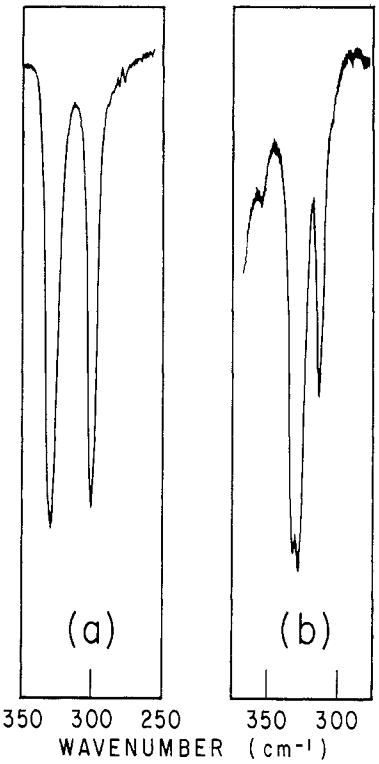


Figure 2.—Infrared spectrum of P_2I_4: (a) Nujol mull; (b) saturated CS_2 solution.

plete agreement with the X-ray crystallographic result[11] that this molecule has the *trans* configuration in the solid state. Four infrared frequencies were observed in CS_2 solutions of P_2I_4. The two strong bands are probably the asymmetric P–I stretching modes, $\nu_8(B)$ and $\nu_9(B)$, and the lower intensity bands can be assigned to the P–I symmetric stretching modes $\nu_1(A)$ and $\nu_2(A)$. Another possibility is that the band at 355 cm.$^{-1}$ is a combination, overtone, or impurity peak since it is less intense and somewhat higher in frequency than other P–I stretching modes. If this is so then one must also consider the possibility of a *cis* (C_{2v}) configuration for which three infrared-active P–I stretching frequencies are predicted [$\nu_2(A_1)$, $\nu_8(B_2)$, and $\nu_9(B_1)$]. However, this configuration is rather unlikely on steric grounds, hence we tend to favor the *gauche* conformation for P_2I_4 in solution, although it is important to realize that the above data could also correspond to an average over a number of configurations.

In accordance with its C_{3v} configuration,[26] PI_3 exhibits two infrared-active P–I stretches in CS_2 solution (Table III). The strong 327 cm.$^{-1}$ band is assigned to asymmetric P–I stretching [$\nu_3(E)$] and the weak 305 cm.$^{-1}$ band to symmetric P–I stretching [$\nu_1(A_1)$]. This is in excellent agreement with the 325 and 303 cm.$^{-1}$ bands reported for the Raman spectrum of PI_3 in CS_2 solution.[27]

Acknowledgment.—The authors are grateful to the Robert A. Welch Foundation for the financial support of this work, and to Dr. J. C. Davis for the B^{11} n.m.r. data.

---

[26] "Tables of Interatomic Distances and Configurations in Molecules," Special Publication No. 11, The Chemical Society, London, 1958, p. M 57.

[27] H. Stammreich, R. Forneris, and Y. Tavares, *J. Chem. Phys.*, **25**, 580 (1956).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA

The Reactions of Dialkylchlorophosphines with Gaseous Chloramine and Ammonia

BY HARRY H. SISLER AND STEPHEN E. FRAZIER

Received March 25, 1965

The reactions of a mixture of chloramine and excess ammonia with compounds of the general formula R_2PCl where R = CH_3, C_2H_5, and n-C_4H_9 were carried out in dry benzene. The compounds of the formula $[R_2P(NH_2)_2]Cl$ were obtained in each case. Along with these compounds the compounds $[(C_2H_5)_2P(NH_2)NP(NH_2)(C_2H_5)_2]Cl$ and $[(C_4H_9)_2PN]_3$ were obtained in the appropriate instances. Pyrolysis of the $[R_2P(NH_2)_2]Cl$ was shown to yield phosphonitrilic materials of the general formulas $(R_2PN)_3$ and $(R_2PN)_4$. Pyrolysis of $[(C_2H_5)_2P(NH_2)NP(NH_2)(C_2H_5)_2]Cl$ was shown to yield a 4:1 mixture of $[(C_2H_5)_2PN]_4$ and $[(C_2H_5)_2PN]_3$.

In an earlier communication[1] from this laboratory it was reported that the reaction of diphenylchlorophosphine with a gaseous mixture of ammonia and chloramine produces $[(C_6H_5)_2PN]_3$ in about 12% yield and an intermediate $[(C_6H_5)_2P(NH_2)N{=}P(NH_2)(C_6H_5)_2]Cl$ in about 50% yield based on the diphenylchlorophosphine used. A reaction sequence was proposed and is generalized in the following steps.

$$R_2PCl + 2NH_3 \longrightarrow R_2PNH_2 + NH_4Cl \qquad (1)$$

$$R_2PNH_2 + NH_2Cl \longrightarrow [R_2P(NH_2)_2]Cl \qquad (2)$$

$$2[R_2P(NH_2)_2]Cl \longrightarrow [R_2P(NH_2)N{=}P(NH_2)R_2]Cl + NH_4Cl \qquad (3)$$

$$[R_2P(NH_2)_2]Cl + [R_2P(NH_2)N{=}P(NH_2)R_2]Cl \longrightarrow [R_2PN]_3 + NH_4Cl \qquad (4)$$

---

[1] H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, **1**, 84 (1962).

or

$$3[R_2P(NH_2)_2]Cl \longrightarrow [R_2PN]_3 + 3NH_4Cl \qquad (5)$$

This sequence offers the attractive possibility of a general procedure for the production of phosphonitrilic compounds in substantial yields. In addition, if the reaction follows the same general course for a number of monochlorophosphines, the synthesis of an homologous series of useful, reactive intermediates might be possible. For instance, in the case of diphenylchlorophosphine, the intermediate produced in step 3 has been shown to yield diphenylphosphonitrilic trimer and tetramer upon pyrolysis.[1] Furthermore, it produces cyclic polymers by ring closure reactions with PCl_5, $(C_6H_5)PCl_4$, and $(C_6H_5)_2PCl_3$.[2]

This communication reports the results of a study which extends the ammonia–chloramine reaction to dialkylchlorophosphines and demonstrates its usefulness as a general synthetic procedure.

Experimental

Materials.—The gaseous mixture of chloramine and ammonia was produced by the gas-phase reaction of chlorine with ammonia in a generator similar to that described by Sisler, *et al.*[3] The gas flow rates were such that the mole ratio of ammonia to nitrogen to chlorine was approximately 12:3:1, and the production rate of chloramine was approximately 0.1 mole/hr.

Tri-*n*-butylphosphine, used in the preparation of dialkylchlorophosphines, was obtained from Food Machinery and Chemical Corp. and used as received. All solvents used were reagent grade. Benzene and petroleum ether were dried and stored over calcium hydride.

Manipulative Methods.—Liquid reagents and solvents were transferred by pipet to minimize exposure to atmospheric oxygen and water vapor. Dialkylchlorophosphines were stored and transferred in an inert atmosphere box containing dry nitrogen. Solid products which were hygroscopic were also stored in the drybox.

Analyses.—Elementary analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Several nitrogen analyses were obtained in these laboratories using a Coleman Model 27 nitrogen analyzer. Melting points were obtained with a Thomas-Hoover capillary melting point apparatus.

Infrared Spectra.—The infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer using sodium chloride optics and on a Beckman Model IR10 grating infrared spectrophotometer. Solid samples were either mulled with Nujol, pressed into KBr pellets, or melted and examined as thin films when the melting point was below 100°. The infrared spectral absorptions are listed in Table I.

Synthesis of Dialkylchlorophosphines.—Dimethylchlorophosphine was synthesized by the method of Parshall.[4] Diethyl- and di-*n*-butylchlorophosphines were synthesized from the corresponding diphosphine disulfides[5] by cleavage and chlorination with SO_2Cl_2[6] and desulfuration with tri-*n*-butylphosphine.[7] The observed boiling point of dimethylchlorophosphine was 68–74° at atmospheric pressure. This material is spontaneously flammable in air. Diethylchlorophosphine fumes strongly in air and boils at 30–35° (15 mm.) [lit.[8] b.p. 61–62° (72 mm.)]. Di-*n*-butylchlorophosphine fumes in air and boils at 39–47° (0.25 mm.) [lit.[9] b.p. 91–92° (12 mm.)].

TABLE I[a]

INFRARED ABSORPTION DATA (CM.$^{-1}$)

$[(CH_3)_2P(NH_2)_2]Cl$, Nujol mull

3260 (vs), 3000 (vs), 2640 (m), 2400 (m), 2200 (b, sh), 1950 (m), 1570 (s), 1460 (s), 1420 (s), 1370 (m), 1300 (s), 1070 (s, sh), 1040 (s), 990 (s), 960 (s), 905 (m, sh), 892 (m), 865 (m), 765 (s), 695 (s)

$[(C_2H_5)_2P(NH_2)_2]Cl$, Nujol mull

3250 (vs), 3000 (vs), 2690 (m), 2600 (m), 2410 (w), 2280 (w), 2200 (w), 2100 (w), 1940 (w), 1560 (s), 1460 (vs), 1410 (sh), 1380 (s), 1280 (s), 1240 (m), 1070 (s, sh), 1060 (s), 1020 (s), 975 (s), 915 (s), 760 (s), 732 (s), 724 (s)

$[(C_2H_5)_2P(NH_2)N{=}P(NH_2)(C_2H_5)_2]Cl$ melt

3250 (vs), 3120 (s), 3000 (s), 2650 (w), 2390 (w), 2100 (w), 1900 (w), 1850 (w), 1570 (s), 1460 (s), 1410 (s), 1380 (m), 1300 (vs), 1255 (vs), 1060 (s), 1040 (vs), 1020 (s), 995 (m), 925 (vs), 910 (sh), 810 (m), 758 (vs), 726 (s), 688 (vs)

$[(n\text{-}C_4H_9)_2P(NH_2)_2]Cl$, Nujol mull

3220 (vs), 3100 (s), 3000 (vs), 2580 (w), 1555 (s), 1460 (s), 1420 (m), 1380 (s), 1320 (m), 1280 (w), 1230 (m), 1200 (w), 1180 (w), 1090 (s), 1010 (s), 944 (s), 895 (w), 813 (m), 775 (sh), 762 (w), 712 (m)

$[(n\text{-}C_4H_9)_2PN]_3$ melt

2950 (s), 2920 (s), 2855 (s), 1450 (m), 1400 (m), 1370 (w), 1300 (sh), 1260 (w), 1215 (m), 1155 (vs), 1085 (w), 1045 (w, sh), 1000 (w, sh), 950 (b, sh), 910 (w), 889 (vw), 789 (vw), 719 (w)

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

Reaction of Dimethylchlorophosphine with Chloramine and Ammonia.—Dimethylchlorophosphine (0.0206 mole) was dissolved in dry benzene (50 ml.) and exposed to the effluent gases of the chloramine generator. An ice bath was used to cool the mixture during the first 2–3 min. of the chloramine–ammonia addition. A white precipitate formed immediately. The chloramination was continued for 15 min. (0.025 mole of NH_2Cl). At the completion of the reaction the solution was filtered. The solids remaining on the filter were extracted with several 50-ml. portions of a hot, 50–50 ethanol–acetone mixture. White, water-soluble crystals formed as the solution cooled slowly to room temperature. These crystals were removed by filtration and dried under vacuum, m.p. 192–194°. *Anal.* Calcd. for $[(CH_3)_2P(NH_2)_2]Cl$: C, 18.69; H, 7.84; P, 24.10; N, 21.79; Cl, 27.58. Found: C, 18.44; H, 7.84; P, 23.82; N, 22.00; Cl, 28.10. Upon addition of petroleum ether to the mother liquor a larger portion of dimethyldiaminophosphonium chloride was isolated; total yield 1.60 g. (60% of theory).

Pyrolysis of Dimethyldiaminophosphonium Chloride.—In a typical experiment 1.15 g. (8.9 mmoles) of dimethyldiaminophosphonium chloride was placed in a semimicro sublimation apparatus and heated at about 200° (0.2 mm.) for 3 days. The resulting sublimate was extracted with several portions of hot, 30–60° petroleum ether. The residue of this extraction was identified as ammonium chloride. Evaporation of the petroleum ether yielded a white, crystalline material with a melting range of 160–170°; crude yield 0.55 g. (82% of theory). *Anal.* Calcd. for $[(CH_3)_2PN]_n$: C, 32.01; H, 8.06; P, 41.28; N, 18.66. Found: C, 31.83; H, 7.98; P, 41.15; N, 18.73. The mixture was separated into dimethyl phosphonitrilic trimer and tetramer[10] by fractional crystallization from petroleum ether. The molecular weights (cryoscopic in benzene) were 220 (calcd. 225) and 311 (calcd. 300), respectively. The trimer melted with sublimation

---

[2] D. L. Herring and C. M. Douglas, *Inorg. Chem.*, **3**, 428 (1964).

[3] H. H. Sisler, F. T. Neth, R. S. Drago, and D. Young, *J. Am. Chem. Soc.*, **76**, 3906 (1954).

[4] G. W. Parshall, *J. Inorg. Nucl. Chem.*, **12**, 372 (1960).

[5] H. Niebergall and B. Langenfeld, *Ber.*, **95**, 64 (1962).

[6] Farbenfabriken Bayer Aktiengesellschaft, Leverkusen-Bayerwerk (by R. Colln and G. Schrader), German Patent 1,054,453 (April 9, 1959); *Chem. Abstr.*, **55**, 6375*b* (1961).

[7] An excellent discussion of desulfuration reactions using tri-*n*-butylphosphine is given by L. Maier, *J. Inorg. Nucl. Chem.*, **24**, 275 (1962).

[8] I. P. Komkov, K. V. Karavanov, and S. V. Ivin, *J. Gen. Chem. USSR*, **28**, 2992 (1958).

[9] K. Issleib and W. Seidel, *Ber.*, **92**, 2681 (1959).

[10] H. T. Searle, *Proc. Chem. Soc.*, 7 (1959).

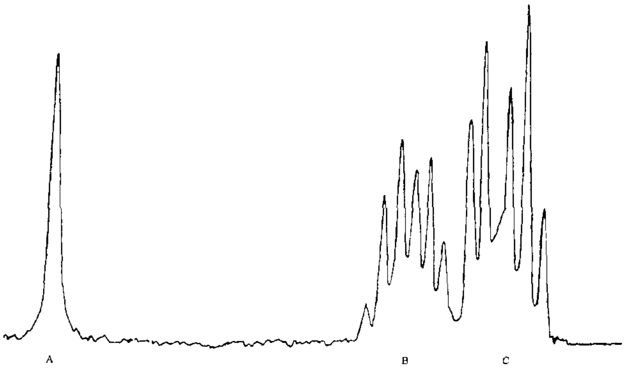


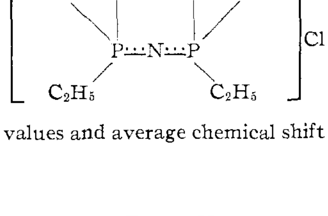
Figure 1.—The n.m.r. spectrum of $[(C_2H_5)_2P(NH_2)NP(NH_2)(C_2H_5)]_2Cl$.

at 187–190° (lit.[10] 195–196°) and the tetramer melted with sublimation at 157–160° (lit.[10] 163–164°). The infrared spectra of these compounds agree quite well with the assignments reported by Searle.[10]

Reaction of Diethylchlorophosphine with Chloramine and Ammonia.—Diethylchlorophosphine (0.0154 mole) was dissolved in 50 ml. of benzene and exposed to the effluent gases of the chloramine generator for 12–15 min. (0.016 mole of NH_2Cl requires 9.6 min.). At the start of the chloramine–ammonia addition the solution grew warm and was cooled with an ice bath. A white precipitate formed immediately. At the completion of the reaction the benzene was removed by filtration and the solids were extracted with two 20-ml. portions of benzene. Upon evaporation of the benzene solution and washings, 2.41 g. of crude material melting at 45–50° was obtained. After purification by repeated recrystallizations from benzene the melting point was raised to 58–61°; yield 1.51 g. (75% of theory). *Anal.* Calcd. for $[(C_2H_5)_2P(NH_2)N{=}P(NH_2)(C_2H_5)_2]Cl$: C, 37.00; H, 9.31; P, 23.85; N, 16.18; Cl, 13.65. Found: C, 37.29; H, 9.35; P, 23.68; N, 15.93; Cl, 13.48.

This material is water-soluble and highly hygroscopic. Peaks attributable to the P=N—P linkage at 1300 and 1255 cm.$^{-1}$ and a broad peak at 925 cm.$^{-1}$ appear in the infrared spectrum. The latter band has been attributed to the PNHP group.[1]

The proton magnetic resonance spectrum (Figure 1) was run at 56.4 Mc. using a $CDCl_3$ solution. The spectrum was obtained by sweeping slowly through the field and interchanging the reference, acetaldehyde, with the sample. Peak A refers to the NH_2 protons, peak B to the methylene protons, and peak C to the methyl protons. The usual methylene quartet and methyl triplet are further split by spin–spin coupling with the phosphorus atom. This spectrum is consistent with the structure[1]



Approximate τ values and average chemical shift values are listed in Table II.

Table II

N.m.r. Spectral Data for $[(C_2H_5)_2P(NH_2)NP(NH_2)(C_2H_5)_2]Cl$

Group	Chemical shift, τ	Coupling, c.p.s.	
NH_2	5.18	H–H	∼8
CH_2	7.98 (av.)	P–CH_2	∼14
CH_3	8.75 (av.)	P–CH_3	∼18

The ratio of areas under the NH_2 peak to those under the CH_2 and CH_3 peaks is approximately 1:5. When the nuclear magnetic resonance spectrum was run at 19.3 Mc. a single, broad peak for phosphorus was observed corresponding to a chemical shift of 41 p.p.m. to low field in comparison to 85% phosphoric acid.

The solids remaining in the reaction flask were extracted with two 25-ml. portions of absolute ethanol. The solution was concentrated to about half the original volume by evaporation, and ammonium chloride was precipitated by the addition of petroleum ether. The solution was filtered and concentrated further. When the formation of crystals was observed in the saturated solution, it was treated with acetone to precipitate the product. Upon filtration and drying, the material melted at 100–103°. Recrystallization from alcohol yielded a product melting at 106–108.5°; yield 0.46 g. (19% of theory). *Anal.* Calcd. for $[(C_2H_5)_2P(NH_2)_2]Cl$: C, 30.08; H, 9.01; P, 19.78; N, 17.89; Cl, 22.64. Found: C, 30.33; H, 8.99; P, 19.51; N, 17.73; Cl, 22.86. This material is water-soluble and highly hygroscopic.

Pyrolysis of Diethyldiaminophosphonium Chloride.—In a typical experiment 0.99 g. (6.3 mmoles) of diethyldiaminophosphonium chloride was placed in a semimicro sublimation apparatus and heated to about 180° (0.2 mm.) for 5 days. This process produced a white sublimate as well as a substantial amount of light-colored residue. The residue was dissolved in boiling benzene and filtered. Upon evaporation of the benzene a white, crystalline material was recorded which melted at 61–64°; yield 0.30 g. This material is hygroscopic, water-soluble, and gives a Cl^- test with aqueous $AgNO_3$. *Anal.* Calcd. for $[(C_2H_5)_2P(NH_2)N{=}P(NH_2)(C_2H_5)_2]Cl$: N, 16.18. Found: N, 16.3. The infrared spectrum confirmed the identity of this substance.

The sublimate was dissolved in benzene and filtered to remove ammonium chloride. The benzene was removed by evaporation and the resulting white, crystalline material was carefully resublimed at about 50° (0.1 mm.). The sublimate melted at 109–112°; yield 0.21 g. (33% of theory). *Anal.* Calcd. for $[(C_2H_5)_2PN]_3$: C, 46.60; H, 9.78; P, 30.04; N, 13.59; mol. wt., 309. Found: C, 46.39; H, 9.92; P, 30.30; N, 13.49; mol. wt., 305. The infrared spectrum agreed with the assignments listed in the literature[11] for diethylphosphonitrilic trimer. The literature value for the melting point of the trimer is 117.5–119°.

The residue from this sublimation was recrystallized from benzene and identified as the intermediate, $[(C_2H_5)_2P(NH_2)N{=}P(NH_2)(C_2H_5)_2]Cl$. The total yield of this intermediate was 0.34 g. (41% of theory).

Pyrolysis of $[(C_2H_5)_2P(NH_2)N{=}P(NH_2)(C_2H_5)_2]Cl$.—In a semimicro sublimation apparatus, 0.85 g. (3.3 mmoles) of $[(C_2H_5)_2P(NH_2)N{=}P(NH_2)(C_2H_5)_2]Cl$ was heated at about 200° (0.15 mm.) for 4–5 days. This process produced a white, oily sublimate and a trace of black residual ash. The sublimate was extracted with several portions of petroleum ether. The residue from this extraction was again extracted with several portions of hot benzene. From the benzene solution 0.25 g. (0.96 mmole) of unreacted starting material was recovered. From the petroleum ether solution 0.36 g. (75% of theory based on the starting material actually reacted) of a mixture of diethylphosphonitrilic tetramer and trimer was recovered by evaporation. The residue of the solvent extractions consisted of ammonium chloride.

The mixture of diethylphosphonitrilic tetramer and trimer was separated by repeated fractional sublimation at 53° (0.1 mm.). By this method the mixture was found to consist of about 20% trimer (m.p. 110–114°) and 80% tetramer (a viscous oil[11]). *Anal.* Calcd. for $[(C_2H_5)_2PN]_4$: C, 46.60; H, 9.78; P, 30.04; N, 13.59; mol. wt., 412. Found: C, 46.36; H, 9.76; P, 29.84; N, 13.30; mol. wt., 401. The infrared spectrum of this material agrees quite well with the assignments listed in the literature[11] for diethylphosphonitrilic tetramer.

Reaction of Di-*n*-butylchlorophosphine with Chloramine and Ammonia.—Di-*n*-butylchlorophosphine (0.0102 mole) was dissolved in 50 ml. of dry benzene and exposed to the effluent gases of the chloramine generator for 12–15 min. A white precipitate formed immediately. An ice bath was used to cool the mixture during the first 2–3 min. of the chloramine–ammonia addition.

---

[11] A. J. Bilbo, *Z. Naturforsch.*, **15b**, 330 (1960).

At the completion of the reaction the benzene was removed by filtration and the solids were washed with two 20-ml. portions of dry benzene and filtered. The solids were then extracted with 25-ml. portions of hot chloroform. The chloroform solution was removed from the insoluble ammonium chloride by filtration. Petroleum ether was added to the chloroform solution and a white, flocculent precipitate formed and was recovered by filtration. After purification by recrystallization from chloroform and drying under vacuum, the material melted at 113.5–115°; yield 0.53 g. (25% of theory). *Anal.* Calcd. for $[(C_4H_9)_2P(NH_2)_2]Cl$: C, 45.17; H, 10.43; P, 14.56; N, 13.17. Found: C, 45.14; H, 10.45; P, 14.34; N, 13.14. The material is water-soluble and highly hygroscopic. Upon evaporation of the benzene solution, 0.89 g. of an unidentified, waxy material was obtained. Its infrared spectrum contains a broad peak in the P=N region (1300–1100 cm.$^{-1}$) as well as N—H peaks. This information and its elemental analysis indicate that it might be the intermediate, $[(C_4H_9)_2P(NH_2)N{=}P(NH_2)(C_4H_9)_2]Cl$. This postulate, however, could not be confirmed. Sublimation of this wax at about 70° (0.1 mm.) yielded a trace (1–2% of theory) of a white sublimate melting at 45–50°. *Anal.* Calcd. for $[(C_4H_9)_2PN]_3$: C, 60.35; H, 11.40; P, 19.45; N, 8.80; mol. wt., 478. Found: C, 60.09; H, 11.37; P, 19.23; N, 8.90; mol. wt., 470. The infrared spectrum of this material contains a sharp peak at 1155 cm.$^{-1}$ attributable to the P=N stretch. This material is soluble in benzene and petroleum ether, but only slightly soluble in cold water.

Pyrolysis of Di-*n*-butyldiaminophosphonium Chloride.—Di-*n*-butyldiaminophosphonium chloride (1.08 g. or 5 mmoles) was placed in a semimicro sublimation apparatus and heated at 190° (0.10 mm.) for 4 days. A white sublimate was observed. Only a trace of black residue remained in the pot at the completion of the reaction. The sublimate was extracted with 30–60° petroleum ether. The insoluble portion was shown to be ammonium chloride. Evaporation of the petroleum ether yielded a white wax which melted at 45–50° and sublimed readily at 70° (0.1 mm.). The infrared spectrum was identical with that of the material identified above as $[(n\text{-}C_4H_9)_2PN]_3$; yield 0.77 g. (95% of theory).

Discussion

The experiments described above not only demonstrate the generality of the ammonia–chloramine reaction with monochlorophosphines but provide strong evidence for the reaction sequence postulated in the earlier communication.[1] In all cases a considerable yield of the dialkyldiaminophosphonium chloride was observed. The analogous intermediate had not been isolated from the diphenylchlorophosphine reaction but its existence had been inferred from the other compounds isolated.

One might question the assumption that chloramination occurs on the phosphorus atom to produce a phosphonium salt in view of the possibility that chloramination occurs on the nitrogen atom forming, instead, a hydrazinium derivative, $[R_2PNH_2NH_2]Cl$. This question was, however, thoroughly considered by Hart and Sisler and it was shown that chloramination of aminophosphines occurs exclusively on the phosphorus atom.[12]

The chloramination of diethylchlorophosphine produces not only the corresponding diaminophosphonium salt, but also the further intermediate $[(C_2H_5)_2P(NH_2)N{=}P(NH_2)(C_2H_5)_2]Cl$. Nuclear magnetic resonance and infrared studies show that its structure is similar to that of the phenyl analog.[1]

In the case of di-*n*-butylchlorophosphine a trace of a new phosphonitrilic derivative, $[(C_4H_9)_2PN]_3$, was isolated from the reaction mixture. However, the predominant product isolated was the di-*n*-butyldiaminophosphonium chloride. A large amount of dark, unresolved oil was also obtained even when the reaction mixture was cooled with an ice bath.

The behavior of the dialkyldiaminophosphonium salts under pyrolytic conditions is also what one would predict on the basis of the assumed reaction sequence. The pyrolyses of the ethyl-substituted phosphonium salts are particularly good examples of the stepwise nature of the process. Upon pyrolysis, diethyldiaminophosphonium chloride produces $[(C_2H_5)_2P(NH_2)N{=}P(NH_2)(C_2H_5)_2]Cl$ and $[(C_2H_5)_2PN]_3$. The intermediate, $[(C_2H_5)_2P(NH_2)N{=}P(NH_2)(C_2H_5)_2]Cl$, is pyrolyzed to produce chiefly diethylphosphonitrilic tetramer. Some cleavage of the intermediate does occur, however, resulting in the formation of some diethylphosphonitrilic trimer and some decomposed material.

This study has demonstrated the generality of the reaction sequence postulated earlier[1] for the reaction of the ammonia–chloramine mixture with diphenylchlorophosphine and has established the general applicability of the reaction of the ammonia–chloramine mixture with halophosphines as a method for synthesizing phosphonitrilic derivatives. The new intermediates isolated from this reaction sequence provide the formal possibility for the synthesis of a great variety of new derivatives for further study. Ring formation reactions involving these intermediates are currently undergoing investigation.

Acknowledgment.—The authors gratefully acknowledge the generous support of this work by W. R. Grace and Co. through a contract with the University of Florida. We also wish to thank Professor Wallace S. Brey, Jr., of the Department of Chemistry of the University of Florida, for his help in the determination and interpretation of the nuclear magnetic resonance spectra.

---

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