oxide.—The solution of 2.26 g. (0.01 mole) of the bis-difluorophosphorane in 10 ml. of water was allowed to stand overnight and was then evaporated on a steam bath to leave a very deliquescent white solid, which was dried *in vacuo* over phosphorupentoxide at 80° (0.1 mm.) for 20 hr. The dried product was sublimed twice at 230-240° (oil bath temperature) (0.2 mm.); a melting point of *ca.* 230° being observed. A determination of the melting point on the sublimed material invariably led to values about 20° lower when the sample was sealed in the capillary at atmospheric pressure. A sample of the diphosphine dioxide was, therefore, placed in a capillary, heated at 130° (0.1 mm.) for 1 hr., and sealed under vacuum. A reproducible m.p. of 236.5-237.5° was thus observed, in excellent agreement with the literature[18] m.p. of 232°.

Anal. Calcd. for $C_6H_{16}O_2P_2$: C, 39.6; H, 8.9. Found: C, 39.3; H, 9.0.

Acknowledgment.—The author is indebted to Mr. R. J. Berndt, Central Research Department, E. I. du Pont de Nemours and Company, for the mass spectroscopic analyses.

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Preparation of Heterosubstituted Phosphonitriles by Ring Closure Reactions

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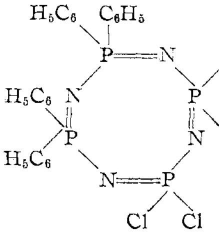
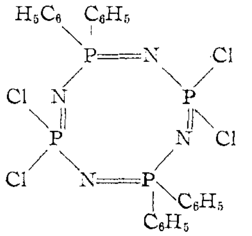
Iminobis(aminodiphenylphosphorane) chloride, $[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$, reacts with pentavalent phosphorus halides to yield cyclic phosphonitrilic trimers and tetramers. Cyclization with phosphorus pentachloride gives 1,1,3,3-tetraphenyl-5,5-dichlorophosphonitrile trimer and 1,1,3,3-tetraphenyl-5,5,7,7-tetrachlorophosphonitrile tetramer. With phenyltetrachlorophosphorane, pentaphenyl monochlorophosphonitrile trimer and two hexaphenyldichlorophosphonitrile tetramers are formed. Reaction of the bis(aminophosphorane) with diphenyltrichlorophosphorane gives $[(C_6H_5)_2PN]_3$ and $[(C_6H_5)_2PN]_4$.

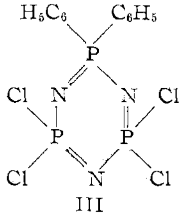
Introduction

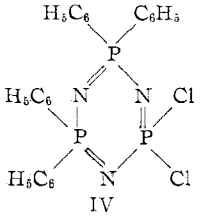
The preparation of cyclic phosphonitriles of the type $R_{2x-y}Cl_yP_xN_x$ (where R = aryl or alkyl and X = 3 or 4) has been reported by several investigators. Bode and Thamer[1] treated dichlorophosphonitrile tetramer with phenylmagnesium bromide and isolated compounds I and II which were assigned the structures


I, m.p. 205°


II, m.p. 176°

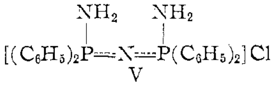
Using the Friedel–Crafts reaction, Bode and Bach[2] prepared III from dichlorophosphonitrile trimer and aluminum chloride; under more vigorous conditions, Shaw and Wells[3] obtained IV employing the same process.


III


IV

In all these instances mixed substitution occurred geminally on the existing phosphonitrile ring systems. The procedures described above offer poor yields and a multiplicity of products. It seemed probable that higher yields of single component products could be obtained by the proper ring closure reaction.

This paper describes the results of ring closure reactions between pentavalent phosphorus halides and a bis(aminodiphenylphosphorane). The latter compound has been prepared by the reaction of diphenyltrichlorophosphorane with ammonia[4-6] and by the reaction of diphenylchlorophosphine with ammonia and chloramine.[7] The structure of the phosphorane has been postulated to be[7]


$$[(C_6H_5)_2\overset{NH_2}{\overset{|}{P}}{=}N{=}\overset{NH_2}{\overset{|}{P}}(C_6H_5)_2]Cl$$
V

Experimental

The phenyldichlorophosphine and diphenylchlorophosphine used in these experiments were obtained from Victor Chemical Works.

The reactions were conducted in all-glass assemblies either on a vacuum line or in an inert atmosphere chamber. All melting points are uncorrected.

Diphenyltrichlorophosphorane.—Dry chlorine gas (48.21 g., 0.68 mole) was condensed into a nickel-plated bomb containing 3000 ml. of carbon tetrachloride and 150.2 g. (0.68 mole) of diphenylchlorophosphine at −196°. After standing overnight at

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(1) H. Bode and R. Thamer, *Ber.*, **76B**, 121 (1943).

(2) H. Bode and H. Bach, *ibid.*, **75B**, 215 (1942).

(3) R. A. Shaw and F. B. G. Wells, *Chem. Ind.* (London), 1189 (1960).

(4) NavOrd Report 4600, July–Sept., 1956, U. S. Naval Ordnance Laboratory, Corona, Calif.

(5) V. V. Korshak, I. A. Gribova, T. V. Artamonova, and A. N. Bushmarina, *Vysokomolekul. Soedin.*, **2**, 377 (1960).

(6) I. I. Bezman and J. H. Smalley, *Chem. Ind.* (London), 839 (1960).

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

$-20°$ the temperature was increased to 25° and the mixture shaken vigorously for 1 hr. The precipitated solid was collected and dried. The crude product weighed 193 g. (97%). After being recrystallized twice from benzene the product was isolated as needles, m.p. 194–200° dec.

Anal. Calcd. for $C_{12}H_{10}PCl_3$: Cl, 36.5. Found: Cl, 36.8.

Preparation of Compound V.—Dry diphenyltrichlorophosphorane (25.7 g., 0.0882 mole) was introduced into a 1-l. round-bottomed flask containing a magnetic stirrer. Then 500 ml. of anhydrous ethanol-free chloroform was transferred *in vacuo* into the flask at $-196°$. Next, 6.2 g. (0.37 mole) of ammonia was condensed into the reaction flask during a 2-hr. period while the temperature of the reaction mixture was allowed to increase gradually to 25°. The reaction mixture was stirred overnight; subsequently the solvent was removed under vacuum. Product V was purified by first extracting the material with water (5°) to remove ammonium chloride, followed by recrystallization of the residue from methanol–benzene to yield compound V (12.9 g., 65%) as white needles, m.p. 245–246°, lit.[6,7] m.p. 245–246.5°.

Anal. Calcd. for $C_{24}H_{24}P_2N_3Cl$: C, 63.8; H, 5.4; P, 13.7; N, 9.3; Cl, 7.8; mol. wt., 452. Found: C, 64.0; H, 5.6; P, 13.8; N, 9.1; Cl, 7.6; mol. wt., 446 (f.p. depression of bromoform).

To demonstrate that self-condensation of V did not occur by heating it below the melting point, 2.0 g. of V was heated *in vacuo* for 12 hr. at 180–185°. After this treatment, V was recovered unchanged, as shown by its infrared spectrum and melting point.

Reaction of V with Phosphorus Pentachloride.—A mixture of 9.0 g. (0.02 mole) of V and 4.2 g. (0.02 mole) of freshly sublimed phosphorus pentachloride was heated under vacuum at 135° for 16 hr. Toward the end of the heating period the evolution of hydrogen chloride (identified by infrared spectral analysis), which had been very vigorous initially, became negligible.

The reaction mixture was extracted with boiling benzene; the insoluble portion was removed by filtration. The benzene solution was concentrated to near dryness, then boiling ligroin (b.p. 90–120°) was added. On cooling, white crystals were formed; recrystallization from ligroin gave IV (2.6 g., 25%), m.p. 142–143° (sealed tube); lit.[3] m.p. 142°.

Anal. Calcd. for $C_{24}H_{20}Cl_2P_3N_3$: C, 56.1; H, 3.9; P, 18.1; N, 8.2; Cl, 13.8; mol. wt., 513. Found: C, 56.2; H, 4.0; P, 18.2; N, 8.3; Cl, 13.8; mol. wt., 509 (f.p. depression of benzene).

The benzene–ligroin solution (remaining after removal of IV) was concentrated, and, upon standing, a white crystalline material was observed. Recrystallization of this material from acetonitrile yielded 0.8 g. (6%) of tetrachlorotetraphenylphosphonitrile tetramer, m.p. 135° (sealed tube).

Anal. Calcd. for $C_{24}H_{20}Cl_4P_4N_4$: C, 45.8; H, 3.2; P, 19.7; N, 8.9; Cl, 22.3; mol. wt., 630. Found: C, 46.1; H, 3.3; P, 19.7; N, 8.7; Cl, 22.4; mol. wt., 615 (f.p. depression of bromoform).

The benzene-insoluble portion of the reaction mixture described above was dissolved in acetonitrile and upon long standing in the air a compound crystallized out, melting sharply at 171°. This melting point is identical with that reported[5] for $(C_6H_5)_2P(O)NH(C_6H_5)_2PN(C_6H_5)_2PNP(O)(C_6H_5)_2$.

Anal. Calcd. for $C_{48}H_{41}P_4N_3O_2$: C, 70.7; H, 5.0; P, 15.2; N, 5.1; O, 4.0. Found: C, 70.8; H, 5.0; P, 14.8; N, 5.5; O, 3.9.

Preparation of Phenyltetrachlorophosphorane.—Dry chlorine gas (33.4 g., 0.47 mole) was condensed into a stainless steel bomb containing 500 ml. of dry carbon tetrachloride and 84.0 g. (0.47 mole) of phenyldichlorophosphine at $-196°$. The temperature was increased to 25° and the mixture shaken vigorously for 1 hr. The solvent was removed by evaporation under vacuum, yielding 112.1 g. (95%) of crude phenyltetrachlorophosphorane. After recrystallization from carbon tetrachloride, the product formed white needles, m.p. 75–76°, lit.[8] m.p. 73°.

Anal. Calcd. for $C_6H_5PCl_4$: C, 28.8; H, 2.0; P, 12.4; Cl, 56.8. Found: C, 28.6; H, 2.1; P, 12.3; Cl, 56.9.

Reaction of V with Phenyltetrachlorophosphorane.—A mixture of 10.2 g. (0.02 mole) of V and 5.2 g. (0.02 mole) of phenyltetrachlorophosphorane was heated gradually over the course of 16 hr. to 140°. During the heating period, 2 equivalents of hydrogen chloride were evolved. The resulting mixture was extracted with ethyl ether. Concentration of the ether solution gave 3.5 g. of white solid material (m.p. 150–165°), which was fractionally recrystallized from ligroin (b.p. 90–120°) to yield 2.0 g. of dichlorohexaphenylphosphonitrile (VI) (m.p. 192–193°) as white needles.

Anal. Calcd. for $C_{36}H_{30}P_4N_4Cl_2$: C, 60.7; H, 4.2; P, 17.4; N, 7.8; Cl, 9.9; mol. wt., 713. Found: C, 60.7; H, 4.2; P, 17.4; N, 8.0; Cl, 9.7; mol. wt., 695 (f.p. depression of benzene).

Concentration of the above ligroin solution yielded 0.8 g. of another material, VII (m.p. 154–155°), with the same elemental analysis. The infrared spectrum, although very similar to that of VI, was not identical.

Anal. Calcd. for $C_{36}H_{30}P_4N_4Cl_2$: C, 60.7; H, 4.2; P, 17.4; N, 7.8; Cl, 9.9; mol. wt., 713. Found: C, 60.9; H, 4.4; P, 17.4; N, 7.9; Cl, 9.7; mol. wt., 690 (f.p. depression of benzene).

Evaporation to dryness of the ethereal solution described above yielded 0.6 g. (5%) of crude VIII, $(C_6H_5)_5ClP_3N_3$ (m.p. 95–100°). Repeated recrystallizations from ligroin (b.p. 90–120°) gave VIII as white needles, m.p. 150–151°.

Anal. Calcd. for $C_{30}H_{25}P_3N_3Cl$: C, 65.0; H, 4.5; P, 16.7; N, 7.6; Cl, 6.3; mol. wt., 556. Found: C, 64.7; H, 4.7; P, 16.7; N, 7.7; Cl, 6.2; mol. wt., 536 (f.p. depression of benzene).

Reaction of V with Diphenyltrichlorophosphorane.—A mixture of 2.9 g. (0.01 mole) of diphenyltrichlorophosphorane and 4.5 g. (0.01 mole) of V was heated gradually under vacuum to 125° during an 8-hr. period. The resulting product mixture was extracted with boiling benzene, then filtered to remove 1.5 g. of crude V. From the benzene solution was isolated diphenylphosphonitrile trimer, m.p. 228–230°, lit.[9] m.p. 230–232°. The yield (1.4 g.) was 35% based on the amount of V used.

In another experiment, a mixture of 2.9 g. (0.01 mole) of diphenyltrichlorophosphorane and 4.5 g. (0.01 mole) of V was heated gradually to 185° during an 8-hr. period. The product mixture was extracted with boiling benzene and then filtered to remove 0.1 g. of ammonium chloride. Diphenylphosphonitrile tetramer (1.9 g. 24%) was isolated as white needles from a benzene solution by fractional recrystallization, m.p. 319.5–321°, lit.[9] m.p. 319.5–321°.

Concentration of the filtrate remaining after removal of the tetramer yielded, by fractional crystallization, 2.0 g. (34%) of diphenylphosphonitrile trimer, m.p. 228–230°.

Discussion

It is evident from the experimental data presented above that the ring closure reactions can be used successfully in the preparation of cyclic phosphonitrile trimers which contain the two equivalent phosphorus atoms of the bisdiphenylaminophosphorane, V, and the third phosphorus atom from the pentavalent halide. These reactions can be summarized in the equations

$$V + (C_6H_5)_2PCl_3 \longrightarrow [(C_6H_5)_2PN]_3 \qquad (1)$$

$$V + C_6H_5PCl_4 \longrightarrow (C_6H_5)_5ClP_3N_3 \qquad (2)$$

$$V + PCl_5 \longrightarrow (C_6H_5)_4Cl_2P_3N_3 \qquad (3)$$

The yields of the expected trimers are modest. The major unexpected result is the formation of significant quantities of tetramers which arise from the interaction of two moles of the monomeric species with V. The

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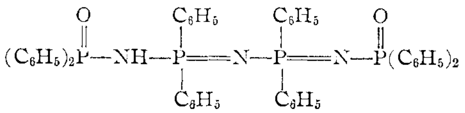
[8] A. Michaelis, *Ber.*, **6**, 816 (1873).

[9] C. P. Haber, D. L. Herring, and E. A. Lawton, *J. Am. Chem. Soc.*, **80** 2116 (1958).

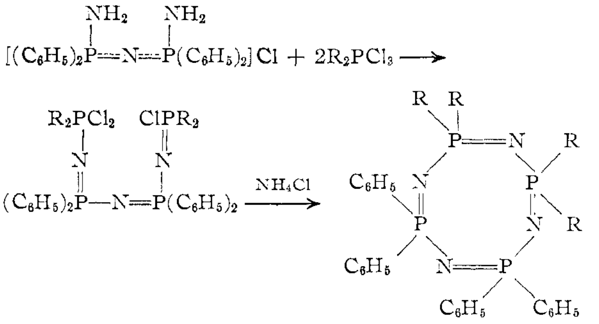
stoichiometry of this reaction requires the availability of a mole of ammonium chloride. One possible source of ammonium chloride would be the condensation of two molecules of V to form diphenylphosphonitrile tetramer. While negligible amounts of the latter compound were recovered from the reactions represented in eq. 2 and 3, in both cases when the reaction mixture was exposed to atmospheric moisture, the compound



$$(C_6H_5)_2\overset{O}{\overset{\|}{P}}-NH-\underset{C_6H_5}{\overset{C_6H_5}{P}}=N-\underset{C_6H_5}{\overset{C_6H_5}{P}}=N-\overset{O}{\overset{\|}{P}}(C_6H_5)_2$$

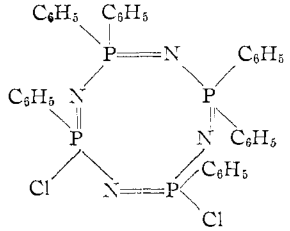
was isolated. This hydrolysis product could arise from a linear or possibly a cyclic precursor of diphenylphosphonitrile tetramer. While the identity of the intermediate has not been established, it, too, is most likely formed from the condensation of two moles of V, with the elimination of ammonium chloride.

This explanation of the formation of the hetero-substituted cyclic tetramers can be depicted as shown below.



The isolation of a cyclic tetraphenyltetrachlorotetraphosphonitrile with a melting point (135°) lower than the two isomers (I, m.p. 205°, and II, m.p. 176°) reported by Bode and Thamer[1] suggests that the conformational isomer of I or II has been obtained. It appears that the new compound reported in this work is probably the isomer of I rather than II because of the structure of the starting materials. While the possibility of the tetrachlorotetraphenylphosphonitrile (m.p. 135°) being a mixture of isomers, can, of course, not be entirely eliminated, it seems unlikely that this is the case since this material can be recrystallized from a variety of solvents without change in melting point or infrared spectrum. The other possible structure for the new compound would be one which has a phenyl group and a chlorine atom on each phosphorus, but this possibility seems unlikely because of the extensive rearrangements required.

In addition to the predicted trimeric pentaphenylmonochlorophosphonitrile, the reaction of V with phenyltetrachlorophosphorane yielded two materials with different melting points and the same chemical analyses. Molecular weight data and the similarity of the infrared spectra with the strong absorption at 7.9 μ indicate that these materials are isomeric hexaphenyldichlorophosphonitrile tetramers (VI).



VI

The isomeric possibilities for such a compound, again excluding rearrangement of V, are two geometrical isomers and two conformational isomers.

In general, the yields of cyclic trimers and tetramers isolated from the reaction mixtures represent, at most, only 50% of the crude products. The significance of this observation is the fact that these relatively simple reactions, performed in an environment not unlike that encountered in the widely-used synthesis of the phosphonitriles *via* R_2PCl_3 and NH_4Cl or NH_3, lead to a multiplicity of products. One must conclude that the formation of phosphonitrile polymers represents a highly complex series of reactions with alternate paths possible with the introduction of each additional phosphorus atom.

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