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The Chloramination of Some Aminophosphines

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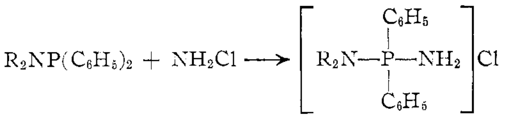
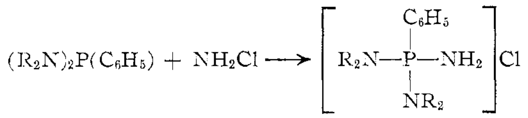
The reactions of NH_2Cl with some substituted aminophosphines—$R_2NP(C_6H_5)_2$, $(R_2N)_2PC_6H_5$, and $(R_2N)_3P$—produce the corresponding aminophosphonium chlorides $[(H_2N)(R_2N)(C_6H_5)_2P]Cl$, $[(H_2N)(R_2N)_2(C_6H_5)P]Cl$, and $[(H_2N)(R_2N)_3P]Cl$, respectively. Several aminophosphonium chlorides were converted to the hexafluorophosphate derivatives. Chemical and physical data indicate that the chloramination occurs on the phosphorus atom rather than the nitrogen atom of the aminophosphine. The reaction of NH_2Cl and NH_3 with $(C_2H_5)_2NP(Cl)(C_6H_5)$ yields $[(H_2N)_2\{(C_2H_5)_2N\}(C_6H_5)P]Cl$.

A variety of reactions have been used to prepare various aminophosphonium salts.[2-6] One of the most interesting of these is the reaction of chloramine with tertiary phosphines to yield aminophosphonium chlorides corresponding to the general formula $[R_3PNH_2]Cl$.[7]

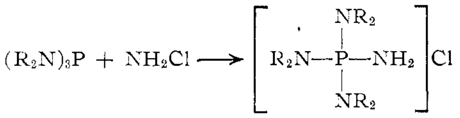
The present work was concerned with the chloramination of aminophosphines. Since the aminophosphines contain at least two potentially basic centers it was of interest to us to determine whether chloramination occurs at the phosphorus atom to yield aminophosphonium salts, or at the nitrogen atom to yield phosphinohydrazinium salts. The data reported herein indicate that the former process occurs and that chloramination of aminophosphines occurs in accordance with the reactions



$$R_2NP(C_6H_5)_2 + NH_2Cl \longrightarrow \left[R_2N-\overset{C_6H_5}{\underset{C_6H_5}{P}}-NH_2 \right] Cl$$



$$(R_2N)_2P(C_6H_5) + NH_2Cl \longrightarrow \left[R_2N-\overset{C_6H_5}{\underset{NR_2}{P}}-NH_2 \right] Cl$$



$$(R_2N)_3P + NH_2Cl \longrightarrow \left[R_2N-\overset{NR_2}{\underset{NR_2}{P}}-NH_2 \right] Cl$$

These studies have thus resulted in the formation of a variety of new di-, tri-, and tetraminophosphonium chlorides. The various new compounds prepared are listed in Table II.

Experimental

Materials.—Solvents used were dried over calcium hydride or sodium–lead alloy. The amines were fractionally distilled prior to the preparations of the aminophosphines. The Victor Chemical Works provided both the phenyldichlorophosphine and the diphenylchlorophosphine which were used as received. The aminophosphines were stored in an inert-atmosphere box.

Analyses.—Elemental analyses were done by Galbraith Microanalytical Laboratories. Several nitrogen analyses were obtained in these laboratories using a Coleman Model 27 nitrogen analyzer. Melting points were obtained in open Pyrex capillary tubes in a Thomas–Hoover capillary melting point apparatus and are uncorrected. Analytical and melting point data are listed in Table II.

Infrared Spectra.—The infrared spectra were determined on a Perkin-Elmer Model 137 spectrometer. The spectra of the solid materials were determined from Nujol mulls and those of the liquids from layers between sodium chloride plates. A summary of the spectral bands between 8.0 and 12.0 μ is found in Table III.

Nuclear Magnetic Resonance Spectra.—Nuclear magnetic resonance spectra, both ^1H and ^{31}P, were determined with a Varian Model V-4300-2 high resolution spectrometer equipped with a field homogeneity control, magnet insulation, and a superstabilizer. The spectra of liquids were determined from pure samples; the spectra of solids, from deuterated chloroform solutions. A summary of the data is found in Table IV.

Preparations of Aminophosphines.—Some of the aminophosphines prepared for chloramination have been reported previously.[8-10] However, using these methods several new aminophosphines were prepared. These include isopropylaminodiphenylphosphine, di-*n*-propylaminodiphenylphosphine, di-*n*-butylaminodiphenylphosphine, diisobutylaminodiphenylphosphine, *t*-butylaminophenylchlorophosphine, (N-methylbutylamino)phenylchlorophosphine, and bis(di-*n*-butylamino)phenylphosphine. Analytical data and boiling points of these compounds are listed in Table II.

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[1] From a dissertation accepted by the University of Florida in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] J. E. Gilpin, *Am. Chem. J.*, **19**, 332 (1897).

[3] A. Michaelis, *Ann.*, **326**, 129 (1903).

[4] W. T. Dye, Jr., U. S. Patent 2,774,658 (Dec. 18, 1956).

[5] H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 4733 (1961).

[6] H. Hoffman, L. Hower, H. G. Wippel, and D. Michael, *Chem. Ber.*, **95**, 523 (1962).

[7] H. H. Sisler, A. Sarkis, H. S. Ahuja, R. I. Drago, and N. L. Smith, *J. Am. Chem. Soc.*, **81**, 2982 (1959).

[8] H. H. Sisler and N. L. Smith, *J. Org. Chem.*, **26**, 611 (1961).

[9] G. Ewart, D. S. Payne, A. L. Porte, and A. P. Lane, *J. Chem. Soc.* 3984 (1962).

[10] A. Michaelis and K. Luxembourg, *Ber.*, **28**, 2205 (1895).

TABLE I

REACTION CONDITIONS FOR THE CHLORAMINATION REACTIONS

Compound	Solvent	Chlorami-nation time at 0°, min.	Stand-ing time at 25°, hr.	Product	Yield
$(i\text{-}C_3H_7)HNP(C_6H_5)_2$ (2.05 g.)	C_6H_6 (75 ml.)	10	3	$[H_2N\{(i\text{-}C_3H_7)HN\}(C_6H_5)_2P]Cl$[a]	1.5 g., 60.3%
$(t\text{-}C_4H_9)HNP(C_6H_5)_2$ (3.50 g.)	C_6H_6 (75 ml.)	12	24	$[H_2N\{(t\text{-}C_4H_9)HN\}(C_6H_5)_2P]Cl$[a]	2.68 g., 63.9%
$(C_2H_5)_2NP(C_6H_5)_2$ (4.68 g.)	C_6H_6 (75 ml.)	14	..	$[H_2N\{(C_2H_5)_2N\}(C_6H_5)_2P]Cl$[b]	3.02 g., 53.8%
$(n\text{-}C_3H_7)_2NP(C_6H_5)_2$ (2.00 g.)	$(C_2H_5)_2O$ (75 ml.)	10	48	$[H_2N\{(n\text{-}C_3H_7)_2N\}(C_6H_5)_2P]Cl$[b]	1.60 g., 67%
$\{(C_2H_5)_2N\}_2PC_6H_5$ (4.82 g.)	$(C_2H_5)_2O$ (75 ml.)	20	3	$[H_2N\{(C_2H_5)_2N\}_2(C_6H_5)P]Cl$[c]	2.76 g., 48%
$\{(n\text{-}C_3H_7)_2N\}_2PC_6H_5$ (4.60 g.)	$(C_2H_5)_2O$ (100 ml.)	15	2	$[H_2N\{(n\text{-}C_3H_7)_2N\}_2(C_6H_5)P]Cl$[c]	4.27 g., 79%
$\{(n\text{-}C_4H_9)_2N\}_2PC_6H_5$ (4.55 g.)	$(C_2H_5)_2O$ (50 ml.)	10	..	$[H_2N\{(n\text{-}C_4H_9)_2N\}_2(C_6H_5)P]Cl$[a]	4.10 g., 79%
$(C_2H_5)_2NPCl(C_6H_5)$ (4.75 g.)	C_6H_6 (100 ml.)	20 (40°)	4	$[(H_2N)_2\{(C_2H_5)_2N\}(C_6H_5)P]Cl$[a]	2.14 g., 43%
$\{(C_2H_5)_2N\}_3P$ (4.41 g.)	Pet. ether (75 ml.)	15	5	$[H_2N\{(C_2H_5)_2N\}_3P]Cl$[d]	3.14 g., 59%
$\{(n\text{-}C_3H_7)_2N\}_3P$ (4.30 g.)	Pet. ether (75 ml.)	10	..	$[H_2N\{(n\text{-}C_3H_7)_2N\}_3P]Cl$[e]	3.61 g., 71.3%
$\{(n\text{-}C_4H_9)_2N\}_3P$ (4.25 g.)	$n\text{-}C_6H_{14}$ (75 ml.)	10	5	$[H_2N\{(n\text{-}C_4H_9)_2N\}_3P]Cl$[f]	3.44 g., 72.1%

[a] Product dissolved in $CHCl_3$ and reprecipitated with petroleum ether. [b] Product dissolved in $CHCl_3$ and reprecipitated with $(C_2H_5)_2O$. [c] Product dissolved in $(CH_3)_2CO$ and reprecipitated with hexane. [d] Product recrystallized from hot hexane. [e] Product recrystallized from hot cyclohexane. [f] Product recrystallized from the mother liquor of the reaction mixture.

TABLE II

ANALYTICAL AND MELTING POINT DATA

		Analytical data							
	B.p., °C. (mm.) or	% C		% H		% N		% P	
Compound	M.p., °C.	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$(i\text{-}C_3H_7)HNP(C_6H_5)_2$	116–119° (0.09 mm.)	74.05	71.85	7.46	7.35	5.76	6.22		
$(n\text{-}C_4H_9)_2NP(C_6H_5)_2$	143° (0.2 mm.)	76.64	76.85	9.01	9.09	4.47	4.52	9.88	9.92
$(i\text{-}C_4H_9)_2NP(C_6H_5)_2$	148° (0.18 mm.)	76.64	76.08	9.01	9.09	4.47	4.46		
$(t\text{-}C_4H_9)HNPCl(C_6H_5)$	78–80° (0.1 mm.)	55.69	55.47	7.01	6.89	6.50	6.41	14.36	14.19
$(n\text{-}C_4H_9)(CH_3)NPCl(C_6H_5)$	103–106° (0.15 mm.)	57.52	57.28	7.46	7.29	6.09	6.21	13.48	13.55
$\{(n\text{-}C_4H_9)_2N\}_2PC_6H_5$	141° (0.14 mm.)					7.69	7.89		
$[(H_2N)\{(i\text{-}C_3H_7)HN\}(C_6H_5)_2P]Cl$	180–181°	61.12	61.03	6.84	6.87	9.50	9.57	10.51	10.53
$[(H_2N)\{t\text{-}C_4H_9)HN\}(C_6H_5)_2P]Cl$	201°[a]	62.23	62.22	7.18	7.36	9.07	9.12	10.03	10.04
$[(H_2N)\{(C_2H_5)_2N\}(C_6H_5)_2P]Cl$	175–177°	62.23	61.85	7.18	7.48	9.07	8.82	10.03	9.78
$[(H_2N)\{(n\text{-}C_3H_7)_2N\}(C_6H_5)_2P]Cl$	174–175°	64.18	64.29	7.78	7.88	8.32	8.20	9.20	9.00
$[(H_2N)\{(C_2H_5)_2N\}_2(C_6H_5)P]Cl$	175–176°	55.34	55.53	8.96	9.08	13.83	13.61	10.20	10.04
$[(H_2N)\{(n\text{-}C_3H_7)_2N\}_2(C_6H_5)P]Cl$	162–163°	60.06	60.09	9.80	10.01	11.68	11.68	8.60	8.75
$[(H_2N)\{(n\text{-}C_4H_9)_2N\}_2(C_6H_5)P]Cl$	82–83°	63.51	63.75	10.42	10.68	10.10	10.05	7.45	7.59
$[(H_2N)\{(C_2H_5)_2N\}_3P]Cl$	85–86°	48.23	48.24	10.79	10.88	18.75	18.60	10.37	10.19
$[(H_2N)\{(n\text{-}C_3H_7)_2N\}_3P]Cl$	153–154°	56.44	56.52	11.58	11.70	14.63	14.87	8.09	8.12
$[(H_2N)\{(n\text{-}C_4H_9)_2N\}_3P]Cl$	159–161°	61.70	61.86	12.08	12.20	11.00	13.06	6.63	6.56
$[(H_2N)\{(i\text{-}C_3H_7)HN\}(C_6H_5)_2P]PF_6$	170–171°	44.56	44.73	4.99	5.08	6.93	6.81	15.32	15.16
$[(H_2N)\{(t\text{-}C_4H_9)HN\}(C_6H_5)_2P]PF_6$	161–162°	45.95	45.93	5.30	5.39	6.70	6.71		
$[(H_2N)\{(C_2H_5)_2N\}(C_6H_5)_2P]PF_6$	169–170°	45.95	46.02	5.30	5.80	6.70	6.64		
$[(H_2N)\{(n\text{-}C_3H_7)_2N\}(C_6H_5)_2P]PF_6$	129–130°	48.43	48.40	5.87	5.98	6.28	6.33	13.88	14.08
$[(H_2N)\{(C_2H_5)_2N\}_3P]PF_6$	219–220°	35.29	35.30	7.90	8.02	13.72	13.98	15.17	15.31
$[(H_2N)_2\{(C_2H_5)_2N\}(C_6H_5)P]Cl$	148–150°	48.48	48.30	7.73	7.54	16.97	16.80	12.50	12.14
$(C_2H_5)_2NP(O)(C_6H_5)_2$	139–141°	70.31	69.19	7.38	7.41	5.13	5.17		

[a] With bubbling.

Procedure for Chloramination Reactions.—The chloramine generator used in this study is similar to those previously described.[11,12] The mixture of chloramine with nitrogen and excess ammonia delivered by this generator was passed into solutions of the compounds being treated. In all the chloraminations the rates of flow of ammonia, nitrogen, and chlorine into the generator were 1.2, 0.3, and 0.1 mole/hr., respectively. The experimental details for the various chloraminations are summarized in Table I. Several attempts to chloraminate di-*n*-butylaminodiphenylphosphine and diisobutylaminodiphenylphosphine produced oily liquids which were soluble in benzene, dioxane, and diethyl ether, but insoluble in petroleum ether. These materials could neither be crystallized nor distilled.

Hexafluorophosphate Derivatives.—With one exception (the amino-*t*-butylaminodiphenylphosphonium salt) the aminophosphonium hexafluorophosphates were prepared by mixing an aqueous solution of the aminophosphonium chloride with a saturated aqueous solution of potassium hexafluorophosphate and filtering off, washing, and drying the resulting white precipitate.

Amino-*t*-butylaminodiphenylphosphonium Hexafluorophosphate.—To an aqueous solution of amino-*t*-butylaminodiphenylphosphonium chloride was added a saturated aqueous solution of potassium hexafluorophosphate. A white precipitate formed immediately. The mixture was allowed to stand for a short time, and the precipitated crude product was filtered off, washed with water, and dried. The product was then dissolved in a small quantity of acetone and the solution treated with diethyl ether to precipitate white crystals of pure amino-*t*-butylaminodiphenylphosphonium hexafluorophosphate (m.p. 161–162°).

Diethylaminodiphenylphosphine Oxide.—The preparation of diethylaminodiphenylphosphine oxide is summarized by the equation

$$2(C_2H_5)_2NH + (C_6H_5)_2P(O)Cl \longrightarrow (C_2H_5)_2NP(O)(C_6H_5)_2 + (C_2H_5)_2NH_2Cl$$

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[11] R. Mattair and H. H. Sisler, *J. Am. Chem. Soc.*, **73**, 1619 (1951).

[12] H. H. Sisler, F. T. Neth, R. S. Drago, and D. Young, *ibid.*, **76**, 3906 (1954).

A solution of 9.44 g. of diphenylchlorophosphine oxide (0.037 mole) in 35 ml. of benzene was added dropwise, with stirring, to a solution of 7.30 g. of diethylamine (0.10 mole) in 50 ml. of benzene. After the addition was completed the reaction mixture was refluxed for 1 hr., allowed to stand overnight at room temperature, and filtered. The amine hydrochloride was washed with three small portions of dry benzene. The filtrate and wash liquor were combined and the solvent was evaporated under vacuum to yield a white solid, the crude diethylaminodiphenylphosphine oxide. The product was recrystallized from benzene by the addition of petroleum ether yielding white crystals of pure diethylaminodiphenylphosphine oxide (m.p. 136–139°, 7.75 g., 75% of theory). This material was also prepared by the reaction of diethylaminodiphenylphosphine in benzene solution with a large excess of activated manganese dioxide at reflux temperature over a 10-hr. period. The product obtained by the addition of petroleum ether to the reaction mixture melted at 139–141°.

The Chloramination of Diethylaminodiphenylphosphine Oxide.—No reaction was observed between diethylaminodiphenylphosphine oxide and chloramine under conditions similar to those used to prepare the aminophosphonium chlorides or at 40°. The aminophosphine oxide was virtually completely recovered with little change in melting point after prolonged exposure to chloramine.

Hydrolysis of Amino-*t*-butylaminodiphenylphosphonium Chloride.—Amino-*t*-butylaminodiphenylphosphonium chloride was hydrolyzed with aqueous sodium hydroxide. The volatile products of the hydrolysis were separated in a vacuum system by fractional condensation and identified as ammonia and *t*-butylamine by vapor pressure measurements. No evidence of the presence of a hydrazine derivative in the hydrolysate was found.

Discussion

Proof of Chloramination on the Phosphorus Atom.—Proof that the chloramination of aminophosphines occurs on the phosphorus atom rather than on the nitrogen atom is furnished by the results of the hydrolysis of amino-*t*-butylaminodiphenylphosphonium chloride, the fact that diethylaminodiphenylphosphine oxide does not undergo chloramination, the results of the chloramination of the hydrazinophosphines,[13] and infrared and nuclear magnetic resonance spectral data on the chloramination products.

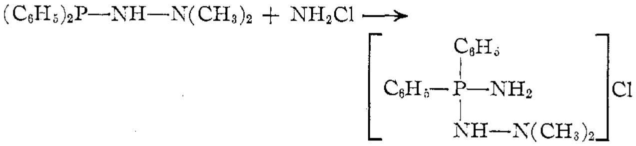
Volatile products from the basic hydrolysis of amino-*t*-butylaminodiphenylphosphonium chloride were found to be ammonia and *t*-butylamine. The equation for the hydrolysis is

$$[(H_2N)\{(t\text{-}C_4H_9)HN\}(C_6H_5)_2P]^+ + H_2O + OH^- \longrightarrow (C_6H_5)_2P(O)OH + NH_3 + t\text{-}C_4H_9NH_2$$

Had chloramination taken place on the nitrogen atom of the aminophosphine, *t*-butylhydrazine would have been isolated after the hydrolysis.

Chloramine does not react with diethylaminodiphenylphosphine oxide. When the phosphorus atom is blocked, no reaction occurs. This supports the argument that the phosphorus atom is the reactive site in the aminophosphine molecule.

The previously reported chloramination of hydrazinophosphines[13] invariably resulted in the chloramination occurring on the phosphorus atoms as illustrated by the equation



$$(C_6H_5)_2P{-}NH{-}N(CH_3)_2 + NH_2Cl \longrightarrow \left[\begin{array}{c} C_6H_5 \\ | \\ C_6H_5{-}P{-}NH_2 \\ | \\ NH{-}N(CH_3)_2 \end{array}\right]Cl$$

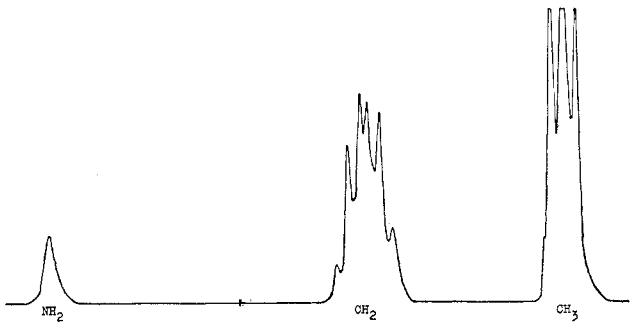


Fig. 1.—Proton magnetic resonance spectrum of aminotris(diethylamino)phosphonium chloride in deuterated chloroform.

The infrared spectra of the chloramination products of the various aminophenylphosphines have a strong absorption band between 1120 and 1110 cm.$^{-1}$. This band has been attributed to the presence of a quaternary phosphorus atom.[14] The infrared data are treated in a more detailed manner below, but the absorption band is cited here as evidence of chloramination on the phosphorus atom rather than the nitrogen atom.

Finally, the proton magnetic resonance spectrum of a deuterated chloroform solution of aminotris(diethylamino)phosphonium chloride (Fig. 1) indicates that all the ethyl groups of the compound are equivalent. Had chloramination occurred on one of the nitrogen atoms; the chemical shift of the ethyl groups on the quaternary nitrogen would be different from that of the other ethyl groups.

Infrared Spectra.—The infrared spectra of the compounds prepared during this study have many absorption bands which may be readily assigned from general infrared data. Among the more readily identified bands is the N–H stretching absorption near 3330 cm.$^{-1}$. The 3120 to 2860 cm.$^{-1}$ region is characterized by the phenyl C–H, the methyl C–H, and the methylene C–H stretching vibration absorptions. Three or four weak absorptions attributed to the phenyl group are found between 2000 and 1760 cm.$^{-1}$. A band of weak to medium intensity at 1590 cm.$^{-1}$ is assigned to the phenyl "C=C" vibration. Another phenyl "C=C" absorption band is found near 1460 cm.$^{-1}$, but in some spectra the band is not completely resolved from the C–H deformation band occurring at about 1450 cm.$^{-1}$. A strong, sharp absorption band found between 1450 and 1430 cm.$^{-1}$ is assigned to a P–phenyl vibration. The carbon–methyl C–H vibration is found at 1370 cm.$^{-1}$. A weak band between 1000 and 990 cm.$^{-1}$ has been assigned to a P–phenyl vibration. A strong, broad band characteristic of the PF_6^- group is found at

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

(14) J. C. Sheldon and S. Y. Tyree, Jr., *J. Am. Chem. Soc.*, **81**, 6177 (1959).

TABLE III[a]

INFRARED DATA IN THE RANGE 1250 TO 833 CM.$^{-1}$

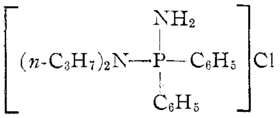
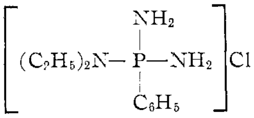
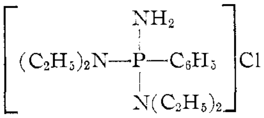
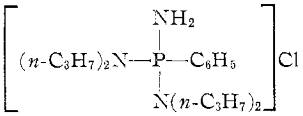
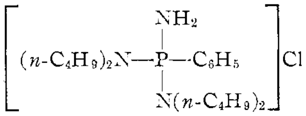
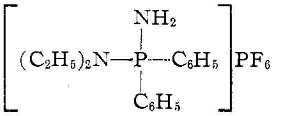
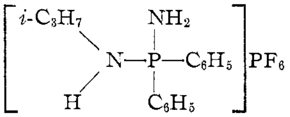
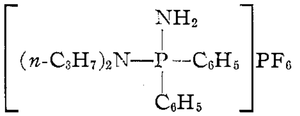
$(i\text{-}C_3H_7)HNP(C_6H_5)_2$	1164 m 1136 m	1093 m 1067 w 1026 w	1000 w, sh 996 m	867 w
$(t\text{-}C_4H_9)HNP(C_6H_5)_2$	1218 s	1091 m 1066 w 1026 w	980 m	
$(C_2H_5)_2NP(C_6H_5)_2$	1181 s	1089 m 1066 w 1021 s	998 w 924 m	
$(n\text{-}C_3H_7)_2NP(C_6H_5)_2$	1175 m	1091 m 1067 w 1038 w 1026 w 1006 m	996 m	877 w
$(n\text{-}C_4H_9)_2NP(C_6H_5)_2$	1166 m	1111 w, sh 1093 s 1070 w 1050 w 1029 s	999 w 990 w 930 s	
$(i\text{-}C_4H_9)_2NP(C_6H_5)_2$	1164 m	1088 s 1066 w 1016 s	1000 m 944 vw	881 w
$(CH_3)(n\text{-}C_4H_9)NPCl(C_6H_5)$	1203 m 1166 m	1091 s 1070 w 1049 m 1019 s 1005 m	1000 m 975 m 954 m 935 m	870 w
$(C_2H_5)_2NPCl(C_6H_5)$	1193 s 1164 s	1087 s 1047 m 1020 s	996 m 927 s 919 m	
$(t\text{-}C_4H_9)HNPCl(C_6H_5)$	1208 s	1093 m 1065 w 1031 m	990 s 926 w	848 s
$\{(C_2H_5)_2N\}_2PC_6H_5$	1183 s	1088 m 1067 w 1048 m 1019 s 1010 s	916 s	
$\{(n\text{-}C_3H_7)_2N\}_2PC_6H_5$	1176 s	1088 m 1026 m	990 s	893 w 875 m
$\{(n\text{-}C_4H_9)_2N\}_2PC_6H_5$	1242 w 1227 m 1170 s 1115 w	1093 s 1064 w 1052 w 1026 s	990 m 980 m 926 s	902 m 864 w
$\{(C_2H_5)_2N\}_3P$	1190 s 1155 s	1101 m 1070 w 1053 m 1010 s		909 s 887 s
 $\left[(n\text{-}C_3H_7)_2N{-}\overset{NH_2}{\underset{C_6H_5}{P}}{-}C_6H_5\right]Cl$	1245 w 1188 m 1152 s 1116 s	1086 m 1030 s, sh 1025 s 1020 s, sh	994 m 971 s	893 w 875 w
 $\left[(C_2H_5)_2N{-}\overset{NH_2}{\underset{C_6H_5}{P}}{-}NH_2\right]Cl$	1244 w 1250 m 1163 s 1124 s	1100 m 1066 m 1026 s	996 m	903 m
 $\left[(C_2H_5)_2N{-}\overset{NH_2}{\underset{N(C_2H_5)_2}{P}}{-}C_6H_5\right]Cl$	1205 s 1160 s 1122 s	1098 w 1064 w 1030 s, sh 1024 s	996 w 982 m 957 m 934 w 923 w	
 $\left[(n\text{-}C_3H_7)_2N{-}\overset{NH_2}{\underset{N(n\text{-}C_3H_7)_2}{P}}{-}C_6H_5\right]Cl$	1193 m 1163 s 1126 s	1109 w 1095 m 1075 w 1035 s 1020 s	983 m	895 w 876 m
 $\left[(n\text{-}C_4H_9)_2N{-}\overset{NH_2}{\underset{N(n\text{-}C_4H_9)_2}{P}}{-}C_6H_5\right]Cl$	1224 w 1176 m 1156 s 1124 s	1095 m 1037 s	999 s 935 s	901 w 877 w
$[\{(C_2H_5)_2N\}_3PNH_2]Cl$	1208 s 1170 s	1099 m 1078 m 1062 m 1020 vs	996 s 963 s 929 m	
$[\{(n\text{-}C_3H_7)_2N\}_3PNH_2]Cl$	1250 w 1193 s 1160 s	1106 m 1094 s 1032 s 1010 s	970 m	895 m

TABLE III (*Continued*)

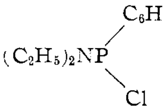
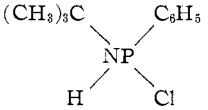
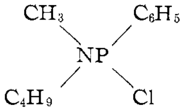
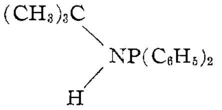
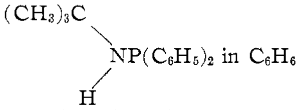
$[\{(n\text{-}C_4H_9)_2N\}_3PNH_2]Cl$	1229 w 1186 m 1161 s 1117 m	1100 m 1042 s	1000 m 933 s	903 w
 $\left[(C_2H_5)_2N\text{—}\overset{NH_2}{\underset{C_6H_5}{P}}\text{—}C_6H_5\right]PF_6$	1206 w 1160 m 1120 m	1105 w 1066 w 1032 m	998 w 978 w 930 w 924 w	840 vs, b
	1164 w 1136 s 1130 s	1106 w 1075 w 1053 m 1026 w	1000 w 963 m 943 w	893 m 840 vs, b
 $\left[(n\text{-}C_3H_7)_2N\text{—}\overset{NH_2}{\underset{C_6H_5}{P}}\text{—}C_6H_5\right]PF_6$	1189 m 1149 m 1117 s	1087 w 1040 m 1016 s	943 w, b	840 vs, b
$[\{(C_2H_5)_2N\}_3PNH_2]PF_6$	1212 s 1168 s	1099 w 1063 w 1026 s	971 m	840 vs, b

[a] s, strong; m, medium; w, weak; b, broad; sh, shoulder; v, very; wave lengths in μ.

TABLE IV

CHEMICAL SHIFTS OF NUCLEAR MAGNETIC RESONANCE PEAKS

τ in p.p.m., multiplet separation in c.p.s.

	^{1}H Shifts in p.p.m. from $(CH_3)_4Si$				^{31}P Shifts in p.p.m. from H_3PO_4 (85%)
Compound	NH	C_6H_5	CH_2	CH_3	
	...	2.76 Double pattern	7.27 Doublet (11.9 c.p.s.) Quartet (6.9 c.p.s.)	9.12 Triplet (6.8 c.p.s.)	−118
	6.98 Doublet (15.1 c.p.s.)	2.84 Double pattern	...	9.02[a] Doublet (1.4 c.p.s.)	−118
	...	2.76 Double pattern	8.92 Multiplet 7.96 (on N) Triplet (6.7 c.p.s.) Doublet (13.4 c.p.s.)	7.82 Doublet (11.8 c.p.s.) 9.36 (on CH_2) Triplet (5.6 c.p.s.)	Not determined
	8.41 Doublet (11.5 c.p.s.)	3.21	...	9.19 Singlet	−22.4
	8.66 Doublet (12 c.p.s.)	Below and under solvent	...	9.40 Singlet	−21.6
$(C_3H_7)_2NP(C_6H_5)_2$	...	2.82	7.07 (on N) Multiplet 8.71 Multiplet	9.35 Triplet (6.2 c.p.s.)	−62
$\{(C_3H_7)_2N\}_2PC_6H_5$	...	2.91	7.38 (on N) Multiplet 8.67 Multiplet	9.60 Triplet	−98
$\{(C_2H_5)_2N\}_2PC_6H_5$	...	3.06	7.25 Doublet (9.4 c.p.s.) Quartet (7.0 c.p.s.)	9.24 Triplet (7.0 c.p.s.)	−98
$\{(C_2H_5)_2N\}_3P$	...	...	7.25 Doublet (7.3 c.p.s.) Quartet (6.7 c.p.s.)	9.17 Triplet (6.7 c.p.s.)	−118
$[\{(C_2H_5)_2N\}_3PNH_2]Cl$	3.53 Singlet	...	6.68 Quartet (7.1 c.p.s.) Doublet (10.7 c.p.s.)	8.67 Triplet (7.1 c.p.s.)	−63

[a] The same splitting is observed at 19.3 Mc.

833 cm.$^{-1}$ in the spectra of the hexafluorophosphates. Two strong absorptions characteristic of the phenyl C–H out-of-plane deformation occur at about 746 and 690 cm.$^{-1}$.

The region between 1250 and 830 cm.$^{-1}$ has a large number of peaks which may not be assigned with certainty. Table III lists the absorption bands in this range for compounds produced in this study and some produced by earlier workers.

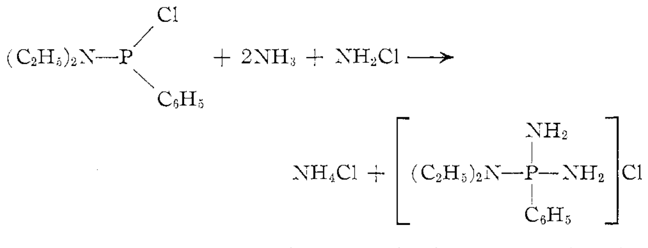
A strong absorption band (in some spectra there appear to be two) at about 1175 cm.$^{-1}$ may possibly be attributed to the C–N vibration in the aminophosphines and in the aminophosphonium salts.

The general occurrence of a band of strong intensity between 1120 and 1110 cm.$^{-1}$ in the spectra of the aminophosphonium salts having a P–phenyl linkage is noted. The peak is also observed in the spectra of other tetracovalent phosphorus compounds having a P–phenyl bond. Sheldon and Tyree[14] associated this peak with the phosphonium cation, but it is better associated with a tetracoordinate phosphorus group having a P–phenyl bond. For example, this band does not appear in the spectrum of $[[(C_2H_5)_2N]_3PNH_2]Cl$.

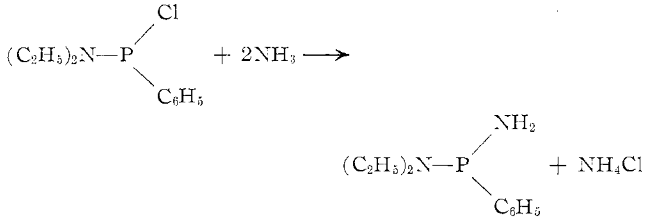
Two bands, one between 1100 and 1085 cm.$^{-1}$ (medium to strong intensity) and the other between 1075 and 1060 cm.$^{-1}$ (weak), are generally observed in the spectra of compounds prepared during this study. These bands have also been observed in many other phosphorus compounds. Because of the generality of their occurrence, no assignments can be made at this time.

The Nitrogen–Phosphorus Bond.—In the light of the proposed mechanism for the chloramination of nitrogen bases,[15–17] it is reasonable to suppose that the chloramination of Lewis bases generally occurs by an S_N2 process. Thus, the site at which chloramine reacts with an aminophosphine should depend on the availability of an unshared electron pair at the basic site. Since chloramination of the aminophosphines occurs only on the phosphorus atoms, we believe that the basicity of the nitrogen atom is reduced in these aminophosphine derivatives. This deactivation of the nitrogen electron pair may be brought about by a partial donation of the free pair of electrons on the nitrogen atom into vacant d-orbitals of the phosphorus atom. Furthermore, the fact that diethylaminodiphenylphosphine oxide is inert to chloramination yields additional evidence that deactivation of the unshared electron pair on the nitrogen atom has taken place.

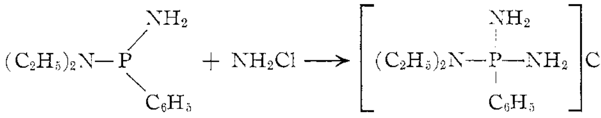
The Reaction of Ammonia, Chloramine, and Diethylaminophenylchlorophosphine.—The reaction of ammonia and chloramine with diethylaminophenylchlorophosphine may be represented by the equation



Since a large excess of ammonia is present in the effluent gas from the chloramine generator and since it is known that ammonolysis of P–Cl bonds occurs very rapidly, the first step in the reaction is probably the ammonolysis of the P–Cl bond.



The aminophosphine then reacts with chloramine.



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(16) R. S. Drago and H. H. Sisler, *ibid.*, **77**, 3191 (1955).
(17) G. M. Omietanski and H. H. Sisler, *ibid.*, **78**, 1211 (1956).