$(BH_3)_2]$ with $NaB(C_6H_5)_4$ in Water.—An approximately 0.6-mmole sample of the appropriate salt in 3 ml of H_2O at 0° was treated with an equimolar quantity of $NaB(C_6H_5)_4$ contained in 15 ml of ice water. The white precipitate which formed was filtered off in about 3 min, washed with ice water, and dried at 100°. The theoretical amount of $[R_2NH_2][B(C_6H_5)_4]$, R = H or CH_3, was obtained from the filter (X-ray powder pattern identification). $NaH_2P(BH_3)_2$ was identified in the filtrate by nmr.

The Hydrolysis of $[NH_4][H_2P(BH_3)_2]$.—A 0.500-mmole sample of $[NH_4][H_2P(BH_3)_2]$ was placed in a reaction tube; the tube was evacuated, then 3–4 ml of 6 *N* HCl was frozen in. After sealing the tube and allowing it to warm to +85° overnight, the contents were cooled to −196° and the tube opened to the vacuum line. The noncondensable gas recovered corresponded to 3.01 mmoles of H_2; the remaining volatile products were distilled through traps held at −78, −112, and −196°. A 0.332-mmole sample of PH_3 was recovered in the −196° trap (when necessary the PH_3 was separated from HCl by forming an azeotrope with H_2O and distilling off the free PH_3). The solid remaining contained NH_4Cl and $B(OH)_3$ (X-ray powder pattern). Boron present in the products was determined by titration in the presence of mannitol as described elsewhere:[13] experimental, 27.5%; theoretical based on equation, 28.7%. The equation which is consistent with all of the observation is

$$M[H_2P(BH_3)_2] + 6H_2O + HCl \longrightarrow H_3P + MCl + 6H_2 + 2B(OH)_3$$

The Reaction of $[(CH_3)_2NH_2][H_2P(BH_3)_2]$ with $NaNH_2$.—A 1.07-mmole sample of $[(CH_3)_2NH_2][H_2P(BH_3)_2]$ was mixed in a vacuum line reaction tube with a 1.74-mmole sample of $NaNH_2$[14] in a drybox. Immediate evolution of ammonia required rapid transfer of the tube to the vacuum line and freezing of the contents to −196°. After evacuation of the air, the system was allowed to warm to 25°, held for 30 min, and then raised to 100° for 45 min. Gaseous products which were evolved were fractionated and identified by vapor pressure measurements as NH_3 and $(CH_3)_2NH$. The white solid which remained was identified by infrared spectroscopy as $Na[H_2P(BH_3)_2]$.

This reaction was also run in formamide; a sample (0.88 mmole) of $[(CH_3)_2NH_2][H_2P(BH_3)_2]$, 1.00 mmole of $NaNH_2$, and 2 ml of formamide were mixed. The $NaNH_2$ was added to a frozen solution of $[(CH_3)_2NH_2][H_2P(BH_3)_2]$ by rapidly removing the nitrogen-filled reaction tube from the line, adding solid $NaNH_2$, then rapidly replacing the reaction tube and evacuating the system. A sample (0.92 mmole) of gas was identified as NH_3 and a 0.84-mmole sample of gas was identified as $(CH_3)_2NH$. Formamide could not, however, be removed from the solid product.

Attempted Preparation of $Na[H_2P(BH_3)_2]$ by the Reaction of $NaPH_2$ and B_2H_6.—A solution of $NaPH_2$ in liquid NH_3, prepared by the reaction of Na with PH_3 in NH_3,[15] was filtered in the vacuum filtration apparatus. The volatiles were then removed at −78° (12 hr); then the N_2-filled, stoppered tube was transferred to the drybox where a sample (0.238 mmole) of $NaPH_2$ was weighed into a vacuum line reaction tube. After evacuation of the tube on the vacuum line, a 1.36-mmole sample of B_2H_6 was distilled into the system. The B_2H_6 was allowed to melt and held in contact with the solid phase for about 1 hr; the system was then warmed to room temperature and held for 12 hr. All but 0.07 mmole of B_2H_6 was recovered from the system. No evidence for $NaH_2P(BH_3)_2$ was found in the solid.

Attempts to dissolve $NaPH_2$ in diethyl ether and diglyme were unsuccessful. When NH_3 was used as a solvent, only $[(H_3N)_2BH_2]BH_4$ was detectable as a solid product [nmr in liquid NH_3 at −45°].

Physical Measurements.—Infrared spectra were obtained using a Beckman IR-12. Nmr spectra for ^{11}B and ^{31}P were obtained with a Varian Associates H-R 100 instrument operating at 94.1 and 40.4 Mc, respectively. Chemical shifts were determined by tube interchange. Proton nmr spectra were obtained with a Varian Associates HA-60 instrument.

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Studies in the Synthesis and Chloramination of Some Hydrazinophosphines

BY JOSEPH M. KANAMUELLER AND HARRY H. SISLER

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The new hydrazino phosphine derivatives $P[N(CH_3)N(CH_3)_2]_3$ and $C_6H_5P[N(CH_3)N(CH_3)_2]_2$ were prepared. The chloraminations of $C_6H_5P[N(CH_3)N(CH_3)_2]_2$, $[(C_6H_5)_2P]_2NN(CH_3)_2$, and $[(C_6H_5)_2P]_2NN[P(C_6H_5)_2](CH_3)$ were carried out in both the presence and absence of ammonia. As found in previous studies of P–N compounds, the phosphorus atoms are the sites of the chloramination reaction. In the absence of ammonia no dehydrochlorination occurs and multiply charged complex aminophosphonium ions are obtained from the chloramination of the bis- and trisphosphinohydrazines.

Recent work has shown that hydrazinophosphines can be prepared by allowing chlorophosphines to react, in the presence of an HCl acceptor, with hydrazines containing an N–H group.[1] We have used this method to prepare tris(1,2-trimethylhydrazino)phosphine and bis(1,2,2-trimethylhydrazino)phenylphosphine.

The reactions of chloramine with hydrazinophosphines and aminophosphines have indicated that the hydrazino or amino nitrogens apparently are inert to attack by chloramine;[2–5] it is rather the phosphorus

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[1] R. P. Nielsen and H. H. Sisler, *Inorg. Chem.*, **2**, 753 (1963).

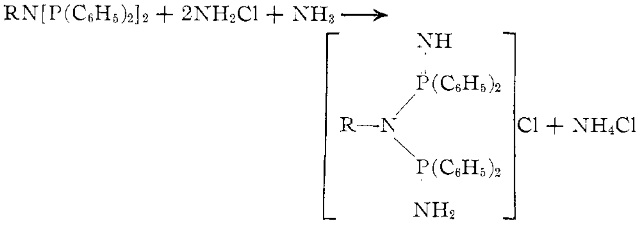
[2] R. P. Nielsen, J. P. Vincent, and H. H. Sisler, *ibid.*, **2**, 760 (1963).

[3] H. H. Sisler and J. Weiss, *ibid.*, **4**, 1514 (1965).

[4] W. A. Hart and H. H. Sisler, *ibid.*, **3**, 617 (1964).

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

atom that is the site for amination by the chloramine molecule. Furthermore, if bis(diphenylphosphino)-hydrazines or amines are allowed to react with chloramine in the presence of ammonia dehydrohalogenation occurs,[2,5] as indicated by the equation



$$RN[P(C_6H_5)_2]_2 + 2NH_2Cl + NH_3 \longrightarrow \left[R{-}N\begin{matrix} \overset{NH}{\overset{\|}{P}}(C_6H_5)_2 \\ \underset{NH_2}{P}(C_6H_5)_2 \end{matrix} \right]Cl + NH_4Cl$$

In the present study, we have also carried out the reaction of ammonia-free chloramine[6] with 1,1-bis(diphenylphosphino)2,2-dimethylhydrazine. A double chloramination product which does not undergo dehydrohalogenation results. 1,1,2-Tris(diphenylphosphino)2-methylhydrazine was allowed to react with chloramine both in the presence and in the absence of ammonia yielding two products. With ammonia present, the expected dehydrohalogenated product was obtained as a chloroform adduct. In the absence of ammonia, however, a doubly chloraminated product appears to have resulted, with no dehydrohalogenation occurring. We have also carried out the reaction of chloramine with $(C_6H_5)P[NCH_3N(CH_3)_2]_2$ and found it to yield the expected aminophosphonium chloride, $[C_6H_5P(NH_2)[NCH_3N(CH_3)_2]_2]Cl$.

Experimental Section

Material.—Phosphorus trichloride was obtained from J. T. Baker Chemical Co. and was distilled under nitrogen prior to use, bp 75.5° (760 mm). Phenyldichlorophosphine, Victor Chemical Co., was vacuum distilled, bp 65° (2 mm). 1,1,1-Trimethylhydrazine was prepared according to the method of Class, *et al.*,[7] and was distilled from calcium hydride, bp 59.5–61.0° (760 mm). Triethylamine, obtained from the Eastman Kodak Co., was refluxed over potassium hydroxide for 18 hr and then distilled, bp 88–89° (760 mm).

The hydrazinophosphines, 1,1-bis(diphenylphosphino)2,2-dimethylhydrazine, mp 137–39°, and 1,1,2-tris(diphenylphosphino)2-methylhydrazine, mp 155.5–157.0°, were prepared according to the procedures given by Nielsen and Sisler.[1]

The gaseous mixture of ammonia and chloramine was produced by the reaction of chlorine and ammonia in a generator according to the Sisler–Mattair process.[8,9] The rate of production of chloramine was 0.1 mole/hr. Ethereal chloramine solutions were freed from ammonia by passing the solutions over anhydrous copper sulfate.[6] The chloramine contents of the solutions were determined by allowing aliquot samples of the chloramine solution to react with acidified potassium iodide solution, the iodine released being titrated with a standard sodium thiosulfate solution.

Manipulations and reactions were carried out in an atmosphere of nitrogen.

Analyses.—Elementary analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. Melting points were determined using sealed capillary tubes and are corrected.

Infrared Spectra.—Infrared spectra were obtained on a Beckman IR-10 spectrophotometer. The spectra of the crystalline solids were obtained in Halocarbon oil–Nujol mulls, those of the liquids as films between potassium bromide disks. The principal bands in the spectra of the various compounds are listed in Table I.

TABLE I

INFRARED ABSORPTION FREQUENCIES (CM^{-1})[a]

$P[NCH_3N(CH_3)_2]_3$ (pure liquid between KBr disks)

2970 (s), 2920 (s), 2840 (s), 2780 (s), 1450 (s), 1395 (m), 1225 (m), 1145 (m), 1090 (s), 1060 (m), 1015 (m), 985 (m), 840 (s), 815 (s), 640 (s), 625 (sh), 540 (m), 490 (sh), 480 (m), 450 (s)

$C_6H_5P[NCH_3N(CH_3)_2]_2$ (pure liquid between KBr disks)

3060 (w, db), 2980 (m), 2940 (s), 2880 (sh), 2850 (s), 2830 (sh), 2770 (m), 1585 (w), 1480 (m), 1450 (m), 1445 (s), 1400 (sh), 1300 (w), 1260 (w), 1225 (m), 1180 (w), 1150 (w), 1115 (m), 1090 (s), 1030 (w), 1015 (m), 985 (m), 970 (m), 920 (w, br), 845 (s), 750 (s), 705 (s), 650 (m), 620 (w, db), 540 (m), 500 (sh), 475 (m)

$[C_6H_5P(NH_2)[NCH_3N(CH_3)_2]_2]Cl$ (halocarbon oil–Nujol mull)

3080 (m), 3050 (m), 2980 (sh), 2940 (s), 2895 (sh), 2790 (w, db), 2560 (w, br), 2250 (w, br), 1950 (w, br), 1880 (w), 1820 (w), 1590 (m), 1560 (m), 1530 (sh), 1510 (w), 1455 (s), 1435 (s), 1410 (w, db), 1260 (w), 1230 (m), 1210 (w), 1185 (w), 1150 (w), 1130 (s), 1105 (m), 1090 (sh), 1080 (m), 1020 (m), 995 (m), 965 (m), 870 (s), 850 (m), 745 (s), 730 (m), 690 (m), 670 (sh), 650 (w), 520 (s), 505 (s), 470 (w), 445 (w)

$[[(C_6H_5)_2PNH_2]_2NN(CH_3)_2]Cl_2$ (halocarbon oil–Nujol mull)

3150 (s), 3040 (s), 2980 (sh), 2820 (sh), 2300 (w, br), 1900 (w, br), 1810 (w, br), 1590 (m), 1560 (m), 1540 (sh), 1480 (m), 1475 (w), 1435 (s), 1370 (sh), 1290 (sh), 1250 (s, br), 1180 (w), 1160 (w), 1120 (s), 1070 (w), 1025 (w), 995 (m), 970 (m), 935 (w), 920 (sh), 850 (w), 750 (s), 720 (s), 690 (s), 670 (sh), 550 (sh), 525 (s), 510 (sh), 450 (w)

$[[(C_6H_5)PNH_2][(C_6H_5)_2PNH]NNCH_3[H_2NP(C_6H_5)_2]]Cl_2 \cdot CHCl_3$ (halocarbon oil–Nujol mull)

3160 (s), 3050 (s), 2550 (w, br), 2250 (w, br), 1950 (w, br), 1880 (w, br), 1805 (w), 1760 (w, br), 1655 (w, br), 1585 (m), 1565 (s), 1475 (m), 1435 (s), 1370 (sh), 1300 (sh), 1250 (s), 1185 (w), 1120 (s), 1010 (w), 995 (w), 965 (s), 945 (m), 745 (s), 720 (s), 685 (s), 670 (sh), 535 (sh), 520 (s), 500 (m), 440 (w)

$[[(C_6H_5)_2PNH_2]_2NNCH_3[P(C_6H_5)_2]]Cl$ (halocarbon oil–Nujol mull)

3150 (s), 3050 (s), 2960 (s), 2860 (sh), 2520 (w), 2280 (w, br), 1900 (w, br), 1820 (w, br), 1760 (w, br), 1665 (w, br), 1590 (s), 1565 (m), 1540 (sh), 1480 (m), 1435 (s), 1380 (w), 1300 (sh), 1250 (s), 1180 (s), 1155 (sh), 1120 (s), 1100 (sh), 1070 (w), 1025 (w), 995 (m), 975 (m), 935 (sh), 880 (w), 850 (w), 780 (m), 750 (s), 725 (s), 690 (s), 670 (sh), 560 (s, db), 530 (s), 510 (s), 450 (w).

[a] s, strong; m, moderate; w, weak; br, broad; sh, shoulder; db, doublet.

Nuclear Magnetic Resonance Spectra.—Proton nuclear magnetic resonance spectra were obtained on a Varian Model A-60-A nmr spectrometer. For the ^{31}P resonance spectra, a Varian high-resolution Model V-4300 nmr spectrometer was used. The chemical shift values are listed in Table II.

Preparation of Tris(1,2,2-trimethylhydrazino)phosphine.—With stirring, cooling in an ice bath, and under a dry nitrogen atmosphere, 20.6 g of phosphorus trichloride (0.15 mole) in 25 ml of dry toluene was slowly added to a solution of 33.3 g of 1,1,2-trimethylhydrazine (0.45 mole) with 54.7 g of triethylamine (0.54 mole) in 75 ml of dry toluene. Upon completion of this addition, the mixture was allowed to warm to room tempera-

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TABLE II

NUCLEAR MAGNETIC RESONANCE DATA

Chemical shift, ppm[a]				Peak-area ratios		
^1H[b]	^{31}P[c]	Assignment	Coupling constants, cps	Assignment	Theory	Found
		$P[N(CH_3)N(CH_3)_2]_3$[d]				
7.63		N-Methyl	$J_{PNCH} = 4.5$			
7.57		N-Dimethyl				
7.55		N-Methyl				
	−101.5					
		$C_6H_5P[NCH_3N(CH_3)_2]_2$[d]				
7.66		N-Dimethyl	$J_{PNCH} = 5.0$	Phenyl : methyl	1:3.60	1:3.52
7.60		N-Methyl				
7.52		N-Methyl				
3.00		Phenyl				
	−80.2					
		$[C_6H_5P(NH_2)[NCH_3N(CH_3)_2]_2]Cl$[e]				
7.57		N-Dimethyl	$J_{PNCH} = 9.0$	Phenyl : amino	2.5:1	2.92:1
7.02		N-Methyl		N-Methyl: N-dimethyl	3:6	3.0:6.6
7.17		N-Methyl	$J_{PNH} = 6.0$			
3.13 d		Amino				
2.38–2.60		Phenyl				
1.64-1.87		Phenyl				
	−39.9					
		$[[(C_6H_5)_2PNH_2]_2NN(CH_3)_2]Cl_2]$				
7.38		Methyl		Phenyl:amino	5:1	12.4:1
7.28		Methyl				
3.63		Amino				
2.83 v br		Amino				
2.51 cm		Phenyl				
	−1.51 ± 1.3					
		$[[(C_6H_5)_2PNH][(C_6H_5)_2PNH_2]NNCH_3[H_2NP(C_6H_5)_2]]Cl_2 \cdot CHCl_3$[e,f]				
4.02		Amino		Phenyl:amino	30:4	30:5[e]
2.47 cm		Phenyl				
	−12.6 ± 2.6 v br					
		$[[(C_6H_5)_2PNH_2]_2NNCH_3[P(C_6H_5)_2]]Cl_2$[c]				
7.32		Methyl	$J_{PNCH} = 10.5$	Phenyl:amino	5:1	4.75:1
7.07		Methyl				
6.42		Amino				
3.85 w, br		Amino				
2.53		Phenyl				
	−36.7 ± 2.6[g]					

[a] b, broad; cm, complex multiplet; d, doublet; v, very; w, weak. [b] τ value. [c] Referred to H_3PO_4, saturated dimethyl sulfoxide solutions. [d] Pure liquid, TMS external standard. [e] Saturated deuteriodimethyl sulfoxide solution, TMS internal standard. [f] Methyl protons not observed due to undeuterated dimethyl sulfoxide present. The proton resonance signal attributable to $CHCl_3$ is mixed with that from the phenyl proton, which is a complex multiplet. [g] Two signals appear to be present.

ture and refluxed gently for several hours. The white solid reaction product, triethylammonium chloride, was filtered off and washed with small portions of toluene; weight 38.9 g (93.5% of theory), mp 252–254° (lit. 254°). The solvent was removed from the combined filtrate and washings yielding 31.1 g of a yellow oil (83% of theory based on PCl_3). This oil was then fractionated at 0.45 mm, the fraction distilling between 82.5 and 83.0° being collected; yield 10.0 g (26.7% of theory) of a colorless liquid. *Anal.* Calcd for $C_9H_{27}N_6P$: C, 43.18; H, 10.87; N, 33.57; P, 12.37. Found: C, 41.96; H, 10.58; N, 31.52; P, 12.10. The method of preparation and analytical data indicate this product to be $P[NCH_3N(CH_3)_2]_3$ but not of high purity. The infrared and nmr spectra are also consistent with this formulation.

Preparation of Bis(1,2,2-trimethylhydrazino)phenylphosphine.—In a reaction procedure similar to that described above, a solution of 11.1 g of 1,1,2-trimethylhydrazine (0.15 mole), 21.7 g of triethylamine (0.22 mole), and 25 ml of dry benzene was slowly added to 13.4 g of phenyldichlorophosphine (0.075 mole) in 50 ml of dry benzene. Stirring, cooling at 0–5°, and a nitrogen atmosphere were maintained throughout the procedure. Upon completion of the addition of the hydrazine–amine solution, the reaction mixture was stirred several additional hours at room temperature. A quantitative yield of triethylammonium chloride was obtained upon filtration. The solvent was removed from the filtrate yielding 16.5 g of a yellow oil (86.5% of theory based on $C_6H_5PCl_2$). The oil was fractionated at 0.5 mm, the fraction distilling between 120 and 133° being collected; yield 6.0 g (36.3% of theory) of a colorless liquid. *Anal.* Calcd for $C_{12}H_{23}N_4P$: C, 56.67; H, 9.12; N, 22.02; P, 12.18. Found: C, 56.77; H, 9.21; N, 21.90; P, 12.32. The analytical data, method of preparation, and infrared and nmr spectra are consistent with the formula $C_6H_5P[NCH_3N(CH_3)_2]_2$ for this product.

Reaction of Bis(1,2,2-trimethylhydrazino)phenylphosphine with Chloramine.—Bis(1,2,2-trimethylhydrazino)phenylphosphine (2.64 g, 0.0104 mole) in 100 ml of dry diethyl ether was allowed to react with the effluent gases of the chloramine generator at 0° for 30 min (0.05 mole of chloramine). The reaction mixture was then allowed to remain at room temperature for 4 hr, thed vented through a KOH-filled drying tube. The solid reaction product, containing ammonium chloride, was recrystallizen from benzene, yielding 4.41 g (21.6% of theory) of a white crystalline solid, mp 161° dec. *Anal.* Calcd for $C_{12}H_{25}N_5PCl$: C, 47.13; H, 8.24; N, 22.91; P, 10.13; Cl, 11.59. Found: C, 47.66; H, 8.72; N, 21.74; P, 10.13; Cl, 11.35.

Reaction of 1,1-Bis(diphenylphosphino)2,2-dimethylhydrazine with Ammonia-Free Chloramine.—A 100-ml sample of an ammonia-free ethereal solution of 0.022 mole of chloramine was slowly added to 1.5 g of 1,1-bis(diphenylphosphino)2,2-dimethylhydrazine (0.0035 mole) in 50 ml of ether. Stirring, cooling in an ice bath, and a blanket of nitrogen were maintained during the procedure. The reaction mixture was stirred an additional 1 hr at room temperature after the addition of the chloramine solution at this point, indicating that chloramine was no longer present. The solid reaction product, containing ammonium chloride from the decomposition of chloramine, was filtered from the solution, weight 2.18 g. This mixture was recrystallized from a chloroform–ether mixture yielding 1.09 g of a pale yellow, crystalline solid. The product begins to decompose at 65° with frothing; at 135° it is a deep yellow viscous liquid. *Anal.* Calcd for $C_{26}H_{30}N_4P_2Cl_2$: C, 58.76; H, 5.59; N, 10.54; P, 11.66; Cl, 13.34. Found: C, 58.84; H, 5.91; N, 9.73; P, 11.40; Cl, 13.53. The analysis and infrared and nmr spectra show this product to be a double chloramination product or dichloride salt.

Reaction of 1,1,2-Tris(diphenylphosphino)2-methylhydrazine with the Gaseous Mixture of Ammonia and Chloramine.—1,1,2-Tris(diphenylphosphino)2-methylhydrazine (0.00342 mole) in 100 ml of dry ether was allowed to react with the effluent gases of the chloramine generator for 2 hr (0.2 mole of chloramine) at 0°. The reaction mixture was then kept at room temperature for 18 hr vented through a KOH-filled drying tube. The solid reaction product, containing ammonium chloride, was recrystallized from a chloroform–ether mixture; 0.55 g of a white crystalline solid, mp 236.5–240.5° dec, was obtained. *Anal.* Calcd for $C_{38}H_{39}N_5P_3Cl_5$: C, 54.59; H, 4.70; N, 8.38; P, 11.11; Cl, 21.23. Found: C, 53.62; H, 5.05; N, 8.24; P, 10.86; Cl, 22.50.

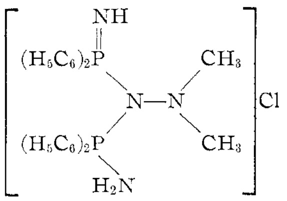
Reaction of 1,1,2-Tris(diphenylphosphino)2-methylhydrazine with Ammonia-Free Chloramine.—An ammonia-free ethereal solution of 0.022 mole of chloramine was added with stirring, ice-bath cooling, and under a blanket of nitrogen to 1.50 g of 1,1,2-tris(diphenylphosphino)2-methylhydrazine (0.00257 mole). Upon completion of the addition of the chloramine solution, the reaction mixture was stirred for 1 hr at room temperature. The solvent, when tested with an acidified potassium iodide solution, gave no reaction, indicating that all the chloramine had been consumed. The solid reaction product, after filtration (weight 2.09 g), was recrystallized from a chloroform–ether mixture to remove the ammonium chloride present. One gram of a white crystalline solid which begins to decompose at 65° was obtained; as the temperature is raised the material froths. At 170° a viscous yellow liquid is formed. *Anal.* Calcd for $C_{37}H_{37}N_4P_3Cl_2$: C, 63.34; H, 5.32; N, 7.99; P, 13.24; Cl, 10.11. Found: C, 62.00; H, 6.64; N, 7.50; P, 12.89; Cl, 9.82. The analytical data, though obviously imperfect, indicate that the product isolated from this reaction probably results from double chloramination.

Discussion

The hydrazinophosphines prepared by the hydrazinolysis of halophosphines include $P[NCH_3N(CH_3)_2]_3$ and $C_6H_5P[NCH_3N(CH_3)_2]_2$. It is interesting to note that for each of these compounds, three ^1H nmr signals for methyl hydrogens are observed. The signal resulting from the N-methyl hydrogens adjacent to the phosphorus atom presumably is split because of coupling with the phosphorus atom. Peak–area ratios were not obtainable since the signals were close together and overlapped somewhat. The ^1H nmr signal for N-methyl protons in the product of the chloramination of $C_6H_5P[NCH_3N(CH_3)_2]_2$, which the analytical and spectroscopic data indicate to have the structure $[C_6H_5P(NH_2)[NCH_3N(CH_3)_2]_2]Cl$, is also split. In this case the various signals were sufficiently separated from each other to allow determination of the peak–area ratio for the N-methyl and N-dimethyl hydrogens. This ratio was found to be approximately 1:2, as predicted from the formula.

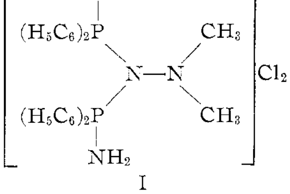
The products of the chloramination reactions described indicate that the phosphorus atom, and not the hydrazino nitrogens, is the site of attack of the chloramine. The infrared spectra of all the chloramination products contain strong bands at or very near 1120 cm^{-1} showing the presence of tetracoordinate phosphorus atoms with P–phenyl bonds. The relatively low yields of chloramination product may result from chloramine exerting a destructive action on the hydrazinophosphine. However, the large excess of chloramine required to carry the reaction to completion and the major amounts of ammonium chloride found may be attributed to catalytic decomposition of the chloramine by the hydrazino group.

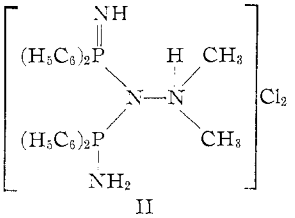
The ammonia-free chloramination of 1,1-bis(diphenylphosphino)2,2-dimethylhydrazine was shown to result in double chloramination yielding a dichloride. This is in contrast to the product obtained by Nielsen, *et al.*,[2] when the same hydrazinophosphine was chloraminated in the presence of ammonia. In the latter instance, dehydrohalogenation occurs, resulting in the formation of



Similar products were obtained with bis(diphenylphosphino)amines when allowed to react with the gaseous ammonia–chloramine mixture.[5] In the absence of ammonia, dehydrohalogenation does not occur.

Structures that can be suggested for this product include I and II. Structure I would result from the

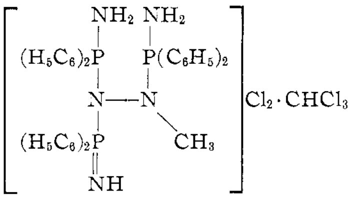

I


II

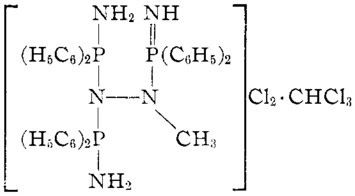
direct chloramination of each phosphorus atom. An intense absorption in the infrared spectrum at 1250 cm^{-1} is consistent with the presence of a P=N group. Thus, structure II in which a proton has transferred to one of the hydrazino nitrogens is probable.

It may be assumed in these reactions that chloramination on the phosphorus atoms occurs first, followed by loss of a proton from an NH_2 group if a proton acceptor is present. If ammonia is present, it would act as a proton acceptor; however, in the absence of ammonia, or other base, the hydrazino nitrogens could be the proton acceptor sites, thus giving structure II. The ^{1}H nmr spectrum does show signals attributable to the NH group at values of 2.83 and 3.63 ppm, but the peak–area ratio of phenyl to amino hydrogens does not agree with the theoretical value for two NH_2 groups. The hydrogen resonance signals due to H—N=P and N—NH groups are not clearly observed and may not be observable because of the complexity of the phenyl hydrogen signals.

The chloramination of 1,1,2-tris(diphenylphosphino)-2-methylhydrazine in the presence and in the absence of ammonia clearly results in the formation of two different products. The data indicate that dehydrohalogenation occurs in the presence of ammonia. In similar cases it was postulated that one phosphorus atom is initially chloraminated, then dehydrohalogenated by ammonia. This is followed by chloramination of the second phosphorus atom resulting in the final product.[2] The compound $[(C_6H_5)_2P]_2NNCH_3P(C_6H_5)_2$ contains three phosphorus atoms as sites for attack by chloramine. All three of the phosphorus atoms are chloraminated in the presence of ammonia, followed by the loss of one mole of hydrogen chloride resulting in the formation of a =NH group. The data given do not allow a decision as to which phosphorus atom has the =NH group. The data obtained suggest that the product has crystallized with one mole of chloroform. Structures III and IV are possible.

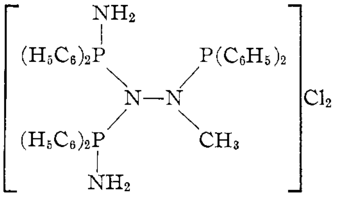


III

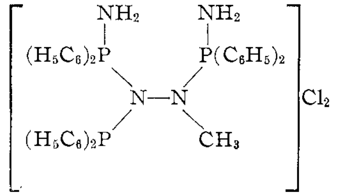


IV

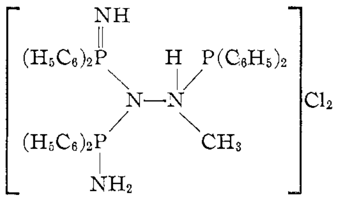
The chloramination of this same hydrazinophosphine in the absence of ammonia does not result in a trichloramination product, but rather in what appears to be a dichloramination product. As in the case of the other chloramination products, the infrared spectrum shows the presence of the quaternized phosphorus atom with a P–phenyl bond. Furthermore, a strong absorption in the infrared at 1250 cm^{-1} indicates that a P=N group may be present. The ^{1}H nmr spectrum shows two signals which can be attributed to N—H hydrogens and the ^{31}P nmr spectrum shows two signals close together. These data indicate that two different N—H groups and two different phosphorus atoms are present in the product. Feasible formulations are V–VII. The available data do not discriminate between them. It is true that formulas VI and VII have three nonequivalent phosphorus atoms. However, in the absence of more definitive information concerning ^{31}P chemical shifts in such compounds as these, it is not safe to eliminate these possible structures. In fact, rapid exchange of protons would result in two of the phosphorus atoms in VII becoming equivalent.



V



VI



VII

Acknowledgments.—We are pleased to acknowledge the support of this work in large part by the National Science Foundation through project No. GP-4505 with the University of Florida. Our appreciation is also expressed to Dr. Kurt Utvary, Visiting Associate Professor at the University of Florida from the Technical University of Vienna, for assistance in obtaining and interpreting the nmr data and his helpful suggestions.