[CONTRIBUTION FROM CHEMISTRY DIVISION, U. S. NAVAL ORDNANCE LABORATORY]

Synthesis of Cyclic Trimeric and Cyclic Tetrameric Diphenylphosphinic Nitride

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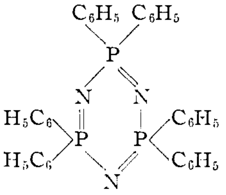
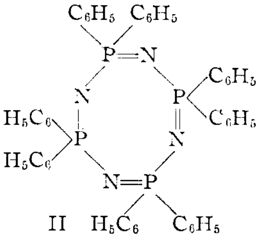
Cyclic trimeric diphenylphosphinic nitride and cyclic tetrameric diphenylphosphinic nitride were synthesized by two methods: (a) the reaction of diphenylphosphorus trichloride with ammonium chloride; and (b) the reaction of diphenylphosphorus trichloride with liquid ammonia.

The preparation of cyclic trimeric diphenylphosphinic nitride was first reported by Rosset[2] in 1925. In the method which he employed, phenylmagnesium bromide reacted with cyclic trimeric dichlorophosphinic nitride to give a low yield of the cyclic trimeric diphenylphosphinic nitride. At a later date, Bode and Thamer[3] using similar methods prepared both the cyclic trimeric and the cyclic tetrameric diphenylphosphinic nitrides in low yields.

In the present investigation, the cyclic trimeric diphenylphosphinic nitride (I) and the cyclic tetrameric diphenylphosphinic nitride (II) were prepared by two methods: (a) the reaction of diphenylphosphorus trichloride[4] with ammonium chloride in *sym*-tetrachloroethane at 130–135°, which is described by the equation


I


II

$$(C_6H_5)_2PCl_3 + NH_4Cl \longrightarrow [(C_6H_5)_2PN]_n + 4HCl$$

gave low yields of cyclic trimer I and cyclic tetramer II; (b) the reaction of diphenylphosphorus trichloride with excess liquid ammonia took place according to the expression

$$(C_6H_5)_2PCl_3 + 4NH_3 \longrightarrow [(C_6H_5)_2PN]_n + 3NH_4Cl$$

From the second reaction, a white, crystalline, moisture-sensitive product was obtained which, when separated from NH_4Cl, was converted quantitatively to a mixture of diphenylphosphinic nitride polymers by heating the intermediate product *in vacuo* at 275°. From the mixture of diphenylphosphinic nitride polymers, which was obtained in 65% over-all yield, a 7% yield of cyclic trimeric diphenylphosphinic nitride (I), m.p. 230–232° (lit. m.p. 228°, 232°) and a 48% yield of cyclic tetrameric diphenylphosphinic nitride (II), m.p. 319.5–321° (lit. m.p. 310°) was obtained. The residual mixture of higher homologs of diphenylphosphinic nitrides was not separated or further characterized.

Both of the cyclic diphenylphosphinic nitrides were unaffected by prolonged boiling with water. The cyclic trimeric diphenylphosphinic nitride (I) was readily soluble in benzene and glacial acetic acid while the cyclic, tetrameric diphenylphosphinic nitride (II) was sparingly soluble in these solvents.

Experimental[5]

Diphenylchlorophosphine.[6]—The phenyldichlorophosphine used in this experiment was obtained from Victor Chemical Works.[7]

Phenyldichlorophosphine, 502 g. (2.82 moles), was heated for a period of 120 hours at 320–340° in a heavy walled Pyrex glass ampoule. The mixture was fractionated through a three-plate column yielding 37.9 g. (20%) of diphenylchlorophosphine, b.p. 110–112° at 0.2–0.3 mm., and 197 g. of unchanged phenyldichlorophosphine.

Anal. Calcd. for $C_{12}H_{10}PCl$: Cl, 16.1. Found: Cl, 16.4.

Diphenylphosphorus Trichloride.—Dry chlorine gas, 48.21 g. (0.68 mole) was condensed into a nickel-plated bomb tube containing 300 ml. of carbon tetrachloride and 150.2 g. (0.68 mole) of diphenylchlorophosphine at −196°. After standing overnight at −20° the temperature was increased to 25° and the mixture shaken vigorously for two hours. The precipitated solid was collected and dried in an inert atmosphere drybox.[8] The crude product weighed 193 g. (97%). After being recrystallized twice from benzene the product was isolated as glistening white needles, m.p. 194–200° dec.

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

The Reaction of Diphenylphosphorus Trichloride with Liquid Ammonia.—Liquid ammonia, 250 ml. was condensed under vacuum at −196° into a reaction vessel containing 50.0 g. (0.172 mole) of diphenylphosphorus trichloride. The temperature was increased to −40° and the mixture was agitated for two hours by means of an o-ring sealed stirrer. After evaporation of the excess ammonia, the resulting solid was treated with $CHCl_3$. One-half of the solid material dissolved, leaving behind essentially pure NH_4Cl. From the $CHCl_3$ solution two distinct compounds were isolated by fractional crystallization, both of which on subsequent heating yielded a mixture of diphenylphosphinic nitride polymers and NH_4Cl. Because of the extremely hygroscopic nature of these materials, purification was difficult and no discrete composition could be assigned from the results of an elementary analysis and the infrared spectra. Both compounds were soluble in $CHCl_3$ and CH_3OH and gave on hydrolysis diphenylphosphonic acid.

Pyrolysis of the mixture of the two intermediate compounds, by heating gradually to 275° over the course of four hours, yielded a mixture of diphenylphosphinic nitride polymers and ammonium chloride. The phosphinic nitride material was isolated by extraction with benzene and amounted to 22.2 g. (65%).

Anal. Calcd. for $C_{12}H_{10}PN$: N, 7.0. Found: N, 7.0.

This mixture of diphenylphosphinic nitride polymers was redissolved in one liter of benzene, and from the resulting solution after standing overnight a precipitate of crystalline tetramer was collected. Evaporating off approximately 500 ml. of solvent benzene yielded, after cooling and filtration, a second precipitate of tetramer. The two precipitates were combined and recrystallized from benzene. When dried,

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[1] Battelle Memorial Institute, Columbus, Ohio.

[2] H. Rosset, *Compt. rend.*, **110**, 750 (1925).

[3] H. Bode and R. Thamer, *Ber.*, **76**, 121 (1943).

[4] W. A. Higgins, P. W. Vogel, W. G. Craig, THIS JOURNAL, **77**, 1864 (1955).

[5] All observed melting points are uncorrected.

[6] A. Broglie, *Ber.*, **10**, 628 (1877).

[7] Victor Chemical Works, Chicago Heights, Ill.

[8] NAVORD report No. 4567 (U. S. Naval Ordnance Laboratory report no. 318), Inert-Atmosphere Chamber for Chemical Operations, by D. L. Herring, Jan. 13, 1956.

the product as white needles, m.p. 319.5–321°, weighed 10.6 g. (48%).

Anal. Calcd. for $C_{48}H_{40}P_4N_4$: C, 72.3; H, 5.1; P, 15.6; N, 7.0; mol. wt., 797. Found: C, 72.6; H, 5.2; P, 15.5; N, 7.1; mol. wt., 833 (b.p. elevation of benzene).

The filtrate (remaining after removal of the tetramer) was concentrated to about 100 ml. and then extracted with three 50-ml. portions of hot 0.08 *N* NaOH. The filtrate was washed with water until neutral to litmus. After setting overnight, a precipitate of trimer was collected. Further concentration of the filtrate yielded, after cooling and filtration, a second precipitate. The two precipitates were combined and recrystallized three times from benzene to give a 7% yield of trimer, m.p. 230–232°.

Anal. Calcd. for $C_{36}H_{30}P_3N_3$: C, 72.3; H, 5.1; P, 15.6; N, 7.0; mol. wt., 597. Found: C, 72.3; H, 5.0; P, 15.4; N, 7.0; mol. wt. 585 (f.p. depression of $CHBr_3$).

The Reaction of Diphenylphosphorus Trichloride with Ammonium Chloride.—To a slurry of 11 g. (0.206 mole) of ammonium chloride in 200 ml. of *sym*-tetrachloroethane was added under nitrogen 27.8 g. (0.095 mole) of diphenylphosphorus trichloride. The mixture was heated at 130–135° for 18 hours. Hydrogen chloride, which formed during the course of the reaction, was removed on a current of nitrogen. The mixture was filtered to remove excess ammonium chloride and then concentrated at reduced pressure. The product mixture was dissolved in 300 ml. of benzene. After standing overnight, a precipitate of tetrameric diphenylphosphinic nitrite was collected. Concentration of the filtrate yielded a second precipitate of tetramer. The two precipitates were combined and recrystallized from benzene to give a 7% yield of tetramer, m.p. 314–318°. Two additional recrystallizations from benzene gave needles, m.p. 319–321°.

Anal. Calcd. for $C_{48}H_{40}P_4N_4$: mol. wt., 796. Found: mol. wt., 796 (60° Nier mass spectrometer).

The filtrate that remained after removal of the tetramer (described above) was concentrated to near dryness. After standing overnight, the precipitated trimeric diphenylphosphinic nitride was collected, and then stirred with 50 ml. of 2.5% NaOH solution for 2 hours to remove moisture-sensitive by-products. The trimer was collected, washed with water and then recrystallized from benzene. The product, m.p. 233–234°, as white needles, weighed 0.8 g. (4%).

Anal. Calcd. for $C_{36}H_{30}P_3N_3$: C, 72.3; H, 5.1; P, 15.6; N, 7.0; mol. wt., 597. Found: C, 72.2; H, 5.3; P, 14.7; N, 7.0; mol. wt., 597 (60° Nier mass spectrometer).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NORTH CAROLINA]

Triphenylphosphonium Salts

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Triphenylphosphonium salts of HCl, $HClO_4$, HI, $HSbCl_4$, $HFeCl_4$, H_2SnCl_6, $HFeBr_4$ and H_2SnBr_6 have been prepared and characterized briefly. It is suggested that absorption spectroscopy is the most definitive means of establishing the presence of the -onium structure.

Introduction

While studying reactions of substituted phosphines with metal halides, it was observed that triphenylphosphine forms a number of stable crystalline complexes with metal halides and the corresponding hydrohalic acids. The ternary complexes can be formulated as $(C_6H_5)_3PHMX_4$ and $[(C_6H_5)_3PH]_2MX_6$, suggesting immediately that they are phosphonium salts and that, as a class, they may exhibit greater stability than hitherto suspected. Previous examples of triphenylphosphonium salts are rare. $(C_6H_5)_3PHBr$ and $[(C_6H_5)P]$-$NiBr_2{\cdot}HBr$ have been mentioned in the patent literature.[1] $(C_6H_5)_3PHI$ and $[(C_6H_5)_3PHCl]_2PtCl_4$ were reported in 1885.[2]

A variety of triphenylphosphine–metal halide addition compounds are known, specifically those of cobalt, nickel and platinum. In spite of the low donor strength of the phosphorus atom in the environment of three phenyl groups, the stability of such addition compounds appears to be considerable. The unexpected stability can be ascribed to π-bonding between a filled d orbital of the metal and a vacant d orbital of the phosphorus atom. Such π-bonding would augment the σ-type coördinate bond formed using the lone pair on the phosphorus. Triphenylphosphonium compounds might well be considered unstable since no d-d π-bonding is possible between phosphorus and a proton.

The present work is directed toward enlarging the scope of triphenylphosphonium salts and to developing means of their characterization.

Experimental

Preparation of Compounds. Triphenylphosphonium Chloride.—The compound cannot be isolated from aqueous solutions even when present in high concentrations. When dry hydrogen chloride is passed into a dry ethereal solution of triphenylphosphine, a white oily suspension is produced, which crystallizes on stirring. After filtration and drying in a stream of dry air, the crystals are homogeneous, short, deliquescent needles. The crystals melt over a range of 70–73°, and recrystallization is very slow. The crystals are easily and irreversibly soluble in polar organic solvents. They are only slowly decomposed by water, due, we believe, to the formation of the insoluble triphenylphosphine on the crystal surfaces.

Anal. Calcd. for $(C_6H_5)_3PHCl$: Cl, 11.9; P, 10.35. Calcd. for $[(C_6H_5)_3PHCl]_3{\cdot}HCl$: Cl, 15.2; P, 9.95. Found: Cl, 15.1; P, 10.05.

Triphenylphosphonium Iodide.—$(C_6H_5)_3PHI$ has been reported previously.[2] The original method of preparation was followed. Triphenylphosphine dissolves readily in hot, concentrated hydriodic acid. On cooling the solution, colorless needles slowly separate. The crystals can be washed with small portions of cold glacial acetic acid and sucked dry with air. Like the other salts described below (though unlike the chloride), the crystals are not hygroscopic. They decompose slowly at 100°, more rapidly at higher temperatures. No melting occurs when a melting point tube containing some of the crystals is placed in a

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(1) German Patent 824,047, *C. A.*, **49**, 6998a (1955).

(2) A. Michaelis and H. v. Soden, *Ann.*, **229**, 295 (1885).