(O^{16} = 16) of 107.9028 ± 0.0013, where the indicated uncertainty is an over-all estimate of limit of error based on 95% confidence limits for the mean and including allowances for effects of known sources of possible systematic error. If, in conformity with the International Commission on Atomic Weights, the factor 1.000275 is used to convert to the chemical scale, we obtain 107.8731 ± 0.0020 for the chemical atomic weight (O = 16). Furthermore, using the factor 1.000317917 ± 17 × 10^{-9} [17] to convert from the physical scale to the recently proposed[18] unified physical and chemical scale (C^{12}=12), we obtain an atomic weight of 107.8685 ± 0.0013. In this case, an entirely negligible increase in uncertainty results from the scale conversion. These data with the identified uncertainty components are summarized in Table IV. The chemical scale (O=16) value differs significantly from the 1957 international value of 107.880.[19] However, the uncertainty in the present physical determination of this atomic weight is nearly an order of magnitude less than that previously reported.[20]

Summary and Conclusions.—A determination of the absolute isotopic abundance ratio of silver results in a new value for the chemical atomic weight of this element, which is one of the key elements in chemical determinations of atomic weights. Also of great importance are the atomic weights of chlorine and bromine through which the atomic weights of many elements are determined with respect to silver. Absolute isotopic abundance measurements of these halogens together with the present absolute abundance measurement of silver would be of inestimable value in establishing the chemical atomic weights of many isotopic elements.

Acknowledgments.—The authors are indebted to Ernest Garner for many of the careful mass spectrometric measurements included in this study, to W. J. Hamer for supplying the separated isotopes, to P. E. Desautels for supplying the native silver samples, to Mrs. M. M. Darr for spectroscopic analyses of the separated isotopes, to J. M. Cameron for statistical analysis and to W. H. Johnson, Jr., and A. O. Nier for communicating data on the nuclidic masses of silver. We also gratefully acknowledge helpful and encouraging discussions with F. L. Mohler and many other colleagues.

[17] "Atomic Masses of Nuclides, $A \leq 70$," F. Everling, L. A. König, J. H. E. Mattauch and A. H. Wapstra, submitted for publication (by private communication with Professor Mattauch).

[18] J. Mattauch, THIS JOURNAL, **80**, 4125 (1958); *Z. Naturforsch.*, **13a**, 572 (1958); T. P. Kohman, J. H. E. Mattauch and A. H. Wapstra, *Science*, **127**, 1431 (1958); *Physics Today*, **12**, 30 (1959); E. Wichers, *ibid.*, **12**, 28 (1959).

[19] E. Wichers, Report on the 1957 meeting of the International Committee on Atomic Weights, THIS JOURNAL, **80**, 4121 (1958).

[20] A. O. Nier, *Science*, **121**, 737 (1955).

[CONTRIBUTION FROM THE ORGANIC CHEMICALS DIVISION, ST. LOUIS RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY, ST. LOUIS, MISSOURI]

Hexaalkyl Phosphorous Triamide Borines

BY THEODOR REETZ AND B. KATLAFSKY

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Methods of preparation and properties of hexaalkyl phosphorous triamide borines are discussed. It was found that $P[N(CH_3)_2]_3$ is a stronger base than $N(CH_3)_3$, the order of coördination thus being P > N with respect to BH_3 as the reference acid. Accordingly, the reactivity of the hexaalkyl phosphorous triamide borines is lower than that of trimethylamine borine. The structure of the new compounds was established as being $(R_2N)_3PBH_3$.

G. Kodama[1] recently described the reaction of phosphorous trifluoride borine and ammonia. This reaction proceeds by direct substitution of the fluorine atoms with NH_2 groups without rupture of the phosphorus–boron bond, according to the equation

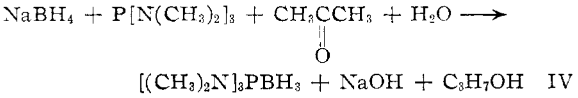
$$F_3PBH_3 + 6NH_3 \longrightarrow (NH_2)_3PBH_3 + 3NH_4F$$

Prior to this report we had prepared the hexamethyl phosphorous triamide borine, $[(CH_3)_2N]_3PBH_3$, by methods entirely different from that of Kodama. Our methods may be illustrated by the equations

$$(CH_3)_3NBH_3 + P[N(CH_3)_2]_3 \longrightarrow [(CH_3)_2N]_3PBH_3 + N(CH_3)_3 \qquad \text{I}$$

$$NaBH_4 + P[N(CH_3)_2]_3 + CO_2 \longrightarrow HCOONa + [(CH_3)_2N]_3PBH_3 \qquad \text{II}$$

$$NaBH_4 + P[N(CH_3)_2]_3 + CH_3COOH \longrightarrow CH_3COONa + [(CH_3)_2N]_3PBH_3 + H_2 \qquad \text{III}$$



$$NaBH_4 + P[N(CH_3)_2]_3 + CH_3\underset{\underset{O}{\|}}{C}CH_3 + H_2O \longrightarrow [(CH_3)_2N]_3PBH_3 + NaOH + C_3H_7OH \qquad \text{IV}$$

$$NaBH_4 + P[N(CH_3)_2]_3 + HCl \longrightarrow [(CH_3)_2N]_3PBH_3 + NaCl + H_2 \qquad \text{V}$$

$$B_2H_6 + 2P[N(CH_3)_2]_3 \longrightarrow 2[(CH_3)_2N]_3PBH_3 \qquad \text{VI}$$

High yields were obtained in all cases except III, where the yield was relatively poor due to competing reactions. Sodium borohydride alone does not react with $P[N(CH_3)_2]_3$. Apparently a conversion of $NaBH_4$ into a more reactive intermediate is required to enable $P[N(CH_3)_2]_3$ to react. The course of reaction II appears to be

$$NaBH_4 + CO_2 \longrightarrow Na[BH_3OOCH] \qquad \text{VII}$$

$$Na[BH_3OOCH] + P[N(CH_3)_2]_3 \longrightarrow NaOOCH + [(CH_3)_2N]_3PBH_3 \qquad \text{VIII}$$

Similarly, reaction III possibly proceeds through an intermediate of the same type

$$NaBH_4 + HOOCCH_3 \longrightarrow Na[BH_3OOCCH_3] + H_2 \qquad \text{IX}$$

$$Na[BH_3OOCH_3] + P[N(CH_3)_2]_3 \longrightarrow NaOOCCH_3 + [(CH_3)_2N]_3PBH_3 \qquad \text{X}$$

In these reactions possible intermediates are sodium formato borohydride (VII) and sodium acetato borohydride (IX).

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[1] G. Kodama, Abstracts of Papers, 135th Meeting of American Chemical Society, p. 33M.

Reaction I is interesting theoretically, since it indicates that hexamethyl phosphorous triamide, $P[N(CH_3)_2]_3$, is a stronger Lewis base than trimethylamine, with respect to borine, BH_3, as the reference acid. The displacement of $N(CH_3)_3$ by $P[N(CH_3)_2]_3$ in $(CH_3)_3NBH_3$ occurs even at room temperature, although slowly. At moderate temperatures (80–100°) this reaction is completed in a short time. To determine the equilibrium of reaction I, some experiments were carried out in a closed system in order to prevent escape of trimethylamine. The equilibrium was found to be over 80% in favor of $[(CH_3)_2N]_3PBH_3$. Thus, the order of coördination is $P > N$ with respect to BH_3 as the reference acid. This is in accordance with Graham and Stone,[2] who established the order of coördination of $P(CH_3)_3$ and $N(CH_3)_3$ as being $P > N$ toward BH_3. In accordance with the greater base strength of $P[N(CH_3)_2]_3$ compared with $N(CH_3)_3$, the borine coördination compound $[(CH_3)_2N]_3PBH_3$ is less reactive than $(CH_3)_3NBH_3$. When $(CH_3)_3NBH_3$ was treated at room temperature with a mixture of concentrated hydrochloric acid and methanol (1:1), 90% reacted within 2 hr. Under the same conditions only 18% $[(CH_3)_2N]_3PBH_3$ was used up. Another test is also illustrative for the different reactivities of these two compounds. Trimethylamine borine does not seem to be very soluble in concentrated hydrochloric acid, yet it reacts quickly with the acid to form H_2, H_3BO_3, $N(CH_3)_3 \cdot HCl$ and an insoluble compound[3] which was not identified but which contained B, N, H and Cl. Under the same conditions hexaalkyl phosphorous triamide borines, $(R_2N)_3PBH_3$, particularly $[(CH_3)_2N]_3PBH_3$ and $[(CH_2CH_2)_2N]_3PBH_3$, are readily soluble in concentrated hydrochloric acid with only slow evolution of hydrogen at low temperature. It is believed that a salt-like adduct, $[(CH_3)_2N]_3PBH_3 \cdot HCl$, is formed. By dilution with water this adduct is hydrolyzed and the starting material, $[(CH_3)_2N]_3PBH_3$, is precipitated and recovered almost quantitatively. The HCl adduct, $[(CH_3)_2N]_3PBH_3 \cdot HCl$, could be obtained in the absence of water as a crystalline product. It is not a stable compound and could not be purified. However, the titration of HCl and the recovery of $[(CH_3)_2N]_3PBH_3$ showed that the ratio of $[(CH_3)_2N]_3PBH_3$ to HCl was approximately 1:1. Thus, $[(CH_3)_2N]_3PBH_3$ still displays weak electron donor power, probably produced by the nitrogen atoms.

The relative inertness shown by the hexaalkyl phosphorous triamide borines, particularly hexamethyl phosphorous triamide borine, toward aqueous acids, alkyl halides, carbon disulfide and others is remarkable. It is known that $P[N(CH_3)_2]_3$ reacts quickly with these reagents whereas the coördination compound $[(CH_3)_2N]_3PBH_3$ is practically not affected under the same conditions. The coördination compound can even be steam distilled without any indication of decomposition. The relatively lower reactivity of $[(CH_3)_2N]_3PBH_3$ and related compounds compared with $(CH_3)_3NBH_3$ may be explained by the greater base strength of $P[N(CH_3)_2]_3$ *per se* which is due to the greater inductive effect of the dimethylamido groups. Another perhaps more important and decisive factor may be that interpreted by Burg and Wagner[4] in their explanation of the unusual stability of the phosphino borine, $[H_2BP(CH_3)_2]_3$. According to these authors the BH bonding electrons enter hybrid orbitals (3 d) of the P-atom weakening the hydridic character of hydrogen in BH_2. This cannot happen in $(CH_3)_3NBH_3$ due to absence of d-orbitals in nitrogen. This concept might be applicable in our case and contribute to the explanation of why $[(CH_3)_2N]_3PBH_3$ is less reactive than $(CH_3)_3NBH_3$. The composition of the hexaalkyl phosphorous triamide borines, particularly of hexamethyl phosphorous triamide borine, is proved by its almost quantitative formation from $(CH_3)_3NBH_3$ and $P[N(CH_3)_2]_3$ (Reaction I) as well as from B_2H_6 and $P[N(CH_3)_2]_3$ (Reaction VI). Furthermore, the hexamethyl phosphorous triamide borine consumed 8 equivalents of iodine in aqueous CH_3OH solution

$$[(CH_3)_2N]_3PBH_3 + 4I_2 + 4H_2O = H_3BO_3 + OP[N(CH_3)_2]_3 + 8HI \quad \text{XI}$$

On prolonged heating of $[(CH_3)_2N]_3PBH_3$ with concentrated hydrochloric acid in the presence of CH_3OH the BH_3 moiety was destroyed. The sample obtained contained boric acid and phosphorous acid and thus consumed only 2 equivalents of iodine. The formation of 3 moles of hydrogen is another proof for the borine group in the molecule.

Also, the infrared spectra of $[(CH_3)_2N]_3PBH_3$, $[(C_4H_9)_2N]_3PBH_3$ and $[(CH_2CH_2)_2N]_3PBH_3$ were run as dilute chloroform solutions in the rocksalt region of the spectrum. All the spectra showed a pair of bands in the region of 2260 and 2370 cm.$^{-1}$ for the B–H stretching modes and a band in the region of 1150–1180 cm.$^{-1}$ for the H–B–H deformation mode. Very weak or no absorption was noted in the 1250 cm.$^{-1}$ region where Rice[5] has found a medium intensity band assigned to a B–N stretching mode in $(CH_3)_3NBH_3$. The spectra of hexamethyl phosphorous triamide and hexamethyl phosphorous triamide borine complement each other with only minor shifts of some of the bands in the 900–1100 cm.$^{-1}$ region. Since the BH_3 entity undoubtedly adds to the pyramidal phosphorus atom of the alkyl phosphorous triamide molecule, the high degree of symmetry of the parent molecule would be maintained in the complex and the infrared spectra of the two compounds should be closely related. Therefore, the close similarity of the spectra of hexamethyl phosphorous triamide and hexamethyl phosphorous triamide borine coupled with the presence of B–H and absence of B–N absorption bands in the latter is indirect proof of the structure as being $[(CH_3)_2N]_3PBH_3$.

Experimental

Hexamethyl Phosphorous Triamide Borine—Method I.—A mixture of 3.64 g. of trimethylamine borine and 8.20 g.

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[2] W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nuclear Chem.*, **3**, 164 (1956).

[3] This substance probably was identical with $ClBH_2N(CH_3)_3$, see H. I. Schlesinger, N. W. Flodin and A. B. Burg, THIS JOURNAL, **61**, 1081 (1939).

[4] A. B. Burg and R. I. Wagner, *ibid.*, **75**, 3872 (1953).

[5] B. Rice, R. J. Galiano and W. J. Lehmann, *J. Phys. Chem.*, **61**, 1222 (1957).

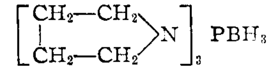
of hexamethyl phosphorous triamide was heated with stirring up to 90°, maintained at that temperature for about 20 minutes and then raised to 110° and held there for a short time. At 70–80° a moderate and at 90° a strong evolution of trimethylamine was observed. 2.6 g. (88% of calcd.) of trimethylamine was condensed in a trap. The reaction product, 9.2 g., was distilled at 61–63° (0.5 mm.). The distillate was dissolved in dioxane. Addition of water to the dioxane solution caused an oily product to separate. This product became crystalline on standing for a short time. It was then dried and distilled. One fraction, b.p. 49–50° (0.1 mm.), was taken, m.p. 32.5°. This compound has a distinct camphor-like odor.

Anal. Calcd. for $C_6H_{21}BN_3P$: P, 17.50; N, 23.72; B, 6.10. Found: P, 17.30; N, 23.54; B, 6.20. Mol. wt. of $C_6H_{21}BN_3P$: 177.03. Found: 180.30.

A sample of the substance dissolved in a small portion of CH_3OH was added to a mixture of 50 ml. of 0.1 *N* I_2, 50 ml. of CH_3OH and *ca.* 5 g. of $NaHCO_3$. After 60 minutes the excess I_2 was titrated with 0.1 *N* sodium arsenite solution, and 7.82 equivalents of iodine was consumed per mole of substance; calcd. 8 (see equation VII). A sample was refluxed with concd. HCl + CH_3OH (1:1) until the BH_3 moiety was destroyed as indicated by the termination of the H_2 evolution. It was analyzed for trivalent P by titration with I_2, and 1.94 equivalents of iodine was consumed per mole (calcd. 2). Evolution of 2.9 moles of H_2 (calcd., 3) was found by treatment of the substance with concd. $HClO_4$ and 1-butanol.

Hexamethyl Phosphorous Triamide Borine–Method Ia.—Dioxane was used as a solvent to prevent sublimation during the reaction of method I. A solution of 14.56 g. of trimethylamine borine and 35.8 g. of hexamethyl phosphorous triamide in 50 ml. of dioxane was gradually heated to about 112° over a period of 90 minutes. Trimethylamine, 11.0 g. (93% of theor.), was collected in a trap. The reaction product was filtered and treated with dilute hydrochloric acid. An oil separated which became crystalline on standing. It was washed with water and dried. The yield was 30.5 g. (86% of theor.) of hexamethyl phosphorous triamide borine; m.p. 32.5°.

N,N,N-Tris-(tetramethylene) Phosphorous Triamide Borine–Method I.—A mixture of 5.3 g. of N,N,N-tris-(tetramethylene) phosphorous triamide, 1.46 g. of trimethylamine borine and 2 ml. of dioxane was gradually heated to about 130°. Trimethylamine was evolved at 60–70°. The mixture was then treated with sufficient 0.5 *N* hydrochloric acid to dissolve the excess of N,N,N-tris-(tetramethylene) phosphorous triamide. A white crystalline precipitate appeared which was dissolved in concentrated hydrochloric acid and precipitated by the addition of water. The latter precipitate was then filtered, washed with water and dried in vacuum. A yield of 4.8 g. (94% of theor.) of N,N,N-tris-(tetramethylene) phosphorous triamide borine was obtained; m.p. 58°.



Anal. Calcd. for $C_{12}H_{27}BN_3P$: P, 12.18; B, 4.23; N, 16.42. Found: P, 11.98; B, 4.16; N, 15.66.

Hexamethyl Phosphorous Triamide Borine–Method II.—Carbon dioxide was gradually introduced at 25 to 30° into a stirred mixture of 17.9 g. of hexamethyl phosphorous triamide, 3.78 g. of sodium borohydride and 50 ml. of tetrahydrofuran until the reaction was completed and no further carbon dioxide was absorbed. The reaction product was treated with sufficient dilute hydrogen chloride to separate an oily product and dissolve the excess hexamethyl phosphorous triamide as well as the solvent. The oily product was taken up with hexane and filtered from a small amount of yellow insoluble solid. The filtrate was evaporated, and the residue was dissolved in dioxane. The addition of water to this solution caused an oil to precipitate which became crystalline upon standing. The crystalline product was filtered and dried. A yield of 11.5 g. (65% of theor.) of hexamethyl phosphorous triamide borine was obtained. When 5 g. of this product was steam distilled, 4.8 g. was recovered; m.p. 32.5°.

Hexamethyl Phosphorous Triamide Borine–Method III.—Acetic acid, 3 g., dissolved in 10 ml. of tetrahydrofuran, was added dropwise to a mixture of 1.9 g. of sodium borohydride and 25 ml. of tetrahydrofuran at −20 to −30° with vigorous stirring over a period of 45 minutes. When the evolution of hydrogen ceased, 12 g. of hexamethyl phosphorous triamide was added to the reaction mixture at about 0°. This reaction mixture was then stirred at room temperature for about 3 hr. and at about 60° for an additional hr. Dilute hydrochloric acid was then added to render the mixture acidic. The resulting mixture now was shaken with hexane and a small amount of a yellow precipitate was removed by filtration. The filtrate consisted of two layers which were separated. The hexane layer was evaporated, leaving an oily residue which was then treated with a small amount of water. The oily product crystallized on standing. It was water washed and dried. A yield of 4.1 g. (46% of theor.) of hexamethyl phosphorous triamide borine was obtained.

Hexamethyl Phosphorous Triamide Borine–Method IV.—A solution of 3 g. of water and 12 g. of acetone was added portionwise to a mixture of 1.9 g. of sodium borohydride, 9 g. of hexamethyl phosphorous triamide and 27 ml. of tetrahydrofuran with vigorous stirring at about 27° over a period of 3 hr. The mixture was then heated at about 55° for 30 minutes, after which 25 ml. of water was added dropwise at 40°. The resulting reaction mixture was rendered acidic with dilute hydrochloric acid and stirred until the unreacted hexamethyl phosphorous triamide was destroyed. An oil separated and became crystalline on cooling. The product was filtered, washed with water and dried in air. A yield of 4.7 g. (53% of theor.) of hexamethyl phosphorous triamide borine was obtained.

Hexamethyl Phosphorous Triamide Borine–Method V.—A solution of 1.82 g. of hydrogen chloride dissolved in 10 ml. of tetrahydrofuran was added to a mixture of 1.9 g. of sodium borohydride and 25 ml. of tetrahydrofuran at about −60° within a period of 1 hr. When the evolution of hydrogen ceased, 12 g. of hexamethyl phosphorous triamide was added. The reaction mixture was slowly heated to room temperature and maintained at that point for about 2 hr. It then was heated for one additional hr. at about 45°. The reaction mixture next was treated with sufficient dilute hydrochloric acid to hydrolyze the excess of hexamethyl phosphorous triamide and dissolve the solvent. Hexane was then added and the resulting mixture shaken. A small amount of a yellow precipitate formed which was insoluble in hexane and was removed by filtration of the hexane layer. The filtrate was evaporated and the residue crystallized. A yield of 5.6 g. (63% of theor.) of hexamethyl phosphorous triamide borine was obtained.

Hexamethyl Phosphorous Triamide Borine–Method VI.—Diborane was generated by a modification of Schlesinger's method.[6] Boron trifluoride etherate, 29.75 g., diluted with 30 ml. of ether was added to a stirred mixture of 5.7 g. of sodium borohydride and 80 ml. of tetrahydrofuran in a flask at −40° in about 45 minutes. Then the reaction mixture was heated gradually to about 58°. Nitrogen then was passed slowly through the contents of the flask. The diborane evolved was introduced into another flask which contained a solution of 35 g. of hexamethyl phosphorous triamide in 50 ml. of tetrahydrofuran. Vigorous stirring and cooling at about −20° was maintained. After all of the diborane was introduced, the reaction mixture was heated to room temperature, and most of the solvent was removed by distillation. A sufficient amount of dilute hydrochloric acid was added to dissolve the remaining solvent and the excess hexamethyl phosphorous triamide. The oil which separated crystallized on standing. The product was filtered and dried in air. A yield of 31.6 g. (89% of theor.) of hexamethyl phosphorous triamide borine, m.p. 32.0°, was obtained.

Hexa-*n*-butyl Phosphorous Triamide Borine–Method VI.—Diborane was generated from the reaction of 18.6 g. of boron trifluoride etherate, 4.1 g. of sodium borohydride and 70 ml. of tetrahydrofuran. The diborane so generated was introduced into a flask containing 41.5 g. of hexa-*n*-butyl phosphorous triamide and 30 ml. of tetrahydrofuran. The reaction mixture was stirred vigorously, and a temperature of 25–30° was maintained. The mixture was then treated with sufficient dilute hydrochloric acid to dissolve the solvent and destroy any excess of hexa-*n*-butyl phosphorous triamide. An oily product separated which was washed with a dilute solution of sodium sulfate, separated and dried in vacuum; 39.5 g. (92% of theor.) of essentially pure

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[6] H. I. Schlesinger, *et al.*, THIS JOURNAL, **75**, 202 (1953).

hexa-*n*-butyl phosphorous triamide borine was obtained. The infrared spectrum showed the bands at 2370 and 2260 cm.$^{-1}$ as in other cases for the B–H absorption.

Anal. Calcd. for $C_{24}H_{57}BN_3P$: P, 7.25; B, 2.52; N, 9.79. Found: P, 7.02; B, 2.53; N, 9.74.

Hexaethyl Phosphorous Triamide Borine–Method VI.—Diborane was generated from the reaction of 15.5 g. of boron trifluoride etherate and 3.4 g. of sodium borohydride in 70 ml. of tetrahydrofuran. The diborane thus generated was introduced into a flask and reacted with 24.7 g. of hexaethyl phosphorous triamide dissolved in 50 ml. of tetrahydrofuran. Throughout the reaction vigorous stirring and a temperature of about 10° were maintained. The reaction mixture was then shaken with dilute hydrochloric acid to destroy and dissolve any unreacted hexaethyl phosphorous triamide. An oil separated which was washed with water and dried in vacuum. A yield of 22.5 g. (86% of theor.) of hexaethyl phosphorous triamide borine was obtained; b.p. 89° (0.15 mm.).

Anal. Calcd. for $C_{12}H_{33}BN_3P$: P, 11.87; B, 4.17. Found: P, 11.66; B, 3.75.

Hexamethyl Phosphorous Triamide Borine Hydrochloride.—Gaseous HCl, 0.7 g., dissolved in 10 ml. ether was added dropwise to a stirred solution of 2.0 g. $[(CH_3)_2N]_3PBH_3$ in 30 ml. ether at −30°. The precipitate, a fine white crystalline product, was filtered at low temperature and carefully washed with cold ether. Without drying, the product was immediately transferred into a separatory funnel and shaken with water and a little ether. The ether layer was dried with Na_2SO_4, evaporated and the crystalline residue was air dried to constant weight. There was recovered 1.61 g. $[(CH_3)_2N]_3PBH_3$, 9.2 mmoles. Found HCl in the water layer, 9.4 mmoles. Thus, the ratio $[(CH_3)_2N]_3PBH_3$:HCl was 1:1.022.

An attempt to obtain the adduct in a dry state failed. Nitrogen was passed over the product to remove the ether. When the ether-free product was warmed to room temperature, a sudden reaction took place increasing the temperature to about 80°. HCl and H_2 escaped. Only a little $[(CH_3)_2N]_3PBH_3$ was recovered. The substance mainly decomposed into a yellow-brown unidentified product.

Determination of the Equilibrium.—

$$P[N(CH_3)_2]_3 + (CH_3)_3NBH_3 \rightleftharpoons [(CH_3)_2N]_3PBH_3 + N(CH_3)_3$$

A mixture of 7.25 g. of $(CH_3)_3NBH_3$ (0.1 mole) and 16.3 g. of $P[N(CH_3)_2]_3$ (0.1 mole) was placed in an ampoule which was sealed. After 5 days at room temperature the content was treated with 200 ml. of H_2O. An oil separated which became crystalline on cooling. It was filtered, treated with dilute HCl, dissolved in a little dioxane, precipitated with H_2O, filtered and dried; 14.5 g. (81.5% of theor.) of hexamethyl phosphorous triamide borine was obtained; m.p. 32.0°. Trimethylamine was determined in the water layer by titrating with 0.1 *N* HCl; found, 0.083 mole or 83%.

[CONTRIBUTION FROM THE ORGANIC CHEMICALS DIVISION, ST. LOUIS RESEARCH DEPARTMENT, MONSANTO CHEMICAL COMPANY, ST. LOUIS, MISSOURI]

Trialkyl Phosphite Borines. A New Type of Phosphorus-boron Compound

BY THEODOR REETZ

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Properties and methods of preparation of trialkyl-(aryl)-phosphite borines, a new type of PB compound, are reported. Trialkyl phosphites were found to be strong Lewis bases; in the case of triisopropyl phosphite, of the same strength as $N(CH_3)_3$. Several methods of preparing trialkyl phosphite borines are described. A possible course of the reaction of $NaBH_4$ with $P(OR)_3$ is discussed. The composition of the trialkyl phosphite borines was established as being $(RO)_3PBH_3$.

Graham and Stone[1] have found that $(CH_3)_3P$ displaces $(CH_3)_3N$ in the coördination compound $(CH_3)_3NBH_3$ to form the very stable $(CH_2)_3PBH_3$, the equilibrium being 80% in favor of the latter. It has been shown[2] that $[(CH_3)_2N]_3P$ also displaces $(CH_3)_3N$ in $(CH_3)_3NBH_3$ to form $[(CH_3)_2N]_3PBH_3$. The equilibrium has been found to be about 80% in favor of $[(CH_3)_2N]_3PBH_3$. Consequently, the Lewis base strength of $(CH_3)_3P$ and $[(CH_3)_2N]_3P$ must be greater than that of $(CH_3)_3N$ toward BH_3. On the other hand, in comparison with the above substances, the electron donor power of PF_3 is weak. Accordingly, the coördination compound F_3PBH_3 is rather unstable. Trimethylamine displaces PF_3 from F_3PBH_3 quantitatively.[3] Thus, toward BH_3, the order of the base strength of the compounds mentioned should be

$$(CH_3)_3P,\ [(CH_3)_2N]_3P > (CH_3)_3N >> PF_3$$

These considerations evoke the question as to what place in the above sequence trialkyl phosphites would have to be assigned. It was a surprising result to find that tertiary phosphites are strong Lewis bases. They displace $(CH_3)_3N$ from $(CH_3)_3NBH_3$ even at room temperature to form stable phosphite borines, $(RO)_3PBH_3$. The equilibrium of the reaction

$$(CH_3)_3NBH_3 + (\text{iso-}C_3H_7O)_3P \rightleftharpoons (\text{iso-}C_3H_7O)_3PBH_3 + (CH_3)_3N \quad \text{I}$$

was found to be about 53% in favor of $(\text{iso-}C_3H_7O)_3PBH_3$, thus showing the base strength of $(\text{iso-}C_3H_7O)_3P$ toward BH_3 to be similar to that of $(CH_3)_3N$. Based on displacement reactions the order of the coördination compounds discussed appears to be

$$(CH_3)_3PBH_3,\ [(CH_3)_2N]_3PBH_3 > (CH_3)_3NBH_3,\ (RO)_3PBH_3 >> F_3PBH_3$$

The trialkyl phosphite borines are unusually resistant toward reagents such as water, dilute acids and iodine. In this respect, it is interesting to compare them with $[(CH_3)_2N]_3PBH_3$, $(CH_3)_3NBH_3$ and the starting material, $(RO)_3P$. The latter three react quickly and completely (within minutes) with a dilute (0.05 *N*) aqueous-methanol solution of iodine. In contrast, the reaction of $(RO)_3PBH_3$ with I_2 under the same conditions is extremely slow.

Also, the resistance of $(RO)_3PBH_3$ toward HCl is significant. For example, $(\text{iso-}C_3H_7O)_3PBH_3$ does not seem to react with a 3 *N* solution of HCl in water–methanol (1:3) at room temperature,

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(1) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nuclear Chem.*, **3**, 166 (1956).

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