

357. *The Reaction of Boron Hydrides with Trialkyl and Triaryl Phosphines.*

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The reactions of pentaborane and decaborane with alkyl- and aryl-phosphines are described. Reaction schemes are suggested and the thermal and hydrolytic stabilities of the products are discussed. A simple laboratory method for the preparation of pentaborane and decaborane by pyrolysis of diborane is described.

BORON HYDRIDES react with phosphines to form adducts which lose hydrogen when heated and give stable boron-phosphorus polymers. Most of the work in this field has been published by Burg¹ and his co-workers who investigated the preparation of the adduct $\text{Me}_2\text{PH}\cdot\text{BH}_3$ and its thermal decomposition to the trimer $(\text{Me}_2\text{P}\cdot\text{BH}_2)_3$ and tetramer $(\text{Me}_2\text{P}\cdot\text{BH}_2)_4$; various derivatives of the trimer have also been mentioned.² At the same time reference³ has been made to three-dimensional polymers, which remain light-coloured and transparent up almost to 500° , from B_5H_9 and bases such as PMe_3 , $\text{Me}_2\text{N}\cdot\text{PMe}_2$, and P_2Me_4 .

In the work now reported, thermal decomposition of compounds made from penta- and decaborane and trimethyl- and triphenyl-phosphine has been investigated. The

¹ *E.g.*, Burg and Wagner, *J. Amer. Chem. Soc.*, 1953, **75**, 3872.

² Burg and Brendel, *J. Amer. Chem. Soc.*, 1958, **80**, 3198; Biddulph, Brown, Cass, Long, and Silver, *J.*, 1961, 1822.

³ Burg, 133rd Meeting Amer. Chem. Soc., 1958; Burg, *Angew. Chem.*, 1960, **72**, 183.

reactions were carried out at $\sim 200^\circ$ for 0.3–4 hours in sealed tubes which were then opened to a vacuum line, the volatile materials being removed and the residues analysed for boron and phosphorus.

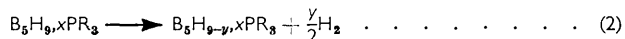
The compounds formed from higher boron hydrides and trialkyl- or triaryl-phosphines were very pale yellow, brittle solids at room temperature, unaffected by air, and insoluble in water or organic solvents, which precluded determination of their molecular weights. They were thermoplastic at 150° , at which temperature, owing to evolution of hydrogen, large bubbles were formed which slowly collapsed. In several cases, a compound $\text{H}_3\text{B}\cdot\text{PR}_3^+$ (R = Me or Ph) was a decomposition product at elevated temperatures. At 200° the products from pentaborane or decaborane with trimethylphosphine, and from pentaborane with triphenylphosphine were yellow liquids whose viscosities increased with rising temperature until at 300° the polymers solidified. The product from decaborane and triphenylphosphine was not thermoplastic, even at 450° , and although it lost hydrogen no sublimate of $\text{H}_3\text{B}\cdot\text{PPh}_3^+$ was formed.

It has been suggested⁴ that pentaborane, which has B–B bonds, should readily form polymers with bases by removal of two BH_3 groups from the B_5H_9 , leaving a B_3H_3 unit which can then combine with other such units. Trimethylphosphine can be trapped in these aggregates, the phosphorus donating electrons to the electron-deficient boron³ while being stabilised by partial isolation in the boron hydride aggregate. In the work reported here it was found that a boron hydride polymer, *i.e.*, one containing no phosphorus, was not obtained when the ideal molar ratio for the abstraction of two BH_3 groups from pentaborane was used ($\text{PMe}_3 : \text{B}_5\text{H}_9 = 2 : 1$); in this case less than two BH_3 groups were removed per B_5H_9 unit. The reaction of triphenylphosphine with pentaborane was different, because hydrogen was the main by-product and only a trace of $\text{H}_3\text{B}\cdot\text{PPh}_3^+$ was formed.

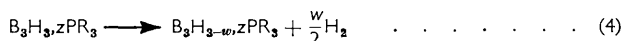
The reaction of pentaborane with a trialkyl- or triaryl-phosphine gave results (Table 1) that suggest there may be an initial reaction:



followed by:



or



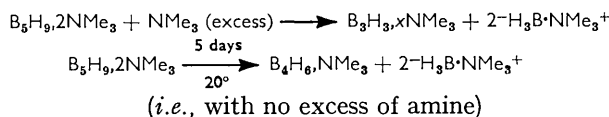
Thus, the reaction of pentaborane and an excess of trimethylphosphine was carried out at room temperature, yielding a solid product only, which was not isolated but could well have been the product suggested for reaction (1). Raising the temperature of reaction to $\sim 200^\circ$ gave hydrogen, the compound $\text{H}_3\text{B}\cdot\text{PMe}_3^+$, and a solid of approximate formula $\text{BH}(\text{PMe}_3)_{0.2}$, supporting reactions (2) and (3). Although an excess of trimethylphosphine was used, only in one experiment were 2 moles of the compound $\text{H}_3\text{B}\cdot\text{PMe}_3^+$ produced per mole of B_5H_9 (experiment 1, Table 1).

Treating an excess of triphenylphosphine with pentaborane gave a solid product of approximate formula $\text{BH}(\text{PPh}_3)_{0.2}$; but, because hydrogen was the main by-product and only a trace of the compound $\text{H}_3\text{B}\cdot\text{PPh}_3^+$ was obtained it appears that the main reaction was according to steps 1 and 2 above. Nevertheless, isolation of a little triphenylphosphine–borine adduct indicates that some reaction took place according to step 3, even though the molar ratio $\text{PPh}_3 : \text{B}_5\text{H}_9$ was slightly less than 2 : 1.

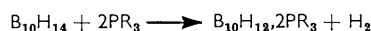
We made no attempt to isolate the postulated addition compound $\text{B}_5\text{H}_9 \cdot x\text{PR}_3$; an analogous nitrogen compound, $\text{B}_5\text{H}_9 \cdot 2\text{NMe}_3$, has been prepared by Burg⁴ and by Hough

⁴ Burg, *J. Amer. Chem. Soc.*, 1957, **79**, 2129.

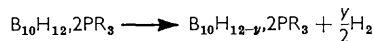
et al.,⁵ who suggest two alternative mechanisms for its cleavage which supports the reaction course given above:



The terminal hydrogens in decaborane can readily be replaced⁴⁻⁶ and it is probable that a $\text{B}_{10}\text{H}_{12}, 2\text{PR}_3$ unit takes part in polymerisation by further loss of hydrogen. The first reaction would be:



followed by:



The above course of reaction has been given by Hawthorne and Pitochelli⁶ who isolated the compound $\text{B}_{10}\text{H}_{12}, 2\text{PPh}_3$ by carrying out the reaction of decaborane with triphenylphosphine in ether. Our work has also shown that only hydrogen, and no phosphine-borane adduct, $^{-}\text{H}_3\text{B}\cdot\text{PMe}_3^+$, is formed; further heating of the product causes only loss of hydrogen. Treating decaborane with triphenylphosphine at 280° in the absence of solvent gave a material of empirical composition $\text{B}_{10}\text{H}_6, 2\text{PPh}_3$ which lost more hydrogen

TABLE 1.
Reaction of boron hydrides with trimethylphosphine and triphenylphosphine
(amounts of materials are given in mmoles).

B_5H_9	PMe_3 used	PMe_3 recovered	PMe_3 reacted	H_2 formed	$^{-}\text{H}_3\text{B}\cdot\text{PMe}_3^+$ formed	Temp.	Time (hr.)	Product
2.6	7.95	0.93	7.02	1.14	5.2	230°	0.5	$\text{B}_1\text{H}_{0.7}(\text{PMe}_3)_{0.22}$
2.3	4.6	0	4.6	2.14	2.6	220	4.0	$\text{B}_1\text{H}_1(\text{PMe}_3)_{0.23}$
$\text{B}_{10}\text{H}_{14}$								
1.27	3.25	0.87	2.38	3.63	0	100, then 230	1.0 0.5	$\text{B}_1\text{H}_{0.8}(\text{PMe}_3)_{0.19}$
B_5H_9 used	PPh_3	B_5H_9 recovered	B_5H_9 reacted	H_2 formed	$^{-}\text{H}_3\text{B}\cdot\text{PPh}_3$	Temp.	Time (hr.)	Product
1.27	0.97	0.46	0.81	1.17	Trace	220°	0.3	$\text{B}_1\text{H}_1(\text{PPh}_2)_{0.19}$
1.74	0.75	1.33	0.41	0.8	Trace	220	0.3	$\text{B}_1\text{H}_1(\text{PPh}_2)_{0.22}$
$\text{B}_{10}\text{H}_{14}$		$\text{B}_{10}\text{H}_{14}$ recovered	$\text{B}_{10}\text{H}_{14}$ reacted					
0.41	0.93	Nil	0.41	1.66	Nil	220	0.3	$\text{B}_1\text{H}_{0.6}(\text{PPh}_3)_{0.22}$

TABLE 2.
Heat stability of the boron-phosphorus compounds *in vacuo*.

Material	Formed from	Temp.	Time (hr.)	H_2 lost by 1 g. (c.c.)(N.T.P.)	Residue
$\text{B}_1\text{H}_1(\text{PMe}_3)_{0.22}$	B_5H_9	430°	2.0	275	*
$\text{B}_1\text{H}_{0.8}(\text{PMe}_3)_{0.19}$	$\text{B}_{10}\text{H}_{14}$	230	3.5	32	$\text{B}_1\text{H}_{0.75}(\text{PMe}_3)_{0.19}$
$\text{B}_1\text{H}_{0.8}(\text{PMe}_3)_{0.19}$	$\text{B}_{10}\text{H}_{14}$	360	2	114	$\text{B}_1\text{H}_{0.54}(\text{PMe}_3)_{0.19}$
$\text{B}_1\text{H}_{0.8}(\text{PMe}_3)_{0.19}$	$\text{B}_{10}\text{H}_{14}$	450	3	168	$\text{B}_1\text{H}_{0.4}(\text{PMe}_3)_{0.19}$
$\text{B}_1\text{H}_1(\text{PPh}_3)_{0.22}$	B_5H_9	450	0.5	90	*
$\text{B}_1\text{H}_{0.6}(\text{PPh}_3)_{0.22}$	$\text{B}_{10}\text{H}_{14}$	450	2.6	114	$\text{B}(\text{PPh}_3)_{0.22}$

* In these experiments borane-phosphine (alkyl or aryl) was produced but not recovered, hence the empirical formula of residue is not reported.

at 450° . Similarly, the product from decaborane and trimethylphosphine at 220° gave a material $\text{B}_{10}\text{H}_8, 2\text{PMe}_3$ which at 450° (3 hr.) gave a material $\text{B}_{10}\text{H}_4, 2\text{PMe}_3$. The thermal

⁵ Hough, Ford, Heffernan, and Edwards, papers M 100, M 102, 135th Meeting, Amer. Chem. Soc., 1959.

⁶ Hawthorne and Pitochelli, *J. Amer. Chem. Soc.*, 1958, **80**, 6685.

1922 Reaction of Boron Hydrides with Trialkyl and Triaryl Phosphines.

degradation of these compounds is shown in Table 2, and the hydrolytic stability in Table 3.

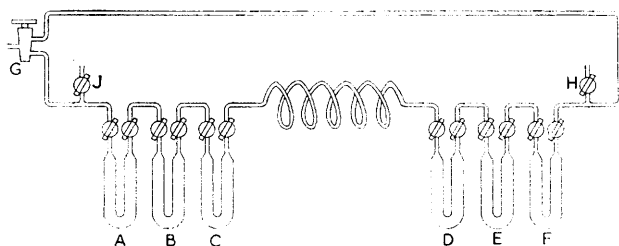
TABLE 3.
Hydrolytic stability of boron-phosphorus compounds with water and 10% aq. NaOH at 100°.

Material	Formed from	Time (at 100°) (hrs.)	ml. H ₂ (produced by 1 g.)	Observation
B ₅ H _{0.7} (PMe ₃) _{0.23}	B ₅ H ₉	16 (with H ₂ O)	76	No B-O bond detected in residue by I.R.
B ₅ H _{0.8} (PMe ₃) _{0.19}	B ₁₀ H ₁₄	16 (with H ₂ O)	12.5	
B ₅ H ₁ (PPh ₃) _{0.22}	B ₅ H ₉	5 (with NaOH)	83	White gelatinous ppt. Not all of polymer attacked.
B ₅ H ₁ (PPh ₃) _{0.19}	B ₅ H ₉	5 (with NaOH)	0	Slight attack of polymer.

EXPERIMENTAL

Diborane, prepared by the reaction of anhydrous stannous chloride and sodium borohydride at about 250° *in vacuo*,⁷ was fractionated in a high vacuum until pure (v. p.⁸ at -112° = 225 mm.).

Preparation of Pentaborane and Decaborane.—Pentaborane and decaborane were prepared by pyrolysis of diborane in a simple gas-circulatory system (Figure). The temperature of pyrolysis was 200—220° and the yields of pentaborane and decaborane were about 60% and 6% respectively, based on a 90% conversion of the diborane.



Pyrolysis apparatus (for key, see text).

Diborane (2—5 g.) was condensed in the U-trap A at -196° (liquid nitrogen), and the system was evacuated. Oxygen-free dry nitrogen was then passed through the apparatus and out to a vented hood. Meanwhile, the bath surrounding trap A was replaced by one at -90° (freezing toluene); thus, the diborane was swept through the heated spiral tube at 200° where pyrolysis took place and any B₅H₉ and B₅H₁₁ formed were collected in trap D at -78°; unconverted diborane was collected in traps E and F at -196°. When all the diborane had been passed through the spiral, the nitrogen flow was reversed by turning the double oblique tap G, closing tap H, and opening tap J. The unconverted diborane was then warmed to -90° and again passed through the spiral, and the pyrolysis was continued until complete. The pentaborane produced was then collected in one trap, transferred to a conventional Stock-type high-vacuum apparatus, and fractionated until pure, as indicated by its infrared spectrum; the vapour pressure at 0° was 66 mm. (lit.,⁹ 66 mm.), and its molecular weight 63 (determined from the vapour density). The crystals of decaborane near the cool ends of the glass spiral tube were washed from the apparatus with carbon disulphide, recovered by evaporation, and purified by vacuum sublimation, the criterion of purity being a sharp m. p. of 99.5° (lit.,⁹ 99.5°) and the infrared spectrum.

Trimethylphosphine.—Trimethylphosphine was prepared by the reaction of phosphorus trichloride and methylmagnesium iodide in ether and purified by precipitation as the silver iodide complex from aqueous potassium iodide-silver iodide.¹⁰ The complex was dried over phosphoric oxide and the trimethylphosphine regenerated by heating at ~200° under a vacuum.

⁷ Jeffers, B.P. 853,727.

⁸ Stull, *Ind. Eng. Chem.*, 1947, **39**, 540.

⁹ Hurd, "Chemistry of the Hydrides," Wiley, New York, 1952.

¹⁰ Mann, Wells, and Purdie, *J.*, 1937, 1828.

Reaction of Pentaborane with Trimethylphosphine.—A typical experiment was as follows: Pentaborane (2.3 mmoles) and trimethylphosphine (4.6 mmoles) were allowed to react in a seal-off tube at 20° for 18 hr., after which the temperature was raised to 220° for 4 hr. The solid which had been produced at the lower temperature thus melted to an amber-coloured liquid and colourless crystals sublimed to the cooler parts of the tube. The products of reaction were hydrogen, (2.14 mmoles), crystalline trimethylphosphine-borine, $^{-}\text{H}_3\text{B}\cdot\text{PMe}_3^{+}$ (2.6 mmoles), and a glass $\text{B}_1\text{H}_1(\text{PMe}_3)_{0.22}$.

Analysis.—The polymer (20—30 mg.) was fused with sodium peroxide in a small bomb and the resulting borate and phosphate were dissolved in water. Phosphate was precipitated as magnesium ammonium phosphate and reprecipitated as quinoline phosphomolybdate, and the phosphorus determination completed acidimetrically on the precipitate.

The filtrate was transferred to a stainless-steel beaker and when all ammonia and ammonium salts had been driven off by repeated additions of concentrated sodium hydroxide solution boron determination was completed by use of mannitol and sodium hydroxide.

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