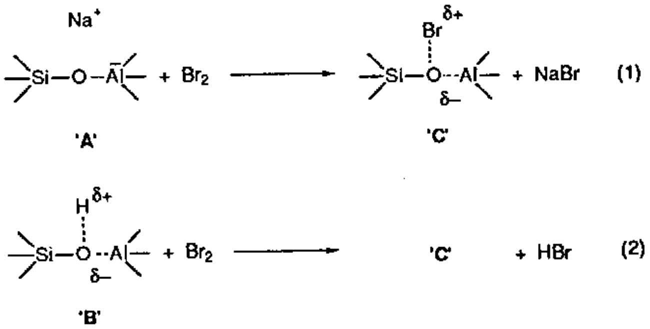
Table 1 Bromination of aromatic compounds

Conditions	Relative rate constants of bromination k_2/k_1	k_3/k_1	k_4/k_1	Ratio of bromotoluenes, *para/ortho*	Ref.
Br_2, Na–Y, CCl_4	6	4	5	13	[a]
Br_2, H–Y, CCl_4	202	923	330	2	[a]
Br_2, $FeBr_3$, $MeNO_2$	3.6	3.9	4.3	0.4	[6]
Br_2, $MeCO_2H$	605	5320	2520	2.0	[7]

[a] This work.

zeolite/Br_2 = 30) in 10 ml of CCl_4 was added to a stirred suspension of 4–5 g of zeolite ($\approx$ 10–20 μm crystals, calcined at 500 °C) in 15 ml or CCl_4 at 30 °C. After 15 min stirring, a tenfold molar excess of an equimolar mixture of two competing substrates was added and stirring was continued for 1 h at 30 °C. After addition of aqueous NaOH and extraction with $CHCl_3$, the reaction mixture was subjected to GLC analysis.†

The results of the selectivity of bromination on zeolites Na–Y and H–Y are listed in Table 1, which gives for comparison the respective data on bromination in homogeneous media. It should be noted that there are large differences in substrate selectivity for the reaction on Na– *vs.* the decationized form of zeolite Y. The bromination on Na–Y gives relative rate values which are typical for the strongly electrophilic brominating agent $Br^+FeBr_4^-$.[6] Zeolite H–Y shows a much higher substrate selectivity, which is similar to that obtained in the case of bromination with molecular Br_2.[7] These facts may be rationalized by assuming that the bromine molecule being adsorbed on zeolite Na–Y is significantly polarized (*cf.* ref. 8) and subsequently dissociates to form an active brominating agent [eqn. (1)]. In the case of the decationized form, such a process [eqn. (2)] is assumed to be unfavourable and the reaction apparently proceeds *via* the less polarized and thus less active bromine molecule (*cf.* ref. 2). This assumption is consistent with calculations performed in molecular approximation by the *ab initio* STO-3G method (the active centres of zeolites Na–Y and H–Y were simulated by structures **A** and **B** respectively, structure **C** has been assumed for the brominating agent), which show process (1) to be ~ 10 kcal mol^{-1} more favourable than (2).‡



The decrease in the relative bromination rates of compounds **2–4** on passing from zeolite H–Y to Na–Y would result from their more difficult diffusion in zeolite channels as compared with benzene. However, the expected changes in relative rate constants due to diffusion limitations are probably negligible in the light of data indicating the absence of significant differences in the ability of the compounds examined to diffuse in zeolite Na–Y.[9,10]

It is noteworthy that, despite the low substrate selectivity, in the case of toluene bromination on zeolite Na–Y the *para/ortho* ratio is higher than that in the case of H–Y and in solution. This is probably due to the greater steric limitations imposed on the transition state of the reaction by an electrophile of type **C** which is more 'bulky' than Br_2 [eqn. (2)] and additional restrictions caused by the Na^+ ions, which are present in the cavities of zeolite Na–Y but not in those of H–Y.

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† The yields of bromoaromatic compounds were > 70%. In the case of zeolite Na–Y formation of some dibromosubstituted products were observed, and the amount of these was taken into account in the calculation of relative rates.

‡ 1 cal = 4.184 J.

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N-Nitrohydrazines and their Salts

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The interaction of N_2O_5 with trimethylsilyl derivatives of functionally substituted hydrazines has for the first time resulted in the formation of nitrohydrazines; the relationship of the nitrohydrazine stability with the nature of the functional group and the molecular geometry is established.

The problem of the connection between the structure and stability of polynitrous and polynitrogen–oxygen systems has not been sufficiently developed so far and was first discussed in ref. 1. Therefore the production of previously unknown structures containing nitrogen and oxygen atoms directly bonded with each other is now of great interest.

The absence of precise data on the synthesis of nitrohydrazines[2–4] which are close analogues of the well-studied nitroamines might result either from a principal improbability of the existence of a nitro group and the amine function of one N atom, or from the instability of nitrohydrazines under the conditions of an ordinary acid nitration.

In order to minimize the possibility of nitrohydrazine decomposition during the reaction we applied our own method of substitute nitration of the N—Si bond which allows us to carry out reactions under mild conditions in a completely aprotic medium.

Thus for the first time nitrohydrazines have been obtained by the action of N_2O_5 on trimethylsilyl derivatives of functionally substituted hydrazines (Scheme 1).

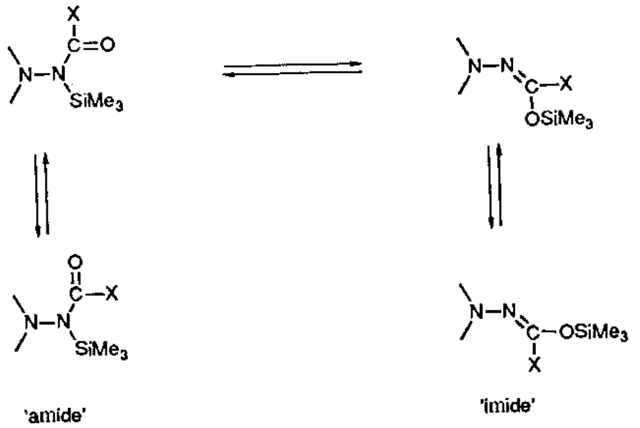
$$\underset{\mathbf{1}}{R^1R^2NNR^3SiMe_3} \xrightarrow{\text{i}} \underset{\substack{\mathbf{2}\\ 80\text{–}90\%}}{R^1R^2NNR^3NO_2} + Me_3SiONO_2$$

a; $R^1 = Me, R^2 = R^3 = CO_2Me$
b; $R^1 = Me, R^2 = R^3 = Ac$
c; $R^1 = Me, R^2 = Ac, R^3 = CO_2Me$
d; $R^1 = Me, R^2 = CO_2Et, R^3 = Ac$
e; $R^1 = Ac, R^2 = R^3 = CO_2Me$
f; $R^1 = R^2 = R^3 = Ac$
g; $R^1 = SiMe_3, R^2 = R^3 = CO_2Me$
h; $R^1 = NO_2, R^2 = R^3 = CO_2Me$
i; $R^1 = SiMe_3, R^2 = R^3 = Ac$

Scheme 1 *Reagents and conditions*: i, N_2O_5, CH_2Cl_2, $-40 \rightarrow +20$°C

The Me_3SiONO_2 formed during the course of the reaction is inert to the other components of the reaction mixture and is easily evaporated in vacuum. Quantitative observation of the reaction course was achieved using ^1H NMR to detect the disappearance of a peak corresponding to the Me_3Si group in **1** and the appearance of a peak characteristic of Me_3SiONO_2. The reaction proceeds smoothly at 20 °C and sharply accelerates when $SnCl_4$ is added.

It should be emphasized that each product obtained has the *N*-nitrohydrazine structure despite the fact that the original trimethylsilyl derivatives containing the NCO fragment exist in solution as mixtures of structural and spatial isomers, the distribution of which depends on the nature of the substituents[5,6] (Scheme 2).



Scheme 2

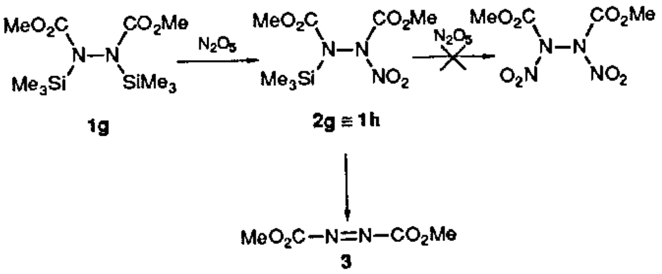
The structure of the *N*-nitrohydrazines was clearly detected by means of ^{15}N NMR spectroscopy using characteristic values of the N atom chemical shifts of the hydrazine fragment (δ − 80 to − 100 ppm for the 'imide' nitrogen) and of $J_{^{15}N^{15}NO_2}$.

The obtained mononitrohydrazines containing the N(R)COX fragment (X = R = Me; X = OMe, R = Me, $SiMe_3$) exist in solution as mixtures of conformers due to impeded rotation around the amide N—CO bond. This impediment disappears with the introduction of acceptor substituents (R = Ac, NO_2) which readily conjugate a lone electron pair on the N atom.

The nature of the substituents directly bonded to the $NSiMe_3$ fragment determines the structure of the silylated derivatives and affects the nitration rate.

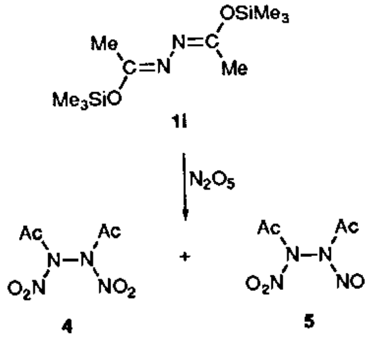
Silylated carbalkoxy-substituted hydrazines (Scheme 2, X = OMe) characterized by the 'amide' structure are more slowly nitrated than those (X = Me) which are inclined to the 'imide' form. This is obviously connected with the greater vulnerability of the 'imide' N atom to attack by an electrophilic reagent.

Substitution of the N atom next to the reaction site also affects the nitration rate. This is clearly seen in the cases of carbalkoxy derivatives. Thus the addition of electron acceptor substituents that lower hydrazine nucleophility hampers the interaction with N_2O_5. Thus for a high product yield in the transition from (**1a**, R^1 = Me) to (**1e**, R^1 = Ac) it is necessary to apply stricter nitration conditions. In the first case of catalysis by $SnCl_4$ the reaction proceeds at − 20 °C for 50 min, in the second case at 0 °C for 90 min (**1h**, $R^1 = NO_2$; $R^2 = R^3 = CO_2Me$) nitration does not occur even at + 20° and further heating leads to decomposition of the silylated nitrohydrazine, yielding **3**. Thus the first Me_3Si group of (**1g**, $R^1 = SiMe_3$) is smoothly nitrated (− 20 °C, 120 min) though without yielding a dinitro derivative (Scheme 3).



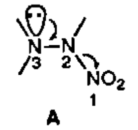
Scheme 3

We were able to synthesize a product containing an *N*,*N*-dinitrohydrazine fragment using a bis(trimethylsilyl) derivative of diacetylhydrazine (**1i**; $R^1 = SiMe_3$, $R^2 = R^3 = Ac$) which exists exceptionally in a readily nitrated 'imide' form[5] as a starting compound. In the reaction, along with the expected **4**, nitronitrosohydrazine **5** is also formed. Its formation, as proved by special tests, is not connected with the presence of N_2O_4 in the nitrating agent.

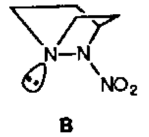


Scheme 4

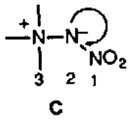
The nitrohydrazines obtained are in most cases thermally unstable, **2a–d** decompose almost completely after 24 h under normal conditions, **2e–f** are more stable and start to decompose only at > 70 °C. Therefore the introduction of electron acceptor substituents delocalizing a free electronic pair on the N atom into the molecule increases the relative stability of nitrohydrazines, thus confirming the course of the decomposition *via* **A**.



A



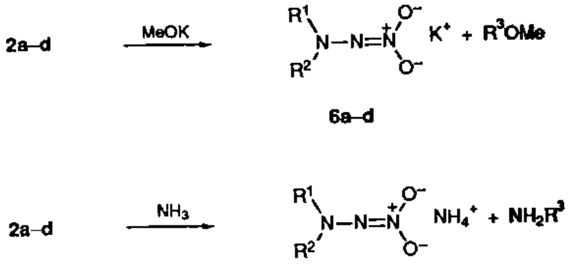
B



C

This decomposition can only be realized with an antiperiplanar conformation of the nitrogen lone pair and the nitro group. In cases where the nitrohydrazine structure excludes an antiperiplanar conformation, as in 7-nitro-1,7-diazabicyclo[2.2.1]heptane,† which was specially synthesized for the purpose, the stability of the product increases markedly. Intensive decomposition starts only at 150 °C.‡

Compounds containing the NNNO$_2$ fragment have the highest stability since there is no lone electron pair on the N-3 atom§ and a stronger N—NO$_2$ bond owing to the interaction of the nitro group with the negative charge on the N-2 atom, similar to that in C. Stabilization due to the latter factor was also observed in nitrohydrazine salts obtained by the action of ammonia or alcoholic MeOK solution on **2a–d** (Scheme 5).



Scheme 5

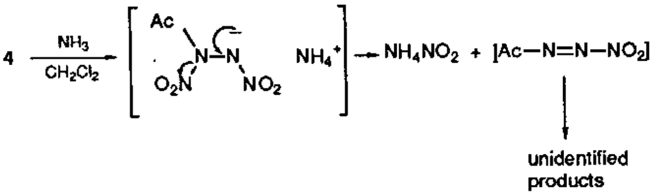
Salts **6a–d** gradually decompose in aqueous solutions, the corresponding tetrazenes being identified in the reaction products (Scheme 6).

$$\mathbf{6a\text{–}d} \xrightarrow{H_2O} R^1R^2N\text{—}N\text{=}N\text{—}NR^1R^2$$

Scheme 6

Under the action of MeOK on **2f** the methoxide ion can attack both the NR^{3}NO$_2$ and the NR^{1}R^2 fragments which contain two electron acceptor groups. As a result, after evaporation of the volatile compounds some complex mixtures are observed in the residue in which KNO$_3$, KNO$_2$ and AcOK can be identified.

During treatment of a solution containing **4** with ammonia instead of a diammonium salt, dinitrohydrazine NH$_4$NO$_2$ was obtained. This result can be accounted for by a scheme similar to that for the decomposition of **2** (Scheme 7).



Scheme 7

Therefore the specific character of compounds containing the nitrohydrazine fragment may be connected with both the presence of and the spatial arrangement of the lone electron pair and the N—NO$_2$ bond.

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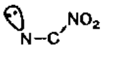
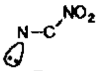
† For preparation of 1,7-diazabicyclo[2.2.1]heptane, see G. V. Shustov, N. B. Tavakalyon and R. G. Kostyanovskii, *Izv. Akad. Nauk, Ser. Khim*, 1981, 1677.

NMR data for 7-nitro-1,7-diazabicyclo[2.2.1]heptane: ^{1}H NMR(300 MHz, CDCl$_3$, rel. Me$_4$Si) δ 1.58(m), 2.03(m, CH$_2$C), 2.8(m), 3.32(m, CH$_2$N), 4.98(t, CH); ^{13}C NMR (75 MHz, CDCl$_3$, rel. Me$_4$Si) δ 25.0 (C-3, C-5), 49.3(C-2, C-6), 60.1(C-4); ^{14}N NMR(22 MHz, CDCl$_3$, rel. MeNO$_2$) δ −23.5(NO$_2$).

‡ This observation correlates well with the previously established sharp increase of stability in systems of type **D** in comparison with systems **E** in bicyclic heterocycles.[7]



D



E

§ We have failed to detect any Me$_2$N—NMeNO$_2$ when the isomeric Me$_3\overset{+}{N}$—$\overset{-}{N}$NO$_2$ is a stable compound with m.p. 212 °C.[8]

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On the Concerted Mechanism of Thiophene Hydrogenolysis by Bimetallic Sulphide HDS Catalysts in terms of the Interacting Bonds Method

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The enthalpy of adsorption of thiophene, tetrahydrothiophene and H$_2$S on the Ni(Co) atoms of the sulphide bimetallic species (SBMS) of hydrodesulphurisation catalysts has been estimated in terms of the Interacting Bonds Method (IBM).

Recently a new mechanism of C—S bond hydrogenolysis mediated by bimetallic sulphide catalysts has been put forward.[1–3] According to this hypothesis thiophene hydrogenolysis is considered to be a process proceeding in the coordination sphere of the sulphide bimetallic species (SBMS): the active component of hydrodesulphurisation (HDS) catalysts. Adsorption of thiophene is proposed to occur on the Ni(Co) atoms, which are in a square-planar environment of S atoms, and H$_2$ activation occurs with participation of the Mo(W) atoms. This hypothesis has been experimentally proved by selenophene adsorption studied by EXAFS.[4] A similar conclusion was obtained in ref. 5.

On consideration of this mechanism of thiophene hydrogenolysis two questions arise: (*i*) Why is thiophene adsorbed, but H$_2$S desorbed on the active centre? (*ii*) Why are none of the possible intermediates [*e.g.* tetrahydrothiophene (THT)]