Jahresb.* **1849**, 325.

[6] *Ann. Chim. Phys.* **67**, 269; *Pogg. Ann.* **44**, 81.

cluded that diphenyl must be present in coal tar, an assumption which was proved by Fittig and Buchner,[1] and by Schultz.[2]

Its formation, together with benzene, by heating phthalic anhydride with lime,[3] or phenol with potassium,[4] may be readily understood. It is also formed in quantity by passing a mixture of benzene and stannic chloride through a red-hot tube:[5]

$$2C_6H_6 + SnCl_4 = C_{12}H_{10} + 2HCl + SnCl_2.$$

It is best and most simply prepared by Berthelot's method,[6] in which small quantities of acetylene, diphenylbenzene, isodiphenylbenzene and other hydrocarbons, together with free hydrogen and carbon, are also obtained.[7] Lüddens recommends passing a mixture of benzene vapour and carbon dioxide through an iron tube filled with pumice-stone, and heated to a bright-red heat, the dilution with carbon dioxide lessening the formation of carbon and hydrogen. The product is returned to the distillation flask, two-thirds again distilled over, and this process repeated several times, the product being finally heated on the water-bath, and the diphenyl driven over with steam.[8]

According to Schmidt and Schultz, the following process is more suitable. An iron tube, heated in an inclined combustion furnace, has at the upper end a separating funnel, from which benzene may be slowly dropped at the rate of 20 drops per minute; the funnel also forms a safety tube. The lower end of the tube is connected with a flask, which is heated in the water-bath, where the diphenyl condenses, whilst the benzene vapour passes on to a condenser, the condensed liquid retaining any diphenyl which is carried along by the acetylene and hydrogen formed in the reaction.[9]

For the preparation of large quantities of diphenyl the apparatus of La Coste and Sorger (Fig. 1) is employed, which allows the benzene vapour to be continuously kept at a red heat for several weeks, and may be suitably employed for other similar purposes.[10]

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[1] *Ber.* **8**, 22.
[2] *Ber.* **17**, 1203.
[3] Anschütz and Schultz, *Annalen*, **196**, 48.
[4] Christomanos, *Ber.* **9**, 83.
[5] Aronheim, *Ber.* **9**, 1898; W. Smith, *Ber.* **17**, 722.
[6] Fittig and Doebner, *Annalen*, **172**, 109.
[7] Berthelot, *loc. cit.*; Schmidt and Schultz, *Annalen*, **203**, 118.
[8] *Ber.* **8**, 870.
[9] *Annalen*, **203**, 108.
[10] *Annalen*, **230**, 1.

A bolt-head of 6—8 litres capacity is half filled with benzene, and heated by means of a gas-stove covered with a double layer of wire gauze. The bolt-head is closed by a trebly-bored india-rubber stopper. Through one of the holes is passed a leaden tube cut off obliquely, the upper portion of which forms a T joint with a wider tube of the same metal. During the operation the lower end of the latter is closed by a glass stopper, surrounded by an india-rubber ring, whilst the upper end is soldered to an iron tube, which is heated to a bright-red heat in an inclined furnace. The upper portion of the iron tube is bent downwards, and soldered to a tube connected with a leaden cylinder 30 cm. in length and 6 cm. in diameter. To prevent the joint being melted, the portion of the iron tube between the furnace and the condenser is kept cool by allowing the water from the condenser to pour over it. The leaden cylinder has an outlet near the top leading to a reflux condenser, from the top of which a tube passes downwards to a flask half filled with water, serving as an outlet for the gases formed in the reaction. To the bottom of the cylinder a narrow leaden tube about 70 cm. in length is attached, and connected by a screw joint to a similar tube which conveys the condensed products back to the distillation flask. The benzene vapours thus pass continuously through the heated tube, whilst the diphenyl accumulates in the flask. The latter is also connected with an empty safety flask.

FIG. 1.

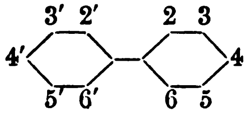
The apparatus requires very little watching; losses can scarcely take place, as if the tubes become blocked the distillate and contents of the distillation flask simply pass into the safety flask. The contents of the bolt-head are collected from time to time and distilled; after removal of the benzene, the diphenyl, of which the yield is very satisfactory, only contains slight quantities of higher boiling products, and is pure enough for ordinary purposes after a single distillation.

Diphenyl may also be obtained from aniline by diazotizing, and adding first alcohol and then gradually copper powder, stirring vigorously during the operation, allowing to stand for an hour, and distilling with steam. As soon as the distillate gives a solid precipitate with water it is collected until no more crystals of diphenyl pass over, the yield being about 22 per cent. In place of copper, zinc dust or iron powder may be employed.[1] Diphenyl is also one of the products of the action of stannous chloride on diazobenzene chloride.[2]

2709 Diphenyl is readly soluble in hot alcohol and ether, less so in the cold liquids, and crystallizes in large transparent, lustrous, brittle plates or monosymmetric tablets,[3] which have the sp. gr. 1·165. It has a pleasant though peculiar odour, melts at 70·5°, and boils at 254°, yielding a vapour of sp. gr. 5·36.[4]

It is not attacked by dilute nitric acid, or by dilute sulphuric acid and potassium dichromate (Fittig), but is converted by chromium trioxide in acetic acid solution into benzoic acid. Most of its substitution products yield substituted benzoic acids on similar treatment, and the reaction is employed for ascertaining their constitution.

To distinguish the numerous substitution products of diphenyl the carbon atoms are numbered in the following manner:



They are frequently termed also ortho- meta- and para-compounds, but this leads in many cases to a good deal of confusion, and the numbers will therefore be here employed throughout.

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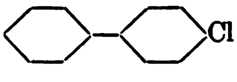
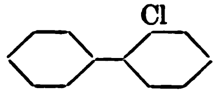
[1] Gattermann and Ehrhardt, *Ber.* **23**, 1226.
[2] Culmann and Gasiorowsky, *J. Pr. Chem.* II. **40**, 97.
[3] Bodewig, *Zeitsch. Krystallog.* **3**, 411.
[4] Schmidt and Schultz, *Annalen*, **203**, 123.

By the action of chlorine on diphenyl two monochlorodiphenyls are obtained, one of which yields on oxidation *p*-chlorobenzoic acid, and the other *o*-chlorobenzoic acid; they have therefore the following constitutional formulæ:

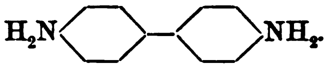
4-Chlorodiphenyl.



2-Chlorodiphenyl.

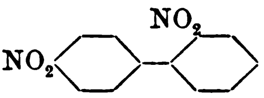


On further treatment with chlorine a dichlorodiphenyl is obtained which likewise yields *p*-chlorobenzoic acid on oxidation, and would therefore appear to be a 2:4-compound. This is however not the case, as it is also obtained by the diazo-reaction from 4:4′-diamidodiphenyl:



The constitution of the diamido derivative is shown by the fact that it is formed by the reduction of the 4:4′-dinitro-compound. The latter may be converted into nitramidodiphenyl, $C_{12}H_8(NO_2)NH_2$, and this into nitrobromodiphenyl, $C_{12}H_8(NO_2)Br$, which on oxidation yields a mixture of *p*-nitrobenzoic acid and *p*-bromobenzoic acid.

By the action of nitric acid, diphenyl yields first a mixture of two mononitro-compounds, one of which is converted on oxidation into *p*-nitrobenzoic acid, whilst the second is completely oxidized by chromic acid, a reaction characteristic of ortho-compounds. That the nitro-group does really occupy the position 2-, is shown by the fact that, if the nitro-group be replaced by bromine, a bromodiphenyl is formed which on oxidation yields *o*-bromobenzoic acid. Of the two mononitrodiphenyls, the first yields the 4:4′-compound on further nitration, whereas the second forms a dinitrodiphenyl, which on oxidation is converted into *p*-nitrobenzoic acid, and has therefore the constitution:



The constitution of the other diphenyl derivatives has been determined in a similar manner.

Dihydrodiphenyl, $C_{12}H_{12}$, is obtained by the action of alcoholic potash on tetrahydrodiphenyl dibromide, and forms an oily liquid which has a smell resembling diphenyl, and boils at 247—249°. Like all partially hydrogenized aromatic hydrocarbons it yields a dibromide which evolves hydrogen bromide on heating, and is converted into hydrogen bromide and diphenyl by alcoholic potash.[1]

Tetrahydrodiphenyl, $C_{12}H_{14}$, is prepared by the action of sodium on a boiling solution of diphenyl in amyl alcohol. It is a clear thick liquid, has a faint smell resembling diphenyl, and boils at 244·8° (716 mm.), diphenyl under the same pressure boiling at 232·9°.[2]

Tetrahydrodiphenyl dibromide, $C_{12}H_{14}Br_2$, is formed when a dilute chloroform solution of the calculated quantity of bromine is added to a similar solution of the foregoing compound cooled with ice and salt. It is a heavy yellow oily liquid, which evolves hydrogen bromide on gently warming.

Bromotetrahydrodiphenyl dibromide, $C_{12}H_{13}Br_3$, is formed when twice the above quantity of bromine is taken, and crystallizes from a mixture of boiling alcohol and benzene in refractive glassy, rhombic tablets, which are sparingly soluble in alcohol and ether, and melt at 134°. It is converted by alcoholic potash into *bromodihydrodiphenyl*, $C_{12}H_{11}Br$, a yellow oil which splits up completely on distillation into hydrogen bromide and diphenyl. It combines with bromine, forming *bromodihydrodiphenyl dibromide*, $C_{12}H_{11}Br_3$, which readily decomposes into hydrogen bromide and bromodiphenyl.

HALOGEN SUBSTITUTION PRODUCTS OF DIPHENYL.

2710 Chlorine alone acts on the fused hydrocarbon with great difficulty, but on addition of antimony pentachloride two monochlorodiphenyls and a dichlorodiphenyl are obtained.

2-*Chlorodiphenyl*, $C_{12}H_9Cl$, crystallizes in beautiful monosymmetric pyramids, melts at 34°, and boils at 267—268°. It dissolves in benzene like sugar in hot water, and is also readily

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[1] Bamberger and Lodter, *Ber.* **21**, 836.

[2] Bamberger and Lodter, *Ber.* **20**, 3073.

soluble in light petroleum. Chromium trioxide converts its acetic acid solution into *o*-chlorobenzoic acid.[1]

4-*Chlorodiphenyl*, $C_{12}H_9Cl$, was first obtained by Schultz by the action of phosphorus pentachloride on 4-hydroxydiphenyl,[2] and crystallizes from alcohol or light petroleum in plates which melt at 75°, and evolve an odour resembling oranges, especially on warming. It is somewhat less soluble in benzene than the ortho-compound, boils at 282°, and is oxidized by chromium trioxide to *p*-chlorobenzoic acid.

4 : 4′-*Dichlorodiphenyl*, $ClC_6H_4.C_6H_4Cl$, was prepared by Griess from tetrazodiphenyl platinochloride by the action of heat.[3] It is also formed, together with benzene, diphenyl, and *p*-chlorodiphenyl, when the vapour of chlorobenzene is passed through a red-hot tube,[4] by acting on diphenyl with chlorine in presence of iodine, and also by treating 4 : 4′-dihydroxydiphenyl with phosphorus pentachloride.[5] It crystallizes from hot alcohol in small needles or lustrous prisms, melts at 148°, boils at 315°, and is oxidized by chromic acid to *p*-chlorobenzoic acid.

Pentachlorodiphenyl, $C_{12}H_5Cl_5$, is prepared, together with the foregoing compound and other products, by the action of phosphorus pentachloride on dihydroxydiphenyl, and is a crystalline substance which melts at 179°, sublimes in long needles, and boils much higher than 360°.

Perchlorodiphenyl, $C_{12}Cl_{10}$, is formed by the exhaustive chlorination of diphenyl or ditolyl in presence of iodine[6] or antimony chloride,[7] or by heating diphenyl or phenanthrene quinone with an excess of antimony chloride to 360°.[8] It crystallizes in tablets or prisms, which do not melt at 270°, and are not converted into perchlorobenzene on further heating with antimony chloride, but remain unaltered.

2-*Bromodiphenyl*, $C_{12}H_9Br$, is obtained from *o*-amidodiphenyl by the diazo-reaction, and is an oily liquid, which has a smell resembling that of oranges, boils at 296—298°, and is oxidized by chromium trioxide in acetic acid solution to *p*-bromobenzoic acid.[9]

4-*Bromodiphenyl*, $C_{12}H_9Br$, is formed, together with the following compound, when bromine is added to a cooled solution of

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[1] Kramers, *Annalen*, **189**, 174.

[2] *Annalen*, **174**, 207.

[3] *Jahresb.* **1866**, 463.

[4] Kramers, *Annalen*, **189**, 135

[5] Schmidt and Schultz, *Annalen*, **207**.

[6] Ruoff, *Ber.* **9**, 1941.

[7] Merz and Weith, *Ber.* **12**, 677 ; Weber and Söllscher, *Ber.* **16**, 882.

[8] Merz and Weith, *Ber.* **16**, 2869.

[9] Schultz, Schmidt, and Strasser, *Annalen*, **207**, 353.

diphenyl in twice its weight of carbon disulphide, and the mixture allowed to stand till no more hydrogen bromide is evolved. It crystallizes from hot water in plates, melting at 89°, and has a pleasant odour, especially on warming, also resembling oranges. It boils at 310°, and yields *p*-bromobenzoic acid on oxidation.[1]

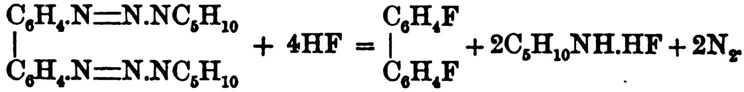
4 : 4′-*Dibromodiphenyl*, $C_6H_4Br.C_6H_4Br$, is a very characteristic compound, which was prepared by Fittig by triturating diphenyl with bromine under water,[2] whilst Griess prepared it from 4 : 4′-diamidodiphenyl by the diazo-reaction. It is insoluble in cold, sparingly soluble in hot alcohol, and crystallizes from benzene in thin monosymmetric prisms,[3] which melt at 164°, are very refractive and have a strong diamond lustre. According to Carnelley and Thomson, when it is crystallized from carbon disulphide, beautiful octohedra are obtained together with the prisms. These have the same melting-point, but are less readily soluble in a mixture of alchohol and ether.[4]

4 : 4′-Dibromophenyl boils at 355—360°, its vapour smelling like oranges; chromic acid converts it into *p*-bromobenzoic acid.[5]

Tribromodiphenyl, $C_6H_4Br.C_6H_3Br_2$, was obtained by Carnelley and Thomson from diphenyl by the action of an excess of bromine. It is very sparingly soluble in alcohol, crystallizes in silky needles, melts at 90°, and also yields *p*-bromobenzoic acid on oxidation.

4 : 4′-*Di-iododiphenyl*, $C_6H_4I.C_6H_4I$, was obtained by Schmidt and Schultz by means of the diazo-reaction from 4 : 4′-diamidodiphenyl. It forms yellow plates melting at 202°, sparingly soluble in cold, readily in hot acetic acid, and on oxidation yields *p*-iodobenzoic acid.

4 : 4′-*Difluodiphenyl*, $C_6H_4F.C_6H_4F$, is obtained in a similar manner to the fluo-derivatives of benzene (Part III., p. 100). Benzidine, or 4 : 4′-diamidodiphenyl, is converted into a tetrazo-compound, which on addition of piperidine yields *diphenyltetrazo-piperidide*, crystallizing in needles. When this is covered with concentrated hydrofluoric acid and gently warmed, the following reaction takes place:



$$\begin{array}{l} C_6H_4.N{=}N.NC_5H_{10} \\ | \\ C_6H_4.N{=}N.NC_5H_{10} \end{array} + 4HF = \begin{array}{l} C_6H_4F \\ | \\ C_6H_4F \end{array} + 2C_5H_{10}NH.HF + 2N_2$$

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[1] Schultz, *Annalen*, **174**, 207.

[2] *Annalen*, **132**, 201.

[3] Shadwell, *Annalen*, **203**, 123.

[4] *Journ. Chem. Soc.* **1885**, I. 586.

[5] Schultz, *Annalen*, **174**, 216.

Difluodiphenyl crystallizes well, is readily soluble in alcohol and ether, melts at 88—89°, and boils at 254—255°.[1]

NITRO-SUBSTITUTION PRODUCTS OF DIPHENYL.

2711 2-*Nitrodiphenyl*, $C_{12}H_9.NO_2$, is formed by dissolving 15 grams of diphenyl in 60 grams of hot acetic acid, and after cooling to 60° adding a mixture of 48 grams of fuming nitric acid mixed with an equal quantity of acetic acid, the temperature of the latter being 30°. A slight evolution of gas takes place, which is moderated by cooling. When the solution is cold, the 4-derivative, which is formed simultaneously, separates out and is removed, water being then added to the solution as long as a crystalline precipitate is formed. On further addition of water an oil separates, which is dissolved in boiling alcohol; on cooling 4-nitrodiphenyl again separates out, and the mother-liquor on evaporation over sulphuric acid deposits compact crystals of the 2-derivative, which are purified by recrystallization.[2] It forms thin plates, or thick rhombic tablets, melts at 37°, boils at about 320° (Schultz, Schmidt, and Strasser), and is only attacked with great difficulty by oxidizing agents, but is then completely oxidized.

4-*Nitrodiphenyl*, $C_{12}H_9.NO_2$, is obtained by boiling 5 parts of diphenyl with 4 parts of concentrated nitric acid and 10 parts of acetic acid, or by pouring 3 parts of concentrated nitric acid on to 2 parts of the finely-divided hydrocarbon, and after some days washing the product with water, distilling with steam to remove unaltered diphenyl, and recrystallizing the residue from alcohol.[3] It may further be prepared by dissolving diphenyl in 8 parts of acetic acid, gradually adding about the same quantity of concentrated nitric acid diluted with 11 parts of acetic acid, and precipitating the pale-yellow solution with water.[4] It crystallizes from hot alcohol in long, colourless needles, melts at 113°, boils at 340°, and is converted by chromium trioxide into *p*-nitrobenzoic acid.

2 : 2′-*Dinitrodiphenyl* is prepared from the corresponding 2 : 2′-dinitrobenzidine (p. 406) by eliminating the amido-groups. It crystallizes from alcohol in straw-yellow needles, which melt

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[1] Wallach, *Annalen*, **235**, 255; Wallach and Heusler, *Annalen*, **243**, 219.

[2] Osten and Lüddens, *Annalen*, **209**, 339.

[3] Schultz, *Annalen*, **174**, 210.

[4] Schultz and Osten, *Annalen*, **209** 340.

at 124°, and when further heated become black and explode. It is almost insoluble in water, sparingly soluble in light petroleum, readily in hot alcohol, benzene, and acetic acid.[1]

4 : 4'-*Dinitrodiphenyl*, $NO_2.C_6H_4.C_6H_4.NO_2$, is formed, together with the following compound by the action of concentrated nitric acid on diphenyl.[2] In order to prepare it, 6 parts of concentrated nitric acid and 1 part of sulphuric acid are poured on to 3 parts of diphenyl, and the mixture boiled for a short time as soon as the first violent reaction is over. The product is boiled with water, washed and purified by extraction with alcohol.[3] 4 : 4'-Dinitrodiphenyl crystallizes in long slender white needles, which melt at 233°, and are very sparingly soluble in cold, somewhat more readily in hot alcohol. It is not attacked by chromium trioxide in acetic acid solution, and may be purified in this manner if it still possesses a yellowish colour.

2 : 4'-*Dinitrodiphenyl* is contained in the mother-liquors of the foregoing compound, and is also formed by the nitration of 2-nitrodiphenyl. It crystallizes from hot alcohol in long monosymmetric spear-shaped crystals, which are readily soluble, and melt at 93·5°. On addition of chromic acid to its acetic acid solution no action takes place, but on warming it is slowly and completely oxidized.

3 : 3'-*Dinitrodiphenyl* is prepared from 3 : 3'-dinitrobenzidine, $C_{12}H_6(NO_2)_2(NH_2)_2$, by triturating it with sulphuric acid, and adding sufficient water to the solution to form a paste, then carefully adding sodium nitrite, cooling well with ice, and boiling the clear solution with absolute alcohol. It crystallizes from acetic acid or alcohol in reddish-yellow needles, which melt at 197—198°.[4]

Dichlorodinitrodiphenyl, $C_{12}H_6Cl_2(NO_2)_2$, is prepared by dissolving dichlorodiphenyl in concentrated nitric acid; it crystallizes from hot alcohol in small needles, and from benzene in long asymmetric transparent prisms, which melt at 140° (Schmidt and Schultz).

4-*Bromo*-4'-*nitrodiphenyl*, $C_6H_4Br.C_6H_4NO_2$, was obtained by Schultz by warming 4-bromodiphenyl with nitric acid, and by converting amidonitrodiphenyl into the diazoperbromide, and boiling the latter with alcohol. It is scarcely soluble in cold, and only with difficulty in boiling alcohol, and crystallizes from boiling toluene in long white needles consisting of chains of

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[1] Täuber, *Ber.* **24**, 197.

[2] Fittig, *Annalen*, **124**, 275.

[3] Schultz, *Annalen*, **174**, 221.

[4] Brunner and Witt, *Ber.* **20**, 1023.

small rhombohedra, which melt at 173°, and boil above 360° almost without decomposition. On warming it with chromium trioxide in acetic acid solution, it yields a mixture of *p*-bromobenzoic acid and *p*-nitrobenzoic acid.[1]

4-Bromo-2′-nitrodiphenyl is formed together with the foregoing compound by nitrating 4-bromodiphenyl, and has also been obtained from the corresponding amidodinitrodiphenyl by the diazo-reaction. It separates from alcohol in beautiful, lustrous, monosymmetric prisms, melts at 65°, boils at about 360°, and is oxidized by chromium trioxide to *p*-bromobenzoic acid.[2]

Dibromonitrodiphenyl, $C_6H_4Br.C_6H_3Br.NO_2$, is formed by the addition of the most concentrated nitric acid to a cold acetic acid solution of dibromodiphenyl, and separates from hot alcohol in crystals melting at 127°.[3]

Dibromodinitrodiphenyl, $C_{12}H_6Br_2(NO_2)_2$, is prepared by warming dibromodiphenyl with fuming nitric acid. It is very sparingly soluble in alcohol, and crystallizes from benzene in long hair-like needles, which melt at 148°, and are not attacked by chromium trioxide.[4]

Dibromotrinitrodiphenyl, $C_{12}H_5Br_2(NO_2)_3$, was obtained by Lellmann by dissolving dibromodiphenyl in a large excess of nitric acid of sp. gr. 1·55; it is sparingly soluble in alcohol, from which it crystallizes in small needles, melting at 177°.

DIPHENYL-SULPHONIC ACIDS.

2712 *Diphenyl-4-sulphonic acid*, $C_{12}H_9.SO_3H$, is formed together with the disulphonic acid by warming diphenyl with sulphuric acid. If the product after dilution with water be boiled with cupric oxide and then cooled, *cupric diphenylsulphonate* $(C_{12}H_9.SO_3)_2Cu$ separates in pale-green plates, which are sparingly soluble in water and alcohol, but much more readily in 40 per cent. alcohol.

Potassium diphenylsulphonate, $C_{12}H_9SO_3K + 2H_2O$, forms hair-like needles, which dissolve readily in water and 40 per cent. alcohol. On heating it diphenyl sublimes, and almost pure potassium diphenyldisulphonate remains behind:[5]

$$2C_{12}H_9SO_3K = C_{12}H_{10} + C_{12}H_8(SO_3K)_2.$$

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[1] *Annalen*, **174**, 218. *Annalen*, **207**, 351.

[3] Lellmann, *Ber.* **15**, 2837.

[4] Fittig, *Annalen*, **132**, 201; Schultz, *Annalen*, **174**, 218.

[5] Latschinow and Engelhardt, *Ber.* **4**, 163; **6**, 191; *Beilstein's Handb.* **2**, 163.

Ethyl diphenylsulphonate, $C_{12}H_9SO_3C_2H_5$, is obtained by acting with ethyl iodide on the *silver* salt, and crystallizes in long needles, melting at 73—74°.[1] The silver salt itself forms rhombic tablets.

Diphenylsulphochloride, $C_{12}H_9.SO_2Cl$, is prepared by the action of phosphorus pentachloride on the potassium salt, and crystallizes from acetic acid in prisms, melting at 115°. If its moist ethereal solution be treated with sodium amalgam, it yields *diphenylsulphinic acid,* $C_{12}H_9.SO_2H$, which separates on addition of hydrochloric acid as a fine granular crystalline precipitate. At the same time the reduction proceeds further, diphenyl being formed in considerable quantity (Gabriel and Deutsch):

$$C_{12}H_9SO_2Cl + H_2 = C_{12}H_{10} + SO_2 + HCl.$$

Diphenylsulphamide, $C_{12}H_9.SO_2.NH_2$, is formed by heating the chloride with alcoholic ammonia at 100°, and crystallizes from alcohol in spherical aggregates of slender needles, melting at 227—230°.

4-Nitrodiphenyl-4′-sulphonic acid, $NO_2.C_6H_4.C_6H_4.SO_3H$, is obtained by warming 4-nitrodiphenyl with concentrated sulphuric acid. Its *sodium* salt crystallizes in anhydrous, sparingly soluble nacreous plates, and is converted by phosphorus pentachloride into *nitrodiphenyl sulphochloride,* $C_{12}H_8(NO_2)SO_2Cl$, which is also formed when diphenyl-4-sulphochloride is dissolved in fuming nitric acid, showing that it is a 4 : 4′-compound. It crystallizes from acetic acid in needles, melting at 178°.[2]

Diphenyl-4-4′-disulphonic acid, $C_6H_4(SO_3H)C_6H_4.SO_3H$, was prepared by Fittig by dissolving diphenyl in warm sulphuric acid. Its solution solidifies over sulphuric acid in long prisms, which melt at 72·5°, and deliquesce in the air, forming an oil having the strongest resemblance to concentrated sulphuric acid. Its salts also so closely resemble the sulphates that an admixture of the latter is very difficult to detect.

Potassium diphenyldisulphonate, $2C_{10}H_8(SO_3K)_2 + 5H_2O$, crystallizes in long transparent prisms, which are less soluble in water than potassium sulphate. An acid salt could not be obtained; on adding to a solution of the acid one-half the quantity of potassium carbonate necessary for complete saturation, and evaporating, large rhombohedra of the composition $C_{10}H_8(SO_3K)_2 + 2H_2O$ separate out.

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[1] Gabriel and Deutsch, *Ber.* **13**, 386.

[2] Gabriel and Dambergis, *Ber.* **13**, 1408.

The cold solution is not precipitated by calcium chloride; on warming, however, the *calcium* salt separates as a crystalline precipitate which is scarcely soluble in boiling water. This reaction is very characteristic, and may be used for the detection of the acid.

Barium chloride, when added to a boiling solution of the potassium salt, gives a crystalline precipitate, which is almost as insoluble in water and acids as barium sulphate.

The *lead* salt is a heavy crystalline precipitate soluble in acids, whilst the *silver* salt, obtained by adding silver nitrate to a hot saturated solution of the potassium salt crystallizes in small plates.[1]

Diphenyldisulphochloride, $C_{12}H_8(SO_2Cl)_2$, crystallizes from acetic acid in prisms which have a glassy lustre, and become brown and melt at 203°.

Diphenyldisulphamide, $C_{12}H_8(SO_2NH_2)_2$, separates from boiling water in slender white needles, which melt above 300°, and are sparingly soluble in alcohol and benzene, more readily in ether (Gabriel and Deutsch).

4-Nitrodiphenyl-4′-sulphonic acid, $C_6H_4(NO_2)C_6H_4.SO_3H$, is formed by warming 4-nitrodiphenyl with sulphuric acid, and separates on addition of water as a white precipitate which dissolves on further dilution.[2]

The *sodium* salt, $C_{12}H_8(NO_2)(SO_3Na)$, forms small plates sparingly soluble in water, and the *barium* salt $[C_{12}H_8(NO_2)SO_3]_2Ba$, crystallizes in slender, lustrous needles, readily soluble in water and alcohol, whilst the *cupric* salt $[C_{12}H_8(NO_2)SO_3]_2Cu + 4H_2O$, is sparingly soluble and forms small blue rhombohedral crystals.

Nitrodiphenylsulphochloride, $C_{12}H_8(NO_2)SO_2Cl$, is obtained by acting on the sodium salt with phosphorus pentachloride, or more readily by dissolving diphenylsulphochloride in fuming nitric acid. It crystallizes from acetic acid in needles melting at 178°.

Nitrodiphenylsulphamide, $C_{12}H_8(NO_2)SO_2.NH_2$, forms crystals melting at 228°.

Nitrodiphenyldisulphochloride, $C_{12}H_7(NO_2)(SO_2Cl)_2$, separates from hot acetic acid in thick yellowish lustrous crystals, melting at 130—131°.

Dinitrodiphenyldisulphochloride, $C_{12}H_6(NO_2)_2(SO_2Cl)_2$, melts at 166° (Gabriel and Dambergis).

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[1] *Annalen*, **132**, 209.

[2] Gabriel and Dambergis, *Ber.* **13**, 1408; Lüddens, *Annalen*, **209**, 349.

HYDROXY-DERIVATIVES OF DIPHENYL.

HYDROXYDIPHENYLS, $C_{12}H_9.OH$.

2713 4-*Hydroxydiphenyl*, or *Diphenylol*, is prepared by melting diphenyl-4-sulphonic acid with potash,[1] or by acting with potassium nitrite on a solution of 4-amidodiphenyl sulphate.[2] It crystallizes in silky plates, is sparingly soluble in cold, more readily in hot water, melts at 164—165°, and is volatile with steam. It boils at 305—308°, and is readily taken up by hot ammonia or sodium carbonate solution, but may be extracted from the solutions by ether.

Acetyl-4-hydroxydiphenyl, $C_{12}H_9.O.CO.CH_3$, forms plates which are readily soluble in alcohol and ether, and melt at 88—89°.

Benzoyl-4-hydroxydiphenyl, $C_{12}H_9.O.CO.C_6H_5$, crystallizes in tablets, melting at 152°.

Nitro-4-hydroxydiphenyl, $C_{12}H_8(NO_2)OH$, is formed in the preparation of diphenylol from amidodiphenyl, and also, together with the following compound, by the action of nitric acid of sp. gr. 1·2 on diphenylol, and volatilizes on distillation with steam. It crystallizes from ether in large citron-yellow prisms, melting at 67°, and forms red salts with alkalis, which on warming or dissolving in water readily lose part of the acid.

Dinitro-4-hydroxydiphenyl, $C_{12}H_7(NO_2)_2OH$, crystallizes from alcohol in lustrous golden plates, which melt at 154°. Its sparingly soluble *potassium* salt, $C_{12}H_7(NO_2)_2OK + 2H_2O$, crystallizes in ring- or ringlet-shaped aggregates of plates.

4-*Nitro-4'-hydroxydiphenyl*, $C_6H_4(NO_2).C_6H_4.OH$, is obtained by the action of nitrous acid on 4-nitro-4'-amidodiphenyl, and crystallizes in needles, melting at 170°.[3]

2-*Nitro-4'-hydroxydiphenyl*, prepared in a similar manner forms small yellow needles, which melt at 138°.[4]

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[1] Latschinow, *Beilstein's Handb.* **2**, 572.

[2] Hübner, *Annalen*, **209**, 348; Kaiser, *Annalen*, **257**, 101.

[3] Schmidt and Schultz, *Annalen*, **207**, 347.

[4] Schmidt and Schultz, *Annalen*, **207**, 351.

DIHYDROXYDIPHENYLS, $C_{12}H_8(OH)_2$.

2714 At the present time five of these are known; they are also termed *diphenols*, and are all converted on heating with zinc dust into diphenyl.

a-Diphenol is formed, together with the β-compound, salicylic acid, hydroxybenzoic acid, and a resin which yields diphenylbenzene on heating with zinc dust, when phenol is heated with an excess of caustic potash till the melt has attained a syrupy consistency. It is then dissolved in water, acidified with sulphuric acid, and extracted with ether. The solution thus obtained is treated with aqueous ammonium carbonate, the ether distilled off, and the residue fractionated under 150 mm. pressure. The greater portion passes over at 310—330°, and solidifies to a hard crystalline cake, which is dissolved in a large quantity of hot water, and mixed with a little lead acetate. The brown flakes which separate are filtered off, the filtrate precipitated with lead acetate, and the precipitate after washing triturated with hot water and decomposed by sulphuretted hydrogen. The mixture of a- and β-diphenol is extracted with ether, and the two compounds separated by fractional crystallization from hot water, in which the β-compound is much less soluble.

a-Diphenol forms long slender flat needles, melts at 123°, and is readily soluble in alcohol, ether, and benzene. Its aqueous solution gives with ferric chloride a pure corn-flower blue colouration, which remains for weeks, but is destroyed by the addition of soda. It is volatile without decomposition, the sp. gr. of the vapour being 6·4. On heating with methyl iodide, caustic potash, and a little methyl alcohol, it yields the *dimethyl ether*, or *dianisoïl*, $C_{12}H_8(OCH_3)_2$, which is a liquid, and boils at 310—320°.

On heating phenol with sulphuric acid, *a-diphenoldisulphonic acid*, $C_{12}H_6(OH)_2(SO_3H)_2$, is formed as a readily soluble crystalline substance; its *sodium* salt, $C_{12}H_6(OH)_2(SO_3Na)_2 + 2H_2O$, forms stellate groups of needles.

β-Diphenol is formed only in small quantity in the above reaction, and crystallizes in small glistening plates, which melt at 190°, and are readily soluble in alcohol, &c. Its aqueous solution is coloured pale-green by ferric chloride, the solution soon depositing green flakes, and becoming colourless. Its vapour has the sp. gr. 6·39, and its *dimethyl* ether crystallizes in microscopic octahedra.[1]

γ-Diphenol, or 4:4′-*Dihydroxydiphenyl*, was first prepared by Griess by the action of nitrous acid on benzidine,[2] and is also formed by melting diphenyldisulphonic acid with potash,[3] or diphenylsuccinic acid with lime.[4]

In order to prepare it, 50 grams of benzidine are dissolved in 60 c.c. of hydrochloric acid, and 1 litre of water; the mixture is then diluted to 5 litres, and 200 grams of sulphuric acid added. On addition of a solution of 37 grams of sodium nitrite in five times the quantity of water, the benzidine sulphate dissolves, and the solution is then heated by a current of steam. After twenty minutes the hot liquid is filtered, and on cooling pure γ-diphenol separates out.[5]

It is sparingly soluble in water and benzene, readily in alcohol or ether, and crystallizes from alcohol in lustrous plates or fascicular aggregates of needles, which dissolve easily in alkalis and in ammonia. It melts at 270°, and boils far above 360°, its vapour having the sp. gr. 6·5.

On solution in pure sulphuric acid and addition of a trace of nitrogen peroxide, a beautiful blue coloration is obtained, which is also given by common sulphuric acid. Its aqueous solution is not coloured by ferric chloride.

γ-Diphenol ethyl ether, $C_{12}H_8(OC_2H_5)_2$, is formed by boiling γ-diphenol with alcohol, potash, and ethyl iodide. It crystallizes from acetic acid in needles which are sparingly soluble in cold, more readily in hot alcohol, and melt at 174—176° (Hirsch).

γ-Diphenylene acetate, $C_{12}H_8(O.CO.CH_3)_2$, is obtained from γ-diphenol and acetic anhydride, and forms needles melting at 159—160°.

2715 *Tetrachloro-γ-diphenol*, $C_6H_2Cl_2OH.C_6H_2Cl_2.OH$, is prepared by acting with chlorine on γ-diphenol suspended in acetic acid, and crystallizes from dilute alcohol in transparent needles, melting at 233°. When fuming nitric acid is added to its acetic acid solution, *tetrachlorodiphenolquinone*, $C_{12}H_4Cl_4O_2$, separates out in scales which have a beautiful violet colour by reflected light, but appear dark-red by transmitted light. It

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[1] Barth, *Annalen*, **156**, 93; Barth and Schreder, *Ber.* **11**, 1332.

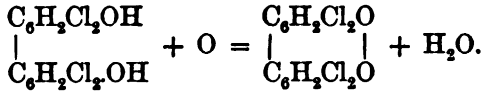
[2] *Jahresb.* **1866**, 461; Schmidt and Schultz, *Annalen*, **207**, 334.

[3] Engelhardt and Latschinow, *Zeitsch. Chem.* **1871**, 259; Schmidt and Schultz, *loc. cit.* p. 336.

[4] Schmidt and Schultz, *loc. cit.* p. 344.

[5] Hirsch, *Ber.* **22**, 335.

does not melt, is insoluble in the usual solvents, but dissolves in concentrated sulphuric acid with a dirty blood-red colour, which disappears on warming. Its formation is represented by the following equation:



$$\begin{array}{l} C_6H_2Cl_2OH \\ | \\ C_6H_2Cl_2.OH \end{array} + O = \begin{array}{l} C_6H_2Cl_2O \\ | \qquad\quad | \\ C_6H_2Cl_2O \end{array} + H_2O.$$

Tetrabromo-γ-diphenol, $C_6H_2Br_2(OH).C_6H_2Br_2OH$, is obtained by adding bromine to a warm solution of the phenol, and separates from absolute alcohol in crystals melting at 264°. On addition of fuming nitric acid to its acetic acid solution, it assumes a deep-red colour, and on cooling, scales of *tetrabromodiphenolquinone*, $C_{12}H_4Br_4O_2$, are obtained. These have a steel-blue colour by reflected light, and a dark brownish-red colour by transmitted light, and dissolve in sulphuric acid with a beautiful violet colouration. On heating with sulphurous acid it is reduced to tetrabromodiphenol.[1]

3 : 3′-*Dinitro-γ-diphenol*, $C_6H_3(NO_2)(OH).C_6H_3(NO_2)OH$, is formed when a solution of γ-diphenol in acetic acid is treated with the requisite quantity of nitric acid of sp. gr. 1·45, and crystallizes in reddish-yellow needles, which have a golden lustre, and melt at 280°; its *diacetate* forms straw-yellow needles melting at 215°.[2]

3 : 3′-*Dinitro-γ-diphenol ethyl ether*, $C_{12}H_6(NO_2)_2(OC_2H_5)_2$, was obtained by Hirsch by nitrating γ-diphenol ethyl ether in acetic acid; it separates from this solvent in needles which melt at 192—193°, and are converted into 3 : 3′-dinitro-γ-diphenol by caustic potash.

Tetranitro-γ-diphenol, $C_6H_2(NO_2)_2(OH).C_6H_2(NO_2)_2OH$, was first prepared by Griess. It is formed not only by the nitration of γ-diphenol, but also by the action of nitric acid on benzidine,[3] whilst Caro also obtained it by converting the latter into a tetrazodiphenyl salt, and treating this with nitric acid. It is most conveniently prepared by adding an excess of concentrated nitric acid to a warm acetic acid solution of γ-diphenol (Kunze). It crystallizes from alcohol in yellow needles, melts at 225° (Schütz), and is a true colouring matter which dyes wool and silk a beautiful orange-yellow.

Its sparingly soluble *ammonium* salt, $C_{12}H_4(NO_2)_4(ONH_4)_2$,

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[1] Magatti, *Ber.* **13**, 224.

[2] Kunze, *Ber.* **21**, 3331; Schütz, *Ber.* **21**, 3530.

[3] Schmidt and Schultz, *Annalen*, **207**, 335.

was formerly brought into commerce as "*Palatine orange.*" The *sodium* salt crystallizes in small red lustrous needles, which are very sparingly soluble in caustic soda; if it be dissolved in hot water, the acid salt, $C_{12}H_4(NO_2)_4(ONa)(OH)$, separates on cooling in brownish-red needles. The *diacetate* forms yellow needles, melting at 236° (Schütz).

The constitution of the nitrodiphenols is discussed together with that of the amidodiphenols.

γ-Diphenoldisulphonic acid, $C_{12}H_6(OH)_2(SO_3H)_2$, is prepared by the action of fuming sulphuric acid on γ-diphenol, and forms a *potasssium* salt which crystallizes in anhydrous prisms, and is sparingly soluble in cold water.[1]

γ-Diphenoltetrasulphonic acid, $C_{12}H_4(OH)_2(SO_3H)_4$, was prepared by Griess by warming tetrazodiphenyl sulphate with sulphuric acid. The product, after dilution with water, is neutralized with barium carbonate, and the solution evaporated. From the residue hot-water extracts the trisulphonic acid simultaneously formed, whilst the tetrasulphonic acid remains behind. To purify it, the crude acid is boiled with a solution of ammonium carbonate, the solution concentrated, and the ammonium salt which separates recrystallized from hot water.

Barium diphenoltetrasulphonate, $C_{12}H_4(OH)_2(SO_3)_4Ba_2 + 6H_2O$ separates on addition of the barium chloride to a boiling solution of the ammonium salt in white needles or prisms.

The free acid, prepared from the latter salt, remains on evaporating the solution as a syrup, which on standing over sulphuric acid crystallizes in white non-deliquescent needles or small tablets; the trisulphonic acid is very similar.[2]

δ-Diphenol, or 2:4′-*Dihydroxydiphenyl*, was first obtained by melting phenol-*p*-sulphonic acid with potash,[3] and is also formed together with catechol from phenol-*o*-sulphonic acid.[4] It is also obtained in large quantity by saturating a well-cooled solution of diphenyline sulphate, $C_{10}H_8(NH_2)_2H_2SO_4$ (p. 411), with nitrogen trioxide, and boiling with water the oily tetrazodiphenyl sulphate which separates on addition of alcohol and ether.[5] It crystallizes in slender needles or small monosymmetric prisms, which are sparingly soluble in water, but readily in alcohol and ether. It melts at 161°, and boils at 342°, its vapour having the sp. gr. 6·25. It forms a colourless solution

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[1] Doebner, *Ber.* **9**, 129.

[2] *Journ. Chem. Soc.* **1867**, 98.

[3] Lincke, *J. Pr. Chem.* II. **8**, 43.

[4] Herzig, *Ber.* **13**, 2233.

[5] Schultz, Schmidt, and Strasser, *Annalen*, **207**, 357.

in pure sulphuric acid, but gives a bluish-green colour with the commercial acid.

δ-Diphenylene diacetate crystallizes from alcohol in lustrous plates, melting at 94°.

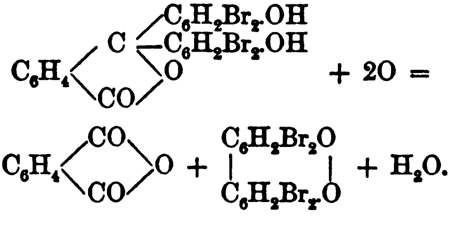
ε-Diphenol, or 2 : 2′-*Dihydroxydiphenyl* is obtained, together with other products, by adding fluorene, $(C_6H_4)_2CH_2$, to fused potash, and forms yellowish needles, which are soluble in boiling water, and melt at 98°.[1]

The following substitution-products of diphenols have been prepared, but their exact constitution is as yet unknown:

Perchlorodiphenol, $C_{12}Cl_8(OH)_2$, is formed by heating perchlorodiphenyl with alcoholic soda at 140—160°, and crystallizes from benzene in thick, almost quadratic tablets, which melt at 233·5—234·5°, and are readily soluble in alkalis and ammonia. On heating with methyl iodide, potash, and methyl alcohol, it yields the *dimethyl ether*, $C_{12}Cl_8(OCH_3)_2$, which crystallizes from alcohol in long needles, melting at 226°. On treatment with acetic anhydride and sodium acetate, it yields the *diacetate*, $C_{12}Cl_8(O.CO.CH_3)_2$, which forms spear-shaped crystals, melting at 194°.[2]

Dinitrodiphenol, $C_6H_3(NO_2)(OH).C_6H_3(NO_2)(OH)$, was prepared by Goldstein by the action of potassium permanganate on *o*-nitrophenyl. It crystallizes from benzene in microscopic prisms, sublimes at 150° without melting, in golden-yellow needles, and dissolves in alkalis with a blood-red colouration. On heating with benzoyl chloride it is converted into the *dibenzoate*, $C_{12}H_6(NO_2)_2(O.CO.C_6H_5)_2$, crystallizing in colourless needles, which melt at 191°.[3]

2716 *Bromorosoquinone*, $C_{12}H_4Br_4O_2$, was obtained by Schraube, together with phthalic acid, by dissolving 5 grams of tetrabromophenolnaphthaleïn in 250 grams of sulphuric acid, adding a mixture of 5 grams of potassium nitrate and 50 grams of sulphuric acid, and cooling well during the process:



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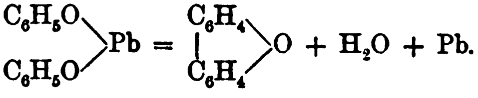
[1] Hodgkinson and Matthews, *Journ. Chem. Soc.* **1883**, I. 168.

[2] Weber and Söllcher, *Ber.* **16**, 882.

[3] *Ber.* **7**, 734 ; **11**, 1848.

The whole is well shaken, and after a few minutes poured into water, which causes the separation of a granular precipitate; the latter, after washing and drying, is boiled with a mixture of alcohol and chloroform, and is thus obtained in beautiful red crystals, with a steel-blue lustre, which dissolve in sulphuric acid with an intense violet colouration, but are insoluble in alkalis and the ordinary solvents. Reducing agents, such as sulphurous acid, or alcoholic potash, convert it into *bromoroso-quinol*, $C_{12}H_4Br_4(OH)_2$. The latter crystallizes from alcohol in slightly yellowish plates, which are soluble in alkalis, melt at 264°, and sublime with slight decomposition in microscopic needles. If it be dissolved in 60—70 parts of acetic acid, and the necessary quantity of fuming nitric acid added to the boiling solution, with frequent shaking, the quinone again separates in splendid crystals.[1]

Diphenylene oxide, $C_{12}H_8O$, was first prepared by distilling phenyl phosphate with lime,[2] and is also formed by distilling phenol with lead oxide,[3] the lead phenate first formed undergoing the following decomposition:



$$\begin{matrix} C_6H_5O \\ C_6H_5O \end{matrix}\!\!>\!Pb = \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!O + H_2O + Pb.$$

It also occurs in the products of distillation of calcium phenate,[4] and of mucic acid,[5] and also in "Stuppfett" (p. 357).

In order to prepare it phenol is mixed with 1—1½ times its weight of lead oxide, and heated carefully in a retort filled at most to one-half its capacity, in order to avoid overflowing. Phenol first passes over, then a mixture of the latter with phenylene oxide, which may be separated by the action of caustic soda, as the oxide is insoluble in that liquid. It is purified by distillation and recrystallization from alcohol.

It is fairly soluble in alcohol, from which it crystallizes in small plates, readily soluble in ether, acetic acid, and benzene. It melts at 80—81°, boils at 287—288° (mercury completely in vapour), and has a vapour density of 5·97. It is not attacked

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[1] *Annalen*, **202**, 121.

[2] Lesimple, *Annalen*, **138**, 376; Hoffmeister, *Annalen*, **159**, 191; see also Kreysler, *Ber.* **18**, 1720.

[3] Graebe, *Ber.* **7**, 396; *Annalen*, **174**, 190; Behr and v. Dorp, *Ber.* **7**, 398.

[4] Niederhausen, *Ber.* **15**, 1119.

[5] Klinkhardt, *J. Pr. Chem.* II. **25**, 45.

by hydriodic acid at 250°, and may be distilled without alteration over red-hot zinc dust.

With picric acid it forms the compound $C_{12}H_8O+C_6H_3(NO_2)_3O$, which separates from alcohol in yellow crystals, melting at 94°.[1]

Dibromodiphenylene oxide, $C_{12}H_6Br_2O$, was prepared by Hoffmeister by adding bromine to a carbon disulphide solution of diphenylene oxide. It crystallizes from alcohol in small plates melting at 185°.

Dinitrodiphenylene oxide, $C_{12}H_6(NO_2)_2O$, forms indistinct crystals, sparingly soluble in water, and melts at 200°.

TETRAHYDROXYDIPHENYLS, $C_{12}H_6(OH)_4$.

2717 *Dicatechol*, $(OH)_2C_6H_3.C_6H_3(OH)_2$, is formed by fusing *a*-phenoldisulphonic acid with potash, and crystallizes in slender matted needles, which are extremely unstable, and very sensitive to the action of light. On heating in a current of hydrogen it sublimes in small quantity, and then melts at 84°. Its aqueous solution is coloured pale green by ferric chloride, the colour on addition of soda changing first to dark blue, then becoming violet, and finally red. It shows therefore the same colour reactions as catechol, on which account it obtained the above name.[2]

Diresorcinol, $C_{12}H_6(OH)_4 + 2H_2O$, is obtained together with a large quantity of phloroglucinol when resorcinol is heated with an excess of caustic soda. It is sparingly soluble in cold water, and crystallizes from the hot liquid according to the concentration in microscopic oblique prisms or long flat needles, which melt at 310°, and are almost insoluble in acetic acid. Its aqueous solution is coloured a somewhat pale blue by ferric chloride, and on heating with zinc dust it is reduced to diphenyl.[3]

Diresorcinol, and also its tetra-ethyl ether and tetracetate, may be recognized by the fact that they dissolve in sulphuric acid with an intense citron-yellow colouration, which changes on addition of acetic anhydride to a beautiful bluish-violet, the latter disappearing when a large quantity of water or an excess of alkali is added.[4]

Tetra-ethoxydiresorcinol, or *Diresorcinol tetra-ethyl ether*, $C_{12}H_6(OC_2H_5)_4$, is formed by heating diresorcinol with the requisite

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[1] Goldschmiedt and Schmidt, *Monatsh.* **2**, 14.

[2] Barth and Schreder, *Ber.* **11**, 1336.

[3] Barth and Schreder, *Ber.* **11**, 1336; Benedikt, *Monatsh.* **1**, 355; Benedikt and Julius, *Monatsh.* **5**, 177.

[4] Herzig and Zeisel, *Monatsh.* **11**, 421.

quantity of ethyl iodide and alcohol potash; it crystallizes from hot alcohol in large plates, melting at 110°.[1]

Tetracetyldiresorcinol, $C_{12}H_6(OCO.CH_3)_4$, is formed when anhydrous diresorcinol is boiled with acetic anhydride and sodium acetate, and crystallizes from alcohol in lustrous prisms melting at 259°.

Hexbromodiresorcinol, $C_{12}Br_6(OH)_4$, is prepared by the action of bromine on an ethereal solution of diresorcinol, and crystallizes in microscopic transparent granules. Its *tetracetate*, $C_{12}Br_6(O.CO.CH_3)_4$, forms crystals, melting at 259°, and almost insoluble in alcohol.

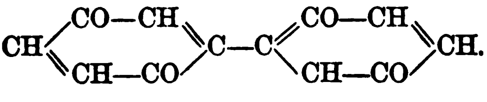
Decabromodiresorcinol is formed when an alkaline solution of diresorcinol is mixed with a solution of bromine in fuming hydrobromic acid, and separates in beautiful crystals which lose bromine in the air, and are converted into hexbromodiresorcinol by sulphurous acid.

Hexnitrodiresorcinol, $C_{12}(NO_2)_6(OH)_4$, is obtained by warming the acetate with fuming nitric acid, and forms yellow crystals, which unlike other similar compounds are readily soluble in water. It decomposes with explosion on heating to 230°.

Diquinol, $C_{12}H_6(OH)_4$. This compound is formed together with other products (Part III., p. 199) when quinol is fused with 10 times its weight of caustic soda, and crystallizes from hot water in fairly large though badly developed crystals, which have a pure sweet taste, and melt at 237°, becoming brown at the same time.

On addition of ferric chloride to its aqueous solution the latter is coloured red, and *diquinhydrone*, $C_{12}H_8O_4$, separates out in needles which have a bluish-violet or green surface lustre; these dissolve in alcohol, forming a red solution, and decompose on heating without melting.

On addition of ferric chloride to the hot concentrated solution, it assumes a light yellow colour; and on quickly cooling, *diquinone*, $C_{12}H_6O_4$, separates out in straw-yellow needles, which melt with decomposition at 186—187°.[2] Its constitution is probably represented by the formula:



$$CH\begin{array}{l}\diagup CO-CH\diagdown\\ \diagdown CH-CO\diagup\end{array}C-C\begin{array}{l}\diagup CO-CH\diagdown\\ \diagdown CH-CO\diagup\end{array}CH.$$

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[1] Pukall, *Ber.* **20**, 1143.

[2] Barth and Schreder, *Monatsh.* **5**, 589.

Sappanin, $C_{12}H_6(OH)_4 + 2H_2O$. When the commercial extract of the East Indian sappan-wood, employed as a red colouring matter, is fused with caustic soda, the above compound is obtained, together with resorcinol and a little catechol. It crystallizes from hot water in glistening plates, which are readily soluble in alcohol and ether, sparingly in cold water, and insoluble in chloroform and benzene. Its aqueous solution is coloured deep cherry-red by ferric chloride, and grass-green by soluble hypochlorites, the latter colour quickly passing to brown. It becomes anhydrous at 100°, melts on further heating, and distils almost unchanged; it reduces ammoniacal silver solution and Fehling's solution, yields trinitroresorcinol with nitric acid,[1] and is reduced by heating with zinc dust to diphenyl.[2] On addition of bromine to its acetic acid solution, *pentabromosappanin*, $C_{12}HBr_5(OH)_4$, is formed, and crystallizes from alcohol in brown needles.[3]

Tetracetylsappanin, $C_{12}H_6(O.CO.CH_3)_4$, crystallizes from alcohol in small prisms.

Baphiin, which has the same composition as Sappanin, is found in the red dye wood known as bar wood or cam wood from *Baphia nitida*, a tree growing on the West Coast of Africa, and used by the native women for painting their bodies. Baphiin crystallizes from alcohol in glistening plates, smelling like orris root, and assumes a reddish-yellow or light-purple colour when exposed to the air;[4] it has not yet been sufficiently examined, and is probably not a diphenyl derivative.

HEXHYDROXYDIPHENYLS, $C_{12}H_4(OH)_6$.

2718 *a-Hexhydroxydiphenyl* was discovered by Liebermann in the course of his investigation of a blue compound which is obtained in the purification of crude pyroligneous acid, and which he termed *coerolignone*, $C_{16}H_{16}O_6$. This is a quinone-like substance which on reduction is converted into the colourless hydrocoerolignone, $C_{16}H_{18}O_6$. On heating the latter with hydrochloric acid at 200°, it yields methyl chloride and the compound $C_{12}H_{10}O_6$, which on distillation with zinc dust yields diphenyl.

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[1] Schreder, *Ber.* **5**, 372.

[2] Barth and Schreder, *Ber.* **12**, 506.

[3] Benedikt, *Monatsh.* **1**, 356.

[4] Anderson and Mills, *Journ. Chem. Soc.* **1876**, II. 582.

It is therefore *a*-hexhydroxydiphenyl, and hydrocoerolignone its tetramethyl ether.

a-Hexhydroxydiphenyl crystallizes from hot water in silvery plates, which are so thin that when laid one on the other they have the appearance of silver-foil. It dissolves in dilute caustic potash with a bluish-violet colour which remains for days. Baryta-water gives with the aqueous solution a white precipitate, which quickly becomes blue, and on drying assumes a green metallic lustre. This could not, however, be obtained pure, as was also the case with the potassium compound precipitated from the alkaline solution by alcohol in violet plates, which immediately undergo further oxidation.[1]

Liebermann remarked that this hexhydroxydiphenyl, no isomerides of which were then known, was probably the pyrogallol of the diphenyl series. The correctness of this supposition was shown later on by Hofmann, who proved that coerolignone is an oxidation-product of pyrogallol dimethyl ether. In each phenyl group, therefore, the three hydroxyl groups are in the adjacent position; their exact position in each ring is unknown, but it is probable that two of them occupy the para-position (p. 393).

a-Hexhydroxydiphenyl tetramethyl ether, *a-Dihydroxytetramethoxydiphenyl*, or *Hydrocoerolignone*, $C_{12}H_4(OCH_3)_4(OH)_2$, is best obtained by passing sulphuretted hydrogen into boiling water containing coerolignone in suspension, or boiling the latter with zinc dust and hydrochloric acid. It is scarcely soluble in water or ether, but dissolves somewhat readily in alcohol and benzene, crystallizing out in lustrous monosymmetric prisms. From superheated aqueous solution it separates in long asbestos-like needles, which melt at 190°. On further heating a portion distils over, the remainder undergoing carbonization, and on oxidation it readily reforms coerolignone.[2]

Potassium hydrocoerolignone, $C_{12}H_4(OCH_3)_4(OK)_2 + 4H_2O$, is obtained by boiling hydrocoerolignone with caustic potash, and separates on cooling in long golden-yellow plates.

a-Hexmethoxydiphenyl, or *Dimethylhydrocoerolignone*, $C_{12}H_4(OCH_3)_6$, is formed by heating the potassium salt with methyl alcohol and potassium methyl sulphate at 140°, and crystallizes from alcohol in silky needles, melting at 126°.[3]

Diacetylhydrocoerolignone, $C_{12}H_4(OCH_3)_4(OCOCH_3)_2$, is spar-

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[1] *Annalen*, **169**, 241.

[2] *Annalen*, **169**, 226.

[3] Ewald, *Ber.* **11**, 1623.

ingly soluble in alcohol, from which it crystallizes in needles melting at 225°.

a-Hexacetoxydiphenyl, $C_{12}H_4(OCO.CH_3)_6$, crystallizes in beautiful prisms, and melts at 145°.

Dichlorohydrocoerolignone, $C_{12}H_2Cl_2(OCH_3)_4(OH)_2$. When diacetylhydrocoerolignone is heated with phosphorus pentachloride, substitution takes place in the diphenyl residue, with formation of *diacetyldichlorohydrocoerolignone*, which crystallizes in small well-developed prisms, melting at 172°, and is decomposed by alcoholic potash with formation of dichlorohydrocoerolignone. The latter crystallizes from hot alcohol in small very lustrous rhombic tablets, melting at 220°. Its *potassium* salt, $C_{12}H_2Cl_2(OCH_3)_4(OK)_2$, is insoluble in alcohol, and crystallizes from water in needles.[1]

Hexmethoxydichlorodiphenyl, $C_{12}H_2Cl_2(OCH_3)_6$, is formed by adding chlorine water to an acetic acid solution of the hexmethyl ether, and crystallizes from alcohol in colourless needles.[2]

The corresponding bromine derivatives have also been prepared.

2719 *Tetrahydroxydibenzoquinone*, $C_{12}H_4(OH)_4O_2$, is formed, together with hydrogen iodide, when an aqueous solution of *a*-hexhydroxydiphenyl is mixed with an alcoholic iodine solution, and forms a blue precipitate, consisting of microscopic needles, soluble in alkalis with a beautiful blue colouration.[3]

Tetramethoxydibenzoquinone, $C_{12}H_4(OCH_3)_4O_2$. In the year 1835, Reichenbach obtained from wood-tar a peculiar compound, which was not contained ready formed, but was prepared in the following manner:

"The rectified oil, which is obtained by the distillation of beech-wood tar, was freed from acetic acid by carbonate of potash, treated with concentrated potash ley, the alkaline solution separated from insoluble matter, and saturated with acetic acid. A portion of the oil separates, and another portion is obtained by distilling the acetate of potash. When about one-third has passed over, a small portion is collected and treated with a solution of ferric sulphate. If this forms a red precipitate the remainder of the distillate may be collected. The latter has the property of giving with ferric sulphate or bichromate of potash a red solution, and after five minutes a

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[1] Hayduck, *Ber.* 9, 928.
[2] Ewald, *loc. cit.*
[3] Liebermann and Bung, *Ber.* 9, 1887.

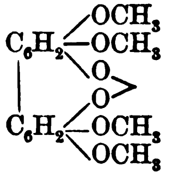
precipitate of slender red needles, the solution becoming colourless.

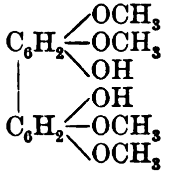
"These red crystals have been termed by Reichenbach *cedriret*, from *cedrium*, an old name for the acid water, obtained in tar burning, and *rete*, a net, because the crystals form a net-shaped mass on filter paper."[1]

Cedriret dissolves in pure sulphuric acid with an indigo-blue colour, which on warming or treatment with water becomes yellowish-brown, the compound undergoing decomposition. It is insoluble in water, alcohol, all the ethers, and most other liquids, but dissolves in creosote, forming a purple solution, from which alcohol precipitates it in a crystalline form. It does not melt, but decomposes at a moderate temperature, and carbonizes on further heating.

Voelcker, who repeated Reichenbach's experiments, was unable to obtain cedriret.[2] About thirty years later, Lettemayer observed that when raw pyroligneous acid is mixed with a small quantity of potassium dichromate solution for purification purposes, a blue film is formed on the surface which gradually sinks to the bottom as a bluish-violet sediment. This was more closely examined by Liebermann, who found that its chief constituent is a compound, the smallest portions of which when suspended in water have a strong surface lustre, and on examination under the microscope are found to consist of small violet needles. An attempt to purify it by sublimation resulted in its total decomposition, and it is practically insoluble in the usual solvents; phenol, however, dissolves it in considerable quantity, and on addition of alcohol it separates in dark steel-blue lustrous needles.

Liebermann termed it coerolignone, as it has a blue colour, is obtained from wood-tar, and also has the properties of a quinone; it passes on reduction into the corresponding quinol, termed hydrocoerolignone. For these compounds Liebermann gave the following constitutional formulæ:





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[1] Berzelius, *Jahresb.* **15**, 408.

[2] *Annalen*, **86**, 102.

He found that coerolignone has the characteristic property of dissolving in concentrated sulphuric acid with a corn-flower blue colour. This is so intense that the smallest grain can be thus readily recognized. The colouration is comparatively stable; on careful addition of water it at first passes into a deep fuchsin-red, and then a brown precipitate is formed.

Liebermann endeavoured in vain to discover the mother-substance of coerolignone in the distillation-products of the wood, although he examined a number of different varieties of genuine creosote. Hofmann, however, found that it occurs in the last products of the distillation of beech-wood tar, and obtained it in needles with a violet surface lustre.[1]

Later on, he drew attention to the fact, already mentioned by Marx,[2] that coerolignone was identical with cedriret, and remarked that it was astonishing how a compound of such remarkable and interesting properties should remain for thirty years uninvestigated, or one might say fall into oblivion.[3]

Liebermann in reply stated that he had already noticed the similarity of the two compounds, but as cedriret formed red crystals, and was obtained from a high-boiling wood-tar oil, and coerolignone was obtained from pyroligneous acid and crystallized in blue needles, he had supposed them, although closely related, to be different compounds.

Hofmann next attempted, and with success, to discover the mother-substance of cedriret. He showed that it is easily formed from pyrogallol dimethyl ether; on dissolving the latter in acetic acid and adding potassium dichromate the mixture becomes warm, and after a few seconds is filled with beautiful needles, which have a dark reddish-brown colour in transmitted light, and a beautiful steel-blue colour in reflected light. The dimethyl ether may also be dissolved in caustic soda, and after addition of an excess of potassium dichromate heated to boiling. On addition of hydrochloric acid, a mass of reddish-brown matted needles separates. The same change may be effected by the elements of the chlorine group, nitric acid, ferric chloride, and potassium ferricyanide.[4]

This formation of cedriret is readily understood, the reaction taking place according to the equation:

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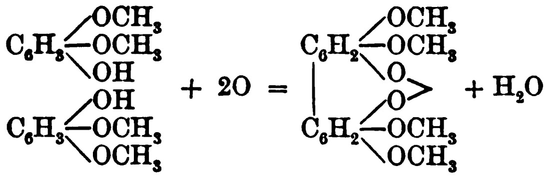
[1] *Ber.* **7**, 78.

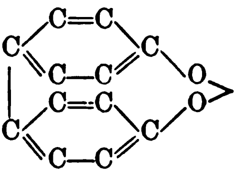
[2] Wagner's *Jahresber.* **1872**, 827.

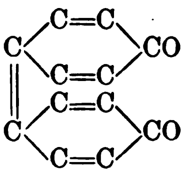
[3] *Ber.* **8**, 68.

[4] *Ber.* **11**, 329.



This, as well as tetrahydroxydibenzoquinone, of which it is the methyl ether, shows great similarity with tetrachlorodibenzoquinone and the corresponding bromine compound, whence it is probable that in tetrahydroxydibenzoquinone the quinone oxygen atoms also occupy the para-position. The compound, like other quinones, may either be represented as a peroxide or a diketone, as shown in the following formulæ:





Tetra-ethoxydibenzoquinone, $C_{12}H_4(OC_2H_5)_4O_2$, was obtained by Hofmann by the action of potassium dichromate on an acetic acid solution of pyrogallol diethyl ether, and termed by him *ethylcedriret*, which name, as he himself remarks, is not quite legitimate. The solution first becomes warm, and assumes a dark red colouration; on allowing it to cool slowly, large prisms separate, which have a crimson colour by transmitted light, and in reflected light a golden-green lustre like cantharides, with a tinge of blue. It is insoluble in water or ether, and crystallizes from dilute alcohol in long thin needles, which form a pale red powder. It dissolves in sulphuric acid, like cedriret, with a corn-flower blue colouration. By the action of sulphurous acid on its alcoholic solution it yields *hydro-ethylcedriret*, or *dihydroxytetra-ethoxydiphenyl*, $C_{12}H_4(OC_2H_5)_4(OH)_2$, which crystallizes in long silky needles, and is readily oxidized to ethylcedriret.[1]

2720 *β-Hexhydroxydiphenyl*, $C_{12}H_4(OH)_6$, is formed by fusing ellagic acid, $C_{14}H_6O_8$, with potash:

$$C_{14}H_6O_8 + 2H_2O = C_{12}H_{10}O_6 + 2CO_2.$$

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[1] Hofmann, *Ber.* **11**, 797.

It crystallizes from hot water in needles which decompose with blackening on heating, a small portion subliming at the same time. On addition of a trace of caustic potash to its aqueous solution, the latter is coloured deep bluish-violet, which then changes, probably by absorption of oxygen, beginning at the upper layer, to blood-red, and finally to yellowish-red. The very dilute solution is coloured yellowish-brown by ferric chloride, which changes to blue on addition of a little soda, whilst a larger quantity of soda converts it into reddish-violet. Ferrous salts give a blue colouration, and blue-black flakes separate out.

On heating β-hexhydroxydiphenyl with zinc dust, it yields diphenyl, and is converted by acetic anhydride into the acetate, crystallizing in large hard prisms, which melt at 170°.[1]

γ-*Hexhydroxydiphenyl*, $C_{12}H_4(OH)_6$, is formed together with a small quantity of the β-compound by fusing ellagic acid with caustic soda, and also in small quantity by the action of sodium amalgam and water on ellagic acid.[2] It crystallizes from hot water in needles which are less soluble than the β-compound. Its aqueous solution is immediately coloured blood-red by caustic potash, the colour passing, on shaking or diluting, through brown to dark emerald-green. A little ferric chloride causes a green colouration, which quickly disappears, and is converted by soda first into bluish-violet and then into reddish-violet. On heating with zinc dust it yields diphenyl in quantity (Barth and Goldschmiedt).

δ-*Hexhydroxydiphenyl* is formed, together with hydroxyquinol and diquinol (p. 387), by fusing quinol with soda, and crystallizes from hot water in lustrous plates, which when moist rapidly become dark blue in the air. Its aqueous solution is coloured blood-red by caustic potash, and ferric chloride gives first a similar colouration, and then a dirty blue precipitate. Its *acetate* crystallizes in needles melting at 172°, which are sparingly soluble in alcohol.[3]

[1] Barth and Goldschmiedt, *Ber.* **12**, 1237.

[2] Cobenzl, *Monatsh.* **1**, 670.

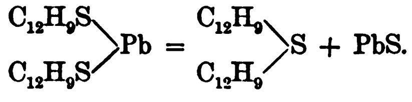
[3] Barth and Schreder, *Monatsh.* **5**, 589.

SULPHUR DERIVATIVES OF DIPHENYL.

2721 *Thiodiphenylol*, or *Diphenylmercaptan*, $C_{12}H_9SH$, is prepared by the action of tin and hydrochloric acid on diphenylsulphochloride, and on distillation with steam passes over as a snow-white mass, which is soluble in alcohol and ether, more readily in benzene and carbon disulphide, and melts at 110—111°. The *lead* salt, $(C_{12}H_9S)_2Pb$, is a dark brown, and the *mercuric* salt a white, crystalline precipitate.[1]

Methylthiodiphenylol, $C_{12}H_9SCH_3$, is formed by heating the above lead salt with methyl iodide, and crystallizes from alcohol in floccular aggregates of extremely slender needles melting at 107—108°.[2]

Diphenyl sulphide, $(C_{12}H_9)_2S$, is obtained by the dry distillation of the lead salt:



$$\begin{matrix} C_{12}H_9S \\ C_{12}H_9S \end{matrix}\Big>Pb = \begin{matrix} C_{12}H_9 \\ C_{12}H_9 \end{matrix}\Big>S + PbS.$$

It crystallizes from acetic acid in large lustrous plates melting at 171—172°, and is oxidized by potassium permanganate in acetic acid solution to *di-diphenyl sulphone*, $(C_{12}H_9)_2SO_2$, which is sparingly soluble in ether, readily in alcohol, and crystallizes in fascicular aggregates of plates, melting at 214—216°.

Diphenyl disulphide, $(C_{12}H_9)_2S_2$, is readily obtained by the oxidation of diphenylol in the air, or more quickly by the action of nitric acid. It crystallizes from acetic acid in long colourless needles, melting at 148—150°.

Dithiophenol, or *Diphenylenedihydrosulphide*, $C_{12}H_8(SH)_2$, is obtained by the reduction of diphenyldisulphochloride, and crystallizes from alcohol in colourless plates, melting at 176°. The *lead* salt is a brownish-red precipitate, and on heating with methyl iodide yields the *methyl* ether, $C_{12}H_8(SCH_3)_2$, which separates from alcohol in yellowish glistening plates, melting at 185—186°.

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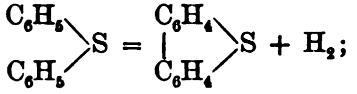
[1] Gabriel and Deutsch, *Ber.* **13**, 386.

[2] Obermeyer, *Ber.* **20**, 2918.

Diphenylene sulphide, $C_{12}H_8S$, is prepared by passing the vapour of phenyl sulphide through a red-hot tube :[1]



$$\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\rangle S = \left.\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\right\rangle S + H_2;$$

the hydrogen set free reduces another portion of the phenyl sulphide to benzene :

$$(C_6H_5)_2S + 4H = 2C_6H_6 + H_2S.$$

Diphenylene sulphide crystallizes from hot alcohol in long needles, which have a silky lustre, and dissolve readily in ether and benzene. It melts at 97°, boils at 332—333°, and is unacted on by phosphorus and hydriodic acid at 250—280°. On warming with dilute sulphuric acid and potassium dichromate, it yields *diphenylene sulphone*, $C_{12}H_8SO_2$, which crystallizes from alcohol in long needles, melting at 230°, and soluble in warm sulphuric acid and concentrated nitric acid without decomposition.

AMIDO-DERIVATIVES OF DIPHENYL.

AMIDODIPHENYLS, $C_{12}H_9.NH_2$.

2722 *2-Amidodiphenyl*, was obtained by Hübner by the reduction of 2-nitrodiphenyl with tin and acetic acid. After diluting with water, and removing the dissolved tin by sulphuretted hydrogen, caustic soda precipitates the crystalline base, which melts at 44—45°.

2-Amidodiphenyl hydrochloride, $C_{12}H_9.NH_3Cl$, forms long colourless needles which readily sublime, and the *platinochloride*, $(C_{12}H_9.NH_3)_2PtCl_6 + 4H_2O$, crystallizes in small lustrous orange plates. The *nitrate* forms large colourless crystals, and the *sulphate* crystallizes in thin readily soluble plates.

By the action of tin and hydrochloric acid on nitrodiphenyl, Hübner and Lüddens obtained *chloro-2-amidodiphenyl*, $C_{12}H_8Cl.NH_2$, the reaction being represented by the following equation :

$$C_{12}H_9.NO_2 + 5HCl + 2Sn = C_{12}H_8Cl.NH_2 + 2SnCl_2 + 2H_2O.$$

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[1] Stenhouse, *Annalen*, **156**, 332 ; Graebe, *Annalen*, **174**, 185.

It crystallizes from alcohol in long needles, which melt at 48°.[1]

4-*Amidodiphenyl.* In the higher-boiling by-products, formed in the manufacture of aniline, Hofmann found a compound, $C_{12}H_{11}N$, which he termed *xenylamine*.[2] Kekulé suggested that it was an amidodiphenyl, a supposition which was proved correct later on by Schulz,[3] and by Hübner and Osten,[4] who obtained it by the reduction of 4-nitrodiphenyl with tin and hydrochloric acid.

4-Amidodiphenyl forms pleasant-smelling plates, which melt at 49°, are readily soluble in alcohol and hot water, and volatile with steam.

4-*Amidodiphenyl hydrochloride,* $C_{12}H_9.NH_3Cl$, forms small lustrous plates, readily soluble in hot, but sparingly in cold water, and scarcely soluble in concentrated hydrochloric acid.

4-*Amidodiphenyl sulphate,* $(C_{12}H_9.NH_3)_2SO_4$, crystallizes from hot water in lustrous plates, which are only sparingly soluble in cold water.

4-*Amidodiphenyl oxalate,* $(C_{12}H_9.NH_3)_2C_2O_4$, forms long needles, also sparingly soluble in cold water. The *platinochloride,* $(C_{12}H_9NH_3)_2PtCl_6 + 2H_2O$, crystallizes in yellow plates, and the *nitrate* in tablets which are readily soluble in cold water.

The following substances are all derivatives of the 4-compound:

Diethylamidodiphenyl, $C_{12}H_9N(C_2H_5)_2$, crystallizes in long needles, melts below 100°, and is insoluble in water, but fairly soluble in alcohol (Hofmann).

Acetamidodiphenyl, $C_{12}H_9NH.CO.CH_3$, is formed by boiling the base with glacial acetic acid, and crystallizes from alcohol in needles melting at 167° (Hübner and Osten).

Benzamidodiphenyl, $C_{12}H_9NH.CO.C_6H_5$, crystallizes in plates, melting at 226°, which are very sparingly soluble in alcohol.

Ethyl diphenylcarbamate, $C_{12}H_9NH.CO.OC_2H_5$. Zimmermann prepared this compound by the action of ethyl chloroformate on an ethereal solution of the base. It crystallizes from ether in microscopic needles, which melt at 110°, and on treating with phosphorus pentoxide yield *diphenyl carbimide,* $C_{12}H_9.NCO$. This distils over as a colourless pungent-smelling liquid, which soon solidifies to a crystalline mass.

Diphenylthiocarbimide, or *Diphenyl mustard-oil,* $C_{12}H_9.NCS$, is

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[1] *Annalen,* **209,** 349.

[2] *Zeitsch. Chem.* **1866,** 1.

[3] *Annalen,* **174,** 212.

[4] *Annalen,* **209,** 342.

formed by heating the base with carbon disulphide and alcohol, and distilling the *di-diphenylthiocarbamide*, $CS(NHC_{12}H_9)_2$, thus obtained with phosphorus pentoxide. It crystallizes from ether in long needles, which melt at 58°, and have a pungent odour resembling that of the other mustard-oils.[1] The above di-diphenylthiocarbamide crystallizes in plates melting at 228°.

4-*Nitro-4′-amidodiphenyl*, $C_6H_4(NO_2).C_6H_4(NH_2)$, was obtained by Fittig by mixing 4 : 4′-dinitrodiphenyl with alcohol and ammonium sulphide, and passing in sulphuretted hydrogen till all had dissolved.[2] It crystallizes from alcohol in small bright-red needles, which melt at 198°, are oxidized by chromium trioxide to *p*-nitrobenzoic acid, and may be converted by the diazo-reaction into 4-nitro-4′-bromodiphenyl.[3]

4-Nitro-4′-amidodiphenyl is an extremely weak base, which dissolves in boiling hydrochloric acid, but separates out unchanged on evaporation; the *platinochloride* is a floccular precipitate, which quickly decomposes. Its *acetyl* compound, $C_6H_4(NO_2)C_6H_4(NH.CO.CH_3)$, forms yellow needles, melting at 264°.[4]

2-*Nitro-4′-amidodiphenyl* is readily obtained when 2:4′-dinitrodiphenyl is gently warmed with a mixture of 5 parts of ammonium sulphide and an equal quantity of alcohol till solution takes place, and crystallizes from alcohol in short reddish-brown monosymmetric prisms, which melt at 97—98°, and may be converted by the diazo-reaction into 2-nitro-4′-bromodiphenyl. It is a fairly strong base, and forms a *hydrochloride* crystallizing in long white needles.[5]

4:4′-*Amidodiphenylsulphonic acid*, $C_{12}H_8(NH_2)SO_3H$, is formed by heating amidodiphenyl with sulphuric acid at 130°, and is precipitated on addition of water. Its *sodium* salt, $C_{12}H_8(NH_2)SO_3Na + 2H_2O$, crystallizes from hot water in needles resembling those of saltpetre.[6]

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[1] Zimmermann, *Ber.* **13**, 1963.

[2] *Annalen*, **124**, 277.

[3] Schultz, *Annalen*, **174**, 222.

[4] Schultz, *Annalen*, **207**, 347.

[5] Schultz, *Annalen*, **174**, 225 ; Schultz, Schmidt, and Strasser, *Annalen*, **207**, 350.

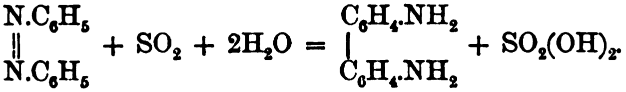
[6] Carnelley and Schlesselmann, *Journ. Chem. Soc.* **1886**, I. 380.

4-4′-DIAMIDODIPHENYL, $C_{12}H_8(NH_2)_2$.

2723 By the action of sulphuretted hydrogen on a solution of azobenzene in alcoholic ammonia, Zinin in 1845 obtained a colourless crystalline compound, which became yellow on keeping. For purification he converted it into the sulphate, from which, by the action of ammonia, he separated the new base, and termed the latter *benzidine*.[1] He found that it does not, after purification, become yellow in the air, and that the sulphate may also be directly prepared by passing sulphur dioxide into an alcoholic solution of azobenzene.[2] He regarded benzidine as a direct reduction-product of azobenzene, but Hofmann afterwards found that the latter on reduction first forms hydrazobenzene (Part. III., p. 356), which is then converted by the action of mineral acids into its isomeride benzidine. The constitution of this was shown by Fittig, who obtained it by the reduction of 4 : 4′-dinitrodiphenyl.[3]

Some time later, Griess also showed that it is a derivative of diphenyl, for by the diazo-reaction it may be converted into this hydrocarbon.[4]

Its formation from azobenzene and sulphurous acid may be now readily understood, inasmuch as sulphuric acid is also formed, and converts the hydrazobenzene first formed into benzidine. The final result is represented by the following equation :



$$\begin{array}{l} N.C_6H_5 \\ \| \\ N.C_6H_5 \end{array} + SO_2 + 2H_2O = \begin{array}{l} C_6H_4.NH_2 \\ | \\ C_6H_4.NH_2 \end{array} + SO_2(OH)_2.$$

Benzidine is also formed when azobenzene is heated with fuming hydrochloric acid at 115°, the chlorine set free causing the formation of a blue resinous by-product,[5] and may further be obtained by boiling azobenzene with hydrobromic or hydriodic acid.[6] Organic acids also bring about this change.

In order to prepare it, 4 : 4′-dinitrodiphenyl is warmed with tin and hydrochloric acid, or hydrazobenzene may be warmed with hydrochloric acid, in which case 2 : 4′-diamidodiphenyl, or

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[1] *J. Pr. Chem.* **36**, 93.

[2] *Annalen*, **85**, 328.

[3] *Annalen*, **124**, 275.

[4] *J. Pr. Chem.* **101**, 91.

[5] Zinin, *Annalen*, **137**, 376.

[6] Werigo, *Annalen*, **165**, 202.

diphenyline, is also obtained. It is, however, unnecessary to prepare pure hydrazobenzene; 70 grams of azobenzene may be dissolved in hot alcohol, and a solution of 55 grams of tin in concentrated hydrochloric acid gradually added, the flask being connected with a reflux condenser. A vigorous reaction takes place, and aniline is formed in addition to the two diamidodiphenyls, but the method has the advantage that the azobenzene is completely decomposed, and that the reaction may be quickly carried out. When the reaction is over, the alcohol is distilled off, the residue mixed with sulphuric acid, and the separated benzidine sulphate filtered off, carefully washed with hydrochloric acid to remove all tin, recrystallized and decomposed with ammonia. The filtrate is evaporated, decomposed with potash, extracted with ether, which takes up the bases, and the latter separated by fractional distillation. Thirteen grams of diphenyline and a similar amount of aniline are obtained, whilst the quantity of benzidine is 30 grams.[1]

On the large scale nitrobenzene is heated with caustic soda and the calculated quantity of zinc dust, the hydrazobenzene formed washed with cold dilute hydrochloric acid, then added to the hot acid, from which solution benzidine sulphate separates on addition of sulphuric acid.[2]

Benzidine dissolves in 2500 parts of cold and in 105 parts of boiling water,[3] and crystallizes out in large lustrous plates, which melt at 122°.[4]

It boils with partial decomposition far above 360°, dissolves easily in alcohol, and still more readily in commercial ether, but requires 45 parts of the latter when free from alcohol and water. The solutions have an alkaline, and at the same time sharp pepper-like taste. On heating with manganese dioxide it yields benzoquinone in large quantity. Both benzidine and its salts, as Zinin found, are decomposed by chlorine in aqueous or alcoholic solution; a transient indigo-blue colour is frequently first seen, and then a crystalline cinnabar-red precipitate separates out. This characteristic reaction was more closely examined by Claus and Risler, who found that a cold saturated solution of benzidine hydrochloride is coloured a beautiful blue by a little chlorine water, the colouration

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[1] Schmidt and Schultz, *Annalen*, **207**, 324.

[2] Friedländer, *Theerfarbenfabr.* 459.

[3] Schiff and Vanni, *Annalen*, **258**, 363.

[4] Wald, *Ber.* **10**, 137.

disappearing after a time, especially on shaking, but reappearing on further addition of chlorine water. If the addition be continued the solution assumes a green colour, and a red floccular precipitate is formed, which is very unstable. Bromine water gives the same colour reactions, and on bringing bromine vapour in contact with a solution of the base in ether or chloroform, a dark blue precipitate is at once obtained; the latter dissolves in water, forming a beautiful blue solution, which quickly becomes orange-yellow. If weak bromine water be poured on to a solution of benzidine in carbon disulphide, the base absorbs the bromine with a blue colouration, which changes to dark-green on addition of more bromine water, after which the aqueous solution becomes discoloured, and the carbon bisulphide solution assumes a dark red colour. If an excess of bromine be allowed to act on a solution of the base in a large excess of hydrochloric acid, a precipitate of tetrabromobenzidine is obtained.[1] On addition of potassium dichromate to a solution of the base, a deep blue precipitate of the chromate described below is obtained, even in very dilute solution. Potassium ferricyanide also yields a precipitate of the same colour.[2]

Benzidine and some of its homologues are largely used in the manufacture of azo-colours.

Benzidine hydrochloride, $C_{12}H_8(NH_3Cl)_2$, crystallizes in thin rhombic plates or tablets, which are readily soluble in water, and still more easily in alcohol, but almost insoluble in ether. An excess of water converts it into the basic salt $C_{12}H_8(NH_2)NH_3Cl$, crystallizing from water, in which it is sparingly soluble, in long needles (Schmidt and Schultz). The *platinochloride*, $C_{12}H_8(NH_3)_2PtCl_6$, is a yellow lustrous crystalline precipitate, which is scarcely soluble in alcohol, sparingly in water, and decomposes on boiling with the latter.

Benzidine sulphate, $C_{12}H_8(NH_3)_2SO_4$, crystallizes in small lustrous scales, and is a very characteristic salt, as it is practically insoluble in alcohol and boiling water. On warming with a little water and sulphuric acid it forms a clear solution, and solidifies on cooling to a radiating crystalline mass, which is probably an acid sulphate, and on addition of large quantities of water yields the finely divided normal salt (Zinin).

The *nitrate* crystallizes from warm water in rectangular plates.

Benzidine chromate, $C_{12}H_8(NH_3)_2CrO_4$, is obtained as a volumi-

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[1] *Ber.* **14**, 82.

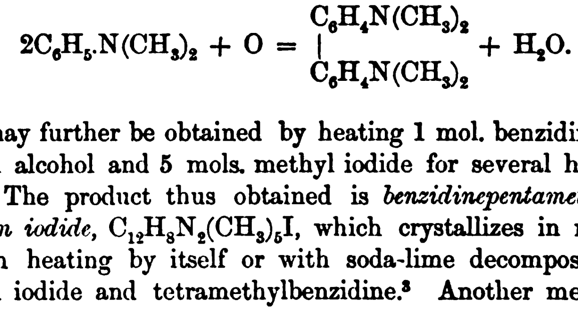
[2] Barzilowsky, *Beilstein's Handb.* **3**, 1036.

nous deep blue precipitate of matted needles by adding potassium dichromate to a hot saturated solution of benzidine. It is insoluble in the ordinary solvents, and on boiling with dilute ammonia decomposes with separation of benzidine. The formation of this salt is a most delicate reaction for benzidine, as a solution only containing 0·01 per cent. gives with a concentrated potassium dichromate solution so large a precipitate that the liquid becomes opaque; even with a solution of 0·022 grams in a litre of water it may be still recognized if the liquid be previously warmed.[1]

Benzidine oxalate, $C_{12}H_8(NH_3)_2C_2O_4$, is fairly soluble in water and alcohol, and crystallizes in spherical or stellate aggregates of needles.

The *acetate* and *tartrate* are readily soluble in water, and crystallize in plates or flat needles.

2724 *Tetramethylbenzidine* was first prepared by Michler and Salathé by heating dimethylaniline with concentrated sulphuric acid.[2] It is also formed when a solution of dimethylaniline in concentrated sulphuric acid is heated on the water-bath with lead dioxide:



$$2C_6H_5.N(CH_3)_2 + O = \begin{array}{l} C_6H_4N(CH_3)_2 \\ | \\ C_6H_4N(CH_3)_2 \end{array} + H_2O.$$

It may further be obtained by heating 1 mol. benzidine with methyl alcohol and 5 mols. methyl iodide for several hours at 120°. The product thus obtained is *benzidinepentamethylammonium iodide*, $C_{12}H_8N_2(CH_3)_5I$, which crystallizes in needles, and on heating by itself or with soda-lime decomposes into methyl iodide and tetramethylbenzidine.[3] Another method of preparation is to heat dimethylaniline with aluminium chloride in the air.[4] It crystallizes from alcohol in beautiful needles, melts at 195°, boils above 360°, and gives with oxidizing agents, such as ferric chloride, a green colouration.

Tetramethylbenzidine hydrochloride, $C_{12}H_8N_2(CH_3)_4,2HCl$, crystallizes in slender needles, and is sparingly soluble in water.

Diethylbenzidine, $C_{12}H_8(NH.C_2H_5)_2$, is readily obtained by heating benzidine with alcohol and ethyl iodide, and crystallizes in plates resembling those of benzidine, which melt at 65°,[5] and

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[1] Julius, *Monatsh.* **5**, 193.

[2] *Ber.* **12**, 1171.

[3] Michler and Pattinson, *Ber.* **14**, 2161; **17**, 115.

[4] Giraud, *Bull. Soc. Chim.* [3], **1**, 692.

[5] P. W. Hofmann, *Annalen*, **115**, 362.

are coloured a beautiful indigo-blue by bromine water.[1] The further action of ethyl iodide converts it into *tetra-ethylbenzidine*, $C_{12}H_8N_2(C_2H_5)_4$, which is also obtained by heating diethylaniline with sulphuric acid and lead dioxide. It likewise crystallizes in a similar form to benzidine, melts at 85°, gives a green colouration with bromine water and ferric chloride, and only combines with ethyl iodide with difficulty. Methyl iodide at 100°, on the other hand, readily converts it into *tetra-ethylbenzidinedimethylammonium iodide*, $C_{12}H_8N_2(C_2H_5)_4(CH_3I)_2$, which crystallizes from hot water in long needles, and is converted by moist silver oxide into the strongly alkaline *tetra-ethylbenzidinedimethylammonium hydroxide*. The latter is readily soluble in water, and yields well-crystallized salts.

Diethidenebenzidine, $C_{12}H_8(N{:}CH.CH_3)_2$, is prepared by the action of acetaldehyde on benzidine, and forms a very sparingly soluble crystalline meal.

Dibenzidenebenzidine, $C_{12}H_8(N{:}CH.C_6H_5)_2$, is obtained in a similar manner from benzaldehyde,[2] and is also formed by heating the latter with azobenzene and zinc chloride at 100—140°.[3] It crystallizes from benzene in large silvery plates, and melts at 231—232°.

Schiff and Vanni have prepared a series of analogous compounds from other aldehydes.

Diformylbenzidine, $C_{12}H_8(NH.COH)_2$, is prepared by heating hydrazobenzene or benzidine with formic acid, and is insoluble in most solvents, but separates from nitrobenzene as a crystalline powder.[4]

Monacetylbenzidine, $C_{12}H_8(NH_2)NH.CO.CH_3$, is formed together with the diacetyl compound by boiling benzidine with glacial acetic acid, and crystallizes from dilute alcohol in long stellate groups of needles, which are sparingly soluble in water, readily in alcohol, melt at 199°, and give sparingly soluble gelatinous precipitates with aqueous acids. It readily dissolves in concentrated sulphuric acid, and on addition of water the sulphate separates out.

Diacetylbenzidine, $C_{12}H_8(NH.CO.CH_3)_2$, forms needles which melt at 317°, are insoluble in water, sparingly soluble in alcohol, and somewhat more readily in acetic acid. It does not combine with acids, and sublimes with partial decomposition on heating.[5]

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[1] Schiff and Vanni, *Annalen*, **258**, 367.

[2] Schiff, *Ber.* **11**, 830.

[3] Barzilowsky, *Beilstein's Handb.* **3**, 1040.

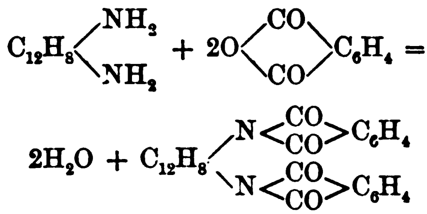
[4] Stern, *Ber.* **17**, 379.

[5] Strakosch, *Ber.* **5**, 236; Schmidt and Schultz, *Annalen*, **207**, 332.

Dibenzoylbenzidine, $C_{12}H_8(NH.CO.C_6H_5)_2$, is formed not only by heating benzidine with benzoyl chloride at 100°, but also by warming the latter with hydrazobenzene. It is insoluble in alcohol, ether, chloroform, acids, alkalis, aniline, &c., but crystallizes from boiling nitrobenzene in beautiful needles. These unite together, forming nacreous plates, which melt at a very high temperature, and sublime without decomposition (Stern).

Oxalylbenzidine, $C_{12}H_8(N_2H_2)C_2O_2$, is obtained on heating benzidine oxalate at 200—210° as a white powder, insoluble in water, alcohol, acids, and alkalis, which is resolved by boiling caustic potash into benzidine and oxalic acid.[1]

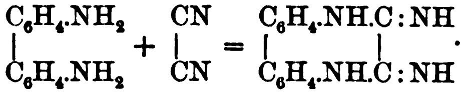
Diphthalylbenzidine, $C_{12}H_8[N(CO)_2C_6H_4]_2$, is formed by heating benzidine or hydrazobenzene with phthalic anhydride:



It crystallizes from boiling nitrobenzene in deep yellow spear-shaped silky needles, which melt above 360°, and may be sublimed in a current of carbon dioxide almost without decomposition. On heating with concentrated sulphuric acid, it is converted into phthalic acid and benzidine sulphate.[2]

Phthalyldiethylbenzidine, $C_{12}H_8N_2(C_2H_5)_2(CO)_2C_6H_4$, is prepared by heating diethylbenzidine with phthalic anhydride at 150—160°. and forms small yellowish crystals which melt at 250° with decomposition (Schiff and Vanni).

Cyanobenzidine, $C_{14}H_{12}N_4$, is formed in a similar manner to cyananiline (Part. III., p. 249), when an alcoholic solution of benzidine is saturated with cyanogen gas:



$$\begin{array}{l} C_6H_4.NH_2 \\ | \\ C_6H_4.NH_2 \end{array} + \begin{array}{l} CN \\ | \\ CN \end{array} = \begin{array}{l} C_6H_4.NH.C:NH \\ | \qquad\qquad\quad | \\ C_6H_4.NH.C:NH \end{array} .$$

On standing, cyanobenzidine separates as a red powder, which is resolved on heating with acids into benzidine and oxalic acid.[3]

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[1] Borodin, *Jahresb.* **1860**, 356.

[2] Bandrowski, *Ber.* **17**, 1181.

[3] Wittenstein, *Ber.* **3**, 723.

Diphenylenedicarbimide, $C_{12}H_8(N.CO)_2$, is obtained when carbonyl chloride is passed into benzidine hydrochloride heated to 250°, and crystallizes in long beautiful needles, which melt at 122°, and may be readily sublimed. Its vapour has an odour resembling that of phenylcarbimide.[1]

Benzidinediurethane, $C_{12}H_8(NH.COOC_2H_5)_2$, is prepared by acting on benzidine in ethereal solution with ethyl chloroformate, and forms flat needles, melting at 230°. At the same time *amidodiphenyl ethylcarbamate*, or *benzidine semiurethane* is formed, and crystallizes from ether in small needles, melting at 90—91° (Schiff and Vanni).

Benzidinediphenyldicarbamide, $C_{12}H_8(NH.CO.NH.C_6H_5)_2$, is formed when 1 mol. benzidine is mixed with 2 mols. phenylisocyanate in ethereal solution. It is thus obtained as a white precipitate, which dissolves in boiling aniline, and separates out on cooling in concentric aggregates of acute needles, melting above 300°.[2]

SUBSTITUTION-PRODUCTS OF BENZIDINE.

2725 2 : 2′-*Dichlorobenzidine*, $C_6H_3Cl(NH_2)C_6H_3Cl(NH_2)$, was obtained by Laubenheimer by warming *m*-dichlorhydrazobenzene (Part III., p. 357) with hydrochloric acid.[3] Schultz also prepared it by the action of hydrochloric acid and stannous chloride on *m*-dichlorazobenzene.[4] It crystallizes from alcohol in small flat lustrous prisms melting at 163°.

p-Dichlorobenzidine was obtained in a similar manner from *p*-dichlorazobenzene; it crystallizes from alcohol in lustrous plates, melting at 60°, and is coloured blood-red by ferric chloride.

2 : 2′-*Dibromobenzidine*, $C_6H_3Br(NH_2).C_6H_3Br(NH_2)$, was prepared by Gabriel from *m*-dibromohydrazobenzene; it forms small lustrous rhombic crystals, melting at 151·5—152°.[5]

p-Dibromobenzidine was obtained from *p*-dibromazobenzene, and crystallizes in small reddish scales melting at 108°.

The position of the halogen atoms in the so-called para-compounds is unknown, but cannot naturally be in the para-position to the amido-group.

Tetrabromobenzidine, $C_{12}H_4Br_4(NH_2)_2$, separates out on addition

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[1] Snape, *Journ. Chem. Soc.* **1886**, I. 245.
[2] Kühn, *Ber.* **18**, 1478.
[3] *Ber.* **8**, 1621.
[4] *Ber.* **17**, 463.
[5] *Ber.* **9**, 1405.

of bromine to a solution of benzidine in an excess of hydrobromic acid. On heating it sublimes in small lustrous needles, melting at 284—286°.[1]

2-*Nitrobenzidine*, $C_{12}H_7(NO_2)(NH_2)_2$, is prepared by dissolving 28·2 grams of pure benzidine sulphate in 300 grams of distilled sulphuric acid, stirring well, and warming, if necessary for complete solution, to 50—60°, cooling subsequently to 10—20°, but not lower, as otherwise benzidine sulphate separates out. 10·1 grams of potassium nitrate are then added, and the mixture well stirred for some hours, and poured into three times its volume of water; nitrobenzidine sulphate separates out, and is purified by recrystallization from hot water with addition of animal charcoal. On addition of ammonia to its hot aqueous solution, nitrobenzidine separates as an oil, which quickly solidifies to a red crystalline mass. If a very dilute solution of the sulphate be employed, the base separates on slow cooling, in long red needles resembling those of chromium trioxide, which melt at 143°.

2-*Nitrobenzidine sulphate*, $2C_{12}H_7(NO_2)(NH_3)_2SO_4 + H_2O$, forms small yellowish crystals, which dissolve in hot water much more readily than benzidine sulphate, but are much more sparingly soluble in cold water than 2 : 2′-dinitrobenzidine sulphate; 2-nitrobenzidine can therefore be readily separated from a mixture of the other two bases.

2 : 2′-*Dinitrobenzidine*, $C_{12}H_6(NO_2)_2(NH_2)_2$, is prepared in a similar manner to the foregoing compound, using double the quantity of potassium nitrate, and crystallizes from alcohol in yellow plates melting at 214°.[2]

3 : 3′-*Dinitrobenzidine* is formed when diacetylbenzidine[3] or diphthalylbenzidine[4] is treated with fuming nitric acid, and separates from the product on addition of caustic potash or sulphuric acid. It crystallizes from alcohol in deep red hemispherical aggregates of very thin needles, which melt at 218—222°, and explode on further heating with a flash. It is converted by nitrous acid and alcohol into 3 : 3′-dinitrodiphenyl.

An isomeric compound is also formed in the reaction, which is readily soluble in alcohol, and crystallizes in short saffron-yellow needles melting at 196—197°.

Dinitrotetramethylbenzidine, $C_{12}H_6(NO_2)_2N_2(CH_3)_4$, is formed

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[1] Claus and Risler, *Ber.* **14**, 82.

[2] Täuber, *Ber* **23**, 794.

[3] Strakosch, *Ber.* **5**, 236; Brunner and Witt, *Ber.* **20**, 1023.

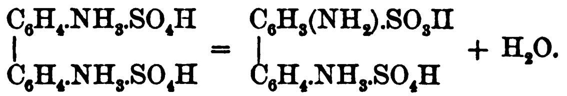
[4] Bandrowski, *Monatsh.* **8**, 471.

by the action of sodium nitrite on a hydrochloric acid solution of tetramethylbenzidine, and crystallizes from alcohol in beautiful yellowish-red needles, which melt at 188°.[1]

Tetranitrotetramethylbenzidine, $C_{12}H_4(NO_2)_4N_2(CH_3)_4$, is obtained by treating tetramethylbenzidine or dimethylaniline with dilute nitric acid, and crystallizes from phenol in beautiful sparkling golden-brown needles, which decompose on heating.

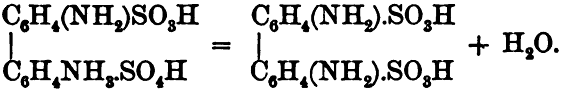
Hexnitrodimethylbenzidine, $C_{12}H_2(NO_2)_6(NH.CH_3)_2$, is formed when the previous compound or dimethylaniline is boiled with fuming nitric acid, and separates on addition of water in transparent yellow laminæ, which explode on heating. On boiling with a little phenol, nitric oxide is evolved, and *tetranitrodimethylbenzidine*, $C_{12}H_4(NO_2)_4(NH.CH_3)_2$, is formed. The latter crystallizes in slender scarlet needles, hardly to be distinguished from those of mercuric iodide. It decomposes on heating, and is reconverted by nitric acid into the hexnitro-compound.[2]

2726 *Benzidinesulphonic acid*, $C_{12}H_7(NH_2)_2SO_3H$, is prepared by heating benzidine sulphate with 6 parts of sulphuric acid at 170° for two hours, or better by heating acid benzidine sulphate at 170° for 24 hours:



$$\begin{array}{l} C_6H_4.NH_3.SO_4H \\ | \\ C_6H_4.NH_3.SO_4H \end{array} = \begin{array}{l} C_6H_3(NH_2).SO_3H \\ | \\ C_6H_4.NH_3.SO_4H \end{array} + H_2O.$$

The 3 : 3′-disulphonic acid is formed at the same time, and in larger quantity if the temperature rises above 170°:



$$\begin{array}{l} C_6H_4(NH_2)SO_3H \\ | \\ C_6H_4NH_3.SO_4H \end{array} = \begin{array}{l} C_6H_4(NH_2).SO_3H \\ | \\ C_6H_4(NH_2).SO_3H \end{array} + H_2O.$$

The black mass is extracted with caustic soda solution, and the extract acidified with acetic acid; the monosulphonic acid then separates as a crystalline tasteless powder, which is sparingly soluble in boiling water, almost insoluble in alcohol and ether. If it be dissolved in hot hydrochloric acid, the *hydrochloride*, $C_{12}H_7(NH_3Cl)(NH_2)SO_3H$, separates on cooling in nodules, which completely lose their hydrochloric acid on boiling with water.

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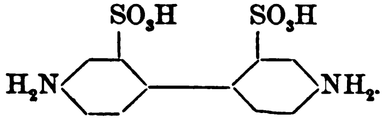
[1] Michler and Pattinson, *Ber.* **14**, 2161; **17**, 115.

[2] Mertens, *Ber.* **19**, 2123; Romburgh, *Ber.* **20**, 469 R.; *Beilstein's Handb.* **3**, 1038.

Barium benzidinesulphonate, $(C_{12}H_{11}N_2SO_3)_2Ba + 5H_2O$, crystallizes from hot water in small needles or plates.[1]

Benzidine-2 : 2'-disulphonic acid, or *4 : 4'-Diamidodiphenyl-2 : 2'-disulphonic acid*, $C_{12}H_8(NH_2)_2(SO_3H)_2 + 3H_2O$, was first obtained by the reduction of *m*-nitrobenzenedisulphonic acid, and was therefore regarded as *m*-hydrazobenzenedisulphonic acid.[2] Schultz[3] first suggested that it was really a benzidine derivative, which was then experimentally confirmed by Limpricht.[4] In order to prepare it, *m*-nitrobenzenedisulphonic acid is warmed with zinc dust and caustic soda until the solution is colourless, after which it is filtered and treated with an excess of hydrochloric acid. It may also be readily obtained by the action of stannous chloride and hydrochloric acid on *m*-azobenzenesulphonic acid. It crystallizes in beautiful monosymmetric prisms, which are scarcely soluble in alcohol and ether, very sparingly in cold, somewhat more readily in hot water, and lose their water of crystallization at 170°.

It is distinguished from the isomeric acid next described by the fact that it forms azo-colouring matters which are not fixed by unmordanted cotton.[5] Its constitution, which follows from its method of preparation, is represented by the formula:



Barium 2 : 2'-benzidinedisulphonate, $C_{12}H_6(NH_2)_2(SO_3)_2Ba + 4H_2O$, forms beautiful prisms, which are sparingly soluble in water, and lose water in the air.

Benzidine-3 : 3'-disulphonic acid, or *4 : 4'-Diamidodiphenyl-3 : 3'-disulphonic acid*, was prepared by Griess by heating benzidine with twice its weight of fuming sulphuric acid at 170°;[6] it is, however, preferable to employ benzidine sulphate and ordinary sulphuric acid, heating them together at 210° for 36—48 hours. Small quantities of the monosulphonic acid still

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[1] Griess and Duisberg, *Ber.* **22**, 2459; *Ber.* **21**, 873 c.; Friedländer's *Theerfarbenfabr.* 500.

[2] Mahrenholtz and Gilbert, *Annalen*, **202**, 331; Brunnemann, *Annalen*, **202**, 340; Balentine, *Annalen*, **202**, 351; Jordan, *Annalen*, **202**, 360; Neumann, *Ber.* **21**, 3419.

[3] *Annalen*, **207**, 314.

[4] *Ber.* **23**, 1052.

[5] Actiengesell. Anilinfabr. *Ber.* **21**, 323 c.

[6] *Ber.* **14**, 300.

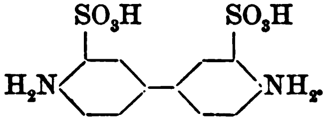
present may be separated by solution in caustic soda and precipitation with acetic acid (Griess and Duisberg).

It crystallizes usually in small four-sided plates, which are almost tasteless, and very sparingly soluble in boiling water. Its very dilute solution is coloured green by bromine water. It is employed in the preparation of azo-colours, which dye cotton directly.

Barium benzidine-3 : 3′-disulphonate, $C_{12}H_6(NH_2)_2(SO_3)_2Ba + 5H_2O$, is fairly soluble in boiling water, and separates on slowly cooling in lustrous white, thin, four- or six-sided plates, which become anhydrous at 150°. On boiling the anhydrous salt with a quantity of water insufficient for complete solution, it forms short thick needles containing 2 mols. of water.

The *silver* salt is a white crystalline precipitate.

The constitution of this benzidinedisulphonic acid is in all probability represented by the following formula:



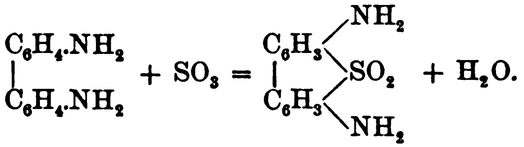
Benzidinetrisulphonic acid, $C_{12}H_5(NH_2)_2(SO_3H)_3 + 2H_2O$, is formed, together with the tetrasulphonic acid, when benzidine sulphate is heated with a large quantity of sulphuric acid at 180—190°. On pouring the liquid into five times its volume of water, the disulphonic acid present separates out. To separate the tri- and tetrasulphonic acids, the filtrate is neutralized with barium carbonate, and the barium salts treated with hot water, in which the tetrasulphonate is less soluble.

Benzidinetrisulphonic acid separates from hot fairly concentrated solutions in thin white lustrous plates, which are readily soluble in cold water, but do not deliquesce in the air.

Barium benzidinetrisulphonate, $(C_{12}H_9N_2)_2(SO_3)_6Ba_3 + 12H_2O$, is sparingly soluble in cold water, and crystallizes from the hot liquid in small indistinct prisms.

Benzidinetetrasulphonic acid, $C_{12}H_4(NH_2)_2(SO_3H)_4 + 6H_2O$, is precipitated by hydrochloric acid in small lustrous needles, which are not deliquescent, but very readily soluble in water. The *barium* salt, $C_{12}H_8N_2(SO_3)_4Ba_2$, forms white needles or small prisms, which are sparingly soluble even in hot water.

Benzidinesulphone, $C_{12}H_6(NH_2)_2SO_2$, is obtained by slowly adding benzidine sulphate to an excess of fuming sulphuric acid containing 20 per cent. SO_3, and warming on the water-bath, till a small portion on solution in water and addition of caustic soda no longer gives a precipitate of benzidine. The formation of the sulphone takes place according to the equation:



The solution is poured into ice, the benzidinesulphone sulphate filtered off after long-continued standing, and boiled with caustic soda. The yellow precipitate thus formed is extracted with alcohol, dissolved in hot hydrochloric acid, and precipitated with caustic soda. The sulphone is then obtained as a yellow powder consisting of exceedingly small needles, which are insoluble in water, alcohol, ether, and benzene; it melts at 350°, is not volatile without decomposition, and is a weak base, forming salts which are decomposed by water. The *hydrochloride*, $C_{12}H_6(NH_3Cl)_2SO_2$, separates from hot hydrochloric acid in almost colourless delicate plates, and the *sulphate*, $2C_{12}H_6(SO_2)(NH_3)_2SO_4 + 3H_2O$, crystallizes in white needles or long narrow plates.

On replacing the amido-groups of benzidinesulphone by hydrogen, it is converted into diphenylenesulphone.

Benzidinesulphonesulphonic acid, $C_{12}H_5(SO_2)(NH_2)_2SO_3H + 2H_2O$, is formed, together with the following compounds, when the sulphone is heated above 100° with fuming sulphuric acid. The solution is poured on to ice, which precipitates the mono- and disulphonic acid, whilst the tri- and tetrasulphonic acid remain in solution; they are precipitated, however, by the addition of sodium chloride.

To separate the monosulphonic acid the mixture is treated with sodium carbonate solution, which leaves the sulphone undissolved. On addition of acetic acid to the filtrate, benzidinesulphonesulphonic acid separates after some time; it is very sparingly soluble in hot water, and crystallizes out on cooling in small pale yellow needles. It has at first a bitter and then a sweet taste, and like benzidinesulphonic acid separates on addition of acetic acid to solutions of its salts as a yellowish-green jelly. The *barium* salt, $2(C_{12}H_9N_2SO_2)(SO_3)_2Ba + 7H_2O$ forms aggregates of golden-yellow needles.

Benzidinesulphonedisulphonic acid, $2C_{12}H_4(SO_2)(NH_2)_2(SO_3H)_2 + 3H_2O$, is precipitated from the acetic acid solution by the addition of a large excess of hydrochloric acid; it is fairly soluble in hot water and separates on cooling as a yellowish jelly; but on boiling the solution it forms small pale yellow needles or prisms, which are also formed by adding hydrochloric acid to the hot solution. The *barium* salt, $2C_{12}H_4(SO_2)(NH_2)_2(SO_3)_2Ba + 9H_2O$, is very sparingly soluble even in boiling water, and crystallizes in needles or very small prisms (Griess and Duisberg).

The disulphonic acid and several other sulphone derivatives of benzidine are used in the preparation of blue azo-colours, which will be described later.

ISOMERIDES OF BENZIDINE.

2727 4 : 2′-*Diamidodiphenyl*, *β-Benzidine*, or *Diphenyline*, $C_{12}H_8(NH_2)_2$, is formed, as already described, together with benzidine, by the action of acids on hydrazobenzene, and is also readily prepared by the action of stannous chloride on 4-amido-2′-nitrodiphenyl.[1] It crystallizes in long needles, which melt at 45°, and become resinous and assume a red colour when exposed to air and light. It differs from benzidine inasmuch as it is very sparingly soluble in water, and distils at 363° without decomposition. The distillate is a pale yellow, strongly refractive liquid, which gradually solidifies to a resinous mass, rarely becoming crystalline. It gives with chlorine water a reddish-brown amorphous compound, and is converted by ethyl nitrite into diphenyl. With potassium dichromate it gives the same colour reactions as benzidine (Julius).

Diphenyline hydrochloride, $C_{12}H_8(NH_3Cl)_2$, is exceedingly soluble in water, and crystallizes in long needles when hydrochloric acid is present; its solution is not precipitated by platinic chloride even on addition of alcohol and ether. The *basic* salt, $C_{12}H_8(NH_2)NH_3Cl$, crystallizes from water in plates.

Diphenyline sulphate, $C_{12}H_8(NH_3)_2SO_4$, is readily soluble in water, and crystallizes in clear compact concentric aggregates of prisms. On careful addition of an alkali to its solution, the *basic* salt, $[C_{12}H_8(NH_2)NH_3]_2SO_4$, which is fairly easily soluble in water and acids, is formed.

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[1] Schultz, Schmidt, and Strasser, *Annalen*, **207**, 354.

Tetramethyldiphenyline, $C_{12}H_8[N(CH_3)_2]_2$, is prepared by heating diphenyline hydrochloride with the requisite quantity of methyl alcohol at 180°. The mixture of bases thus obtained is precipitated by caustic potash, and boiled with acetic anhydride to convert the diphenyline and dimethyldiphenyline into the acetyl compounds; tetramethyldiphenyline is then separated from the product by fractional distillation. It crystallizes from alcohol in monosymmetric prisms, which melt at 51—52°, and on rubbing or breaking show a blue phosphorescence. Platinum chloride and hydrochloric acid give a precipitate which at once decomposes, and chloranil gives a blue colouration. On mixing alcoholic solutions of the base and of picric acid a deep red crystalline precipitate of the *picrate*, $C_{12}H_8N_2(CH_3)_4 + C_6H_3(NO_2)_3O$, is obtained, which on recrystallization from hot alcohol separates in long red needles resembling chromium trioxide. On allowing an alcoholic solution of 1 mol. of the base and 2 mols. of methyl iodide to evaporate, white needles of $C_{12}H_8N(CH_3)_2.N(CH_3)_3I$ separate out, which melt at 184°. If 4 mols. methyl iodide are employed, and the mixture heated at 100°, *hexmethyldiphenylium iodide*, $C_{12}H_8N_2(CH_3)_6I_2$, separates in beautiful yellow crystals, melting at 196°.[1]

Diacetyldiphenyline, $C_{12}H_8(NH.CO.CH_3)_2$, is formed by boiling the base with an excess of acetic acid, and crystallizes from alcohol in needles, melting at 202°.

3 : 3′-*Diamidodiphenyl*, $C_{12}H_8(NH_2)_2$, is obtained by the reduction of *m*-dinitrodiphenyl with tin and hydrochloric acid. It separates from its salts on treatment with alkalis as an oil, which solidifies after a time to a crystalline mass, sparingly soluble in water. On addition of hydrochloric acid to its ethereal solution the *hydrochloride* separates in beautiful white needles; and when platinum chloride is added to its alcoholic solution, the *platinochloride*, $C_{12}H_8(NH_3)_2PtCl_6$, is precipitated in straw-yellow granules. The *sulphate*, $C_{12}H_8(NH_3)_2SO_4$, crystallizes in long needles, which are insoluble in cold water, sparingly soluble in hot water and alcohol.

Diacetyl-3 : 3′-*diamidodiphenyl*, $C_{12}H_8(NH.CO.CH_3)_2$, likewise forms long needles, which melt at 257°.[2]

2 : 2′-*Diamidodiphenyl*, $C_{12}H_8(NH_2)_2$, is prepared by the reduction of the corresponding dinitro-compound with tin and hydrochloric acid in presence of alcohol. It crystallizes from

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[1] Reuland, *Ber.* **22**, 3011.

[2] Brunner and Witt, *Ber.* **20**, 1023.

aqueous alcohol in slender, colourless needles, which melt at 81°, and distil without decomposition when quickly heated in small quantities. Its *hydrochloride* is readily soluble in water, but sparingly in hydrochloric acid; the *sulphate*, unlike that of benzidine, is readily soluble in water, and even in aqueous alcohol. It yields azo-colours which do not dye unmordanted cotton directly. Its *diacetyl* compound crystallizes from absolute alcohol in small colourless prisms, melting at 161°.[1]

Another diamidodiphenyl is formed when dinitro-4 : 4′-dibromodiphenyl is reduced with tin and hydrochloric acid, and the solution obtained treated with sodium amalgam till the bromine is replaced by hydrogen, a process which requires several weeks for completion. The base is extracted from the alkaline solution by ether, the latter evaporated off and the residue distilled. A yellow oil passes over above 360°, and solidifies in the cold to a clear turpentine-like mass, the alcoholic solution of which has a beautiful blue fluorescence. The sulphate could not be obtained crystalline, and the solution of the hydrochloride gives no precipitate with platinic chloride; with chlorine water it yields a dark, dirty green, and with bromine water a white precipitate. Its constitution is not yet satisfactorily proved.[2]

Isobenzidine, $C_{12}H_8(NH_2)$, is obtained, according to Bernthsen, together with carbazole (p. 415) and other compounds when aniline vapour is passed through a red-hot tube. It crystallizes in small lustrous plates, which melt at 125°, and like benzidine forms a sparingly soluble sulphate, but is distinguished from the latter inasmuch as on addition of chlorine water to its aqueous solution it gives a greyish-brown colouration, and then a brown precipitate. It is sparingly soluble in carbon disulphide, the solution gradually assuming a red colour on shaking with bromine water.[3]

TRIAMIDODIPHENYLS, $C_{12}H_7(NH_2)_3$.

2728 2-*Amidobenzidine* was obtained by Täuber by reducing 2-nitrobenzidine with tin and hydrochloric acid, removing the tin with sulphuretted hydrogen, and evaporating the filtrate. The *hydrochloride* then separates as a white crystalline compound; if ammonia be added to the warm solution

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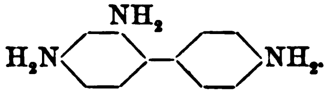
[1] Täuber, *Ber.* **24**, 198.

[2] Strasser and Schultz, *Annalen*, **210**, 194.

[3] *Ber.* **19**, 420.

the free base crystallizes out on cooling in long colourless needles, which melt at 134°. As it yields a brown colouring matter on treatment with nitrous acid or a diazo-chloride, its constitution must be represented by the formula:



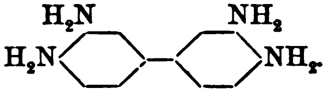
Tetramidodiphenyls, $C_{12}H_6(NH_2)_4$.

2 : 2′-*Diamidobenzidine* was likewise obtained by Täuber from 2 : 2′-dinitrobenzidine. It crystallizes in plates resembling those of benzidine, melts at 165°, does not react with *o*-diketones, but yields brown colouring matters with diazo-salts and nitrous acid, and must therefore be a di-meta-compound.

3 : 3′-*Diamidobenzidine* is prepared by reducing 3 : 3′-dinitrobenzidine with a hydrochloric acid solution of stannous chloride, and is precipitated by ammonia from solutions of its salts in silvery plates, which blacken rapidly in the air.

3 : 3′-*Diamidobenzidine hydrochloride*, $C_{12}H_6(NH_3Cl)_4+2H_2O$, crystallizes in needles, which readily dissolve in water, and quickly become brown in the moist condition. On addition of dilute sulphuric acid to its solution, the *basic sulphate*, $C_{12}H_6(NH_2)_2(NH_3)_2SO_4$, separates out in slender needles.

On heating the hydrochloride with benzaldehyde copious evolution of hydrogen chloride takes place, which, together with other reactions, shows that the base is a 3 : 3′-diamido-compound, of the following constitution:



From this follows also the constitution of 3 : 3′-dinitrobenzidine and of 3 : 3′-dinitrodiphenyl.[1]

Tetramethyltetramidodiphenyl, $C_{12}H_6(NH_2)_2N_2(CH_3)_4$, is obtained by the reduction of dinitrotetramethylbenzidine, and crystallizes from alcohol in beautiful silvery plates, melting at 168°. Its solution in hydrochloric acid is coloured violet by ferric chloride.[2]

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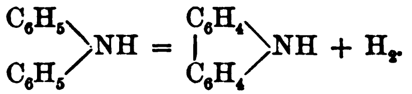
[1] Brunner and Witt, *Ber.* **20**, 1023.

[2] Michler and Pattinson, *Ber.* **17**, 115.

IMIDODIPHENYL OR CARBAZOLE, $C_{12}H_9N$.

2729 This compound was discovered by Graebe and Glaser together with other substances in crude anthracene. As it gave a crystalline picrate, it was regarded as a new hydrocarbon until analysis showed that it contained nitrogen.[1] Graebe then prepared it synthetically by passing the vapour of aniline or diphenylamine through a red-hot tube, which shows its constitution:

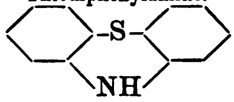


$$\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right>NH = \left.\begin{matrix}C_6H_4\\|\\C_6H_4\end{matrix}\right>NH + H_2.$$

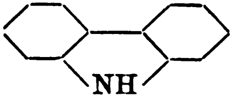
Only a portion of the diphenylamine is converted into carbazole, as the hydrogen set free acts on the remainder with formation of aniline, benzene, and ammonia.[2]

Carbazole is also formed when thiodiphenylamine is boiled for some hours with freshly reduced copper,[3] which is of interest inasmuch as it proves the exact constitution of the compound, Bernthsen having shown that thiodiphenylamine (Part III., p. 376) is formed by heating *o*-amidothiophenol with catechol.[4] The constitution of the two compounds is therefore represented by the formulæ:

Thiodiphenylamine.



Carbazole.



Carbazole likewise occurs in crude aniline, and is formed in quantity by the distillation of azodiphenyl-blue with lime.[5] It may also be prepared by heating 2:2′-diamidodiphenyl with 25 per cent. sulphuric acid or 15 per cent. hydrochloric acid at 200°, the yield being almost quantitative,[6] or by distilling 2-amidodiphenyl over lime.[7]

In order to obtain it, crude anthracene is washed with water containing sulphuric acid, and then extracted with ethyl acetate;

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[1] *Annalen*, **163**, 343.

[2] *Annalen*, **167**, 125; **174**, 180.

[3] Goske, *Ber.* **20**, 232.

[4] *Ber.* **19**, 3255.

[5] Witt, *Ber.* **20**, 1541.

[6] Täuber, *Ber.* **24**, 200.

[7] Blank, *Ber.* **24**, 306.

after evaporating off the latter, the residue is washed with carbon bisulphide, dissolved in hot toluene, and picric acid added. On cooling, the compound, $C_{12}H_9N + C_6H_3(NO_2)_3O$, crystallizes out in large red prisms, which melt at 182°. These are readily decomposed by ammonia and the carbazole purified by recrystallization from alcohol or toluene.[1] It may also be obtained by distilling crude anthracene with caustic potash, when potassium carbazole, $C_{12}H_8NK$, remains behind, and may be decomposed by water.[2]

It is sparingly soluble in alcohol, ether, acetic acid, benzene, &c., in the cold, but more readily on warming,[3] and crystallizes in plates or tablets, melting at 238°. It readily sublimes, and boils at 354—355°, the sp. gr. of its vapour being 5·86—5·90. It may be distilled without alteration over red-hot zinc dust, and is not attacked by concentrated hydrochloric acid, or alcoholic potash at 300°.

It dissolves in concentrated sulphuric acid with a yellow or brownish-yellow colour, which changes to a beautiful green on addition of chlorine, oxides of nitrogen, or other oxidizing agents. If a piece of pine-wood be saturated with an alcoholic solution of carbazole, and exposed to the action of hydrogen chloride, it assumes a deep red colour; and if a mixture of carbazole and isatin be dissolved in concentrated sulphuric acid, a deep blue colouration is produced. If sulphuric acid be diluted with two volumes of acetic acid, and a mixture of quinone and carbazole added, an intense carmine-red solution is obtained, from which water precipitates a red or reddish-violet colouring matter.[4]

Methylcarbazole, $C_{12}H_8NCH_3$, is formed when carbazole is fused with twice its weight of caustic potash, and the product heated with methyl iodide at 170—190°. It crystallizes from alcohol in needles or nacreous plates, melts at 87°, and forms a *picrate*, crystallizing in dark red needles, which melt at 141°.[5]

Ethylcarbazole, $C_{12}H_8NC_2H_5$, crystallizes from ether in plates, melts at 67—68°, and likewise forms a *picrate*, which crystallizes in pale red needles, melting at 97°.

Acetylcarbazole, $C_{12}H_8.N.CO.CH_3$, is formed by heating carbazole with acetic anhydride at 250°, and crystallizes from dilute alcohol in flat prisms, melting at 69°.

Benzoylcarbazole, $C_{12}H_8N.CO.C_6H_5$, is prepared by heating

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[1] Zeidler, *Annalen*, **191**, 296.

[2] Graebe, *Annalen*, **202**, 19.

[3] Zechi, *Ber.* **12**, 1976.

[4] Hooker, *Ber.* **21**, 3299.

[5] Graebe and B. v. Adderskron, *Annalen*, **202**, 23.

carbazole with benzoyl chloride at 160—170°, and crystallizes from alcohol in pale green silky needles, melting at 98·5°. It is decomposed by alcoholic potash, but not by the aqueous solution, and does not unite with hydroxylamine or phenylhydrazine.[1]

Nitrosocarbazole, $C_{12}H_8N.NO$, is obtained when carbazole is suspended in a mixture of ether and acetic acid, and potassium nitrite added. It crystallizes from alcohol in flat yellow needles, which have a golden lustre, and melt at 82° (Zeidler).

Trichlorocarbazole, $C_{12}H_6Cl_3N$, was obtained by Graebe and Knecht by the action of chlorine on carbazole suspended in acetic acid, the solution becoming first bluish-green, then pale green, yellow, and finally orange. On addition of water to the pale green solution, trichlorocarbazole separates out, and crystallizes from benzene in long greenish-yellow needles, which melt at 180°, sublime in beautiful needles, and boil at about the same temperature as sulphur. It dissolves in pure sulphuric acid with a pale green colour, which is changed to emerald green by a trace of nitric acid, and disappears on warming. It is not attacked by alcoholic potash, and forms an unstable *picrate* crystallizing in red needles, and melting at 100°.[2]

Hexchlorocarbazole, $C_{12}H_3Cl_6N$, is obtained by passing in chlorine till the solution has assumed a deep red colour, and no more chlorine is absorbed. It crystallizes from benzene in long yellow needles, which melt with decomposition at 225°, and dissolve without alteration in hot concentrated nitric acid. It dissolves with difficulty in sulphuric acid, forming a yellowish-green solution, which on addition of a trace of nitric acid becomes blue, violet, red, and finally yellow.

Octochlorocarbazole, $C_{12}HCl_8N$, is formed by the action of antimony pentachloride on the foregoing compound, and crystallizes from benzene in slender white needles, melts at 275°, and sublimes without decomposition. It is insoluble in pure sulphuric acid, but in presence of a trace of nitric acid goes into solution with a beautiful blue colour, which then changes to golden-yellow. On heating with antimony pentachloride it forms hexchlorobenzene.

Nitrocarbazole, $C_{12}H_7(NO_2)NH$, is obtained by the hydrolysis of benzoylnitrocarbazole, and crystallizes from boiling alcohol in plates or scales, which melt at 210° to a red liquid. It is very sparingly soluble in hot acetic acid, chloroform and benzene, and almost insoluble in ether and light petroleum.

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[1] Mazzara, *Ber.* **24**, 278.

[2] *Annalen*, **202**, 27.

Benzoylnitrocarbazole, $C_{12}H_7(NO_2)N.CO.C_6H_5$, is prepared by the action of nitric acid of sp. gr. 1·48 on a solution of benzoylcarbazole in hot acetic acid, and crystallizes from the latter in yellow lustrous plates, which melt at 180°, are fairly soluble in warm ether and benzene, very sparingly in alcohol and light petroleum.[1]

Carbazoledisulphonic acid, $C_{12}H_7N(SO_3H)_2$, is prepared by warming carbazole with concentrated sulphuric acid. In order to separate the compound it is converted into the barium salt, and the latter decomposed by sulphuric acid. The solution is then treated with a 3 per cent. solution of potassium permanganate as long as it is decolourized, whereby certain impurities are oxidized which would otherwise prevent the crystallization of the acid. On evaporation the *potassium salt* separates out in microscopic cubes. To obtain the free acid, hydrofluosilicic acid and alcohol are added to a concentrated solution of the potassium salt, the precipitate filtered off after some days, and the filtrate concentrated. Carbazoledisulphonic acid then crystallizes out in white silky needles.[2]

Dinitrocarbazole, $C_{12}H_6(NO_2)_2NH$, is formed when 4 parts of nitric acid (sp. gr. 1·38) are slowly added with constant stirring to a mixture of 4 parts of carbazole and 15 parts of acetic acid, and the whole heated for half an hour at 100°; on cooling it separates out as a yellow crystalline powder.[3]

Tetranitrocarbazole, $C_{12}H_4(NO_2)_4NH$, is obtained by gradually adding carbazole to 30 parts of concentrated nitric acid and warming to 100°. It is almost insoluble in alcohol, ether, and benzene, and separates from acetic acid in slender, citron-yellow crystals, which on boiling with dilute caustic potash yield the reddish-brown crystalline *potassium* salt, $C_{12}H_4(NO_2)_4NK$; the latter is insoluble in water, and is readily decomposed by acids (Graebe and Behaghel).

According to Ciamician and Silber, when carbazole is added to 12 parts of fuming nitric acid and the whole warmed, a mixture of four tetranitrocarbazoles is formed. On cooling, the first three described below are precipitated, and may be separated by crystallization from acetic acid; from the nitric acid mother-liquor water precipitates the δ-compound, which is formed in the largest quantity.[4]

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[1] Mazzara, **24**, 280.
[2] Bechhold, *Ber.* **23**, 2144.
[3] Bad. Anilin. u. Soda. Fabrik. *Ber.* **22**, 177 c.
[4] *Gazzetta*, **12**, 277.

α, small needles, melting at 308° with decomposition.

β, pale-yellow hexagonal tablets, which do not melt at 320°.

γ, pale-yellow rhombic tablets, melting at 285° with decomposition.

δ, small yellow quadratic prisms, which decompose without melting.

4-*Amidocarbazole*, $C_{12}H_7(NH_2)NH$, is formed by distilling diphenyline over quicklime, and crystallizes from water in slender needles, melting at 238°, very similar in appearance to those of benzidine.[1]

Diamidocarbazole, $C_{12}H_6(NH_2)_2NH$, is obtained by the reduction of dinitrocarbazole with tin and hydrochloric acid, and crystallizes in silvery plates, which are sparingly soluble in water and do not melt at 250°. The *hydrochloride* forms long slender needles, which are sparingly soluble in hydrochloric acid, whilst the *sulphate*, which crystallizes in slender needles, is sparingly soluble in water, but readily in dilute acids. It is employed in the manufacture of carbazole yellow.

4 : 4′-*Diamidocarbazole*, $C_{12}H_6(NH_2)_2NH$, is prepared by heating 2 : 2′-diamidobenzidine hydrochloride with 6 times its weight of 18 per cent. hydrochloric acid at 180—190°. The somewhat dark-coloured product is evaporated to dryness, the aqueous solution of the residue boiled with animal charcoal, and mixed with an excess of dilute sulphuric acid. 4 : 4′-*Diamidocarbazole sulphate*, $C_{12}H_{11}N_3.H_2SO_4$, separates in colourless needles, or if the solution be concentrated, as a white crystalline precipitate, which is almost insoluble in boiling water. The *hydrochloride* is fairly soluble in water, and separates out in a crystalline condition on adding hydrochloric acid. The free base is readily obtained from the hydrochloride, and crystallizes from alcohol in flat silvery needles, which blacken at 200° and then form a tarry mass. It yields tetrazo-colours which dye cotton fabrics directly, in similar shades to the benzidine colours.[2]

2730 *Carbazoline*, $C_{12}H_{15}N$, is formed by heating carbazole with hydriodic acid and amorphous phosphorus at 220—240°, and is a weak base, which separates from solutions of its salts on addition of an alkali as a precipitate of microscopic needles, which soon unite to form large needles. It crystallizes from alcohol, ether, benzene, &c., in long flat silky needles, which readily sublime, melts at 99°, and boils at 296—297°, its vapour having the sp. gr. 6·06. Its smell is characteristic, and

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[1] Blank, *Ber.* **24**, 306.

[2] Täuber, *Ber.* **23**, 3266.

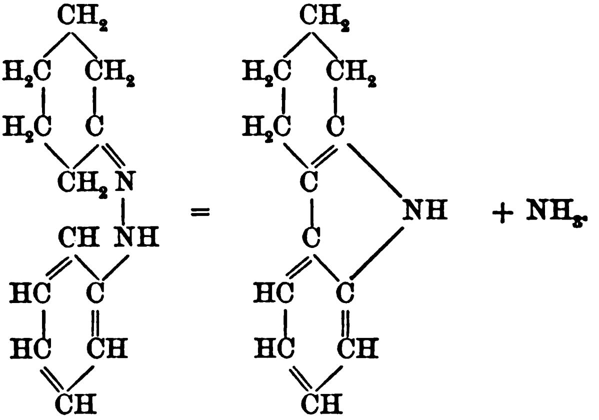
exceedingly pungent when warm; it is readily attacked by oxidizing agents with formation of dirty-green or brown products, and on heating at 300—360° yields a hydrocarbon, $C_{12}H_{20}$, boiling at 225°, which has not been further examined.

Carbazoline hydrochloride, $C_{12}H_{15}N.HCl$, remains as a syrup on evaporating the aqueous solution, and separates in the same form when hydrogen chloride is passed into an ethereal solution of the base; on standing, however, it gradually crystallizes in thick, hard tablets. On long-continued heating at 300°, it loses hydrogen chloride and hydrogen, forming the non-basic compound *a-hydrocarbazole*, $C_{12}H_{13}N$, which forms crystals having a smell resembling that of *a*-naphthylamine, melts at 120°, boils at 325—330°, and forms a *picrate* crystallizing in brown plates.[1]

Ethylcarbazoline, $C_{12}H_{14}N.C_2H_5$, is formed by heating carbazoline with ethyl iodide and alcohol. The *hydriodide* then crystallizes out in tablets.

Acetylcarbazoline, $C_{12}H_{14}N.CO.CH_3$, is prepared by heating carbazoline with acetic anhydride; it is readily soluble in alcohol, crystallizing from the solution in beautiful, white needles, which melt at 98° (Graebe and Behaghel).

β-Hydrocarbazole, $C_{12}H_{13}N$. By the electrolysis of phenol with alternating currents Dreschel obtained the compound *hydrophenoketone* or *ketohexhydrobenzene*, $C_6H_{10}O$. This forms a crystalline hydrazone, which is converted by the action of dilute acid into *hydrophenanilide* or *β-hydrocarbazole*.[2] This reaction corresponds to the indole syntheses of Emil Fischer:[3]



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[1] Glaser and Graebe, *Annalen*, **163**, 352; **170**, 88. [2] *J. Pr. Chem.* II. **38**, 65.
[3] Baeyer and Tutein, *Ber.* **22**, 2184; E. Fischer, *Annalen*, **236**, 116.

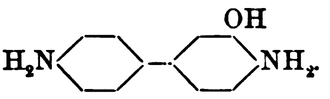
Tetrahydrocarbazole crystallizes in colourless plates, which melt at 108°, and are sparingly soluble in water, readily in alcohol.

AMIDOHYDROXYDIPHENYLS.

2731 4:4'-*Diamido-3-hydroxydiphenyl*, or *Hydroxybenzidine*, $C_{12}H_7(OH)(NH_2)_2$. By the action of a solution of phenol-*p*-sulphonic acid in caustic soda on diazobenzene chloride, *sodium benzeneazophenolsulphonate*, $C_6H_5.N_2.C_6H_3(OH)SO_3Na$, is obtained, and crystallizes in yellow plates. When this is triturated with water and gradually added to a hydrochloric acid solution of stannous chloride, reduction accompanied by intermolecular change takes place, and on evaporating the solution after removal of the tin by sulphuretted hydrogen, the hydrochloride of *diamidohydroxydiphenylsulphonic acid* separates out in large clear crystals; these are converted on heating with water at 180° into *diamidohydroxydiphenyl sulphate*, $C_{12}H_7(OH)(NH_3)_2SO_4$, which is almost insoluble in water, but dissolves more readily in dilute hydrochloric acid. The free base separates out on addition of caustic soda in colourless plates, which melt at 185°, and are sparingly soluble in water, alcohol, and ether, but readily in alkalis, the latter solution quickly undergoing oxidation in the air.[1] It is also formed when benzidinesulphone is fused with caustic soda:[2]

$$C_{12}H_6(NH_2)_2SO_2 + 2NaOH = C_{12}H_7(NH_2)_2OH + Na_2SO_3.$$

Its constitution is represented by the following formula:



4:4'-*Diamido-3-ethoxydiphenyl*, $C_{12}H_7(OC_2H_5)(NH_2)_2$, is prepared in a similar manner from benzeneazophenetoïlsulphonic acid, $C_6H_5.N_2.C_6H_3(OC_2H_5)SO_3H$, and crystallizes in lustrous flat needles, which melt at 134—135°, and are sparingly soluble in water, readily in alcohol, but insoluble in alkalis. Its difficultly soluble *sulphate* forms prisms, and dissolves in hydrochloric acid with formation of a basic salt. On heating the ethyl compound with hydrochloric acid under pressure it yields ethyl chloride and diamidohydroxydiphenyl hydrochloride.

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[1] Weinberg, *Ber.* **20**, 3171.

[2] Griess and Duisberg, *Ber.* **22**, 2468.

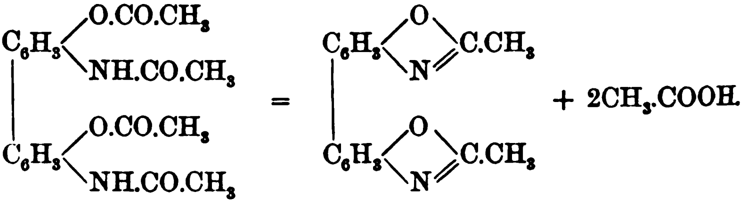
AMIDO-DIPHENOLS.

2732 3 : 3'-*Diamido-γ-diphenol*, $C_{12}H_6(NH_2)_2(OH)_2$, is obtained by the reduction of 3 : 3'-dinitro-γ-diphenol; it crystallizes in colourless needles or plates, and its readily soluble *hydrochloride*, $C_{12}H_6(NH_3Cl)_2(OH)_2$, forms needles or nodules. The alcoholic ammoniacal solution assumes a deep-green colour in the air.

Diacetyldiamido-γ-diphenol, $C_{12}H_6(NH.CO.CH_3)_2(OH)_2$, was obtained by Schütz by the action of acetic acid on diamido-γ-diphenol, and crystallizes in white needles which melt at 210°, and are soluble in alkalis but not in acids.

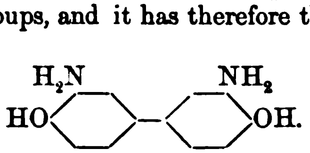
Tetracetyldiamido-γ-diphenol, $C_{12}H_6(NH.CO.CH_3)_2(O.CO.CH_3)_2$, was prepared by Kunze by boiling diamido-γ-diphenol with acetic anhydride; it crystallizes in white needles, which melt at 225°, and on more strongly heating lose acetic acid, passing into the following compound.

Diethenyldiamido-γ-diphenol is formed according to the equation



Schütz also obtained it by heating diamido-γ-diphenol with acetyl chloride at 150°. It crystallizes in colourless prisms, melting at 195°, and is soluble in acids but not in alkalis.

The formation of this anhydro-compound shows that the amido-groups in diamido-γ-diphenol, occupy the ortho-position to the hydroxyl groups, and it has therefore the constitution:



This also shows the constitution of 3 : 3'-dinitro-γ-diphenol.[1]

Tetramido-γ-diphenol, $C_{12}H_4(NH_2)_4(OH)_2$, is prepared by the reduction of the corresponding dinitro-compound, and crystallizes in white needles or silvery plates, which become blue in the air. On passing air through its solution in alcoholic ammonia,

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[1] Kunze, *Ber.* **21**, 3331; Schütz *Ber.* **21**, 3530.

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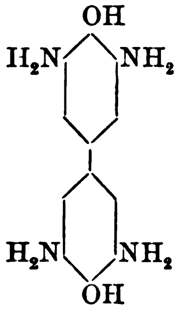
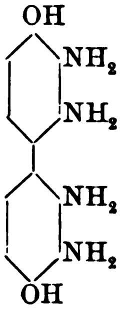
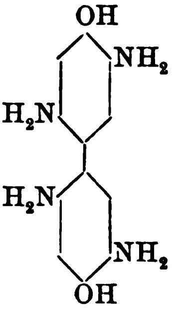
tetramidodibenzoquinone, $C_{12}H_4(NH_2)_4O_2$, separates out in blue-black needles, which have a bronze lustre.

Hexacetyltetramido-γ-diphenol, $C_{12}H_4(NH.CO.CH_3)_4(O.CO CH_3)_2$, separates as a crystalline powder on boiling the base with acetic anhydride, and on warming with caustic soda yields the *tetracetyl* compound, $C_{12}H_4(NH.CO.CH_3)_4(OH)_2$, which crystallizes in lustrous needles, melting at 280°.

The constitution of tetramido-γ-diphenol may be represented in different ways, as for example:







Künze assumed the first of these formulæ, but Schütz found that it yields with acetyl chloride a diethenyl base, which he states is soluble in alkalis, and must therefore contain a hydroxyl group. Such a compound can only be formed if the constitution of the base is represented by the second or third formula, and of those Schütz gives preference to the second.

2:2′-*Diamidodiphenetoïl*, or *Diphenetidine*, $[C_6H_3(OC_2H_5)NH_2]_2$, is obtained from *o*-nitrophenetoïl, $C_6H_4(NO_2)OC_2H_5$, by converting it into hydrazophenetoïl and heating the latter with concentrated hydrochloric acid, or better by adding the hydrazo-compound to a warm hydrochloric acid solution of stannous chloride, boiling for a short time and concentrating. On cooling, the double-salt, $C_{12}H_6(OC_2H_5)_2(NH_3Cl)_2 + 2SnCl_2$, crystallizes out in beautiful rhombic plates. On decomposition with sulphuretted hydrogen the *hydrochloride* is obtained, and crystallizes in tablets or concentric aggregates of needles. The base, which may be separated by ammonia, forms plates or needles, which are scarcely soluble in cold, more readily in hot water, and easily in alcohol. On shaking its ethereal solution with a trace of bromine a beautiful moss-green compound separates, which readily becomes brown.[1]

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[1] Möhlau, *J. Pr. Chem.* II. **19**, 381.

Dianisidine, $[C_6H_3(OCH_3)NH_2]_2$, is obtained on the large scale in a similar manner from *o*-nitranisoïl, and likewise crystallizes in plates. Both this and the previous compound are employed in the colour industry.[1]

Diamido-diphenylene oxide, $C_{12}H_6(NH_2)_2O$, is formed by heating benzidinedisulphonic acid with caustic soda under pressure, and crystallizes from hot water in white needles, melting at 150—152°. Its *hydrochloride* is readily, and its *sulphate* sparingly soluble. It is also employed in the preparation of azo-colours.[2]

4 : 4′-*Diamido*-2 : 2′ : 3 : 3′-*tetrahydroxydiphenyl*, $C_{12}H_4(NH_2)_2(OH)_4$. The *ethyl* ether of this compound is formed when nitro-*p*-diethoxybenzene is warmed with zinc dust and alcoholic potash, and the *tetra-ethoxyhydrazobenzene* thus obtained, heated with hydrochloric acid. It crystallizes from dilute alcohol in plates, melting at 120°, and forms a *hydrochloride* which crystallizes in slender silky needles; on addition of oxidizing agents to its solutions these assume a dark-brown colour, and a precipitate which has a metallic lustre is formed.[3]

TETRAZO-DERIVATIVES OF DIPHENYL.

2733 These compounds, which contain the diazo-group twice, were also discovered by Griess.[4]

Tetrazodiphenyl nitrate, $(C_6H_4.N{=}N.NO_3)_2$, is readily formed when nitrogen trioxide is passed into a cold concentrated solution of benzidine nitrate. On addition of alcohol and ether it separates in white or yellowish needles, which are readily soluble in water, sparingly in alcohol, insoluble in ether, and on heating explode as violently as diazobenzene nitrate. Hot water decomposes it into nitric acid, nitrogen and γ-diphenol. On addition of platinum chloride to its solution, the *platinochloride*, $C_{12}H_8N_4PtCl_6$, separates out in pale-yellow narrow plates or small six-sided tablets greater in length than in width, according to the concentration. On heating with soda it decomposes, forming 4 : 4′-dichlorodiphenyl.

Tetrazodiphenyl sulphate, $(C_{12}H_8N_4SO_4)_2H_2SO_4$, separates on addition of sulphuric acid and alcohol to a solution of the

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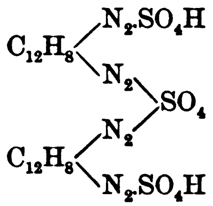
[1] Farbenfabr. vorm. Bayer and Co., *Friedländer's Theerfarben*, 488.

[2] Farbenfabr. vorm. Bayer and Co., *Chem. Zeit.* **1889**, 1240; Schultz, *Steinkohlentheer*, **2**, 1179.

[3] Nietzki, *Annalen*, **215**, 146.

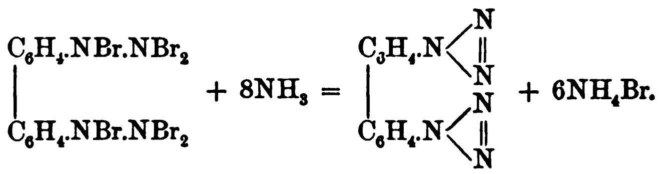
[4] *Journ. Chem. Soc.* **1867**, 94.

nitrate as a crystalline precipitate or in white needles, which have the following constitution :



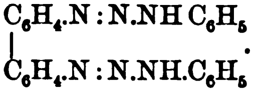
• It is very explosive when dry, and yields diphenyl on boiling with alcohol.

Tetrazodiphenyl perbromide, $C_{12}H_8N_4Br_6$, separates in rounded reddish crystals when bromine water is added to a solution of the nitrate. It is a very unstable compound, which is converted by boiling alcohol into 4 : 4′-dibromodiphenyl, and by aqueous ammonia into *tetrazodiphenylimide* or *ditriazodiphenyl* :

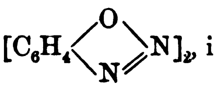


It is insoluble in cold water, sparingly soluble in cold, more readily in hot alcohol, and crystallizes in very lustrous white or yellowish plates, which melt at 127°, and on further heating decompose with a crackling noise.

Tetrazodiphenylamidobenzene separates as a yellow crystalline mass on addition of aniline to a solution of the nitrate. It crystallizes from hot alcohol, in which it is only sparingly soluble, in spear-shaped crystals, which are generally united in stellate aggregates, and explode on heating. Its constitution is represented by the following formula :



$$\begin{array}{l} C_6H_4.N:N.NH\,C_6H_5 \\ | \\ C_6H_4.N:N.NH.C_6H_5 \end{array}.$$

Tetrazodiphenol,  is formed by the action of sodium nitrite on a solution of 3 : 3′-diamido-γ-diphenol, crystallizes in red needles, and when freshly prepared dissolves in hydrochloric acid forming a red solution, which is reprecipitated by ammonia.[1]

HYDRAZINE-DERIVATIVES OF DIPHENYL.

2734 *Diphenylenehydrazine*, $(C_6H_4.NH.NH_2)_2$, is most readily obtained by dissolving 50 grams of benzidine hydrochloride in 40 grams of 37 per cent. hydrochloric acid, and 500 c.c. of water, and diazotizing the well-cooled solution with the calculated quantity of sodium nitrite. The product is then added to a cooled hydrochloric acid solution of stannous chloride, and heated for about two hours on the water-bath till the scum has disappeared, and the diphenylenehydrazine hydrochloride has separated as a dirty-brown precipitate. An equal volume of water and some animal charcoal is then added, and the whole boiled and filtered hot. The salt which separates on cooling is decomposed by ammonia, or better by sodium acetate in hot solution, when diphenylenehydrazine separates out in lustrous plates, which quickly become yellow and then brown, and melt at 167° with decomposition. It reduces Fehling's solution, is sparingly soluble in alcohol and ether, more readily in acetic acid, and also fairly soluble in hot water, from which it crystallizes in slightly coloured, very slender needles.

Its *hydrochloride* crystallizes from hot water in rosette-shaped aggregates of small needles, which are sparingly soluble in water, and still less in hydrochloric acid and alcohol. The *sulphate* is likewise sparingly soluble in cold water, and crystallizes from the hot liquid in spherical aggregates of needles.

Diphenylenedinitrosohydrazine, $[C_6H_4.N(NO).NH_2]_2$, separates on mixing solutions of the hydrochloride and sodium nitrite as a pale yellow precipitate, which melts at 112—113° with decomposition, is sparingly soluble in alcohol, more readily in acetone. It is fairly stable in the dry state, but rapidly decomposes in solution.

Diphenylenedisemicarbazide, $(C_6H_4.NH.NH.CO.NH_2)_2$, is formed by adding potassium cyanate to a solution of the diphenylenehydrazine hydrochloride, and is sparingly soluble in

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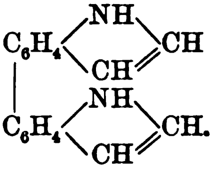
[1] Künze, *Ber.* **21**, 3331.

water, alcohol, and ether, more readily in acetic acid, and crystallizes from alcohol in slender needles, which melt with decomposition at 306—308°. Its *hydrochloride* separates from hot water in colourless plates.

Diphenylenediacetonehydrazone, $[C_6H_4.N_2H{=}C(CH_3)_2]_2$, is prepared by dissolving the hydrazine in acetone; on evaporating off the excess of the latter, and pouring the dark-red liquid into water, a reddish-yellow precipitate is formed, which may be recrystallized from ether. The compound is very unstable, especially when moist, and melts at 197—198° with decomposition.

On heating with zinc chloride at 215—220° it is converted into *diphenodimethylindole*, $C_{18}H_{18}N_2$, which is purified by distillation in vacuo and washing with ether. It forms a pale yellow mass, which melts at 270°, and in alcoholic solution slowly colours pine-wood dipped in hydrochloric acid, first orange and then dark-red.[1] It has the following constitution:



Diphenoldihydrazine, $C_{12}H_6(OH)_2(N_2H_3)_2$. On addition of stannous chloride to a hydrochloric acid solution of tetrazodiphenol, the *hydrochloride* of this compound is obtained. It crystallizes in slender white needles, and on treatment with ammonia yields diphenolhydrazine in colourless crystalline spangles, which melt with complete decomposition at 140°. It reduces Fehling's solution and ammoniacal silver solution, even in the cold.

Diphenoldiacetonehydrazone, $C_{12}H_6(OH)_2[N_2H.C(CH_3)_2]_2$. On addition of acetone to a solution of the hydrochloride till it commences to become turbid, this compound separates out in rhombic plates, melting at 200°, which are insoluble in alcohol and ether, sparingly soluble in ammonia, but readily in caustic soda.[2]

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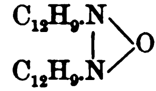
[1] Arheidt, *Annalen*, **239**, 206.

[2] Kunze, *Ber.* **21**, 3331.

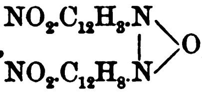
AZO-DERIVATIVES OF DIPHENYL.

2735 4-*Azodiphenyl*, $C_{12}H_9.N_2.C_{12}H_9$, is formed by the action of sodium amalgam on an ethereal solution of 4-nitrodiphenyl, but is best prepared by mixing hot alcoholic solutions of 4-hydrazodiphenyl and ferric chloride; it separates as a red precipitate, which is insoluble in alcohol and acetic acid, but dissolves readily in ether, and crystallizes from benzene in well-developed orange-red tablets, melting at 249—250°.

4-*Hydrazodiphenyl*, $C_{12}H_9.NH.NH.C_{12}H_9$. Zimmermann prepared this compound by heating azoxydiphenyl with alcoholic ammonium sulphide. It crystallizes from alcohol in small white satiny tablets, which melt at 247°, and become brown in the air. On distillation it forms azodiphenyl and 4-amidodiphenyl, but is unaltered by hydrochloric acid at 280°.



Azoxydiphenyl, $\left.\begin{array}{l} C_{12}H_9.N \\ \quad | \\ C_{12}H_9.N \end{array}\right\rangle O$, is formed by boiling 4-nitrodiphenyl with alcoholic potash, and crystallizes in yellowish scales, which melt at 205°, are sparingly soluble in acetic acid, and insoluble in alcohol.[1]



Dinitroazoxydiphenyl, $\left.\begin{array}{l} NO_2.C_{12}H_8.N \\ \qquad\quad | \\ NO_2.C_{12}H_8.N \end{array}\right\rangle O$, is formed when sodium amalgam is added to 4 : 4′-dinitrodiphenyl suspended in alcohol. It is insoluble in the common solvents, but dissolves in boiling aniline with a beautiful orange-red colour, and separates on cooling as a brick-red crystalline powder, which melts at 255°, By the action of tin and hydrochloric acid, or of alcoholic ammonium sulphide at 115°, it is reduced to benzidine.[2]

Derivatives of 4-azodiphenylsulphonic acid are obtained by diazotizing a hydrochloric acid solution of 4-amidodiphenylsulphonic acid with sodium nitrite, and adding an alkaline phenol solution.

Sodium phenolazodiphenylsulphonate, $C_6H_4(OH)N_2.C_{12}H_8.SO_3Na$, is an amber-yellow precipitate, which readily dissolves in hot water, and colours wool or silk a beautiful yellow.

Sodium resorcinolazodiphenylsulphonate, $C_6H_3(OH)_2N_2.C_{12}H_8.SO_3Na$, is a brick-red crystalline precipitate, which on drying becomes brown. It is readily soluble in hot water, and dyes wool, silk, and unbleached jute a beautiful orange.

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[1] Zimmermann, *Ber.* **13**, 1960.

[2] Wald, *Ber.* **10**, 137.

Sodium quinolazodiphenylsulphonate, $C_6H_3(OH)_2.N_2.C_{12}H_8.SO_3Na$, is readily soluble in water, and dyes silk and unbleached jute amber-yellow.

Sodium a-naphtholazodiphenylsulphonate, $C_{10}H_6(OH)N_2.C_{12}H_8 SO_3Na$, is a fairly soluble brownish-black precipitate, which dyes the above fabrics deep reddish-brown. The corresponding β-compound is a pale red precipitate, easily soluble in hot water, and dyes a beautiful red.[1]

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[1] Carnelley and Schlesselman, *Journ. Chem. Soc.* **1886**, I. 380.

METHYLDIPHENYL GROUP.

2736 *o-Phenyltolyl* or *2-Methyldiphenyl*, $C_6H_5.C_6H_4.CH_3$, was prepared by Barbier, by acting with sodium on a mixture of bromobenzene and liquid bromotoluene. It is a liquid which boils at 258—260°, and has an odour resembling that of diphenyl.[1]

m-Phenyltolyl or *3-Methyldiphenyl* is formed together with other hydrocarbons by the action of methyl chloride on a mixture of diphenyl and aluminium chloride, and is a strongly refractive liquid, which boils at 272—277°, and is oxidized by chromium trioxide to *m*-phenylbenzoic acid.[2]

4 : *4′-Diamido-3-methyldiphenyl*, $C_6H_4(NH_2).C_6H_3(NH_2)CH_3$, is prepared on the large scale by heating *o*-toluidine with nitrobenzene and powdered caustic soda at 180°, whereby a mixture of methylazobenzene and methylazoxybenzene is obtained, which on reduction with zinc dust and caustic soda yields the hydrazo-compound. The latter is converted by the action of hydrochloric acid into the isomeric 4 : 4′-diamido-3-methyldiphenyl, which separates on addition of caustic soda as a thick syrup, and gradually solidifies to a glassy mass.[3]

4 : *4′-Diamido-3′-hydroxy-3-methyldiphenyl*, $C_6H_3(NH_2)(OH)$ $C_6H_3(NH_2)CH_3$, is prepared by heating *o*-toluene-azophenylsulphonic acid with water, and crystallizes in nacreous plates which melt at 177°, and are readily soluble in alkalis. Its *sulphate* forms crystals sparingly soluble in water.

4 : *4′-Diamidoethoxyphenyltolyl*, $C_{12}H_5(CH_3)(NH_2)_2OC_2H_5$, is prepared in a similar manner, and crystallizes in flat needles which melt at 117·5°, and are converted by heating with hydrochloric acid into the foregoing compound, which has the constitutional formula:[4]

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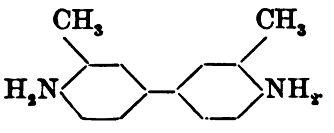
[1] *Ber.* **7**, 1548.

[2] Adam, *Bull. Soc. Chim.* **49**, 57 ; *Ann. Chim. Phys.* [6] **15**, 239.

[3] *Farbenfabr.* vorm. Bayer and Co. ; *Chem. Zeit.* **14**, 1144.

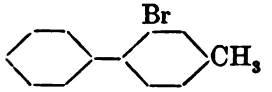
[4] Weinberg, *Ber.* **20**, 3171.

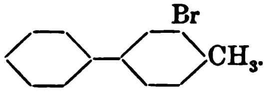


p-Phenyltolyl or *4-Methyldiphenyl* was prepared by Carnelley by the action of sodium on a mixture of bromobenzene and pure *p*-bromotoluene, benzene, toluene, diphenyl, ditolyl, and other products of high boiling-point being also formed.[1] A larger yield is obtained by passing a mixture of benzene and toluene vapours through an iron tube filled with pumice stone and heated to dull redness; a series of other hydrocarbons, including naphthalene, diphenyl, *o*-*p*-ditolyl, phenanthrene, anthracene, diphenylbenzene, &c., is also formed.[2]

The fractionation of the product, weighing 1453 grms., yielded 231 grms. of *p*-phenyltolyl. This substance is a strongly refractive, pleasantly-smelling liquid, boils at 263—267°, and solidifies at a low temperature to crystals which melt between 2 and 3°. It is oxidized by dilute nitric acid to *p*-phenylbenzoic acid and by chromic acid to terephthalic acid.

p-Phenylbromotolyl, $C_6H_5.C_6H_3Br.CH_3$, is obtained, together with the substance next to be described, when the calculated quantity of bromine is gradually added to a solution of the hydrocarbon in carbon disulphide. The solvent is then distilled off and the residue heated with caustic soda solution, washed with water and extracted with boiling alcohol. The crude product crystallizes out on cooling and is purified by recrystallization. It forms nacreous tablets, melts at 127—129°, and is scarcely soluble in cold, slightly in boiling alcohol, and readily in benzene. An acetic acid solution of chromic acid converts it into bromoterephthalic acid, no other product being formed, so that its constitution must be represented by one or other of the following formulæ:[3]





p-Bromo-p-phenyltolyl, $C_6H_4Br.C_6H_4.CH_3$, separates out as a yellow oil when the mother liquor of the preceding compound is evaporated, and after being freed from alcohol and water,

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[1] *Journ. Chem. Soc.* 1876, **1**, 13.
[2] *Journ. Chem. Soc.* 1880, **1**, 701.
[3] Carnelley and Thomson, *Journ. Chem. Soc.* 1885, **1**, 588 ; 1887, **1**, 87.

solidifies on cooling to a yellow crystalline mass, melting at 27—30°. On oxidation it first yields *p*-bromophenylbenzoic acid and then *p*-bromobenzoic acid, and is therefore a dipara-compound.

a-Dibromo-p-phenyltolyl, $C_6H_4Br.C_6H_3Br.CH_3$, is formed, together with the *β*-compound, when two molecules of bromine are employed, the liquid being cooled at first, but afterwards heated gently for some time. After the evaporation of the carbon disulphide, the residue is repeatedly extracted with boiling alcohol, the small amount of the *a*-compound which is present being thus dissolved. It crystallizes in frond-shaped tablets, and on oxidation passes first into *a*-bromophenylbromobenzoic acid and then into *p*-bromobenzoic acid.

β-Dibromo-p-phenyltolyl, $C_6H_4Br.C_6H_3Br.CH_3$, is scarcely soluble in alcohol, but readily in benzene, and crystallizes from ether in needles, melting at 148—150°. It is converted by oxidation into *β*-bromophenylbromobenzoic acid and *p*-bromobenzoic acid.

Each of these compounds therefore contains one bromine atom in the para-position; the second atom of bromine is present in one compound in the position $CH_3 : Br = 1 : 2$, and in the other 1 : 3.

Nitro-p-phenyltolyl, $C_{12}H_8(NO_2)CH_3$, is formed when one part of nitric acid of sp. gr. 1·45 is added to a solution of one part of the hydrocarbon in three parts of glacial acetic acid, and crystallizes from hot alcohol in hard lustrous needles, melting at 141°. An oily mononitro-compound is also formed in the reaction, but has not been obtained pure.

Dinitro-p-phenyltolyl, $C_{12}H_7(NO_2)_2CH_3$, is prepared by the action of a mixture of six parts of nitric acid and one part of sulphuric acid, on three parts of the hydrocarbon. It crystallizes from alcohol in slender white needles, and melts at 153—157°.

Amido-p-phenyltolyl, $C_{12}H_8(NH_2)CH_3$, is obtained by the reduction of the mononitro-compound with tin and hydrochloric acid, and crystallizes in fascicular groups of needles, melting at 93—97°. The *hydrochloride* forms small silky needles or tablets.[1]

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[1] Carnelley, *Journ. Chem. Soc.* 1876, **1**, 20.

PHENYLBENZYL COMPOUNDS.

2737 *Phenylbenzyl alcohol*, $C_6H_5.C_6H_4.CH_2.OH$, was prepared by Adam by heating *m*-phenyltolyl to 150° with bromine, boiling the product with alcoholic potash and finally treating the ethyl ether thus obtained with hydriodic acid in the cold :

$$C_{12}H_9.CH_2.OC_2H_5 + HI = C_{12}H_9.CH_2.OH + C_2H_5I.$$

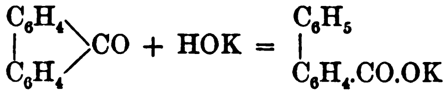
It is a thick liquid, without taste or odour, is not volatile with steam and is insoluble in water, but soluble in alcohol, ether, &c.

Phenylbenzyl methyl ether, $C_{12}H_9.CH_2OCH_3$, was prepared in a similar manner to the ethyl ether; it is a syrupy liquid, has a characteristic not unpleasant odour, and is volatile with steam.

Phenylbenzyl ethyl ether, $C_{12}H_9.CH_2.OC_2H_5$, is a similar substance.[1]

THE PHENYLBENZOIC ACIDS, $C_6H_5.C_6H_4.CO_2H$.

2738 *o-Phenylbenzoic acid* was first obtained by Fittig and Ostermayer, by fusing diphenyleneketone with caustic potash :[2]



$$\left.\begin{array}{l}C_6H_4\\ |\\ C_6H_4\end{array}\right\rangle CO + HOK = \begin{array}{l}C_6H_5\\ |\\ C_6H_4.CO.OK\end{array}$$

It is also formed, together with carbonyldiphenyl oxide, $CO(C_6H_4)_2O$, and other products, by the distillation of sodium salicylate with phenyl phosphate, and has been synthetically prepared from *o*-amidodiphenyl by diazotizing, converting the diazo-chloride into phenylbenzonitrile by a solution of cuprous potassium cyanide and heating this with alcoholic potash.[3] It is insoluble in cold, only very sparingly soluble in boiling water, and crystallizes from boiling alcohol in small transparent needles, or from a more dilute solution in well-developed, lustrous, four-

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[1] *Bull. Soc. Chim.* **49**, 97 ; *Ann. Chim. Phys.* VI. **15**, 242.
[2] *Annalen*, **166**, 374 ; Schmitz, *Annalen*, **193**, 120.
[3] Kaiser, *Annalen*, **257**, 99.

sided flat prisms with oblique terminations, the crystals being often an inch in length. It melts at 110—111°, and solidifies to a crystalline mass when slowly cooled; on rapid cooling, however, a transparent, viscid, glutinous mass is obtained, which becomes crystalline if it be stirred with a platinum wire. When it is heated with slaked lime, diphenyleneketone is again formed, together with a little diphenyl, the yield of which is larger when the calcium salt is heated by itself or the acid fused with potash, its production being accompanied by carbonization of the mass. Dilute nitric acid does not attack it even on boiling, whilst on heating with potassium dichromate and dilute sulphuric acid it is, like other ortho-compounds, completely destroyed.

Potassium o-phenylbenzoate, $C_{13}H_9O_2K + H_2O$, crystallizes in small, transparent prisms, and is readily soluble in water, but scarcely in concentrated caustic potash solution.

Calcium o-phenylbenzoate, $(C_{13}H_9O_2)_2Ca + 2H_2O$, is sparingly soluble in water, and forms small crystals, which redissolve very slowly even in a large quantity of boiling water, but do not then separate out again until the solution has been sufficiently concentrated.

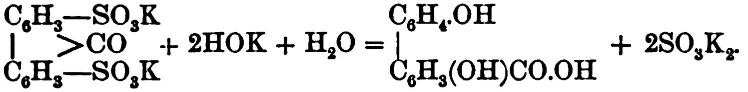
Barium o-phenylbenzoate, $(C_{13}H_{10}O_2)_2Ba + H_2O$, separates on the evaporation of a dilute solution in fascicular groups of crystals. When the mother liquor is cooled, no more of the salt separates out, and if it then be allowed to evaporate over sulphuric acid, crystallization does not occur until it is very concentrated; the amount of salt which separates out is increased by raising the temperature, but it does not appear to redissolve on cooling.

Silver o-phenylbenzoate, $C_{13}H_9O_2Ag$, is a flocculent precipitate, which crystallizes from hot water in transparent needles.

Ethyl-o-phenylbenzoate, $C_{13}H_9O_2.C_2H_5$, is prepared by passing hydrogen chloride into the alcoholic solution of the acid; it is a thick colourless liquid, boils at 300—305° and does not solidify at $-20°$.

Nitro-o-phenylbenzoic acid, $C_{12}H_8(NO_2)CO_2H$, is readily formed when *o*-phenylbenzoic acid is brought into fuming nitric acid; it crystallizes from alcohol in transparent monosymmetric tablets, and melts at 221—222°. The *calcium* salt is readily soluble in water, and separates out in anhydrous nodules on the spontaneous evaporation of its solution, this property being shared by the *barium* salt.

p-Dihydroxy-o-phenylbenzoic acid, $C_6H_4(OH)C_6H_3(OH)CO_2H$, is obtained when diphenyleneketonedisulphonic acid is fused with caustic potash:



$$\begin{array}{l}C_6H_3\text{—}SO_3K\\ |\quad >CO\\ C_6H_3\text{—}SO_3K\end{array} + 2HOK + H_2O = \begin{array}{l}C_6H_4.OH\\ |\\ C_6H_3(OH)CO.OH\end{array} + 2SO_3K_2.$$

It forms crystals melting at 270°, is sparingly soluble in water, readily in alcohol, and decomposes on heating with lime into carbon dioxide and γ-diphenol.[1]

m-Phenylbenzoic acid is formed, together with salicylic acid, *p*-hydroxybenzoic acid, α-hydroxyisophthalic acid, *p*-phenylbenzoic acid, and other amorphous yellow and brown products, when one part of benzoic acid is fused with six parts of caustic potash. It can also be obtained by the oxidation of *m*-phenyltolyl and also by brominating this substance and boiling the product with a solution of copper nitrate (Adam). It is only sparingly soluble in water, crystallizes from alcohol in dazzling white plates, melts at 160—161°, and decomposes into carbon dioxide and diphenyl when heated with slaked lime. Potassium dichromate and dilute sulphuric acid oxidize it to isophthalic acid.

Calcium m-phenylbenzoate, $(C_{13}H_9O_2)_2Ca + 3H_2O$, separates out in crusts when its solution is evaporated, and becomes anhydrous at 200°.

Barium m-phenylbenzoate, $2(C_{13}H_9O_2)_2Ba + 7H_2O$, is readily soluble in water, and crystallizes in fascicular groups of needles, which lose their water of crystallization at 180°.

The *silver* salt is a white, flocculent precipitate, which is not much acted on by light.

Ethyl m-phenylbenzoate, $C_{13}H_9O_2C_2H_5$, is a thick oily liquid, which distils without decomposition at a high temperature.[2]

p-Phenylbenzoic acid was obtained by Schultz by the oxidation of *p*-diphenylbenzene, $(C_6H_5)_2C_6H_4$, with an acetic acid solution of chromium trioxide.[3] It has been prepared synthetically by Doebner from the nitrile, which is formed by the distillation of potassium diphenylsulphonate with potassium cyanide, and on boiling with alcoholic potash is converted into the acid.[4]

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[1] Schultz, *Annalen*, **207**, 344.

[2] Barth and Schreder, *Monats.* **3**, 808.

[3] *Ber.* **6**, 415 ; *Annalen*, **174**, 213.

[4] *Annalen*, **172**, 111.

The latter is also formed, as already mentioned, by fusing benzoic acid with caustic potash, and by the oxidation of phenyltolyl.

It is scarcely soluble in cold, only sparingly in boiling water, readily in alcohol and ether, crystallizes from hot dilute alcohol in fascicular groups of long needles, melts at 218—219°, and readily sublimes in long, lustrous needles. On heating with an excess of lime it decomposes quantitatively into carbon dioxide and diphenyl, whilst chromium trioxide in acetic acid solution oxidizes it to terephthalic acid.

Calcium p-phenylbenzoate, $(C_{13}H_9O_2)_2Ca$, is obtained as a granular precipitate when calcium chloride is added to a solution of the ammonium salt. It is scarcely soluble in cold, sparingly in boiling water, and crystallizes on cooling in small plates.

Barium p-phenylbenzoate $(C_{13}H_9O_2)_2Ba$, closely resembles the calcium salt, and crystallizes from a hot saturated solution in thin lustrous plates.

The remaining salts, including even the ammonium salt, are either sparingly soluble or insoluble.

Ethyl p-phenylbenzoate, $C_{12}H_9.CO.OC_2H_5$, crystallizes from alcohol in hard colourless prisms, and melts at 46°.

p-Phenylbenzonitrile, $C_6H_5.C_6H_4.CN$, has in addition to the method described above, been prepared by Kaiser from p-amidodiphenyl in a similar manner to the ortho-compound. It separates from alcohol in hard compact crystals, melts at 84—85°, and distils without decomposition at a high temperature.

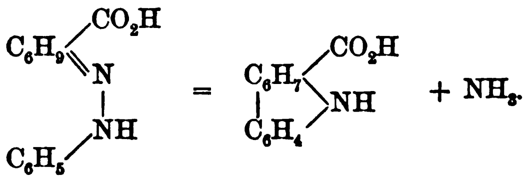
The following compounds, formed as already mentioned by the oxidation of the bromophenyltolyls, have only been slightly investigated:

	Melting-point.
p-Bromophenylbenzoic acid, $C_6H_4Br.C_6H_4.CO_2H$	193—194°
a-*p*-Bromophenylbromobenzoic acid, $C_6H_4Br.C_6H_3Br.CO_2H$, small needle-shaped prisms	202—204°
β-*p*-Bromophenylbromobenzoic acid, sublimes easily	231—232°

p-o-Dinitro-p-phenylbenzoic acid, $C_6H_4(NO_2)C_6H_3(NO_2)CO_2H$, is formed when *p*-phenylbenzoic acid is heated with ten parts of fuming nitric acid, and crystallizes from hot alcohol in small needles, melting at 252°. Its *methyl ester* forms long flat needles, and melts at 156°.

When the acid is reduced with stannous chloride and hydrochloric acid, and the hydrochloride of diamido-*p*-phenylbenzoic acid thus obtained distilled with lime, diphenyline is formed.[1]

β-Hydrocarbazolecarboxylic acid, $C_{13}H_{13}NO_2$, is obtained in a similar manner to β-hydrocarbazole (p. 420) by heating the hydrazone of ketohydrobenzoic acid with a mineral acid:



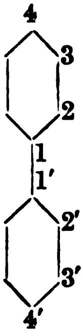
It dissolves in the alkali carbonates, and is re-precipitated by acids. On heating it melts at 230°, and decomposes at a somewhat higher temperature, products of a fæcal odour being formed, which redden a pine splinter moistened with hydrochloric acid.[2]

[1] Strasser and Schultz, *Annalen*, **210**, 191.

[2] Baeyer and Tutein, *Ber.* **22**, 2184.

DIMETHYLDIPHENYL GROUP.

2739 Twelve dimethyldiphenyls are theoretically possible, six of the formula $C_6H_5.C_6H_3(CH_3)_2$, and six *ditolyls*, $CH_3.C_6H_4.C_6H_4.CH_3$. Only the latter have hitherto been prepared, their constitutions being as follows:



2 : 2′ = diortho,
3 : 3′ = dimeta,
4 : 4′ = dipara,
2 : 3′ = orthometa,
2 : 4′ = orthopara,
3 : 4′ = metapara.

THE DITOLYLS.

o-Ditolyl is formed by the action of sodium on *o*-bromotoluene,[1] and is a strongly refractive liquid, which has a characteristic odour, somewhat resembling that of poplar buds, boils at 272°, and has a sp. gr. of 0·9945 at 16·5°. A crystalline hydrocarbon which was obtained by Fittig as a by-product and was considered by him to be dibenzyl, was probably *p*-ditolyl, since the liquid bromotoluene employed for the reaction certainly contained *p*-bromotoluene.

m-Ditolyl is prepared by acting upon an alcoholic solution of diamido-*m*-ditolyl with nitrogen trioxide,[2] and also occurs among

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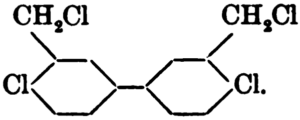
[1] Fittig, *Annalen*, **139**, 178; Luginin, *Ber.* **4**, 514.
[2] Schultz, *Ber.* **17**, 467; Stolle, *Ber.* **21**, 1096.

the products which are obtained by the action of methyl chloride on diphenyl in the presence of aluminium chloride.[1] It is an oily liquid, boils at 289°, and has a sp. gr. of 0·9993 at 16°. On oxidation it yields diphenyl-*m*-dicarboxylic acid and isophthalic acid.

Dichloro-m-ditolyl, $C_6H_3Cl(CH_3)C_6H_3Cl(CH_3)$, is formed when a solution of diamido-*m*-ditolyl in hydrochloric acid is diazotized and then treated with a hydrochloric acid solution of cuprous chloride; the intermediate compound, $C_{12}H_6(CH_3)_2(N_2Cl)_2 + Cu_2Cl_2$, is first formed as a dark-yellow or brown powder (p. 248) which readily decomposes. Dichloro-*m*-ditolyl crystallizes from alcohol in white plates with a fatty lustre, melts at 51°, and is oxidized to chloro-*m*-toluic acid by chromic acid. On heating to 220—240° with an acetic acid solution of hydriodic acid and phosphorus, it is converted into *m*-ditolyl.

Tetrachloro-m-ditolyl, $C_{14}H_{10}Cl_4$, is obtained when the substance just described is heated to 200° with phosphorus pentachloride. It is an oily liquid, but solidifies in a freezing mixture. On treatment with dilute nitric acid it yields dichlorodiphenyl-*m*-dicarboxylic acid and must therefore have the following constitution:



Dibromo-m-ditolyl, $C_{14}H_{12}Br_2$, has been prepared, as also the following compound, from diamido-*m*-ditolyl by the diazo-reaction; it crystallizes in yellow needles or plates, melting at 58—59°.

Di-iodo-m-ditolyl, $C_{14}H_{12}I_2$, crystallizes in yellow needles, melting at 99—100°.[2]

p-Ditolyl is formed by the action of sodium on *p*-bromotoluene dissolved in ether or light petroleum.[3] It crystallizes from hot alcohol in aggregates of small white plates, or when its ethereal solution is slowly evaporated in splendid monosymmetric prisms, with a vitreous lustre, melts at 121°, and boils at 283—288° without decomposition. Chromium trioxide acts upon it in acetic acid solution, with formation of tolylphenylcarboxylic acid,

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[1] Adam, *Bull. Soc. Chim.* **49**, 97; *Ann. Chim. Phys.* VI. **15**, 247.
[2] Stolle, *Ber.* **21**, 1096.
[3] Zincke, *Ber.* **4**, 369; Luginin, *Ber.* **4**, 514.

$CH_3.C_6H_4.C_6H_4.CO_2H$, melting at 245°, which is then converted by further oxidation into diphenyl-*p*-dicarboxylic acid.[1]

o-p-Ditolyl was found by Carnelley among the products obtained by the action of sodium on a mixture of bromobenzene and *p*-bromotoluene, and by passing the vapours of benzene and toluene through a red-hot tube (p. 431). The same hydrocarbon is without doubt a constituent of the liquid ditolyl which was obtained by Zincke and Luginin in the preparation of the para-compound, and which was probably a mixture of *o-p-* and *p*-ditolyl. The production of the former of these compounds is explained by the fact that the *p*-bromotoluene employed contained a little of the ortho-derivative. *o-p*-Ditolyl has not yet been obtained pure, since even after repeated fractionation it boils between 272—280°. On oxidation it yields a tolylphenylcarboxylic acid, melting at 180°, and terephthalic acid (Carnelley). Bromine converts it into the following substitution-products, by means of which its constitution has been determined.

a-Brom-o-p-ditolyl, $C_{12}H_7Br(CH_3)_2$, crystallizes from hot alcohol in slender, matted, microscopic needles, and melts at 95°. On oxidation it yields bromoterepthalic acid.

β-Brom-o-p-ditolyl is an oily liquid and is converted by chromium trioxide in acetic acid solution into a bromodiphenylcarboxylic acid, which, on further action, passes into *a*-bromophthalic acid.

Dibrom-o-p-ditolyl, $C_{12}H_6Br_2(CH_3)_2$, crystallizes from alcohol in long, very lustrous, hair-like needles, and melts at 156°.[2]

o-m-Ditolyl was obtained by Schultz by mixing orthometatolidine, (p. 446) with a solution of nitrogen trioxide in alcohol. It is an oily liquid with a pleasant odour and boils at 280°. Chromic acid oxidizes it to isophthalic acid.[3]

m-p-Ditolyl was prepared by the same chemist in a similar manner from the tolidine obtained from *p*-azotoluene. It crystallizes in slender needles or plates, melts at 91°, and is volatile with steam. On oxidation it yields an acid which melts at 273°, and is insoluble in water. Its constitution follows from the fact that those of all the other isomerides are known.

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[1] Doebner, *Ber.* **9**, 271; Carnelley, *Journ. Chem. Soc.* 1877, **2**, 653.

[2] Carnelley and Thomson, *Journ. Chem. Soc.* 1885, **1**, 590.

[3] *Ber.* **17**, 471; Schultz, *Steinkohlentheer*, **1**, 195.

THE HYDROXYDITOLYLS

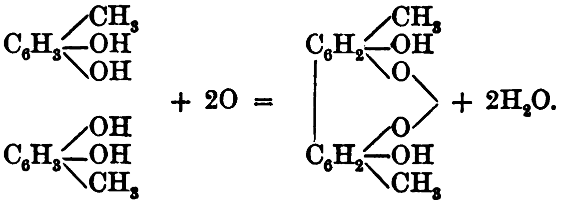
2740 *Dihydroxy-m-ditolyl*, or *o-Dicresol*, $C_{14}H_{12}(OH)_2$, is formed when a solution of tetrazo-*m*-ditolyl chloride is boiled, and separates on cooling in large, broad needles, melting at 157°.[1] On heating with zinc dust it is reduced to *m*-ditolyl.[2]

Diethoxy-m-ditolyl, $C_{14}H_{12}(OC_2H_5)_2$, is obtained as a by-product in the preparation of the hydrocarbon, and crystallizes from hot alcohol in white, glistening plates, melting at 156° (Schultz). Hobbs prepared it and several other ethers from the potassium compound of dicresol and the corresponding alcoholic iodide.

Diacetoxy-m-ditolyl, $C_{14}H_{12}(O.CO.CH_3)_2$, is formed when the potassium compound of dicresol is heated with acetic anhydride; it forms long needles and melts at 131° (Hobbs).

Dinitrodihydroxy-m-ditolyl, $C_{14}H_{10}(NO_2)_2(OH)_2$, is obtained by boiling the tetrazochloride with ordinary nitric acid (Gerber), and by heating dicresoldicarboxylic acid with nitric acid.[3] It crystallizes from glacial acetic acid in golden-yellow needles, melts at 272—273°, is insoluble both in water and alcohol, and gives a blue colouration with ferric chloride. The *potassium* and *sodium* salts form reddish-violet stellate groups of crystals, whilst the *ammonium* salt is orange-red; they form orange-red solutions in water.

Tetrahydroxyditolyl, $C_{14}H_{10}(OH)_4$. When toluquinol is oxidized in a well-cooled acetic acid solution by means of manganese dioxide and sulphuric acid, *dihydroxyditolylquinone* is formed, the reaction being similar to that by which cedriret is obtained from dimethylpyrogallol (p. 392):



This substance separates from alcohol in small black crystals with a green metallic lustre, and is readily reduced by zinc and

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[1] Gerber, *Ber.* 21, 749; Hobbs, *Ber.* 21, 1065.

[2] *Ber.* 21, 1096.

[3] Denninger, *Ber.* 21, 1641.

acetic acid to tetrahydroxyditolyl. The latter crystallizes from alcohol in transparent wine-yellow, four-sided prisms, and is readily soluble in hot water. The warm solution assumes a reddish colour in the air, and on cooling deposits the *quinhydrone* in blue flakes.

Tetrahydroxyditolyl becomes brown and melts at 202°; its alkaline solution changes colour in the air, becoming yellowish-green, yellowish-brown, cherry-red, and finally black-brown.[1]

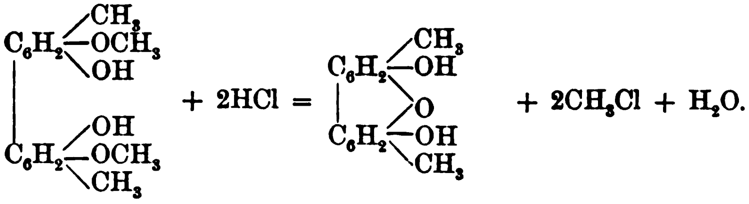
Dimethyltetrahydroxyditolyl, $C_{14}H_{10}(OH)_2(OCH_3)_2$, is obtained by heating dimethoxyditolylquinone, $C_{14}H_{10}O_2(OCH_3)_2$, which is described below, with ammonium sulphide, and crystallizes from benzene in slender colourless needles; it melts at 173° and readily becomes reoxidized to the quinone.[2]

Tetramethoxyditolyl, $C_{14}H_{16}(OCH_3)_4$, is formed when tetrahydroxyditolyl is heated with methyl iodide and a solution of sodium in methyl alcohol at 115—125°. A partially methylated compound is also formed, which contains the dimethyl ether.

It crystallizes from alcohol in colourless prisms or tablets, melts at 129°, and sublimes when carefully heated.

Tetracetoxyditolyl, $C_{14}H_{10}(O.CO.CH_3)_4$, is prepared by heating tetrahydroxyditolyl with sodium acetate and acetic anhydride to 155—165°, and crystallizes from alcohol in matted needles, melting at 135°.

Dihydroxyditolylene oxide, $C_{14}H_{10}O(OH)_2$, is obtained by heating the dimethyl ether with concentrated hydrochloric acid to 180—190°.



It crystallizes from benzene in long, flat needles, which rapidly effloresce in the air with loss of benzene of crystallization, and from dilute alcohol in lustrous plates, containing one molecule of water, which is completely lost at 120°. It melts at 232°, but sublimes at a lower temperature in lustrous plates. On heating with zinc dust it yields a small amount of a semi-liquid hydrocarbon possessing a pleasant smell of lemons.

Dimethoxyditolylquinone, $C_{14}H_{10}(OCH_3)_2O_2$, is obtained,

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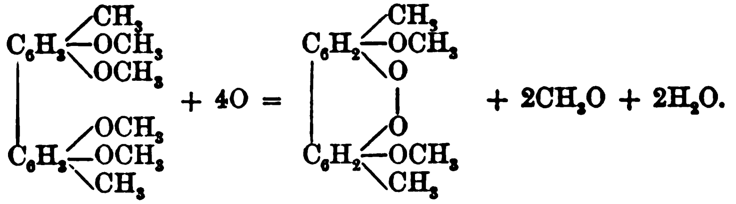
[1] Brunner, *Monatsh.* **10**, 174.

[2] Nietzki, *Annalen*, **215**, 160.

together with formaldehyde, when dimethyltoluquinol is oxidized in acetic acid solution with potassium dichromate and sulphuric acid:



It is moreover formed when an alcoholic solution of the by-product obtained in the preparation of the tetramethyl ether, as described above, is heated with ferric chloride, and then separates out in brownish-red needles. It is soluble in alcohol, ether, and glacial acetic acid with a yellowish-red colour, and crystallizes from a dilute solution in brick-red needles, but from a stronger as a mass of hair-like needles, which appear almost black by reflected light, take a violet-grey colour and a silky lustre on drying, and melt at 153°.

Diethoxyditolylquinone, $C_{14}H_{10}(OC_2H_5)_2O_2$, is prepared from diethyltoluquinol in a similar manner to the methyl compound. It forms very slender needles, of a greenish-black colour, and melts at 139°.

Diethyltetrahydroxyditolyl, $C_{14}H_{10}(OC_2H_5)_2(OH)_2$, is obtained by reducing the preceding compound. It forms slender white needles, and readily oxidizes in solution. It is only slightly soluble in water, readily in alcohol, and sublimes with partial decomposition.[1]

Ditolyldiquinone, $C_{14}H_{10}O_4$, is obtained by treating an alcoholic solution of tetrahydroxyditolyl with a concentrated solution of ferric chloride. It crystallizes from alcohol in lustrous tablets or prisms, which are coloured light-yellow to orange-yellow, according to their thickness, and sublimes with partial decomposition on heating.

Ditolylquinhydrone, $C_{14}H_{14}O_4 + C_{14}H_{10}O_4$, is formed by the partial oxidation of tetrahydroxyditolyl, and when an alcoholic solution of this substance is mixed with a hot concentrated solution of the quinone. It crystallizes in bluish-violet, oblong plates, and melts at 217—220°.

Which of the three ditolyls first described is the parent hydrocarbon of the preceding compounds is not yet known.

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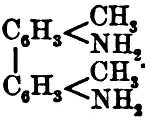
[1] Noelting and Werner, *Bull. Soc. Chim.* **1890**, 804.

DIAMIDODITOLYLS or TOLIDINES,



$$\begin{array}{l} C_6H_3<\substack{CH_3\\NH_2} \\ | \\ C_6H_3<\substack{CH_3\\NH_2} \end{array}.$$

2741 *Orthotolidine* or *p-Diamido-m-ditolyl* is formed by the action of hydrochloric acid on *o*-hydrazotoluene,[1] and when an alcoholic solution of *o*-azotoluene is heated with stannous chloride and hydrochloric acid.[2] It crystallizes in nacreous plates, melts at 128°, is slightly soluble in water, readily in alcohol and ether, and is coloured blue by chlorine and bromine vapour.

Its *sulphate* is sparingly soluble in water, and even less readily in alcohol, and the *hydrochloride*, crystallizing in plates, is also only slightly soluble in water. The solutions of its salts are coloured blue by ferric chloride.

The *m*-ditolyl obtained from this compound is converted by oxidation into isophthalic acid, from which it follows that in the conversion of *o*-hydrazotoluene into orthotolidine the amido-groups take the para-positions, as in benzidine. This is also shown by the fact that when orthotolidine is converted into tetrazoditolyl perbromide and the latter boiled with alcohol, a bromo-*m*-ditolyl is formed, in addition to the diethyl ether described above, which yields bromo-*m*-toluic acid, melting at 205°, on oxidation (Schultz).

Orthotolidine is employed in the manufacture of azo-colours and prepared on the large scale from *o*-nitrotoluene in a similar manner to benzidine from nitrobenzene.

Diacetylorthotolidine, $C_{14}H_{12}(NH.CO.CH_3)_2$, is obtained by boiling the base with glacial acetic acid, and crystallizes in white lustrous needles, melting at 314°.[3]

Tetracetylorthotolidine, $C_{14}H_{12}N_2(CO.CH_3)_4$, is formed when the preceding compound is heated with acetic anhydride at 160—170°, and crystallizes from alcohol in snow-white lustrous needles, melting at 211° (Gerber).

m-Ditolyl mustard oil, $C_{14}H_{12}(NCS)$, is obtained by the action of carbon disulphide on the base and treatment of the product with sulphuric acid. It crystallizes from benzene in splendid thick, transparent tablets, and melts at 157° (Hobbs).

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[1] Petriew, *Ber.* **6**, 557.

[2] Schultz, *Ber.* **17**, 467 ; *Steinkohlentheer*, **1**, 369.

[3] Gerber, *Ber.* **21**, 746 ; Hobbs, *Ber.* **21**, 1065.

Dinitro-orthotolidine, $C_{14}H_{10}(NO_2)_2(NH_2)_2$, was prepared by Gerber by nitrating the diacetyl-compound and heating the product with dilute sulphuric acid. It is only slightly soluble in alcohol, from which it crystallizes in flat, garnet-red, glistening tablets, melts at 266—267°, and deflagrates at a few degrees above this temperature.

Orthotolidinesulphonic acid, $C_{12}H_5(CH_3)_2(NH_2)_2SO_3H$, is obtained in a similar manner to benzidinesulphonic acid, and is only slightly soluble both in hot and cold water; its salts crystallize badly.

Orthotolidine-m-disulphonic acid, $C_{12}H_4(CH_3)_2(NH_2)_2(SO_3H)_2$, is also prepared in a similar manner to the corresponding benzidinedisulphonic acid; it crystallizes from hot water, in which it is readily soluble, in delicate white needles, and forms crystalline salts. When orthotolidine is heated with fuming sulphuric acid, the *sulphone*, $C_{12}H_4(CH_3)_2(NH_2)_2SO_2$, is formed as a greenish-yellow amorphous mass; its salts resemble those of benzidinesulphone.[1]

Orthotolidine-o-disulphonic acid, $2C_{12}H_4(CH_3)_2(NH_2)_2(SO_3H)_2 + 5H_2O$, is formed by the action of stannous chloride on a concentrated solution of *o*-azotoluene-*p*-disulphonic acid, and forms a crystalline powder, sparingly soluble in water; its salts crystallize well. Neale looks upon it as hydrazotoluenesulphonic acid;[2] the fact that it forms a tetrazo-compound however, shows that is derived from orthotolidine.[3]

Metatolidine or *p-Diamido-o-ditolyl* was obtained by Goldschmidt by adding dilute sulphuric acid to an alcoholic solution of *m*-hydrazotoluene, the *sulphate*, $C_{12}H_6(CH_3)_2(NH_3)_2SO_4$, being deposited in small plates with a velvet lustre.[4] It is also formed when sulphuretted hydrogen is passed into a solution of *m*-azotoluene in alcoholic ammonia and hydrochloric acid then added. On evaporation the *hydrochloride* separates out in splendid lustrous plates, which become bluish in the air. The free base is obtained by adding ammonia to a solution of this salt as a brown oily liquid, but solidifies after a few days to crystals melting at 108—109°. The aqueous solutions of its salts become coloured violet-red on heating or on the addition of ferric chloride.[5]

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[1] Griess and Duisberg, *Ber.* **22**, 2473.

[2] *Annalen*, **203**, 76.

[3] Friedländer, *Theerfarben*, 502.

[4] *Ber.* **11**, 1624.

[5] Buchka and Schachtebeck, *Ber.* **22**, 837.

Diacetylmetatolidine, $C_{12}H_6(CH_3)_2(NHCO.CH_3)_2$, forms light yellow crystals, and melts at 274—275°.

Paratolidine or *Diamido-m-p-ditolyl* was obtained by Melms by passing sulphur dioxide into an alcoholic solution of *p*-hydrazotoluene,[1] but it is better to simply add dilute sulphuric acid to the solution (Goldschmidt).

It is also formed when 10 grams of *p*-azotoluene are brought into 100 grams of alcohol and 100 cc. of a solution of 200 grams of tin in a litre of concentrated hydrochloric acid, and a few drops of concentrated sulphuric acid added. After 8—14 days the red crystals of azotoluene have almost completely disappeared and caustic soda solution is then added, the liquid boiled and the tin oxide filtered off. On cooling paratolidine separates out in silvery plates,[2] melting at 103°, which are soluble in hot water and more freely in alcohol or ether.

Its *sulphate* crystallizes in needles, the *hydrochloride* in tablets, whilst with platinum chloride a dark red precipitate is produced; the *picrate* crystallizes in lustrous reddish-yellow needles.

Paratolidine also gives a blue colour with ferric chloride. The position of the amido-groups is not known, but these cannot, as in benzidine and orthotolidine be situated in the para-position to the carbon atoms which unite the two benzene residues. Moreover, only one of these groups can be in the para-position to a methyl group, because if both occupied this position the ditolyl obtained from paratolidine would be either the meta- or ortho-compound.

Orthometatolidine or *p-Diamido-o-m-ditolyl* was prepared by Schultz from *o*-toluidine, which he converted into amido-*o-m*-azotoluene, and then by the action of an alcoholic solution of nitrous acid into *o-m*-azo-toluene, which was finally reduced by stannous chloride in alcoholic solution. The free base could not be obtained in crystals; its *hydrochloride* is readily soluble in water and crystallizes in silky needles, whilst the sparingly soluble *sulphate* forms small plates. The amido-groups of this tolidine are shown to be probably in the para-position, because the ditolyl obtained from it yields isophthalic acid on oxidation.[3]

Several substituted benzidines and tolidines have been prepared by Noelting and Werner,[4] by the action of hydro-

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[1] *Ber.* **3**, 554.

[2] Schultz, *Ber.* **17**, 472.

[3] *Ber.* **17**, 469.

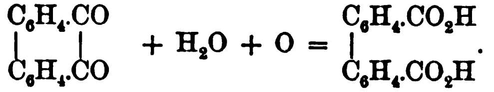
[4] *Bull. Soc. Chim.* **1890**, 798.

chloric acid on the corresponding hydrazo-derivatives. The most important of these are:

	Melting-point.
Methylethoxybenzidine	107°
Dimethylethoxybenzidine	73°

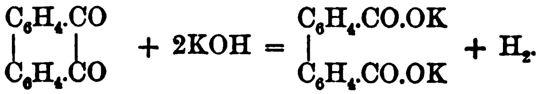
DIPHENYLDICARBOXYLIC ACIDS, $C_{12}H_8(CO_2H)_2$.

2742 *o-Diphenyldicarboxylic acid* was first obtained by Fittig and Ostermayer, who termed it *diphenic acid* by the oxidation of phenanthrenequinone with potassium dichromate and dilute sulphuric acid. It is formed according to the following equation:[1]



$$\begin{array}{l}C_6H_4.CO\\ |\qquad\ |\\ C_6H_4.CO\end{array} + H_2O + O = \begin{array}{l}C_6H_4.CO_2H\\ |\\ C_6H_4.CO_2H\end{array}.$$

It may also be obtained by boiling phenanthrenequinone for a considerable time with alcoholic potash:[2]



$$\begin{array}{l}C_6H_4.CO\\ |\qquad\ |\\ C_6H_4.CO\end{array} + 2KOH = \begin{array}{l}C_6H_4.CO.OK\\ |\\ C_6H_4.CO.OK\end{array} + H_2.$$

Free hydrogen is not however actually evolved but reduces a portion of the quinone. It has also been prepared synthetically from benzoic acid, which is first converted into *m*-hydrazobenzoic acid. On boiling this substance with hydrochloric acid it passes into diamidodiphenic acid, which yields di-iododiphenic acid by the diazo-reaction; the iodine atoms of the latter acid being then replaced by hydrogen by the action of sodium amalgam on its alkaline solution.[3]

Diphenic acid is only slightly soluble in cold, more freely in hot water, and very readily in alcohol and ether. When its hot aqueous solution is rapidly cooled it separates in lustrous plates, but when more slowly deposited it forms well-developed, trans-

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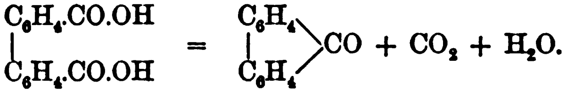
[1] *Annalen*, **166**, 367; Schmitz, *Annalen*, **193**, 116; Gräbe and Aubin, *Annalen*, **247**, 263.

[2] Anschütz and Schultz, *Annalen*, **196**, 50.

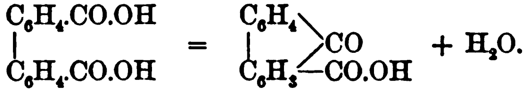
[3] Schultz, *Annalen*, **196**, 21; **203**, 96.

parent, monosymmetric prisms; if the solution is evaporated in a basin, the acid crystallizes out in forms resembling those of common salt.[1] It melts at 228—229° (Schultz), and sublimes when carefully heated in long transparent needles. On heating with quicklime diphenyleneketone is formed :



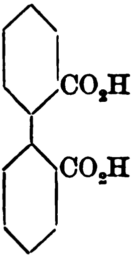
$$\begin{array}{l} C_6H_4.CO.OH \\ | \\ C_6H_4.CO.OH \end{array} = \begin{array}{l} C_6H_4 \diagdown \\ | \qquad >CO \\ C_6H_4 \diagup \end{array} + CO_2 + H_2O.$$

If, however, slaked lime or soda lime be used, it decomposes into carbon dioxide and diphenyl (Anschütz and Schultz), whilst on heating with sulphuric acid, water and diphenyleneketocarboxylic acid are formed :[2]



$$\begin{array}{l} C_6H_4.CO.OH \\ | \\ C_6H_4.CO.OH \end{array} = \begin{array}{l} C_6H_4 \diagdown \\ | \qquad >CO \\ C_6H_3 \diagup\!-CO.OH \end{array} + H_2O.$$

Other dehydrating agents convert it into the anhydride, described below. It is not attacked by boiling dilute nitric acid or by potassium permanganate in acid or alkaline solution, even on heating for a considerable time, whereas it is completely oxidized to water and carbon dioxide on heating with dilute sulphuric acid and potassium dichromate.[3] Its constitution is expressed by the following formula :



Calcium diphenate, $2C_{14}H_8O_4Ca + 5H_2O$, is readily soluble in water, and separates on evaporation in badly developed crystals.

Barium diphenate, $C_{14}H_8O_4Ba + 4H_2O$, forms transparent, probably rhombic crystals, effloresces in the air, and is less readily soluble than the calcium salt.

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[1] Schultz, *Annalen*, **203**, 97.

[2] Gräbe and Mensching, *Ber.* **13**, 1302 ; Gräbe and Aubin, *Ber.* **20**, 845 ; *Annalen*, **247**, 257.

[3] Hummel, *Annalen*, **193**, 129.

Magnesium diphenate, $C_{14}H_8O_4Mg + 4H_2O$, crystallizes in readily soluble plates.

Silver diphenate, $C_{14}H_8O_4Ag_2$, is a white, voluminous precipitate, soluble in a large quantity of water (Fittig and Ostermayer).

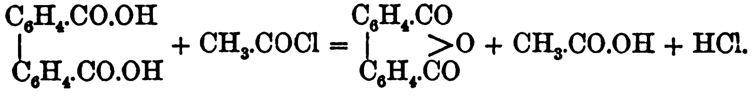
Methyl diphenate, $C_{14}H_8O_4(CH_3)_2$, is formed when a solution of the acid in methyl alcohol is saturated with hydrogen chloride and then heated on the water bath. It crystallizes in large, lustrous, monosymmetric tablets,[1] melts at 73·5°, and volatilizes without decomposition at a higher temperature (Schultz).

Acid methyl diphenate, $C_{12}H_8(CO_2.CH_3)CO_2H$, is obtained by boiling diphenic anhydride for a short time with methyl alcohol; it crystallizes in tablets, melts at 110°, and volatilizes without decomposition (Gräbe and Aubin).[2]

Ethyl diphenate, $C_{14}H_8O_4(C_2H_5)_2$, has a great tendency to separate from alcohol as an oil or to remain after evaporation as a thick syrup; if however the latter be completely dehydrated and well cooled, it solidifies to a crystalline mass. A trace of the crystalline substance brought into a moderately concentrated solution of the ester in dilute alcohol is sufficient to cause it to crystallize out in lustrous, transparent cubes, which sometimes form skeleton crystals like common salt, and melt at 42° (Hummel).

Acid ethyl diphenate, $C_{12}H_8(CO_2.C_2H_5)CO_2H$, crystallizes in tablets, melts at 88°, and is also volatile without decomposition, whereas the acid esters of phthalic acid decompose into the alcohol and anhydride on heating (Gräbe and Aubin).

2743 *Diphenic anhydride*, $(C_6H_4.CO)_2O$, was obtained by Anschütz by the action of acetyl chloride on the acid; the reaction taking place even in the cold, more rapidly on heating:



$$\begin{array}{l} C_6H_4.CO.OH \\ | \\ C_6H_4.CO.OH \end{array} + CH_3.COCl = \begin{array}{l} C_6H_4.CO \\ | \qquad >O \\ C_6H_4.CO \end{array} + CH_3.CO.OH + HCl.$$

It is also readily formed when diphenic acid is heated with acetic anhydride at 140—150°,[3] and when the acid is boiled with tin tetrachloride, or heated with the chlorides of phosphorus.

Diphenic anhydride crystallizes from a warm mixture of acetic anhydride and glacial acetic acid in long needles or

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[1] Calderon, *Jahresber.* **1881**, 842.

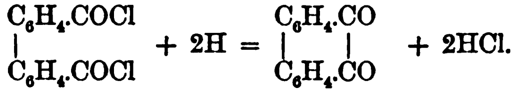
[2] *Ber.* **10**, 326.

[3] Anschütz, *Ber.* **10**, 1884; Gräbe and Aubin, *Annalen*, **247**, 263.

prisms, melts at 217°, and sublimes on careful heating; when it is more rapidly distilled, however, it partially decomposes into carbon dioxide and diphenylene ketone, complete decomposition into these substances occurring when its vapour is heated to the temperature of boiling sulphur. Boiling water slowly reconverts it into diphenic acid, and the same effect is produced by alkalis, slowly in the cold, rapidly on heating. Methyl and ethyl alcohol do not attack it in the cold, but on boiling for a short time the acid esters are formed, and at 180—200° the normal esters. When it is heated with sulphuric acid it is converted into the isomeric diphenyleneketocarboxylic acid.

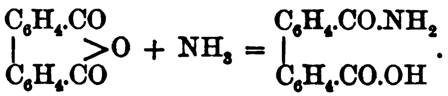
Diphenic chloride, $C_{14}H_8O_2Cl_2$, is prepared by heating the anhydride with phosphorus pentachloride at 180°, the somewhat violent reaction being moderated by removing the flask from the oil bath; the phosphorus oxychloride is then removed at 130—140° and a current of air finally passed through the heated flask. The chloride is readily soluble in ether, glacial acetic acid and benzene, can be obtained from the last of these in crystals, melts at 93—94°, and can be distilled without decomposition.

On heating with caustic soda solution it is converted into diphenic acid, the methyl ester of this being formed when it is boiled with methyl alcohol. When it is treated in ethereal solution with zinc and hydrochloric acid, phenanthrenequinone and its reduction products are obtained. This reaction and the formation of the methyl ester from the chloride show that it does not possess an analogous constitution to phthalyl chloride (Part IV., p. 460), but is a true acid chloride (Gräbe and Aubin). The conversion into phenanthrenequinone takes place in the following manner:



$$\begin{array}{l} C_6H_4.COCl \\ | \\ C_6H_4.COCl \end{array} + 2H = \begin{array}{l} C_6H_4.CO \\ |\quad\ \ | \\ C_6H_4.CO \end{array} + 2HCl.$$

Diphenamic acid, $C_{12}H_8(CO.NH_2)CO_2H$, is formed when the anhydride is boiled for 20—30 minutes with ammonia:

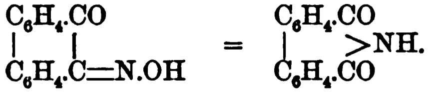


$$\begin{array}{l} C_6H_4.CO \\ |\qquad\ >O \\ C_6H_4.CO \end{array} + NH_3 = \begin{array}{l} C_6H_4.CO.NH_2 \\ | \\ C_6H_4.CO.OH \end{array}.$$

The ammonium salt is thus obtained and the free acid precipitated by hydrochloric acid. It crystallizes from alcohol in tablets, melting at 193°, and is converted into sodium diphenate by boiling with caustic soda solution.

Diphenamide, $C_{12}H_8(CO.NH_2)_2$, is formed when the anhydride is heated with alcoholic ammonia, and crystallizes from hot water in thick, transparent hexagonal tablets, which melt at 212° and are insoluble in alkalis.

Diphenimide, $C_{12}H_8(CO)_2NH$, is obtained by heating ammonium diphenate in closed vessels at 250—260°, or the amide above its melting point. It is, moreover, formed when the isomeric phenanthrenequinonoxime is dissolved in ten parts of acetic acid, hydrogen chloride passed in to saturation and the liquid heated at 130—140°:



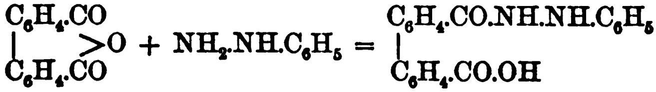
$$\begin{array}{l} C_6H_4.CO \\ |\quad\;\; | \\ C_6H_4.C{=}N.OH \end{array} = \begin{array}{l} C_6H_4.CO \\ |\qquad\;\; >NH. \\ C_6H_4.CO \end{array}$$

It crystallizes from hot alcohol, in which it is only slightly soluble, in very lustrous needles, melts at 217°, and is insoluble in water and ether. Concentrated hydrochloric acid decomposes it into ammonia and diphenic acid, whilst boiling caustic potash solution converts it into diphenamic acid, and diphenamide soon separates out when it is dissolved in dilute ammonia. Diphenimide is simultaneously a weak base and an acid, and therefore dissolves in alkalis.

Sodium diphenimide, $C_{12}H_8(CO)_2NNa$, separates out on the addition of ether to an alcoholic solution of the imide as a white crystalline powder, readily soluble in water. The *silver* salt is a light-yellow precipitate. When the sodium salt is heated with methyl iodide, the oily *methyl ether* is formed.

Acetyldiphenimide, $C_{12}H_8(CO)_2N.CO.CH_3$, occurs as a by-product in the preparation of the imide from the quinonoxime and has also been obtained by the action of acetyl chloride on the imide. It crystallizes from alcohol in hard colourless prisms, and melts at 92°.[1]

Anilidodiphenamic acid, $C_{20}H_{16}N_2O_3$, is formed when diphenic anhydride is heated with phenylhydrazine:



$$\begin{array}{l} C_6H_4.CO \\ |\qquad\;\; >O \\ C_6H_4.CO \end{array} + NH_2.NH.C_6H_5 = \begin{array}{l} C_6H_4.CO.NH.NH.C_6H_5 \\ | \\ C_6H_4.CO.OH \end{array}$$

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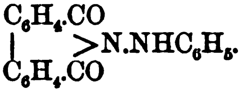
[1] Wegerhoff, *Annalen*, **252**, 14.

It is readily soluble in water and separates from alcohol in light-yellow crystals, melts at 174°, and dissolves in the alkalis and their carbonates. On heating to 230—250° it loses water and leaves a residue, melting at 150°, of *anilidodiphenimide:*



$$\begin{array}{l} C_6H_4.CO \\ | \qquad > N.NHC_6H_5. \\ C_6H_4.CO \end{array}$$

2744 *Bromodiphenic acid*, $C_{12}H_7Br(CO_2H)_2$, is formed, together with *a*-dibromodiphenic acid, when diphenic acid is heated with bromine at 200°. The product is washed with chloroform to remove resinous products, and the acids separated by means of their barium salts.

Bromodiphenic acid crystallizes from hot glacial acetic acid in small, well-developed, acicular prisms, melts at 235—236°, is scarcely soluble in cold, very slightly in boiling water, sparingly in chloroform, but readily in alcohol and acetic acid. On heating with slaked lime it decomposes into carbon dioxide and bromodiphenyleneketone.

Barium bromodiphenate, $C_{14}H_7BrO_4Ba + 3H_2O$, crystallizes in long, thin pointed needles, is very sparingly soluble in cold and only slightly more freely in hot water.

Ethyl bromodiphenate, $C_{14}H_7BrO_4(C_2H_5)_2$, was obtained as a thick, viscid liquid, which solidified after eighteen months to a crystalline mass, melting at 65°.

Bromodiphenic acid bromide, $C_{12}H_7Br(CO_2H)_2Br_2$, is obtained when diphenic acid is heated with bromine at 100° for a week. It is very sparingly soluble in cold alcohol, and crystallizes from the hot solution in small lustrous needles, which melt and decompose at 256°. When it is heated for some hours in a sealed tube at 200° dibromodiphenic acid and resinous products are formed. The same acid is obtained when the dibromide is dissolved in warm alkalis, whilst it dissolves without decomposition in hot sulphuric acid and fuming nitric acid, and crystallizes from the latter in beautiful large needles. In spite of the fact that it is only sparingly taken up by most solvents it has, like diphenic acid and all its derivatives, an extremely unpleasant, intensely bitter taste.

When it is dissolved in sodium carbonate at 50—60°, the *sodium* salt, $C_{14}H_7Br_3O_4Na_2$, is formed, which crystallizes on evaporation of the solution over sulphuric acid in silky plates, and decomposes on boiling with water into sodium bromide and sodium dibromodiphenate.

a-Dibromodiphenic acid, $C_{12}H_6Br_2(CO_2H)_2$, is scarcely soluble in cold water, readily in alcohol or ether, and crystallizes from glacial acetic acid in small lustrous needles, melting at 245°. On heating with slaked lime it decomposes into carbon dioxide and dibromodiphenyleneketone.

Calcium dibromodiphenate, $C_{14}H_6Br_2O_4Ca + 3H_2O$, crystallizes in scaly plates and, as well as the *barium* salt, is readily soluble in water.

Ethyl dibromodiphenate, $C_{14}H_6Br_2O_4(C_2H_5)_2$, separates out as a buttery mass, which gradually becomes crystalline and then melts at 105—106°.[1]

β-Dibromodiphenic acid is slowly formed when dibromophenanthrenequinone is boiled with dilute sulphuric acid and potassium dichromate, and separates from alcohol in small crystalline druses, melts at 295—296°, and is scarcely soluble in cold, only very slightly in hot water, more readily in alcohol and in ether; it has also an exceptionally bitter, persistent taste. The *calcium* and *barium* salts form very slender scale-like plates, sparingly soluble in water, whilst the *ethyl ester* is a colourless, heavy liquid which decomposes on boiling, an odour resembling that of the allyl compounds being produced.[2]

Di-iododiphenic acid, $C_{12}H_6I_2(CO_2H)_2$, was obtained by Schultz by suspending the nitrate of *a*-diamidodiphenic acid in water, and saturating the cooled liquid with nitrogen trioxide. The nitrate of tetrazodiphenic acid separates out as a white crystalline mass, sparingly soluble in water, and is converted into di-iododiphenic acid by boiling with hydriodic acid. It can also be readily prepared from *a*-diamidodiphenic acid hydrochloride, and separates from its solution in ammonia in white flakes, melting at 262°, which are very sparingly soluble in water, readily in alcohol, glacial acetic acid, ether, &c., but cannot be obtained from these solvents in the crystalline form. The salts are also amorphous, the *silver* salt being a light-yellow precipitate, which swells up on heating, forming a mass resembling the so-called "Pharaoh's serpents." When the acid is suspended in water and acetic acid and sodium amalgam added, it is converted into diphenic acid, which can also be obtained from it in a similar manner in alkaline solution.[3]

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[1] Claus and Erler *Ber.* **19**, 3149.

[2] Ostermayer, *Ber.* **7**, 1091

[3] Schultz, *Annalen*, **196**, 96; **203**, 23.

p-Nitrodiphenic acid, $C_{12}H_7(NO_2)(CO_2H)_2$, is quantitatively formed when nitrophenanthrenequinone is heated with dilute sulphuric acid and potassium dichromate. It is almost insoluble in cold water, and crystallizes from boiling water in yellowish, sharply-pointed, prismatic needles.[1]

a-Dinitrodiphenic acid, $C_{12}H_6(NO_2)_2(CO_2H)_2$, was obtained by Struve by the oxidation of dinitrophenanthrenequinone.[2] It is also formed, together with the β-acid, when diphenic acid is heated with 4 parts of fuming nitric acid,[3] the two acids being separated by means of their barium salts.

α-Dinitrodiphenic acid is best prepared by heating pure dinitrophenanthrenequinone with potassium dichromate and dilute sulphuric acid.[4] It is sparingly soluble in cold, moderately in hot water, and crystallizes from the latter or from dilute alcohol in faintly-yellowish, lustrous, long, broad needles, containing one molecule of water which is lost at 150—160°, the crystals becoming white, and then melting at 253°.

Barium a-dinitrodiphenate, $C_{14}H_6(NO_2)_2O_4Ba + 6H_2O$, is somewhat sparingly soluble in cold, readily in hot water, and crystallizes in fascicular or concentric groups of long, slender, lustrous needles.

Methyl a-dinitrodiphenate, $C_{14}H_6(NO_2)_2O_4(CH_3)_2$, is sparingly soluble in alcohol, and crystallizes in needles, melting at 176—177°, or from toluene in masses of short, yellowish, lustrous, monosymmetric prisms.[5]

β-Dinitrodiphenic acid is best obtained by heating the by-products formed during the preparation of dinitrophenanthrene, with dilute sulphuric acid and potassium dichromate, a little of the α-acid being simultaneously formed, which is separated as described above.[6]

β-Dinitrodiphenic acid crystallizes in slender needles, melting at 297°, is insoluble in cold, very sparingly soluble in hot water, and readily in alcohol.

Barium β-dinitrodiphenate, $C_{14}H_6(NO_2)_2O_4Ba + 4H_2O$, is very readily soluble in cold water, and crystallizes in large, thick, lustrous, pale-yellow asymmetric prisms.

Methyl β-dinitrodiphenate is readily soluble in alcohol, and forms pale-yellow, thick, monosymmetric tablets, melting at 131—132°.

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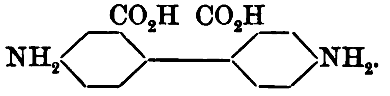
[1] Strassburger, *Ber.* **16**, 2346.
[2] *Ber.* **10**, 75.
[3] Hummel, *Annalen*, **193**, 131; Schultz, *Annalen*, **203**, 105.
[4] Schultz, *Annalen*, **196**, 25.
[5] Schultz, *Annalen*, **203**, 111.
[6] Schultz, *Annalen*, **203**, 105.

p-Amidodiphenic acid, $C_{12}H_7(NH_2)(CO_2H)_2$, was prepared by Strassburger by the reduction of nitrodiphenic acid by tin and hydrochloric acid, the *hydrochloride* being thus obtained in white, silvery plates.

p-Diamidodiphenic acid, $2C_{12}H_6(NH_2)_2(CO_2H)_2 + 3H_2O$, was obtained by Griess by the continued heating of *m*-azobenzoic acid with tin and hydrochloric acid, and by boiling *m*-hydrazobenzoic acid with hydrochloric acid.[1] It is also formed by the reduction of *α*-dinitrodiphenic acid with tin and hydrochloric acid,[2] and is precipitated by acetic acid from the solution of its ammonium salt as a heavy white powder, or, when the solution is dilute, in short, white, tasteless needles, which are only very slightly soluble in water and alcohol, and scarcely in ether. When it is heated to 150° it becomes anhydrous, and at 170° is converted into a new amido-acid, which on ignition with lime yields diamidofluorene, $C_{13}H_8(NH_2)_2$. The same substance is formed when the original diamidodiphenic acid is heated with lime, benzidine being however simultaneously formed, and being the sole product of the dry distillation of the barium salt. Diamidodiphenic acid has therefore, the following constitution, that of *α*-dinitrodiphenic acid and di-iododiphenic acid being at the same time determined:



When it is dissolved in concentrated sulphuric acid and a drop of fuming sulphuric acid added, the liquid becomes brown on warming, then green, and finally yellow.

Silver diamidodiphenate, $C_{14}H_{10}N_2O_4Ag_2 + H_2O$, is a white amorphous precipitate, which rapidly changes to stellate groups of small plates.

Diamidodiphenic acid hydrochloride, $C_{12}H_6(NH_3Cl)_2(CO_2H)_2$, crystallizes in white prisms, is readily soluble in hot, sparingly in cold water, and even less readily in hydrochloric acid.

When platinum chloride is added to its dilute solution, the compound, $C_{12}H_6(CO_2H)_2(NH_3)_2PtCl_6 + 2H_2O$, separates out in well developed yellow rhombic tablets or prisms (Griess).

The *nitrate* crystallizes from hot water in long slender needles (Schultz).

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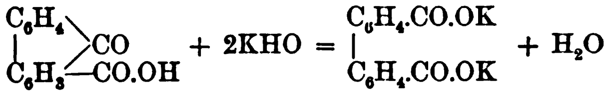
[1] *Ber.* **7**, 1609.

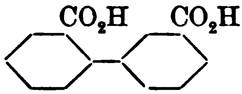
[2] Schultz, *Annalen*, **196**, 25; **203**, 99.

2745 *o-m-Diphenyldicarboxylic acid,* or *Isodiphenic acid,* is formed when diphenyleneketonecarboxylic acid is fused with potash:[1]



$$\begin{matrix} C_6H_4 \\ | \\ C_6H_3 \end{matrix} \!\!\begin{matrix} \diagdown \\ \diagup \end{matrix}\!\! \begin{matrix} CO \\ -CO.OH \end{matrix} + 2KHO = \begin{matrix} C_6H_4.CO.OK \\ | \\ C_6H_4.CO.OK \end{matrix} + H_2O$$

It is readily soluble in alcohol, scarcely in cold, with difficulty in boiling water, and crystallizes in fine groups of small needles, melts at 216°, and on gradual cooling solidifies to a crystalline mass, but when rapidly cooled forms a vitreous mass. On heating with lime it decomposes into carbon dioxide and diphenyleneketone, a small amount of diphenyl being also formed. It is oxidized to isophthalic acid by dilute sulphuric acid and potassium dichromate, and has the following constitution:



Calcium isodiphenate, $C_{14}H_8O_4Ca + 2H_2O$, separates during evaporation from a somewhat dilute solution in crusts, which only redissolve with great difficulty.

Barium isodiphenate, $C_{14}H_8O_4Ba + 6H_2O$, crystallizes, when its concentrated solution is evaporated over sulphuric acid, in fascicular groups of thick transparent prisms. If the solution be evaporated to dryness on the water-bath, the residue can only be redissolved by continued heating with a large quantity of water.

Silver isodiphenate, $C_{14}H_8O_4Ag_2$, is a white precipitate, and does not become coloured when exposed to light or heated to 100°.

Methyl isodiphenate, $C_{14}H_8O_4(CH_3)_2$, crystallizes from alcohol in small thick asymmetric tablets, whilst the *ethyl ester* is a thick liquid.

m-Diphenyldicarboxylic acid is formed, according to Stolle, by the oxidation of *m*-ditolyl, but has not been described.

Dichloro-m-diphenyldicarboxylic acid, $C_{12}H_6Cl_2(CO_2H)_2$, is obtained by boiling tetrachloro-*m*-ditolyl with dilute nitric acid; it is only sparingly soluble in cold, more readily in hot water, and melts at 267—268°.[3]

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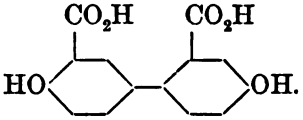
[1] Fittig and Gebhard, *Annalen,* **193**, 155.

[2] Fittig and Liepmann, *Annalen,* **200**, 9.

[3] Stolle, *Ber.* **21**, 1096.

Dihydroxy-m-diphenyldicarboxylic acid, or *p-Diphenol-m-dicarboxylic acid*, $C_{12}H_6(OH)_2(CO_2H)_2$, is formed when the sodium compound of *p*-diphenol is mixed with liquid carbon dioxide and heated to 200°. It is slightly soluble in water, readily in alcohol, and separates out on cooling, when water is added to the boiling alcoholic solution until a permanent turbidity is produced, in microscopic needles, melting at 131° with evolution of carbon dioxide. When ferric chloride is added to the acid suspended in water, it becomes coloured bluish-violet and dirty brown on heating, whilst in the solution of its sodium salt a deep blue colour and an indigo-blue precipitate are produced.[1] It therefore behaves in a manner similar to salicylic acid, and has probably the following constitution:



Diamido-m-diphenyldicarboxylic acid, $C_{12}H_6(NH_2)_2(CO_2H)_2$, was obtained by Griess by boiling *o*-hydrazobenzoic acid with hydrochloric acid. When the hot boiling solution is treated with ammonia and then acetic acid, it separates out as a siskin-green precipitate, consisting of slender needles, which are also but slightly soluble in alcohol and ether. The *platinochloride* forms light yellow needles, almost insoluble in water.[2]

p-Diphenyldicarboxylic acid was first prepared by Doebner by heating the nitrile, described below, with concentrated hydrochloric acid at 180°,[3] and afterwards by the oxidation of *p*-ditolyl with chromium trioxide in acetic acid solution.[4] It separates from solutions of its alkali salts on addition of hydrochloric acid in thick white flakes, and after drying forms an amorphous white powder, which closely resembles terephthalic acid and, like this, is almost insoluble in boiling water, alcohol, &c., does not melt nor sublime, and only decomposes at a very high temperature. Almost all its salts, with the exception of those of the alkalis, are insoluble in water. On heating with an excess of lime it decomposes quantitatively into carbon dioxide and diphenyl.

Barium p-diphenyldicarboxylate, $C_{14}H_8O_4Ba$, is a white granular precipitate, almost insoluble even in boiling water. The *calcium* salt resembles it and the *silver* salt is also a

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[1] Schmitt and Kretschmar, *Ber.* **20**, 2703

[2] *Ber.* **7**, 1612.

[3] *Annalen*, **172**, 116.

[4] *Ber.* **9**, 271.

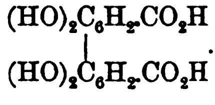
granular precipitate, which on boiling with water coagulates and dissolves to a small extent.

Ethyl p-diphenyldicarboxylate, $C_{14}H_8O_4(C_2H_5)_2$, is not formed when hydrochloric acid is passed through alcohol in which the acid is suspended. It can however be readily prepared by heating the silver salt with ethyl iodide; it crystallizes from hot alcohol in large flat prisms and melts at 112°.

p-Diphenonitrile or *p-Dicyanodiphenyl*, $C_{12}H_8(CN)_2$, is obtained by heating potassium diphenyldisulphonate with potassium cyanide. It crystallizes from hot alcohol in thin arborescent needles, melts at 234°, and when more strongly heated sublimes in lustrous serrated plates. On boiling with alcoholic potash it is only slowly converted into the acid, since the insoluble *amide*, $C_{12}H_8(CONH_2)_2$, is first formed and is not easily further attacked, the *amido-acid*, $C_{12}H_8(CONH_2)CO_2H$, which is also insoluble, being probably the next product. In order to obtain the pure acid the product is dissolved in a large excess of caustic potash and repeatedly evaporated to a small bulk. It is however better to heat the nitrile for twelve hours at 180° with concentrated hydrochloric acid, but it is still advisable to purify it by evaporation with caustic potash.

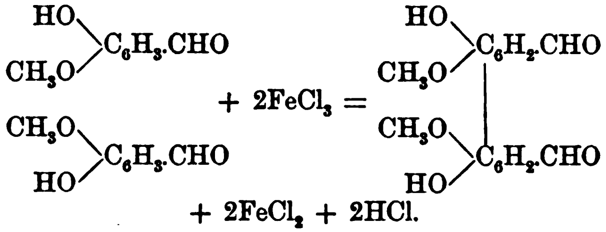
o-p-Diphenyldicarboxylic acid is obtained from diphenyline by diazotizing it and running the solution into heated potassium cuprous cyanide solution; the *nitrile* is thus formed and crystallizes from alcohol in well-formed plates, melting at 152—153°. The acid prepared from it by boiling with caustic potash separates on the evaporation of its solution in white plates, melting at 251—252°.[1]

DIHYDROXYDIPHENYLDICARBOXYLIC ACID,



$$\begin{array}{l}(HO)_2C_6H_2.CO_2H\\ \quad\;|\\ (HO)_2C_6H_2.CO_2H\end{array}.$$

2746 *Dehydrodiprotocatechuic acid.* When vanillin is heated with ferric chloride, *dehydrodivanillin* is formed:



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[1] Reuland, *Ber.* **22**, 3018.

This substance forms white needles, melts at 303—304°, is sparingly soluble in water and alcohol, but readily in alkalis, and on fusion with caustic potash is converted into the acid mentioned above. The latter is precipitated by hydrochloric acid in flakes, which form hard brown masses on drying, melts above 300°, is somewhat soluble in water, more readily in alcohol, and behaves towards ferric chloride like protocatechuic acid.[1]

Diresorcinoldicarboxylic acid is obtained by heating diresorcinol (p. 386) with water and acid potassium carbonate at 130°, and forms a powder, insoluble in water, sparingly soluble in alcohol.

Potassium diresorcinoldicarboxylate, $C_{14}H_8O_8K_2$, crystallizes in slender white needles, soluble in water.

Barium diresorcinoldicarboxylate, $C_{14}H_8O_8Ba + 6H_2O$, forms lustrous needles, and is moderately soluble in water.[2]

ETHYLDIPHENYL AND DERIVATIVES.

2747 *Ethyldiphenyl*, $C_6H_5.C_6H_4.C_2H_5$, is obtained by the action of ethyl chloride, ethyl iodide, or better ethylene on a mixture of aluminium chloride and fused diphenyl. It is a liquid, boils at 283—284°, and is oxidized by chromic acid solution to *m*-phenylbenzoic acid.

Methyldiphenylketone, $C_6H_5.C_6H_4.CO.CH_3$, is formed by the action of acetyl chloride on a solution of diphenyl and aluminium chloride in carbon disulphide. It forms white, faintly nacreous pliable crystals, melts at 121°, boils at 325—327°, and is also oxidized by chromic acid to *m*-phenylbenzoic acid. When sodium amalgam is added to its alcoholic solution, *methyldiphenylcarbinol*, $C_6H_5.C_6H_4.CH(OH)CH_3$, is formed, which melts at 85—86°, and decomposes on distillation.[3]

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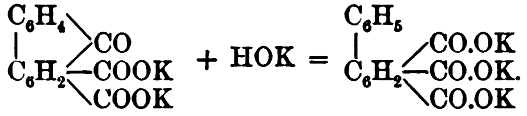
[1] Tiemann, *Ber.* **18**, 3493.

[2] Will and Albrecht, *Ber.* **17**, 2105.

[3] Adam, *Bull. Soc. Chim.* **47**, 686 ; **49**, 97 ; *Ann. Chim. Phys.* VI. **15**, 255.

DERIVATIVES OF DIPHENYL CONTAINING MORE THAN FOURTEEN ATOMS OF CARBON.

2748 *Diphenyltricarboxylic acid*, $C_6H_5.C_6H_2(CO_2H)_3$, is obtained by fusing diphenylketonedicarboxylic acid with 6—8 parts of caustic potash and a little water at the lowest possible temperature:



It is readily soluble in ether and alcohol, from which it separates in flakes. Cold water only dissolves traces of it, and it is only slightly soluble in boiling water, separating out on cooling as a crystalline powder, which can be heated to 270° without undergoing any change. When its alcoholic solution is mixed with a little water, it soon crystallizes in cellular masses of interlocked needles. On distillation with lime it decomposes into carbon dioxide and diphenyl.

Silver diphenyltricarboxylate, $C_{15}H_7Ag_3O_6$, is a heavy white precipitate, which on heating suddenly becomes incandescent and swells up to a voluminous vermiform mass.[1]

HYDROCARBONS, C_nH_{2n-14}, AND THEIR DERIVATIVES.

2749 *m-Dixylyl*, $(CH_3)_2.C_6H_3.C_6H_3(CH_3)_2$, was obtained by Fittig by the action of sodium on bromo-*m*-xylene, and forms a strongly refractive liquid, boiling at 290—295°.[2] Probably identical with this substance is the dixylyl prepared by Oliveri by shaking commercial xylene with sulphuric acid, which is a strongly refractive fluorescent liquid, boiling at 293—297°, and smelling like Copaiva balsam.[3]

p-Dixylyl was obtained by Jacobsen as a product of the distillation of mercury *p*-xylyl, $(CH_3)_2C_6H_3HgC_6H_3(CH_3)_2$; it

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[1] Bamberger and Hooker, *Annalen*, **229**, 159.

[2] *Annalen*, **147**, 37.

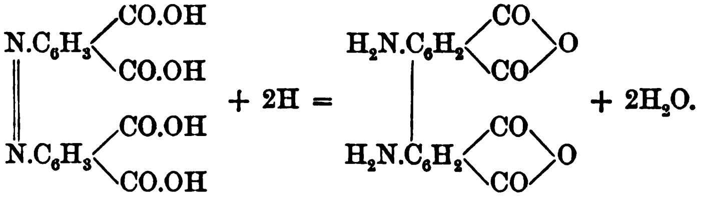
[3] *Gazz. Chim. Ital.* **12**, 158.

crystallizes from hot alcohol in long, arborescent needles, and melts at 125°.[1]

The various azo-xylenes can readily be converted into diamidodixylyls, which, like their lower homologues, can be employed for the manufacture of dyes, but have not been carefully examined.[2]

Dicresoldicarboxylic acid, $(CH_3)_2C_{12}H_4(OH)_2(CO_2H)_2$, is formed when the sodium compound of dicresol is heated at 160° with liquid carbon dioxide; it crystallizes from alcohol in small needles, does not melt even at 290°, and is coloured blue by ferric chloride. On heating with acetic anhydride the compound $(CH_3)_2C_{12}H_4(O.CO.CH_3)_2(CO_2H)_2$, is formed, and crystallizes in white needles, which are also coloured blue by ferric chloride.[3]

Benzidinetetracarboxylic acid, $C_{12}H_4(NH_2)_2(CO_2H)_4$, is not known in the free state; its anhydride is formed when azophthalic acid, prepared from γ-nitrophthalic acid, is boiled with a solution of stannous chloride:



It is a light, pale-yellow powder, does not dissolve in water, alcohol, and dilute acids, but is soluble in alkalis.

The *potassium* salt, $C_{12}H_{11}(NH_2)_2(C_2O_3)(CO_2K)_2 + 5H_2O$, crystallizes in large amber-yellow prisms. When silver nitrate is added to its solution, a light yellow precipitate of $C_{12}H_8Ag_2N_2O_7$ is produced; if, however, the anhydride be dissolved in ammonia and the excess of the latter allowed to evaporate, silver nitrate produces a similar precipitate of the composition $C_{12}H_4(NH_2)_2(CO_2Ag)_4$. On heating the anhydride, carbonization takes place and the compound $C_{14}H_8N_2O_2$ sublimes in light yellow, delicate needles. It probably has the following constitution:[4]

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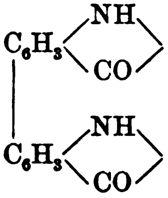
[1] *Ber.* **14**, 2112.

[2] Nölting and Stricker, *Ber.* **21**, 3143.

[3] Deninger, *Ber.* **21**, 1639.

[4] Claus and Hemmann, *Ber.* **16**, 1759.



Diethyldiphenyl, $C_{12}H_8(C_2H_5)_2$, is a liquid, boils at 304—310°, and on oxidation yields, like *m*-ditolyl, an acid, which on heating neither melts nor sublimes (Adam).

Diamidodiethyldiphenyl, $C_{12}H_6(NH_2)_2(C_2H_5)_2$, was obtained by Schultz by heating *o*-azoethylbenzene with an acid solution of stannous chloride. The free base separates from alcohol as a viscid mass. The *sulphate*, $C_{12}H_6(C_2H_5)_2(NH_3)_2SO_4$, forms lustrous needles, only slightly soluble in cold water; the *acetyl* compound, $C_{12}H_6(C_2H_5)_2(NH.COCH_3)_2$, crystallizes from hot glacial acetic acid in lustrous needles, melts at 307°, and sublimes almost at the same temperature in snow-white needles. In endeavouring to prepare the corresponding hydrocarbon by means of the diazo-reaction, Schultz chiefly obtained the *diethyl ether*, $C_{12}H_6(C_2H_5)_2(OC_2H_5)_2$. This substance crystallizes from hot alcohol in lustrous plates, melting at 120°, and was accompanied by a small amount of an oily hydrocarbon, which yielded isophthalic acid on oxidation.[1]

PHENOLS, $C_nH_{2n-14}O_2$.

2750 *Dipseudocumenol*, or *Hexmethyldiphenol*, $(CH_3)_3C_6H(OH)$—$C_6H(OH)(CH_3)_3$, is formed in small quantity during the preparation of *a*-pseudocumenol from *a*-pseudocumidine by means of the diazo-reaction. In order to prepare it, pseudocumenol is dissolved in glacial acetic acid and an acetic acid solution of potassium dichromate added.[2] It is also formed when pseudocumenol is heated with dilute nitric acid or ferric chloride,[3] and separates from hot glacial acetic acid in lustrous white needles or small crystals, having a diamond lustre. It melts at 173°, is slightly soluble in alcohol, acetic acid, and alkalis, readily in ether and chloroform, and does not volatilize with steam.

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[1] *Ber.* **17**, 473.

[2] Auwers, *Ber.* **17**, 2982.

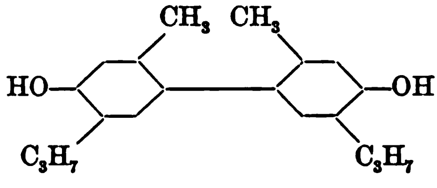
[3] *Ber.* **18**, 2659.

Dipseudocumenol methyl ether, $C_{18}H_{20}(OCH_3)_2$, is obtained by heating dipseudocumenol with caustic potash, methyl alcohol, and methyl iodide; it crystallizes from alcohol in white needles, melts at 126°, and is insoluble in alkalis.

Dibromodipseudocumenol, $C_{18}H_{18}Br_2(OH)_2$, is formed when the phenol is brominated in acetic acid solution; it occurs in small lustrous crystals, melts at 186—187°, is insoluble in water, slightly soluble in alkalis and readily in alcohol.

Dithymol, $C_3H_7(CH_3)C_6H_2(OH)—C_6H_2(OH)CH_3(C_3H_7)$, is prepared by oxidizing a warm mixture of 1 part of thymol and 10 parts of water with ferric chloride, or better, a solution of iron alum, the liquid being kept neutral by the addition of sodium carbonate. It is also obtained when iodine is added to an alkaline thymol solution, the brownish-red precipitate dissolved in ether, alcoholic potash added, and zinc dust then gradually introduced.[1] It crystallizes in prisms or tablets, melts at 165·5°, a portion subliming at the same time, readily dissolves in alcohol, and forms an orange-yellow coloured solution in alkalis.

On treatment with nitrous acid it does not yield a nitrosophenol or quinonoxime, and has therefore probably the following constitution:



Dibenzoyldithymol, $C_{20}H_{24}(O.CO.C_6H_5)_2$, forms colourless microscopic plates, and melts at 215°.

Dicarvacrol is isomeric with dithymol, and is obtained from carvacrol in a similar manner. It crystallizes from dilute alcohol in long, thin, silky needles, melts at 154°, and is readily soluble in alcohol.[2]

THE AZO-DYES OF THE DIPHENYL GROUP.

2751 In 1881 Schultz found that when the tetrazodiphenyl nitrate obtained from benzidine is brought into an alkaline solution of phenol, a colouring matter is formed which dyes silk

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[1] Messinger and Pickersgill, *Ber.* **23**, 2761.

[2] Dianin, *Ber.* **15**, 1194; *Beilstein's Handb.* **2**, 637.

a beautiful and fast yellow.[1] Shortly after this several of these benzidine dyes were prepared, and since they contain the diazo-group twice, were known as diazo- or tetrazo-colours. It was, however, found that most of them were not suitable for dyeing wool, and they appeared to be of no practical importance until P. Böttiger in 1883 made the remarkable discovery that the colouring matter known as Congo Red, prepared from benzidine and naphthionic acid, which is not stable towards acids, and is quite unfitted for dyeing wool, is notwithstanding capable of dyeing unbleached cotton a fine and moderately stable red in alkaline solution. Since that time a large number of such azo-dyes for cotton, or colouring matters of the Congo-group has been manufactured, the shades which they produce depending upon their composition. Thus, combinations of benzidine with the hydroxybenzoic acids give yellow, those with the various naphthylaminesulphonic acids red, and those with the naphtholsulphonic acids violet to violet-blue shades. Numerous compound shades can be produced by combining the tetrazo-compound of benzidine with one molecule of a phenol or amine, or one of their sulphonic acids, and then bringing the resulting unstable diazo-compound together with a second molecule of a different phenol, amine, &c.[2] If benzidine be replaced by orthotolidine or dianisidine the yellow dyes take a redder shade, and the red or violet become much bluer and in some cases almost a pure blue.

The property possessed by these substances of being fast on cotton does not depend upon the diphenyl residue alone, since the monamido-diphenyls and diphenyline do not yield dyes, whereas such are given by orthotolidine, dianisidine, and other diparamido-compounds. The meta-substitution products also give dyes, but not the ortho-compounds. They are, however, obtained from *p*-diamidobenzene, 1 : 4′-diamidonaphthalene and from diamidostilbene, $C_6H_4(NH_2)C_2H_2.C_6H_4(NH_2)$, the derivatives of which will be subsequently described.

Azo-dyes for cotton are therefore only obtained from *p*-diamido-compounds and, among the derivatives of diphenyl, from such substances in which, in addition, the ortho-hydrogen is not replaced.

The preparation of these dyes is similar to that of other azo-colouring matters, the diamido-compound being diazotized

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[1] *Annalen*, **207**, 334.

[2] Schultz, *Ber.* **17**, 461; *Steinkohlentheer*, **2**, 305.

and a solution of the phenol, sulphonic acid, &c., in caustic soda added.

The dyeing usually takes place in a bath heated to 80—100°, which is made strongly alkaline by the addition of soap, borax, sodium silicate, sodium stannate, &c., and sodium sulphate added to aid the absorption of the colour.

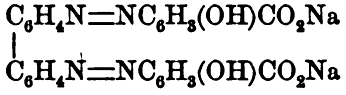
Almost all of these dyes are altered by acids, the red being most delicate and the violet rather more stable, whilst the blue are not affected. On the other hand, the last are sensitive to light, the reds more stable and the yellow chrysamines fast both to light and soap. Only a few of the most important or better known are here described. For an account of the others reference may be made to the works cited in the footnote.[1]

Chrysamine G, $C_{26}H_{16}N_4O_6Na_2$, is prepared from benzidine and salicylic acid and occurs in commerce as a brownish red powder, only slightly soluble in water, readily in dilute caustic soda solution, a brownish red solution of the basic salt, $C_{26}H_{14}N_4O_6Na_4$ being formed. Hydrochloric acid produces a brownish red precipitate in this solution. It forms a reddish violet coloured solution in concentrated sulphuric acid, the addition of water to which produces a brown precipitate of the free acid. It dyes wool a fine yellow in a soap bath.

Chrysamine R, $C_{25}H_{20}N_4O_6Na_2$, is obtained from orthotolidine and is very similar to the preceding compound but produces a redder yellow.

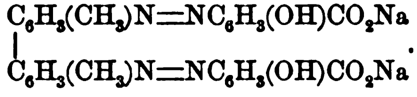
The constitution of these compounds is expressed by the following formulæ :

G.



$$\begin{array}{l}C_6H_4N{=}NC_6H_3(OH)CO_2Na\\ |\\ C_6H_4N{=}NC_6H_3(OH)CO_2Na\end{array}$$

R.



$$\begin{array}{l}C_6H_3(CH_3)N{=}NC_6H_3(OH)CO_2Na\\ |\\ C_6H_3(CH_3)N{=}NC_6H_3(OH)CO_2Na\end{array}.$$

Congo red, $C_{32}H_{22}N_6S_2O_6Na_2$, is obtained from benzidine and naphthionic acid, and forms a brownish red powder, which yields a reddish brown coloured solution in water and separates from the hot liquid in lustrous green crystals. Hydrochloric acid produces a blue and caustic soda a reddish brown precipitate;

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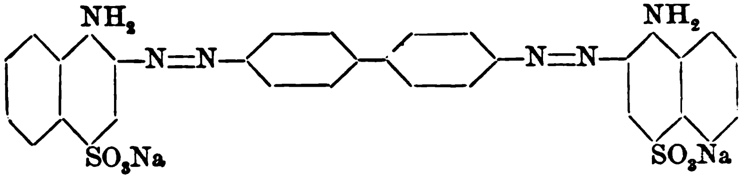
[1] Schultz, *Steinkohlentheer*, 2, 256 ; Friedländer, *Theerfarbenfabr.* 455.

in sulphuric acid it forms a blue solution from which water precipitates the free blue acid. It is decomposed by the action of zinc dust on its solution in ammonia into benzidine and 1 : 2-diamidonaphthalenesulphonic acid[1] and has therefore the following constitution:



Cotton is dyed with it in a soap bath to which Glauber's salt has been added, the shades produced varying from a delicate pink to a fiery scarlet or Turkey red according to the amount of colouring matter employed.

On account of its sensitiveness towards acids, even acetic acid, Congo red has been recommended as a reagent for acids and as an indicator for titrations of acids and alkalis. Julius proposed to employ it in the titration of aniline and Herberg used it to detect free acid in paper. According to Erdmann it exceeds litmus in delicacy. Vulpius and Dietrich, on the other hand, maintain that it is only useful for certain titrations, especially for aniline.[2]

Brücke, who has carefully studied the behaviour of various acids and salts towards Congo red, has found that it is coloured purple violet by carbon dioxide and violet by boric acid. An aqueous solution of arsenic trioxide does not affect it. If sufficient sulphuric, phosphoric, oxalic, lactic, tartaric or salicylic acid be added to an aqueous solution of Congo red to turn it violet, and the liquid be then heated, the colour becomes purple at 50° and above 60° red, but changes to violet again on cooling. If, however, sufficient acid be added to turn it blue, no change occurs on heating. The blue colour becomes violet, brown or red on the addition of an acetate or acid tartrate, but it passes back to blue on the further addition of acid. Even sulphuric and hydrochloric acid are affected in this way by the salts of weaker acids. He therefore considers that Congo red is not suited for use in volumetric analysis, and that unlike litmus, it does not possess the property of being only affected by free acid.[3]

[1] Witt, *Ber.* **19**, 1719.

[2] Schultz, *Steinkohlentheer*, **2**, 303.

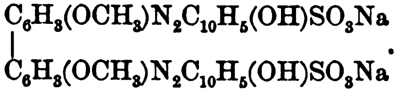
[3] *Monatsh. Chem.* **9**, 31.

Benzopurpurine B, $C_{34}H_{26}N_6S_2O_6Na_2$, prepared from tolidine and β-naphthylamine-β-sulphonic acid, is a brown powder and forms a reddish brown solution in water which is not altered by caustic soda, whilst hydrochloric acid produces a brown precipitate. It forms a blue solution in sulphuric acid in which water produces a brown flocculent precipitate. It dyes wool red, the colour being stable to acetic acid.

If naphthionic acid is used instead of the β-acid, a very similar substance, *benzopurpurine 4B*, is produced, whilst with 1 : 4′-naphthylaminesulphonic acid, *benzopurpurine 6B*, which dyes cotton a bluish red is obtained.

Deltapurpurine 5B, $C_{34}H_{26}N_6S_2O_6Na_2$, is obtained from tolidine and commercial β-naphthylamine-δ-sulphonic acid, which contains about 50 per cent. of β-naphthylamine-β-sulphonic acid. Since each of these acids is easily acted on, the deltapurpurine obtained is naturally a mixture of the colouring matters and contains together with benzopurpurine B, the sodium salt of ditolyldiazo-β-naphthylamine-δ-sulphonic acid or *deltapurpurine 7B* and the mixed azo-colour which is produced from equal molecules of tetrazoditolyl chloride and the two sulphonic acids, and which is present to the extent of 50 per cent. When common salt is added to an aqueous solution of the product, deltapurpurine 7B is first precipitated, the difficultly soluble magnesium salt of which can be obtained by adding magnesium sulphate to a boiling solution of the deltapurpurine 5B.[1] The solution of the latter gives with hydrochloric acid a brown and with caustic soda a red precipitate. Both the deltapurpurines form blue solutions in sulphuric acid, in which water produces a brown precipitate. A characteristic property of deltapurpurine 7B, which is actually extracted from the mixture, is that concentrated acetic acid added to its aqueous solution produces a brownish violet precipitate of the colouring matter, which is therefore also given by a concentrated solution of the 5B. The latter dyes cotton a somewhat bluer shade than benzopurpurine B, whilst deltapurpurine 7B produces a bluish red.

Benzazurine G, $C_{34}H_{24}N_4S_2O_{10}Na_2$, is prepared from dianisidine and 1 : 4-naphtholsulphonic acid and has therefore the following constitution :



$$\begin{array}{l} C_6H_3(OCH_3)N_2C_{10}H_5(OH)SO_3Na \\ | \\ C_6H_3(OCH_3)N_2C_{10}H_5(OH)SO_3Na \end{array}.$$

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[1] Schultz, *Ber.* **20**, 3160.

It comes into the market as a blue black powder, and forms a bluish violet solution in water, which becomes magenta red on the addition of caustic soda, whilst hydrochloric acid produces a violet precipitate. It dissolves in sulphuric acid with a blue colour, a bluish violet colouration being produced by the addition of water. It dyes cotton, silk, and wool a bluish violet to blue shade, and is employed for the production of indigo shades, a little chrysamine being added to the bath; this mixture has the advantage over indigo of dyeing cotton uniformly and not rubbing off.

When a piece of cotton dyed with benzazurine G is boiled for some time with a weak solution of copper sulphate, a copper compound of the colouring matter is formed, which is of a greener shade and therefore more valuable. This is also the case to a much greater extent with *benzazurine* 3G, prepared from anisidine and the so-called Cleve's α-naphtholsulphonic acid. The colour is in this case so greatly improved that it can scarcely be recognized as benzazurine 3G.

In the same manner azo-violet, prepared from anisidine, α-naphtholsulphonic acid and α-naphthylaminesulphonic acid, is converted into a blue with only a faint violet shade, which is not reconverted into the original reddish violet by soaping. The violet red *heliotrope* from anisidine and β-naphthylaminesulphonic acid forms a fine violet compound with copper, and in fact all the colours of this nature become bluer and more stable towards soap.

The latter effect can also be attained by the use of zinc sulphate or nickel sulphate, without an accompanying alteration of the shade. Moreover, the colours are thus rendered absolutely fast to light and even surpass indigo in this respect. Dyed wool is altered by copper sulphate in the same manner as cotton, and at the same time becomes faster to milling whilst nickel sulphate makes it faster to soap.[1]

Benzidine Blue, $C_{32}H_{18}N_4S_4O_{14}Na_4$, was obtained by Schultz from benzidine and β-naphthol-α-disulphonic acid.[2] It is a powder with a bronze lustre, and forms a blue solution in cold water, which on boiling, becomes Bordeaux red, but passes back to blue on cooling; caustic soda solution also colours it Bordeaux red, whilst acetic acid produces a brownish-red colouration, and hydrochloric acid a reddish-violet flocculent precipitate. It

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[1] *Farbenfabr.* vorm. Baeyer and Co.; Schultz, *Steinkohlentheer*, **2**, 1258.

[2] Schultz, *Ber.* **17**, 461.

forms a blue solution in sulphuric acid, from which water precipitates it as a violet mass.

If anisidine is employed instead of benzidine, a greenish blue is obtained. If, however, only one molecule of the disulphonic acid be allowed to act on a molecule of the tetrazo-compound, a product is formed which still contains one diazo group and from which a series of reddish-blue to greenish-blue dyes can be prepared by combination with naphthols, or their sulphonic acids.[1]

Other blue colouring matters are prepared from benzidine-sulphodisulphonic acid, and secondary or tertiary β-naphthylamines such as methyl-β-naphthylamine or o-tolyl-β-naphthylamine, which give a redder but clearer blue than phenyl-β-naphthylamine, whilst that obtained from xylyl-β-naphthylamine is of a greener shade.[2]

Reddish-brown and brown cotton colours are obtained by combining the diazo-compounds prepared from the sulphonic acids of the naphthylamines, of benzidine, &c., with phenylene brown.

Black cotton colours are prepared from amidonaphtholsulphonic acid and benzidine, tolidine, or dianisidine. These are all of a red shade, but since they contain an amido-group they can be diazotized on the fibre and then converted by the action of phenols, amidobases, &c., into deep blue or black dyes. If, for example, cotton goods dyed with *diamine black* prepared from benzidine, be dipped into a faintly acid sodium nitrite solution they take a greenish-blue colour. If they are then washed out and brought into a cold alkaline β-naphthol solution, they become deep blue-black, the shade being more than twice as deep as the original colour, and at the same time very fast towards acids and alkalis. When the benzidine is replaced by dianisidine or tolidine, greener shades are obtained.[3]

Carbazole-yellow, $C_{12}H_6(NH)[N_2C_6H_4(OH)CO_2Na]_2$, is prepared by diazotizing diamidocarbazole sulphate and bringing it into an alkaline solution of salicylic acid, a deep-red solution being formed which on standing becomes yellowish-brown. The liquid is boiled and salt added, which precipitates the colouring matter as a brown crystalline mass. It is readily soluble in water, dyes cotton a full golden-yellow, and imparts a bright yellow colour to silk and wool, which is fast to milling.[4]

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[1] *Farbenfabr.* vorm. Baeyer and Co. ; Schultz, *Steinkohlentheer*, **2**, 1072.

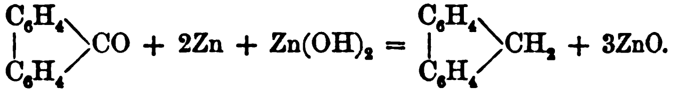
[2] *Farbenfabr.* vorm. Baeyer and Co. ; *Ber.* **23**, 441 c.

[3] *Farbenfabr.* vorm. Baeyer and Co. ; *Chem. Zeit.* **14**, 1356.

[4] Bad. *Anilin- and Sodafabr.* ; *Ber.* **22**, 177 c.

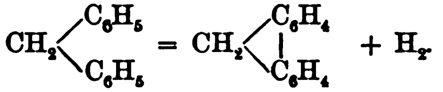
THE FLUORENE GROUP

2752 *Fluorene,* $C_{13}H_{10}$. This name was given by Berthelot to a hydrocarbon which he discovered in 1867 in crude anthracene and in heavy coal-tar oil, and which was distinguished by its magnificent violet fluorescence.[1] Fittig in 1873 then found that when diphenyleneketone is heated with zinc dust, the corresponding *diphenylenemethane* is formed:[2]



$$\begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array} > CO + 2Zn + Zn(OH)_2 = \begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array} > CH_2 + 3ZnO.$$

Gräbe moreover found that it is also formed when the ketone is heated with phosphorus and hydriodic acid at 130—140°,[3] and when the vapour of diphenylmethane is passed through a red-hot tube:[4]



$$CH_2 < \begin{array}{l} C_6H_5 \\ C_6H_5 \end{array} = CH_2 < \begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array} + H_2.$$

He pointed out that diphenylenemethane is very similar to fluorene, which had been more closely examined by Barbier,[5] and Fittig and Schmitz then showed that the two are identical.[6]

Fluorene is also obtained by heating ellagic acid, $C_{14}H_6O_8$, with zinc dust,[7] and in a very pure condition by heating *o*-diphenylenecarboxylic acid with hydriodic acid and phosphorus.[8] Adam prepared it by the action of methylene chloride on a mixture of diphenyl and aluminium chloride.[9]

[1] *Ann. Chim Phys.* IV. **12**, 222.
[2] *Ber.* **6**, 187.
[3] *Ber.* **7**, 1625.
[4] *Annalen,* **174**, 194.
[5] *Ann. Chim. Phys.* V. **7**, 479.
[6] *Annalen,* **193**, 134.
[7] Barth and Goldschmidt, *Ber.* **11**, 846.
[8] Graebe and Aubin, *Annalen,* **247**, 277.
[9] *Ann. Chim. Phys.* VI. **15**, 253.

In order to isolate fluorene from heavy coal-tar oil, the latter is first of all freed from phenanthrene and anthracene by crystallization and the portion boiling between 290 and 340° fractionated about six times, until the larger part passes over at 300—320°. On strongly cooling, the fluorene separates out and is well pressed, the portion boiling at 295—305° isolated by fractional distillation, repeatedly crystallized from a mixture of benzene and alcohol, and finally recrystallized from glacial acetic acid. The crude fluorene may also be dissolved in ether, picric acid added and the compound thus obtained decomposed with ammonia. The hydrocarbon purified in this manner shows the beautiful fluorescence already mentioned (Barbier), but according to Fittig and Schmitz, this is due to an impurity. They prepared fluorene by distilling diphenyleneketone over zinc dust, a red substance being also formed in small quantity which can be separated from the hydrocarbon by a single distillation. The fluorene was then purified by recrystallization from alcohol. It forms colourless, lustrous plates, showing only a faint fluorescence, like that of other similar hydrocarbons, is sparingly soluble in cold, readily in hot alcohol, ether, benzene, and carbon disulphide. It melts at 113°, boils at 296°, and forms a vapour of the sp. gr. 5·77.[1] When it is heated with 40 parts of concentrated hydriodic acid to 275°, it is converted into tridecane, $C_{13}H_{28}$, boiling at about 240°; in addition some hexane and heptane are formed (Barbier). On fusion with caustic potash it yields ε-diphenol.

In order to detect fluorene in a mixture of phenanthrene and anthracene, 15 grms. of the substance are boiled with 90 grms. of sulphuric acid, diluted with 3 vols. of water, and 60 grms. of potassium dichromate for 6 hours in an apparatus provided with a reflux condenser; the oxidation product is then filtered off, distilled with steam and the distillate allowed to crystallize slowly from alcohol, by which means diphenyleneketone is obtained in compact crystals, which can be readily picked out from any adhering hydrocarbon.[2]

Fluorene picric acid, $C_{13}H_{10} + C_6H_3(NO_2)_3O$, is formed when an ethereal solution of the constituents is allowed to evaporate, and crystallizes according to Barbier in red needles, but according to Fittig and Schmitz in compact, reddish-brown prisms, which melt at 79—80°, and are decomposed by boiling with

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[1] Knecht, *Ber.* **10**, 2074.

[2] Anschütz, *Ber.* **11**, 1216.

water or alcohol. Gräbe and Aubin, on the other hand, obtained golden yellow needles, of the same melting point.

Fluorene picryl chloride $C_{13}H_{10} + C_6H_2(NO_2)_3Cl$, crystallizes from an alcoholic solution of its constituents in orange-yellow needles, melting at 69—70°.[1]

Octohydrofluorene, $C_{13}H_{18}$, is formed, together with the following compound, when 3·6 grms. of fluorene are heated for 8 hours at 250—260° with 3 grms. of red phosphorus and 9 grms. of hydriodic acid of sp. gr. 1·7, and is a liquid, boiling at 272—275°.

Decahydrofluorene, $C_{13}H_{20}$, boils at 254—256°, has a faint violet fluorescence, a penetrating odour, resembling that of diphenylmethane, and solidifies at — 73° to a white crystalline mass.[2]

Perhydrofluorene, $C_{13}H_{22}$, is obtained by heating 1 part of fluorene with 1·25 parts of phosphorus and 5—6 parts of hydriodic acid of sp. gr. 1·7 for 12—16 hours at 250—260°. It is a liquid, which resembles perhydroacenapthene and boils at 230°.[3]

Dichlorofluorene, $C_{13}H_8Cl_2$, separates out when dry chlorine is passed into a solution of fluorene in chloroform; it crystallizes in tablets, which melt at 128°, and sublime without decomposition. Chromic acid oxidizes it to dichlorophenyleneketone.[4]

Trichlorofluorene, $C_{13}H_7Cl_3$, was obtained by Holm by passing chlorine for a long time through a solution of fluorene in carbon disulphide. It crystallizes in small white plates, is sparingly soluble in alcohol and ether, and melts at 147°.[5]

Bromofluorene, $C_{13}H_9Br$, is formed, together with the following compound when bromine is carefully added to a cooled solution of fluorene in chloroform. It crystallizes from alcohol in needles, melting at 101—102°, is very soluble in chloroform, and on oxidation yields bromodiphenyleneketone (Hodgkinson and Matthews).

Bromofluorene dibromide, $C_{13}H_9Br_3$, was obtained by Barbier by passing a mixture of bromine vapour and air into a cold solution of fluorene in carbon disulphide. It crystallizes from benzene in light yellow, strongly lustrous long needles, and is converted by alcoholic potash into the following compound.

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[1] Liebermann and Palm, *Ber.* **8**, 377.

[2] Guye, *Bull. Soc. Chim.* III. **4**, 266.

[3] Liebermann and Spiegel, *Ber.* **22**, 779.

[4] Hodgkinson and Matthews, *Journ. Chem. Soc.* 1883, **1**, 163.

[5] *Ber.* **16**, 1081.

Dibromofluorene, $C_{13}H_8Br_2$, is formed, according to Barbier when the calculated quantity of bromine is added to a solution of fluorene in 6 parts of carbon disulphide, the latter distilled off and the residue washed with ether and recrystallized from carbon disulphide. He thus obtained large, transparent, monosymmetric tablets, which were measured by Bouchardat. It melts at 166—167°, is sparingly soluble in alcohol, can be distilled without decomposition, and is not attacked by boiling alcoholic potash, but decomposes on ignition with lime, diphenyl being formed.

Fittig and Schmitz, who also prepared this compound, obtained it in the form of small, transparent, colourless tablets, which melt at 162—163°, and according to Arzruni, are also monosymmetric, but with quite a different axial ratio.[1]

By recrystallizing a specimen of the substance prepared by Barbier from carbon disulphide they first obtained colourless tablets, precisely similar to those obtained by themselves, and then a single yellow crystal, followed by a further crop of the colourless substance.

Lehmann has shown that dibromofluorene also exists in two other forms and is tetramorphous, since both the forms already described are converted by heating into the γ-modification, which is also formed when the fused substance is allowed to cool, and is readily soluble in benzene. On cooling this solution a portion crystallizes out unaltered, a second is converted into the form observed by Barbier, and a third separates in the cold in long needles of the δ-modification, which are readily converted by heating into the stable γ-form.[2]

Tribromofluorene, $C_{12}H_6Br_2.CHBr$, was obtained by Barbier by adding the calculated quantity of bromine to a solution of fluorene in carbon disulphide. Since it is almost as soluble in benzene and carbon disulphide as dibromofluorene it can only be separated from the latter, which is simultaneously formed, by repeated recrystallization. It forms slender, yellowish needles, united in spherical masses, and melts at 161—162°. Chromic acid oxidizes it in acetic acid solution to dibromophenyleneketone (Holm).

p-Nitrofluorene, $C_{13}H_9NO_2$, is formed when nitric acid of sp. gr. 1·4 is added to a cooled solution of fluorene in glacial acetic acid, and the liquid then heated to boiling. It crys-

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[1] *Zeitschr. Krystallogr.* **1**, 625.

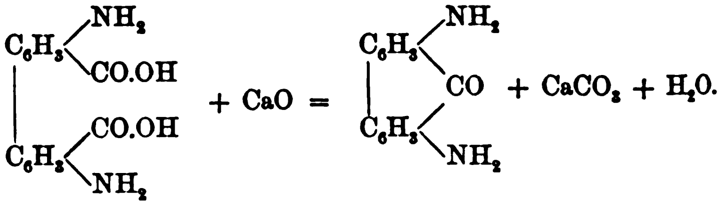
[2] *Zeitschr. Krystallogr.* **1**, 626.

tallizes in yellowish needles, melts at 154°, and is oxidized by chromium trioxide to *p*-nitrodiphenyleneketone.[1]

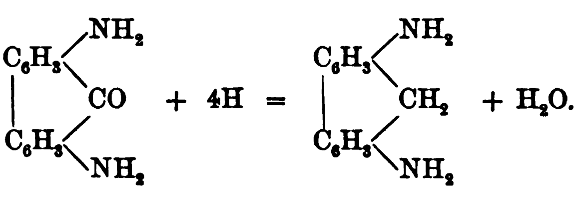
Dinitrofluorene, $C_{13}H_8(NO_2)_2$, is obtained by bringing fluorene into a mixture of equal volumes of fuming nitric acid and glacial acetic acid. It crystallizes from hot glacial acetic acid in colourless needles, and from boiling alcohol, in which it is only very sparingly soluble, in lustrous pointed needles, melting at 199—201° (Fittig and Schmitz).

Amidofluorene, $C_{13}H_9.NH_2$, was prepared by Strassburger by the distillation of the hydrochloride of *p*-amidodiphenic acid with lime,[2] and by the reduction of nitrofluorene with tin and hydrochloric acid. It crystallizes from alcohol in pale grey needles, and melts at 124—125.° Its *hydrochloride* is only sparingly soluble in water, and its *acetyl compound* melts at 187—188°.

Diamidofluorene, $C_{13}H_8(NH_2)_2$, is formed by the reduction of dinitrodiphenyleneketone with tin and hydrochloric acid, and, together with benzidine when diamidodiphenic acid is distilled with lime. Diamidodiphenyleneketone is the first product of the reaction:



A portion of the substance is simultaneously carbonized, hydrogen being evolved which exercises a reducing action:



Diamidodifluorene crystallizes in grey or brownish needles, rapidly becomes bluish in the air, and is slightly soluble in cold, more readily in boiling water, and readily in alcohol. On heat-

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[1] Strassburger, *Ber* **17**, 107.

[2] *Ber.* **16**, 2346.

ing with a solution of ethyl nitrite it is converted into fluorene. Its *sulphate* is sparingly soluble in water and crystallizes in small lustrous plates. Its solution gives with potassium ferricyanide a blue precipitate, soluble in hot water and acids; chlorine water or bleaching powder solution also produce a blue precipitate, which soon becomes green and finally reddish-brown.

Diacetamidofluorene, $C_{13}H_8(NH.CO.CH_3)_2$, crystallizes in white lustrous plates.[1]

2753 *Isomerides of fluorene* were found by Carnelley among the products formed by heating a mixture of benzene and toluene to redness. Since he considered Berthelot's fluorene to be different from Fittig and Schmitz's diphenylenemethane, he distinguished his hydrocarbons as γ and δ.[2]

γ-*Diphenylenemethane* appears also to occur in coal-tar,[3] and crystallizes from alcohol in nacreous plates or prismatic needles, melts at 118°, boils at 295°, and forms a *picric acid compound*, which crystallizes from ether in blood-red needles, melting at 79—81°.

γ-*Diphenylenemethoquinone*, $C_{13}H_8O_2$, is obtained by the oxidation of the hydrocarbon with chromium trioxide, and crystallizes from alcohol in long golden-yellow needles, which melt at 280—281°, but sublime at a lower temperature.

γ-*Dibromodiphenylenemethane*, $C_{13}H_8Br_2$, crystallizes in needles or octohedra, and melts at 162°.

δ-*Diphenylenemethane* forms nacreous tablets, melting at 208°. It boils at 320° and on oxidation yields a *quinone*, which is a white powder, sublimes in needles, and at 288° melts to a yellowish-green liquid, fluorescing like uranium glass.

A third isomeric *quinone* was obtained by Barbier, together with diphenyleneketone, by the oxidation of fluorene in small granular yellow masses, melting at 180—181°, whilst Fittig and Schmitz were unable to obtain any trace of such a substance. It was probably due to some impurity.

Sequoiene, $C_{13}H_{10}$, occurs, together with a terpene and other substances, in the needles of the Wellingtonia of our gardens (*Sequoia gigantea*), which have such a characteristic odour. It is a crystalline substance, dissolves readily in most solvents, but does not easily crystallize well. It is obtained in small plates when a layer of water is poured on to its solution in acetic

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[1] Schultz, *Annalen*, **203**, 99.

[2] *Journ. Chem. Soc.* 1880, **1**, 708.

[3] Hodgkinson and Matthews, *Journ. Chem. Soc.* 1883, **1**, 163.

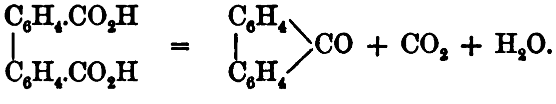
acid; these show a faint bluish fluorescence, melt at 105°, and in the pure state are odourless. It boils at 290—300°, gives with picric acid a compound crystallizing in red needles, and a yellowish-red nitro-product with nitric acid.[1]

2754 *Fluorenyl alcohol* or *Diphenylene carbinol*, $C_{12}H_8{:}CH.OH$, is formed by the action of sodium amalgam on an alcoholic solution of diphenyleneketone,[2] and by heating diphenyleneglycollic acid to 160° with caustic soda solution.[3] It crystallizes from boiling water in hair-like matted needles, and is soluble in alcohol and ether, more readily in benzene, from which it crystallizes in hexagonal tablets, with a vitreous lustre, containing benzene of crystallization which is gradually lost in the air, rapidly on heating.[4] It melts at 153°, is coloured blue by concentrated sulphuric acid and is reconverted into the ketone by oxidation. When it is heated somewhat strongly, water is lost and *fluorenyl ether*, $(C_{13}H_9)_2O$, formed as a resinous mass.

Fluorenyl acetate, $C_{13}H_9.O.CO.CH_3$, was obtained by Barbier by heating the alcohol with acetic anhydride at 100°; it crystallizes from a mixture of ether and alcohol in rhombic tablets, melting at 75°.

Fluorenylamine, $C_{12}H_8.CH.NH_2$, is formed when diphenyleneketoxime, $C_{10}H_8{:}CNOH$, is boiled with zinc and acetic acid; its *hydrochloride* crystallizes from dilute alcohol in long needles. The free base is insoluble in water, and melts at 50—60°.[5]

Diphenyleneketone, $C_{13}H_8O$, is obtained by the distillation of diphenic acid with lime:[6]



$$\begin{array}{l} C_6H_4.CO_2H \\ | \\ C_6H_4.CO_2H \end{array} = \begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!>CO + CO_2 + H_2O.$$

It is also formed by the oxidation of fluorene (Barbier). In order to prepare it, equal parts of diphenic acid and quicklime are heated in a combustion furnace in a tube bent at an obtuse angle, the temperature being allowed to rise very slowly; a red substance is also formed, which remains behind on distilling the product with steam. Since however the ketone is only slightly volatile, it is better to purify it by recrystallization from

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[1] Lunge and Reinkauler, *Ber.* **13**, 1656; **14**, 2202.

[2] Barbier, *loc. cit.*; Bamberger and Hooker, *Annalen*, **229**, 157.

[3] Friedländer, *Ber.* **10**, 534.

[4] Bamberger, *Beilstein's Handb.* **2**, 684.

[5] Wegerhoff, *Annalen*, **252**, 36.

[6] Fittig and Ostermayer, *Annalen*, **166**, 372.

a mixture of equal volumes of alcohol and water, in which the red substance is scarcely soluble.[1]

It is also readily obtained by passing the vapour of phenanthrenequinone over heated lead oxide,[2] or by boiling it for some time with caustic soda solution and then adding potassium permanganate to oxidize the diphenyleneglycollic acid, $C_{13}H_8(OH)CO_2H$, which is first formed.[3]

The latter is insoluble in water, and sparingly soluble in dilute alcohol, from which it crystallizes in small yellow needles, whilst it separates from alcohol, in which it is readily soluble in light yellow, large, transparent, rhombic tablets or thick prisms, melting at 83·5—84°. It boils above 300°, is converted by fused potash into *o*-phenylbenzoic acid (p. 433) and on heating with chromic acid is completely oxidized, whilst an alkaline permanganate solution oxidizes it slowly to phthalic acid.

Dichlorodiphenyleneketone, $C_{13}H_6Cl_2O$, is obtained by the oxidation of dichlorofluorene with chromium trioxide and forms yellow microscopic crystals, melting at 158°.

a-Bromodiphenyleneketone, $C_{13}H_7BrO$, was prepared in a similar manner from bromofluorene, and crystallizes in dark yellow needles, melting at 104° (Hodgkinson and Matthews).

β-Bromodiphenyleneketone is formed by the distillation of bromodiphenic acid with slaked lime, and crystallizes from hot alcohol in light yellow delicate plates, melts at 122°, and on heating with zinc dust is converted into fluorene.[4]

a-Dibromodiphenyleneketone, $C_{13}H_6Br_2O$, is obtained by adding the calculated quantity of chromium trioxide to a solution of dibromofluorene in acetic acid. It crystallizes from alcohol in long, yellow needles, and melts at 142·5°.[5]

β-Dibromodiphenyleneketone is formed when a small excess of chromium trioxide is employed and by the oxidation of tribromofluorene. It also crystallizes in yellow needles, melts at 197°, and on heating with phosphorus and hydriodic acid is reconverted into dibromofluorene (Holm, Hodgkinson, and Matthews).

γ-Dibromodiphenyleneketone was obtained by the distillation of dibromophenylbenzoic acid with slaked lime, and crystallizes

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[1] Schmitz, *Annalen*, **193**, 115.
[2] Wittenberg and Meyer, *Ber.* **16**, 502.
[3] Anschütz and Japp, *Ber.* **11**, 211.
[4] Claus and Erler, *Ber.* **19**, 3155.
[5] Holm, *Ber.* **16**, 1081.

from alcohol in light yellow, thin plates, melts at 133° and sublimes in long, thin, wine-yellow needles, giving rise to the pleasant odour of unripe oranges, in the same manner as β-bromodiphenyleneketone (Claus and Erler).

Nitrodiphenyleneketone, $C_{13}H_7(NO_2)O$, is formed when diphenyleneketone is added in small quantities to fuming nitric acid, and crystallizes from alcohol in yellow needles or plates, which melt at 220° and readily sublime.[1]

Dinitrodiphenyleneketone, $C_{13}H_6(NO_2)_2O$, is formed when the ketone is heated with fuming nitric acid, by the oxidation of dinitrofluorene or dinitrophenyleneglycolic acid and by the action of concentrated nitric acid on fluorene alcohol. It is slightly soluble in boiling alcohol, and crystallizes from glacial acetic acid in long, slender, light-yellow needles, melting at 290.° Tin and hydrochloric acid convert it into *diamidodiphenyleneketone*, $C_{13}H_6(NH_2)O$, which is a crystalline substance (Schultz).

Diphenyleneketoxime, $C_{12}H_8: C=NOH$, is prepared by heating an alcoholic solution of diphenyleneketone with hydroxylamine hydrochloride and separates from alcohol in pale yellow crystals, melting at 192°.[2]

Its *sodium salt*, $C_{13}H_8NONa$, crystallizes from hot concentrated caustic soda solution in elongated light yellow plates, readily soluble in water. The *acetate*, $C_{13}H_8NO.CO.CH_3$, is formed by boiling the oxime with acetic anhydride, and crystallizes from dilute alcohol in short, broad needles, melting at 76°, whilst the *benzoate* forms long, narrow, yellow prisms, and melts at 179°.[3]

Diamidodiphenyleneketoxime, $C_{12}H_6(NH_2)_2NOH$, is obtained by heating diamidodiphenyleneketone with a solution of hydroxylamine hydrochloride and sodium carbonate. It is an orange-coloured powder which forms a yellowish-brown solution in alcohol. It is employed for the manufacture of cotton colours; the compounds formed with salicylic acid are yellow, whilst those given by the naphthylamine sulphonic acids are amaranth-red.[4]

Hydroxydiphenyleneketone, $C_{12}H_7(OH)CO$, is prepared by heating sodium salicylate with phosphorus oxychloride,[5] and together with phenylsalicylic acid, by heating *o*-diazobenzoic acid sulphate with phenol:[6]

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[1] Schultz, *Annalen*, **203**, 103.

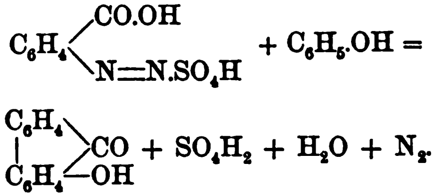
[2] Spiegler, *Monatsh. Chem.* **5**, 195.

[3] Wegerhoff, *Annalen*, **252**, 36.

[4] Bad. Anilin. and Sodafabr. *Ber.* **23**, 535 c.

[5] Richter, *J. Pr. Chem.* II. **28**, 294.

[6] Griess, *Ber.* **21**, 981.



$$C_6H_4\left\langle\begin{matrix}CO.OH\\ N{=}N.SO_4H\end{matrix}\right. + C_6H_5.OH =$$

$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\begin{matrix}>CO\\ -OH\end{matrix} + SO_4H_2 + H_2O + N_2.$$

It crystallizes from alcohol in white needles, melting at 95°, readily soluble in alkalis. On ignition with lime it yields benzophenone, diphenylene dioxide, carbon dioxide, and hydrogen, whilst on heating with zinc-dust it is reduced to diphenyl. Potassium permanganate and chromic acid oxidize it completely.

Hexhydroxydiphenyleneketone, $C_{12}H_2(OH)_6CO$, is formed when ellagic acid is boiled for a few minutes with concentrated caustic potash solution. It crystallizes from boiling water, in which it is only slightly soluble, in microscopic, acicular prisms, is readily soluble in alkali, and on heating with zinc-dust is converted into fluorene. When a trace of alcohol is added to its aqueous solution, it is first coloured yellowish-brown, then, more rapidly on shaking, dark yellowish-red, and finally a fiery carmine-red. If alkali be added to the alcoholic solution a green precipitate is produced, which forms a carmine-red solution in water. Ferrous salts produce a blue colouration followed by a precipitate of the same colour, whilst ferric chloride colours dilute solutions bluish-green and gives a blue-black precipitate, soluble in a large quantity of water, in more concentrated solutions. Sodium carbonate produces in these solutions, according to the concentration, a red to brown colouration or a precipitate of the same colour.[1]

Isodiphenyleneketone, $C_{13}H_8O$, is formed when the vapours of phenol and carbon disulphide are passed over red-hot copper turnings:

$$2C_6H_6O + CS_2 + 4Cu = C_{13}H_8O + H_2O + 2Cu_2S + H_2.$$

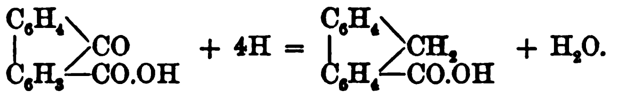
It crystallizes from alcohol in feathery needles or plates, melts at 83° and is not affected either by an acetic acid solution of chromium trioxide or fused potash.[2]

[1] Barth and Goldschmidt, *Ber.* **12**, 1247.

[2] Carnelley and Dunn, *Ber.* **21**, 2005.

FLUORENECARBOXYLIC ACIDS.

2755 *Fluorenic acid*, or *m-Fluorenecarboxylic acid*, $C_{13}H_9.CO_2H$, is the product of the action of sodium amalgam on *m*-diphenyleneketocarboxylic acid suspended in water, the liquid being neutralized with hydrochloric acid at intervals:



$$\begin{array}{l}C_6H_4\diagdown\\ |\qquad\quad >CO\\ C_6H_3\diagup\!\!-CO.OH\end{array} + 4H = \begin{array}{l}C_6H_4\diagdown\\ |\qquad\quad >CH_2\\ C_6H_3\diagup\!\!-CO.OH\end{array} + H_2O.$$

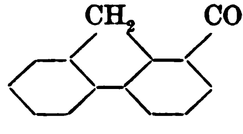
It is scarcely soluble in boiling water, readily in hot, more sparingly in cold alcohol, and separates from dilute alcohol in groups of small crystals, which melt at 245—246°, and sublime without decomposition. On heating with lime it decomposes into fluorene and carbon dioxide; potassium dichromate and dilute sulphuric acid oxidize it completely on boiling, whilst potassium permanganate in alkaline solution oxidizes it to the ketonic acid.

Calcium fluorenate, $2(C_{14}H_9O_2)_2Ca + 5H_2O$, crystallizes from hot water, in delicate white needles.

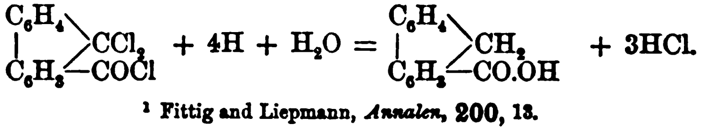
Barium fluorenate, $(C_{14}H_9O_2)_2Ba + 3H_2O$, separates from a hot dilute solution in thin plates, which show splendid interference colours, and after drying look like small silvery fish scales.

Ethyl fluorenate, $C_{14}H_9O_2.C_2H_5$, forms long lustrous prisms, melting at 53·5°.[1]

The constitution of the acid follows from that of fluorene, and is expressed by the following formula:



o-Fluorenecarboxylic acid, $C_{12}H_7(CH_2)CO_2H$, is formed by the action of zinc dust and dilute acetic acid on *o*-dichlorodiphenylenecarboxylic chloride:



$$\begin{array}{l}C_6H_4\diagdown\\ |\qquad\quad >CCl_2\\ C_6H_3\diagup\!\!-COCl\end{array} + 4H + H_2O = \begin{array}{l}C_6H_4\diagdown\\ |\qquad\quad >CH_2\\ C_6H_3\diagup\!\!-CO.OH\end{array} + 3HCl.$$

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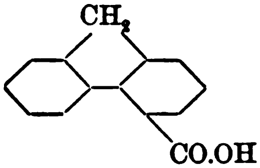
[1] Fittig and Liepmann, *Annalen*, **200**, 13.

It forms crystals, is slightly soluble in cold, moderately in hot water, readily in alcohol and ether, and melts at 175°. Its *methyl ester* forms well-developed transparent crystals, melting at 64°.

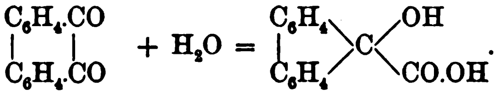
It has the following constitution:



o-Fluorenehydroxycarboxylic acid, $C_{12}H_7(CH.OH)CO_2H$, is formed when an ammoniacal solution of *o*-diphenyleneketo-carboxylic acid is treated with zinc dust. It is scarcely soluble in cold, moderately in hot water or alcohol, and melts at 203°. It forms a green solution in sulphuric acid, and is re-oxidized to the ketonic acid by an alkaline solution of potassium permanganate.

Diphenyleneacetic acid, $C_{14}H_{10}O_2$, is obtained by heating diphenyleneglycollic acid with hydriodic acid and red phosphorus at 140°; it forms small indistinct crystals, melts at 220—222°, is scarcely soluble in water, and moderately in alcohol. When it is heated for some time above its melting point, fluorene sublimes, and on heating with soda lime it decomposes quantitatively into carbon dioxide and the same hydrocarbon Its *ethyl ester* forms hard crystals, melting at 165°.

Diphenyleneglycollic acid, $2C_{14}H_{10}O_3 + H_2O$, is prepared by boiling phenanthrenequinone with concentrated caustic soda solution:



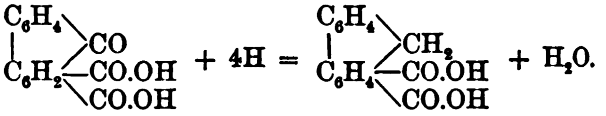
$$\begin{array}{l} C_6H_4.CO \\ | \qquad | \\ C_6H_4.CO \end{array} + H_2O = \begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array}\!\!>C<\!\!\begin{array}{l} OH \\ CO.OH \end{array}.$$

It is only very slightly soluble in cold, readily in hot water, from which it crystallizes in lustrous white plates, melting at 162°. On heating with sulphuric acid a deep blue solution is formed, from which water precipitates Barbier's fluorenyl ether, a substance also formed by heating the acid above its melting point. When the acid is heated with an excess of caustic soda solution at 160°, it decomposes into carbon dioxide and fluorenyl alcohol, whilst chromic acid oxidizes it to diphenyleneketone.

Ethyl diphenyleneglycollate, $C_{12}H_8 : C(OH)CO.OC_2H_5$, crystallizes from dilute alcohol in small hard prisms, melting at 92°.

Dibromodiphenyleneglycollic acid, $C_{12}H_6Br_2 : C(OH)CO_2H$, is produced by the addition of bromine to the acid suspended in water, and crystallizes from glacial acetic acid in small distorted needles, melting at 225°. Its *ethyl ester* forms small lustrous prisms, melting at 150—151°.[1]

Fluorenedicarboxylic acid, $C_{13}H_8(CO_2H)_2$, is obtained by the action of sodium amalgam on a weak alkaline solution of diphenyleneketonedicarboxylic acid:



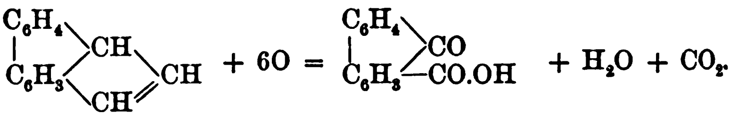
$$\begin{array}{l} C_6H_4\diagdown \\ |\qquad\;\; >CO \\ C_6H_2\!<\!-CO.OH \\ \qquad\;\; \diagdown CO.OH \end{array} + 4H = \begin{array}{l} C_6H_4\diagdown \\ |\qquad\;\; >CH_2 \\ C_6H_4\!<\!-CO.OH \\ \qquad\;\; \diagdown CO.OH \end{array} + H_2O.$$

It is slightly soluble in alcohol and ether, more readily in glacial acetic acid, from which it separates as a heavy crystalline powder. On heating with lime it decomposes into carbon dioxide and fluorene.

Its *silver salt* is a heavy white precipitate, which decomposes on heating, a sublimate of net-like aggregates of needles, probably consisting of fluorenyl alcohol, being obtained.[2]

DIPHENYLENEKETONECARBOXYLIC ACIDS.

2756 *m-Diphenyleneketonecarboxylic acid*, $C_{12}H_7(CO)CO_2H$, is formed when fluoranthrene is heated with dilute sulphuric acid and potassium dichromate:



$$\begin{array}{l} C_6H_4\diagdown \\ |\qquad\;\; >CH\diagdown \\ C_6H_3\!<\qquad\quad >CH \\ \qquad\;\; \diagdown CH\!\!\nearrow \end{array} + 6O = \begin{array}{l} C_6H_4\diagdown \\ |\qquad\;\; >CO \\ C_6H_3\!<\!-CO.OH \end{array} + H_2O + CO_2.$$

It is scarcely soluble in cold, slightly in hot water, readily in alcohol and ether, and crystallizes from dilute alcohol in orange-red needles, often an inch in length, melting at 191—192°.

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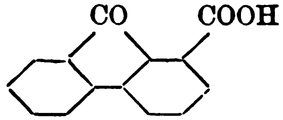
[1] Friedländer, *Ber.* **10**, 534.

[2] Bamberger and Hooker, *Annalen*, **229**, 161.

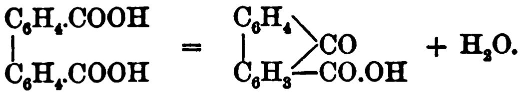
On heating with zinc dust it yields fluorene, and on dry distillation decomposes into carbon dioxide and diphenyleneketone. It is scarcely attacked by potassium dichromate and sulphuric acid, whilst water and sodium amalgam reduce it to fluorenic acid, and fused potash converts it into isodiphenic acid. Its constitution is expressed by the following formula:



The *calcium* salt, $(C_{14}H_7O_3)_2\,Ca + 2H_2O$, separates on evaporating its solution in small yellow needles, which are not perceptibly more soluble in hot than in cold water. The *barium* salt, $(C_{14}H_7O_3)_2Ba + 4H_2O$, crystallizes from a hot dilute solution in voluminous aggregates of slender silky needles, and is sparingly soluble in cold water.

Nitro-m-diphenyleneketonecarboxylic acid, $C_{14}H_7(NO_2)O_3$, is prepared by dissolving the acid in warm fuming nitric acid. It is insoluble in water, but crystallizes from absolute alcohol in lustrous golden yellow needles, melting at 245—246°. Its *barium* salt, $(C_{14}H_6NO_5)_2Ba + 4H_2O$, forms very sparingly soluble pale yellow slender needles.[1]

o-Diphenyleneketonecarboxylic acid is obtained by heating diphenic acid with sulphuric acid at 150°:



$$\begin{array}{l} C_6H_4.COOH \\ | \\ C_6H_4.COOH \end{array} = \begin{array}{l} C_6H_4 \\ |\quad >CO \\ C_6H_3-CO.OH \end{array} + H_2O.$$

It crystallizes from alcohol in yellow needles, which are scarcely soluble in water, melts at 227°, and distils at a higher temperature almost without decomposition. If, however, its vapour be heated to 450°, it splits up into diphenyleneketone and carbon dioxide. On fusion with potash it yields diphenic acid, and is converted by hydriodic acid and phosphorus at 180° into pure fluorene.

The *sodium* salt, $C_{14}H_7O_3Na + 6H_2O$, crystallizes from hot water in yellow needles; the *ammonium* salt, $C_{14}H_7O_3(NH_4) + H_2O$,

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[1] Fittig and Gebhard, *Annalen*, **193**, 149; Fittig and Liepmann, *Annalen* **200**, 6.

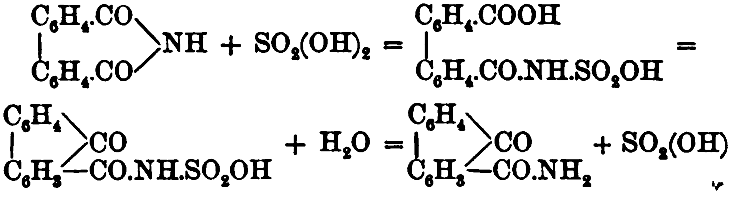
forms dark yellow needles; and the *silver* salt a pale yellow precipitate somewhat soluble in water:

	Melting-point.
Methyl ester, $C_{14}H_7O_3(CH_3)$, yellow needles . . .	132°
Ethyl ester, $C_{14}H_7O_3(C_2H_5)$, golden yellow needles	103°

o-Diphenyleneketonecarboxylic chloride, $C_{12}H_7(CO)COCl$, is obtained by the action of phosphorus trichloride on the acid, and separates from light petroleum in large yellow crystals, melting at 128°. It is only slowly attacked by water, but quickly by alkalis, and is converted by ammonia into the amide.

Dichlorodiphenyleneketonecarboxylic chloride, $C_{12}H_7(CCl_2)COCl$, is formed by heating the foregoing compound with phosphorus pentachloride, and separates from light petroleum in colourless crystals, melting at 95°. From its alcoholic solution the *ester*, $C_{12}H_7(CCl_2)CO.OC_2H_5$, separates out at the ordinary temperature in colourless needles, which melt at 73°, but on boiling, the ester of the ketonic acid is formed. On treatment with zinc and dilute acetic acid, the trichloride is converted into fluorene-*o*-carboxylic acid.[1]

o-Diphenyleneketonecarboxylic amide, $C_{12}H_7(CO)CO.NH_2$, is obtained by the action of ammonia on the chloride, or by warming diphenimide or phenanthrenequinonoxime (p. 506) with sulphuric acid. Its formation from diphenimide, which corresponds to diphenic anhydride, may possibly take place in the following manner:



$$\left.\begin{matrix}C_6H_4.CO\\ |\\ C_6H_4.CO\end{matrix}\right>NH + SO_2(OH)_2 = \begin{matrix}C_6H_4.COOH\\ |\\ C_6H_4.CO.NH.SO_2OH\end{matrix} =$$

$$\begin{matrix}C_6H_4\\ |\\ C_6H_3\end{matrix}\begin{matrix}>CO\\ \\ -CO.NH.SO_2OH\end{matrix} + H_2O = \begin{matrix}C_6H_4\\ |\\ C_6H_3\end{matrix}\begin{matrix}>CO\\ \\ -CO.NH_2\end{matrix} + SO_2(OH)_2$$

It crystallizes from alcohol in slender pale yellow needles, containing 1 mol. alcohol, which is evolved at 125°; it melts at 225°, but commences to sublime above 150°. By the action of zinc on its acetic acid solution it is converted into *o-diphenylenehydrolcarboxylic amide*, $C_{12}H_7(CH.OH)CONH_2$, which crystallizes from hot water in long plates, melts at 206—210°, sublimes on strongly heating, and dissolves in sulphuric acid with a green

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[1] Graebe and Aubin, *Annalen*, **247**, 275.

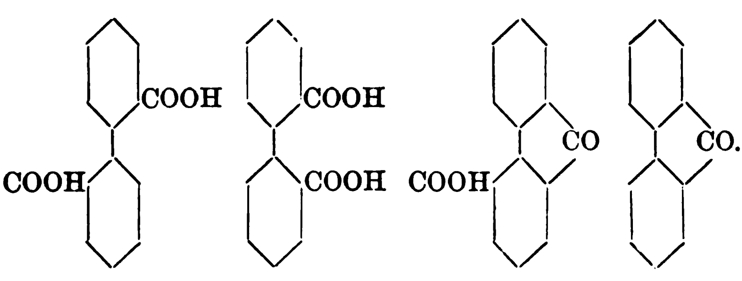
colour. On warming the amide with alcoholic ammonia at 150° it yields the *imido-amide*, $C_{12}H_7(C:NH)CO.NH_2$, which crystallizes from hot water in microscopic prisms, and melts at 220—221°.[1]

o-Diphenyleneketoximecarboxylic acid, $C_{12}H_7(C:N.OH)COOH$, is obtained by boiling the sodium salt of the acid with alcohol and hydroxylamine. Water precipitates it as a crystalline substance, which melts at 263°, and decomposes on more strongly heating. It dissolves in alkalis and alkaline carbonate solutions with a yellow colour; on addition of silver nitrate to a solution of the ammonium salt, the *silver* salt is obtained as a pale yellow crystalline precipitate.

o-Diphenyleneketoximecarboxylic amide, $C_{12}H_7(N.OH)CO.NH_2$, is obtained by acting on the amide of the ketonic acid with hydroxylamine, and forms a yellow crystalline powder, which is very sparingly soluble in alcohol, and melts at 272°. On heating with acetic anhydride it forms the *acetate*, $C_{12}H_7(N:O.CO.CH_3)CONH_2$, which crystallizes in colourless prisms, and melts at 177—178° (Wegerhoff).

o-Diphenylenehydrazonecarboxylic acid, $C_{12}H_7(C:N_2H.C_6H_5)COOH$, is prepared by heating the ketonic acid with phenylhydrazine. It crystallizes from alcohol in yellow or brownish-yellow needles or prisms, melts at 205°, and decomposes at 210°. It is reprecipitated from its alkaline solutions by acids.[2]

o-Diphenyleneketonedicarboxylic acid is formed from diphenic acid by elimination of water. The latter is a di-ortho-compound, and its constitution may be represented by two formulæ; these must, however, be regarded as identical, in order to explain the formation of both diphenyleneketone and of diphenyleneketonecarboxylic acid from it:[3]



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[1] Wegerhoff, *Annalen*, **252**, 25.

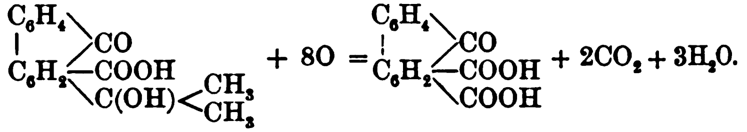
[2] Graebe and Aubin, *Annalen*, **247**, 275.

[3] Graebe, *Ber.* **20**, 848.

In other words, it is assumed that the two benzene residues in diphenyl and its derivatives can rotate freely around the common axis.

p-Diphenyleneketonecarboxylic acid is formed, together with large quantities of diphenyleneketone, when the silver salt of diphenyleneketonedicarboxylic acid is heated. It crystallizes from alcohol, in which it is sparingly soluble, in slender lustrous pale yellow needles, which sublime on heating in woolly frond-shaped aggregates. It is also obtained in lustrous yellow plates by heating the dicarboxylic acid. On warming its ammonium salt with hydroxylamine hydrochloride the corresponding *oxime* separates out in pale yellow flakes.[1] Its constitution is not yet finally proved.

Diphenyleneketonedicarboxylic acid, $C_{12}H_6(CO)(COOH)_2$, is prepared by the oxidation of retenequinone, or of hydroxyisopropyldiphenyleneketonecarboxylic acid, prepared from the latter by the action of sulphuric acid and potassium dichromate:



It crystallizes from acetic acid in sulphur yellow microscopic needles, which are very sparingly soluble in alcohol, and still less in water. On heating it decomposes without melting into carbon dioxide and *p*-diphenyleneketonecarboxylic acid, and on ignition with slacked lime yields diphenyl:

$$C_{12}H_6(CO)(CO_2H)_2 + H_2O = C_{12}H_{10} + 3CO_2.$$

The *silver* salt is a heavy yellow precipitate, which is unalterable in the light, and on heating splits up into carbon dioxide, diphenyleneketone, *p*-diphenyleneketonecarboxylic acid, and silver. On addition of barium chloride to a concentrated solution of the acid, a heavy yellow precipitate is obtained, but if the solution be dilute, sulphur yellow crystalline nodules separate after some time.

The *ethyl ester*, $C_{15}H_6O_5(C_2H_5)_2$, crystallizes from alcohol in flat

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[1] Bamberger and Hooker, *Annalen*, **229**, 138.

golden yellow needles with a vitreous lustre, and melts at 114·5°.

Diphenyleneketoximedicarboxylic acid, $C_{12}H_6(C:N.OH)(CO_2H)_2$, separates in yellow flakes when the ammonium salt is warmed with hydroxylamine hydrochloride. It remains unaltered at 280°.[1]

2757 *Ellagic acid,* $C_{14}H_6O_8 + 2H_2O$, was first discovered by Chevreul, together with gallic acid, in a gall-nut extract which had been prepared some time, and was recognized as a distinct compound by Braconnot. Taylor[2] states that it also occurs in the oriental "Bezoars," whilst Lipowitz regarded the acid contained in the latter as a different compound, and termed it bezoaric acid. The identity of the two compounds was, however, proved by Merklein and Wöhler, who also correctly determined the composition of the substance.[3] Wöhler wrote at the time to Liebig as follows:

"Bezoaric acid is, in fact, nothing but ellagic acid. The beasts from which the 'bezoars' are obtained, in all probability eat fodder containing tannic or gallic acid, from which the ellagic acid is formed, or else they eat plants containing ellagic acid ready formed, and are unable to digest it."[4]

According to Merklein and Wöhler the substances known as "bezoar," which formerly stood in high repute as medicine, may be divided into three groups:

1. Those which consist of calcium phosphate and ammonium magnesium phosphate.

2. Those which contain lithofellic acid, $C_{20}H_{36}O_4$, and are the gall-stones of a Persian antelope.

3. The true oriental bezoars, which contain ellagic acid, and consist of layers arranged concentrically around a kernel, the latter consisting usually of the seed of a leguminous plant.[5] They have a faint pleasant smell, similar to that of ambergris or musk. These were previously described under the name *Coagulum Resinorum Bezoarticum* by Kämpfer, who stated that when thrown on to burning coals they evolve an odour similar to rosin or incense. Monardes states that they are found in the intestines of a Persian wild goat.[6]

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[1] *Annalen,* **229**, 151.

[2] *Phil. Mag.* III. **28**, 192.

[3] *Annalen,* **55**, 129; see also A. Goebel, *Annalen,* **83**, 280.

[4] Liebig and Wöhler's *Briefwechsel,* **1**, 253.

[5] See also Hankel, *Pogg. Ann.* **55**, 481.

[6] Taylor *loc. cit.*

Wöhler and Merklein suggested that it would be most suitable to retain the name bezoaric acid for the acid; but this suggestion was not adopted, as it might have caused confusion between ellagic acid and lithofellic acid, which was also known as bezoaric acid.

Wöhler's supposition that ellagic acid occurs in the vegetable kingdom was confirmed later. Löwe showed its presence in "divi-divi," the seed-pods of *Cæsalpinia coriaria*, and in "myrobalans," the fruit of *Terminalia Chebuli*, both of which are used as substitutes for gall-nuts, and contain, in addition, *ellagitannic acid*, $C_{14}H_{10}O_{10}$; the latter on heating with water at 110° yields ellagic acid,[1] and Rembold has also shown that the tannic acid of the root of the pomegranate decomposes on boiling with dilute acids into sugar and ellagic acid.[2] The latter also occurs in oak-bark,[3] pine-bark (*Abies excelsa*),[4] and in various other plants.

It is also obtained under varying conditions from gallic acid and digallic acid or tannin. Thus it is always formed if, in the preparation of gallic acid, the gall-nut extract be allowed to stand in the air, and remains behind when the gallic acid is extracted with water. It is further formed by heating gallic acid with arsenic acid,[5] or with iodine and water at 92°,[6] and may be prepared in large quantity by warming ethyl gallate with sodium carbonate solution.[7] To isolate it from divi-divi, the pounded pods are extracted with cold alcohol, the solution evaporated, and the residue poured into cold water. Crude ellagic acid is thus precipitated, and is washed with cold alcohol. The aqueous filtrate is evaporated, and the ellagitannic acid thus converted into ellagic acid; on treatment with hot water the latter remains behind, and is digested with hot alcohol to remove colouring matters. From the alcoholic extract of 30 kilos. of divi-divi, Barth and Goldschmiedt obtained 250 grams of ellagic acid, and nearly a kilo. from the aqueous solution of ellagitannic acid.[8]

It may be more simply prepared from the coarsely-powdered divi-divi, separated by sifting from the shells and kernels, by digesting it for a few days with water, and evaporating the

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[1] *Fresenius Zeitschr.* **14**, 35.

[2] *Annalen*, **143**, 288.

[3] Etti, *Monatsh.* **1**, 262.

[4] Stromer, *Monatsh.* **2**, 539.

[5] Löwe, *Zeitschr. Chem.* **1868**, 603.

[6] Griessmayer, *Annalen*, **160**, 55.

[7] Ernst and Zwenger, *Annalen*, **159**, 32; Schiff, *Ber.* **12**, 1533.

[8] *Ber.* **11**, 846.

solution to a syrup with addition of sulphuric acid or gall-nut extract. The syrup is treated with boiling water, and the separated acid repeatedly washed with water and alcohol. In this manner Cobenzl obtained 6—7 per cent. of somewhat brownish-coloured ellagic acid.[1]

It is a light, pale yellow powder, consisting of microscopic transparent prisms, and is insoluble in ether, scarcely soluble in water, and only slightly in alcohol, forming a pale yellow solution which has a faintly acid reaction. It becomes anhydrous at 120°, but takes up water again in moist air; if, however, it be heated to 200° it absorbs moisture very slowly. At a higher temperature it carbonizes without melting, a small portion subliming in slender sulphur-yellow needles. It dissolves in caustic potash, forming a deep yellow-coloured solution, which, on remaining in the air, becomes deep yellowish-red to blood-red, and then deposits *potassium glaucomelanate*, $C_{12}H_4K_2O_7 + H_2O$, as a lustrous black powder. This has a tinge of blue, and under the microscope is seen to consist of thin, broad transparent prisms, which have a deep blue-black colour. On treatment with neutral ferric chloride it assumes a greenish colour, which becomes first greyish-green, and finally forms a blue-black liquid resembling ink, from which no solid is deposited. On mixing it with sulphurous acid it first gelatinizes, but quickly liquefies again, and becomes decolorized, especially on warming, with separation of well-crystallized ellagic acid.

Ellagic acid is coloured purple-red by nitrogen trioxide (Merklein and Wöhler), and if it be treated with nitric acid containing nitrous acid forms a deep blood-red solution, which, on addition of water, becomes bright red, and finally yellow; this reaction is extremely characteristic.[2]

On heating with zinc dust, ellagic acid is reduced to fluorene,[3] and with boiling caustic potash solution it yields hexhydroxydiphenyleneketone (p. 479); fused caustic potash converts it into β-hexhydroxydiphenyl, whilst with caustic soda a mixture of the β- and γ- hexhydroxydiphenyls is obtained.[4] The latter is also the final product of the action of sodium amalgam on its alkaline solution (Cobenzl).

The acid forms different series of salts.

Monosodium ellagate, $C_{14}H_5NaO_8 + H_2O$, is obtained by

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[1] *Monatsh.* **1**, 670.

[2] Griessmayer, *Annalen*, **160**, 51.

[3] Barth and Goldschmiedt, *Ber.* **11**, 846.

[4] Barth and Goldschmiedt, *Ber.* **12**, 1237.

heating ethyl gallate with sodium carbonate solution and forms a lemon-yellow silky crystalline precipitate, which is slightly soluble in boiling water, and imparts to it a faintly acid reaction. The water of crystallization is only evolved at a high temperature, the salt then becoming dull yellow.

Disodium ellagate, $C_{14}H_4Na_2O_8 + H_2O$, was prepared by Merklein and Wöhler by passing a current of carbon dioxide into a solution of the acid in caustic soda. It is a deep yellow crystalline precipitate, which becomes anhydrous at 110° (Barth and Goldschmiedt).

Dipotassium ellagate, $C_{14}H_4K_2O_8$, is obtained in a similar manner, and after drying forms a greenish or pale yellow paper-like mass, which is very light and loosely aggregated. It consists of microscopic transparent prisms often united to fan-shaped aggregates, and separates in this form from its solution in hot water. On warming its saturated solution it is coloured yellow and becomes anhydrous.

Tripotassium ellagate, $C_{14}H_5K_3O_9$, is formed when the acid is treated with alcoholic potash, and is a lemon-yellow powder, consisting of transparent microscopic prisms. It quickly becomes greyish-black in the air, and is converted into a mixture of the previous salt and potassium carbonate.

Barium ellagate, $(C_{14}H_5O_9)_2Ba_3$, is prepared by pouring baryta water on to the acid, and is a deep yellow powder, which, after drying at 140°, has the above composition. It assumes a dark pistachio-green colour in the air, and simultaneously absorbs carbon dioxide.

Tetracetylellagic acid, $C_{14}H_2(C_2H_3O)_4O_8$, was obtained by Schiff by heating anhydrous ellagic acid with acetic anhydride. It also forms a yellow powder, but gives no coloration with ferric chloride.[1] Barth and Goldschmiedt, on the other hand, obtained a compound, having approximately the composition of a pentacetyl derivative, by the action of acetic anhydride and anhydrous sodium acetate on the acid.

Ellagic acid is a derivative of diphenyleneketone, and is formed by the oxidation of gallic acid; its constitution, therefore, probably corresponds to that of digallic acid or tannin,[2] and may be represented as derived from the latter in the following manner:

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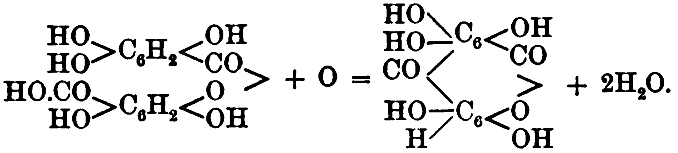
[1] *Annalen*, **170**, 75.

[2] See also Barth and Goldschmiedt, *Ber.* **12**, 1252.



It is now prepared on the manufacturing scale from divi-divi, and is employed as a pale yellow colouring-matter, chiefly in combination with other dyes.

Tetrahydroellagic acid, $C_{14}H_{10}O_8$, is prepared by adding potassium permanganate to a cold concentrated solution of gallic acid, containing sulphuric acid. It crystallizes in beautiful yellow microscopic needles, and is very sparingly soluble in water, forming a yellow solution, but dissolves readily in alcohol, with an intense yellowish-red colour. It also dissolves in causti cpotash solution, with a beautiful green colouration, which speedily changes to a fine blue and then to yellow; in absence of air, however, a deep red solution is obtained, which on exposure to the air shows the above changes of colour.[1]

On ignition with zinc dust it is converted into fluorene,[2] and when fused with caustic potash yields an isomeric compound, which is very sparingly soluble in cold water, and crystallizes from the hot liquid in slender greenish-yellow microscopic needles, the solution being coloured reddish-brown by ferric chloride. On addition of an alkali to the finely-divided substance suspended in water, it dissolves, forming an olive-green solution, which in presence of air and excess of alkali becomes carmine-red. The colour is so intense that a few drops impart a distinctly red tinge to a large quantity of water; it is unaltered by carbon dioxide, but changes to yellow in presence of the slightest excess of a mineral acid, and is therefore well suited for an indicator in alkalimetry. The carbonates of the alkaline earths also cause the formation of the red colour, and it can therefore be used in the estimation of combined carbonic acid in water, and of permanent hardness.[3]

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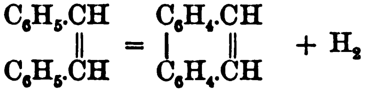
[1] Oser and Flögl, *Ber.* **9**, 135.

[2] Oser and Böcker, *Jahresb.* **1879**, 684.

[3] Oser and Kalmann, *Monatsh.* **2**, 50.

PHENANTHRENE GROUP.

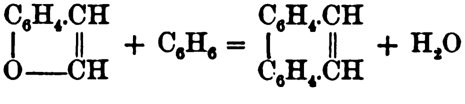
2758 *Phenanthrene*, $C_{14}H_{10}$, was discovered by Fittig and Ostermayer in a "neutral tar-oil, distilling between 300° and 400°," which was obtained as a by-product in the preparation of anthracene.[1] They gave it the above name in view of its isomerism with anthracene and close relationship to diphenyl. It is also a constituent of crude anthracene[2] and of "stuppfett" (p. 357), and is formed together with other hydrocarbons when toluene vapour is passed through a red-hot tube.[3] It may also be obtained in the same manner from dibenzyl, $C_6H_5.CH_2.CH_2.C_6H_5$, and stilbene, $C_6H_5.CH{=}CH.C_6H_5$:[4]



$$\begin{array}{l} C_6H_5.CH \\ \qquad\;\, \| \\ C_6H_5.CH \end{array} = \begin{array}{l} C_6H_4.CH \\ \;|\qquad\; \| \\ C_6H_4.CH \end{array} + H_2$$

the hydrogen set free reduces a portion of the dibenzyl or stilbene to toluene.

Phenanthrene is also formed in a similar manner from a mixture of ethylene and diphenyl vapour,[5] and also by acting on coumaron (Part V., p. 247) with benzene at a dark red heat:[6]



$$\begin{array}{l} C_6H_4.CH \\ |\qquad\;\; \| \\ O\text{——}CH \end{array} + C_6H_6 = \begin{array}{l} C_6H_4.CH \\ |\qquad\;\; \| \\ C_6H_4.CH \end{array} + H_2O$$

or when morphine is heated with zinc dust.[7]

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[1] *Annalen*, **166**, 361.
[2] Graebe, *Annalen*, **167**, 131; Hayduck, *Annalen*, **167**, 177.
[3] Graebe, *Ber.* **7**, 48.
[4] Graebe, *Annalen*, **167**, 156.
[5] Barbier, *Ann. Chim. Phys.* V. **7**, 532.
[6] Krämer and Spilker, *Ber.* **23**, 84.
[7] Gerichten and Schrötter, *Annalen*, **210**, 396.

In order to prepare it, crude anthracene may be fractionated, and the portion boiling at 320—350° boiled with a large quantity of alcohol. The anthracene which separates on cooling is removed, the alcohol distilled off, and the residue repeatedly crystallized from alcohol.[1] A better method is to take the crude phenanthrene obtained as a by-product in the manufacture of anthracene, and fractionate repeatedly; the portion boiling at 339—342° is then purified by crystallization.[2]

Anthracene is more readily attacked by sulphuric acid and potassium dichromate than phenanthrene; hence crude anthraquinone, which is obtained on the large scale, is a suitable material for the preparation of phenanthrene, the anthraquinone being removed by extraction with alcohol and the residue recrystallized. On the small scale the pure hydrocarbon may be readily obtained by dissolving crude phenanthrene in alcohol or coal-tar naphtha, adding picric acid, and decomposing the compound formed with ammonia. In all these cases it is advisable to treat the raw material first with caustic soda and then with sulphuric acid, to remove phenols and bases.[3]

Phenanthrene crystallizes in white plates or tablets with a bluish fluorescence, melts at 103°,[4] boils at 340°, but readily sublimes at a lower temperature. Its vapour has the sp. gr. 6·29 (Graebe). 100 parts of 95 per cent. alcohol dissolve 2 parts of phenanthrene at 13—14° (Graebe), whilst 100 parts of absolute alcohol dissolve 2·62 parts at 16°, and 10·08 parts at the boiling-point.[5] It also dissolves readily in ether, carbon disulphide, acetic acid, and benzene. 100 parts of toluene dissolve 32·02 parts at 16·5°, and at 100° almost any proportion (Becchi).

Fittig and Ostermayer found that phenanthrene is converted by oxidation into phenanthrenequinone and then into diphenic acid; the latter on heating with lime yields diphenyleneketone, which on fusion with potash yields phenylbenzoic acid; this in turn splits up on distilling with quicklime into diphenyl and carbon dioxide. Hence they proposed the following formula for phenanthrene:

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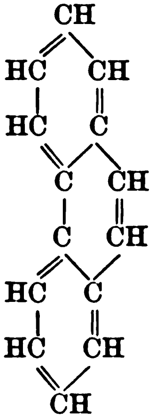
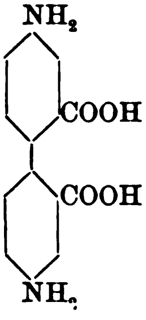
[1] Ostermayer, *Ber.* **7**, 1089.
[2] Schmidt, *Ber.* **12**, 1159.
[3] Schultz, *Steinkohlentheer*, **1**, 214.
[4] Reissert, *Ber.* **23**, 2243.
[5] Becchi, *Ber.* **12**, 1976.



Schultz proved this formula to be correct in the following manner: Phenanthrene passes on oxidation into diphenic acid, which may also be obtained from *m*-nitrobenzoic acid, by converting it into *m*-hydrazobenzoic acid, and treating the latter with hydrochloric acid; it then passes by a molecular interchange into the corresponding diamidodiphenic acid. This is converted by distillation with quicklime into benzidine, which is a 4:4′ derivative, and hence the diamido-acid must have the formula



On replacing the amido-groups by hydrogen the same diphenic acid is formed as is obtained by the oxidation of phenanthrene.[1] By further oxidation with alkaline potassium permanganate it is slowly converted into phthalic acid, which is more readily obtained from phenanthrenesulphonic acid, and as no trace of the isomeric phthalic acids is formed, this is a further confirmation of the above formula.[2] The same may be said with regard to its formation from coumaron, which occurs in large quantity in coal-tar, and will be subsequently described.

[1] *Annalen*, **203**, 95.

[2] Anschütz and Japp, *Ber.* **11**, 211.

At present the only practical application of phenanthrene is for the preparation of lampblack. According to Schultz it is very suitable for obtaining casts of models which can withstand a temperature of 120°, and may well replace sulphur for this purpose. In order to prevent its solidifying in large crystals, burnt gypsum should be previously added to the melted mass.[1]

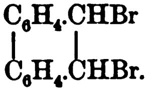
Phenanthrene picric acid, $C_{14}H_{10} + C_6H_3(NO_2)_3O$, separates in slender needles on mixing cold saturated solutions of the constituents, and crystallizes from hot alcohol or benzene in long golden-yellow prisms, melting at 145° (Graebe).

Phenanthrene picryl chloride, $C_{14}H_{10} + C_6H_2(NO_2)_3Cl$, crystallizes in lemon-yellow needles,[2] and melts at 88°. Phenanthrene likewise combines with chloro-*m*-dinitrobenzene to form a compound which crystallizes in long orange-red needles, and melts at 44°.[3]

Tetrahydrophenanthrene, $C_{14}H_{14}$, is prepared by heating phenanthrene with phosphorus and hydriodic acid at 210—240°, and is a liquid boiling at about 310°, and possessing a peculiar faint smell. It solidifies on cooling to a crystalline mass, melting at 0°. When heated with more phosphorus above 240°, it yields *octohydrophenanthrene,* $C_{14}H_{18}$, which boils below 300°.[4]

Perhydrophenanthrene, $C_{14}H_{24}$, is obtained by heating 1 part of phenanthrene with 1·25 parts of phosphorus and 5—6 parts of hydriodic acid (sp. gr. 1·7) to 250° for 12—16 hours. It is a liquid which boils at 270—275°, and solidifies in a freezing mixture to a crystalline mass, melting at − 3°.[5]

Phenanthrene dibromide, $C_{14}H_{10}Br_2$, is formed when bromine is added drop by drop to a solution of phenanthrene in ether or carbon disulphide, and crystallizes in flat four-sided prisms, which quickly decompose on keeping. On heating alone or with water it is converted into bromophenanthrene and hydrogen bromide, whilst alcoholic potash or potassium cyanide simply eliminate the bromine, reforming phenanthrene.[6] It has the following constitution (see bromophenanthrene):



$$\begin{array}{l} C_6H_4.CHBr \\ \;| \qquad\;\; | \\ C_6H_4.CHBr. \end{array}$$

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[1] *Steinkohlentheer,* **1**, 215.

[2] Liebermann and Palm, *Ber.* **8**, 377.

[3] Willgerodt, *Ber.* **11**, 601.

[4] Graebe, *Ber.* **8**, 1054 ; *Annalen,* **167**, 153.

[5] Lucas, *Ber.* **22**, 779.

[6] Fittig and Ostermayer, *Annalen,* **166**, 363 ; Hayduck, *Annalen,* **167**, 180 ; Anschütz, *Ber.* **11**, 1217.

HALOGEN DERIVATIVES OF PHENANTHRENE.

2759 When chlorine is passed into a solution of phenanthrene in acetic acid the chief product is dichlorophenanthrene tetrachloride ; smaller quantities of chloro- and dichlorophenanthrene are simultaneously formed, and may with difficulty be separated by repeated solution in acetic acid, and fractional precipitation with water.[1]

Chlorophenanthrene, $C_{14}H_9Cl$, is an oily liquid which carbonizes on heating.

Dichlorophenanthrene, $C_{14}H_8Cl_2$, is obtained in tough white flakes, which readily melt to an oily liquid and carbonize above 100°.

Dichlorophenanthrene tetrachloride, $C_{14}H_8Cl_6$, crystallizes in long colourless spear-shaped needles, readily soluble in alcohol, ether, &c., melts at 145°, and on boiling with alcoholic potash yields the following compound.

Tetrachlorophenanthrene, $C_{14}H_6Cl_4$, is also obtained by heating phenanthrene with iodine trichloride at 100—110°, but is most simply prepared by allowing antimony pentachloride to drop on to powdered phenanthrene. It crystallizes from benzene in short needles, which are scarcely soluble in alcohol, melts at 171—172°, and sublimes with slight carbonization in thin yellowish spear-shaped needles. Like the higher substitution products it is not attacked by boiling alcoholic potash.

Hexchlorophenanthrene, $C_{14}H_4Cl_6$, is prepared by heating phenanthrene with antimony pentachloride at 120—140°, and sublimes in feathery aggregates of needles, which melt at 249—250°.

Octochlorophenanthrene, $C_{14}H_2Cl_8$, obtained in a similar manner at 180—200°, forms granular crystals, melts at 270—280°, and sublimes in needles. On heating with antimony pentachloride to its melting point, it yields tetrachloromethane and hexchlorobenzene without forming perchlorodiphenyl.[2]

Bromophenanthrene, $C_{14}H_9Br$, was prepared by Hayduck by heating the dibromide on the water-bath ; it crystallizes from alcohol in thin white prisms, melts at 63°, readily sublimes, and boils above 360°. It is oxidized by chromium trioxide in

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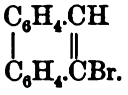
[1] Zetter, *Ber.* **11**, 164.

[2] Ruoff, *Ber.* **9**, 1490 ; Zetter, *Ber.* **11**, 169 ; Merz and Weith, *Ber.* **12**, 677.

acetic acid solution to phenanthrenequinone, and has therefore the following constitution :[1]



$$\begin{array}{l} C_6H_4.CH \\ \;|\quad\;\; \| \\ C_6H_4.CBr. \end{array}$$

a-Dibromophenanthrene, $C_{14}H_8Br_2$, separates from an ethereal solution of 1 mol. phenanthrene and 4 mols. bromine on long-continued standing in small delicate needles, which are very soluble in alcohol, and crystallize from it in long colourless spear-shaped needles. It melts at 146—148°, and readily sublimes in yellowish fascicular aggregates of needles.

β-Dibromophenanthrene, $C_{14}H_8Br_2$, separates out on evaporating the mother liquor from the *a*-compound. It crystallizes in plates, which melt at 158° but do not sublime. Both compounds are unacted upon by boiling alcoholic potash (Zetter).

Tribromophenanthrene, $C_{14}H_7Br_3$, is formed by heating phenanthrene with bromine, and crystallizes in slender silky needles melts at 126°, and readily sublimes.

Tetrabromophenanthrene, $C_{14}H_6Br_4$, is obtained by heating the hydrocarbon with the necessary quantity of bromine at 200—210°; it separates from acetic acid in granular crystals, which are almost insoluble in alcohol and ether, melts at 183—185°, and sublimes in feathery aggregates of needles.

Hexbromophenanthrene, $C_{14}H_4Br_6$, sublimes in snow-white needles, which unite, forming druses or feathery aggregates.

Heptabromophenanthrene, $C_{14}H_3Br_7$, can only be obtained by heating phenanthrene with bromine and a large quantity of iodine at 360° or higher; it sublimes in small yellow needles, melting above 270°, and is not attacked by bromine even at 400° (Zetter).

NITRO-DERIVATIVES OF PHENANTHRENE.

2760 By the action of moderately concentrated nitric acid on phenanthrene, three mono-nitro-compounds are formed. These are best prepared by adding 1 part of nitric acid of sp. gr. 1·35 to 1 part of phenanthrene, which is mixed with 3·5 parts of coarse sand to facilitate the action of the acid, as the mass soon becomes thick and pasty. It is well kneaded from time to

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[1] Anschütz, *Ber.* **11**, 1217.

time until it becomes friable, then washed with water and sodium carbonate solution, and extracted repeatedly with boiling alcohol. The product obtained from the extract can be separated into its constituents by repeated fractional crystallization from alcohol, ether, acetic acid, and benzene.[1]

α-Nitrophenanthrene, $C_{14}H_9NO_2$, is the chief product, and crystallizes in straw-yellow fascicular aggregates of needles, which melt at 73—75°.

β-Nitrophenanthrene is more sparingly soluble in ether, and also forms straw-yellow needles, melting at 126—127°.

γ-Nitrophenanthrene crystallizes from alcohol in lustrous yellow plates, melts at 170—171°, and is more sparingly soluble in alcohol and ether than its isomerides.

Dinitrophenanthrene, $C_{14}H_8(NO_2)_2$, is obtained by heating phenanthrene with concentrated nitric acid at 100°, and separates from acetic acid in yellow crystals, melting at 150—160° (Graebe).

Nitrobromophenanthrene, $C_{14}H_8Br.NO_2$, was prepared by Anschütz by warming an acetic acid solution of bromophenanthrene with nitric acid. It crystallizes from carbon disulphide in yellow transparent slender prisms, or, on slow evaporation, in well-developed compact crystals, which melt at 195—196°, and sublime in beautiful long spear-shaped needles.

AMIDO-DERIVATIVES OF PHENANTHRENE.

2761 These were obtained by Schmidt by the reduction of the nitro-compounds with tin and hydrochloric acid or ammonium sulphide.

α-Amidophenanthrene, $C_{14}H_9.NH_2$, crystallizes from dilute alcohol in yellowish faintly lustrous plates; its *hydrochloride* is a granular precipitate, sparingly soluble in water, which decomposes in the air, becoming brown, whilst the *sulphate*, which forms a powder sparingly soluble in water and alcohol, is much more stable.

β-Amidophenanthrene crystallizes also in lustrous plates; its granular *hydrochloride* is sparingly soluble in water and fairly stable.

γ-Amidophenanthrene resembles its isomerides, and forms a

[1] Schmidt, *Ber.* **12**, 1153.

stable *hydrochloride*, which crystallizes from alcohol containing hydrochloric acid in small yellow lustrous scales.

SULPHONIC ACIDS OF PHENANTHRENE.

2762 *a-Phenanthrenesulphonic acid*, $C_{14}H_9SO_3H$, is formed when phenanthrene is heated with an equal weight of sulphuric acid at 100°, and remains on evaporation of its aqueous solution as a crystalline mass, more soluble in hot than in cold water. The *calcium* salt, $(C_{14}H_9SO_3)_2Ca + 4H_2O$, crystallizes from hot water in small tablets. The *lead* and *barium* salts form indistinct crystals, and are scarcely more soluble in hot than in cold water.[1]

A small quantity of an isomeric acid is formed in the above reaction, the calcium salt of which is very soluble in water.[2]

β-Phenanthrenesulphonic acid is obtained by heating phenanthrene with sulphuric acid at 180—190°. It crystallizes in white nacreous needles, and is readily soluble in water; its salts, however, are less soluble than those of the *a*-acid. The *potassium* salt, $C_{14}H_9SO_3K$, forms lustrous tablets, and the *barium* salt, $(C_{14}H_9SO_3)_2Ba + 3H_2O$, crystallizes in scales.[3]

Phenanthrenedisulphonic acid, $C_{14}H_8(SO_3H)_2$, is formed when phenanthrene is added with vigorous shaking to four parts of commercial pyrosulphuric acid, and the mixture heated for some time on the water-bath. It is a brownish-yellow syrup, and has a very sour and bitter taste. The salts are readily soluble in water, but insoluble in alcohol.[4]

HYDROXY-DERIVATIVES OF PHENANTHRENE.

2763 *Hydroxyphenanthrene* or *Phenanthrol*, $C_{14}H_9.OH$, is prepared by fusing *a*-phenanthrenesulphonic acid with potash, and crystallizes from a mixture of benzene and light petroleum in beautiful plates, which have a blue fluorescence, are readily soluble in alcohol and ether, melt at 112°, and become red or brown on exposure to the air. It forms well-crystallized compounds with alkalis.

Phenanthryl acetate, $C_{14}H_9O.CO.CH_3$, is obtained by heating

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[1] Graebe, *Annalen*, **167**, 152.

[2] Japp, *Journ. Chem. Soc.* 1880, **1**, 83.

[3] Morton and Geyer, *Am. Chem. Journ.* **1880**, 203.

[4] Fischer, *Ber.* **13**, 314.

phenanthrol with acetic anhydride, and crystallizes from alcohol in beautiful lustrous plates, melting at 117—118°.[1]

Dihydroxyphenanthrene or *Phenanthrenequinol*, $C_{14}H_8(OH)_2$, was obtained by Graebe by subjecting phenanthrenequinone to the action of an alcoholic solution of sulphur dioxide, which gradually dissolves it. On addition of water the colourless quinol separates out; it may be obtained more quickly by warming, and is also rapidly formed by exposing a solution of the quinone in aqueous ether to sunlight.[2]

$$2C_{14}H_8O_2 + (C_2H_5)_2O = 2C_{14}H_8(OH)_2 + 2C_2H_4O.$$

It crystallizes in colourless needles or prisms, which are fairly soluble in water, and readily in alcohol, ether, and benzene. In the dry state it is moderately stable, but when freshly precipitated from alcoholic solution rapidly absorbs oxygen, and on evaporating its solutions it is partially converted into the quinhydrone described below. This is also readily obtained by evaporating its alkaline solution in the air.

Acetophenanthrenequinol, $C_{14}H_8(OH)O.CO.CH_3$, is formed by a remarkable reaction when a mixture of acetaldehyde and phenanthrenequinone is exposed to sunlight. The mixture becomes dark, and the acetyl compound commences to separate before the whole of the quinone has dissolved. Its formation proceeds equally quickly if the light be previously passed through a solution of cupriammonium chloride, but is considerably retarded if this be replaced by one of potassium dichromate. It crystallizes from a mixture of benzene and chloroform in white lustrous flat needles, becomes yellow at 140°, and melts at 168—170°. On warming with dilute caustic soda solution it is resolved into acetic acid and the quinol, the latter quickly undergoing further oxidation.[3]

Diacetophenanthrenequinol, $C_{14}H_8(O.CO.CH_3)_2$, is obtained by heating the quinol with acetic anhydride at 140—150°, and crystallizes in colourless tablets, which melt at 202°, and sublime with difficulty. It is insoluble in water, sparingly soluble in alcohol or ether, readily in hot benzene. On heating with caustic potash solution it is hydrolyzed with difficulty, and is unaltered by boiling with sulphuric acid and potassium

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[1] Rehs, *Ber.* **10**, 1252.

[2] *Annalen*, **249**, 137.

[3] Klinger, *Ber.* **19**, 1869.

dichromate; on heating its acetic acid solution with chromium trioxide it reforms the quinone (Graebe).

Valerophenanthrenequinol, $C_{14}H_8(OH)(O.CO.C_4H_9)$, was prepared by Klinger by exposing a mixture of the quinone and valeraldehyde to the sunlight. It forms flat white needles, melts at 149°, and is sparingly soluble in alcohol, ether, and cold benzene.

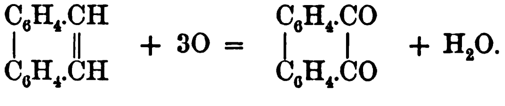
Benzophenanthrenequinol, $C_{14}H_8(OH)(O.CO.C_6H_5)$, is obtained in a similar manner, and crystallizes in matted aggregates of elastic white needles, which when seen in quantity resemble cotton wool. It melts at 177—178°.

p-Amidophenanthrenequinol, $C_{14}H_7(NH_2)(OH)_2$, is prepared by the long-continued boiling of nitrophenanthrenequinone with tin and hydrochloric acid, amidophenanthrenequinone being formed as an intermediate product. Its *hydrochloride* crystallizes in white needles.

p-Diamidophenanthrenequinol, $C_{14}H_6(NH_2)_2(OH)_2$, is formed in a similar manner from dinitrophenanthrenequinone.[1] Its *hydrochloride*, $C_{14}H_6(NH_3Cl)_2(OH)_2 + 3H_2O$, crystallizes in long lustrous needles, which on treatment with caustic potash solution first become green, then bluish-violet, and finally black. If the dilute alcoholic solution be shaken with ether and a little ammonia, it assumes a beautiful blue colour. The hydrochloride, when heated with acetic anhydride and sodium acetate, yields the compound $C_{14}H_6(NH.CO.CH_3)_2(O.CO.CH_3)_2$, which crystallizes in slender colourless needles, very sparingly soluble in alcohol and acetic acid, and does not melt at 300°.[2]

PHENANTHRENEQUINONE OR DIPHENYLENEDIKETONE.

2764 This compound is formed by warming phenanthrene with potassium dichromate and dilute sulphuric acid, or by treating it with chromium trioxide in acetic acid solution:[3]



$$\begin{array}{l} C_6H_4.CH \\ |\quad\ \ \| \\ C_6H_4.CH \end{array} + 3O = \begin{array}{l} C_6H_4.CO \\ |\quad\ \ | \\ C_6H_4.CO \end{array} + H_2O.$$

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[1] Anschütz and Meyer, *Ber.* **18**, 1942.

[2] Kleemann and Wense, *Ber.* **18**, 2168.

[3] Fittig and Ostermayer, *Annalen*, **166**, 365; Graebe, *Annalen*, **167**, 139; Hayduck, *Annalen*, **167**, 183.

It is best prepared on the small scale by dissolving phenanthrene in 4—5 parts of warm acetic acid, and gradually adding a solution of 2·2 parts of chromium trioxide in 5—6 parts of hot acetic acid in such a manner as to keep the whole nearly at the boiling point. It is then boiled for some time in connection with a reflux condenser, after which the acetic acid is distilled off, and the residue mixed with water. The precipitated quinone is washed with water and warmed with a solution of sodium bisulphite, the quinone going into solution and leaving unaltered phenanthrene behind. The filtrate is precipitated with hydrochloric acid, and the washed precipitate recrystallized from alcohol, acetic acid or benzene (Graebe).

On the large scale a mixture of 0·5 litre of sulphuric acid, 1·5 litres of water, and 300 grams of potassium dichromate is warmed in a porcelain dish, 100 grams of crude phenanthrene added, the whole well stirred, and the flame removed to moderate the reaction. It is then again gently warmed, another 300 grams of powdered potassium dichromate gradually added, and the boiling continued till the product has become granular; it is then filtered on a linen filter, and well washed. After drying it is finely powdered and treated with strong sulphuric acid to remove organic chromium compounds and acridine; the next day water is added, the mixture warmed and filtered, the residue washed with water and dilute soda solution to remove diphenic acid, &c., washed again with water, dried, and extracted with ether or benzene, which removes diphenyleneketone and phenanthrene. The insoluble portion is then treated with sodium bisulphite solution, in which anthraquinone is insoluble. The phenanthrenequinone is precipitated from the filtrate with a solution of potassium dichromate in dilute sulphuric acid, to avoid reduction by the sulphur dioxide evolved, and the precipitate recrystallized from dilute acetic acid.[1]

Phenanthrenequinone crystallizes in long lustrous orange-coloured needles, which are mostly united to fascicular aggregates. It melts at 198° (Fittig), sublimes on heating in orange-red tablets, and boils above 360°. It is very slightly soluble in boiling water, sparingly in cold alcohol, but readily in hot alcohol, acetic acid, and benzene.

Phenanthrenequinone forms additive compounds with different chlorides and cyanides, such as $C_{14}H_8O_2 + ZnCl_2$, which

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[1] Anschütz and Schultz, *Annalen*, **196**, 37.

crystallizes in dark red needles, and does not melt even above 300°; the compound with mercuric chloride, $C_{14}H_8O_2 + HgCl_2$, forms red oblique prisms, and melts at 222—223°. The compound, $C_{14}H_8O_2 + Hg(CN)_2$, melts at the same temperature, and likewise forms red crystals. The quinone does not combine with oxy-salts.[1]

Its conversion into diphenic acid, diphenyleneketone, diphenyleneglycollic acid, &c., has already been described. On heating it with antimony pentachloride at 360° it yields perchlorodiphenyl, together with a little hexchlorobenzene,[1] and on ignition with soda-lime,[2] splits up into diphenyl, carbon dioxide, and hydrogen (Anschütz and Schultz):

$$C_{14}H_8O_2 + 4NaOH = C_{12}H_6 + 2Na_2CO_3 + H_2.$$

Its solution in alcoholic potash phosphoresces with a pure white light when shaken in the dark, oxidation to diphenic acid taking place; if, however, a drop of aqueous caustic potash be added to its hot alcoholic solution a dark red or almost black colouration is produced,[3] which disappears on shaking in the air, a reaction very characteristic of orthodiketones.[4] It dissolves in sulphuric acid with a dark green colour, and is reprecipitated by water.

Laubenheimer found that a bluish-green colouration is formed when 5cc. of a ½ per cent. solution of phenanthrene in acetic acid are mixed with 1cc. of toluene, and 4cc. sulphuric acid carefully added with constant cooling and shaking. If the mixture be poured into water after a few minutes, and the solution shaken with ether, the latter assumes an intense violet colour. The reaction is so delicate that it may be observed with even a single drop of the acetic acid solution. On evaporating the ether the colouring matter remains behind as a black mass.[5]

The colouration is not formed, however, if pure toluene be employed, but only when the latter contains methylthiophen, $C_4H_3(CH_3)S$.[6] The pure colouring-matter, $C_{19}H_{12}SO$, forms a deep blue powder, which on subjection to pressure assumes a cupreous lustre, and dissolves in alcohol, benzene, &c., forming

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[1] Japp and Turner, *Proc. Chem. Soc.* **1889**, 160.

[2] Merz and Weith, *Ber.* **16**, 2869.

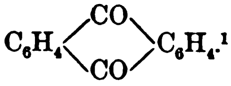
[3] Bamberger, *Ber.* **18**, 865, 1932.

[4] V. Meyer, *Ber.* **16**, 1624, 2970.

[5] Lachowicz, *Ber.* **16**, 332.

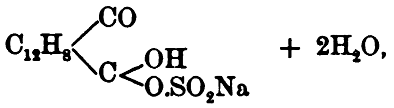
[6] *Ber.* **8**, 224.

beautiful violet solutions. On heating with zinc dust it yields phenanthrene, but on ignition with lead chromate yields, instead of phenanthrenequinone, the isomeric anthraquinone.



$$C_6H_4\langle{}^{CO}_{CO}\rangle C_6H_4.$$[1]

Phenanthrenequinone-sodium-bisulphite,



$$C_{12}H_8\langle{}^{CO}_{C\langle{}^{OH}_{O.SO_2Na}} + 2H_2O,$$

separates from a concentrated solution in plates, which are partially decomposed by acids and completely by alkalis with separation of the quinone. Potassium bisulphite forms a similar compound (Graebe).

Phenanthrenequinhydrone, $C_{14}H_8O_2+C_{14}H_8(OH)_2$, was prepared by Graebe by boiling phenanthrenequinol with water in presence of air. It is, however, most readily prepared by boiling the solution of the quinone and sulphurous acid with hydrochloric acid for a short time, and separates out on cooling in long lustrous black needles, which pass into the quinone on boiling with alcohol,[2] or even on long-continued boiling with water.

Dibromophenanthrenequinone, $C_{14}H_6Br_2O_2$, is prepared by heating phenanthrenequinone with bromine and a little water at 180°, and is readily soluble in xylene, less easily in alcohol and acetic acid, from which it crystallizes in yellow nodular aggregates, melting at 203°.

p-Nitrophenanthrenequinone, $C_{14}H_7(NO_2)O_2$, is obtained by boiling the quinone with a mixture of fuming nitric acid and acid of sp. gr. 1·4; it crystallizes from acetic acid in lustrous golden plates, which melt at 257°, and are almost insoluble in alcohol.[3] On oxidation it yields *p*-nitrodiphenic acid.

Three other nitrophenanthrenequinones were obtained by Schmidt by oxidizing the three nitrophenanthrenes with chromium trioxide in acetic acid solution. A fourth was prepared by Lachowicz by warming with nitric acid the chlorophenanthrone described below.[4]

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[1] Odernheimer, *Ber.* **17**, 1338.

[2] Liebermann and Jacobsen, *Annalen,* **211**, 69.

[3] Anschütz and Schultz, *Ber.* **9**, 1404.

[4] *J. Pr. Chem.* II. **28**, 172.

		Melting-point.
α-Nitrophenanthrenequinone,	orange-yellow plates	215—220°
β „ „ „	orange-yellow flat needles	260—266°
γ „ „ „	orange-yellow long needles	263°
δ „ „ „	orange-yellow plates	281—282°

p-Dinitrophenanthrenequinone, $C_{14}H_6(NO_2)_2O_2$, is prepared by boiling the quinone with a mixture of sulphuric and fuming nitric acids, and crystallizes from acetic acid in silky yellow plates, which melt at 294°.[1] On oxidation it yields α-dinitrodiphenic acid.

An isomeric compound is formed together with the foregoing, which could not be obtained pure, but yields β-dinitrodiphenic acid on oxidation (Schultz).

p-Amidophenanthrenequinone, $C_{14}H_7(NH_2)O_2$, is obtained by boiling nitrophenanthrenequinone for not too long a time with tin and hydrochloric acid, and crystallizes in violet-black needles, which dissolve readily in alcohol, and sparingly in water, forming a reddish-violet solution. Its *hydrochloride* forms yellowish-red feathery aggregates of needles, and is completely dissociated by water.

p-Diamidophenanthrenequinone, $C_{14}H_6(NH_2)_2O_2$, crystallizes in small violet-black needles, which do not melt at 310°; its *hydrochloride* forms yellow plates, which are likewise decomposed by water with separation of the diamidoquinone.

p-Hydroxyphenanthrenequinone, $C_{14}H_7(OH)O_2$, is obtained from the amido-compound by means of the diazo-reaction, and crystallizes in slender brownish-red needles, which sublime on careful heating, and dissolve in aqueous caustic soda with a yellowish-green colour.

p-Acetoxyphenanthrenequinone, $C_{14}H_7(O.CO.CH_3)O_2$, is formed by heating the foregoing compound with acetic anhydride, and crystallizes from alcohol in small reddish-yellow needles.[2]

α-Hydroxyphenanthrenequinone, $C_{14}H_7(OH)O_2$, is obtained by the oxidation of phenanthryl acetate, and sublimes in long yellowish-red needles; it dissolves in alkalis with a dark red colour.[3]

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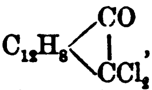
[1] Graebe, *Annalen*, **167**, 144; Schultz, *Annalen*, **203**, 107; Strassburger, *Ber.* **16**, 2346.

[2] Anschütz and Meyer, *Ber.* **18**, 1942.

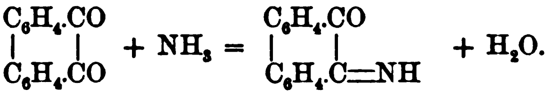
[3] Simienski, *Ber.* **18**, 1943.

p-Dihydroxyphenanthrenequinone, $C_{14}H_6(OH)_2O_2$, forms microscopic transparent brownish-black needles; its *acetate*, $C_{14}H_6(O.CO.CH_3)_2O_2$, crystallizes from alcohol in beautiful yellowish-red needles (Anschütz and Meyer).



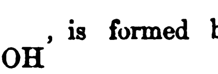
Dichloroketophenanthrene or *Dichlorophenanthrone*, $C_{12}H_8\left\langle\begin{array}{l}CO\\ |\\ CCl_2\end{array}\right.$, is obtained by the action of phosphorus pentachloride on phenanthrenequinone, and crystallizes from chloroform in pale yellow rhombic prisms, which are sparingly soluble in alcohol, and melt at 165°. Its solution in alcoholic potash phosphoresces like that of phenanthrenequinone, into which it is indeed thus converted. When warmed with acetic acid, and a little iron powder added, it is converted into *chlorophenanthrone*, $C_{14}H_9ClO$, which crystallizes in large yellowish prisms, and melts at 122—123°. By the further action of iron on its acetic acid solution it is converted into *phenanthrone*, $C_{14}H_{10}O$, which crystallizes in lustrous brownish-red tablets, melts at 148—149°, is readily soluble in alcohol, and also in alkalis with a green colour.[1]

Phenanthrenequinonimide, $C_{14}H_9NO$, is prepared by treating the quinone in alcoholic solution with ammonia:



$$\begin{array}{l}C_6H_4.CO\\ |\quad\ \ |\\ C_6H_4.CO\end{array} + NH_3 = \begin{array}{l}C_6H_4.CO\\ |\quad\ \ |\\ C_6H_4.C{=}NH\end{array} + H_2O.$$

It crystallizes in yellow elastic needles, melting at 158—159°, and is reconverted into the quinone by warming with alcohol or acids.[2]



Phenanthrenequinonoxime, $C_{12}H_8\left\langle\begin{array}{l}CO\\ |\\ C:NOH\end{array}\right.$, is formed by bringing together phenanthrenequinone and an alcoholic solution of hydroxylamine hydrochloride in the cold, or more quickly on heating.[3] It crystallizes in golden yellow fascicular aggregates of needles, melts at 158°, and dissolves in sulphuric acid with a blood-red colour, the solution being reprecipitated by water. It dissolves in hot caustic soda solution with a green colour, and on cooling the *sodium* salt separates out in greenish

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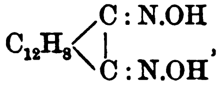
[1] Lachowicz, *Ber.* **16**, 330; *J. Pr. Chem.* II. **28**, 168.

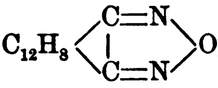
[2] Anschütz and Schultz, *Annalen*, **196**, 51; Zincke, *Ber.* **12**, 1624.

[3] Goldschmidt, *Ber.* **16**, 2176; Auwers and Meyer, *Ber.* **22**, 1985.

shimmering plates. Like other orthoquinonoximes it is a colouring-matter (p. 227), and dyes green with iron mordants.[1] Its conversion into the isomeric diphenimide has already been described (p. 451).

Phenanthrenequinonedioxime,  $C_{12}H_8 \left\langle \begin{array}{l} C:N.OH \\ | \\ C:N.OH \end{array} \right.$, is prepared by the continued warming of phenanthrenequinone with an excess of hydroxylamine hydrochloride. It crystallizes from a large quantity of hot alcohol or acetic acid in yellow microscopic prisms, which melt with decomposition at 202°, and dissolve in sulphuric acid with a blood-red colour. Its sparingly soluble *sodium* salt crystallizes in nacreous plates. If it be treated with acetic anhydride and acetic acid, and hydrogen chloride passed in to the cooled mixture, a red solution is formed from which glittering yellow oblique microscopic crystals of the *diacetate*, $C_{14}H_8(N.O.CO.CH_3)_2$, quickly separate out.

On heating the dioxime with absolute alcohol at 150°, or by heating the monoxime with hydroxylamine hydrochloride, alcohol, and a little hydrochloric acid, the *anhydride*,



, is formed; it crystallizes in slender reddish-yellow needles, melts at 182—183°, is insoluble in alkalis, and gives no colouration with sulphuric acid.

Phenanthrenequinonehydrazone, $C_{14}H_8(N_2H.C_6H_5)O$, is prepared by heating the quinone with phenylhydrazine hydrochloride; it separates in broad, pale-yellow, lustrous needles or plates, is sparingly soluble in hot alcohol, melts at 165°, and dissolves in sulphuric acid with a violet colour.[2]

METHANTHRENE, $C_{15}H_{12}$.

2765 This hydrocarbon was obtained by Oudemans by distilling podocarpic acid over red-hot zinc dust; it crystallizes in white plates having a violet fluorescence, melts at 117°, boils above 360°, is readily soluble in boiling alcohol, and still more easily in acetic acid. Even at its melting-point it sublimes, evolving a peculiar unpleasant smell, resembling that of molten asphalte. With picric acid it forms the compound $C_{15}H_{12} + C_6H_3(NO_2)_3O$,

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[1] Kostanecki, *Ber.* **22**, 1349.

[2] Zincke, *Ber.* **16**, 1563.

which crystallizes in slender orange-coloured needles, and melts at 117°.

Methanthraquinone, $C_{15}H_{10}O_2$, is readily prepared by adding chromium trioxide to the warm acetic acid solution of methanthrene, and is a yellow powder consisting of rhombic plates; it melts at 187°, and is readily soluble in alcohol with a reddish-yellow colour.

Podocarpic acid, $C_{17}H_{22}O_3$, is the chief constituent of the resin of *Podocarpus cupressina*, one of the Javan forest trees, and is found as a crystalline separation in the stems of the old trees. This is dissolved in alcohol, the solution precipitated with water, and the acid purified by converting it into the sodium salt, and decomposing the latter with hydrochloric acid.

Podocarpic acid is insoluble in water, but readily soluble in alcohol, ether, and acetic acid; it crystallizes in dextro-rotatory rhombic tablets or prisms, melts at 187—188°, and on further heating slowly volatilizes, evolving a peculiar aromatic smell. It decomposes only at a much higher temperature, and yields as chief product a thick oily distillate.

The salts are difficult to obtain pure and of constant composition, with the exception of the following:

Sodium podocarpate, $C_{17}H_{21}NaO_3 + 7H_2O$, crystallizes in beautiful white lustrous needles, and is readily soluble in water.

Ethyl podocarpate, $C_{17}H_{21}(C_2H_5)O_3$, is formed by heating the silver salt with ethyl iodide, and crystallizes from alcohol in slender needles, melting at 143—146°.

Acetylpodocarpic acid, $C_{16}H_{20}(O.CO.CH_3)CO.OH$, is formed by warming the acid with acetyl chloride, and crystallizes in small needles.

Nitropodocarpic acid, $C_{17}H_{21}(NO_2)O_3$, is obtained by the action of dilute nitric acid on the acid; it forms small yellow lustrous crystals, melting at 205°.

Dinitropodocarpic acid, $C_{17}H_{20}(NO_2)_2O_3$, is formed together with the foregoing compound, and is readily obtained pure by warming the sulphonic acid with nitric acid. It forms pale yellow crystals, resembling those of potassiun ferrocyanide, and melts at 203°.

Both nitro-acids contain two hydrogen atoms readily replaceable by metals, yielding beautiful, red, well-crystallized salts.

Sulphopodocarpic acid, $C_{17}H_{21}(SO_3H)O_3$, is prepared by gently warming the acid with sulphuric acid, and remains on evaporating the aqueous solution as a wax-like mass. It forms two series of salts, which crystallize well.

Especially remarkable is its susceptibility to nitric acid; thus if a milligram be dissolved in 3—4cc. of water, and a few drops of nitric acid added, a precipitate of the dinitro-compound is obtained on warming. *Vice versâ*, small quantities of nitric acid may be detected by boiling with a solution of the sulphonic acid, especially if a little sulphuric acid be added.

On distilling the calcium salt of podocarpic acid, the following products are obtained together with *p*-cresol:

Carpene, C_9H_{14}, a liquid boiling at 155—157°, which has an odour simultaneously resembling that of turpentine and styrolene, and quickly becomes resinous in the air.

Methanthrol, $C_{15}H_{12}O$, separates from ether on spontaneous evaporation as a woolly crystalline mass, or if evaporated at a higher temperature, as an oil which solidifies to a crystalline mass, melting at 122°, and insoluble in caustic potash.

Hydrocarpol, $C_{16}H_{20}O$, is a peculiarly smelling, turpentine-like mass, which boils at 220° *in vacuo*, and decomposes at a higher temperature into carpene and *p*-cresol. These are also formed, together with carbon dioxide, by the dry distillation of the acid.[1]

PHENANTHRENECARBOXYLIC ACIDS.

2766 *a-Phenanthrenecarboxylic acid*, $C_{14}H_9.CO_2H$, was obtained by Schultz and Japp by distilling the potassium salt of phenanthrenesulphonic acid with potassium ferrocyanide, and boiling the yellowish semi-solid nitrile with alcoholic potash. It is scarcely soluble in water, readily in alcohol and acetic acid, and crystallizes in long bent plates, which melt at 266°, and sublime with partial decomposition in fern-shaped aggregates of plates. On heating with soda-lime it decomposes into carbon dioxide and phenanthrene. The *barium* salt, $(C_{14}H_9.CO_2)_2Ba + 7H_2O$, crystallizes in long, slender, elastic needles, which usually unite in fascicular or spherical aggregates.[2]

β-Phenanthrenecarboxylic acid was prepared by Japp from the phenanthrenesulphonic acid which forms a very soluble calcium salt (p. 499). It crystallizes from acetic acid in stellate groups of needles, melts at 150—152°, and sublimes in fern-like aggregates

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[1] *Annalen*, **170**, 213.

[2] *Annalen*, **196**, 10; *Journ. Chem. Soc.* 1880, **1**, 83.

of plates. On heating with soda-lime it yields carbon dioxide and phenanthrene, and it is oxidized by chromium trioxide to phenanthrenequinone. The *barium* salt, $(C_{14}H_9.CO_2)_2Ba+6H_2O$, crystallizes in long, rectangular, brittle plates.

Phenanthrenequinonecarboxylic acid, $C_{14}H_7O_2(CO_2H)$, is formed when an acetic acid solution of the α-acid is treated with chromium trioxide. It resembles phenanthrenequinone, and like this, dissolves in sodium bisulphite solution, but is distinguished from it by its solubility in cold sodium carbonate solution.

RETENE GROUP.

2767 In the fossil fir-wood (*Pinus uliginosa*),[1] which occurs in a peat bed at Redwitz in the Fichtelgebirge, Fikentscher found a resinous or fatty substance, and submitted it for investigation to Trommsdorf. The latter purified it by recrystallization from alcohol, and thus obtained it in delicate white plates, the analysis of which showed that it was a hydrocarbon isomeric with benzene.[2] Krauss found the same composition for *Scheererite*, which likewise occurs in the fir stems of the lignite beds at Uznach in Switzerland.[3] According to Steenstrup, the stems and roots of the firs in the great peat moors of Denmark likewise contain solid hydrocarbons, one of which, termed by Forchhammer *Phylloretine*, as it crystallizes in slender plates, has the greatest resemblance with Scheererite, and appeared from the analysis to have the empirical formula C_4H_5 or C_6H_6.[4]

In 1858 Knauss, in Archangel, found a new hydrocarbon in the tar formed in the distillation of fir-wood (see Part V. p. 464), which was further examined by Fehling[5] and Fritsche,[6] with different results. The latter first proposed the formula $C_{19}H_{18}$, but two years later altered it to the correct one, $C_{18}H_{18}$, and simultaneously showed that the above-mentioned hydrocarbons obtained from fossil fir stems were identical with the compound from the fir-wood tar. He gave to it the name Retene, inasmuch as it is probably derived from the resin (ῥητίνη) of the fir either by a slow mouldering process or by the action of a high temperature. Knauss states that, in Archangel, only wood rich in resin is employed for distillation, which is a further confirmation of the above supposition. In order to

[1] A. Schmidt, *Ber.* **22**, 499.

[2] *Annalen*, **28**, 125.

[3] *Annalen*, **106**, 388.

[4] *Annalen*, **21**, 226.

[5] *Annalen*, **41**, 39.

[6] *Annalen*, **109**, 250.

ensure the wood containing large quantities of resin, the tree is continuously deprived of its bark for a number of years.[1]

Fritsche proved the molecular weight of retene by the analysis of its compound with picric acid, this being the first employment of the method not only for that purpose, but also for the recognition and separation of aromatic hydrocarbons.

Further investigation of this hydrocarbon was then undertaken by Wahlforss, who obtained it from Finnish wood-tar. By its oxidation he obtained *dioxyresistene*, $C_{16}H_{14}O_2$, which was derived not from retene, but from *resistene*, $C_{16}H_{14}$, this hydrocarbon being obtained by heating the dioxy-compound with zinc dust.[2]

Ekstrand, who examined retene obtained from Swedish tar, and prepared a number of its substitution products, confirmed the existence of dioxyresistene, but found that resistene is a mixture of retene with other hydrocarbons; hence he concluded that dioxyresistene has a more complicated constitution, especially as he obtained from it, by the action of baryta and bromine, substances whose formulæ did not stand in any simple relation to the formula $C_{16}H_{14}O_2$.[3]

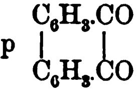
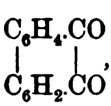
Bamberger and Hooker, however, found that dioxyresistene is in reality *retenequinone*, $C_{18}H_{16}O_2$, which is extremely difficult to burn, and thus readily gives too small a quantity of carbon on analysis. When heated with zinc dust or hydriodic acid the quinone is reconverted into retene, which has the greatest resemblance to phenanthrene, just as retenequinone has to phenanthrenequinone. The latter on boiling with caustic potash, yields diphenyleneglycollic acid, whilst the former yields reteneglycollic acid, $C_{16}H_{16}.C(OH)CO_2H$, which on oxidation yields reteneketone, $C_{16}H_{16}{=}CO$. This behaves in an analogous manner to diphenyleneketone, inasmuch as on reduction it yields retenefluorenyl alcohol, $C_{16}H_{16}.CH.OH$, and retenefluorene, $C_{16}H_{16}.CH_2$.

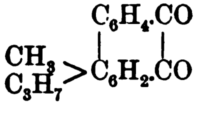
In their physical properties the corresponding compounds in both groups show the greatest similarity; they differ, however, inasmuch as the phenanthrene derivatives are very stable and are readily prepared, whereas the formation of retene and its derivatives depends upon the exact fulfilment of certain conditions; on account of their instability great care is required in their preparation.

[1] *J. Pr. Chem.* **82**, 321.

[2] *Jahresb.* **1869**, 501.

[3] *Annalen*, **185**, 75.

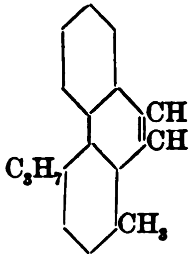
The constitution of retenequinone has been determined by Bamberger in the following manner: On oxidation with alkaline potassium permanganate it yields a monobasic ketonic acid, $C_{16}H_{13}O_2.CO_2H$, which on further oxidation yields the diphenyleneketonedicarboxylic acid already described (p. 486), the silver salt of which splits up on heating into carbon dioxide and diphenyleneketone. The ketone carbonyl group is undoubtedly formed by the oxidation of the quinone group CO.CO, and hence retenequinone must contain the group  $\begin{array}{l} C_6H_3.CO \\ | \qquad\ | \\ C_6H_3.CO \end{array}$ or  $\begin{array}{l} C_6H_4.CO \\ | \qquad\ | \\ C_6H_2.CO \end{array}$, with which four carbon atoms and ten hydrogen atoms are also combined. It is very improbable that these form a closed chain in combination with the diphenyl residue, but they are probably present in the form of two alkyl-groups, which would readily explain the formation of the dicarboxylic acid. The only possible alternatives in that case are that the compound contains two ethyl groups or a methyl and propyl group. This question is decided by the formation of the acid, $C_{16}H_{13}O_2.CO_2H$, which as it is a ketonic acid must contain both the carbonyl and carboxyl groups. The latter can only be obtained by the oxidation of a methyl group, and hence retenequinone must be a methylpropylphenanthrenequinone:

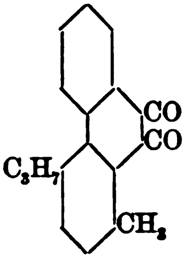


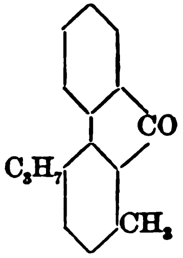
$$\begin{array}{l} CH_3 \\ C_3H_7 \end{array}\!\!>\begin{array}{l} C_6H_4.CO \\ | \qquad\ | \\ C_6H_2.CO \end{array}$$

The acid obtained by the oxidation of this compound contains 5 atoms of oxygen, which is readily understood if the C_3H_7 is an isopropyl group, as the latter on oxidation in alkaline solution is readily converted into hydroxyisopropyl; the acid is therefore hydroxyisopropyldiphenyleneketonedicarboxylic acid (see below). As the diphenyleneketonedicarboxylic acid splits up on heating into carbon dioxide and a diphenyleneketonemonocarboxylic acid, and does not form an anhydride, the two side chains can scarcely occupy the ortho-position to one another. One of them, however, probably occupies the ortho-position to the ketone-carbonyl group, as on fusion with potash the ketone-dicarboxylic acid is converted into a tricarboxylic acid which yields an anhydride.

The constitution of retene and of its quinone and ketone may be represented, therefore, by the following formulæ:[1]







It is especially noteworthy that retene contains the same side-chains as oil of turpentine. Whether these also occupy the para-position to one another in the manner shown above has not yet been proved, although, as this combination is so frequent in compounds obtained from firs and pines, it is very probably the case. Against this view is the fact that the diphenyleneketonecarboxylic acid is not, as would be expected if the above view is correct, identical with either the ortho- or meta-acid.

Retene or *Methylisopropylphenanthrene*, $C_{14}H_8(CH_3)C_3H_7$. When fir-wood tar is subjected to distillation a thick oil passes over towards the end of the operation, which solidifies to a granular mass on cooling. This is employed for greasing purposes under the name "tar-tallow," and consists almost solely of retene, which may be obtained pure by subjecting the mass to strong pressure, thus removing adhering oil, and recrystallizing the residue from boiling alcohol.[2]

Retene is also obtained in large quantity, together with sulphuretted hydrogen, by distilling pine-wood resin or colophony, and heating the "resin oil" thus obtained with sulphur (Kelbe); it may be obtained in this manner on the large scale.[3] It crystallizes in mica-like plates, or very lustrous white nacreous tablets, and melts at 98·5 to a liquid having a slight violet fluorescence. It boils at 390°,[4] but sublimes far below this temperature in microscopic scales; its vapour has the sp. gr. 8·28.[5]

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[1] Bamberger and Hooker, *Annalen*, **229**, 102.

[2] Ekstrand, *Annalen*, **185**, 75; Bamberger and Hooker, *Annalen*, **229**, 115.

[3] *Chem. Fabr. Rheinau*, Germ. Patent, 15 September, 1887.

[4] Berthelot, *Bull. Soc. Chim.* **8**, 389.

[5] Knecht, *Ber.* **10**, 2073.

100 parts of 95 per cent. alcohol dissolve 3 parts of retene at the ordinary temperature, and 69 parts at the boiling-point; the hydrocarbon also dissolves readily in ether, carbon disulphide, light petroleum, and boiling acetic acid, and crystallizes out for the most part on cooling.

Retene may be distilled over lead oxide without undergoing alteration; it yields resinous products with nitric acid, and is not attacked by potassium permanganate in alkaline or neutral solution, but is completely oxidized in acetic acid solution. On warming with dilute sulphuric acid and potassium dichromate it yields retenequinone, phthalic acid, and acetic acid.

Retene picric acid, $C_{18}H_{18} + C_6H_3(NO_2)_3O$, is formed by dissolving retene and an excess of picric acid in alcohol, and crystallizes out on cooling in pure yellow or orange-yellow lustrous needles, which melt at 123—124°, and are decomposed by alkalis and even by water and alcohol. From a solution in benzene the compound $C_{18}H_{18} + C_6H_6 + C_6H_3(NO_2)_3O$ crystallizes out, and becomes opaque in the air owing to the loss of benzene. If retene and dinitroanthraquinone (which was also employed by Fritsche for detecting hydrocarbons) be dissolved in acetic acid, a compound crystallizing in deep orange-coloured needles is formed with difficulty (Ekstrand).

Tetrahydroretene, $C_{18}H_{22}$, is prepared by acting with sodium on a boiling amyl alcoholic solution of retene, and is a yellowish oily liquid, which boils at 280° under 50 mm. pressure, and gradually solidifies in the air owing to the re-formation of retene.[1] Towards bromine it behaves as a partially reduced compound.[2]

Dodecahydroretene, $C_{18}H_{30}$, is formed when 4 parts of retene are heated with 5 parts of phosphorus and 20—24 parts of hydriodic acid of sp. gr. 1·7, for 12—16 hours at 250—260°, and is a bluish fluorescent liquid, boiling at 336°.[3]

The hydrides also probably occur in pine-wood tar and in "resin oil," as these yield large quantities of retene on heating with sulphur. Moreover the pitch from pine-wood tar yields such hydrides on distillation, for the distillate which passes over above 360° as a thick yellowish oil with a faint blue fluorescence yields retene on exposure to the air.[4]

Fichtelite, $C_{18}H_{32}$, was discovered by Fikentscher at the same time as retene, with which it usually occurs; it has also been found

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[1] Bamberger and Lodter, *Ber.* **20**, 3073.

[2] *Ber.* **21**, 836.

[3] Liebermann and Spiegel, *Ber.* **22**, 779.

[4] Boyen, *Chem. Zeit.* **1889**, 870.

in the peat moors at Franzensbad,[1] and at Kolbermoor near Rosenheim in Upper Bavaria,[2] whilst Mallet observed its presence in the stem of the American pine (*Pinus australis*), which yields the greater portion of the American oil of turpentine.[3]

It was first analysed by Bromeis[4] and Clark;[5] the latter also examined the action of chlorine upon it, and suggested the formula $C_{40}H_{70}$, whilst Mallet regarded it as a sesquiterpene, $(C_5H_8)n$, and Hell concluded that it was either a dihydrosesquiterpene, $C_{15}H_{26}$, or a tetrahydrosequiterpene, $C_{15}H_{28}$; the analyses, however, agreed better with the intermediate composition, which made it appear possible that the correct formula was $C_{30}H_{64}$.[6] It was finally recognized by Bamberger and Strasser as *perhydroretene*,[7] and appears to be formed by the further heating of dodecahydroretene with phosphorus and hydriodic acid.[8]

Fichtelite crystallizes from a mixture of alcohol and ether in long monosymmetric prisms, and separates in still finer crystals from light petroleum. It melts at 46°, boils at 355° under 719 mm. pressure, yielding a vapour of sp. gr. 8·7. It is unaltered after boiling for days with potassium dichromate and dilute sulphuric acid or potassium permanganate, and is not attacked by lead oxide below a red heat. It appears to be completely oxidized by chromium trioxide in acetic acid solution, and forms large quantities of oxalic acid on boiling with nitric acid. On heating with iodine it yields dodecahydroretene and hydriodic acid.

Dibromoretene, $C_{18}H_{16}Br_2$, is formed by gradually adding two molecules of bromine to a molecule of retene suspended in water, and gently warming till no more hydrogen bromide is evolved; the product is then treated with alcohol and dilute caustic potash, digested with alcoholic potash, and washed successively with water, alcohol, and ether. It is thus obtained as a white crystalline powder, which crystallizes from carbon disulphide or hot light petroleum in lustrous tablets, melting at 180°. The yield is small owing to the formation of by-products.

Tetrabromoretene, $C_{18}H_{14}Br_4$, is obtained by heating retene with bromine on the water-bath till the excess of the latter has

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[1] Gmelin, *Handb. Org. Chem.* **4**, 2194.
[2] Bamberger, *Ber.* **22**, 635.
[3] *Ber.* **5**, 817.
[4] *Annalen*, **37**, 304.
[5] *Annalen*, **103**, 236.
[6] *Ber.* **22**, 498.
[7] *Ber.* **22**, 3361.
[8] Spiegel, *Ber.* **22**, 3369.

disappeared. It crystallizes from boiling benzene or carbon disulphide in flat prisms, and melts at 210—212°.

Retenedisulphonic acid, $C_{18}H_{16}(SO_3H)_2 + 10H_2O$, is prepared by gradually adding finely divided retene to a mixture of equal volumes of fuming and concentrated sulphuric acid as long as it continues to dissolve. After two or three weeks a hair-like mass of slender needles is obtained, these having the composition $C_{18}H_{16}(SO_3H)_2 + 5H_2SO_4$ (Fritsche and Ekstrand). This is converted into the barium or lead salt, which are reconverted into the acid by the action of sulphuric acid and hydrogen sulphide respectively. The concentrated solution yields a magma of slender needles, which are very soluble in alcohol and ether, and crystallize from acetic acid on evaporation in well-developed prisms or stellate aggregates of needles. On addition of sulphuric acid to its solution the above double compound again separates out.

Ekstrand also prepared a number of its salts, which are insoluble in alcohol, somewhat soluble in cold, and readily in hot water.

Retenedisulphochloride, $C_{18}H_{16}(SO_2Cl)_2$, crystallizes from acetic acid in stellate aggregates of small hard prisms, melts at 175°, and is only decomposed by water at 160°.

Retenetrisulphonic acid, $C_{18}H_{15}(SO_3H)_3$, is obtained by warming retene with fuming sulphuric acid, and crystallizes in small readily soluble prisms. Its *barium* salt, $[C_{18}H_{15}(SO_3)_3]_2Ba_3 + 18H_2O$, forms hair-like needles or long prisms.

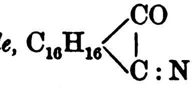
2768 *Retenequinone*, $C_{18}H_{16}O_2$, can only be obtained in quantity by careful adherence to certain conditions. According to Bamberger and Hooker the most suitable method is the following: 19 grams of chromium trioxide are dissolved in 100 cc. of acetic acid, and carefully added through a reflux condenser to a luke-warm solution of 10 grams of retene in 35 cc. of acetic acid, the reaction proceeding quietly without evolution of carbon dioxide; the solution is then boiled until it has a pure green colour and the gas evolution has ceased. On cooling, retenequinone is obtained as a mass of long orange-red prisms, having a metallic lustre, which are washed with 80 per cent. alcohol. The quinone remaining in the mother liquor is obtained by partially distilling off the acetic acid, recrystallizing from alcohol, and treating with sodium carbonate solution and ether to remove acids and resinous products. About 60 per cent. of crude quinone is thus obtained, from which 55 grams of the pure compound may be prepared.

Retenequinone melts at 197—197°·5, and may be partially sublimed by careful heating. 10,000 parts of 83 per cent. alcohol only dissolve 1—2 parts at the ordinary temperature, whilst 1,000 parts of 95 per cent. alcohol dissolve 1—5 parts at 0°·5, and 22—23 parts at the boiling-point.[1] It dissolves readily in boiling carbon disulphide, and crystallizes out on cooling in woolly needles, and is soluble in hot aniline, separating out on addition of $\frac{1}{3}$ vol. of alcohol in reddish-yellow satiny plates.

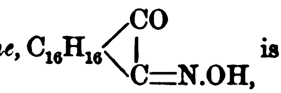
Sulphuric acid dissolves retenequinone with a green colour. On addition of a drop of aqueous potash to its alcoholic solution and warming, a fine bordeaux-red colouration is obtained, which disappears on shaking; after a few seconds, or still better on warming, the colour reappears and again disappears on shaking; this can be repeated several times, the colour becoming continuously fainter, until at last it disappears altogether. By means of this reaction, which is characteristic of *o*-diketones,[2] traces of the quinone may be readily detected.

That it is in reality an *o*-diketone is proved by the fact that it combines directly with *o*-diamidobenzene with elimination of water, forming retenequinoxaline, which will be described in a later volume.

Dibromoretenequinone, $C_{18}H_{14}Br_2O_2$, is obtained by adding a slight excess of bromine to the quinone, stirring well during the operation. It crystallizes in pale orange-red prisms, melts at 250—252°, is sparingly soluble in alcohol and acetic acid, readily in chloroform. Towards alcoholic potash it behaves in a similar manner to the quinone.



Retenequinonimide, $C_{16}H_{16}\left<\begin{array}{l}CO\\ |\\ C:NH\end{array}\right.$, is prepared by allowing a chloroform solution of the quinone to remain with alcoholic ammonia for several days, and crystallizes on evaporating the solution in golden yellow slender prisms, having a vitreous lustre. It melts at 109—111°, and on remaining in moist air, or on treatment with dilute acids or alkalis is resolved into retenequinone and ammonia.



Retenequinonoxime, $C_{16}H_{16}\left<\begin{array}{l}CO\\ |\\ C{=}N.OH\end{array}\right.$, is formed by heating

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[1] Ekstrand, *Annalen*, **185**, 75.

[2] Bamberger, *Ber.* **18**, 865, 1932.

an alcoholic solution of 1 mol. of the quinone with an aqueous solution of 2 mols. of hydroxylamine hydrochloride, and the equivalent quantity of sodium carbonate for 1—2 days at 30—40°. It crystallizes from alcohol in golden yellow needles or plates, melts at 128°·5, and though scarcely attacked by aqueous hydrochloric acid, is readily decomposed by the alcoholic solution.

Like other *o*-quinonoximes it gives beautifully coloured lakes with salts of iron, nickel, and cobalt; it colours iron mordants green, but not so strongly as phenanthrenequinone, probably because it is insoluble in water.[1]

When retenequinone is boiled with a hydrazinesulphonic acid of phenyl, naphthyl, &c., a red solution is obtained, from which the colouring matter separates on neutralization and addition of sodium chloride. The azo-colours thus obtained dye wool with an orange to blood-red colour.[2]

Retenequinol, $C_{18}H_{16}(OH)_2$. To prepare this compound, 0·5 gram retene is dissolved in 60 cc. of alcohol, mixed with a saturated aqueous solution of sulphur dioxide, warmed for several hours in a sealed tube at 60—70°, then filtered into a vessel containing no air, and water free from air added; after some hours retenequinol separates in silver-white satiny tablets. These readily pass on warming or remaining in the air, especially if moist, into the quinone, which is thus obtained in flat tablets, which are really pseudomorphs. If the quinol be placed under water so that the air only comes in contact with it slowly, the tobacco-brown *quinhydrone* is formed; the *potassium* salt of the latter is also formed when the quinone is boiled with zinc dust and dilute potash, the solution filtered into boiling caustic potash, and the whole boiled in the air. It forms a voluminous green precipitate, which may be washed with hot water, and then only undergoes a surface oxidation in the air.

Retenedicarboxylic acid, $C_{16}H_{16}(CO_2H)_2$, is formed by boiling the alcoholic solution of the quinone with sodium amalgam, the dark red colour changing to brown. The alcohol is evaporated off, the residue taken up with water, filtered from undissolved resinous matter, cooled in a freezing mixture, and treated with hydrochloric acid. It is thus obtained as a white granular precipitate, which forms a brown sticky resin on exposure to the air. If it be dissolved in ammonia and shaken with ether, a

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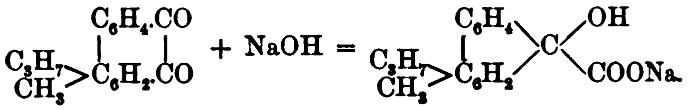
[1] Kostanecki, *Neues Handwörterbuch*, **5**, 1210.

[2] *Ges. Chem. Ind. Rheinau*, *Chem. Zeit.* **1889**, 565; Schultz, *Steinkohlentheer*, **2**, 1153.

slightly yellow solution of the ammonium salt is obtained, which with silver nitrate gives a precipitate of the *silver* salt, $C_{16}H_{16}(CO_2Ag)_2$, a heavy white compound, which is very susceptible to light. The *barium* salt is a heavy crystalline, sparingly soluble precipitate.

Reteneglycollic acid, $C_{16}H_{16}.C(OH).COOH$. To prepare this acid the quinone is dissolved in sulphuric acid, and the green solution poured into cold water with constant stirring, which precipitates the quinone in amorphous flakes. After washing, these are added to boiling caustic soda solution of 16 per cent. strength :



After a quarter of an hour the quinone has gone into solution with separation of a green resin ; the solution is first neutralized with hydrochloric acid, and then treated with an excess of the latter in a freezing mixture. Reteneglycollic acid is thus obtained as a granular crystalline product, which quickly becomes sticky and discoloured in the air. The *silver* salt is a flocculent precipitate, very susceptible to light ; the characteristic *copper* salt is a pale green precipitate, almost white in thin layers, and somewhat soluble in boiling water. The yield of reteneglycollic acid amounts only to about 6 per cent. of the quinone.

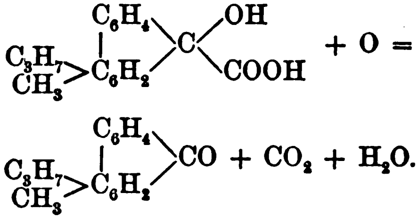
Retenefluorene, $C_{17}H_{18}$, is obtained by distilling reteneketone with zinc dust, or heating it with hydriodic acid and phosphorus at 150° ; it crystallizes from alcohol in silver-white nacreous plates, melts at 96·5—97°, and yields a vapour having the sp. gr. 7·78. On addition of chromium trioxide to its acetic acid solution, no quinone is formed, but the hydrocarbon is almost completely oxidized. It unites with picric acid, forming a compound crystallizing in orange-red lustrous needles ; these are, however, too unstable for analysis.

Dinitroretenefluorene, $C_{17}H_{16}(NO_2)_2$, is formed by adding nitric acid to a hot acetic acid solution of retenefluorene, and crystallizes in straw-yellow matted needles, which are sparingly soluble in alcohol.

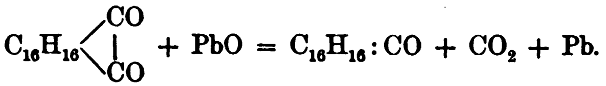
Retenefluorenyl alcohol, $C_{16}H_{16}:CH.OH$, is obtained by the action of sodium amalgam, or of zinc and hydrochloric acid, on an alcoholic solution of reteneketone, and crystallizes on evaporating the alcoholic solution in long white silky needles, melting at 133—134°.

Retenefluorenyl acetate, $C_{16}H_{16}$: CH.O.CO.CH_3, is prepared by boiling the alcohol for a short time with acetic anhydride and sodium acetate, and forms slender white silky needles, melting at 70—71°.

Reteneketone, $C_{16}H_{16}$.CO, is obtained by acting with dilute sulphuric acid and potassium dichromate on copper reteneglycollate:

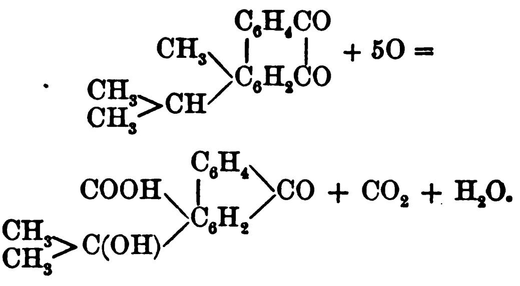


It is also formed when retenequinone is heated with caustic baryta, and in large quantity by distilling the former over lead oxide:



Reteneketone crystallizes from alcohol in flat rhombic sulphur-yellow tablets with a vitreous lustre, which melt at 90°, and show a golden-yellow and greenish-yellow pleochroism.

Hydroxyisopropyldiphenyleneketonecarboxylic acid is formed together with reteneketone by boiling amorphous retenequinone with alkaline potassium permanganate:



It crystallizes from alcohol in lustrous golden-yellow plates, which become red on heating, and melt at 190°. Further oxidation converts it into diphenyleneketonedicarboxylic acid (p. 486). The *barium* salt, $(C_{17}H_{13}O_4)_2Ba + 2H_2O$, forms rosette-shaped aggregates of golden needles. The *oxime*, $HO.N : C : C_{12}H_6(C_3H_6.OH)CO_2H$, is formed by adding hydroxylamine hydrochloride to a solution of the ammonium salt and warming for several hours; it is sparingly soluble in boiling alcohol, from which it crystallizes in straw-yellow fern-like aggregates of needles, which remain unaltered at 270°.

Tectoquinone, $C_{18}H_{16}O_2$, is isomeric with retenequinone, and is found in teak wood (*Tectona grandis*) and in the tar obtained by its distillation. It crystallizes from alcohol in oblique amber yellow prisms, melts at 171°, and sublimes slowly even at the ordinary temperature in rhombic tablets. It dissolves in sulphuric acid with a yellow colour, and is reprecipitated by water. When heated with absolute alcohol and caustic potash it yields a crimson solution, which on addition of water becomes first green and then yellow with separation of the quinone. Bromine converts it at 100—140° into *dibromotectoquinone*, which crystallizes in thin orange-yellow needles, and melts at 165°.[1]

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[1] Romanis, *Journ. Chem. Soc.* **1887**, I. 868; *Proc. Chem. Soc.* **1889**, 116.

FLUORANTHENE GROUP

2769 *Fluoranthene*, $C_{15}H_{10}$, is found in coal-tar,[1] and is also identical with *idryl*, one of the constituents of "stuppfett" (p. 357).[2] It is prepared from the fractions of coal-tar boiling higher than anthracene, and soluble in benzene, which consist mainly of pyrene and fluoranthene, together with small quantities of phenanthrene and other hydrocarbons. To separate the other hydrocarbons the mixture is fractionated under 60mm. pressure, fluoranthene boiling then at 250—251°, and pyrene at 260°. The fraction, 240—250°, is dissolved in alcohol and mixed with a similar solution of picric acid. The fluoranthene picric acid is then separated by repeated crystallization from the less soluble pyrene compound, and converted into the hydrocarbon by the action of ammonia.

Fluoranthene is sparingly soluble in cold, readily in hot alcohol, in ether and acetic acid, and crystallizes from a concentrated alcoholic solution in long slender needles, and from a dilute solution in lustrous monosymmetric tablets, which melt at 109° and dissolve in warm concentrated sulphuric acid with a blue colour. Its vapour has the sp. gr. 6·637.

On oxidation it is converted into fluoranthenequinone and *m*-diphenyleneketonecarboxylic acid (p. 482); the latter on fusion with potash yields isodiphenic acid, and on distilling with zinc dust is reduced to fluorene, whilst when heated with lime it yields diphenyleneketone. Hence fluoranthene stands to fluorene in the same relation as phenanthrene to diphenyl, for which reason it received the above name; its constitution is represented by the formula:

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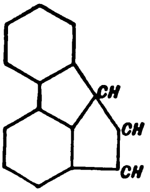
[1] Fittig and Gebhard, *Ber.* **10**, 2141; *Annalen*, **193**, 142.

[2] Goldschmiedt, *Ber.* **10**, 2022.



Fluoranthene picric acid, $C_{15}H_{10} + C_6H_3(NO_2)_3O$, crystallizes in pale reddish-yellow lustrous needles, melts at 182—183°, is sparingly soluble in cold alcohol, and decomposes on boiling with water.

Dihydrofluoranthene, $C_{15}H_{12}$, is formed when fluoranthene is heated with phosphorus and hydriodic acid at 180°, or when its alkaline solution is treated for a long time with sodium amalgam. It crystallizes from alcohol in beautiful needles, melts at 76°, and yields with picric acid a sparingly soluble compound, which crystallizes in yellow or red needles, and melts at 186°.

Octohydrofluoranthene, $C_{15}H_{18}$, is obtained by heating the hydrocarbon with phosphorus and hydriodic acid at 250°; it is a liquid boiling at 311°, and combines with picric acid, forming a red crystalline compound, which is easily soluble and very unstable.[1]

Trichlorofluoranthene, $C_{15}H_7Cl_3$, was obtained by Goldschmiedt by acting on a chloroform solution of fluoranthene with chlorine gas. It forms small white needles, which do not melt at 300°, are almost insoluble in ether, very sparingly soluble in alcohol, and somewhat more readily in benzene.

Dibromofluoranthene, $C_{15}H_8Br_2$, is formed by adding bromine to a solution of fluoranthene in carbon disulphide, and crystallizes in yellowish-green lustrous needles, which melt at 204—205°, and are very sparingly soluble in alcohol and ether (Fittig and Gebhard).

Tribromofluoranthene, $C_{15}H_7Br_3$, was prepared by Goldschmiedt together with the foregoing compound by the action of bromine on an acetic acid solution of the hydrocarbon. It forms soft needles, which do not melt at 345°, and are hardly dissolved by any of the usual solvents.

Trinitrofluoranthene, $C_{15}H_7(NO_2)_3$, is formed by the action of fuming nitric acid on the hydrocarbon, and crystallizes from hot nitric acid in lustrous yellow needles, which do not melt at

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[1] Goldschmiedt, *Monatsh.* **1**, 221.

300°, and are also very sparingly soluble in the common solvents (Fittig and Gebhard).

Fluoranthenedisulphonic acid, $C_{15}H_8(SO_3H)_2$, is prepared by warming fluoranthene with concentrated sulphuric acid, and is a brownish-yellow syrup which undergoes decomposition at 100°. The *barium* salt, $2C_{15}H_8(SO_3)_2Ba + 5H_2O$, is very soluble in water, and separates on evaporation in crystalline crusts (Goldschmiedt).

Fluoranthenequinone, $C_{15}H_8O_2$. Goldschmiedt obtained this compound by mixing acetic acid solutions of fluoranthene and chromium trioxide,[1] whilst Fittig and Gebhard found that in this case and also if dilute sulphuric acid and potassium dichromate are employed, *m*-diphenyleneketonecarboxylic acid is the chief product; this may be removed by treatment with sodium carbonate solution, and the residue on recrystallizing from alcohol yields the compound of fluoranthenequinone and fluoranthene described below. The former may be dissolved out by a solution of sodium bisulphite, and the extract acidified with hydrochloric acid; the corresponding quinol is first formed, but quickly oxidizes, reforming the quinone (Fittig and Liepmann).

Fluoranthenequinone crystallizes from alcohol in small red needles, melting at 188°, and combines with fluoranthene to form the compound, $C_{15}H_8O_2 + 2C_{15}H_{10}$, which separates from alcohol in very lustrous ruby-red flat needles, and melts at 102.° If the quinone be heated with soda-lime diphenyl is formed, whereas it is completely oxidized by boiling with dilute sulphuric acid and potassium dichromate; hence, in the oxidation of fluoranthene, the formation of the quinone does not precede that of diphenyleneketonedicarboxylic acid, but both are formed simultaneously.

Fluoranthenecarboxylic acid, $C_{15}H_9.CO_2H$, was obtained by Goldschmiedt in place of the dicarboxylic acid, by heating potassium fluoranthenedisulphonate with potassium cyanide, and fusing the distillate with caustic potash. It crystallizes from hot alcohol in yellowish-white flakes, melts at 165°, and on heating with lime yields carbon dioxide and fluoranthene.[2]

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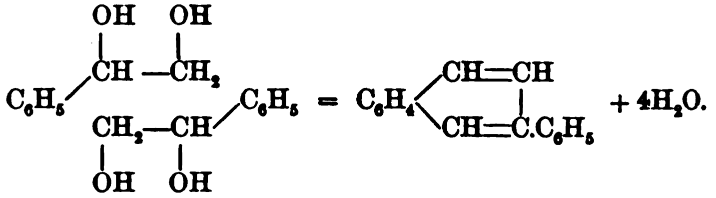
[1] *Ber.* **10**, 2022.

[2] *Monatsh.* **1**, 221.

PHENLYNAPHTHALENE GROUP

2770 *β-Phenylnaphthalene*, $C_{10}H_7.C_6H_5$, is formed together with diphenyl and β-dinaphthyl when the vapour of equal parts of bromobenzene and naphthalene is passed through a red-hot tube filled with pumice stone.[1] It is also obtained by mixing 80 grams of sulphuric acid with 34 grams of water, and pouring at once into a solution of 5 grams of styrolene alcohol in 10 grams of water:



The mixture is boiled, well shaken for a few minutes, and then poured into water,[2] phenylacetaldehyde being formed as an intermediate product in the reaction. It may also be prepared by heating α-phenyllactic acid with dilute sulphuric acid at 200°.[3]

β-Phenylnaphthalene crystallizes from alcohol in lustrous plates with a bluish fluorescence, melts at 101—101·5°, and boils at 345—346°. Its vapour, the odour of which resembles that of oranges, has the sp. gr. 7·1. It is oxidized by sulphuric acid and potassium dichromate to benzoic acid, whilst potassium permanganate yields in addition some phthalic acid (Zincke and Breuer).

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[1] W. Smith, *Ber.* **12**, 2049; *Proc. Chem. Soc.* **1889**, 70; Smith and Takamatsu, *Journ. Chem. Soc.* **1881**, I. 546.

[2] Zincke and Breuer, *Annalen*, **226**, 23; Zincke, *Annalen*, **240**, 137.

[3] Erlenmeyer, *Ber.* **13**, 305; Miller and Rohde, *Ber.* **23**, 1078.

β-Phenyl-α-naphthoquinone, $C_6H_5.C_{10}H_5O_2$, is prepared by adding a solution of 3 parts of chromium trioxide in 10 parts of acetic acid to a solution of 1 part of phenylnaphthalene in 10 parts of warm acetic acid, and after the first violence of the reaction is over, boiling till the oxidation is complete. To purify the product it must be recrystallized from alcohol, without exposure to daylight.

Phenylnaphthoquinone crystallizes in lustrous golden-yellow needles, melts at 109—110°, and is fairly soluble in alcohol, ether and benzene, more sparingly in light petroleum. In the dry condition it is stable towards light, but in solution it is converted into two polymeric modifications, which form a crystalline precipitate, and may be separated by means of hot chloroform.

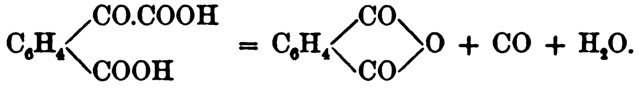
"Yellow polyquinone" crystallizes from hot acetic acid, in which it is sparingly soluble, in small yellow rhombic tablets, melts at 229°, and carbonizes when more strongly treated.

"White polyquinone" forms small plates, which are insoluble in the ordinary solvents, melt at 207—207°·5, and at higher temperatures give a sublimate of phenylnaphthoquinone (Zincke and Breuer).

Phenylnaphthoquinol, $C_6H_5.C_{10}H_5(OH)_2$, is obtained by warming the quinone with a solution of stannous chloride or hydriodic acid, and crystallizes in colourless needles or plates, which melt at 92—93°, and quickly undergo oxidation in moist air. Its acetate, $C_6H_5.C_{10}H_5(O.CO.CH_3)_2$, forms nodular aggregates of slender yellow needles, and melts at 151·5—152°·5.

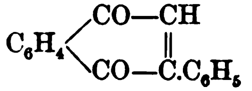
Phenylnaphthoquinhydrone, $C_{16}H_{10}(OH)_2 + C_{16}H_{10}O_2$, is formed together with the quinol by heating the quinone with aqueous sulphurous acid at 120°; it crystallizes from a mixture of benzene and light petroleum in thick opaque needles with a steel-blue lustre, which melt at 132—133°, and readily undergo oxidation in alcoholic solution, reforming the quinone.

Phenylhydroxynaphthoquinone, $C_6H_5.C_{10}H_4(OH)O_2$, is formed together with the corresponding quinol by heating the quinone with dilute caustic soda, and is precipitated from the deep red solution by hydrochloric acid in reddish-yellow flakes or slender needles. It crystallizes from hot alcohol in lustrous golden-yellow prisms or needles, showing a faint dichroism, melts at 143·5—144°·5, and sublimes with difficulty and simultaneous decomposition. Dilute potassium permanganate solution oxidizes it to benzoic and phthalic acids; in alkaline solution, however, benzoic acid and *phenyleneketonedicarboxylic acid* are formed. The latter separates from solution as an oil, which, after remaining for months, solidifies to a radial crystalline mass, melting at 177—179°; on strongly heating it decomposes, with formation of a sublimate of phthalic anhydride:

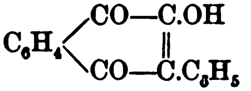


$$C_6H_4\left\langle\begin{matrix}CO.COOH\\COOH\end{matrix}\right. = C_6H_4\left\langle\begin{matrix}CO\\CO\end{matrix}\right\rangle O + CO + H_2O.$$

The quinone and hydroxyquinone must therefore have the following constitutional formulæ:



$$C_6H_4\left\langle\begin{matrix}CO-CH\\ \| \\CO-C.C_6H_5\end{matrix}\right.$$



$$C_6H_4\left\langle\begin{matrix}CO-C.OH\\ \| \\CO-C.C_6H_5\end{matrix}\right.$$

The alkaline salts of the hydroxyquinone have a deep red colour, and are readily soluble in water and alcohol, but hardly in concentrated alkalis. The *barium* salt $(C_{16}H_9O_3)_2Ba$ separates from dilute alcohol in small brown needles, of thick, almost black, crystals. The *acetate*, $C_{16}H_9(O.CO.CH_3)O_2$, crystallizes in transparent yellow tablets, melting at 110—111°, and the *benzoate*, $C_{16}H_9(O.CO.C_6H_5)O_2$, in large yellow monosymmetric prisms resembling gypsum.

Phenyltrihydroxynaphthalene, $C_6H_5.C_{10}H_4(OH)_3$, is formed by heating the hydroxyquinone with hydriodic acid, and crystallizes in long white needles, which melt at 72—73°, and quickly undergo oxidation in presence of water or alcohol.

Phenylnaphthohydroxyquinhydrone, $C_{16}H_9(OH)_3 + C_{16}H_9(OH)O_2$, is prepared by heating the hydroxyquinone with sulphurous acid at 120—130°, and forms thick plates or needles with a steel blue lustre, which melt at 154—155°.

Phenylamidonaphthoquinone, $C_6H_5.C_{10}H_4(NH_2)O_2$, is obtained by the action of ammonia on an alcoholic solution of the quinone, and crystallizes from alcohol in broad red lustrous plates, which melt at 173·5—174°, and sublime in small red plates. On boiling with caustic soda or heating with hydrochloric acid at 140—150° it is reconverted into the hydroxyquinone.

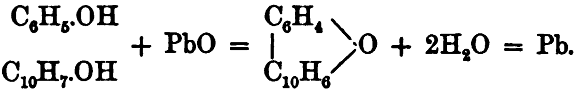
Phenylmethylamidonaphthoquinone, $C_6H_5.C_{10}H_4(NH.CH_3)O_2$, crystallizes in broad dark red plates.

Phenylanilidonaphthoquinone, $C_6H_5.C_{10}H_4(NHC_6H_5)O_2$, forms dark red needles or plates, and melts at 158—158°·5.

The quinone forms similar compounds with the toluidines and α-naphthylamine, and corresponds therefore exactly to α-naphthoquinone (Zincke).

Phenyl-β-ethoxy-p-diamidonaphthalene, $C_6H_5.C_{10}H_4(OC_2H_5).(NH_2)_2$, is formed by the action of stannous chloride and hydrochloric acid on an alcoholic solution of the ethyl ether of benzeneazo-β-naphthol (p. 257). The *hydrochloride* crystallizes in silky needles, and the *normal sulphate* is very sparingly soluble in water. Alkalis precipitate the base in white flakes, which melt at 72°, and readily darken in the moist condition; it dissolves in alcohol with a greenish-blue, and in ether with a violet fluorescence. Nitrous acid converts it into the tetrazo-compound, which yields pure blue colouring matters with naphtholsulphonic acids.[1]

2771 *α-Naphthylenephenylene oxide*, $C_{16}H_{10}O$, is obtained by heating equal parts of phenol and α-naphthol with four parts of lead oxide:



$$\begin{matrix} C_6H_5.OH \\ C_{10}H_7.OH \end{matrix} + PbO = \begin{matrix} C_6H_4\diagdown \\ | \quad\quad O \\ C_{10}H_6\diagup \end{matrix} + 2H_2O = Pb.$$

It crystallizes from benzene in yellowish needles, sparingly soluble in alcohol and acetic acid, melts at 178°, sublimes at 280°, and boils above 360°. It is not reduced by heating with zinc dust.

With picric acid it forms the compound $C_{16}H_{10}O + 2C_6H_3(NO_2)_3O$, which crystallizes from benzene in dark red needles or prisms, melts at 165°, and is decomposed by alcohol.

Dichloronaphthylenephenylene oxide, $C_{16}H_8Cl_2O$, is prepared by the action of phosphorus pentachloride or chlorine on the oxide, and crystallizes from benzene in needles melting at 245°.

Dibromonaphthylenephenylene oxide, $C_{16}H_8Br_2O$, crystallizes from benzene in white needles, and melts at 284°.

Dinitronaphthylenephenylene oxide, $C_{16}H_8(NO_2)_2O$, is obtained crystalline with difficulty from toluene, and melts at 235°.

α-Naphthylenequinonephenylene oxide, $C_{16}H_8O_3$, is formed by adding chromium trioxide to an acetic acid solution of the oxide.

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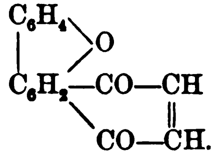
[1] Weinberg, *Ber.* **20**, 3177.

It is readily soluble in alcohol and benzene, and crystallizes in reddish-yellow prisms, melting at about 140°. Alkalis dissolve it forming a red solution, and with sulphuric acid it yields a yellow solution showing a green fluorescence. On heating with zinc dust it is reduced to naphthylenephenylene oxide, and is oxidized by potassium permanganate to phthalic acid.

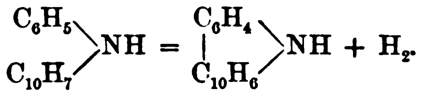
As diphenyl yields no similar quinone, it is probable that the quinone group is in the naphthalene nucleus, as shown in the following constitutional formula:



β-Naphthylenephenylene oxide is obtained from β-naphthol, phenol and lead oxide, and separates on addition of alcohol to its toluene solution in yellow plates, which melt at 296°, are only slightly soluble in alcohol and ether, and somewhat more readily in acetic acid. Its solutions according to their concentration show a strong violet to blue fluorescence. It dissolves in sulphuric acid with a pink colour, which gradually changes to blue; on dilution with water the solution shows an orange-red fluorescence.[1]

β-Naphthylenequinonephenylene oxide, $C_{16}H_8O_3$, was prepared by Graebe and Knecht by the oxidation of naphthylphenylcarbazole, and crystallizes from benzene in reddish-yellow prisms, which dissolve in alkalis with a red colour, and when heated with zinc dust yield the previous compound.

Naphthylphenylcarbazole is a constituent of crude anthracene, in which it was discovered by Brunck; it is also formed when the vapour of phenyl-β-naphthylamine is passed through a red-hot tube:



When prepared from crude anthracene, and purified by crystallization or sublimation, it contains an intense greenish or

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[1] Arx, *Annalen*, **209**, 141.

golden-yellow impurity which is even more difficult to remove than in the case of chrysene. It is however destroyed by fusion with potash, or by preparing the acetyl derivative and reconverting the latter into the carbazole.

It then forms colourless plates, which are almost insoluble in cold alcohol, benzene, and toluene; at the boiling-point 100 parts of alcohol dissolve 0·25 parts, and 100 parts of toluene 0·3 parts.[1] It only dissolves slightly in boiling acetic acid, but readily in hot aniline, the solution showing a blue fluorescence. It melts at 330°, and boils above 436°, yielding a vapour having the sp. gr. 7·42. It combines with picric acid, forming an unstable compound.

Acetylnaphthylcarbazole, $C_{16}H_{10}:N.CO.CH_3$, is prepared by heating the carbazole with acetic anhydride at 220—240°, and crystallizes from alcohol in flat prisms, which melt at 121° and dissolve readily in ether, benzene, and hot alcohol with a blue fluorescence.

Nitrosonaphthylcarbazole, $C_{16}H_{10}:N.NO$, is formed by pouring ether and 50 per cent. acetic acid on to the carbazole and adding sodium nitrite. After some days the ethereal solution is evaporated, the nitroso-compound being then deposited in long reddish prisms, which melt at 240° and dissolve in sulphuric acid, forming a beautiful violet solution.

Naphthylphenylcarbazoline, $C_{16}H_{15}N$, is prepared by heating the carbazole with phosphorus and hydriodic acid at 200—220°. It crystallizes from alcohol in needles, and forms salts which are decomposed by boiling water.

Naphthoquinonephenylcarbazole, $C_{16}H_9NO_2$, is formed together with phthalic acid and the above β-naphthoquinonephenylene oxide, by the oxidation of the carbazole with dilute sulphuric acid and potassium permanganate, and may be readily obtained pure, as it is insoluble in sodium carbonate solution. It crystallizes from acetic acid in reddish-yellow needles, melts at 307°, and sublimes in red needles. It forms a beautiful reddish-violet solution in sulphuric acid, and on heating with zinc dust re-forms the carbazole; with potassium permanganate it is oxidized to phthalic acid.[2]

These compounds have the following constitution:

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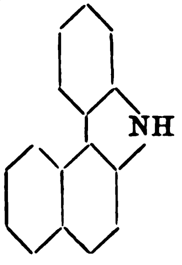
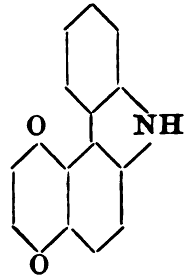
[1] Becchi, *Ber.* **12**, 1976.

[2] Graebe and Knecht, *Annalen*, **202**, 1.

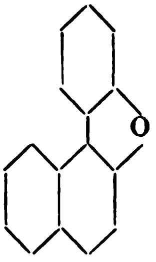
Naphthylphenylcarbazole.



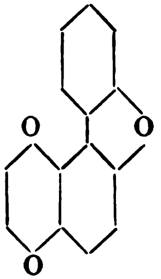
Naphthoquinonephenylcarbazole.



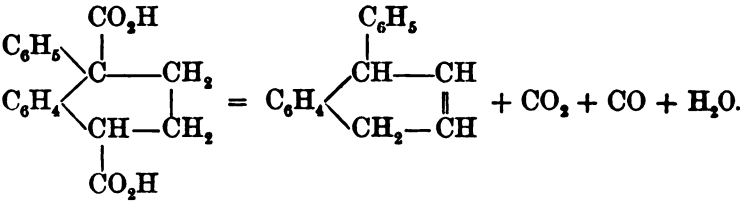
β-Naphthylenephenylene oxide.



β-Naphthoquinonephenylene oxide.



2772 *Phenyldihydronaphthalene* or *Atronol*, $C_{16}H_{14}$, is formed by the dry distillation of *a*-isatropic acid (Part V., p. 234):



$$C_6H_4\left\langle\begin{array}{l} C(C_6H_5)(CO_2H)—CH_2 \\ CH(CO_2H)—CH_2 \end{array}\right. = C_6H_4\left\langle\begin{array}{l} CH(C_6H_5)—CH \\ CH_2—CH \end{array}\right. + CO_2 + CO + H_2O.$$

It is a transparent, somewhat thick liquid, which has a faint pleasant odour and boils at 325—326°; at —18° it forms a very viscous mass without crystallizing, and is oxidized by chromic acid to *o*-benzoylbenzoic acid, $C_6H_5.CO.C_6H_4.CO_2H$.

Atronolsulphonic acid, $C_{16}H_{13}.SO_3H$, is obtained by gently warming atronol with sulphuric acid, and crystallizes in colourless very soluble needles. The *barium* salt, $(C_{16}H_{13}SO_3)_2Ba$, is so little soluble in cold water that even a dilute solution of the acid is precipitated by barium chloride; it crystallizes from a boiling solution on cooling in silvery plates.

Atronic acid, $C_{16}H_{13}.CO_2H$, is formed in small quantity together with atronol, and crystallizes from alcohol in thick colourless transparent prisms, melting at 164°. The *calcium* salt, $(C_{16}H_{13}.CO_2)_2Ca + 6H_2O$, is obtained on addition of calcium chloride to a solution of the ammonium salt, as a flocculent precipitate, which quickly changes to needles. These are sparingly soluble in hot water, and crystallize out on cooling in lustrous needles, which on filtering and drying form a mass resembling silver foil. The *barium* salt, $(C_{16}H_{13}CO_2)_2Ba + 4H_2O$, is very similar to the calcium salt, but dissolves much more readily in boiling water.

Isatronic acid, $C_{16}H_{13}.CO_2H$, is obtained by warming α- or β-isatropic acid with sulphuric acid, and is scarcely soluble in water, but readily in alcohol. Its solution in a warm mixture of equal volumes of alcohol and water, even when very dilute, yields on cooling a magma of nacreous plates, which melt at 156—157°, and split up when more strongly heated into carbon dioxide and atronol. The *calcium* salt, $(C_{16}H_{13}.CO_2)_2Ca$, is obtained as a voluminous precipitate on addition of calcium chloride to a solution of the ammonium salt. When warmed this increases so much that the whole resembles a mass of silica-jelly; on heating with more water to the boiling-point, it separates as a powder which is scarcely soluble in both cold and hot water. The *barium* salt, $(C_{16}H_{13}.CO_2)_2Ba + 6H_2O$, is an amorphous glutinous precipitate, which crystallizes from boiling water in small thick prisms.

Atronylenesulphonic acid, $C_{16}H_{11}.SO_3H$, is formed by heating isatropic acid or isatronic acid with sulphuric acid at 90°. It is insoluble in water, and crystallizes from dilute acetic acid in large colourless transparent prisms, which decompose above 200°, but are unaffected by water and hydrochloric acid at 150°. Its solution in aqueous sodium carbonate shows a characteristic and remarkable behaviour towards light; if kept in the dark the liquid remains quite clear even after several months, but on exposure to light becomes turbid, and in direct sunlight quickly yields a thick white precipitate of *atroninsulphone*:

$$C_{16}H_{11}.SO_3Na = C_{16}H_{10}:SO_2 + NaOH.$$

This compound crystallizes from alcohol in small lustrous needles, melting at 193°.[1]

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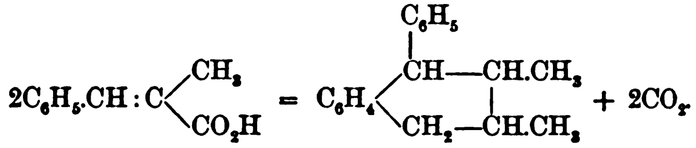
[1] Fittig, *Annalen*, **206**, 46.

Phenyldimethyltetrahydronaphthalene or *Methronol*, $C_{18}H_{20}$, was prepared by Erdmann by the continued boiling of phenylmethacrylic acid with a mixture of two parts of sulphuric acid and three parts of water:



$$2C_6H_5.CH:C\left\langle\begin{array}{l}CH_3\\CO_2H\end{array}\right. = C_6H_4\left\langle\begin{array}{l}\overset{C_6H_5}{\overset{|}{C}H}—CH.CH_3\\ CH_2—\overset{|}{C}H.CH_3\end{array}\right. + 2CO_2.$$

It is a yellow, oily, aromatic-smelling liquid, which boils at 322—323°, and is oxidized by chromic acid to *o*-benzoylbenzoic acid; acetic acid, benzoic acid, and anthraquinone are formed as by-products.[1]

Pseudophenanthrene, $C_{16}H_{12}$, is isomeric with the phenylnaphthalenes, but its constitution is unknown. It occurs in crude anthracene, from which it is obtained by repeated extraction with ethyl acetate, distilling off the latter, and warming the residue with alcohol at 40°. After cooling, the insoluble portion is filtered off and treated with a quantity of benzene insufficient for complete solution, and a saturated benzene solution of picric acid added. The picric acid compound is allowed to crystallize out in fractions, the first portion decomposed by ammonia, and the separated hydrocarbon recrystallized from alcohol. It is then again dissolved in alcohol and treated with a cold saturated alcoholic solution of picric acid; the compound thus obtained yields pure pseudophenanthrene, which crystallizes in large lustrous plates and melts at 115°, whilst its *picric acid compound* forms pale red needles and melts at 147°. When treated with chromium trioxide in acetic acid it yields a yellow quinone, which melts at 170°, and sublimes with great difficulty.[2]

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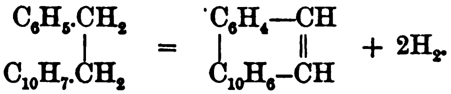
[1] Erdmann, *Annalen*, **227**, 247.

[2] Zeidler, *Annalen*, **191**, 285.

CHRYSENE GROUP.

2773 *Chrysene*, $C_{18}H_{12}$. This name was given by Laurent on account of its yellow colour to a hydrocarbon found in the last fractions obtained in the distillation of the tar from coal or fat.[1] The same compound in a more or less pure condition had frequently been observed previously; thus Vogel in 1805 showed that amber yields on distillation a "volatile-amber resin," which, as Pelletier and Walter found, contained a hydrocarbon[2] undoubtedly identical with chrysene. By passing the vapour of coal-tar through a red-hot tube, Kidd obtained together with naphthalene and other products a "yellow meal," which certainly contained chrysene.[3] It is also obtained by the direct distillation of coal-tar, as was shown by Galletly (who was the first to characterize the hydrocarbon with any exactitude),[4] and occurs in fir-wood tar[5] and in lignite-tar.[6]

Graebe and Bungener obtained it synthetically by passing the vapour of phenylnaphthylethane through a red-hot tube:[7]



$$\begin{array}{c} C_6H_5.CH_2 \\ | \\ C_{10}H_7.CH_2 \end{array} = \begin{array}{c} C_6H_4\text{—}CH \\ |\qquad \| \\ C_{10}H_6\text{—}CH \end{array} + 2H_2.$$

It is also formed when the vapours of coumaron (Part V., p. 247) and naphthalene are passed through a tube heated to dull redness:[8]

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[1] *Ann. Chim. Phys.* II. **66**, 163; G. Williams, *Jahresb.* **1855**, 633.

[2] *Annalen*, **48**, 345.

[3] *Phil. Trans.* **1821**, 309; Mansfield, *Quart. Journ. Chem. Soc.* **1**, 248; *Gmelin's Handb. Org. Chem.* **4**, 473; Liebermann, *Annalen*, **158**, 299; Schmidt, *J. Pr. Chem.* II. **9**, 270.

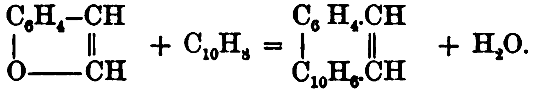
[4] *Jahresb.* **1865**, 532.

[5] Berthelot, *Jahresb.* **1867**, 599.

[6] *Ber.* **12**, 1078.

[7] Ader, *Ber.* **12**, 1889.

[8] Krämer and Spilker, *Ber.* **23** 84.



$$\begin{array}{l}C_6H_4-CH\\ |\qquad \| \\ O——CH\end{array} + C_{10}H_8 = \begin{array}{l}C_6H_4.CH\\ |\qquad \| \\ C_{10}H_6.CH\end{array} + H_2O.$$

From these syntheses it appears that chrysene stands to phenylnaphthalene in the same relation as phenanthrene to diphenyl.

For its thorough investigation we are indebted in the first place to Liebermann, who obtained it from the material employed by Graebe for the preparation of pyrene (p. 357). The substance remaining after repeated extraction with carbon disulphide was crystallized from coal-tar xylene, and thus obtained in lustrous yellow scales or plates. The colour, however, is due to a minute quantity of an impurity, which is destroyed by boiling with alcohol and a little nitric acid.

Schmidt isolated chrysene from crude anthracene by boiling the latter with alcohol and nitric acid, which causes the formation of the compound of chrysene and dinitroanthraquinone described below; this was then decomposed by tin and hydrochloric acid, and the chrysene recrystallized from benzene.

It is sparingly soluble in cold ether, carbon disulphide, or acetic acid, and crystallizes from boiling benzene or acetic acid in scales or small rhombic tablets, which like the solutions show a reddish-violet fluorescence. According to Becchi 100 parts of absolute alcohol dissolve 0·097 parts of chrysene at 16°, and 0·17 parts at the boiling-point, whilst 100 parts of toluene dissolve 0·24 parts at 18°, and 5·39 parts at the boiling-point.[1] Chrysene melts at 250°, sublimes at a lower temperature in loose aggregates of lustrous plates, and boils at about 440°, yielding a vapour of the sp. gr. 7·95.[2] When gradually heated with antimony pentachloride to 360° it yields tetrachloromethane, hexchlorethane, and hexchlorobenzene.[3]

Chrysene picric acid, $C_{18}H_{12} + C_6H_3(NO_2)_3O$, was prepared by Galletly by mixing the constituents in alcoholic solution, and crystallizes in long red needles. It is also formed, according to Berthelot, by boiling an alcoholic chrysene solution with an excess of picric acid, whilst cold alcohol converts it into pseudomorphs of chrysene (Liebermann).

Chrysene dinitroanthraquinone, $C_{18}H_{12}+C_{14}H_6(NO_2)_2O_2$, crystallizes in slender red needles, melts at 294°, and is almost in-

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[1] *Ber.* **12**, 1976.

[2] Knecht, *Ber.* **10**, 2073.

[3] Ruoff, *Ber.* **16**, 2881.

soluble in boiling alcohol, ether, and benzene; it dissolves somewhat more readily in acetic acid. Oxidizing or reducing agents convert it into its constituents, which may then undergo further alteration according to the nature of the agent. When carefully heated it sublimes in beautiful red needles, but decomposes into chrysene and dinitroanthraquinone on repeated sublimation at a high temperature.

Hekkaidecahydrochrysene, $C_{18}H_{28}$, is formed together with the following compound by heating 1 part of chrysene with 1 part of amorphous phosphorus and 5 parts of hydriodic acid (sp. gr. 1·7) at 250—260° for sixteen hours, and is a thick, oily, slightly fluorescent liquid, which boils at about 360°.

Perhydrochrysene, $C_{18}H_{30}$, crystallizes from alcohol in snow-white needles, melts at 115°, boils at 353°, and is not attacked in the cold by bromine or concentrated nitric acid. On boiling with chromium trioxide in acetic acid solution it does not yield chrysoquinone, but undergoes complete oxidation. It may be distilled over pumice-stone at a moderate red heat without decomposition, but is converted for the most part into chrysene by red-hot zinc dust. Hekkaidecahydrochrysene behaves in a very similar manner.[1]

Dichlorochrysene, $C_{18}H_{10}Cl_2$, is formed by passing chlorine over chrysene at 100°, and crystallizes from benzene in delicate white needles, melts at 267°, and on more strongly heating sublimes in beautiful needles. It is scarcely soluble in boiling alcohol or ether (Schmidt).

Trichlorochrysene, $C_{18}H_9Cl_3$, is obtained by the action of chlorine on chrysene at 160—170°. The only liquid in which it dissolves to any extent is benzene; from this solution it crystallizes in slender needles, melting above 300°.

Dibromochrysene, $C_{18}H_{10}Br_2$, is prepared by treating a carbon disulphide solution of chrysene with bromine, and crystallizes in lustrous white needles, which melt at 273°, and dissolve only in benzene. It sublimes without decomposition in beautiful needles, and is converted by alcoholic potash at 170—180° into chrysene, the alcohol probably undergoing oxidation.

Nitrochrysene, $C_{18}H_{11}(NO_2)$, is readily obtained by triturating 10 grams of chrysene with 100 grams of acetic acid, adding 4·5 grams of nitric acid of sp. gr. 1·415, and warming for several hours on the water-bath. It is sparingly soluble in acetic acid

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[1] Liebermann and Spiegel, *Ber.* **22**, 135.

and benzene, and crystallizes from the latter in yellow stellate groups of prisms, whilst from nitrobenzene, in which it readily dissolves, it separates in beautiful red crystals resembling potassium dichromate, which melt at 205°·5, and sublime in needles.[1]

Dinitrochrysene, $C_{18}H_{10}(NO_2)_2$, is formed by warming the hydrocarbon for a long time with nitric acid of sp. gr. 1·3. The reddish-yellow powder thus formed contains also the nitro- and tetranitro-derivatives, and was described by Laurent as "*Nitrite de chrysenase*," $C_{12}H_6O + N_2O_3$. On heating it, the tetranitro-compound decomposes, whilst the nitro- and dinitro-compounds sublime, and are separated by means of benzene, in which the latter is very slightly soluble. Dinitrochrysene crystallizes from acetic acid, in which it also dissolves but sparingly, in slender yellow needles, melting above 300°.

Tetranitrochrysene, $C_{18}H_8(NO_2)_4$, is formed by the action of fuming nitric acid on chrysene (Liebermann), or by heating the foregoing compound with concentrated acid (Schmidt), and crystallizes from acetic acid in yellow needles, which do not melt at 300°, and on further heating explode somewhat violently.

Tribromodinitrochrysene, $C_{18}H_7Br_3(NO_2)_2$, was prepared by Adler by the action of bromine on the foregoing compound; it crystallizes from alcohol in red needles, and is sparingly soluble in ether and benzene.

Amidochrysene, $C_{18}H_{11}.NH_2$, was obtained by Abegg by heating nitrochrysene with hydriodic acid and phosphorus. It is also formed when 10 grams of nitrochrysene are dissolved in boiling acetic acid, 7 grams of granulated tin added, and then hydrochloric acid drop by drop till the solution is colourless. The stannochloride then separates out, and is decomposed by boiling with dilute caustic soda, the liberated base dissolved in alcohol and mixed with hydrochloric acid, which yields the hydrochloride in the pure condition.

Amidochrysene is obtained from its salts as a white crystalline powder, which is insoluble in water, but dissolves readily in alcohol, benzene, and especially in chloroform, with a bluish-violet fluorescence. The solutions very readily become brown, and the recrystallized base has therefore generally a slight

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[1] Schmidt, *loc. cit.*; Abegg, *Ber.* **23**, 792; Bamberger and Burgdorf, *Ber.* **23**, 2444.

chocolate tinge. It melts at 199°, and gives with diazobenzenesulphonic acid a raspberry-red colouring matter, which dissolves in dilute alcohol with a beautiful blue fluorescence.

The *hydrochloride* and *sulphate* are almost insoluble in water and alcohol, but the latter dissolves readily in concentrated sulphuric acid (Bamberger and Burgdorf).

2774 *Chrysoquinone*, $C_{18}H_{10}O_2$, is best prepared by mixing loosely aggregated crystallized chrysene with acetic acid, and adding a little chromium trioxide. After the first reaction is over the mixture is heated to boiling; as soon as the liquid has partially cooled more chromium trioxide is added, and the process repeated till 3 parts of chromium trioxide have been used for every 2 parts of chrysene; the boiling solution is then filtered, and the filtrate precipitated with water. The precipitate is washed with boiling water, and dissolved in sulphuric acid to remove unaltered chrysene; water is again added to the solution, and the precipitate repeatedly crystallized from boiling benzene (Liebermann). It forms beautiful reddish-yellow needles, melts at 235°, and sublimes in splendid red needles (Schmidt). Cold concentrated sulphuric acid dissolves it, forming a cornflower-blue solution, the colour of which is so intense that an unweighable particle of chrysenequinone may be thus recognized. On addition of water the quinone separates out, and the solution is completely decolourized. Its hot alcoholic solution gives with a drop of caustic potash the dark-red colouration characteristic of *o*-diketones, which disappears on shaking.[1] On heating with zinc dust it is reduced to chrysene, and with potassium permanganate it yields phthalic acid, which is also formed in the preparation of the quinone.

Chrysoquinone also dissolves in a warm solution of acid sodium bisulphite, and if the solution is sufficiently concentrated, colourless crystals separate out, which are decomposed by water.[2]

Chrysoquinol, $C_{18}H_{10}(OH)_2$. Liebermann prepared this compound by boiling the quinone with caustic potash and zinc dust, and Graebe obtained it by heating the former with sulphurous acid at 100°. It forms colourless needles, which readily undergo oxidation in the moist condition. This also takes place if the anhydrous compound be heated to 200°, or by dissolving it in

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[1] Bamberger, *Ber.* **18**, 865, 1931.

[2] Graebe, *Ber.* **7**, 782.

sulphuric acid and shaking the yellowish-green solution in the air, when it assumes the characteristic cornflower-blue colour.

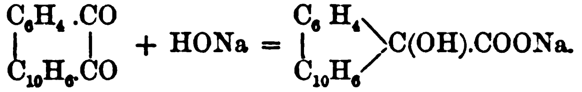
Dichlorochrysoquinone, $C_{18}H_8Cl_2O_2$, is formed by heating the quinone with phosphorus chloride at 200°, and separates on addition of alcohol in pale yellow flakes.

Dibromochrysoquinone, $C_{18}H_8Br_2O_2$, was prepared by Adler by the action of bromine, and crystallizes from carbon disulphide in red plates, melting at 160—165°.

Dinitrochrysoquinone, $C_{18}H_8(NO_2)_2O_2$, is formed by dissolving the quinone in nitric acid of sp. gr. 1·4, and is precipitated from the beautiful red solution by addition of water. It crystallizes from a mixture of acetic acid and alcohol in red needles, melting at 230° (Adler).

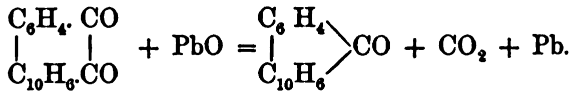
Tetranitrochrysoquinone, $C_{18}H_6(NO_2)_4O_2$, was obtained by Liebermann by the action of fuming nitric acid on chrysoquinone. It is an orange-yellow powder, insoluble in most of the usual solvents.

Chrysoglycollic acid is prepared by boiling amorphous chrysoquinone with caustic soda, the latter being best obtained by precipitating the sulphuric acid solution with water:



$$\begin{array}{l} C_6H_4.CO \\ | \qquad\;\; | \\ C_{10}H_6.CO \end{array} + HONa = \begin{array}{l} C_6H_4 \\ | \\ C_{10}H_6 \end{array}\!\!>C(OH).COONa.$$

It is precipitated in flakes on addition of acids, and readily undergoes decomposition. On warming with dilute sulphuric acid and potassium dichromate it is oxidized to *chrysoketone*, which is more readily obtained by heating the quinone with lead oxide:

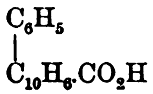


$$\begin{array}{l} C_6H_4.CO \\ | \qquad\;\; | \\ C_{10}H_6.CO \end{array} + PbO = \begin{array}{l} C_6H_4 \\ | \\ C_{10}H_6 \end{array}\!\!>CO + CO_2 + Pb.$$

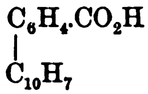
It sublimes in thin golden-yellow silky needles or orange-red prisms, which melt at 132°·5, and crystallizes on cooling in long ruby-red needles (Bamberger and Burgdorf). It is reduced by zinc and hydrochloric acid to *chrysofluorenyl alcohol*, $C_{17}H_{11}.OH$, which crystallizes in silky needles or plates, melts at 166—167°, dissolves in sulphuric acid with a reddish-violet, and in alcohol with a blue colour.

Chrysofluorene, $C_{17}H_{12}$, is obtained by heating the ketone with hydriodic acid and phosphorus at 150—160°, and crystallizes in silver-white satiny plates, melting at 187—188°.[1]

Chrysenic acid, $C_{16}H_{11}.CO_2H$, is prepared by fusing chrysenequinone or chryseneketone with potash, and also crystallizes in silver-white satiny plates. It is sparingly soluble in water, readily in alcohol, and melts at 186°·5. If it is dissolved in sulphuric acid, and the solution poured into ice-water, chrysoketone is re-formed. Its constitution is represented by one of the following formulæ :



$$\begin{array}{l} C_6H_5 \\ | \\ C_{10}H_6.CO_2H \end{array}$$



$$\begin{array}{l} C_6H_4.CO_2H \\ | \\ C_{10}H_7 \end{array}$$

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[1] Bamberger and Kranzfeld, *Ber.* **18** 1931.

DINAPHTHYL GROUP.

2775 *a-Dinaphthyl*, $C_{20}H_{14}$, was obtained by Lossen together with phthalic acid and other products by boiling naphthalene with dilute sulphuric acid and manganese dioxide, and also in small quantity by the action of sodium on *a*-bromonaphthalene.[1] It is obtained, further, together with its two isomerides, when a mixture of the vapours of naphthalene and antimony trichloride or tin tetrachloride is passed through a red-hot tube,[2] and is also readily prepared by distilling *β*-dinaphthol with 10—15 parts of zinc dust.[3] It crystallizes from alcohol in octohedra, and from light petroleum in rhombic tablets, melts at 154°, and boils above 360°, yielding a vapour of sp. gr. 8·67. Its solutions show a blue fluorescence, and it gives with picric acid the compound $C_{20}H_{14} + 2C_6H_3(NO_2)_3O$, which crystallizes from benzene in reddish-brown needles, melting at 145°; it becomes yellow and decomposes in the air.[4]

Dibrom-a-dinaphthyl, $C_{20}H_{12}Br_2$, was prepared by Lossen by acting on *a*-dinaphthyl with bromine vapour; it crystallizes from benzene in thin, strongly refractive prisms, melts at 215°, and is volatile without decomposition.

Nitro-a-dinaphthyl, $C_{20}H_{13}.NO_2$, is formed by dissolving 10 grams of *a*-dinaphthyl in 150 cc. of acetic acid, and adding 20 grams of concentrated nitric acid. The product which has separated after some hours is crystallized from benzene, and then forms orange-yellow lustrous plates, melts at 188°, and dissolves in hot sulphuric acid with a dark blue colour.

Dinitro-a-dinaphthyl, $C_{20}H_{12}(NO_2)_2$. Julius obtained this compound in a similar manner to the foregoing, using 80 grams

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[1] *Annalen*, **144**, 71.

[2] W. Smith, *Journ. Chem. Soc.* **1877**, II. 559; **1879**, I. 224.

[3] Julius, *Ber.* **19**, 2549.

[4] Walder, *Ber.* **15**, 2166.

of nitric acid, and finally warming to 60°. It crystallizes from benzene in small pale yellow needles, which melt at 280°, and only dissolve to any appreciable extent in acetic acid, benzene, and xylene.

Dihydroxy-a-dinaphthyl, $C_{20}H_{12}(OH)_2$. This substance was obtained by Dianin by the action of ferric chloride on an aqueous solution of β-naphthol, and was termed by him *β-dinaphthol*.[1] A better yield is obtained by adding anhydrous ferric chloride to an ethereal solution of β-naphthol, and boiling the solution when the first reaction has moderated (Walder). It crystallizes from alcohol in flat lustrous white needles, from benzene in rounded plates, and from a mixture of carbon disulphide and alcohol in large oblique prisms, which melt at 218°, and decompose into β-naphthol on distillation. With ferric chloride it gives a pale green colouration, which changes on warming to bright red and then to brown. It is reduced to α-dinaphthyl on heating with zinc dust, and is oxidized by potassium permanganate to hydroxynaphthoylbenzoic acid, $C_{10}H_6(OH).CO.C_6H_4.CO_2H$. Its *picric acid compound*, $C_{20}H_{14}O_2 + 2C_6H_3(NO_3)_2O$, crystallizes from benzene in yellowish-white spear-shaped needles, melts at 174°, is more readily soluble in benzene than β-dinaphthol, and becomes yellow in the air.

Dimethoxy-a-dinaphthyl, $C_{20}H_{12}(OCH_3)_2$, is formed by heating β-dinaphthol with alcoholic potash and methyl iodide, and crystallizes in pyramid-shaped crystals, melting at 190°.

Diethoxy-a-dinaphthyl, $C_{20}H_{12}(OC_2H_5)_2$, forms spherical aggregates of needles, and melts at 90°.[2]

a-β-Dinaphthylene oxide, $C_{20}H_{12}O$, is obtained by heating β-dinaphthol with zinc chloride at 270°, and separates from benzene solution on addition of alcohol in yellowish satiny plates; it readily sublimes in yellowish plates which have a green fluorescence, and melt at 157°. It dissolves in concentrated sulphuric acid, forming a red solution, which gradually becomes brown. Its *picric acid compound*, $C_{20}H_{12}O + C_6H_3(NO_3)_2O$, crystallizes in red needles, melting at 135°.[3]

Tetrahydroxy-a-dinaphthyl or *dinaphthyldiquinol*, $C_{20}H_{10}(OH)_4$. When 1 part of β-naphthoquinone is warmed for ten minutes at 55° with 1 volume of sulphuric acid and 2 volumes of water, it yields the isomeric *dinaphthyldiquinhydrone*, $C_{20}H_{10}O_2(OH)_2$,

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[1] *Ber.* **7**, 1252.

[2] Ostermeyer and Rosenhek, *Ber.* **17**, 2453.

[3] Walder, *Ber.* **15**, 2166.

which forms a blue-black powder, and is converted by a saturated solution of sulphur dioxide into the quinol.[1] The latter is also formed by treating β-naphthoquinone with stannous chloride and hydrochloric acid,[2] and together with β-naphthoquinonephenylhydrazone by the action of phenylhydrazine hydrochloride on β-naphthoquinone.[3]

It crystallizes from dilute acetic acid containing sulphurous acid in colourless needles, melts at 176—178°, and darkens on drying owing to partial oxidation.

Tetracetyldinaphthyldiquinol, $C_{20}H_{10}(O.CO.CH_3)_4$, is prepared by heating the diquinol with acetic anhydride and sodium acetate, and crystallizes from acetic acid in white silky needles, which melt with decomposition at 165—166° (Korn).

a-Dinaphthyldiquinone, $C_{20}H_{10}O_4$, is formed by boiling the quinhydrone with nitric acid, or dilute sulphuric acid and potassium dichromate, or by shaking the diquinol with bromine water (Stenhouse and Groves). It is also obtained when 2-amido-a-naphthol is oxidized with ferric chloride or chromic acid (Zincke and Rathgen). In order to prepare it a solution of the quinhydrone in 30 per cent. acetic acid is poured into nitric acid of sp. gr. 1·45; the diquinone then separates in small orange-red lustrous prisms, which are scarcely soluble in the ordinary solvents, but may be recrystallized from nitric acid. It is converted by reducing agents into the diquinol, and on distillation with zinc dust yields a-dinaphthyl. Potassium permanganate oxidizes it to diphthalylic acid, $HO.CO.C_6H_4.CO.CO.C_6H_4.CO.OH$, which on boiling with caustic potash yields phthalic acid, thus showing the constitution of the quinone (Korn, *v. infra*).

Dinaphthyldiquinonetetranilide, $C_{20}H_8O_2(N.C_6H_5)_2(NHC_6H_5)_2$, is prepared by boiling the quinone with aniline and a little alcohol, and crystallizes in dark red plates, which have a metallic lustre, and melt at 248—250°. If water be added to its solution in concentrated hydrochloric acid, the *hydrochloride* separates in fascicular aggregates of needles.

Dihydroxydinaphthyldiquinone, $C_{20}H_8O_4(OH)_2$, is formed when a mixture of the quinone and dilute alkali is allowed to stand in the air; the former gradually dissolves with a beautiful green colour, which afterwards changes to brownish red. On

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[1] Stenhouse and Groves, *Annalen*, **194**, 202.

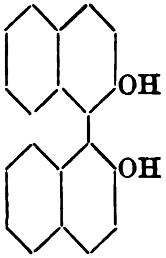
[2] Liebermann and Jacobson, *Annalen*, **211**, 58; Korn, *Ber.* **17**, 3019.

[3] Zincke and Rathgen, *Ber.* **19**, 2492.

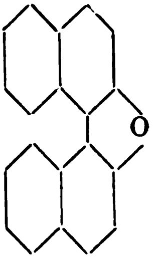
addition of hydrochloric acid, the new compound separates as a yellow crystalline powder, which melts at 245—250°, is readily soluble in alcohol, and also in alkalis, forming a brownish-red solution. In the oxidation of the quinone with potassium permanganate, the formation of this compound probably precedes that of diphthalylic acid.

The constitution of the *a*-dinaphthyl derivatives may be represented by the following formulæ:

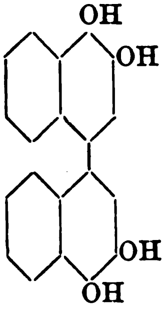
Dihydroxydinaphthyl.



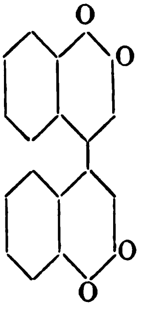
Dinaphthylene Oxide.



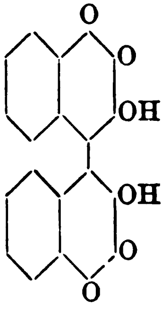
Dinaphthyldiquinol.



Dinaphthyldiquinone.



Dihydroxydinaphthyl-diquinone.



2776 *Naphthidine*, $C_{20}H_{12}(NH_2)_2$, is obtained by dissolving *a*-*a*-azonaphthalene in 45 parts of hot acetic acid, and adding a mixture of 1 part of stannous chloride, 3 parts of hydrochloric acid, and 2—3 parts of water until the solution is colourless. Concentrated hydrochloric acid is then added, the precipitated salt washed with dilute acid, dissolved in hot water, and again precipitated with concentrated acid. The naphthidine obtained from the purified hydrochloride crystallizes from alcohol in silvery plates resembling benzidine, and from benzene in tablets, melting at 198°.

The *hydrochloride*, $C_{20}H_{12}(NH_3Cl)_2$, crystallizes in silvery plates, which form a milky solution with boiling water. Addition of a drop of hydrochloric acid immediately causes the formation of a clear solution, and the turbidity is therefore probably due to a slight dissociation.

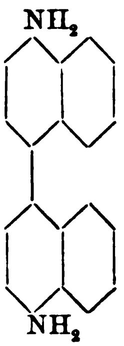
The *sulphate*, $C_{20}H_{12}(NH_3)_2SO_4$, is, if anything, less soluble than that of benzidine, and crystallizes in lustrous plates.

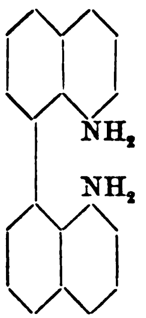
Ferric chloride, chromic acid, or chlorine cause with solutions of the salts a beautiful crimson colouration, or with concentrated solutions a red precipitate. On warming the base with chromic acid, *a*-naphthoquinone and phthalic acid are formed.

If the sulphate be diazotized, and alcohol and ether added to the solution, yellowish plates of the *diazo-sulphate* separate out, which on boiling with alcohol yield *a*-dinaphthyl.

Dinaphthyline, $C_{20}H_{12}(NH_2)_2$, is obtained by carefully warming *a*-*a*-hydrazonaphthalene with the calculated quantity of dilute hydrochloric acid to 70—80°. A little naphthidine simultaneously formed separates out on addition of concentrated hydrochloric acid; dinaphthyline is obtained from the filtrate, and crystallizes from benzene in colourless plates, melting at 273°. Its readily soluble salts lose ammonia on boiling with even weak acids, forming the corresponding carbazole. The solutions are readily turned brown by oxidizing agents, and yield phthalic acid alone on warming with chromic acid. By means of the diazo-reaction it also yields *a*-dinaphthyl.[1]

These two bases correspond exactly to benzidine and diphenyline (pp. 399, 411); as dinaphthyline so readily yields a carbazole, the amido-groups must be close together, and the constitution of the two compounds may be represented by the following formulæ:





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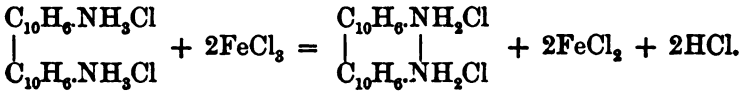
[1] Nietzki and Goll, *Ber.* **18**, 3252.

Diamido-a-dinaphthyl, $C_{20}H_{12}(NH_2)_2$, was prepared by Julius by the reduction of the nitro-compound with zinc dust and hydrochloric acid. The *hydrochloride* thus obtained crystallizes from water containing hydrochloric acid in small needles, which become green in the air. If it be treated with ammonia, extracted with ether, and the ethereal solution evaporated, the base remains as a green amorphous residue. On addition of ferric chloride to a solution of the hydrochloride, *di-imidodinaphthalene hydrochloride* is obtained in dark brown needles, having a bronze lustre:

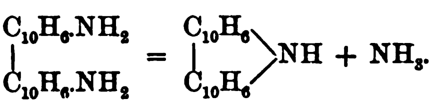


$$\begin{array}{l} C_{10}H_6.NH_3Cl \\ | \\ C_{10}H_6.NH_3Cl \end{array} + 2FeCl_3 = \begin{array}{l} C_{10}H_6.NH_2Cl \\ |\quad\;\; | \\ C_{10}H_6.NH_2Cl \end{array} + 2FeCl_2 + 2HCl.$$

It is reconverted by reducing agents into the diamido-compound.

Ditolyldiamido-a-dinaphthyl, $C_{20}H_{12}(NH.C_6H_4.CH_3)_2$, is formed when *p*-tolyl-β-naphthylamine is warmed with nitrosodimethylaniline hydrochloride, zinc chloride, and acetic acid, or boiled with ferric chloride and acetic acid. It is purified by washing with acetic acid, boiling water, and alcohol, and is thus obtained in shimmering white crystals, which melt at 224—225°, and are only dissolved sparingly by the ordinary solvents, forming solutions which show a beautiful blue fluorescence. Its solution in concentrated sulphuric acid is coloured grass green by a trace of nitrous acid.[1]

a-a-Dinaphthylcarbazole, $C_{20}H_{13}N$, gradually separates out on heating a solution of dinaphthyline in hydrochloric acid to the boiling-point:



$$\begin{array}{l} C_{10}H_6.NH_2 \\ | \\ C_{10}H_6.NH_2 \end{array} = \begin{array}{l} C_{10}H_6\diagdown \\ | \qquad\quad NH \\ C_{10}H_6\diagup \end{array} + NH_3.$$

It crystallizes from acetic acid or benzene in long colourless needles, and from alcohol in silvery plates, melts at 216°, and sublimes in needles. It dissolves in sulphuric acid with a reddish-brown colour, which is changed by a trace of nitric acid to dark green.

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[1] Witt, *Ber.* **21**, 726.

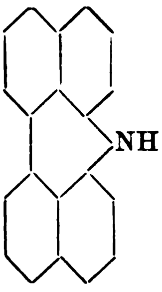
With picric acid it yields the compound $C_{20}H_{13}N$ + $C_6H_3(NO_2)_3O$, which melts at 236°. On addition of sodium nitrite to an acetic acid solution of the carbazole, the *nitrosamine*, $C_{20}H_{12}N.NO$, separates in yellow plates, melting above 300°; and on heating with acetic anhydride, it forms the *acetyl*-compound, $C_{20}H_{12}N.CO.CH_3$, which crystallizes in colourless needles (Nietzki and Goll).

α-β-Dinaphthylcarbazole, $C_{20}H_{13}N$, is formed by heating β-dinaphthol with zinc-chloride-ammonia at 320—330°, and crystallizes from alcoholic ether in white lustrous needles, melts at 159°, and dissolves in sulphuric acid with a blood red colour. Its *picric acid compound*, $C_{20}H_{13}N + 2C_6H_3(NO_2)_3O$, crystallizes from benzene in small black needles, which have a violet-blue lustre, and melt at 219°. The *acetyl*-derivative, $C_{20}H_{12}N.CO.CH_3$, obtained by heating the carbazole with acetic anhydride and sodium acetate, crystallizes from alcoholic ether in white satiny plates, and melts at 144°.

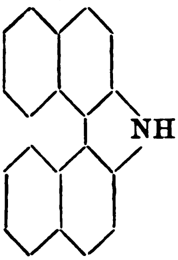
Phenyl-α-β-dinaphthylcarbazole, $C_{20}H_{12}N.C_6H_5$, was prepared by Walder by heating β-dinaphthol with zinc-chloride-aniline, and crystallizes from benzene on addition of alcohol in yellowish prisms, which have a diamond lustre, melt at 144°, and dissolve in sulphuric acid with a violet colour. The *picric acid compound*, $C_{26}H_{17}N + 2C_6H_3(NO_2)_3O$, forms reddish-brown lustrous needles, and melts at 169°.

The constitution of the two carbazoles is represented by the following formulæ:

α-α



α-β



2777 *β-Dinaphthyl* or *Isodinaphthyl*, $C_{20}H_{12}$, is formed in quantity when the mixed vapours of naphthalene and antimony trichloride are passed through a red-hot tube (W. Smith), and is also obtained, together with methylnaphthalenes and dinaphthylnaphthalene, when a mixture of naphthalene and ethylene bromide is heated with aluminium chloride.[1] It crystallizes from benzene in tablets having a blue fluorescence, is sparingly soluble in alcohol and ether, melts at 190°, and boils at about 450°. It is converted by chromium trioxide in acetic acid solution into *isodinaphthyldiquinone*, $C_{20}H_{10}O_4$, which is a yellow amorphous powder. When hot solutions of the hydrocarbon and picric acid are mixed together and allowed to cool, the *picric acid compound*, $C_{20}H_{14} + 2C_6H_3(NO_2)_3O$, separates in orange coloured microscopic prisms, which melt at 184°.[2]

α-β-Dinaphthyl is formed together with the β-β-compound, and is separated from it by recrystallization from light petroleum. It crystallizes in six-sided plates, melts at 79—80°, and is more readily soluble in alcohol and benzene than the foregoing compound.

The *picric acid compound*, $C_{20}H_{14} + C_6H_3(NO_2)_3O$, crystallizes in golden-yellow needles, and melts at 155—156° (Wegscheider).

α-Dinaphthol or *Dihydroxy-β-dinaphthyl*, $C_{20}H_{12}(OH)_2$, was obtained by Dianin by adding ferric chloride to a saturated solution of α-naphthol till the precipitate assumed a pale violet colour. The residue is purified by boiling with water and benzene and recrystallizing from alcohol. α-Dinaphthol is then obtained in silvery rhombic tablets, which melt at 300°, and on distillation are partially reconverted into α-naphthol. Its alcoholic solution gives a violet colouration and precipitate with ferric chloride.

α-Dinaphthol ethyl ether, $C_{20}H_{12}(OC_2H_5)_2$, is formed by warming α-dinaphthol with alcoholic potash and ethyl iodide, and crystallizes from alcohol in white nacreous plates, melting at 211°. The corresponding *dimethyl ether* crystallizes in tablets, and melts at 251°.[3]

β-α-Dinaphthylene oxide, $C_{20}H_{12}O$, is obtained by heating α-naphthol with lead oxide,[4] the reaction possibly taking place in the following manner:

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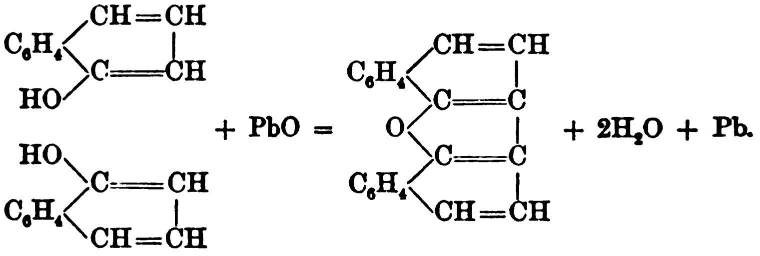
[1] Staub and Smith, *Journ. Chem. Soc.* **1885**, I. 104.

[2] Wegscheider, *Ber.* **23**, 3199.

[3] Ostermayer and Rosenhek, *Ber.* **17**, 2453.

[4] Knecht and Unzeitig, *Annalen*, **209**, 134.



It is also formed when *a*-naphthol is boiled in presence of air,[1] and by heating calcium *a*-naphthate:[2]

$$3(C_{10}H_7O)_2Ca = 2C_{20}H_{12}O + 2C_{10}H_8 + 3CaO + H_2O.$$

β-*a*-Dinaphthylene oxide crystallizes from alcohol in plates, and from benzene in broad needles, melts at 184°, is insoluble in sulphuric acid, and yields with picric acid the compound $C_{20}H_{12}O + C_6H_3(NO_2)_3O$, which crystallizes from benzene in dark red needles, and melts at 171°.

Dichloro-β-a-dinaphthylene oxide, $C_{20}H_{10}Cl_2O$, is obtained by warming the oxide with phosphorus pentachloride, and crystallizes from benzene in needles, which melt at 150—151°, and readily sublime.

Dibromo-β-a-dinaphthyl, $C_{20}H_{10}Br_2O$, is formed when bromine is allowed to drop into a solution of the oxide in carbon disulphide, and separates from benzene, in which it is sparingly soluble, in pale yellow crystals, melting at 287°.

Dinitro-β-a-naphthylene oxide, $C_{20}H_{10}(NO_2)_2O$, is prepared by acting with nitric acid on a warm acetic acid solution of the oxide, and crystallizes from benzene in pale yellow, indistinct needles, which melt at 270°.

β-Dinaphthylene oxide is obtained by heating *β*-naphthol with lead oxide or with phosphorus pentoxide,[3] and crystallizes in silvery plates or broad needles, melts at 161°, and is sparingly soluble in boiling alcohol, cold benzene, or acetic acid, readily in ether. It dissolves in sulphuric acid with a rose-red colour, which changes on warming, first to reddish-violet and then to dark blue. If the solution be poured into water, an orange-red, strongly fluorescent liquid is obtained.

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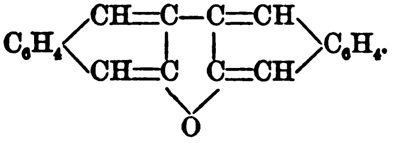
[1] Merz and Weith, *Ber.* **14**, 195.

[2] Niederhausen, *Ber.* **15**, 1119.

[3] Dianin, *Beilstein's Handb.* **2**, 642.

It yields a *picric acid compound*, $C_{20}H_{12}O + 2C_6H_3(NO_2)_3O$, which crystallizes from benzene in cinnabar-red needles, and melts at 171°, and cannot therefore be identical with β-α-dinaphthylene oxide; it has probably the following constitution:



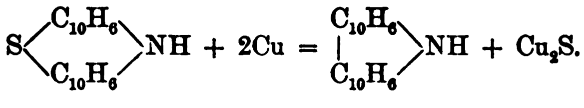
Dichloro-β-dinaphthylene oxide, $C_{20}H_{10}Cl_2O$, crystallizes from benzene in silky needles, melts at 245°, and dissolves in sulphuric acid with a reddish-brown colour, which changes to violet on warming; if nitric acid is present a deep green solution is formed, which becomes red when the solution is slowly warmed and finally almost disappears.

Dibromo-β-dinaphthylene oxide, $C_{20}H_{10}Br_2O$, likewise crystallizes in needles, and melts at 247°. With sulphuric acid and a drop of nitric acid it gives a pale green colouration, which changes to blue, reddish-violet, and finally to cherry-red.

Dinitro-β-dinaphthylene oxide, $C_{20}H_{10}(NO_2)_2O$, crystallizes from benzene in needles, melting at 221°.

γ-Dinaphthol, $C_{20}H_{12}(OH)_2$, is formed together with β-hydroxynaphthoic acid and β-naphthol when β-naphthaldehyde is fused with potash, and crystallizes from alcohol in slender silky needles, which melt at 195°, are insoluble in water, but soluble in alkalis.[1]

β-Dinaphthylcarbazole, $C_{20}H_{13}N$, is obtained by heating β-thiodinaphthylamine with copper powder:



$$S\left\langle\begin{matrix}C_{10}H_6\\C_{10}H_6\end{matrix}\right\rangle NH + 2Cu = \left.\begin{matrix}C_{10}H_6\\|\\C_{10}H_6\end{matrix}\right\rangle NH + Cu_2S.$$

It crystallizes from hot benzene in needles or prisms, melts at 170°, is sparingly soluble in alcohol, moderately in acetic acid, readily in ether, and especially in boiling benzene, the solutions showing a blue fluorescence. Its almost colourless sulphuric acid solution is coloured brown by a trace of nitric acid. The *picric acid compound* crystallizes from benzene in compact, dark

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[1] Kauffmann, *Ber.* **15**, 804.

reddish-brown or almost black needles, and melts at 221°; the *acetyl* compound, $C_{20}H_{12}N.CO.CH_3$, separates from hot benzene in long yellowish needles, and melts at 143°.[1]

Picene, $C_{22}H_{14}$, occurs in the pitch-like mass which remains on the distillation of coal-tar, and passes over at a high temperature as a resinous mass resembling gamboge, which crystallizes from high boiling tar-oil in yellow plates.[2] It is also obtained when the residue from the rectification of Californian petroleum is subjected to dry distillation, and then crystallizes in yellowish-green or deep green plates.[3] It is also found, together with other hydrocarbons, among the products formed by the action of aluminium chloride on a mixture of naphthalene and ethylene bromide,[4] and is identical with *benzerythrene*, a by-product obtained in the preparation of diphenyl,[5] and probably also with *parachrysene*, which is found in the highest boiling portions of coal-tar.[6] By repeated crystallization from boiling pseudocumene it is obtained in pure white lustrous plates, which have a blue fluorescence, and are only very sparingly soluble in any of the usual solvents. It melts at 337—339°, and boils at 518—520°, *i.e.* nearly at a red heat, and has therefore the highest boiling-point of any known hydrocarbon. Its vapour has a sp. gr. of 9·8.

Eikosihydropicene, $C_{22}H_{34}$, is formed together with the following compound by heating picene with phosphorus and hydriodic acid at 250—260°, and is a liquid boiling above 360°.

Perhydropicene, $C_{22}H_{36}$, crystallizes from alcohol in white needles, melts at 175°, and boils above 360°. When distilled over zinc dust it is reconverted into picene.[7]

Hydrides of picene also occur in the high boiling oils obtained from lignite-tar, as these yield picene on heating with sulphur or on remaining for a long time in the air.[8]

Dibromopicene, $C_{22}H_{12}Br_2$, is formed by adding a chloroform solution of bromine to picene suspended in the same liquid, and crystallizes from boiling xylene in slender white needles, melting at 294—296°.

Picenequinone, $C_{22}H_{12}O_2$, is prepared by suspending picene in

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[1] Ris, *Ber.* **19**, 2240.

[2] Burg, *Ber.* **13**, 1834.

[3] Graebe and Walter, *Ber.* **14**, 175.

[4] Lespieau, *Bull. Soc. Chim.* III. **6**, 238.

[5] Schmidt and Schultz, *Annalen*, **203**, 134; Schultz, *Steinkohlentheer*, I. 218.

[6] Rasenack, *Ber.* **6**, 1401.

[7] Liebermann and Spiegel, *Ber.* **22**, 779.

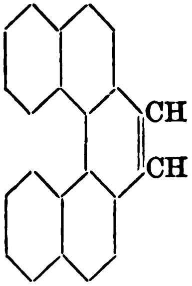
[8] Boyen, *Chem. Zeit.* **1889**, 870, 905.

acetic acid, and adding a solution of chromium trioxide in the same liquid. It is a dark orange-red crystalline powder, which becomes strongly electrified when rubbed, sublimes with partial decomposition in red needles, dissolves readily in hot alcohol and acetic acid, and also in sulphuric acid with a green colour.

Picene is the final member of the following series of hydrocarbons:

Benzene	C_6H_6.
Naphthalene	$C_{10}H_8$.
Phenanthrene	$C_{14}H_{10}$.
Chrysene	$C_{18}H_{12}$.
Picene	$C_{22}H_{14}$.

It has probably the constitution:



Dinaphthylnaphthalene, $(C_{10}H_7)_2C_{10}H_6$, the formation of which has been already mentioned under β-dinaphthyl (p. 549), crystallizes from boiling alcohol, in which it is sparingly soluble, in greenish hexagonal plates, which readily sublime and melt at about 300° (Roux).

DIPHENYLBENZENE GROUP.

2778 *p-Diphenylbenzene*, $C_6H_4(C_6H_5)_2$, was obtained by Riess by the action of sodium on a mixture of bromobenzene and *p*-dibromobenzene,[1] and by Abeljanz by the decomposition of benzene potassium (Part III. p. 89) with water.[2] It is also contained together with isodiphenylbenzene in the by-products obtained in the manufacture of diphenyl by passing benzene vapour through a red-hot tube, and may be isolated from them by fractional distillation and separation of isodiphenylbenzene and other compounds by means of alcohol;[3] from 2,000 grams of benzene, 40 grams of *p*-diphenylbenzene were thus obtained. It is also formed, together with methyldiphenyl, dimethyldiphenyl, and isodiphenylbenzene, by the action of methyl chloride on a mixture of diphenyl and aluminium chloride.[4]

t crystallizes in large plates which are sparingly soluble in boiling alcohol and acetic acid, more readily in ether and light petroleum, and easily in benzene with a blue fluorescence. It melts at 205°, boils at 383°, giving a vapour of sp. gr. 8·08, yields no compound with picric acid, and is oxidized by chromium trioxide in acetic acid solution to *p*-phenylbenzoic acid and terephthalic acid.

Perchlorodiphenylbenzene, $C_{18}Cl_{14}$, is formed by gradually heating *p*-diphenylbenzene to 360° with an excess of antimony pentachloride, and distils, if air be excluded, as a thick oily liquid. It quickly solidifies, and is sparingly soluble in alcohol, somewhat more readily in benzene, and very easily in boiling nitrobenzene, from which it separates in crystalline granules.[5]

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[1] *Annalen*, **164**, 161.

[2] *Ber.* **9**, 10.

[3] Schultz, *Annalen*, **174**, 228; Schmidt and Schultz, *Annalen*, **203**, 118.

[4] Adam, *Ann. Chim. Phys.* VI. **15**, 239

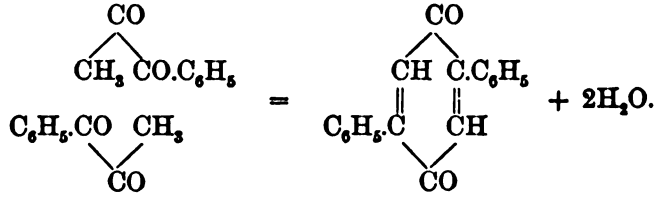
[5] Merz and Weith, *Ber.* **16**, 2884.

Dinitrodiphenylbenzene, $C_{18}H_{12}(NO_2)_2$, is obtained by mixing a solution of the hydrocarbon in acetic acid, with eight times its volume of fuming nitric acid and warming on the water bath; it separates as a yellowish crystalline substance which is sparingly soluble in alcohol, somewhat more readily in acetic acid, and crystallizes from nitrobenzene in long monosymmetric needles melting at 277°.

Trinitrodiphenylbenzene, $C_{18}H_{11}(NO_2)_3$, is obtained by the action of fuming nitric acid on the dinitro-compound or on the hydrocarbon, and crystallizes from acetic acid in concentric aggregates of yellowish rhombic needles, which melt at 195°.

Triamidodiphenylbenzene, $C_{18}H_{11}(NH_2)_3$, is prepared by reducing the trinitro-compound with tin and hydrochloric acid, and crystallizes from alcohol in small needles, melting at 169·5°. The solution assumes a bluish-violet surface colour in the air, and on addition of ferric chloride and warming becomes violet and then brownish black. Its *hydrochloride* crystallizes in long needles (Schmidt and Schultz).

p-Diphenylbenzoquinone, $(C_6H_5)_2C_6H_2O_2$. When ethyl methylbenzoylacetate, $C_6H_5.CO.CH(CH_3).COOC_2H_5$, is dissolved in dilute caustic potash, and sodium nitrite and dilute sulphuric acid added, it is converted into isonitroso-ethylphenylketone, $C_6H_5.CO.C(NOH).CH_3$; the latter on distillation with dilute sulphuric acid yields *methylphenyldiketone* or *acetylbenzoyl*, $C_6H_5.CO.CO.CH_3$, a yellowish oily liquid which boils at 216—218°, forming an extremely pungent vapour. When mixed with twenty parts of water and two parts of 10 per cent. caustic soda solution, preferably with addition of little potassium ferricyanide, it undergoes a similar reaction to diacetyl (Part III. p. 186), and is converted into diphenylbenzoquinone:



The liquid quickly becomes brown and after fifteen minutes is warmed on the water bath and extracted with benzene. After evaporating off the latter a brown residue is left, which is washed with ether, and warmed with a mixture of six parts of alcohol and three parts of moderately dilute nitric acid till it assumes a pure yellow colour.

Diphenylbenzoquinone crystallizes from acetic acid in very lustrous orange-yellow plates, and is only sparingly soluble in the usual solvents, with the exception of benzene. It dissolves in sulphuric acid forming a reddish-violet solution which is reprecipitated by water. On heating with zinc dust and acetic acid it yields *p-diphenylquinol*, $C_{18}H_{12}(OH)_2$, which crystallizes from alcohol in colourless cubes, melts at 218—219°, and is converted by ferric chloride first into the *quinhydrone*, which is also obtained as a greenish-black precipitate by mixing acetic acid solutions of the quinone and quinol and precipitating with water.[1]

Isodiphenylbenzene, $C_{18}H_{14}$, crystallizes from dilute alcohol in long needles, melts at 85°, and boils at 363° giving a vapour of sp. gr. 8·18. On oxidation it yields benzoic acid, together with teréphthalic acid and *p*-phenylbenzoic acid.

Trinitro-isodiphenylbenzene, $C_{18}H_{11}(NO_2)_3$, crystallizes from hot acetic acid in concentric aggregates of needles, melts at 200° and on reduction yields a base which melts at 288°, and gives a dark brown colouration with ferric chloride.

Triphenylene, $C_{18}H_{12}$, is likewise formed in the preparation of diphenyl, and crystallizes from alcohol in needles melting at 196°. It combines with picric acid forming an orange-yellow compound which melts at 212° (Schmidt and Schultz).

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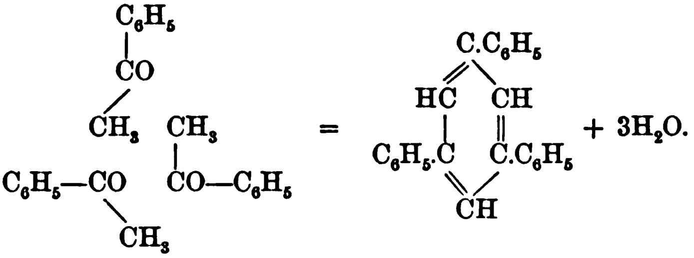
[1] Müller and Pechmann, *Ber.* **22**, 2127.

TRIPHENYLBENZENE GROUP.

2779 *s-Triphenylbenzene*, $C_{24}H_{18}$, is obtained by saturating acetophenone with hydrogen chloride and allowing the mixture to remain in a warm place. Its formation corresponds exactly to that of mesitylene from acetone:



As soon as crystals cease to separate out the mother liquor is filtered off, and may be made to yield more of the hydrocarbon by repeated saturation with hydrogen chloride.[1] A very remarkable formation of this compound was observed by Béhal, from the product of the action of phosphorus pentachloride and acetophenone. This was allowed to stand for a long time and suddenly exploded; the crystals scattered around were found to consist of triphenylbenzene. Béhal showed that chlorostyrolene, $C_6H_5.CCl=CH_2$, is first formed, and that this on saturation with hydrogen chloride and heating to 40°, forms triphenylbenzene with explosive evolution of hydrogen chloride.[2]

s-Triphenylbenzene crystallizes from ether in rhombic tablets, melts at 169—170°, and is moderately soluble in alcohol and ether, readily in benzene. When boiled with dilute nitric acid

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[1] Engler and Berthold, *Ber.* **7**, 11, 23.

[2] *Bull. Soc. Chim.* **50**, 632.

or dilute sulphuric acid and potassium dichromate it is not attacked, but if heated with chromium trioxide in acetic acid solution is oxidized to benzoic acid, the central nucleus being destroyed.[1]

Dodecahydrotriphenylbenzene, $C_{24}H_{30}$, is formed by heating triphenylbenzene with amorphous phosphorus and hydriodic acid for sixteen hours at 270—280°, and is a thick faintly aromatic smelling liquid, which gradually crystallizes in the cold, but melts at the summer temperature. It is not attacked by cold concentrated sulphuric or nitric acids.

Eikosihydrotriphenylbenzene, $C_{24}H_{38}$, is formed if the heating with hydriodic acid be continued for thirty-two hours, and is a somewhat less thick liquid than the foregoing compound (Mellin).

Perchlorotriphenylbenzene, $C_{24}Cl_{18}$, is obtained by gradually heating a mixture of the hydrocarbon and phosphorus pentachloride to 360°, and distils in an atmosphere of chlorine forming an oil which quickly solidifies, and crystallizes from nitrobenzene in needles. It is only attacked with great difficulty by concentrated nitric acid, even at 300—350°.[2]

Bromotriphenylbenzene, $C_{24}H_{17}Br$, is formed by allowing a solution of bromine and triphenylbenzene in carbon disulphide to stand, and crystallizes from alcohol in needles, melting at 104° (Engler and Berthold).

a-Tetranitrotriphenylbenzene, $C_{24}H_{14}(NO_2)_4$, is obtained together with the β-compound by adding nitric acid to an acetic acid solution of the hydrocarbon, and on cooling separates almost completely in small needles which are practically insoluble in the common solvents. It crystallizes from boiling aniline or nitrobenzene in pale yellow needles, and melts at 370°.

β-Tetranitrotriphenylbenzene, $C_{24}H_{14}(NO_2)_4$, separates from the acetic acid solution on addition of water. It dissolves readily in alcohol, ether, &c., and crystallizes in small needles, melting at 108°.

a-Tetramidotriphenylbenzene, $C_{24}H_{14}(NH_2)_4$, is prepared from the corresponding nitro-compound by reduction with tin and hydrochloric acid, and crystallizes from dilute alcohol in small white needles, which melt at 137—138°. When boiled for some

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[1] Mellin, *Ber.* **23**, 2533.

[2] Merz and Weith, *Ber.* **16**, 2883.

time with acetic anhydride and sodium acetate it yields the *octacetyl* compound, $C_{24}H_{14}N_4(CO.CH_3)_8$, which forms microscopic needles, and melts at 156—158°.

β-Tetramidotriphenylbenzene crystallizes in yellowish needles, which become dark in the air, and melt at 96—98° with decomposition. Its *octacetyl* compound forms granular crystals, and melts at 142—143° (Mellin).

Triphenylbenzene is the final member of the following series:

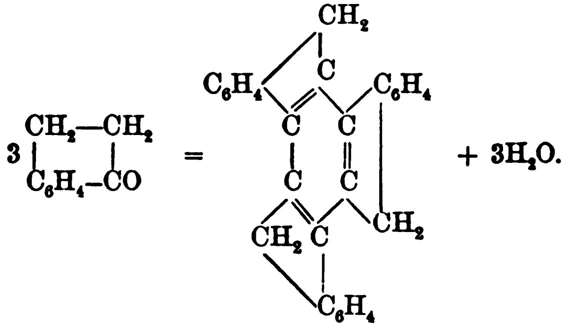
Benzene, C_6H_6
Diphenyl, $C_{12}H_{10}$
Diphenylbenzene, $C_{18}H_{14}$.
Triphenylbenzene, $C_{24}H_{18}$.

Tri-p-tolylbenzene, $C_6H_3(C_6H_4.CH_3)_3$, is obtained by repeatedly saturating *p*-tolylmethylketone with hydrogen chloride, and crystallizes from chloroform in beautiful white needles, and from alcohol in plates, which melt at 171°, and decompose on further heating without subliming.

Tribromotritolylbenzene, $C_{27}H_{21}Br_3$, crystallizes from carbon disulphide in matted needles, and melts at 212°.

Trinitrotritolylbenzene, $C_{27}H_{21}(NO_2)_3$, is a canary-yellow crystalline powder, which decomposes on heating.[1]

Tri-o-benzylenebenzene, $C_{27}H_{18}$, is formed by heating hydrindene (p. 7) with hydrochloric acid at 100°.[2]



It is also formed when truxone, which will be described in a later volume, is heated with hydriodic acid,[3] and crystallizes

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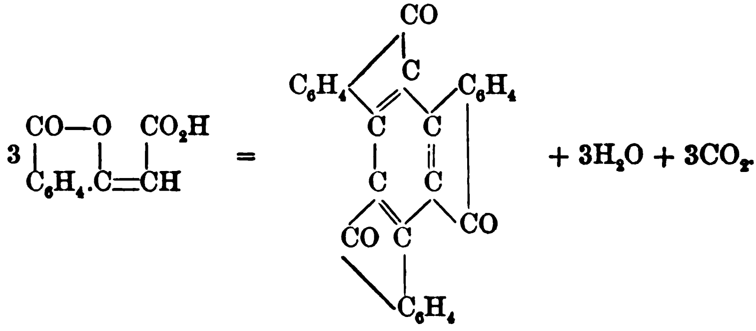
[1] Claus, *J. Pr. Chem.* II. **41**, 405.
[2] Hausmann, *Ber.* **22**, 2019.
[3] Liebermann and Bergami, *Ber.* **22**, 786 ; **23**, 317.

from boiling nitrobenzene in beautiful yellowish needles, which do not melt at 360°, are almost insoluble in boiling alcohol, ether, acetic acid, &c., and also in cold concentrated sulphuric acid, and in boiling nitric acid.

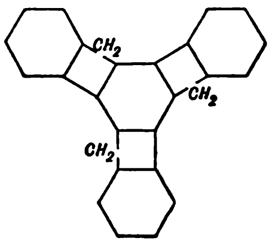
Tri-o-benzoylenebenzene, $C_{27}H_{12}O_3$, is formed when phthalylacetic acid is warmed with 60 parts of sulphuric acid on the water-bath:

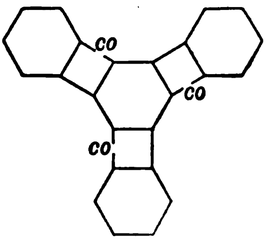


It is also formed by heating phthalic anhydride with ethyl malonate or ethyl acetoacetate,[1] and when tribenzylenebenzene is boiled for a long time with 5 parts of chromium trioxide and 50 parts of acetic acid.[2]

Tribenzoylenebenzene crystallizes in slender yellow hair-like needles, which do not melt at 360°, and only dissolve to any appreciable extent in nitrobenzene.

The exact constitution of these two compounds is represented by the following formulæ:





o-Phenenyltribenzoic acid, $C_6H_3(C_6H_4.CO_2H)_3$, is formed by fusing tribenzoylenebenzene with potash, and crystallizes from dilute alcohol in thick broad prisms, melts at 259—261°, and

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[1] Gabriel and Michael, *Ber.* **10**, 1557; **11**, 1107; Gabriel, *Ber.* **14**, 925.

[2] Hausmann, *loc. cit.*; Liebermann and Bergami, *loc. cit.*

on distillation with lime yields triphenylbenzene and carbon dioxide.

p-Phenenyltribenzoic acid is prepared by heating tritolylbenzene with dilute nitric acid at 160—180°, and separates from alcohol as a crystalline powder, which commences to sublime in needles at 280° without melting; the *normal potassium salt* is readily soluble and remains on evaporation as an indistinct crystalline mass; the di-acid salts are heavy, soluble, crystalline powders (Claus).

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THE END.