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CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
RUTGERS, THE STATE UNIVERSITY, NEW BRUNSWICK, NEW JERSEY 08903

Reactions of Tris(dialkylamino)phosphines with Dialkylchloramines¹

By DONALD B. DENNEY AND STEPHEN M. FELTON

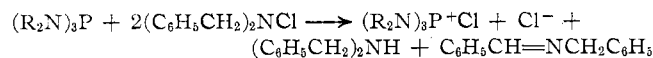
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Tris(dialkylamino)phosphines react with dialkylchloramines to give tris(dialkylamino)chlorophosphonium chlorides, a Schiff base derived from the dialkylchloramine, and the parent amine. The reaction is thought to proceed by initial displacement on halogen to give a tris(dialkylamino)chlorophosphonium dialkylamide. This salt is in equilibrium with the starting materials. Reaction of the dialkylamide anion with dialkylchloramine yields the Schiff base and the parent amine.

Introduction

The reaction of "positive halogen" containing compounds with trialkylphosphines and phosphites have been shown to lead in many cases to phosphonium salts.² Sisler and his co-workers have made an extensive study of the reactions of a variety of phosphines with chloramine.³ In general, aminophosphonium chlorides are the products. One exception involves the reaction of tris(dimethylamino)phosphine with dimethylchloramine which yielded tris(dimethylamino)chlorophosphonium chloride.³ The other products of this reaction were not investigated; however, it was suggested that tetramethylhydrazine was probably formed.

The study now being reported was aimed at preparing tetrakis(dialkylamino)phosphonium halides by allowing tris(dialkylamino)phosphines to react with dialkylchloramines. It has been found that the reaction does not yield these products but as previously reported by Sisler, *et al.*,³ yields the tris(dialkylamino)chlorophosphonium chloride. It has been shown that, in the N-chlorodibenzylamine reaction, the other products are the Schiff base derived from the dibenzylchloramine and dibenzylamine rather than the tetraalkylhydrazine suggested by Sisler, *et al.*³



Experimental Section

Materials.—N-Chlorodialkylamines were prepared by the method of Coleman.⁴ The tris(dialkylamino)phosphines were prepared by condensing the appropriate amine with phosphorus trichloride.⁵

Spectra.—The nuclear magnetic resonance spectra were re-

corded with a Varian Associates A-60 spectrometer at 60 MHz. The spectra were run in a variety of solvents with tetramethylsilane as an internal standard. Chemical shifts are reported in ppm relative to tetramethylsilane. Infrared spectra were recorded with Perkin-Elmer Models 21 and 137 and a Beckman IR-5A instrument.

Reaction of Tris(diethylamino)phosphine (1 Mol) with N-Chlorodiethylamine (2 Mol).—Tris(diethylamino)phosphine, 8.25 g (0.0345 mol) was added to a chilled hexane solution, 75 g, containing 0.0691 mol of N-chlorodiethylamine. The reaction mixture warmed and became milky. The mixture was stirred at room temperature. A yellow-orange oil formed and after 16 hr in the refrigerator two distinct phases were present. An aliquot of the hexane phase gave no iodine when treated with potassium iodide solution. The oil and the hexane phase were separated by decantation and the oil was washed with 50 ml of hexane. The oil was dried in a vacuum oven to give 7.0 g of material. The nmr spectrum was identical in its major absorptions with that of an authentic sample of tris(diethylamino)chlorophosphonium chloride. This reaction was conducted many times with identical results. When the oil was further dried at 90° (2 mm) for 16 hr and then triturated with dry ether, the oil became semicrystalline. The infrared and nmr spectra of this material were identical with that of an authentic sample of tris(diethylamino)chlorophosphonium chloride prepared by allowing chlorine to react with tris(diethylamino)phosphine which is the method used by Nöth and Vetter to prepare tris(dimethylamino)chlorophosphonium chloride.⁶ The materials obtained by both methods were extremely hygroscopic. The nmr spectrum showed a triplet at 1.30 ppm ($J = 7$ cps) and an apparent sextet centered at 3.34 ppm. The 1.30-ppm absorption is due to the methyl group and the absorption at 3.34 ppm is due to the methylene group hydrogens which are coupled to the methyl group hydrogens and phosphorus ($J_{PH} = 14$ cps). The relative areas under these absorptions were 18:12.

Both materials were converted to their hexafluorophosphate derivatives by allowing the salts to react with saturated aqueous solutions of potassium hexafluorophosphate. The salts were recrystallized from ethanol, mp 332–333°. The yield of hexafluorophosphate from the dialkylchloramine reaction was 56%. *Anal.* Calcd for $[(C_2H_5)_2N]_3PClPF_6$: C, 33.70; H, 7.02. Found: C, 34.55; H, 7.20.

The hexane solution was treated with a solution of 6.4 g of 2,4-dinitrophenylhydrazine in 30 ml of concentrated sulfuric acid, 48 ml of water, and 160 ml of ethanol. A yellow solid formed

(1) This research has been supported by the National Science Foundation under NSF GP4997X.

(2) B. Miller, "Topics in Phosphorus Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1965, Chapter 3.

(3) S. R. Jain, L. K. Krannick, R. E. Highsmith, and H. H. Sisler, *Inorg. Chem.*, **6**, 1058 (1967), and references cited therein.

(4) G. H. Coleman, *J. Am. Chem. Soc.*, **55**, 3001 (1933).

(5) C. Steube and H. P. Lankelma, *ibid.*, **78**, 976 (1956).

(6) H. Nöth and H. J. Vetter, *Ber.*, **98**, 1981 (1965).

which was filtered and recrystallized from ethanol, mp 144–147°. There was no depression of melting point on admixture with an authentic sample of acetaldehyde 2,4-dinitrophenylhydrazone. The nmr and infrared spectra were identical with those of an authentic sample. The crude yield was 41% based on 1 mol of Schiff base per 2 mol of N-chlorodiethylamine.

Reaction of Tris(diethylamino)phosphine (1 Mol) with N-Chlorodiethylamine (1 Mol).—The same reaction was repeated using 0.0653 mol of phosphine and 0.0653 mol of chloramine. After 16 hr the hexane phase was concentrated at 35° on an aspirator. The distillate yielded the 2,4-dinitrophenylhydrazone of acetaldehyde, 28%, when treated as before. The pot residue was distilled to give 8.6 g (54%) of recovered tris(diethylamino)phosphine. Some tris(diethylamino)phosphine oxide, *ca.* 1 g, remained as a pot residue. The hexane-insoluble oil was converted into the tris(diethylamino)chlorophosphonium hexafluorophosphate. The yield based on a reaction of 1 mol of phosphine with 2 mol of chloramine was 47%.

Reaction of Tris(diethylamino)phosphine (1 Mol) with N-Chlorodibenzylamine (2 Mol).—N-Chlorodibenzylamine was prepared in benzene. The benzene solution was dried by distilling until a clear distillate was obtained. The resulting solution contained 0.059 mol of the chloramine; to this was added 7.4 g (0.030 mol) of tris(diethylamino)phosphine. An exothermic reaction took place. The reaction mixture remained homogeneous. The nmr spectrum after 16 hr had a triplet at 1.04 ppm ($J = 7$ cps), a triplet at 1.12 ppm ($J = 7$ cps), an octet at 2.96 ppm ($J_{PH} = 14$ cps), an apparent sextet at 3.26 ppm ($J_{PH} = 14$ cps), a singlet at 3.87 ppm, a doublet at 4.71 ppm ($J = 1$ cps), and a poorly defined multiplet at 8.23 ppm. A small triplet was also found at 1.57 ppm ($J = 7$ cps). The triplet at 1.04 ppm and the octet at 2.96 ppm correspond in chemical shift and coupling constants to tris(diethylamino)phosphine oxide. Integration indicated a 16% yield. The triplet at 1.12 ppm and apparent sextet at 3.26 ppm correspond in chemical shift and coupling constant to tris(diethylamino)chlorophosphonium chloride; integration indicated an 84% yield. The absorptions at 4.71 and 8.23 ppm were the same as those of an authentic sample of N-benzylidenebenzylamine. Integration indicated *ca.* 100% yield. The single peak at 3.87 ppm was identified as due to the benzylic protons of dibenzylamine by augmenting this peak with authentic dibenzylamine. The yield was 76% by integration. Absorptions in the aromatic region were also found. The small triplet at 1.57 ppm could not be assigned.

In another experiment, tris(diethylamino)phosphine, 7.41 g (0.030 mol), was allowed to react with 0.060 mol of N-chlorodibenzylamine in hexane. In this experiment a yellowish oil was formed. A few drops of the hexane phase were treated with 2,4-dinitrophenylhydrazine solution. A dark orange-red derivative was obtained, mp 237° (lit.⁷ 237°), for the 2,4-dinitrophenylhydrazone of benzaldehyde. The nmr spectrum of the hexane concentrate indicated that tris(diethylamino)phosphine oxide and N-benzylidenebenzylamine were present.

The hexafluorophosphate derivative was prepared from the insoluble material mp 332–333°. Dibenzylamine hydrochloride was also found in the insoluble oil.

Reaction of Tris(diethylamino)phosphine with N-Chlorodimethylamine.—Tris(diethylamino)phosphine, 10.0 g (0.0405 mol), was added to an ether solution of 0.040 mol of N-chlorodimethylamine dried over phosphorus pentoxide. A white precipitate formed immediately. After 15 min, 8 ml of water was added. The reaction mixture warmed. After 2 hr two clear layers had formed. The aqueous phase was added to 150 ml of dry benzene and water was removed by distillation. The benzene solution on cooling deposited a white solid; mp 168–171° (lit.⁸ 171°); 2.9 g (89%) of dimethylamine hydrochloride. The nmr spectrum was identical with that of an authentic sample.

The ether solution was concentrated to give a liquid whose infrared and nmr spectra were identical with those of tris(diethylamino)phosphine oxide.

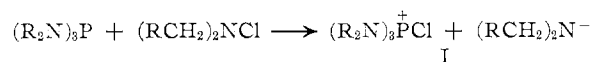
Reaction of Tris(dimethylamino)phosphine with N-Chlorodiethylamine.—Tris(dimethylamino)phosphine, 6.0 g (0.037 mol), was added to an ether solution of 0.04 mol of N-chlorodiethylamine. A white precipitate formed. After 5 min, 3 ml of water was added. White crystals formed on standing. After 2 days they were collected; mp 209–210° (lit.⁹ 219–220°); 1.8 g (44%) of diethylamine hydrochloride. The ether layer was concentrated to give 6.0 g of a liquid whose nmr spectrum was identical with that of tris(dimethylamino)phosphine oxide. No absorptions for diethylamino groups bound to phosphorus were present in the spectrum.

Reaction of Tris(diethylamino)chlorophosphonium Chloride with Lithium Diethylamide.—A solution of butyllithium, 0.02 mol in hexane–benzene, was treated with 2.0 g (0.028 mol) of diethylamine in 25 ml of benzene. The mixture was stirred. A white precipitate of lithium diethylamide formed. Tris(diethylamino)chlorophosphonium chloride, 3.17 g (0.01 mol), was added with stirring. The heterogeneous mixture began to turn yellow and then brown; stirring was continued for 3 hr. An aliquot of the homogeneous reaction solution was concentrated to a viscous oil which was treated with a small amount of benzene. A yellow precipitate was formed which was identified as lithium chloride by titration with perchloric acid in acetic acid in the presence of mercuric acetate. The nmr spectrum of the benzene solution showed absorptions for tris(diethylamino)phosphine and a small amount of tris(diethylamino)phosphine oxide.

Results and Discussion

The reactions of phosphorus-containing nucleophiles with compounds containing N–X bonds have been reviewed² and it has been concluded that the general mechanism involves attack on halogen to give an intermediate halophosphonium cation and an anion. In general these react with each other to give a new phosphonium salt and a halide ion. It should be noted that in many cases this general mechanism has not been distinguished from ones involving a pentasubstituted intermediate which dissociates into ions, or alternatively attack could occur on nitrogen to give halide ion and the phosphonium ion directly.

The results of the present work strongly support an initial attack by the tris(dialkylamino)phosphine on the chlorine of the N-chloroamine to give the chlorophosphonium salt (I). An alternate mode of reaction



which would lead to a pentasubstituted intermediate is eliminated because no mixed products were obtained when tris(diethylamino)phosphine was allowed to react with N-chlorodimethylamine and when tris(dimethylamino)phosphine was allowed to react with N-chlorodiethylamine followed by hydrolysis to the phosphine oxides. If the dialkylamino moiety of the dialkylchloramine had become bonded to phosphorus, then a mixed phosphine oxide would have to be formed in at least one case. These results also eliminate attack by the phosphorus on the nitrogen of the N-chloramine. Such a reaction should have given mixed phosphine oxides.

(7) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 283.

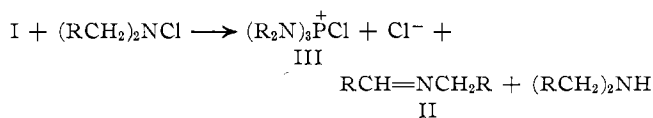
(8) "Handbook of Chemistry and Physics," Chemical Rubber Publishing Co., Cleveland, Ohio, 1961, p 958.

(9) See ref 8, p 957.

The results also agree with those of Sisler and co-workers.³

Formulation of the initial reaction product as I is supported by its rapid reaction with water to give the appropriate phosphine oxide. It was also shown that the initial precipitate reacts with various alcohols to give alkyl halides and olefins. Phenol reacted to give tris(dialkylamino)phenoxyphosphonium chlorides.¹⁰ These results clearly show that the first product is not a tris(dialkylamino)chlorophosphonium chloride. Nöth and Vetter⁶ have shown that tris(dimethylamino)chlorophosphonium chloride is stable in aqueous media. Their findings have been confirmed.¹⁰

It is clear though that I does undergo further reaction to give tris(dialkylamino)chlorophosphonium chloride. A possible path for the generation of this salt involves reaction of the dialkylamide ion with N-chlorodialkylamine to generate chloride ion, Schiff base (II), and tris(dialkylamino)chlorophosphonium chloride (III). There is precedence for such an elimination reaction.¹¹ That a Schiff base is formed as a prod-



uct of the reaction with N-chlorodibenzylamine has been demonstrated and its formation can certainly be inferred by the isolation of the 2,4-dinitrophenylhydrazone of acetaldehyde from the N-chlorodiethylamine reaction. This reaction scheme is supported by the observed stoichiometry which is 1 mol of phosphine to 2 mol of N-chlorodialkylamine. It is also supported by the finding that tris(diethylamino)chlorophosphonium chloride reacted with lithium diethylamide to give tris(diethylamino)phosphine. This demonstrates that the formation of I is reversible and thus a route is available for the formation of the observed products.

It is important to note that this appears to be the first example of direct proof that the phosphine is attacking the halogen of the N-X compound with the production of a halophosphonium salt. Unfortunately these results cannot be generalized to other phosphorus-containing nucleophiles.

(11) (a) W. E. Bachmann, M. P. Cava, and A. S. Dreiding, *J. Am. Chem. Soc.*, **76**, 5554 (1954); (b) H. E. Baumgarten and F. A. Bower, *ibid.*, **76**, 4561 (1954); (c) F. Klages, *Ann.*, **547**, 1 (1941).

(10) The details of these experiments can be found in the Ph.D. thesis of S. M. Felton, Rutgers, The State University, 1967.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

Fragmentation and Rearrangement Processes in the Mass Spectra of Fluoroalkylphosphorus Compounds. I. Trifluoromethylphosphines and Trifluoromethylhalogenophosphines

BY R. G. CAVELL AND R. C. DOBBIE

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The mass spectra of a series of trifluoromethylhalogeno- and hydridophosphines have been studied. In addition to normal bond breaking, extensive rearrangement of the ions was observed leading to species containing P-F bonds in all of the spectra. A mechanism for the transfer of fluorine from carbon to phosphorus is proposed.

Introduction

The mass spectra of pentafluorophenylphosphorus derivatives indicated that both normal fragmentation and molecular rearrangement occurred under electron impact.¹ Also it has been recently demonstrated that the trifluoromethyl derivatives of arsenic undergo extensive rearrangement under electron impact to form ions and neutral fragments containing As-F bonds.² We have made a comprehensive study of the mass spectra of trifluoromethylphosphorus compounds to evaluate the importance of rearrangement processes.

Experimental Section

Standard vacuum techniques were used for all manipulations. The compounds were prepared from the iodophosphines³ by the

most convenient literature methods. The action of antimony trifluoride,^{4,5} mercuric chloride, and mercuric bromide^{5,6} gave the corresponding fluoro, chloro, and bromo compounds, while reduction with hydrogen iodide and mercury gave the hydrides.⁷ Pure samples of the iodophosphines for mass spectroscopic study were obtained from the reaction of iodine with either tetrakis-(trifluoromethyl)diphosphine³ or with a mixture of trifluoromethylphosphorus cyclic tetramer and pentamer.⁸ The compounds were characterized and purified as described in the literature.³⁻⁸ In general, gas-phase molecular weights within 0.5% of the theoretical value were obtained on all compounds. The infrared spectra agreed with the literature and showed no indication of impurities. Comparison of the results of vapor pressure measurements on some of the compounds with the

(3) F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1585 (1953).

(4) A. B. Burg and G. Brendel, *J. Am. Chem. Soc.*, **80**, 3198 (1958).

(5) J. F. Nixon and R. G. Cavell, *J. Chem. Soc.*, 5983 (1964).

(6) A. B. Burg and J. F. Nixon, *J. Am. Chem. Soc.*, **86**, 356 (1964).

(7) R. G. Cavell and R. C. Dobbie, *J. Chem. Soc., Sect. A*, 1308 (1967).

(8) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).

(1) J. M. Miller, *J. Chem. Soc., Sect. A*, 828 (1967).

(2) R. C. Dobbie and R. G. Cavell, *Inorg. Chem.*, **6**, 1450 (1967).