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The Reaction of Chloramine and Chloramine–Ammonia Mixtures with 2-(*N*,*N*-Dimethylhydrazino)-1,3,2-dioxophospholane

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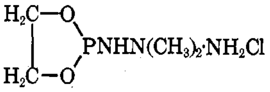
The reactions of 2-(*N*,*N*-dimethylhydrazino)-1,3,2-dioxophospholane with chloramine and with a mixture of chloramine and ammonia have been carried out. The former reaction leads to a 1:1 adduct



whereas the latter results in the formation of dimethylhydrazine, dimethyltriazanium chloride, and a phosphorus-containing polymer. Various experiments were carried out leading to the elucidation of the course of this reaction. It was shown that chloramine does not by itself cleave the P–N bond in the hydrazinophospholane.

Introduction

Utvary and Sisler[1a] have shown that 2-dialkylamino-1,3,2-dioxophospholanes react with chloramine–ammonia mixtures to produce the corresponding 2,2-dialkyltriazanium chlorides and, ultimately, polymers derived from the phospholane fragments. Utvary[1b] interpreted these results to indicate that chloramine first cleaves the P–N bond to give 2-chloro-1,3,2-dioxophospholane and dialkylhydrazine. He postulated further that these products react with chloramine and ammonia to produce the observed results.

This interpretation is interesting because, if true, this would be the first known example of cleavage of a P–N bond by chloramine. The reactions of chloramine with aminophosphines,[2] phosphinoamines,[3] phosphinohydrazines,[4] and hydrazinophosphines[5] have been investigated. In no case has cleavage of the P–N bond by chloramine been demonstrated. In all examples the apparent site of chloramine attack is the phosphorus atom, and the result is an aminophosphonium ion.

Utvary's interpretation also suggests that the chloramination of a 2-(*N*,*N*-dimethylhydrazino)-1,3,2-dioxophospholane would provide a possible route to new linear nitrogen compounds. If P–N bond cleavage occurs, 1,1-dimethyltriazine may be produced. This might react further with chloramine to yield tetraazanium ions.

Therefore, we have investigated the interaction of chloramine and chloramine–ammonia mixtures with 2-(*N*,*N*-dimethylhydrazino)-1,3,2-dioxophospholane in order to resolve the question of P–N bond cleavage and to isolate new compounds which might be formed in the reaction.

Experimental Section

Materials.—1,1-Dimethylhydrazine was obtained from Aldrich Chemical Co. and used as obtained. Triethylamine was obtained from Eastman Kodak Co. and dried over calcium hydride before use. The solvents benzene and diethyl ether were obtained as the reagent grade materials and dried over calcium hydride. All other solvents were reagent grade.

Reaction products and intermediates were rigorously protected from atmospheric water vapor by storage and transfer in a Vacuum Atmospheres Dri-Lab Model HE-43 equipped with a Model HE-93B Dri-Train.

Analyses.—Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn., and by PCR, Inc., of Gainesville, Fla. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrometer or on a Beckman IR-10 spectrometer. Proton magnetic resonance spectra were recorded at room temperature with a Varian Model A-60A spectrometer.

Synthesis of Chloramine.—Chloramine was prepared by the gas-phase reaction of chlorine and ammonia described previously.[6] Gaseous chloramine prepared in this way is always mixed with a large excess of ammonia. Ether solutions of ammonia-free chloramine were prepared by the method of Gilson and Sisler.[7] Stable solutions containing 0.3–0.6 *M* NH_2Cl were prepared and stored at room temperature in the dark. Prior to any experiment, the chloramine content was determined by shaking a measured sample with potassium iodide in acidic solution and titrating the liberated iodine with standard thiosulfate solution.

Synthesis of 2-(*N*,*N*-Dimethylhydrazino)-1,3,2-dioxophospholane.[8]—2-Chloro-1,3,2-dioxophospholane[9] (25.3 g, 0.20 mmol) was added dropwise to a stirred solution of 12 g (0.20 mmol) of 1,1-dimethylhydrazine and 20.6 g (0.20 mmol) of triethylamine in 50 ml of diethyl ether. The precipitated triethylamine hydrochloride was filtered off and washed with three 25-ml portions of ether. The filtrate and washings were combined and concentrated by vacuum evaporation at room temperature. The residual liquid was distilled under vacuum; bp 72–75° (9–11 mm), 64° (8 mm); yield 14.2 g (47% of theory). *Anal.* Calcd for $C_4H_{11}O_2N_2P$: C, 32.01; H, 7.38; N, 18.66. Found: C, 32.21; H, 7.53; N, 18.79.

Reaction of 2-(*N*,*N*-Dimethylhydrazino)-1,3,2-dioxophospholane with Ammonia-Free Chloramine.—In a typical experiment, a 0.365 *N* solution of chloramine in ether was added dropwise to a stirred solution of 1.11 g (7.4 mmol) of the hydrazinosphospholane in 25 ml of benzene. The reaction mixture was maintained at or just above room temperature, the rate of heat evolution being regulated by the rate of addition of chloramine. A white, granular precipitate formed. Chloramine addition was continued until one more drop showed no further precipitation. About 20.5 ml of solution (7.3 mmol of chloramine) was required.

The reaction mixture was transferred to the drybox and the white solid was filtered off, washed with several portions of dry benzene and ether, and dried under vacuum; mp (evacuated tube) 67–70° dec; yield 1.16 g. *Anal.* Calcd for $C_4H_{13}PN_3O_2Cl$ (I): C, 23.83; H, 6.50; N, 20.84; Cl, 17.59. Found: C, 24.04; H, 6.71; N, 20.95; Cl, 18.22.

When freshly precipitated, this product was soluble in water,

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[1] (a) K. Utvary and H. H. Sisler, *Inorg. Chem.*, **5**, 1835 (1966); (b) K. Utvary, *Monatsh. Chem.*, **99**, 1473 (1968).

[2] W. A. Hart and H. H. Sisler, *Inorg. Chem.*, **3**, 617 (1964).

[3] D. F. Clemens and N. N. Sisler, *ibid.*, **4**, 1222 (1965).

[4] J. M. Kanamueller and N. H. Sisler, *ibid.*, **6**, 1765 (1965).

[5] R. P. Nielsen, J. F. Vincent, and H. H. Sisler, *ibid.*, **2**, 760 (1963).

[6] H. H. Sisler, F. T. Neth, R. S. Drago, and D. Yaney, *J. Amer. Chem. Soc.*, **76**, 3907 (1954).

[7] I. T. Gilson and H. H. Sisler, *Inorg. Chem.*, **4**, 273 (1965).

[8] J. B. Faught, unpublished data.

[9] E. L. Gefter, *J. Gen. Chem. USSR*, **26**, 1619 (1956).

alcohols, dimethylformamide, and dimethyl sulfoxide and was insoluble in benzene, ether, and chloroform. On standing, the solubility of the substance slowly decreased. Water solutions gave an immediate precipitate of silver chloride with silver nitrate solution. Reduction of silver ion was also observed when the mixture was allowed to stand in the dark for several hours. The product does not oxidize aqueous solutions of iodide ion. Although a tetraphenylborate salt could be formed by metathesis in aqueous solution, it decomposed when recrystallization from ethanol was attempted.

The solvent and washings from the chloramine reaction were distilled at 0° under a high vacuum system. The residue (0.1–0.4 g) was a viscous oil. Infrared analysis indicated that this material was a mixture of unreacted starting material and products containing P=O groups. These oils were never obtained in high yield and were not investigated further. The distillate was shown to consist only of benzene and ether.

Reaction of 2-(*N*,*N*-Dimethylhydrazino)-1,3,2-dioxophospholane with Chloramine and Ammonia.—In a typical experiment 30 mmol of the hydrazinophospholane was dissolved in 50 ml of dry benzene and exposed to the effluent gases of the chloramine generator. Addition of the chloramine–ammonia mixture was continued for 25–30 min resulting in addition of 40–50 mmol of NH_2Cl assuming a production rate of 0.1 mmol/hr. A voluminous white precipitate was produced. After standing at room temperature for several hours this material was filtered, washed with several portions of dry benzene, dried *in vacuo*, and transferred to the drybox.

Infrared and gas chromatographic analysis of the combined filtrate and washings showed solvent and 2,2-dimethylhydrazine. Addition of this solution to an alcohol solution of oxalic acid produced 2,2-dimethylhydrazine oxalate,[10] mp 140–142°; yield 1.58 g (37% of theory).

The solid reaction product (5.67 g) was hygroscopic, gave a strong test for 2,2-dimethyltriazanium chloride,[11] and showed strong peaks in the infrared spectrum characteristic of NH_4Cl. It was suspended in chloroform and triethylamine and refluxed for several days. The mixture was filtered hot and washed with hot chloroform to remove triethylamine hydrochloride. The residue was then extracted with hot ethanol from which 2,2-dimethyltriazanium chloride (0.80 g, 24% of theory) was crystallized and identified by its melting point and infrared spectrum.[11]

The residue (2.89 g) was an insoluble, light brown solid which decomposed in the range 275–300°. *Anal.* Found: C, 19.92; H, 4.95; P, 24.91; N, 17.7.

Reaction of Adduct I with Ammonia and Chloramine–Ammonia Mixtures. Experiment 1.—A chloramine solution in ether was added to a benzene solution of 2-(*N*,*N*-dimethylhydrazino)-1,3,2-dioxophospholane to precipitate I as before. Upon completion of the addition, the stirred mixture was immediately saturated with ammonia at room temperature. After standing for several days the solution was removed by filtration, the solid product was washed with benzene and the filtrate and washings were combined. The solution was moved to a vacuum line and degassed at −196°. Ammonia was distilled from the solution at −78°. Benzene, ether, and 2,2-dimethylhydrazine were distilled from the mixture at 0°. A little oily residue remained; this was not investigated further.

An alcohol solution of oxalic acid was added to the solution containing 2,2-dimethylhydrazine to precipitate the oxalate, mp 140–142°; yield 0.34 g (26% of theory).

The solid residue (1.19 g) decomposed at 125–135°. Since only 26% of the available dimethylhydrazine was releaased by the action of ammonia, this material was assumed to be a mixture of I and the ammonolized product. The proton magnetic resonance spectrum was consistent with this assumption, the areas under the N–H peaks having increased while the area under the NCH_3 peaks decreased. Several attempts to separate this mixture were unsuccessful.

Experiment 2.—Product I was precipitated as before. Upon completion of the addition of ammonia-free chloramine solution, the stirred mixture was immediately exposed to the gaseous effluent of a chloramine generator for 30 min. The mixture was allowed to stand for several days. The solvent was removed by filtration, the solid product was washed with several portions of dry benzene, and the filtrate and washings were combined. Evaporation of the filtrate yielded 0.15 g of oily residue. No free dimethylhydrazine was detected.

The solid product gave a positive test for dimethyltriazanium chloride.[11] It was analyzed by dissolving a 70-mg sample in a solution of 25 ml of 0.10 *M* potassium iodide and 10 ml of 6 *M* sulfuric acid. After several minutes the liberated iodine was titrated with 0.20 *N* sodium thiosulfate solution. The yield of dimethyltriazanium chloride was 0.37 g (45% of theory).

Experiment 3.—A dry sample of product I (0.71 g) was suspended in benzene. The mixture was saturated with ammonia and allowed to stand for several days. It was then separated by filtration. The filtrate was distilled under a high vacuum system and tested for dimethylhydrazine by addition of alcoholic oxalic acid. No dimethylhydrazine oxalate formed. The solid recovered (0.65 g) was apparently unchanged product I.

Experiment 4.—Product I was dissolved in dry dimethylformamide. After several minutes a white solid precipitated. This mixture was saturated with gaseous ammonia and allowed to stand for several days. The solution was then moved to the vacuum line and distilled. The portion distilled at 0° was tested with alcoholic oxalic acid. No dimethylhydrazine oxalate precipitated. The solid portion was filtered and dried. Its infrared spectrum had a very strong absorption at 1660 cm^{-1} in the C=O stretching region indicating formation of a dimethylformamide adduct.

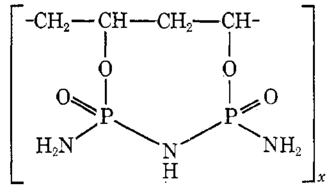
Attempted Transamination of 2-(*N*,*N*-Dimethylhydrazine)-1,3,2-dioxophospholane with NH_3.—Gaseous ammonia was added to a benzene solution of the hydrazinophospholane at room temperature until the solution was saturated. After standing for 1 day in this solution the product was separated by distilling the ammonia and solvent from it at reduced temperature and pressure under a high-vacuum system. Infrared analyses of the residue showed it to be unchanged hydrazinosphospholane. Recovery was quantitative.

No dimethylhydrazine oxalate was precipitated when the benzene distillate was mixed with an alcohol solution of oxalic acid.

Results and Discussion

2-(*N*,*N*-Dimethylhydrazine)-1,3,2-dioxophospholane reacts with ammonia-free chloramine to form a solid addition product. This addition product is water soluble, gives an immediate precipitate of silver chloride with silver nitrate solution, does not oxidize acidic potassium iodide solution, and gives a precipitate with aqueous solution containing the $B(C_6H_5)_4^-$ ion. Furthermore, exposure of the addition product to ammonia results in the formation of 1,1-dimethylhydrazine. This reaction takes place readily when the addition product is freshly precipitated but rapidly disappears as the precipitated addition product is aged. Heating the product causes decomposition at about 65°. Simultaneously a peak at about 1250 cm^{-1} in the infrared spectrum attributed to P=O becomes very pronounced, and solubility in water is reduced.

Chloramine mixed with ammonia reacts with 2-(*N*,*N*-dimethylhydrazino)-1,3,2-dioxophospholane to produce 1,1-dimethylhydrazine, 2,2-dimethyltriazanium chloride, and a hygroscopic, chlorine-containing product. If this product is boiled with an HCl acceptor, an insoluble, intractable solid results which has a P:N ratio of 2:3. The analysis of this material approaches the calculated analysis for the formula



which Utvary reported as a product of the reaction of 2-dialkylamino-1,3,2-dioxophospholane with the chloramine–ammonia mixture.

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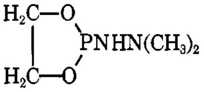
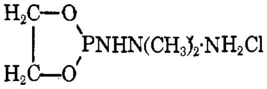
[10] P. Rowe and L. Audrieth, *J. Amer. Chem. Soc.*, **78**, 563 (1956).

[11] K. Utvary and H. H. Sisler, *Inorg. Chem.*, **7**, 698 (1968).

TABLE I

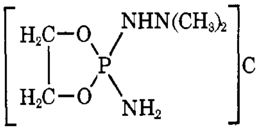
NMR PARAMETERS[a]

	τ				
Compd	N-CH$_3$	H_2C-O-[b] / H_2C-O-	N-H	NH$_2$	J_{P-NH}, cps
	7.65	5.82	4.23 4.85	. . .	37
	7.47	6.0	2.45 2.62	2.45	10

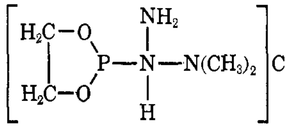
[a] DMSO-d_6; sodium salt of 3-trimethylsilylpropionic acid-2,2,3,3-d_4 (TSP) used as an internal standard. [b] Measured at the center of the broad multiplet.

Of the possible paths by which chloramine may react with 2-(*N*,*N*-dimethylhydrazino)-1,3,2-dioxophospholane, cleavage of the P-N bond to yield 2-chloro-1,3,2-dioxophospholane and a triazane is clearly eliminated. It is also clear that chloramine does not cause rupture of the N-N bond.

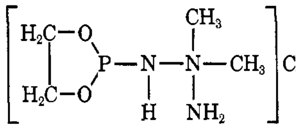
Several possible structures of a 1:1 addition product which fit the chemical and physical properties can be envisioned



I



II



III

Structures II and III seem less likely than structure I because, as substituted triazanium ions, they should oxidize acidic potassium iodide. Instead, the addition product reduces silver ion indicating the presence of the hydrazino group.

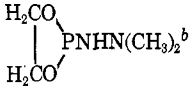
The proton magnetic resonance data (Table I) offer the most convincing evidence in favor of structure I. The resonance of the N-H proton adjacent to the phosphorus atom undergoes a large downfield shift relative to the unreacted hydrazinophospholane. This reflects the decrease in electron density on the phosphorus atom resulting from quaternization. Furthermore, the N-H chemical shifts in the chloraminated product have values in the range observed earlier[12] for aminophosphonium ions. Other protons in the molecule are relatively far removed from the phosphorus atom and quaternization of the phosphorus has a much smaller effect on them. If either nitrogen atom in the hydrazino group had become quaternized, the effect on the chemical shift on the N-CH$_3$ protons should be much greater. For instance, the N-CH$_3$ chemical shift in 2,2-dimethyltriazanium chloride is τ 6.47[11] or about 100 cps downfield from the N-CH$_3$ resonance in the present example.

The magnitude of the coupling constant J_{P-NH} decreases upon reaction of chloramine. This may reflect the change in effective nuclear charge on the phosphorus atom, in addition to the change in "s" character of the P-N bond.[13] Changes in dπ-pπ bonding in P-N groups will change the effective nuclear charge on the phosphorus atom. The study of a series of compounds containing the P-NH- group could clarify this relationship and perhaps lead to a method of estimating the extent of dπ-pπ bonding in phosphorus-nitrogen compounds.

The infrared spectrum of the chloramination product of 2-(*N*,*N*-dimethylhydrazino)-1,3,2-dioxophospholane (Table II) has a number of characteristic features, namely, N-H stretching and deformation bands at 3150 and 1570 cm^{-1}, respectively, C-H vibrations at 3050, 2950, 2815, 1450, and 1410 cm^{-1}, and strong absorptions characteristic of the P-O-C group at 1070, 1030, and 950 cm^{-1}. In the free hydrazinophospholane these P-O-C vibrations occur at 1040, 1015, and 920 cm^{-1}.

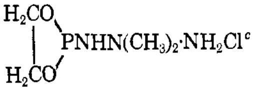
TABLE II

INFRARED DATA,[a] CM^{-1}



[b]

3260 m, 2975 m, 2940 s, 2880 m, 2850, 2810 m, 2760 m, 1470 s, 1460 m, 1440 m, 1400 w, 1215 w, sh, 1205 w, 1148 w, 1085 w, 1040 sh, 1015 s, 920 s, 880 s, 785 sh, 750 m, 695 s, 608 m, 590 w, 505 m

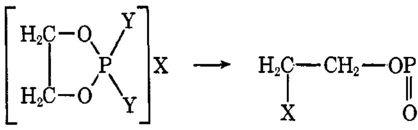


[c]

3150 s, 3050 s, 2950 sh, 2815 m, b, 2000 w, 1760 w, b, 1570 m, 1450 b, sh, 1410 s, 1300 m, b, 1220 m, b, 1070 s, sh, 1030 s, 950 s, 805 s, sh, 780 s, 755 sh, 675 m

[a] Key: s, strong; m, medium; w, weak; sh, shoulder; b, broad. [b] Examined neat between KBr plates. [c] Examined in KBr pellets and mulled in Nujol.

It is known[14] that compounds analogous to I rapidly undergo an Arbuzov rearrangement to a more stable form having a P=O group



Such a rearrangement would explain the low decom-

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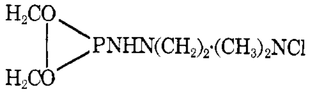
[12] S. R. Jain, W. S. Brey, Jr., and H. H. Sisler, *Inorg. Chem.*, **6**, 515 (1967).

[13] D. M. Grant and W. M. Litchman, *J. Amer. Chem. Soc.*, **87**, 3994 (1965).

[14] P. A. Rossiiskaya and M. I. Kabachnik, *Izv. Akad. Nauk SSR*, 509 (1947); *Chem. Abstr.*, **42**, 2924*b* (1948).

position temperature, the appearance of the P═O absorption in the infrared spectrum after heating, and the change in solubility properties.

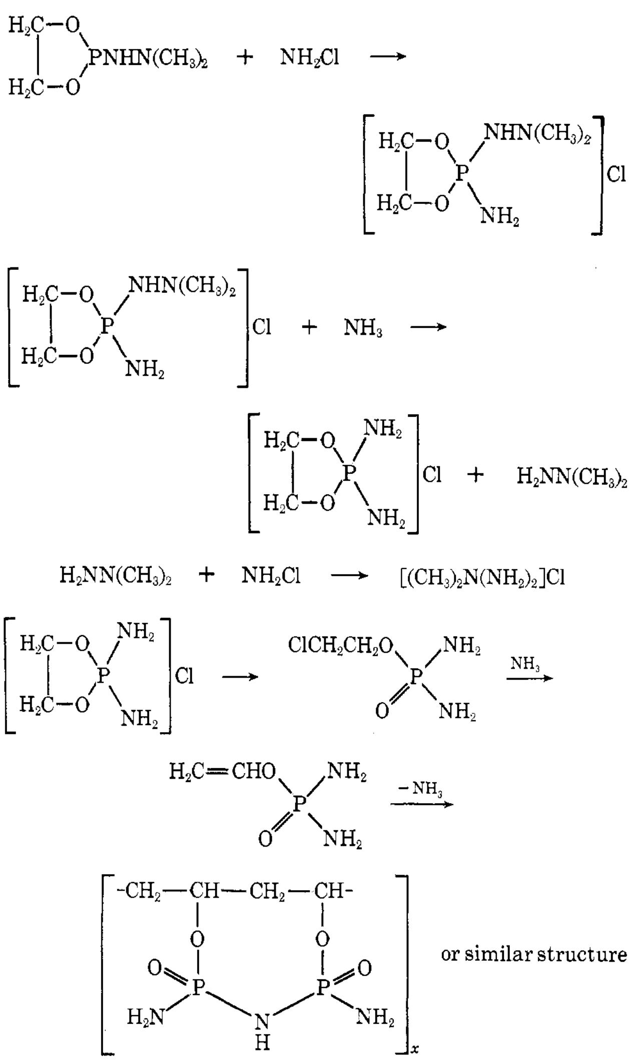
The reaction with ammonia also indicates the presence of a reactive species. The decrease in the amount of transamination with time may be caused by conversion to the oxide form which is inert[15] to transamination under the conditions of the experiment. Alternatively, the extent of transamination may be related to the crystallite size, the larger crystallites being less reactive. A slow rate of crystallization has been demonstrated in the reaction of 2-(*N*,*N*-dimethylhydrazino)-1,3,2-dioxophospholane with dimethylchloramine.[8] The product of this reaction is a viscous liquid which crystallizes with difficulty. The crystalline form melts at 165-167°; its analysis corresponds to the formula



Although dialkylaminophospholanes and arsolanes are known[16,17] to undergo transamination with ammonia and amines, 2-(*N*,*N*-dimethylhydrazino)-1,3,2-dioxophospholane does not react with excess ammonia under the same conditions which result in dimethylhydrazine evolution from the 1:1 addition product.

These considerations lead us to postulate the following sequence of reactions to describe the reaction of 2-(*N*,*N*-dimethylhydrazino)-1,3,2-dioxophospholane with chloramine and ammonia (see Scheme I). The products in this sequence which we have isolated are amino-2,2-dimethylhydrazinodioxophospholanium chloride, 1,1-dimethylhydrazine, 2,2-dimethyltriazanium chloride, and an intractable phosphorus-containing material with a P:N ratio of 2:3.

SCHEME I



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(15) R. P. Nielsen, J. R. Vincent, and H. H. Sisler, *Inorg. Chem.*, **2**, 760 (1963).

(16) R. Burgada, *Ann. Chim. (Paris)*, 15 (1966).

(27) L. Krannich, personal communication.

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Reactions of Dimethylchloramine and Ammonia-Free Chloramine with Trialkylarsines and Phenarsazines

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The reactions of a series of trialkylarsines with chloramine and dimethylchloramine yield in every case examined the corresponding aminoarsonium chlorides. Chloramination of some 5,10-dihydrophenarsazines demonstrates that the preferred site for amination is the arsenic atom rather than the nitrogen atom. Some theoretical implications of these results are discussed.

It has been established[1] in this laboratory that chloramine reacts with triphenylarsine and trimethylarsine to give good yields of the respective aminoarsonium chlorides. Other investigations[2,3] have shown that dimethylchloramine reacts with tertiary phosphines to give the respective aminophosphonium salts whereas dialkylphosphonates[4] and tris(dimethylamino)phosphine[2] behave differently, the latter forming $(R_2N)_3PCl^+Cl^-$. Other dialkylchloramines[5] react with tris(diethylamino)phosphine to give the chlorophospho-

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(1) H. H. Sisler and C. Stratton, *Inorg. Chem.*, **5**, 2003 (1966).

(2) S. R. Jain, L. K. Krannich, R. E. Highsmith, and H. H. Sisler, *ibid.*, **6**, 1058 (1967).

(3) R. M. Kren and H. H. Sisler, *ibid.*, **9**, 836 (1970).

(4) K. A. Petrov and G. A. Sohol'ski, *Zh. Obshch. Khim.*, **26**, 3377 (1956).

(5) D. B. Denney and S. M. Felton, *Inorg. Chem.*, **7**, 99 (1968).