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A New Reaction of Chloramines with Phosphines

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Received April 11, 1968

Phosphine reacts with dimethylchloramine to give elemental phosphorus and with chloramine to give a polymeric phosphorus hydride. Diphenylphosphine and phenylphosphine react with dimethylchloramine or chloramine to give, respectively, tetraphenylbiphosphine and tetraphenylphosphetane. In the chloramine reactions, ammonium chloride is formed, and in the dimethylchloramine reactions, dimethylammonium chloride is produced.

Introduction

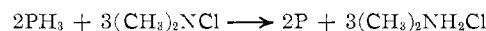
Extensive discussions of the reactions of chloramines of the type R_2NCl , where $R = H$ or alkyl, with tertiary phosphines have appeared in the literature¹⁻⁵ and in all cases reported, except that of tris(dimethylamino)phosphine,⁵ the chloramination reaction produces an aminophosphonium chloride or one of its condensation products. We wish to report that primary and secondary phosphines (containing P-H bonds) react differently with chloramines. The only report in the literature of the reaction of a chloramine with such phosphines was made by Petrov, *et al.*,⁶ and they did not identify the products.

Experimental Section

Materials.—Phosphine was prepared by dropping water on aluminum phosphide (from Rocky Mountain Research) in a nitrogen atmosphere and was purified by passage through traps cooled to -78° . The vapor pressure of the phosphine was found to be 172 mm at the melting point of carbon disulfide (lit.,⁷ 171 mm at the same temperature). Diphenylphosphine was purchased from Alfa Inorganics, Inc. Phenylphosphine was prepared by reduction of phenyldichlorophosphine with lithium aluminum hydride in diethyl ether according to the method of Kuchen and Buchwald.⁸ Ammonia-free chloramine solutions were prepared by the method of Gilson and Sisler.⁹ Dimethylchloramine was prepared by a procedure analogous to the Raschig synthesis of chloramine.¹⁰ All chloramine solutions were dried by vacuum distillation from anhydrous copper sulfate in a conventional glass vacuum system. Reagents and products were generally handled in an inert-atmosphere chamber to prevent hydrolysis or oxidation.

Elemental analyses were carried out by the Schwarzkopf Microanalytical Laboratory, Woodbury, N. Y., and Galbraith Laboratories, Inc., Knoxville, Tenn. Melting points (uncorrected) were obtained using the Thomas-Hoover capillary melting point apparatus. Infrared spectra of Halocarbon and Nujol mulls of the solids, supported between KBr disks, were obtained with a Beckman IR-10 spectrometer. Mass spectral data were obtained using a Hitachi Perkin-Elmer RMU-6E mass spectrometer at an ionizing voltage of 70 eV. The heated inlet to the mass spectrometer was operated at 150° .

Reaction of Phosphine with Dimethylchloramine.—Ten milliliters of 1.0 *M* dimethyl chloramine–diethyl ether solution was distilled into a flask containing 50 ml of diethyl ether and 5.6 mmol of phosphine. The mixture was allowed to warm to room temperature and was stirred for 17 hr. The volatile materials were distilled out of the reaction flask leaving a red solid. Dimethylammonium chloride was extracted from the red solid by washing it with acetonitrile; yield, 0.55 g or 80% of theory based on the amount of phosphine and the stoichiometry expressed by the equation



It was identified by its melting point (170 – 171°) and its infrared spectrum. The insoluble residue was a red solid which ignited when warmed in air or upon contact with concentrated nitric acid. It appeared to be completely unaffected by water or air at room temperature. It was assumed to be principally elemental phosphorus because of its appearance and high phosphorus content, but it could contain polymeric phosphorus hydrides or chlorophosphines whose compositions closely approach that of elemental phosphorus. This would be the case if the long chains (or sheets) of phosphorus atoms were end-stopped with chlorine or hydrogen atoms. Elemental analysis of the solid showed that it contained small percentages of carbon, hydrogen, and chlorine; these could also be the result of the presence of small quantities of solvent and/or dimethylammonium chloride occluded in the solid. The yield of phosphorus was 90% of theory based on the amount of phosphine. *Anal.* Found: P, 89.

Reaction of Phosphine with Chloramine.—Eighty-five milliliters of 0.070 *M* chloramine–diethyl ether solution (6.0 mmol of chloramine) was mixed with 1.0 mmol of phosphine in a flask and the mixture was allowed to warm to room temperature. After 24 hr, the volatile materials were distilled into another flask and no chloramine or phosphine was found to be present. Numerous other experiments showed that excess phosphine is present at the end of the reaction if the ratio of chloramine to phosphine at the start of the reaction is less than 6:1. The white solid (0.28 g) which remained in the reaction flask was washed with diethyl ether and dried under vacuum. Elemental analyses of the solid from two independent sources were inconsistent and uninterpretable. Ammonium chloride was identified as a major component of the solid by its infrared spectrum and mass spectral data. Complete separation of the ammonium chloride from the phosphorus compound could not be obtained by vacuum sublimation or solvent extraction. No elemental phosphorus was detected.

When benzene was used as the solvent, analytical results were more consistent and some separation of products could be obtained. Phosphine (2.1 mmol) was condensed into 4.5 mmol of chloramine in 50 ml of benzene and 0.24 g of bright yellow solid formed. The solid was washed with petroleum ether (bp 30 – 60°) and dried under vacuum. Analytical, infrared, and mass spectroscopic data on the yellow solid could best be interpreted by assuming the solid to contain about 85% ammonium chloride along with small amounts of benzene, hydrogen chloride, and condensed phosphorus hydride species. The data account for 1.6 mmol of

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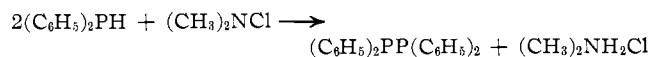
TABLE I
 SUMMARY OF REACTIONS OF CHLORAMINES WITH PHOSPHINES

Reactants				Products			
Chloramine	mmol	Phosphine	mmol	Amine hydrochloride	Yield, %	Phosphorus compound	Yield, %
(CH ₃) ₂ NCl	10.0	PH ₃	5.6	(CH ₃) ₂ NH ₂ Cl	80	P red (impure)	90
H ₂ NCl	4.5	PH ₃	2.1	NH ₄ Cl	...	P _x H _y	76
(CH ₃) ₂ NCl	3.0	(C ₆ H ₅) ₂ PH	10.9	(CH ₃) ₂ NH ₂ Cl	77	[(C ₆ H ₅) ₂ P] ₂	90
H ₂ NCl	3.11	(C ₆ H ₅) ₂ PH	10.0	NH ₄ Cl	61	[(C ₆ H ₅) ₂ P] ₂	11
H ₂ NCl	6.34	(C ₆ H ₅) ₂ PH	6.2	NH ₄ Cl	56	[(C ₆ H ₅) ₂ P] ₂	32
(CH ₃) ₂ NCl	9.00	C ₆ H ₅ PH ₂	15.5	(CH ₃) ₂ NH ₂ Cl	100	(C ₆ H ₅ P) ₄	55
H ₂ NCl	6.23	C ₆ H ₅ PH ₂	7.5	NH ₄ Cl	52	(C ₆ H ₅ P) ₄	19

phosphorus, which means that 76% of the phosphine had reacted. The remainder of the phosphine was found in the benzene. The benzene solution was fractionated on the vacuum line by allowing it to distil into a series of traps, the first cooled to -78° and the next cooled to -196°. The benzene was found in the -78° trap. A mixture of phosphine and hydrogen chloride was found in the -196° trap. They were identified from the infrared spectrum of the gaseous mixture and the observation that the mixture had strongly reducing and acidic properties. When diethyl ether was used as solvent, the phosphine and hydrogen chloride could not be separated from the solvent.

It is known that some polymeric phosphorus hydrides condense by splitting out phosphine. Mass spectral data indicate that phosphine was formed when the solid was heated in the chamber of the mass spectrometer. Hence, it was concluded that the products are ammonium chloride and a polymeric phosphorus hydride. No elemental phosphorus was observed.

Reaction of Diphenylphosphine with Dimethylchloramine.—A diethyl ether solution of 3.02 mmol of dimethylchloramine was distilled onto 2.03 g of diphenylphosphine (10.9 mmol) and the mixture was stirred at room temperature for about 24 hr. The volatile materials were distilled out, leaving a mixture of a white solid and unreacted diphenylphosphine. This was taken into the inert-atmosphere chamber where the excess diphenylphosphine was separated from the solid by washing with acetonitrile. The remaining solid was dried under vacuum; mp 124–126°, lit.¹¹ mp 121°. The yield of tetraphenylbiphosphine was 1.0 or 90% of theory based on the amount of dimethylchloramine and the equation



Its infrared spectrum was identical with that of a known sample of tetraphenylbiphosphine. The acetonitrile was distilled off under vacuum and the residual white solid was washed with boiling benzene and dried under vacuum. The yield of dimethylammonium chloride was 0.19 g or 77% based on the amount of dimethylchloramine (mp 168–170°). Its infrared spectrum was identical with that of a known sample of dimethylammonium chloride.

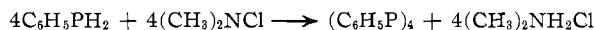
Reaction of Diphenylphosphine with Chloramine.—Eighty-nine milliliters of 0.035 *M* chloramine-diethyl ether solution (3.11 mmol of chloramine) was distilled onto 1.80 g (10.0 mmol) of diphenylphosphine and the mixture was allowed to warm to room temperature with stirring. After 46 hr, the volatile materials were distilled from the reaction flask leaving a mixture of white solid and unreacted phosphine. The mixture was extracted with boiling benzene and diethyl ether. The insoluble white solid was dried under vacuum. Its infrared spectrum was identical with that of ammonium chloride and the yield was 0.10 g or 61% of theory based on the amount of chloramine.

The benzene and diethyl ether were evaporated under vacuum leaving a mixture of white solid and unreacted diphenylphosphine. The phosphine was removed by washing with cold acetonitrile and the solid residue was dried under vacuum. The yield of tetraphenylbiphosphine was 0.13 g or 11% of theory based on the equation

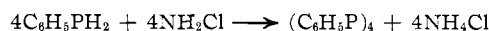


A higher yield of biphosphine was obtained when 96 ml of 0.066 *M* chloramine-diethyl ether solution (6.34 mmol of chloramine) was distilled onto 1.16 g (6.24 mmol) of diphenylphosphine. The products were separated and identified as described previously. The yield of ammonium chloride was 56% of theory and the yield of tetraphenylbiphosphine (mp 119–122°) was 32% of theory based on the amount of diphenylphosphine and the above equation.

Reaction of Phenylphosphine with Dimethylchloramine.—Twenty milliliters of diethyl ether containing 9.0 mmol of dimethylchloramine was dropped into a solution of 1.70 g of phenylphosphine (15.5 mmol) in 10 ml of diethyl ether. The reaction mixture was filtered after 24 hr. Dimethylammonium chloride was retained on the filter (mp 168–170°) in 100% yield based on the amount of dimethylchloramine. The ether was removed from the filtrate by evaporation under vacuum, leaving a white solid which was taken into the drybox and washed with cold acetonitrile. The white solid (0.53 g) melted at 149–151° (lit.⁸ 150.5°) and its infrared spectrum was identical with that published for tetraphenylphosphetane.⁸ The yield was 55% of theory based on the amount of dimethylchloramine and the equation



Reaction of Phenylphosphine with Chloramine.—Eighty-nine milliliters of 0.070 *M* chloramine-diethyl ether solution (6.23 mmol of chloramine) was distilled onto 0.83 g (7.5 mmol) of phenylphosphine and the mixture was stirred for 12 hr at room temperature. The solvent was distilled into another flask leaving a white solid and the excess phenylphosphine. The solid mixture was extracted with boiling benzene and diethyl ether in the inert-atmosphere chamber. The infrared spectrum indicated that the 0.17 g of insoluble white solid was mostly ammonium chloride (52% yield). The benzene and ether were evaporated under vacuum leaving a white solid which was washed with cold acetonitrile and dried under vacuum. This white solid melted at 149–151° and its infrared spectrum was identical with that published for tetraphenylphosphetane.⁸ The yield was 0.13 g or 19% of theory based on the equation



and the amount of chloramine.

Discussion

The reactions described herein illustrate a new method for the formation of phosphorus-phosphorus bonds from primary and secondary phosphines. In this process the hydrogen atoms on the phosphorus atoms are transferred to the nitrogen atoms of the chloramine molecules to form ammonium chlorides. It is reasonable to assume that this type of reaction can be extended to other hydrides which are similar to phosphine in bond strength and acidity. These reactions make possible a new and unexpected application of chloramines to problems in inorganic synthesis.

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It should be noted that the only phosphorus-containing products formed in the reaction of phosphine with chloramine were polymeric phosphorus hydrides in contrast to the apparent red phosphorus formed in the reaction of phosphine with dimethylchloramine. This may be a result of the expected higher basicity of a dimethylamino group compared to that of an amino group.

Chloramine cleaves P-P bonds¹² and yields a mixture of aminophosphonium chlorides, their condensation products, and P-Cl compounds which are difficult to separate. It is probable that dialkylchloramines

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will also cleave P-P bonds. This may have been the difficulty encountered by Petrov⁶ in characterizing the products obtained in his experiments. The products reported herein are obtained only when chloramine or dimethylchloramine is not in excess.

This type of reaction is currently being investigated with respect to hydrides of other elements and is being extended to include other substituted phosphines.

Acknowledgment.—The support of this research by the National Institutes of Health through Grant No. CA08263-03 with the University of Florida is gratefully acknowledged.

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Mass Spectrometric Study of Photoionization. XII. Boron Trifluoride and Diboron Tetrafluoride

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Received March 29, 1968

Mass spectra and photoion yield curves for the molecular and principal fragment ions of BF_3 and B_2F_4 are reported. The threshold regions only are measured for B_2F_3^+ and BF^+ from B_2F_4 . These observations are intercompared in order to derive heats of formation of ions and radicals and bond dissociation energies. The boron-boron bond dissociation energy in B_2F_4 is calculated to be 431 kJ mol^{-1} ($103 \text{ kcal mol}^{-1}$).

Introduction

Recent electron impact studies¹⁻⁴ on BF_3 have given remarkably concordant results of 15.5–15.7 eV for the ionization threshold of the molecule in spite of the relatively low intensity of that ion. Unfortunately, no extrapolated Rydberg series or photoionization measurements on BF_3 have been reported for comparison. The same authors¹⁻⁴ also report consistent values of about 16.2 eV for the threshold of the BF_2^+ ion in BF_3 . The ionization energy of BF_2 necessary for the calculation of bond energies has not been measured directly. Steele, Nichols, and Stone⁵ estimated $I(\text{BF}_2) = 9.4 \pm 0.1 \text{ eV}$ by subtracting an average⁶ B-F bond energy of BF_3 from the electron impact value^{1,2} of $A(\text{BF}_2^+)$. On the other hand, Margrave⁷ used this value and electron impact results to calculate $\Delta H_f(\text{BF}_2)$, thus completing the circular argument.

Domalski and Armstrong⁸ have stated that the ther-

mochemistry of many boron compounds is dependent on the heat of formation of BF_3 and of the lower fluorides of boron. Thus the present study was undertaken in an attempt to obtain additional and more accurate values. To do so, the study includes measurements on B_2F_4 because of its obvious relationship to BF_3 and because it is one of the few volatile boron compounds containing a boron-boron bond. The necessity and advantage of a joint consideration of some of the experimental results for the two molecules will be apparent.

The mass spectrum of an apparently impure sample of B_2F_4 has been reported,⁹ but no published data are available on ionization energies of this molecule. However, Gunn and Green¹⁰ have investigated the heat of reaction for the chlorination of B_2F_4 . The assumed equivalent reaction of $\text{BF}_3 + \text{BCl}_3$ results in a complex equilibrium mixture, and a B-B bond energy of $72.4 \text{ kcal mol}^{-1}$ is calculated from the summation of heats of formation of the components. Unexpectedly, the same method resulted in a B-B bond energy of 79 kcal mol^{-1} for the less stable B_2Cl_4 .

The following conversion factors are used in this report: $1 \text{ eV molecule}^{-1} = 96.4870 \text{ kJ mol}^{-1}$; $1 \text{ kcal mol}^{-1} = 4.1840 \text{ kJ mol}^{-1}$.

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