dipole interaction. It would be expected that the neptunium(V)–methanol interaction would be less than that for a $2+$ ion–methanol interaction and result in a lower ΔF^*.

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The Reaction of Ammonia–Chloramine Mixtures with Phosphorus–Phosphorus Bonds

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The reactions of ammonia–chloramine mixtures with tetramethyldiphosphine, tetraethyldiphosphine, tetraphenyldiphosphine, and tetraphenylcyclotetraphosphine have been shown to result in the fission of the phosphorus–phosphorus bonds and in the formation of the same products as would be expected from the reaction of ammonia–chloramine mixtures with the corresponding mono- or dihalophosphines. The previously postulated but not isolated compounds $[(C_6H_5)_2P(NH_2)_2]Cl$ and $[(C_6H_5)P(NH_2)_3]Cl$ were obtained. It is postulated that the initial products of the P–P bond fission are R_2PCl and R_2PNH_2. It was also shown that dimethyldiaminophosphonium chloride reacts with PCl_5 to yield $(CH_3)_2Cl_4P_3N_3$. The mode of formation and the infrared spectrum indicate that this product is a phosphonitrilic cyclic trimer in which both methyl groups are on the same phosphorus atom.

It has recently been reported[1–3] that the reaction of ammonia–chloramine mixtures with monochlorophosphines produces diaminophosphonium chlorides which undergo self-condensation reactions giving phosphonitrilic polymers. Since halophosphines are formed by cleavage of diphosphines and polyphosphines with free halogens,[4,5] it was interesting to determine if phosphorus–phosphorus bonds would be cleaved by reaction with chloramine. Thus, the reaction of ammonia–chloramine mixtures with substituted diphosphines, for example, might give the same products which are obtained from the analogous reaction with monochlorophosphines.

We now are reporting the results of a study of the reactions of gaseous chloramine and ammonia with tetramethyldiphosphine, tetraethyldiphosphine, tetraphenyldiphosphine, and tetraphenylcyclotetraphosphine. The reaction of dimethyldiaminophosphonium chloride with phosphorus(V) chloride was also studied.

Experimental Section

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.*[6] 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.

All solvents used were reagent grade. Benzene, diethyl ether, and petroleum ether were dried and stored over calcium hydride. Phenyldichlorophosphine and diphenylchlorophosphine were provided by Victor Chemical Works. Tri-*n*-butylphosphine was otained from Food Machinery and Chemical Corp. Dimethyldiaminophosphonium chloride for the reaction with phosphorus(V) chloride was synthesized from dimethylchlorophosphine.

Manipulative Methods.—Liquid reagents and solvents were transferred by pipet to minimize exposure to atmospheric oxygen and water vapor. The substituted diphosphines and tetraphenylcyclotetraphosphine were stored and transferred in an inert-atmosphere box containing dry nitrogen. Hygroscopic reaction products were also stored and handled in the drybox.

Analyses.—Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Several nitrogen analyses were obtained in these laboratories using a Coleman Model 29 nitrogen analyzer. Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

The infrared spectra were recorded on a Perkin-Elmer Model 337 grating infrared spectrometer and on a Beckman Model IR10 spectrophotometer. Solid samples were examined between KBr disks as Nujol mulls. In certain instances thin films could be obtained by carefully evaporating a chloroform solution of the sample on a KBr disk. The infrared spectral absorptions are listed in Table I. Sections of the infrared spectrum of $[(C_6H_5)_2P(NH_2)_2]Cl$ are shown in Figure 1.

Preparation of Substituted Diphosphines and Tetraphenylcyclotetraphosphine.—Tetramethyldiphosphine and tetraethyldiphosphine were prepared by the method of Maier.[7] The observed boiling point of tetramethyldiphosphine was 36° (16 mm) [lit.[7] bp 38–40° (16 mm)]. The observed boiling point of tetraethyldiphosphine was 67° (1.7 mm) [lit.[7] bp 220–223° (740 mm)]. Both liquids are spontaneously flammable in air.

Tetraphenyldiphosphine was synthesized by the reaction of diphenylchlorophosphine with tri-*n*-butylphosphine.[8] The material used in this study melted at 118–121° (lit.[5] mp 120.5). Although strict precautions against oxidation of the diphosphine

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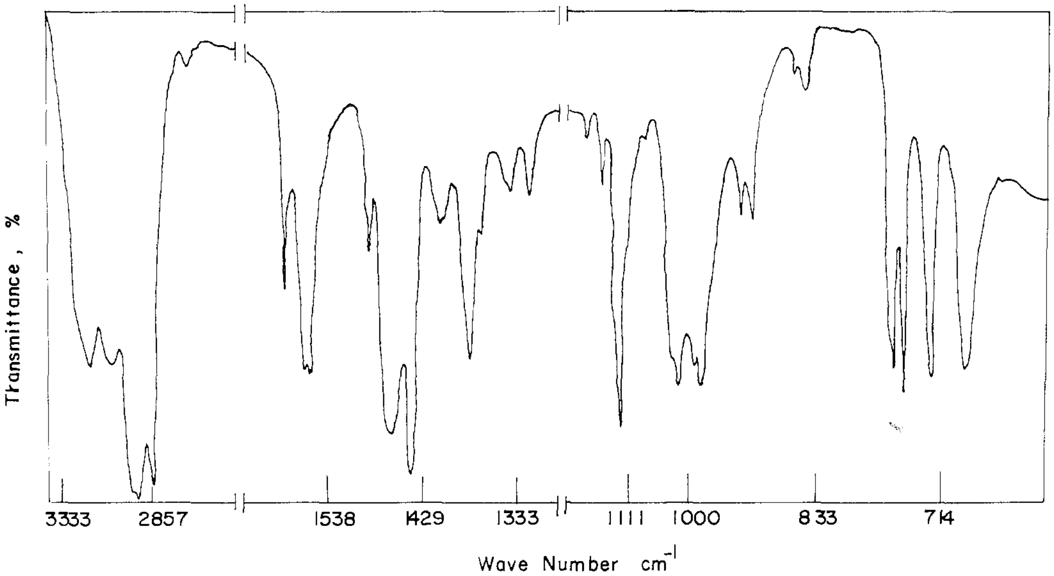


Figure 1.—Infrared spectrum of $[(C_6H_5)_2P(NH_2)_2]Cl$ (Nujol).

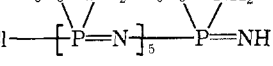
TABLE I[a]
INFRARED ABSORPTION DATA (cm^{-1})

$(C_6H_5)_2P(O)NH_2$, Nujol Mull

3240 s, b, 3125 s, 2940 vs, 2860 vs, 1970 w, 1900 w, 1820 w, 1779 w, 1680 w, 1595 m, 1560 s, 1485 m, 1460 vs, b, 1440 vs, sh, 1439 vs, 1420 w, sh, 1380 s, 1365 m, sh, 1340 w, 1310 m, 1275 w, 1260 w, 1175 s, 1110 s, 1105 s, 1060 m, 1010 w, 990 m, 910 s, 858 w, 849 w, 752 s, 720 s, 695 s, 620 w, 532 s, 518 s, 488 m, 439 w

$[(C_6H_5)_2P(NH_2)_2]Cl$, Nujol Mull

3170 s, 3075 s, 2980 vs, sh, 2940 vs, 2860 vs, 2710 w, 2540 w, b, 2440 w, 1970 w, 1900 w, 1815 w, 1780 w, 1665 w, b, 1595 m, 1560 s, 1485 m, 1460 s, 1440 s, 1410 m, 1380 s, 1365 m, sh, 1340 w, 1320 w, 1280 w, 1190 w, 1160 w, 1110 s, 1075 w, sh, 1025 s, sh, 1010 s, 990 s, sh, 980 s, 922 m, 910 m, 855 w, 840 w, 756 s, sh, 751 s, 742 s, 720 s, 691 s, 638 w, b, 620 w, 549 w, b, 510 s, 505 s, sh, 472 m, 434 w, 413 m

Suspected  Thin Film

$Cl{-}[P(C_6H_5)(NH_2){=}N]_5{-}P(C_6H_5)(NH_2){=}NH$,

3400 s, sh, 3210 vs, 3060 vs, 2950 s, 2940 sh, 2635 w, 2600 w, 2300 m, 2250 w, 1960 m, 1900 m, 1820 m, 1770 w, 1720 w, 1670 m, 1640 m, 1590 s, 1550 vs, 1480 s, 1440 vs, 1280 s, sh, 1205 vs, vb, 1115 s, 1015 m, 910 m, b, 799 m, 742 s, 692 s, 685 sh, 615 w, 502 s, vb

$[(C_6H_5)P(NH_2)_3]Cl$, Nujol Mull

3375 m, 3250 s, sh, 3170 s, 3075 s, 2940 s, sh, 2900 vs, 2850 s, 1590 w, 1559 m, 1460 s, 1440 s, 1415 m, 1380 s, 1135 s, 1084 w, 1070 w, 1025 w, 985 m, 925 w, sh, 875 m, 798 w, 763 s, 721 w, 705 w, 692 m, 620 w, b, 510 m, 474 m

$(C_6H_5)P(O)(NH_2)_2$, Nujol Mull

3350 s, 3275 s, sh, 3220 s, 3110 s, sh, 3055 m, 2940 vs, 2850 vs, 2740 w, 1955 w, 1900 w, 1770 w, 1590 m, 1560 m, 1460 s, 1440 s, 1410 m, b, 1380 s, 1330 w, 1310 w, 1182 m, 1155 vs, 1118 s, 1060 m, 1010 m, 939 s, 915 m, sh, 885 m, 855 w, 745 s, sh, 740 s, 720 m, 694 s, 620 w, 568 w, b, 520 s, 512 s, 494 w, 435 w, b

$(CH_3)_2Cl_4P_3N_3$, Nujol Mull

2940 vs, b, 2850 vs, 2715 w, 2665 w, b, 2299 w, b, 2245 w, 2175 w, 2144 w, 2085 w, 2020 m, 1996 w, sh, 1960 w, 1939 w, 1874 w, 1869 w, 1805 w, 1766 w, 1651 w, 1440 vs, 1418 s, 1405 m, 1380 vs, 1365 s, 1308 vs, 1295 vs, 1242 s, sh, 1220 vs, 1170 vs, 962 s, 935 s, 905 w, 881 vs, 876 s, 787 s, 758 s, 722 w, 694 s, 674 w, 634 vs, 584 vs, b, 510 vs, b, 431 w, 404 vs

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

were taken, some tetraphenyldiphosphine monoxide[9] was probably present in each sample.

Tetraphenylcyclotetraphosphine was synthesized by the reaction of phenyldichlorophosphine with tri-*n*-butylphosphine.[8] The material used in this study melted at 153–155° (lit.[10] mp 153–155°).

Reaction of Tetramethyldiphosphine with Chloramine and Ammonia.—Tetramethyldiphosphine (7.1 mmoles) was dissolved in 75 ml of dry benzene and allowed to react with the gaseous ammonia–chloramine mixture from the chloramine generator. A white precipitate formed immediately, and the temperature of the solution increased to 30–40° as the reaction proceeded. The introduction of the ammonia–chloramine mixture was continued for 15–20 min until the solution became cool from evaporation of the solvent. The benzene was removed by filtration, and the benzene-insoluble solids were extracted with 60 ml of hot, 50:50 ethanol–acetone mixture. White, water-soluble crystals precipitated from the ethanol–acetone solution as it cooled slowly to room temperature. These crystals were removed by filtration and dried under vacuum; mp 191–194°. *Anal.* Calcd for $[(CH_3)_2P(NH_2)_2]Cl$: N, 21.79. Found: N, 21.47. The infrared spectrum of this material is identical with that of dimethyldiaminophosphonium chloride[2] (mp 192–194°) produced by the reaction of a mixture of ammonia and chloramine with dimethylchlorophosphine.

Addition of petroleum ether to the mother liquor caused more of the dimethyldiaminophosphonium chloride to precipitate; total yield: 1.08 g (63% of theory).

Reaction of Tetraethyldiphosphine with Chloramine and Ammonia.—Tetraethyldiphosphine (5.0 mmoles) was dissolved in 75 ml of dry benzene and allowed to react with the gaseous ammonia–chloramine mixture from the chloramine generator. A white precipitate formed immediately, and the temperature of the solution increased to 30–40° as the reaction proceeded. Chloramination was continued for 15–20 min until the solution became cool from evaporation of the solvent. The benzene solution was removed by filtration, and the solids were washed with 25 ml of fresh benzene. The combined filtrate and washings were evaporated to dryness. A trace of oily crystals was observed. This material was purified by recrystallization from petroleum ether (bp 30–60°) and sublimation at 30–40° (0.1 mm); mp 113–115°. This crystalline material was identified

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[9] J. McKechnie, D. S. Payne, and W. Sim, *J. Chem. Soc.*, 3500 (1965).

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by its infrared spectrum as diethylphosphonitrilic trimer;[2,11] yield: trace (1–5 mg).

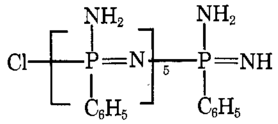
The solids remaining on the filter were extracted with three 10-ml portions of absolute ethanol. This solution was evaporated to dryness, and the resulting crystalline residue was dissolved in 10 to 15 ml of hot 50:50 ethanol–acetone mixture and filtered. This solution was cooled with an ice bath, and to it was added approximately 100 ml of petroleum ether (bp 60–110°). The product crystallized from the solution as well-formed white needles. These crystals were filtered and dried under vacuum; mp 103–105°. *Anal.* Calcd for $[(C_2H_5)_2P(NH_2)_2]Cl$: N, 17.89. Found: N, 17.9. The infrared spectrum of this material was identical with that of diethyldiaminophosphonium chloride (mp 106–108.5°) produced by the chloramination–ammonolysis of diethylchlorophosphine[2]; yield: 1.07 g (68% of theory).

Reaction of Tetraphenyldiphosphine with Chloramine and Ammonia.—In a typical experiment, 1.05 g (2.8 mmoles) of tetraphenyldiphosphine was dissolved in 75 ml of dry benzene and treated with the gaseous ammonia–chloramine mixture from the chloramine generator. A white precipitate formed immediately, and the temperature of the solution increased to 30–40° as the reaction proceeded. Chloramination was continued for 15–20 min until the solution became cool from evaporation of the solvent. The benzene solution was removed by filtration, and the solids were washed with 25 ml of fresh benzene. The combined filtrate and washings were evaporated to dryness yielding 0.39 g of a white powder which melted at 80–110°. After several recrystallizations from benzene the material melted at 162–163°. *Anal.* Calcd for $(C_6H_5)_2P(O)NH_2$: N, 6.48. Found: N, 6.6, 6.5. The infrared spectrum (Table I) is consistent with the formula $(C_6H_5)_2P(O)NH_2$ (lit.[12] mp 165–167°).

The benzene-insoluble solids were extracted with two 10-ml portions of hot chloroform. These extracts were combined and concentrated to about half the original volume by evaporation. White crystals precipitated and were removed by filtration and dried under vacuum; mp 239–241°. *Anal.* Calcd for $[(C_6H_5)_2P(NH_2){-}N{=}P(NH_2)(C_6H_5)_2]Cl$: N, 9.30. Found: N, 8.9. The infrared spectrum of this material is identical with that of $[(C_6H_5)_2P(NH_2){-}N{=}P(NH_2)(C_6H_5)_2]Cl$ (mp 245–246°) produced by the reaction of ammonia and chloramine with diphenylchlorophosphine;[1] yield: 0.42 g (33% of theory based on tetraphenyldiphosphine). If the vacuum-drying process was not prolonged, the 1:1 chloroform adduct[13] of the substance was obtained. *Anal.* Calcd for $[(C_6H_5)_2P(NH_2){-}N{=}P(NH_2)(C_6H_5)_2]Cl\cdot CHCl_3$: N, 7.36. Found: N, 7.3.

The chloroform-insoluble residue was extracted with 25 ml of hot, 4:1 acetone–ethanol mixture. The product was precipitated from this solution by the addition of diethyl ether. This material was recrystallized from 4:1 acetone–ethanol, filtered, and dried under vacuum; mp 207–209°. *Anal.* Calcd for $[(C_6H_5)_2P(NH_2)_2]Cl$: C, 57.04; H, 5.58; P, 12.26; N, 11.09; Cl, 14.03. Found: C, 56.22; H, 5.84; P, 11.78; N, 10.69; Cl, 14.50. Yield: 0.20 g (14% of theory based on tetraphenyl diphosphine). This material hydrolyzes rapidly in water.

Reaction of Tetraphenylcyclotetraphosphine with Chloramine and Ammonia.—In a typical experiment, 1.16 g (2.69 mmoles) of tetraphenylcyclotetraphosphine was dissolved in 75 ml of dry benzene and treated with the gaseous ammonia–chloramine mixture from the chloramine generator. A white precipitate formed, and the temperature of the solution increased to 30–40° as the reaction continued. The chloramine–ammonia mixture was passed through the solution for 15–20 min until the solution became cool from evaporation of the solvent. The benzene solution was removed by filtration, and the solids were washed with 25 ml of fresh benzene. The combined filtrate and washings were evaporated under vacuum. As the solution cooled, a trace of oily product precipitated and was removed and discarded. The evaporation was continued. After evaporation of the solution to dryness, 0.53 g of a white solid was recovered. This material softened in the range of 58–69° and slowly melted in the range of 80–120°. *Anal.* Calcd for



$$Cl{-}\left[{-}P(NH_2)(C_6H_5){=}N{-}\right]_5{-}P(NH_2)(C_6H_5){=}NH$$

C, 49.98; H, 5.01; P, 21.48; N, 19.43; Cl, 4.10; mol wt, 865. Found: C, 49.74; H, 5.21; P, 21.43; N, 19.20; Cl, 4.08; mol wt, 870. Yield: 0.53 g (34% of theory). In several experiments, the yield of this material varied from 30 to 57% of theory. The substance hydrolyzes slowly in moist air.

The benzene-insoluble solids were extracted with 30 ml of hot, 2:1 acetone–ethanol mixture. This solution was carefully filtered twice under dry nitrogen to remove NH_4Cl. Diethyl ether was added to precipitate the product which was filtered under dry nitrogen and dried under vacuum; mp 164–165°. *Anal.* Calcd for $[(C_6H_5)P(NH_2)_3]Cl$: C, 37.61; H, 5.79; P, 16.17; N, 21.93; Cl, 18.50. Found: C, 38.24; H, 6.15; P, 16.37; N, 21.96; Cl, 17.35. Yield: 0.39 g (19% of theory).

This triaminophosphonium chloride is extremely sensitive to hydrolysis giving the diamide, $C_6H_5P(O)(NH_2)_2$,[14] which melts at 187–188° (lit.[14] mp 189°) after several recrystallizations from ethanol. *Anal.* Calcd for $C_6H_5P(O)(NH_2)_2$: C, 46.16; H, 5.81; P, 19.84; N, 17.94; O, 10.25. Found: C, 45.47; H, 5.81; P, 19.86; N, 17.95; O (by difference), 10.43. Attempts to recrystallize phenyltriaminophosphonium chloride yielded the diamide as did subsequent extractions of the reaction mixture with acetone and ethanol; yield of diamide extracted from the reaction mixture: 0.16 g (10% of theory based on tetraphenylcyclotetraphosphine).

Reaction of Dimethyldiaminophosphonium Chloride with Phosphorus(V) Chloride.—In an inert-atmosphere box under dry nitrogen, dimethyldiaminophosphonium chloride (8.25 mmoles) was placed in a 100-ml round-bottom flask equipped with a side arm for introduction of nitrogen. Phosphorus(V) chloride (8.25 mmoles) was added, and the reactants were mixed thoroughly. After adding 25 ml of dry benzene, the mixture was removed to a hood and refluxed. A slow flow (less than 1 l./min) of dry nitrogen was passed over the mixture and then bubbled through a benzene solution of triethylamine. Hydrogen chloride was evolved from the refluxing mixture and was collected as triethylamine hydrochloride. After about 3 days of reaction, 3.86 g of triethylamine hydrochloride had been recovered, and the rate of evolution of HCl from the reaction mixture was negligible The clear benzene solution was evaporated to dryness under vacuum, yielding 1.56 g of crude product. Sublimation of this material at 50° (0.15 mm) yielded 0.75 g of white sublimate and 0.81 g of a hard residue. The sublimate was further purified by several recrystallizations from benzene or hexane and repeated sublimations as 50° (0.1 mm); mp 174–176° subl. Though no complete structural investigation was undertaken, it is interesting to note that in the infrared spectrum of this material (Table I) a doublet near 1300 cm^{-1} occurs. This is similar to the P–CH_3 doublet occurring in the fully substituted derivatives, $[(CH_3)_2PN]_{3,4}$.[15] In addition, two peaks appear in the P=N stretching region at 1220 and 1170 cm^{-1}. *Anal.* Calcd for $(CH_3)_2Cl_4P_3N_3$: C, 7.83; H, 1.97; P, 30.28; N, 13.70; Cl, 46.22; mol wt, 307. Found: C, 8.03; H, 2.20; P, 29.53; N, 14.07; Cl, 46.07; mol wt, 308. In several experiments, the yield of this material varied from 26 to 59% of theory based on the PCl_5 used.

The residue from the sublimation was an air-sensitive substance which, upon pyrolysis at 180–190° (0.1 mm), produced more $(CH_3)_2Cl_4P_3N_3$ as a sublimate and also yielded a glassy residue which was insoluble and infusible up to 300°. The infrared spectrum of this residue contains a broad band in the phos-

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phonitrilic P=N region at 1250 cm^{-1}. Analytical data indicate that this material may be a cross-linked polymer derived from the unit $[(CH_3)_2PN\cdot Cl_2PN]$.

Discussion

The results of this study demonstrate that under the conditions of this experiment, chloramine cleaves the phosphorus–phosphorus bonds in tetramethyldiphosphine, tetraethyldiphosphine, tetraphenyldiphosphine, and tetraphenylcyclotetraphosphine. Indeed, the products in each case are those which are known to form in the reactions of the corresponding monohalo- or dihalophosphines with mixtures of ammonia and chloramine. Apparently, chloramine cleaves the P–P bond in diphosphines, for example, giving an aminophosphine and a chlorophosphine

$$R_2P{-}PR_2 + NH_2Cl \longrightarrow R_2PNH_2 + ClPR_2$$

These products are then presumed to undergo further chloramination and ammonolysis to produce the observed products.

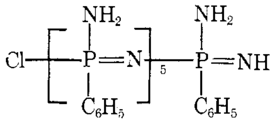
This reaction seems to favor the production of diaminophosphonium chlorides. The reaction of ammonia–chloramine mixtures with tetramethyldiphosphine and tetraethyldiphosphine produces dimethyldiaminophosphonium chloride and diethyldiaminophosphonium chloride as the main products, respectively. This method is more convenient for the preparation of these phosphonitrilic precursors[2,3] than the chloramination–ammonolysis of dialkylchlorophosphines because tetraalkyldiphosphines are easier to synthesize and have longer shelf-lives than dialkylchlorophosphines. The reaction of the ammonia–chloramine mixture with tetraphenyldiphosphine gives diphenyldiaminophosphonium chloride, a material which was a postulated product in the reaction of ammonia and chloramine with diphenylchlorophosphine[1] but was never isolated. Similarly, the reaction of the ammonia–chloramine mixture with tetraphenylcyclotetraphosphine produces phenyltriaminophosphonium chloride.

The reaction of the gaseous mixture of ammonia and chloramine with tetraphenyldiphosphine produces $[(C_6H_5)_2P(NH_2){-}N{=}P(NH_2)(C_6H_5)_2]Cl$ and diphenylphosphinic amide $(C_6H_5)_2P(O)NH_2$ in addition to the diphenyldiaminophosphonium chloride. This amide may arise from the chloramination and ammonolysis of $(C_6H_5)_2P{-}P(O)(C_6H_5)_2$, a possible contaminant in the starting material

$$(C_6H_5)_2P{-}P(O)(C_6H_5)_2 + 2NH_2Cl + 2NH_3 \longrightarrow [(C_6H_5)_2P(NH_2)_2]Cl + H_2NP(O)(C_6H_5)_2 + NH_4Cl$$

or it could result from the hydrolysis of diphenyldiaminophosphonium chloride.

It is interesting to note that the reaction of ammonia and chloramine with tetraphenylcyclotetraphosphine produces a linear phosphonitrilic derivative



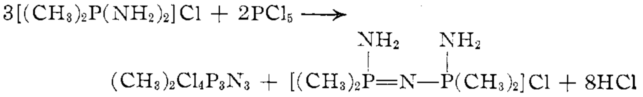
$$Cl{-}\left[\overset{NH_2}{\underset{C_6H_5}{P}}{=}N\right]_5{-}\overset{NH_2}{\underset{C_6H_5}{P}}{=}NH$$

in addition to the triaminophosphonium salt. Pyrolysis of this substance produces ammonium chloride and a polymeric material which has a lower nitrogen content than the original material and is probably a cross-linked phosphonitrilic polymeric material.

Considering the products of the reaction of dimethyldiaminophosphonium chloride with phosphorus(V) chloride, the formation of polymeric $[(CH_3)_2PN\cdot Cl_2PN]_n$ may be rationalized in terms of the equation

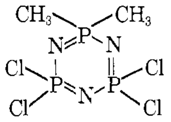
$$n[(CH_3)_2P(NH_2)_2]Cl + nPCl_5 \longrightarrow [(CH_3)_2PN\cdot Cl_2PN]_n + 4nHCl$$

The formation of $(CH_3)_2Cl_4P_3N_3$ probably involves reaction with NH_4Cl produced by self-condensation of $[(CH_3)_2P(NH_2)_2]Cl$. A possible over-all reaction would be



$$3[(CH_3)_2P(NH_2)_2]Cl + 2PCl_5 \longrightarrow (CH_3)_2Cl_4P_3N_3 + [(CH_3)_2\overset{NH_2}{P}{=}N{-}\overset{NH_2}{P}(CH_3)_2]Cl + 8HCl$$

Considering the fact that the temperature of the reactants never exceeded 80°, it seems likely that no $P{-}CH_3$ bonds are broken during the reaction and, therefore, that both methyl groups are on the same phosphorus atom. Thus, the substance $(CH_3)_2Cl_4P_3N_3$ may be assigned the structure



This represents the first report of the synthesis of a geminal dialkyltetrachlorophosphonitrile.

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