

**PATENT SPECIFICATION**

*Inventor:* GEORGE ARCHER SAUL and KENNETH LEROY GODFREY

**744,484**



*Date of Application and filing Complete Specification:* March 2, 1953.

No. 5733/53.

*Complete Specification Published:* Feb. 8, 1956.

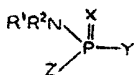
Index at acceptance:—Class 2(3), C1A(12:X), C1B(13:22), C1C(3:5:6:7A:11F), C1D, C2(E:J).

COMPLETE SPECIFICATION

**Production of Dialkylamidophosphoryl Halides, Hexa-Alkyl Phosphorylamides and Octa-Alkyl Pyrophosphorylamides**

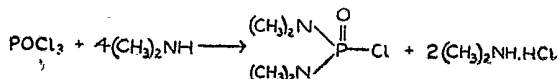
We, MONSANTO CHEMICAL COMPANY, a corporation organized and existing under the Laws of the State of Delaware, United States of America, of 1700, South Second Street, City of St. Louis, State of Missouri, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of dialkylamido phosphoryl halides and hexa-alkyl phosphoryl amides having the general formula



in which R<sup>1</sup> and R<sup>2</sup> are both alkyl groups, X is an oxygen or sulphur atom, Y is a halogen atom or a group having the general formula —NR<sup>3</sup>R<sup>4</sup> and Z is a halogen atom or a group having the general formula —NR<sup>5</sup>R<sup>6</sup> in which R<sup>3</sup>, R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> are alkyl groups. The invention also relates to the production of octaalkylpyrophosphorylamides.

Bis(dialkylamido)phosphoryl halides are important intermediates for the manufacture of insecticidal compositions. They have been made by reacting a phosphoryl halide with a dialkylamine in a molar ratio of 1:4 and separating the product from by-product dialkylamine hydrochloride. The chemical equation for this reaction employing phosphoryl chloride and dimethylamine is as follows:



Although this method is used, it is expensive, time-consuming and inefficient. Amine hydrochlorides are bulky hygroscopic solids. Large volumes of solvent must be used or the reaction mixture cannot be mixed properly. Subsequent removal of the hygroscopic solids is extremely troublesome. Furthermore, it is essential that they be removed and the amine recovered since amines are expensive reagents.

It is an object of the present invention to provide an improved process for the manufacture of dialkylamido phosphoryl halides and hexa-alkyl phosphoryl amides and a more efficient and economical process for the manufacture of octa-alkyl-

pyrophosphorylamides. A further object is to provide a process for the manufacture of octa-alkylpyrophosphorylamides direct from phosphoryl halides and secondary amines and which yields phosphorylamides of satisfactory commercial grade without necessitating purification steps.

According to the present invention there is provided a process for producing dialkylamido phosphoryl halides and hexa-alkyl phosphoryl amides having the above general formula which comprises treating a phosphoryl halide or a thiophosphoryl halide with at least a stoichiometric proportion of dialkylamine for each dialkylamido group desired in the

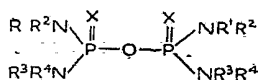
[Price 3s. 0d.]

Price 3s. 0d.

750-

product and either simultaneously or subsequently introducing an inorganic acid acceptor into the reaction mixture in amount at least sufficient to combine with the hydrogen halide generated by the reaction.

The present invention also provides a process of producing an octa-alkylpyrophosphorylamide having the general formula



in which R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are alkyl groups and each X is oxygen or sulphur which comprises treating a phosphoryl halide or a thiophosphoryl halide with substantially two mols of a dialkyl amine for each mol of halide and either simultaneously or subsequently introducing at least three equivalents of an inorganic acid acceptor into the reaction mixture.

The inorganic acid acceptor may be an hydroxide or a salt of a metal which is decomposed by a hydrogen halide, for example, a salt of a weak or easily displaced acid of a metal above yttrium in the electromotive series. The acid acceptor should be present in an amount at least substantially equivalent to the hydrogen halide generated by the reaction.

The product formed depends upon the respective proportions in which the phosphoryl or thiophosphoryl halide, the secondary alkylamine and the acid acceptor are employed.

Examples of hydroxides and salts which may be used include sodium carbonate, sodium bicarbonate, potassium carbonate, trisodium phosphate, lithium hydroxide, barium hydroxide, calcium hydroxide, sodium hydroxide, strontium hydroxide, magnesium hydroxide and mixtures thereof. Probably the most satisfactory results have been obtained with sodium carbonate and with mixtures of sodium hydroxide and calcium hydroxide in molar proportions of approximately 2:1. The amount of base used should be at least substantially equivalent to the total hydrogen halide expected in the desired reaction. It is advisable to employ a quantity in the range of 105—110% of the calculated quantity. Any free acid present rapidly attacks the phosphorylamido groupings. The total amount of acid acceptor used depends on how far the reaction is to be carried. If the reaction is to be terminated at the bis (dialkylamido) phosphoryl halide stage instead of after formation of an octa-alkyl pyrophos-

phorylamide, less acid acceptor should be used. The acid acceptor may be incorporated into the reaction mixture in solid form or in aqueous solution or suspension but excessive quantities of water should be avoided.

In general reaction is facilitated and carried out much more conveniently if an inert organic solvent or diluent is used. The most satisfactory results have been obtained with halogenated hydrocarbon solvents, as for example trichloroethylene, ethylene dichloride and chloroform; those possessing a favourable partition coefficient with respect to water are especially preferred. Other suitable inert water immiscible solvents are toluene, kerosene and benzene. It is preferred to add the amine to the phosphoryl halide gradually and then add the acid acceptor to the mixture of amine and phosphoryl halide although the order of mixing is subject to variation. When carbonates are employed, carbon dioxide is evolved so the gradual addition of the acid acceptor is desirable in order to control foaming.

The conditions of reaction will vary depending upon the product desired. For the preparation of bis(dialkylamido) phosphoryl halides having alkyl groups of one to four carbon atoms a reaction temperature of 0 to 10° C. is desirable throughout. The reason is to avoid loss of amine since the corresponding dialkylamines are highly volatile. For example, only a small yield of bis(dimethylamido) phosphoryl chloride was obtained at 50° C., the main constituent being dimethylamido phosphoryl dichloride. However, reaction in an autoclave or other closed system will avoid the difficulty. In general reacting the phosphoryl halide and amine at a temperature within the range of -15 to 50° C. is feasible. For the subsequent reaction in the presence of the acid acceptor temperatures of -10 to 30° C. proved satisfactory in an open system.

The secondary amine should be employed in proportion substantially equal to that theoretically required by the desired reaction but the amine is preferably used in slight excess since reactions carried out with the phosphoryl halide instead of the amine in slight excess have given less satisfactory results. Especially suitable are secondary dialkylamines containing one to four carbon atoms in the alkyl group, as for example dimethylamine, diethylamine, dipropylamine, di-isopropylamine, dibutylamine and methylethylamine.

For preparation of the octa-alkylpyrophosphorylamides only substantially two

mols of amine per mol of phosphoryl halide should be used but at least three equivalents of an inorganic acid acceptor are required. The water of neutralization formed is sufficient to enable the conversion of the intermediate to the pyrophosphorylamide although additional water may be added if desired. It has been found, however, that the addition of more water than is produced by the neutralization of the hydrogen halide is unnecessary. The hydrolysis and condensation of the bis(dialkylamido) phosphoryl halides is greatly speeded by heating. The reactions can be finished in a short time by gentle heating. A mixture of two moles of phosphoryl chloride and four moles of dimethylamine and three moles of sodium carbonate rapidly evolves carbon dioxide at 0—5° C. The evolution of carbon dioxide substantially ceases and then becomes rapid again at 30—40° C., indicating that conversion of the intermediate to the desired pyrophosphorylamide is taking place rapidly.

The following examples illustrate the nature of the invention and the manner in which it may be carried out.

#### EXAMPLE 1.

206 parts by weight (substantially 1.34 mols) of phosphoryl chloride is admixed with 777 parts by weight of trichloroethylene in a reaction vessel and thereto is slowly added with agitation at -5 to 5° C. 135 parts by weight (substantially 3.0 mols) of dimethylamine. After completion of the amine addition the reaction mixture is agitated for 5 to 10 minutes at 0—5° C. Thereupon, while maintaining the temperature at 0—5° C., 54.9 parts by weight (substantially 0.74 mol) of calcium hydroxide is added over a 40 minute period with agitation. Then 116.4 parts by weight (substantially 1.48 mols) of 50.9% aqueous sodium hydroxide is incorporated in the reaction mixture with stirring over a 20 minute period while maintaining the temperature at 0—5° C. The organic layer is then decanted and filtered. Upon fractionating the filtrate a yield of 80.5% of bis(dimethylamido)phosphoryl chloride of 97.1% purity is obtained.

Employing the same reagents, the same proportions thereof, and the same reaction conditions but replacing the total metal hydroxide reactant with an equivalent proportion of potassium hydroxide in the form of a 60% aqueous solution, an excellent yield of bis(dimethylamido) phosphoryl chloride of high purity is obtained.

#### EXAMPLE 2.

307 parts by weight (substantially 2.0

mols) of phosphoryl chloride is admixed with 1000 parts by weight of ethylene dichloride in a reaction vessel and thereto is slowly added with agitation at -5 to 5° C. 201 parts by weight (substantially 4.46 mols) of dimethylamine. Thereupon, while maintaining the temperature at about 10—15° C., 270 parts by weight (substantially 4.40 mols) of potassium hydroxide (91.5% pure) in the form of a 58.5% aqueous solution is incorporated in the mixture with stirring over a 55 minute period while maintaining the temperature at 10—15° C. After stirring the mixture at approximately 10° C. for one-half hour, the organic layer is decanted and filtered through Attapulugus clay. Upon fractionating the filtrate a yield of 72.9% of bis(dimethylamido)phosphoryl chloride of 88.3% purity is obtained.

Employing the same reagents, the same proportions thereof, and the same reaction conditions but replacing dimethylamine with an equimolar amount of diethylamine, a good yield of bis(diethylamido)phosphoryl chloride of high purity is obtained.

#### EXAMPLE 3.

921 parts by weight (substantially 6.0 mols) of phosphoryl chloride is admixed with 3500 parts by weight of trichloroethylene in a reaction vessel and thereto is slowly added with agitation at 0—5° C. 600 parts by weight (substantially 13.3 mols) of dimethylamine. 1090 parts by weight of aqueous 48.8% sodium hydroxide solution (substantially 13.3 mols) are then incorporated in the mixture with stirring over a 67 minute period while maintaining the temperature at 10—15° C. The mixture is then stirred for 30 minutes at 10—15° C. and the organic layer decanted and fractionated to give a yield of 85% of bis(dimethylamido) phosphoryl chloride of 86.5% purity.

#### EXAMPLE 4.

677.6 parts by weight (substantially 4.0 mols) of thiophosphoryl chloride is mixed with 1349 parts by weight of chloroform in a reaction vessel. Gaseous dimethylamine is then fed into the stirred mixture, a total of 392 parts by weight (substantially 8.7 mols) being added below 30° C., the time of addition depending upon the efficiency of cooling. The reaction mixture is then cooled to 10—15° C. and 645 parts by weight (substantially 8.0 mols) of 49.6% aqueous sodium hydroxide added gradually thereto with stirring. The reaction becomes strongly exothermic after about two-thirds of the caustic soda solution is added but the temperature is kept below 15° by cooling.

The caustic soda solution is added over a period of about 95 minutes. The organic layer is then decanted from the salt cake-water mixture and the solvent removed by distillation under reduced pressure. The crude product, free from solvent, is filtered and fractionated under reduced pressure. A 79.5% yield of bis(dimethylamido)thiophosphoryl chloride based on the thiophosphoryl chloride is obtained. Crystallizing point is 21.6° C.; b.p. 80—82° C./2 mm. and refractive index  $N_D^{25} = 1.5209$ . Chlorine found by analysis is 19.3% as compared with the calculated value of 19.0%.

#### EXAMPLE 5.

Into a reaction vessel is charged 338.8 parts by weight of thiophosphoryl chloride and 800 parts by weight of trichloroethylene. 92 parts by weight of gaseous dimethylamine are fed in while keeping the reaction mixture below 30° C. and 106 parts by weight of finely divided sodium carbonate are then gradually added to the stirred mixture at 0—5° C. After carbon dioxide evolution from the cold reaction mixture ceases the salt is removed by filtration. The solvent is removed by distillation under reduced pressure and the crude product distilled at 16 mm. absolute pressure. There is obtained approximately at 33.4% yield of dimethylamidothiophosphoryl dichloride b.p. 89—90° C./16 mm. Analysis for chlorine gives 39.7% as compared to the calculated value of 39.9%.

#### EXAMPLE 6.

307 parts by weight (substantially 2.0 mols) of phosphoryl chloride is mixed with 1000 parts by weight of ethylene dichloride. Gaseous dimethylamine is slowly run into the mixture at -5 to 5° C., a total of 99 parts by weight (2.2 mols) being added. Thereupon, while maintaining the temperature of 0—5° C., 127 parts by weight (1.2 mols) of finely powdered sodium carbonate are added and the mixture stirred for a short time to complete the neutralization of the amine salt and reaction of the released amine. The reaction mixture is then filtered, the cake washed with ethylene dichloride and the solvent removed from the filtrate and washings by distillation and the crude product fractionated by distillation. A good yield of dimethylamidophosphoryl dichloride is obtained, b.p. 90—91° C./22 mm.

#### EXAMPLE 7.

307 parts by weight (substantially 2.0 mols) of phosphoryl chloride is admixed with 2000 parts by weight of trichloroethylene in a reaction vessel and thereto is slowly added with agitation at a temperature below 35° C. 190 parts by weight

(substantially 4.2 mols) of dimethylamine, 22.6 parts by weight (substantially 2.0 mols) of finely powdered sodium carbonate are then added over a period of one-half hour while keeping the temperature at about 10° C. The reaction mixture is stirred at not more than 50° C. for 4 hours or until carbon dioxide is no longer evolved and then filtered and the salt cake washed with trichloroethylene. The combined filtrate and washings are stripped of solvent by distillation under reduced pressure. A good yield of bis(dimethylamido)phosphoryl chloride is obtained, b.p. 93—99° C./6 mm. containing 20.7% chlorine by analysis as compared to the calculated value of 20.8%.

#### EXAMPLE 8.

306.8 parts by weight of phosphoryl chloride and approximately 880 parts by weight of trichloroethylene are weighed into a reactor equipped with a gas inlet tube, agitator, thermometer, and valve for release of excess pressure. 190 parts by weight of gaseous dimethylamine are passed into the closed flask (vented by the valve) above the surface of the well-agitated contents over a period of one hour the temperature being held below 35° C. by appropriate cooling. The reaction mixture is cooled to 0—10° C., the gas inlet tube removed, and the addition of 340 parts by weight of sodium carbonate begun. During this addition, which requires 50 minutes, the temperature is held at 0—10° C. A steady evolution of carbon dioxide begins during the carbonate feed. The reaction mixture is then agitated at 0—10° C. for 2 hours; over the next 2½ hours it is heated gradually to 70° C. and it is maintained at 70—80° C. for 4 additional hours during which time the carbon dioxide evolution subsides. The reaction mixture is cooled to room temperature and filtered with suction. The salt cake residue is washed with trichloroethylene. Filtrate and washings are combined and freed from solvent by stripping to a pot temperature of 110° C./30 mm. The product is filtered with a small amount of Attapulgis clay for clarification. The filtrate is a clear, yellow liquid. A yield of 87.5%, based on the phosphoryl chloride, of technical octamethylpyrophosphorylamide is obtained.

The foregoing procedure is repeated through the addition of the dimethylamine and the reaction mixture cooled to 3° C. 285 parts by weight of 40.9% aqueous sodium hydroxide solution is added gradually while keeping the temperature below 15° C. 143 parts by weight of flake sodium hydroxide is then added

and the reaction mixture heated at 78—79° C. for 3 hours and then cooled. The salt is removed by filtration and the combined filtrate and washings stripped of solvent to a pot temperature of 110° C./30 mm. The residue is then filtered from by-product solids leaving the crude liquid octamethylpyrophosphorylamide. However, a much higher yield is obtained when sodium carbonate is employed instead of sodium hydroxide.

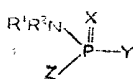
#### EXAMPLE 9.

206 parts by weight of phosphoryl chloride (substantially 1.34 molecular proportions) and 1000 parts by weight of chloroform are charged into a suitable reaction vessel and thereto is slowly added 218 parts by weight (substantially 4.83 molecular proportions) of dimethylamine. 4.82 molecular proportions of sodium hydroxide are then added gradually as a 50% aqueous solution while keeping the temperature at 13—16° C. Stirring is continued for an hour during which time the reaction mixture is allowed to come to room temperature and stirring continued for another hour. The salt is removed by filtration, the filtrate and washings combined and the solvent stripped by distillation to 95° C./25 mm. There is obtained 185 parts by weight of hexamethylphosphorylamide, b.p. 94—96° C./6 mm.,  $N_D^{25}$  1.4569.

While the reactions have been described in detail with reference to phosphoryl chloride and thiophosphoryl chloride since these are preferred for reasons of economy, other phosphoryl halides may be employed. Thus, "halogen" unless otherwise specified may be chlorine, bromine, iodine or fluorine.

What we claim is:—

1. A process of producing a dialkylamidophosphoryl halide or a hexa-alkyl phosphorylamide having the general formula



in which  $R^1$  and  $R^2$  are both alkyl groups,  $X$  is oxygen or sulphur,  $Y$  is a halogen atom or a group having the general formula  $-NR^3R^4$  and  $Z$  is a halogen atom or a group having the general formula  $-NR^5R^6$ ,  $R^3$ ,  $R^4$ ,  $R^5$  and  $R^6$  being alkyl groups, which comprises treating a phosphoryl halide or a thiophosphoryl halide with at least a stoichiometric proportion of a dialkylamine for each dialkylamido group desired in the product and either simultaneously or subsequently introducing an inorganic acid acceptor into the re-

action mixture in an amount at least sufficient to combine with the hydrogen halide generated by the reaction.

2. A process according to claim 1 in which the acid acceptor is sodium carbonate, sodium bicarbonate, potassium carbonate, trisodium phosphate or the hydroxide of lithium, magnesium, calcium, strontium or barium or a mixture thereof.

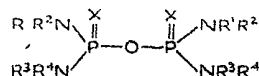
3. A process according to either of the preceding claims in which the reaction is carried out in solution in an inert organic solvent.

4. A process according to claim 3 in which the solvent is trichloroethylene, ethylene dichloride, chloroform, benzene, toluene or kerosene.

5. A process according to any of the preceding claims in which the dialkylamine is one having not more than four carbon atoms in each alkyl group.

6. A process according to any of the preceding claims for the preparation of a bis(dialkylamido)phosphoryl halide having one to four carbon atoms in each of the alkyl groups in which the reaction between the phosphoryl or thiophosphoryl halide and secondary alkylamine is carried out at a temperature of 0 to 10° C.

7. A process of producing an octa-alkyl pyrophosphorylamide having the general formula



in which  $R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are alkyl groups and each  $X$  is oxygen or sulphur which comprises treating a phosphoryl halide or a thiophosphoryl halide with substantially two mols of a dialkylamine for each mol of halide and either simultaneously or subsequently introducing into the reaction mixture at least three equivalents of an inorganic acid acceptor.

8. A process according to claim 7 in which formation of the octa alkyl pyrophosphorylamide is completed by gentle heating.

9. A process for the production of a dialkylamidophosphoryl halide or a hexa-alkyl phosphorylamide according to claim 1 and substantially as hereinbefore described and illustrated with reference to any of Examples 1—7 or 9.

10. A process for the production of an octa-alkyl pyrophosphorylamide according to claim 7 and substantially as hereinbefore described and illustrated with reference to Example 8.

11. A dialkylamidophosphoryl halide or a hexa-alkyl phosphoryl amide when-

ever produced by the process of any of claims 1 to 6 and 9.

12. An octa-alkylpyrophosphorylamide  
whenever produced by the process of any  
5 claims 7, 8 and 10.

STEVENS, LANGNER, PARRY &  
ROLLINSON,  
Chartered Patent Agents,  
Agents for the Applicants.

Leamington Spa: Printed for Her Majesty's Stationery Office, by the Courier Press.—1956.  
Published at The Patent Office, 25, Southampton Buildings, London, W.C.2, from which  
copies may be obtained.