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Some Observations on the Synthesis of Octamethylcyclotetraphosphazene and Hexamethylcyclotriphosphazene

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As part of a general study of the reactions of heteroatom ring systems with transition metal carbonyls, we undertook the synthesis of octamethylcyclotetraphosphazene ($((CH_3)_8P_4N_4)$) and found that previously reported procedures[1,2] were unsatisfactory. The preparation of this compound therefore became a subject of study. Two improved synthetic procedures have been devised and are reported here.

Experimental Section

Method I.—In a typical synthesis 12.0 g of dimethyltrichlorophosphorane, $(CH_3)_2PCl_3$, obtained by chlorinating[3] tetramethylbiphosphine disulfide,[4] $[(CH_3)_2P(S)]_2$, was placed in a Pyrex tube, about 25 cm long and 2 cm in diameter, fitted with a 24/40 outer joint. Dry, finely powdered ammonium chloride (6.7 g), obtained by precipitating the salt from aqueous solution with acetone, was intimately mixed with the dimethyltrichlorophosphorane in the tube. The air in the tube was removed and replaced with prepurified nitrogen, and the tube was connected to a manifold through which a continuous stream of prepurified nitrogen could be passed. A bubbler filled with mineral oil placed at the end of the manifold served to monitor gas flow and maintain a slight positive pressure within the manifold. The tube was heated with an oil bath to 120° over a period of 1 hr at which time the mixture began to shrink and fuse and to evolve a colorless acidic gas, presumably HCl.

After about 30 min the vigorous bubbling had subsided and the tube was carefully evacuated. This caused a resumption of the vigorous bubbling and a sharp smelling gas (presumably HCl) was collected in a trap at $-196°$. The temperature of the reaction mixture was raised to about 150° over a period of 1 hr while pumping was continued. Within 1 hr more the reaction mixture had become a hard gray mass. After cooling the tube and filling it with nitrogen, this mass was chipped from the tube in a nitrogen-filled glove bag and transferred to a 100-ml, three-necked flask fitted with a condenser, stopper, and gas inlet.

With the flask filled with a nitrogen atmosphere 75.0 ml of chloroform, dried over molecular sieves, was added to the flask creating a gray suspension. The gray particles immediately dissolved with the evolution of heat when excess triethylamine, dried over molecular sieves, was added, an excess being determined when a drop of solution gave a positive test for base on damp pH paper. The solvent and excess triethylamine were removed using a rotary evaporator and the fluffy white residue was extracted repeatedly with hot petroleum ether (bp 30–60°) to yield practically pure octamethylcyclotetraphosphazene. Purity was indicated by its infrared spectrum, which was essentially identical with that reported.[1] After recrystallization from petroleum ether the substance had a melting point of 155–156° (uncor). Yields were typically 60% based on $(CH_3)_2PCl_3$. *Anal.* Calcd for $C_8H_{24}P_4N_4$: C, 32.03; H, 8.01; N, 18.68. Found: C, 31.70; H, 8.34; N, 18.90.

The mass spectrum, kindly measured by C. M. Lukehart, had a parent ion peak at *m/e* 300. The infrared spectrum given in Table I agrees with that reported.[1] No cyclic trimer could be detected in the product obtained by the above procedure. X-Ray study[5] of the compound $(CH_3)_8P_4N_4Mo(CO)_3$ prepared from it confirms the identity of the product.

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

$(CH_3)_8P_4N_4$ (in CCl_4 Solution)
2980 m, 2910 w, 1410 w, 1300 s, 1220 s, b, 990 m, 920 s, 870 s, 640 s

$(CH_3)_8P_4N_4 \cdot 2HCl$ (in 1,3-Hexachlorobutadiene Mull)
2970 m, 2900 m, 2810 s, b, 2560 s, b, 1320 s, 1278 s

$(CH_3)_8P_4N_4 \cdot 2HCl$ (in Nujol Mull)
1010 s, 975 m, 940 s, 900 m, 870 m, 790 m, 765 m, 725 w

[a] Key: s, strong; m, medium; w, weak; b, broad.

Method II.—Dimethyltrichlorophosphorane (3.5 g) was suspended in 200 ml of benzene. Ammonia gas, dried over KOH, was bubbled for 0.5 hr through the suspension. Heat was evolved and a white solid separated. This was collected, under nitrogen, on a glass frit and extracted with two 50-ml portions of a hot 1:1 acetone–ethanol mixture. Addition of 50 ml of petroleum ether to the cooled extracts caused precipitation of a solid which was collected on a frit under nitrogen. This compound was identified as dimethyldiaminophosphonium chloride, $(CH_3)_2(NH_2)_2PCl$, on the basis of its infrared spectrum[2] and its subsequent conversion to the cyclic trimeric and tetrameric dimethylphosphazenes. This conversion was accomplished[2] by sublimation at 190° and 0.1 Torr. The presence of both trimer and tetramer, in roughly equimolar proportions, was shown by the infrared spectrum. The yield of $(CH_3)_2P(NH_2)_2Cl$ was 40–50%. The mixture of cyclic trimer and tetramer can be separated by fractional crystallization as previously described.[1,2]

Discussion

Method I.—It has previously been postulated[1] that in method I linear polymers are formed in the initial reaction between dimethyltrichlorophosphorane and ammonium chloride and that the function of the triethylamine used in the second step is to promote cyclization by combining with hydrogen chloride which is formed in the cyclization reaction. This interpretation is similar to that proposed for the process of cyclization of linear alkylborazoles.[6]

We have conducted an extraction of the hard gray mass obtained in method I with boiling benzene in a Soxhlet extractor. Upon evaporation of the benzene no residue was obtained despite the fact that linear polymers of dimethylphosphazene are reported to be soluble in benzene.[7]

However, the infrared spectrum of the gray mass proved to be identical, except for peaks attributable to unreacted NH_4Cl, with that for the dihydrochloride of octamethylcyclotetraphosphazene. The latter was obtained by adding 4 ml of concentrated HCl to a solution of 0.25 g of the cyclic phosphazene in 10 ml of absolute ethanol and evaporating to dryness. Elemental analysis proved the product to be a dihydrochloride. The infrared spectrum of the dihydrochloride is given in Table I. We thus conclude that the intermediate obtained at the end of method I in the procedure does not consist of linear polymers but is instead a mixture of NH_4Cl and the dihydrochloride of the cyclic tetramer. We must then necessarily question the correctness of the reported[1] synthesis of linear polymers.

The previously published description of method I was

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[5] F. A. Cotton, G. Rusholme, and A. Shaver, unpublished work.

[6] H. S. Turner and R. J. Warne, *Chem. Ind. (London)*, 526 (1958).

[7] H. H. Sisler, S. E. Frazier, R. G. Rice, and M. G. Sanchez, *Inorg. Chem.*, **5**, 326 (1966).

very cryptic.[1] In this reaction an enormous amount of HCl is produced, *viz.*

$$4NH_4Cl + 4(CH_3)_2PCl_3 \longrightarrow [P(CH_3)_2N]_4 \cdot 2HCl + 14HCl$$

Our work indicates that it is crucial in order to obtain good yields that this HCl be efficiently removed. Hence the continuous sweeping with nitrogen followed by pumping are of vital importance. The removal of the remaining HCl by treatment with triethylamine is then very facile

$$[P(CH_3)_2N]_4 \cdot nHCl + n(C_2H_5)_3N \longrightarrow [P(CH_3)_2N]_4 + n(C_2H_5)_3NHCl$$

It is also worth stressing that method I has the advantage of giving pure tetramer, uncontaminated with trimer.

Method II.—This method is new although the approach was suggested by previously reported direct ammonolysis reactions.[8,9] It provides an efficient route to the intermediate $(CH_3)_2(NH_2)_2PCl$ which can then be used as previously described by Sisler and Frazier.[2] The equations are

$$(CH_3)_2PCl_3 + 4NH_3 \longrightarrow (CH_3)_2(NH_2)_2PCl + 2NH_4Cl$$

$$n(CH_3)_2(NH_2)_2PCl \longrightarrow x[P(CH_3)_2N]_3 + [(n - 3x)/4][P(CH_3)_2N]_4 + nNH_4Cl$$

This route differs from that in method I by providing, in roughly equimolar quantities, both the trimer and the tetramer, which can be separated by fractional crystallization.

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The Preparation of Hexaborane(10) from Octahydropentaborate(1−) Salts

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The preparation and characterization of alkali metal octahydropentaborate(1−) salts have been described.[1–7] Addition of B_2H_6 to LiB_5H_8 is a potentially useful reaction in that it can yield B_6H_{10} and $B_{10}H_{14}$.[3] We describe herein the preparation of B_6H_{10} in a procedure which offers substantial advantages over previously published methods.[8–13]

Experimental Section

Methods and Materials.—Standard vacuum-line techniques were used in the manipulation of volatile materials. Nonvolatile materials were transferred in a drybox in a nitrogen atmosphere. Pentaborane(9) and diborane(6) were obtained from the Callery Chemical Co. and used directly. Solutions of $LiCH_3$ in diethyl ether were purchased from Foote Chemical Co. and had known concentrations in the range 1.5–1.7 *M*. Reagent grade diethyl ether was dried over $LiAlH_4$ and distilled and stored under vacuum in a glass bulb equipped with a Fisher-Porter Teflon valve. Dimethyl ether was obtained in a cylinder from the Matheson Co. and used directly.

Preparation of LiB_5H_8 Solutions.—In typical syntheses, 30-mmol quantities of LiB_5H_8 were prepared in $(CH_3)_2O$ or $(C_2H_5)_2O$ solutions. In a drybox, a carefully measured volume of $LiCH_3$–ethyl ether solution (about 20 ml of a 1.5 *M* solution) was syringed into a 100-ml reaction flask which contained a Teflon-covered stirring bar (this vessel must be of adequate volume to contain the foam produced by the rapid evolution of methane in the reaction). The flask was fitted with a stopcock, placed on the vacuum line, cooled to −196°, and evacuated. In cases where $(CH_3)_2O$ was used, the $(C_2H_5)_2O$ was pumped away and an equal volume of $(CH_3)_2O$ was then distilled into the vessel. An amount of B_5H_9, equimolar to the $LiCH_3$ present, was condensed into the reaction vessel at −196°. The vessel was opened to an evacuated section of the vacuum line of sufficient volume to contain the anticipated gas evolution and then warmed to −78°. With $(C_2H_5)_2O$ as the solvent, it was sometimes necessary to warm the reaction mixture to about −50° in order to melt the B_5H_9 which was frozen to the side of the bulb. On such occasions, the solution was then quickly cooled to −78° in order to prevent excessive foaming. By observing the increasing pressure in the system the extent of reaction was followed; as it neared completion, the mixture was stirred and allowed to warm briefly in order to hasten completion of the reaction. While it is not possible to isolate LiB_5H_8 free of solvent, solutions thus produced appeared to be stable at room temperature for periods up to 1 hr.

For the preparation of LiB_5H_8 in greater than 30-mmol quantities, the required amount of $LiCH_3$ solution was syringed into the reaction bulb, but it was prudent to add B_5H_9 in 20–30-mmol increments and allow complete reaction before the addition of each successive increment.

Preparation of B_6H_{10}.—In a typical procedure, a 30-mmol quantity of B_2H_6 was allowed to expand into a reaction bulb at −78° which contained a dimethyl ether solution of 30 mmol of LiB_5H_8 that had been prepared by the method described above. The B_2H_6 was completely absorbed in 1–2 hr when the solution was stirred vigorously. Then the reaction vessel was opened to a U trap at −196° and the bulk of the solvent distilled from the reaction vessel at −78°. At this point the remaining material was white and solid at −78°. While constantly pumping through the U trap at −196°, this solid was stirred and slowly warmed to −15° over a period of several hours. The solid liquefied and thickened, first turning yellow and then yellow-brown, as H_2 was given off. The mixture was maintained at −15.3° (benzyl alcohol slush) until removal of volatile material to the U trap became prohibitively slow (several hours for the scale of reaction described herein). Then the mixture was slowly warmed to room temperature over several additional hours while continuously pumping volatile material into the U trap at −196°. The nonvolatile residue which remained consisted of $LiBH_4$ (identified by X-ray powder diffraction and boron-11 nmr), plus unidentified material.

Hexaborane(10) was isolated from the material which was collected in the U trap. This was accomplished by warming the trap to −45° and slowly distilling its contents through a series of traps which were maintained at −78, −95, and −196°. The fractionation process was continued until the material which collected in the −78° trap was shown to have a constant vapor pressure, 7.5 mm at 0°, in excellent agreement with an earlier report for B_6H_{10}.[14] The yield of B_6H_{10} from the −78° trap was about 6.5 mmol. The fraction which collected in the −95° trap consisted primarily of B_5H_9 but also contained some B_6H_{10}. Fractionating this material at −78° yielded another 1.0 mmol of B_6H_{10}, giving a total yield of 25% of the theoretical yield.

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