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.—

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

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

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

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).

[2] See preceding paper, THIS JOURNAL, **82**, 5036 (1960).

[3] R. W. Parry and T. C. Bisson, *ibid.*, **78**, 1524 (1956).

whereas $(CH_3)_3NBH_3$ reacts with HCl under the same conditions.

In terms of Burg's[4] conception, we may presume the electron density on the hydrogen atoms in $(RO)_3PBH_3$ is lowered by the participation of the BH electrons in the 3d orbitals of the phosphorus atom. Thus, the hydridic character of the hydrogen atoms is weakened. This would explain the relatively great resistance of $(RO)_3PBH_3$ toward HCl in comparison with $(CH_3)_3NBH_3$ where a similar transfer of electrons is not possible.[5]

To compare the reactivities of trialkyl phosphite borines among themselves, the slow reaction with dilute aqueous methanol solution of I_2 was employed. The most resistant trialkyl phosphite borines toward I_2 are those which contain nonsubstituted alkyl groups. It has been found that the order of reactivities of these borines toward I_2 is

$$(\text{iso-}C_3H_7O)_3PBH_3 > (C_2H_5O)_3PBH_3 > (CH_3O)_3PBH_3$$

The greater reactivity of the higher trialkyl phosphite borines, particularly of the triisopropyl phosphite borine, toward I_2 might be due to the weaker BP bond caused by steric factors. Phosphite borines containing halogen substituted alkyls are more reactive. For example, only 2% of $(C_2H_5O)_3PBH_3$ reacted with I_2 during 17 hr., whereas 12% of $(ClCH_2CH_2O)_3PBH_3$ was oxidized under the same conditions.[6] Still more reactive is the tris-(beta-trifluoroethyl) phosphite borine which reacts quickly with I_2. In general, the more negative the substituents in the phosphite moiety, the more reactive are the phosphite borines.

The composition of the trialkyl phosphite borines as $(RO)_3PBH_3$ follows from the Experimental Results. When trimethylamine borine is treated with triisopropyl phosphite (equation V), practically no hydrogen is formed, nearly 100% of the $N(CH_3)_3$ is recovered and the yield of the PB compound is very high. An exchange of H and the alkyl group to form $ROH_2BPH(OR)_2$, *i.e.*, a reduction of the phosphorus, did not occur. This was proved by

$$(CH_3O)_3PBH_3 + (\text{iso-}C_3H_7O)_3P \longrightarrow (\text{iso-}C_3H_7O)_3PBH_3 + P(OCH_3)_3\uparrow \qquad \text{II}$$

The recovery of the $P(OCH_3)_3$ shows that the trimethyl phosphite moiety is intact in the trimethyl phosphite borine molecule. Furthermore, since the composition of $[(CH_3)_2N]_3PBH_3$ has been established,[2] the reactions III and IV prove that the BH_3 group is also unchanged in the trialkyl phosphite borines.

$$(\text{iso-}C_3H_7O)_3PBH_3 + P[N(CH_3)_2]_3 \longrightarrow [(CH_3)_2N]_3PBH_3 + (\text{iso-}C_3H_7O)_3P \qquad \text{III}$$

$$(C_6H_5O)_3PBH_3 + P[N(CH_3)_2]_3 \longrightarrow [(CH_3)_2N]_3PBH_3 + (C_6H_5O)_3P \qquad \text{IV}$$

The formation of $(CH_3)_3NBH_3$ in the reaction

$$(RO)_3PBH_3 + N(CH_3)_3 \rightleftarrows (CH_3)_3NBH_3 + P(OR)_3$$

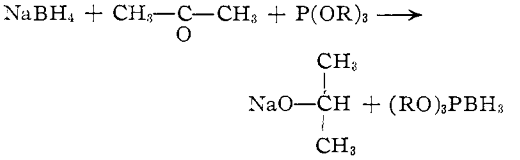
is another proof of the H_3B group in the trialkyl phosphite borine molecule. Finally, nearly 3 moles of H_2 were formed on treatment of $(EtO)_3PBH_3$ with concentrated $HClO_4$ in dioxane. The determination of the structure of the trialkyl phosphite borines by physical means is a goal of further investigation.

A number of methods were employed to prepare the trialkyl phosphite borines. These equations illustrate their formation.

$$(CH_3)_3NBH_3 + P(OR)_3 \longrightarrow (RO)_3PBH_3 + N(CH_3)_3\uparrow \qquad \text{V}$$

$$B_2H_6 + 2P(OR)_3 \longrightarrow 2(RO)_3PBH_3 \qquad \text{VI}$$

$$NaBH_4 + CO_2 + P(OR)_3 \longrightarrow NaOOCH + (RO)_3PBH_3 \qquad \text{VII}$$



$$NaBH_4 + CH_3\underset{\displaystyle O}{-C-}CH_3 + P(OR)_3 \longrightarrow NaO-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{CH}} + (RO)_3PBH_3 \qquad \text{VIII}$$

$$NaBH_4 + C_6H_5OH + P(OR)_3 \longrightarrow NaOC_6H_5 + (RO)_3PBH_3 + H_2 \qquad \text{IX}$$

$$NaBH_4 + HOOCCH_3 + P(OR)_3 \longrightarrow NaOOCCH_3 + (RO)_3PBH_3 + H_2 \qquad \text{X}$$

$$NaBH_4 + HCl + P(OR)_3 \longrightarrow NaCl + (RO)_3PBH_3 + H_2 \qquad \text{XI}$$

$$3NaBH_4 + 4BF_3{\cdot}Et_2O + 4P(OR)_3 \longrightarrow 3NaBF_4 + 4(RO)_3PBH_3 + 4Et_2O \qquad \text{XII}$$

The reaction according to equation V proceeds slowly at room temperature with all trialkyl phosphites used in the present investigation. Nevertheless, the odor of trimethylamine can be detected shortly after trimethylamine borine is mixed with trialkyl phosphite at room temperature. The reaction is rather fast at 80–90°.

The reaction of trialkyl phosphites with B_2H_6 (equation VI) is highly exothermic and is preferably carried out at low temperature in the presence of tetrahydrofuran.

Sodium borohydride is used in reactions VII to XII. This reagent itself does not react with trialkyl phosphites. Additional reagents are required to give rise to the reactions shown in the equations.

Although the role of the additional reagents in these reactions is not entirely clear, it is apparent from the evidence below that these reagents convert the unreactive $NaBH_4$ into a species reactive with $P(OR)_3$. In the case of carbonyl compounds (acetone, for instance) there was speculation[7] about the formation of the complex $Na[BH_3OCH(CH_3)_2]$ from $NaBH_4$ and acetone. In the case of protonated reagents (such as acetic acid) we isolated $Na(BH_2OOCCH_3)$ as the product of $NaBH_4$ and CH_3COOH. Furthermore, $P(OR)_3$ reacts with the isolated material to form $(RO)_3PBH_3$. It is then reasonable to speculate that

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

[5] It is interesting that $[(CH_3)_2N]_3PBH_3$ reacts with HCl in aqueous methanol solution to form H_2. We may presume that here the adduct $[(CH_3)_2N]_3PBH_3{\cdot}HCl$ is formed, being in equilibrium with $[(CH_3)_2N]_3PBH_3$ and HCl. We know[2] that this adduct is not a stable compound *per se*. It decomposes spontaneously at room temperature. On the other hand, there is no evidence of formation of an HCl adduct of $(RO)_3PBH_3$ which might cause an increase of the reactivity of the latter.

[6] Percentages were calculated on the basis of 8 equivalents of iodine per mole of substance.

[7] (a) S. W. Chaikin and W. G. Brown, THIS JOURNAL, **71**, 122 (1949). (b) E. R. Garrett and D. A. Lyttle, *ibid.*, **75**, 6051 (1953). (c) E. H. Jensen, "A Study on Sodium Borohydride," Nyt Nordisk Forlag Arnold Busck, Copenhagen, 1954, p. 133.

TABLE I

RESULTS OF THE REACTION OF $P(OR)_3$ WITH $NaBH_4$

Additional reagents used in these reactions according to method A are shown in column 2.

R in $(RO)_3PBH_3$	Reagent	Temp[a], °C.	Yield, %	B.p., °C., mm.	Analyses Calcd., %	Analyses Found, %	Mol. weight Calcd.	Mol. weight Found	$n^{25}D$
CH_3	CO_2	28	75.0	86/23	P, 22.50	21.85	137.9	145	1.4162
			82.5	45/5	B, 7.87	7.44			
C_2H_5	CO_2	30	73.0	39/0.4	P, 17.20	16.94	180.8	209	1.4200
					B, 6.00	5.94		220	
Iso-C_3H_7	CO_2	30	75.0	42–43/0.1	P, 13.95	13.90	222.0	242	1.4171
			79.0		B, 4.86	4.62			
n-C_4H_9	CO_2	28	85.0	83–85/0.15	P, 11.80	11.84	264.0	287	1.4329
			Crude		B, 4.08	3.97			
$-C_6H_5$	CO_2	28	70.0	M.p. 54.0	P, 9.58	9.56	324.0	349	
					B, 3.34	3.15			
$-CH_2CH_2Cl$	CO_2	28	82.0	Dec.	P, 11.00	11.29	...	..	
			Crude		Cl, 37.50	36.01			
					B, 3.80	3.30			
–Cyclohexyl	CO_2	30	83.0	M.p. 69.0	P, 9.05	9.13	342.0	382	
					B, 3.15	3.10			
C_2H_5	C_6H_5OH	5	75.0	106/22					1.4195
C_2H_5	CH_3COOH	8	88.0						
C_2H_5	Iso-valeric acid	10	75.0						
Iso-C_3H_7	HCl	−25	72.0						1.4169
Iso-C_3H_7	$BF_3(C_2H_5)_2O$	−30	87.0						1.4169
Iso-C_3H_7	$OC(CH_3)_2 + H_2O(1:1)$	18	82.0						
Iso-C_3H_7	CH_3COOH	−40	80.0						
Iso-C_3H_7	H_3BO_3	18	32.0						

$NaBH_4$ and $P(OR)_3$ react readily by the addition of CH_3COCH_3 or CH_3COOH because the reactive complexes such as $Na[BH_3OCH(CH_3)_2]$ and $Na(BH_3OOCCH_3)$ are formed as intermediates.

This work suggests a means of classifying the trialkyl phosphites with respect to their basic character. It also points out the possible usefulness of $(RO)_3P$ and $[(CH_3)_2N]_3P$ in the study of borine coördination compounds and boron hydrides.

Experimental

Method A–$NaBH_4$.—Mixtures of equimolar amounts (0.2 to 0.5 mole) of sodium borohydride, trialkyl phosphite and 80 to 130 ml. of tetrahydrofuran were treated with CO_2 at 25–30° with vigorous stirring until the exothermic reaction was finished and the absorption of CO_2 ceased. When reagents other than CO_2 were used as promoters, solutions of these reagents in a little C_4H_8O were used and added to the phosphite–$NaBH_4$–C_4HO mixtures with vigorous stirring at temperatures indicated in Table I over a period of 1 to 3 hr. The reaction mixture then was heated at 50° for a short time. In some cases most of the solvent was distilled off. The residue was treated with an excess of dilute HCl to dissolve the unreacted phosphite and the solvent. The separated oil was washed with dilute HCl and water and then dried with Na_2SO_4. The distillation was carried out in vacuum. In case the trialkyl phosphite borine was not distillable, it was subjected to vacuum at 50–60° to remove the traces of solvent. The products were not contaminated with phosphite or other reducing agents. Practically no I_2 (0.1 *N*) was consumed.

Method B.—Glacial acetic acid, 6.2 g., was added to a mixture of 3.78 g. of $NaBH_4$ and 80 ml. of tetrahydrofuran at −40° with vigorous stirring over a period of 1 hr. About 0.1 mole (*ca.* 2370 ml.) of H_2 escaped. The reaction mixture then was heated slowly to 55° and maintained at this temperature for 10 minutes. No B_2H_6 escaped the vessel, indicating the formation of a BH_3 complex other than tetrahydrofuran borine. Then 30 g. of (iso-$C_3H_7O)_3P$ was added to the reaction mixture which was heated at 55° for 3 hr. The reaction mixture was worked up as mentioned in the description of the method A to give 17.9 g. of (iso-$C_3H_7O)_3PBH_3$, 81%.

Method C.—A mixture of 14.56 g. of trimethylamine borine, 50 g. of triisopropyl phosphite and 20 ml. of dioxane was heated in a reaction vessel which was connected with a solid carbon dioxide trap. Some trimethylamine was formed at room temperature; pronounced evolution of trimethylamine began at about 50–60°. The mixture was gradually heated to 120°. Finally N_2 was passed slowly through the vessel for a short time. Trimethylamine, 11.1 g. (94%), was collected in the trap. The reaction mixture was treated several times with dilute HCl, dried with Na_2CO_3 and distilled under reduced pressure. Obtained 37.5 g., 84.6% of (iso-$C_3H_7O)_3PBH_3$; boiling point 42–43° (0.1 mm.), $n^{25}D$ 1.4170. No iodine (0.1 *N*) was consumed indicating the product was free of reducing contaminants.

Method D.—The diborane, generated according to Schlesinger,[8] from 5.7 g. of $NaBH_4$ and 30.0 g. of $BF_3 \cdot Et_2O$ in 80 ml. of tetrahydrofuran, was introduced into a solution of 50 g. of $P(OEt)_3$ in 50 ml. of tetrahydrofuran at −20° with vigorous stirring. After a portion of the solvent was removed the reaction mixture was treated with dilute HCl, and an oily product separated. This was washed with water and dried with K_2CO_3. Finally, it was subjected to vacuum, 10 mm. at 50°, until the weight was constant. There was obtained 33.5 g. (92.5% of theor.) of essentially pure triethyl phosphite borine. The titration with I_2 indicated the product was free of triethyl phosphite; $n^{25}D$ 1.4198; b.p. 40° (0.5 mm.).

Sodium Monoacetato Borohydride, $Na[BH_3OOCCH_3]$ and its Reaction with $P(OC_2H_5)_3$.—A solution of 12.0 g. of CH_3COOH in 50 ml. of C_4H_8O was added dropwise to a mixture of 7.5 g. of $NaBH_4$ and 80 ml. of C_4H_8O at −30 to −35° with vigorous stirring over a period of 1.5 hr. Then the reaction mixture was heated at 30–40° for 1 hr. The white precipitate was filtered in the absence of moist air, washed with tetrahydrofuran and dried. Obtained 14.8 g. (theory for $Na[BH_3OOCCH_3]$ 19.16 g., thus, 4.36 g. of the product remained dissolved in the filtrate). It is believed that the precipitate was $Na[BH_3OOCCH_3]$. It used 5.8 equivalents of I_2 and formed 2.8 moles of H_2. A strong evolution of H_2 was observed when the product was dissolved in H_2O. On prolonged heating of 9.58 g. of the precipitate with 20 g. of $P(OC_2H_5)_3$ in tetrahydrofuran, 12.0 g. (65%) of $(C_2H_5O)_3PBH_3$ was formed.

Determination of the Equilibrium.—

$$(CH_3)_3NBH_3 + (\text{iso-}C_3H_7O)_3P \longrightarrow (\text{iso-}C_3H_7O)_3PBH_3 + N(CH_3)_3$$

A mixture of 0.1 mole of $H_3BN(CH_3)_3$ and 0.1 mole of $P(O\text{-iso-}C_3H_7)_3$ was placed in a tube containing some mer-

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[8] H. I. Schlesinger, THIS JOURNAL, **75**, 202 (1953).

cury with an immersed capillary to serve as a manometer. The remaining air was displaced by mercury. The tube was heated at 49° for about 20 hr. The rising Hg in the long capillary indicated a pressure of about 2 atm. Then the reaction mixture was cooled to 0°, transferred into a beaker and immediately treated with an excess of 3 *N* HCl to dissolve the resulting $N(CH_3)_3$ and the unused reactants. The oil was shaken with dilute HCl several times, washed with water, separated and dried with anhydrous Na_2CO_3. A small amount of material was recovered from the aqueous layers by extracting with hexane. In a number of experiments yields in the range of 50 to 56% of $(iso\text{-}C_3H_7O)_3PBH_3$ were obtained, the average being 53%.

Reactivity of Trialkyl Phosphite Borines Toward I_2. Method.—A weighed amount of the substance was dissolved in 2 ml. of CH_3OH and added to a mixture of 50 ml. of 0.1 *N* I_2 and 100 ml. of CH_3OH at 23°. After 70 hr. the unreacted I_2 was titrated with 0.1 *N* arsenite solution in the presence of $NaHCO_3$. The I_2 consumed is calculated in milliequivalents and shown in the table below. The last column contains the number of equivalents of I_2 consumed per mole of substance. According to the equation $(RO)_3PBH_3 + 4I_2 + 4H_2O = H_3BO_3 + 8HI + OP(OR)_3$ one mole of trialkyl phosphite borine should consume 8 equivalents of I_2.

$H_3BP(OR)_3$	Substance used, mmole	I_2 consumed, meq.	Eq. I_2 consumed per mole substance
$R = CH_3$	0.71	0.35	0.49
$R = C_2H_5$	0.92	1.11	1.20
$R = iso\text{-}C_3H_7$	0.66	1.61	2.45

Because of a possible side reaction, the results obtained may not represent the actual extent of the over-all reaction. However, qualitatively these attempts indicate that the order of reactivity of the trialkyl phosphite borines toward I_2 is

$$(CH_3O)_3PBH_3 < (C_2H_5O)_3PBH_3 < (iso\text{-}C_3H_7O)_3PBH_3$$

The ratio of reactivities of $(CH_3O)_3PBH_3$, $(C_2H_5O)_3PBH_3$ and $(i\text{-}C_3H_7O)_3PBH_3$ is 1:2.45:5.0.

Reactivity of Trialkyl Phosphite Borines toward I_2 in the Presence of Pyridine.—The same conditions (23°, 70 hr.) were applied as described above; however, 5 ml. of pyridine was added to the reaction mixture to suppress the side reaction of $(RO)_3PBH_3$ with HI which would be formed by the main reaction. Since I_2 reacts with CH_3OH in the presence of pyridine (1.5 ml. of 0.1 *N* I_2 was consumed in the blank test), this number of milliliters of I_2 was subtracted from the amount of 0.1 *N* I_2 consumed in the tests.

$(RO)_3PBH_3$	Mmoles used	Meq. I_2 consumed	Eq. I_2 consumed per mole substance
$R = CH_3$	1.05	0.32	0.31
$R = C_2H_5$	1.30	0.86	0.66
$R = iso\text{-}C_3H_7$	0.92	1.23	1.34

The results show that the numbers of equivalents of I_2 consumed per mole of substance are smaller than in the previous experiments (in the absence of pyridine). However, the ratio of the reactivities of $(CH_3O)_3PBH_3$, $(C_2H_5O)_3PBH_3$ and $(iso\text{-}C_3H_7O)_3PBH_3$ is 1:2.13:4.3 which is close to the previous results found in the absence of pyridine.

Proof of the Constitution of $(RO)_3PBH_3$.—

$$(C_6H_5O)_3PBH_3 + P[N(CH_3)_2]_3 \longrightarrow [(CH_3)_2N]_3PBH_3 + P(OC_6H_5)_3 \quad (a)$$

A mixture of 2.4 g. of $(C_6H_5O)_3PBH_3$ and 3.6 g. of $P[N(CH_3)_2]_3$ was heated at 100° for 30 minutes. The reaction mixture was steam distilled. The distillate was acidified with HCl, the crystalline product filtered, washed with H_2O and dried in air to a constant weight, producing 0.985 g. = 75.0% of $[(CH_3)_2N]_3PBH_3$; m.p. 32.0°. The constitution of $[(CH_3)_2N]_3PBH_3$ has been established.[2]

$$(iso\text{-}OC_3H_7)_3PBH_3 + P[N(CH_3)_2]_3 \longrightarrow [(CH_3)_2N]_3PBH_3 + (iso\text{-}C_3H_7O)_3P \quad (b)$$

A mixture of 2.22 g. of $(iso\text{-}C_3H_7O)_3PBH_3$ and 4.89 g. of $P[N(CH_3)_2]_3$ was heated at 110° for 45 minutes. The reaction mixture was worked up as in the foregoing experiment; obtained 1.25 g. of $[(CH_3)_2N]_3PBH_3$, 70.5%.

$$(CH_3O)_3PBH_3 + (iso\text{-}C_3H_7O)_3P \longrightarrow (iso\text{-}C_3H_7O)_3PBH_3 + P(OCH_3)_3\uparrow \quad (c)$$

A mixture of 13.78 g. of $(CH_3O)_3PBH_3$ and 40.0 g. of $(iso\text{-}C_3H_7)_3P$ was subjected to distillation at atmospheric pressure. One fraction was taken, the vapor temperature being 110 to 120°. The distillation was interrupted because of fear of a sudden decomposition of the residue. The distillate was redistilled. Obtained 6.5 g. of $P(OCH_3)_3$, b.p. 111-113°. Thus, the phosphite borine contains the unchanged $P(OCH_3)_3$ moiety.

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Cleavage and Disproportionation of Polychlorodisilanes, Trichloromethylchlorosilanes and Hexachlorodisiloxane by Amines and Ammonium Salts

BY GLENN D. COOPER AND ALFRED R. GILBERT

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The cleavage and disproportionation reactions of polychlorodisilanes with amines and ammonium salts had been briefly examined and a mechanism is advanced for these reactions. Trichloromethyl-substituted chlorosilanes were found to undergo similar reactions; trichloromethyltrichlorosilane yields silicon tetrachloride with tri-*n*-butylamine, and a mixture of chloroform and silicon tetrachloride with the amine hydrochloride. Hexachlorodisiloxane disproportionates in the presence of tri-*n*-butylamine to silicon tetrachloride and perchloropolysiloxanes.

The cleavage and disproportionation of polychlorodisilanes by ammonium halides and amines was reported by Wilkins.[1] Hexachlorodisilane reacted with ammonium chloride at 120-130° to form trichlorosilane and silicon tetrachloride, and with ammonium fluoride to yield trichlorosilane, trichlorofluorosilane and silicon tetrachloride. Non-volatile residues which contained nitrogen, presumably in the form of silazanes, also were obtained.

$$Cl_3SiSiCl_3 + NH_4Cl \longrightarrow SiCl_4 + HSiCl_3 \quad (1)$$

Trimethylamine brought about the disproportionation of hexachlorodisilane to silicon tetrachloride and poly-(dichlorosilane).

$$nCl_3SiSiCl_3 \longrightarrow nSiCl_4 + (SiCl_2)_n \quad (2)$$

Recently Kaczmarczyk and Urry[2] found that in the

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(1) C. J. Wilkins, *J. Chem. Soc.*, 3409 (1953).

(2) A. Kaczmarczyk and G. Urry, THIS JOURNAL, **82**, 751 (1960).