CHEMICAL REACTIVITY OF THE BORON HYDRIDES AND RELATED COMPOUNDS

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I. Introduction

Alfred Stock (*131*) and his collaborators were the first to characterize a series of boranes. Properties and many reactions reported by them (1912–1936) have required but little revision to this day. For one hundred years prior to the investigations of Stock and his co-workers, the boron hydrides had been produced intermittently, but they were not identified or analyzed correctly. Stock's work stimulated others, notably Burg and Schlesinger, to enter this field so that from 1930 until 1942, the date of an important review (*111*), structural studies were carried out, and the abandon with which the boranes enter into chemical combination with themselves and with other molecules became evident. Development of improved, or even new, experimental methods has necessitated reinterpretation of most of the early structural results. As would be expected, preparative studies carried out prior to about 1942 have required less revision, providing a firm foundation on which a great extension of synthetic work could be built.

Until fairly recently interest in boron hydride chemistry was largely academic but was sustained by the failure of the boranes, and certain compounds related to them, to conform with the usual rules relating chemical composition with classical valence theory. This has now changed, and in little more than a decade the boron hydrides and their derivatives have assumed an importance far greater than could possibly have been envisaged by pioneer workers in this field. This is a consequence of the production of certain boron compounds on an industrial scale for use as fuels and fuel additives (*143*) and as reducing agents in organic and inorganic chemistry (*56*).

Compounds rich in both boron and hydrogen are especially suitable as chemical fuels because they combine such properties as high energy content per unit weight with high density and with low melting point. Of all the elements hydrogen has the highest heat of combustion, 52,000 BTU/lb at 25°C. Carbon has a heat of combustion of 14,500 BTU/lb. Hydrocarbons, therefore, have intermediate heats of combustion. Thus kerosene burned in jet engines yields about 18,600 BTU/lb. Boron itself releases 25,000 BTU/lb when burned, and when it is combined with hydrogen in the form of diborane (B_2H_6) combustion yields 32,000 BTU/lb. The hydrides B_5H_9 and $B_{10}H_{14}$ are only a little less efficient in this respect. The boranes are thus theoretically far superior fuels to kerosene.[1] However, actual fuels currently being produced are believed to be alkylated boranes. Introduction of carbon decreases efficiency, but the resulting compound would be easier to manipulate than a simple boron hydride.

New principles of propulsion may in time make chemical fuels obsolete. Furthermore, boron is a somewhat rare element. From the point of view of industrial interest in this field, it is fortunate that compounds containing boron and hydrogen have other applications, for example, as reducing agents.

Boron hydride structures and structures of molecules related to them, as well as other properties associated with bonding problems in these compounds, have been reviewed in the first volume of this series (*83*). Here it is intended to survey chemical reactivity of the boranes and of their derivatives.

Rapid expansion of boron research with isolation of many new substances has led to a proposal that there should be a new scheme of nomenclature for boron compounds (*90, 100*). Most workers now reporting their results in the English language literature do so in accordance with the new scheme. Although the subject is still being debated with vigor and there has been no international agreement on the subject, the new system of naming will be used here, except where long-established compounds are involved and trivial designations have received widespread usage. The new system may

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[1] A recent useful article on this subject is by D. R. Martin (*83c*). However, it now appears that performance of the borane fuels has not lived up to expectation, and costs are much higher than anticipated. See *Chem. Eng. News* **37,** No. 36, 38 (1959).

be illustrated by considering the BH_3 group, long referred to as *borine* but now better described as *borane*, thereby emphasizing its relation to the commonest boron hydride, diborane (B_2H_6). A natural extension is to consider most compounds as being derived from borane, thus calling alkyl compounds R_3B, R_2BX, and RBX_2 trialkylboranes, dialkylhaloboranes, and alkyldihaloboranes, respectively; for example, $(CH_3)_3B$, trimethylborane; $(C_2H_5)_2BBr$, diethylbromoborane; and $C_2H_5BF_2$, ethyldifluoroborane. Other new names put forward have received far less support; for example, tetrahydridoborate(III) for the BH_4^- ion.

Through the years the boron hydrides and their derivatives have been reviewed several times, and the reader would do well to refer to these articles (*6, 10, 27, 57, 111, 132, 146, 147*) for a more detailed survey of borane chemistry than is possible in the space available here.

Well-authenticated boron hydrides are listed in Table I. Characterization of these hydrides does not preclude the isolation of others (*83*). Properties known at present to be common to all boranes include thermal instability; susceptibility to hydrolysis, to alcoholysis, and to oxidation; toxicity; ability to react with ammonia and with many electron-pair donor molecules [for example, $(CH_3)_3N$]; and a tendency to undergo substitution of their hydrogen atoms by halogen or alkyl groups.

As might be expected, the hydrides possess these properties to varying degrees. At ambient temperatures decomposition of pure diborane is less than about 10% in a year but at 100° it rapidly forms hydrogen and other hydrides. On the other hand, tetraborane-*10* and pentaborane-*11* decompose into other boranes fairly rapidly at room temperature. Similarly, whether or not a borane will inflame on contact with air depends not only on the borane but also on the conditions of temperature and pressure. Most of these general properties have been known for a long time, but in the last ten years much work has been done to place knowledge of them on a more quantitative basis. The following studies illustrate this point. Pressure and composition explosion limits have been determined for diborane-oxygen (*91, 97*) and pentaborane-*9*-oxygen (*2, 92*) mixtures. The results have been interpreted in terms of branched-chain reactions, with oxygen atoms probably taking part in chain propagation. Experiments have shown (*119, 120, 144*) that the hydrolysis of diborane and of pentaborane-*9* very likely involves the intermediate

$$H_2\overset{+}{O}\cdot\overset{-}{B}H_3,$$

and Stock's (*131*) observation that pentaborane-*9* reacts only slowly with water at room temperature has been shown (*121*) to be due to poor miscibility of the hydride with water. In the presence of a mutually miscible solvent (dioxane) the rate of hydrolysis of pentaborane-*9* is fast. A kinetic study

TABLE I

PHYSICAL CONSTANTS OF THE VOLATILE BORON HYDRIDES

Molecular formula	B_2H_6	B_4H_{10}	B_5H_9	B_5H_{11}	B_6H_{10}	B_9H_{15}	$B_{10}H_{14}$
Name	Diborane-*6*	Tetraborane-*10*	Pentaborane-*9*	Pentaborane-*11*	Hexaborane-*10*	Enneaborane-*15*	Decaborane-*14*
Melting point (°C)	−165.5	−120	−46.6	−123	−63.2	−20	99.7
Boiling point (°C)	−92.5	18	48	63	82.2	—	213

(*7*, *8*) has been made of the reactions between decaborane-*14* and various alcohols, and deuterium exchange of decaborane-*14* and deuterium oxide has been examined (*68*). Partial hydrolysis of pentaborane-*11* below room temperature yields tetraborane-*10* (*13*). This reaction illustrates a new principle—interconversion of boranes by appropriately chosen chemical reagents rather than interconversion *via* thermal decomposition type reactions. A further example of this procedure is the synthesis of the hitherto rare B_6H_{10}, several physical properties of which have recently been reported (*56a*), by treating B_5H_{11} with dimethyl ether or certain other basic reagents (*13a*).

II. Reactions of the Boranes and Their Derivatives

A. GENERAL PRINCIPLES

On the basis of known behavior most boron hydride reactions may be assigned to two main classes. The first class involves removal of a borane group from a boron hydride structure, while the second class involves nonsymmetrical cleavage of the hydrogen bridge bonds in a borane.[2]

Removal of a borane group often occurs when a borane is treated with a nucleophilic reagent. The initial product of this type of reaction is an adduct of the borane group, but the nature of the donor part of the adduct controls the subsequent fate of the whole. For all such compounds there is a tendency, varying from complex to complex, to dissociate reversibly into donor and acceptor parts. Thus whereas $(CH_3)_2S \cdot BH_3$ (*49*) is appreciably dissociated in the gas phase at 50°, the compound $(CH_3)_3P \cdot BH_3$ (*43*) may be heated to 200° without appearance of significant amounts of borane decomposition products.

Some borane adducts decompose irreversibly. Thus if the ligand atom has hydrogen bonded to it, elimination of molecular hydrogen from the complex occurs either as soon as it is formed [ ] or on heating; for example,

$$B_2H_6 + ROH \rightarrow [R(H)O \cdot BH_3] \rightarrow ROBH_2 + H_2 \xrightarrow[\text{disproportionation}]{} (RO)_2BH + (RO)_3B + B_2H_6, \quad (\mathit{38})^{1a}$$

$$(CH_3)_2NH + B_2H_6 \rightarrow (CH_3)_2NH \cdot BH_3 \xrightarrow{\text{heat}} (CH_3)_2NBH_2 + H_2. \quad (\mathit{36}, \mathit{37}, \mathit{148}, \mathit{149})^{3}$$

[1a] In this chapter, parenthesized numbers appearing to the right of chemical equations are reference numbers throughout.

[2] Since this article was submitted to the publisher, two papers concerned with classification of the reactions of the boranes in relation to their structures have appeared (*83a*, *85a*).

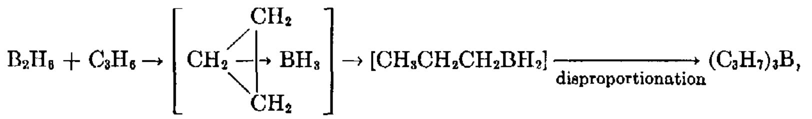
[3] This compound, *N*,*N*-dimethylaminoborane (mp, 75°), like most BH_2 derivatives polymerizes. When prepared by this method, the solid is dimeric but a monomer-dimer equilibrium exists in the gas phase, complicated by some disproportionation to

Reactions related to these are the many which occur in the gas phase between boranes and molecules with insufficient dative bonding power to permit formation of a definite complex even at low temperature; for example,

$$B_2H_6 + H_3As \rightarrow H_2 + (H_2AsBH_2)_n, \qquad (134)$$

$$B_2H_6 + (CF_3)_2PH \rightarrow H_2 + [(CF_3)_2PBH_2]_3. \qquad (31)$$

An alternative route for irreversible decomposition of a borane adduct involves transfer of hydride from boron to the ligand, usually occurring with a rapidity sufficient to prevent isolation of an initial complex. Indeed, existence of an adduct at the first stage of reaction can often only be inferred from the nature of the final product; for example,



$$B_2H_6 + C_3H_6 \rightarrow \left[\begin{array}{c} CH_2 \\ CH_2 \rightarrow BH_3 \\ CH_2 \end{array}\right] \rightarrow [CH_3CH_2CH_2BH_2] \xrightarrow[\text{disproportionation}]{} (C_3H_7)_3B, \qquad (59)$$

$$B_2H_6 + CH_3CHO \rightarrow [CH_3CHO \cdot BH_3] \rightarrow [CH_3CH_2OBH_2] \xrightarrow[\text{disproportionation}]{} (C_2H_5O)_2BH + (C_2H_5O)_3B. \qquad (16)$$

The boron hydrides function as Lewis acids in these reactions involving borane. In this connection important energy factors are dissociation of the boron hydride in the gas phase to give a borane fragment, vaporization of the base if it is a liquid or solid, adjustment of borane and of the base to configurations present in the final product, energy released in dative-bond formation and in condensation of product to a liquid or solid (*132, 133*). Thus each reaction must be examined individually, and although data for component parts of such an energy cycle are lacking, the cycle can be used qualitatively for discussion of real or possible compounds. Physical properties of several borane addition compounds are presented in Table II. Heats of dissociation and heats of formation of a number of borane coordination compounds have been measured. Borane exists in its standard state as B_2H_6, so that the measurements necessarily involve this dimer. However, the enthalpy change for the reaction $B_2H_{6(g)} = 2BH_{3(g)}$ has been estimated as 28.4 kcal/mole (*5, 84*). Hence strength of the dative bond in a borane addition compound can be determined from data involving diborane if

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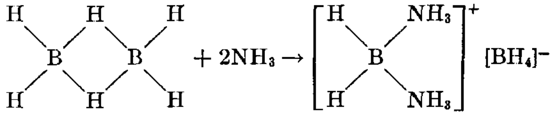
$[(CH_3)_2N]_2BH$ and $(CH_3)_2NB_2H_5$. As will be described in Section II,B, a *trimeric* form of $(CH_3)_2NBH_2$ has also been reported. In most cases occurrence of borane derivatives like $(CH_3)_2NBH_2$ or $(C_2H_5O)_2BH$ as *monomers* can be accounted for in terms of the existence of double bonding involving overlap of a filled p_π-orbital on the donor atom (namely N or O) with the empty boron p_π-orbital. See references (*10*) and (*133*) for a more detailed review of this idea.

strength of the bond is defined (*133*) as the enthalpy change accompanying the reaction,

$$\text{Ligand} \cdot BH_{3(g)} \rightarrow \text{Ligand}_{(g)} + BH_{3(g)}.$$

More recently another mode of reaction of some of the boranes has been recognized. Certain reagents under rather carefully controlled conditions induce nonsymmetrical cleavage of the hydrogen bridge bonds. As will be discussed in more detail later (Section II,B), formation of the "diammoniate of diborane" probably involves this mechanism.



The sodium-diborane reaction (*72*) provides another example of unsymmetrical cleavage of a double bridge bond.

$$2Na + 2B_2H_6 \rightarrow NaBH_4 + NaB_3H_8$$

Besides removal of borane groups and unsymmetrical bridge-bond cleavage, other types of boron hydride reaction are known but at present appear to be much less common;[2] for example, loss of protons, as in the ionization of $B_{10}H_{14}$ in dioxane-water or ethanol-water solutions (*61*, *62*),

$$B_{10}H_{14(aq)} \rightleftharpoons B_{10}H^{-}_{13(aq)} + H^{+}{}_{(aq)},$$

and in salt formation by $B_{10}H_{14}$ (*65*),

$$(C_6H_5)_3P^{+}CH_2^{-} + B_{10}H_{14} \rightarrow [(C_6H_5)_3PCH_3]B_{10}H_{13},$$

or internal exchange of hydrogen atoms as in the reaction between $B_{10}H_{14}$ and acetonitrile to give $B_{10}H_{12}(CNCH_3)_2$. The latter substance is best regarded as a substitution derivative of $B_{10}H_{14}^{-2}$ (*83*), not a derivative of $B_{10}H_{14}$, with the boron-hydrogen arrangement having either the 2632 or 0814 topology (*139*).

B. Reactions Leading to Formation of Boron-Nitrogen Bonds

Discovery of the "diammoniate" of diborane (B_2H_6, $2NH_3$) and borazene ($B_3N_3H_6$), better known by its older name of borazole, by Stock (*131*) indicated that the boron hydrides could be used to prepare interesting boron-nitrogen compounds. This approach to boron chemistry was rapidly extended when the principles discussed in the preceding section were clearly recognized. Thus the compound $(CH_3)_3N \cdot BH_3$, the first borane adduct to be characterized (*39*), pointed the way to the synthesis of a number of similar substances directly from diborane and amines; for exam-

TABLE II

Coordination Compounds of Borane

Compound	Melting point (°C)	Boiling point[a] (°C)	$\log_{10} p(\mathrm{mm}) = -A/T + B$		ΔH (vapor) (kcal/mole)	Trouton constant[a] (eu)	References
			A	B			
$H_3N \cdot BH_3$	Slowly decomposes, liberating H_2 at room temperature						*123, 124*
$CH_3H_2N \cdot BH_3$	54	—	—	—	—	—	*1, 12, 36, 148 149*
$CH_3H_2P \cdot BH_3$	−49.3	150	2329	8.400	10.7	25.3	*43*
$CH_3H_2As \cdot BH_3$	Solid at −78.5 (p_{diss} = 10.5 mm)	Unstable	—	—	—	—	*134*
$(CH_3)_2HN \cdot BH_3$	36	—	—	—	—	—	*1, 36, 148, 149*
$(CH_3)_2HP \cdot BH_3$	−22.6	174	2337	8.100	10.7	23.9	*43*
$(CH_3)_2HAs \cdot BH_3$	−22.4 to −21.5	85.5	2263	9.191	10.3	28.9	*134*
$(CH_3)_3N \cdot BH_3$	94	171	2202	7.846	10.1	22.7	*39*
$(C_2H_5)_3N \cdot BH_3$	−4	Vapor pressure 12 mm at 100°					*80*
$(C_2H_5)_2(n\text{-}C_4H_9)N \cdot BH_3$	−33	Vapor pressure 14 mm at 125°					*80*
$(n\text{-}C_4H_9)_3N \cdot BH_3$	—	Vapor pressure 10^{-3} mm at 87°					*80*
$(CH_3)_3P \cdot BH_3$ (*solid*)	103	—	2933	9.531	—	—	*43*
$(CH_3)_3As \cdot BH_3$	73.5–74.5	154	2420	8.553	11.1	26.0	*134*
$(CH_3)_3Sb \cdot BH_3$	−33	Unstable	—	—	—	—	*34, 71*
$HONH_2 \cdot BH_3$	Solid at −78	Loses H_2 on warming to room temperature					*45*
$HONHCH_3 \cdot BH_3$	—	Loses H_2 on warming to room temperature					*45*
$HON(CH_3)_2 \cdot BH_3$	2–4°	Vapor pressure 6 mm at 25°					*45*
$(CH_3O)NH_2 \cdot BH_3$	55	Slightly volatile at 40°					*11*
$(CH_3O)(CH_3)NH \cdot BH_3$	−23 to −21	Slightly volatile at 25°					*11*
$(CH_3)_2(CH_3O)N \cdot BH_3$	−16.5	Vapor pressure 3.8 mm at 26°					*11*
$F_3P \cdot BH_3$	−116.1	−61.8	1038.9	7.8061	4.760	22.5	*85*
$OC \cdot BH_3$	−137	−64	1040	7.850	4.750	23	*39*

$(CH_3)_2O \cdot BH_3$	Solid at −78.5 (p_{diss} = 18 mm)	Unstable	—	—	—	—	*110*
$(CH_2)_4O \cdot BH_3$	−34	62	1244	6.592	—	17.0	*49, 95, 154*
$(CH_3)_2S \cdot BH_3$	−40 to −38	97	2346	9.220	10.7	29.0	*44, 49, 58*
$(CH_2)_4S \cdot BH_3$	—	132.5	2321	8.602	10.6	26.2	*49*
$(C_2H_5)_2S \cdot BH_3$	—	119.5	2394	8.978	11.0	27.9	*49*
$(CH_3)_2Se \cdot BH_3$	−34 to −32	63.2	1732	8.030	7.9	23.5	*58*

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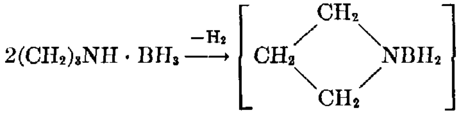
[a] In order to calculate the boiling point, a large extrapolation of the vapor pressure equation is involved, so these values must be considered as approximate. Furthermore, whenever vaporization of an addition compound is accompanied by an increase in dissociation, extrapolation of the vapor pressure equation cannot give the true boiling point. This is exemplified by tetrahydrofuran-borane, the boiling point of which is less than that of the ligand [tetrahydrofuran; bp 64°]. The large entropies of vaporization of molecular addition compounds are a consequence of further dissociation on vaporization, although dipole association in the condensed phase probably enhances the effect to some extent. A few addition compounds do not have high Trouton constants even though they are known to be highly dissociated in the gas phase. Such adducts are no doubt partially dissociated even as liquids.

ple, $C_5H_5N\cdot BH_3$ (*17*)[4] $CH_3NH_2\cdot BH_3$ (*112, 148, 149*), $(CH_3)_2NH\cdot BH_3$ (*36, 148, 149*), and $(CH_2)_5NH\cdot BH_3$ (*33*). Moreover, many adducts of this type provide a route to substituted derivatives of borane, because in those instances where the donor atom carries a proton the complex will eliminate hydrogen, either incipiently or on heating; for example,



Azetidine-borane Azetidinoborane (*33*)

$$3CH_3NH_2\cdot BH_3 \xrightarrow{100^\circ} (CH_3NHBH_2)_3 + 3H_2 \qquad (12)$$

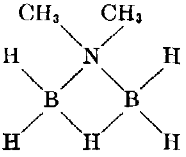
N-methylamineborane *N*-methylaminoborane

$$\downarrow 200^\circ$$

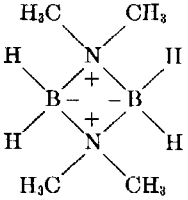
$$(CH_3NBH)_3 + 3H_2 \qquad (112,\ 151)$$

N-trimethylborazole

Aminoboranes undergo an interesting reaction when heated with diborane; a borane group is absorbed and aminodiboranes are formed (*35, 36*). The structure of *N,N*-dimethylaminodiborane has been determined by electron diffraction (*70*); it (I) is related to the structure of diborane and to the probable structure of *dimeric* *N,N*-dimethylaminoborane (II).[3] It is likely that all aminodiboranes have similar structures. The first member of the group, $H_2NB_2H_5$, may be prepared by passing diborane over its



(I)



(II)

diammoniate at 88°, and at a pressure of about 1 atm (*113*). It decomposes slowly into a polymer, $(H_2B\cdot NH_2)_x$, and diborane. Alkylaminodiboranes are more stable. *N,N*-Dimethylaminodiborane may be stored indefinitely at room temperature.

The effect of ammonia on diborane is very complex. A variety of products are produced depending on conditions. At −120° using very specific techniques, diborane and excess of ammonia form the diammoniate, B_2H_6, $2NH_3$ (*89, 110, 131*). The latter was at first formulated as $(NH_4^+)_2(B_2H_4)^{-2}$ (*131, 145*), but this structure was later shown to be incorrect (*26, 110*), con-

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[4] Borane adducts of various alkylpyridines have been prepared. They were studied in order to correlate their stability with certain steric effects in organic chemistry. See Brown and Domash (*13b*).

TABLE III

AMINODIBORANES

Formula	Melting point (°C)	Boiling point[a] (°C)	$\log_{10} p(\text{mm}) = -A/T + 1.75 \log T - BT + C$			Trouton constant[a] (eu)	References
			A	B	C		
$H_2NB_2H_5$	−66.5	76.2	2097	0.00642	6.677	21.0	*113*
$CH_3(H)NB_2H_5$	—	66.8	2158.56	0.00806	7.51883	19.6	*36*
$(CH_3)_2NB_2H_5$	−54.8 to −54.4	50.3	1727.64	0.004661	5.3370	20.6	*36*
$(CH_3)(SiH_3)NB_2H_5$	−39.0	51	$\log_{10} p(\text{mm}) = 8.081 - 1686T^{-1}$			23.8	*35*
$(SiH_3)_2NB_2H_5$	−69.4 to −68.8	54	$\log_{10} p(\text{mm}) = 7.974 - 1669T^{-1}$			23.3	*35*
$C_2H_5(H)NB_2H_5$	−96.4	86.6	2096.3	0.00533	6.15245	21.0	*33*
n-$C_3H_7(H)NB_2H_5$	−146 to −143	121	$\log_{10} p(\text{mm}) = 8.537 - 2117T^{-1}$			25.9	*33*
$(CH_2)_3NB_2H_5$	−45.4	101	2248	0.00616	6.6928	20.2	*33*
$(CH_2)_4NB_2H_5$	−63.5	121.8	2205	0.004539	5.7217	20.6	*33*
$(CH_2)_5NB_2H_5$	—	148	2410	0.00510	6.1606	19.6	*33*

[a] From the vapor pressure equation.

vincing evidence against it coming from an isotopic tracer study using ND_3 (*26*). This showed that H-D exchange between solute and solvent occurred only between N-bonded hydrogens. Later the structure $(NH_4^+)(H_3B \cdot NH_2 \cdot BH_3)^-$ was suggested (*110*) mainly because with sodium in liquid ammonia the diammoniate gave one equivalent of hydrogen. This was taken as evidence for the presence of one ammonium ion per pair of boron atoms in the structure. The constitution of the "diborane diammoniate" has recently been placed on a much firmer basis by studies of Parry and his co-workers (*88, 89, 117, 122, 124, 125*). There is now no doubt that the diammoniate contains the borohydride ion, BH_4^-. This was first indicated by the work of G. W. Schaeffer *et al.* (*101*) who found that when B_2H_6, $2NH_3$ was treated with sodium, sodium borohydride was produced. Later it was shown (*117*) that $[Mg(NH_3)_6](BH_4)_2$ could be precipitated from a liquid ammonia solution of the diammoniate. Furthermore, the Raman spectrum of $B_2H_6 \cdot 2NH_3$ is in accord with the presence of a BH_4^- ion (*136*). It should be noted that the borohydride ion had not been discovered at the time Schlesinger and Burg (*110*) proposed the structure $(NH_4^+)(H_3BNH_2BH_3)^-$. Once the presence of borohydride in the structure was established, the idea of having an ammonium ion simultaneously present became unlikely because ammonium borohydride is unstable (*87*). Moreover, formation of one equivalent of hydrogen by treating the diammoniate of diborane with sodium in liquid ammonia (*110*) is not a specific test for ammonium ion, but merely indicates the presence of a Brönsted-Lowry acid (*117*). The idea (*101*) that ammonium and borohydride ions can exist together in the diammoniate because they are stabilized by a H_2BNH_2 group, namely, $NH_4^+(BH_2NH_2)BH_4^-$, is difficult to reconcile with certain experimental observations (*117*). A reasonable explanation of the results is possible if the presence of the cation $[H_2B(NH_3)_2]^+$ in the diammoniate is assumed. This accords with the isolation of chloride and bromide salts $[H_2B(NH_3)_2]X$ from reactions between the diammoniate and the appropriate ammonium halide, with the inertness of the diammoniate towards sodium borohydride, and with the behavior of the diammoniate on hydrolysis, as well as with certain other properties. Furthermore, an X-ray diffraction study of $(NH_3)_2BH_2Cl$ demonstrates that the cation $[H_2B(NH_3)_2]^+$ is present in this compound (*84a*). Thus the diammoniate of diborane is now best regarded as having the structure $[H_2B(NH_3)_2]^+[BH_4]^-$. Quite distinct from this compound is ammonia-borane (*123, 124*), prepared by the reactions,

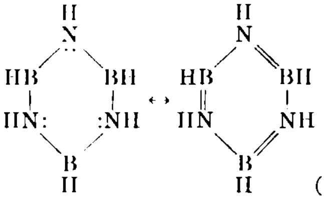
$$LiBH_4 + NH_4Cl \xrightarrow{(C_2H_5)_2O} LiCl + H_3N \cdot BH_3 + H_2$$

$$[H_2B(NH_3)_2]^+[BH_4]^- + NH_4Cl \xrightarrow[\text{trace } NH_3]{(C_2H_5)_2O} [H_2B(NH_3)_2]^+Cl^- + H_3N \cdot BH_3 + H_2$$

$$(CH_3)_2O \cdot BH_3 + NH_3 \rightarrow H_3N \cdot BH_3 + (CH_3)_2O$$

Ammonia-borane is thermally less stable than the "diammoniate" with respect to loss of hydrogen. It is monomeric, and unlike the "diammoniate" is soluble in ether.

When diborane and excess of ammonia are heated together, boron imide and ultimately boron nitride[5] are produced. If diborane and ammonia in a ratio of 1:2 are heated, or if the diammoniate of diborane is heated above 200°, the compound borazole(III) (bp, 53°) is obtained, but in yields only as high as 45%. Borazole decomposes slowly in the liquid phase and even more slowly in the gas phase. Its boron atoms can act as weak electron acceptors and its nitrogen atoms as weak donors; thus hydrogen chloride adds to borazole, and on heating *B,B′,B″*-trichloroborazole is produced. In a similar manner water reacts with borazole. This reactivity emphasizes how borazole differs from benzene and is related to localization of electrons on nitrogen, for which there is additional evidence from spectroscopic studies (*93*). A very large number of substituted borazoles are known. Reactions by which borazole and some of its derivatives have been prepared include:


(two forms)

(III)

$$\underset{\text{(mixture of solids)}}{3LiBH_4 + 3NH_4Cl} \xrightarrow{230^\circ} \underset{\substack{(30\text{–}35\%\\ \text{yield})^{6}}}{B_3N_3H_6} + 9H_2 + 3LiCl \qquad (104)$$

$$\begin{array}{l} LiBH_4 + RNH_3Cl \xrightarrow{(C_2H_5)_2O} LiCl + RNH_2 \cdot BH_3 + H_2 \qquad (75)\\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow 200\text{–}260^\circ \\ (R = CH_3,\ C_2H_5,\ C_3H_7 \text{ and } i\text{-}C_3H_7) \qquad \tfrac{1}{3}\,(RNBH)_3 + 2H_2 \\ \qquad\qquad\qquad\qquad\qquad\qquad\qquad (\text{yields} \sim 90\%) \end{array}$$

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[5] In this reaction the hexagonal or "white graphite" form of this substance is obtained It is composed of condensed $(BN)_x$ rings. A cubic form, borazon, analogous to diamond has recently been prepared. It is often stated that the structures of graphite and hexagonal boron nitride are similar. They are related but differ in an important respect. Localization of electrons on the nitrogen atoms in boron nitride leads to a different mode of layer packing, with boron atoms in one layer directly under nitrogen atoms in another. In accordance with this, hexagonal boron nitride is a poor electrical conductor.

[6] Recently Emeléus and Videla (*50a*) have shown that if hydrazine hydrochloride is used in this reaction instead of ammonium chloride, the yield is near 50%.

$$3NH_4Cl + 3BCl_3 \xrightarrow[140\text{–}150^\circ]{C_6H_5Cl} (HNBCl)_3 + 9HCl \qquad (82)$$[7]

$$\downarrow 3LiBH_4$$

$$B_3N_3H_6 + 3LiCl + \tfrac{3}{2}\,B_2H_6 \qquad (105)$$

(90% yield)

$$3BCl_3 + 3[CH_3NH_3]Cl \xrightarrow[\text{reflux}]{C_6H_5Cl} (CH_3NBCl)_3 + 9HCl$$

$$\downarrow RMgX$$

$$(CH_3NBR)_3$$

$$(R = C_2H_5,\ CH_2{:}CHCH_2^-,\ n\text{-}C_4H_9) \qquad (99)$$

$$3RBCl + 9NH_3 \xrightarrow{\text{heat}} [RBNH]_3 + 6NH_4Cl \qquad (98)$$

$$(R = n\text{-}C_4H_9,\ C_6H_5,\ ClCH{:}CH,\ \text{etc.})$$

$$BCl_3 + RNH_2 \xrightarrow{C_6H_6} RNH_2 \cdot BCl_3 \xrightarrow{(C_2H_5)_3N} [RNBCl]_3 + (C_2H_5)_3NHCl \qquad (137)$$

(84% yield)

$$BCl_3 + C_6H_5NH_2 \xrightarrow{C_6H_5CH_3} C_6H_5NH_2 \cdot BCl_3 \xrightarrow[\text{reflux}]{C_6H_5CH_3} [(C_6H_5)NBCl]_3 + HCl$$

$$\downarrow RMgX$$

$$[(C_6H_5)NBR]_3 \qquad (60)$$

$$(R = CH_3,\ n\text{-}C_4H_9,\ C_6H_5,\ CH_2{:}CHCH_2^-,\ \text{etc. with yields} \sim 70\%)$$

$$(CH_3)_3B + CH_3NH_2 \rightarrow (CH_3)NH_2 \cdot B(CH_3)_3 \xrightarrow[20\ \text{atm}]{450^\circ} [CH_3NBCH_3]_3 \qquad (151)$$

As would be expected, hydrolytic and thermal stability of the substituted borazoles is dependent on the substituent groups. Thus *B*-trimethyl-*N*-triphenylborazole is but little affected by water at 100°, whereas the *N*-trialkylborazoles are readily hydrolyzed.

An extensive field of boron chemistry is associated with reactions between the higher boranes and ammonia or amines. Stock (*131*) was responsible for discovery of a series of "ammoniates" of the higher boron hydrides and for their thermal decomposition into borazole and nonvolatile boron-nitrogen containing materials. The properties of all these ammoniates are worthy of further investigation since recently it has been shown (*77*, *78*) that tetraborane-*10* forms a "diammoniate" and not a "tetraammoniate" as reported by Stock (*131*). The "diammoniate" of tetraborane has properties consistent with the structure $[H_2B(NH_3)_2]^+[B_3H_8]^-$ (*77*, *78*, *79a*). This unsymmetrical cleavage by ammonia of the bridge bonds of a higher borane is in contrast to the behavior of tertiary amines towards tetraborane, pentaborane-*9*, or pentaborane-*11*. The ultimate products of the reaction between

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[7] In the presence of cobalt catalyst yields in this reaction are markedly increased (*50a*).

tetraborane and excess of trimethylamine are three moles of $(CH_3)_3N \cdot BH_3$ and $(BH_x)_n$ polymer (*42*). With a 1:1 molar ratio of reactants, however, tetraborane and trimethylamine yield a mixture of $(CH_3)_3N \cdot BH_3$ and $(CH_3)_3N \cdot B_3H_7$. In a similar manner the adduct $C_5H_5N \cdot B_3H_7$ has been obtained from pyridine and tetraborane (*73*). With excess of the nitrogen bases the B_3H_7-adducts decompose giving an amine-borane and diborane. The B_3H_7 group has a strong affinity for pyridine since the reaction,

$$B_4H_{10} + C_5H_5N \cdot BH_3 \rightarrow C_5H_5N \cdot B_3H_7 + B_2H_6$$

occurs. Adducts are also formed between B_3H_7 and dimethyl sulfide, ethylene glycol ethers (*73*), and ammonia (*77*, *86*),

$$B_4H_{10} \cdot 2NH_3 + HCl \xrightarrow[-78^\circ]{(C_2H_5)_2O} (NH_3)_2BH_2Cl + (C_2H_5)_2O \cdot B_3H_7 + H_2$$

$$(C_2H_5)_2O \cdot B_3H_7 + NH_3 \xrightarrow[-78^\circ]{(C_2H_5)_2O} (C_2H_5)_2O + H_3N \cdot B_3H_7$$

Although the last reaction listed yields ammonia-triborane, this substance is better obtained *via* the reactions (*79a*),

$$B_4H_{10} + (CH_2)_5O \xrightarrow{25^\circ} \tfrac{1}{2}\, B_2H_6 + (CH_2)_5O \cdot B_3H_7$$

$$(CH_2)_5O \cdot B_3H_7 + NH_3 \xrightarrow[-78^\circ]{(C_2H_5)_2O} H_3N \cdot B_3H_7 + (CH_2)_5O$$

In contrast to tetraborane, no reactions were observed between pentaborane-*9* and weak Lewis bases such as tetrahydrofuran or dimethyl sulfide (*74*). With trimethylamine, however, at −78° (*28*) or at room temperature (*74*), pentaborane-*9* affords the white sublimable bistrimethylamine pentaborane-*9*, $[(CH_3)_3N]_2B_5H_9$. If the latter substance is heated (*28*), or left in contact with amine (*74*), cleavage occurs with partial conversion to $(CH_3)_3N \cdot BH_3$ and $(BH_x)_n$. In the absence of excess of amine, bistrimethylamine pentaborane-*9* slowly forms $(CH_3)_3N \cdot BH_3$ and trimethylamine tetraborane-*6*, $(CH_3)_3N \cdot B_4H_6$ (*74*). Dimethylamine or the *N*-methylaminoboranes also remove borane from B_5H_9 on heating, but form as well a compound first formulated as $[(CH_3)_2N]_3B_3H_4$ (*28*).[8]

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[8] Very recently the reaction between B_5H_9 and excess of dimethylaminoborane has been reinvestigated (*46a*). On the basis of new acid-methanolysis data and an NMR study the compound reported as "$[(CH_3)_2N]_3B_3H_4$" has now been formulated as $[(CH_3)_2NBH_2]_3$, a new trimeric form of dimethylaminoborane. This has been confirmed by an X-ray diffraction study by Trefonas and Lipscomb (*136a*). The compound in question is inert to water, acid, and methanol at ambient temperatures (in this respect it is quite comparable (*12*) to the N-methylaminoborane trimer), and is stable in *vacuo* to a little over 300°. With methanol and hydrochloric acid, however, it reacts completely at 80–90° over a period of 16 hr or less. Compared with other borane derivatives the stability of

The interaction of trimethylamine or certain other Lewis bases with pentaborane-*11* also results in symmetrical cleavage of BH_3 groups. Nevertheless, the ultimate reactions are more complicated than the reactions with other boranes because of the instability of pentaborane-*11* (*53*). The decaborane-dimethylamine system is complicated. When solid $B_{10}H_{14}$ is treated with dimethylamine, a series of adducts containing 1, 2, or 3 moles of amine per mole of decaborane tend to form (*52*). Decaborane and pyridine also yield a number of products (*51*). It appears that most of these products consist of two pyridine molecules attached to a decaborane molecule which has lost one or two hydrogen atoms.

As a conclusion to this section it should be mentioned that reactions between diborane and several other nitrogen Lewis bases besides those mentioned above have been investigated. These nitrogen donors include hydrazine and its methyl derivatives (*130*), hydroxylamine and its *N*-methyl derivatives (*45*), and *O*-methylhydroxylamine and its *N*-methyl derivatives (*11*). In general, borane adducts are formed (Table II) which are thermally unstable with respect to release of hydrogen.

C. REACTIONS LEADING TO FORMATION OF BORON-PHOSPHORUS, BORON-ARSENIC, OR BORON-ANTIMONY BONDS

By using boron hydrides as the boron source, a number of compounds may be made in which boron is bonded to phosphorus or its congeners. Thermal stabilities of analogous borane derivatives of these elements decrease from phosphorus to antimony in accord with the general observation that heavier elements form weaker covalent bonds than do lighter elements. However, strength of a bond between a particular Group V element and the borane group is dependent on a number of factors including the nature of substituents on the Group V atom. Thus the compound $(CH_3)_3P \cdot BH_3$ is very stable (*43*) since strong donor groups are on phosphorus, whereas the complex $F_3P \cdot BH_3$ (*85*) with electronegative groups on the ligand atom readily dissociates into its components. Amminolysis of phosphorus trifluoride-borane at low temperatures may be represented by

$$6NH_3 + F_3P \cdot BH_3 \xrightarrow[-111° \text{ to } -35°]{(C_2H_5)_2O} 3NH_4F + (H_2N)_3P \cdot BH_3 \qquad (79)$$

The compound triamido-phosphorus-borane, $(H_2N)_3P \cdot BH_3$, is a sublimable white solid soluble in ether and liquid ammonia. An ethane-like struc-

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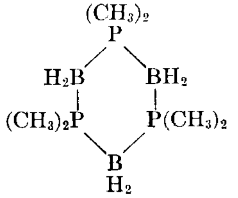
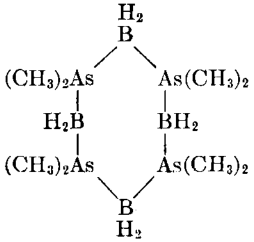
the new substance (mp, 97°) is high, but it does not appear to be so unreactive as the phosphorus analog (Section II,C). It is surprising that $[(CH_3)_2NBH_2]_3$ has not been reported before now, and that its formation from the monomer-dimer mixture of $(CH_3)_2NBH_2$ required the presence of B_5H_9.

ture has been suggested for phosphorus trifluoride-borane with a σ-bond between boron and phosphorus (*85*). However, as will be discussed in Section II,F, it is possible that the bonding may not be as simple as this.

Diborane and phosphine at −110° form a solid $B_2H_6,2PH_3$, dissociation pressure 200 mm at 0° (*55*). Its constitution is unknown but the properties are more like those of ammonia-borane than those of the diammoniate of diborane, so it may be a simple borane adduct $H_3P \cdot BH_3$. Diborane reacts with biphosphine well below room temperature to produce $P_2H_4 \cdot B_2H_6$, a compound thermally more stable than $P_2H_4 \cdot 2BF_3$ (*9*). As might be expected, diborane and phosphine react slowly at room temperature, or more rapidly on heating, forming a polymer $[BPH_x]_n$ and hydrogen. Similarly, $CH_3PH_2 \cdot BH_3$ (*43*), with more than one proton bonded to the ligand atom, releases hydrogen on heating, producing nonvolatile polymeric materials. When adducts such as $(CH_3)_2PH \cdot BH_3$ or $(CH_3)_2AsH \cdot BH_3$ are heated on the other hand, loss of hydrogen ceases after evolution of one mole and formation of borane derivatives, $[(CH_3)_2M^VBH_2]_n$ ($M^V = P$ or As) (*43*, *134*). These dimethylphosphino- and dimethylarsinoboranes are obtained principally as trimers, although some tetrameric and higher polymeric forms are simultaneously produced. The trimers and tetramers are volatile crystalline solids with exceedingly high thermal and hydrolytic stability for molecules containing B-H bonds. Thus dimethylphosphinoborane trimer and tetramer are hydrolyzed only slowly by concentrated hydrochloric acid near 300°, and $[(CH_3)_2PBH_2]_3$ is stable in *vacuo* to 400°, although it ignites in air at about 250°. The arsinoboranes are somewhat less stable, as would be expected from the weaker bonding powers of arsenic. It is likely that these trimeric and tetrameric phosphino- and arsinoboranes have ring structures (IV,V). Indeed, in the case of $[(CH_3)_2PBH_2]_3$ this has been confirmed by an X-ray diffraction study (*63*). It has been suggested (*43*) that the extraordinary stability of these compounds is due to a novel type of bonding in which the regular dative σ-bonds are strengthened by π-bonds. These π-bonds could arise through interaction of vacant *d*-orbitals on phosphorus or arsenic with electron density from the B-H linkages. In



(IV)



(V)

this manner the virtual absence of hydridic character in the B-H bonds can be accounted for. This hypothesis gains some support from the observation that in $[(CH_3)_2PBH_2]_3$ the HBH angle is near 120°, considerably greater than tetrahedral, and as if B-H electrons are attracted to phosphorus above and below the puckered ring (*63*). Any B-P π-bonding in the cyclic phosphinoboranes should increase in importance as electronegativity of the groups on phosphorus is increased. The P-B dative σ-bonds, however, would be weakened. It is interesting, therefore, that the volatile solids $[(CF_3)_2PBH_2]_3$ and $[(CF_3)_2PBH_2]_4$ have been prepared by reaction between diborane and $(CF_3)_2PF$ or $(CF_3)_2PH$ (*31*). These fluorocarbon phosphinoboranes are hydrolytically much less stable than the methyl compounds, but they are thermally stable up to 200°. Their existence is difficult to account for in terms of polymerization of $(CF_3)_2PBH_2$ groups merely by P-B σ-dative bonds because the $(CF_3)_2P$ group is a very weak electron pair donor. The compound $(CF_3)_2PH$ does not form a recognizable adduct with borane.

A number of compounds $[R_2PBH_2]_n$ have now been prepared (*41*, *140*), some by pyrolysis of borane adducts obtained from diborane and secondary phosphines, for example,

$$(CH_3)(i\text{-}C_3H_7)PH \cdot BH_3 \rightarrow \frac{1}{3}\,[CH_3(i\text{-}C_3H_7)PBH_2]_3 + H_2$$

$$cyclo(C_6H_{11})_2PH \cdot BH_3 \rightarrow \frac{1}{3}\,[cyclo(C_6H_{11})_2PBH_2]_3 + H_2$$

$$\underline{CH_2(CH_2)_3PH} \cdot BH_3 \rightarrow \frac{1}{3}\,[\underline{CH_2(CH_2)_3P}BH_2]_3 + H_2$$

others starting from organohalophosphines, for example,

$$\begin{array}{c} R_2PCl + NaBH_4 \rightarrow R_2PH \cdot BH_3 + NaCl \\ \downarrow \text{pyrolysis} \\ [R_2PBH_2]_3 \\ (R = Et, Ph, etc.) \end{array}$$

The discovery (*28a*) that when the adduct $(CH_3)_4P_2(BH_3)_2$ is heated to 170–200° the phosphinoborane $[(CH_3)_2PBH_2]_n$ ($n = 3$, 75% yield; $n = 4$, 15% yield) is produced suggests that diphosphines may also provide routes to phosphorus-boron polymers. In the above reactions the phosphinoboranes are obtained mostly as trimers with small amounts of tetramer and only traces of higher polymers. In the search for truly inorganic polymer systems it would be useful if the phosphinoboranes could be obtained with a high degree of polymerization. Recently a novel technique has been partially successful in increasing the yield from pyrolysis of a phosphine-borane of highly polymeric $[R_2PBH_2]_n$ (*140a*). When a phosphine-borane is pyrolyzed in the presence of about ten mole per cent of a strong Lewis base [for example, $(C_2H_5)_3N$, $(CH_3)_3P$, or $(CH_3)_3N$], a significant proportion (approximately 50%) of the phosphinoborane produced is in the form of high polymer. Under these conditions $(CH_3)_2PH \cdot BH_3$, for example, affords a brittle white polymer with a degree of polymerization of about 80 (molecular weight approximately 6000), while when $CH_3(C_2H_5)PH \cdot BH_3$ is heated in the presence of Lewis base, a truly plastic polymer (mp, 118–126°) is produced. It is probable that in these reactions the Lewis base functions to stabilize the monomer, namely, $R_2PBH_2 \cdot N(C_2H_5)_3$, the phosphorus atom in one such unit then bonding to the boron atom in another. It is likely that treatment of higher boranes with organophosphines will afford interesting substances with phosphorus-boron bonds. In this connection the compound $B_{10}H_{12}[(C_6H_5)_3P]_2$ should be noted (*69*). This substance, stable without melting to above 300°, may be prepared by refluxing decaborane and triphenylphosphine in diethyl ether. One mole of hydrogen is evolved per mole of compound produced. Treatment of $B_{10}H_{12}(CH_3CN)_2$ with triphenylphosphine also yields $B_{10}H_{12}[(C_6H_5)_3P]_2$. The $B_{10}H_{12}$ unit can be transferred from one ligand to another, behaving as a discrete electron-deficient species (*69*).

Recently some stibinoboranes have been reported (*34*), and as would be expected antimony-boron bonds are considerably weaker than those between arsenic and boron. Thus $(CH_3)_3Sb \cdot BH_3$ exists only well below room temperature, whereas $(CH_3)_3As \cdot BH_3$ shows instability only above 80°. Indeed, if Lewis acid-base displacement reactions are used as a criterion of stability, then relative stabilities of the BH_3 adducts of trimethyl compounds of Group V elements are in the order: $(CH_3)_3P \cdot BH_3 > (CH_3)_3N \cdot BH_3 > (CH_3)_3As \cdot BH_3 > (CH_3)_3Sb \cdot BH_3$ (*133*). Reaction between diborane and $(CH_3)_2SbH$, or better $(CH_3)_4Sb_2$ at 100°, yields $(CH_3)_2SbBH_2$ (bp, est. 70°) (*34*). This compound is monomeric. Failure of $(CH_3)_2SbBH_2$ to polymerize *via* antimony-boron bonds is easily understood in terms of the weak dative bonding power of antimony. However, the BH_2 group in $(CH_3)_2SbBH_2$ should then pass to a dimer form as in diborane, because the monomer would not be stabilized by Sb-B p_π-p_π bonding, as is monomeric $(CH_3)_2NBH_2$. Antimony is too large to form double bonds of the p_π-p_π variety. In view of this it has been suggested (*34*) that *monomeric* $(CH_3)_2SbBH_2$ exists through the ability of antimony to hybridize its filled $5p$-orbital with the appropriate $5d$ to give a pd hybrid long enough for effective overlap with the vacant p_π-orbital of a planar boron atom.

D. Reactions Leading to Formation of Boron-Oxygen Bonds

There are oxygen counterparts to many of the reactions which occur between boranes and nitrogen compounds, but with important differences because the donor power of oxygen is less than that of nitrogen, and the O—H bond has a greater protonic activity towards B—H than does the N—H bond. Thus borane forms a series of etherates analogous to the amine-boranes but with much lower stability. In the gas phase at ambient temperatures the borane-etherates (Table II) are completely dissociated, but their relative stabilities as determined from volatility measurements (*49*), phase studies (*154*), and from Raman spectra studies (*96*), are in the order $(CH_2)_4O \cdot BH_3 > (CH_3)_2O \cdot BH_3 > (C_2H_5)_2O \cdot BH_3$. Furthermore, some of the higher boranes react with ethers in a manner analogous to their reactions with tertiary amines. Tetraborane-*10* on treatment with either diethyl ether or tetrahydrofuran forms diborane, and the unstable solids $(C_2H_5)_2O \cdot B_3H_7$ and $(CH_2)_4O \cdot B_3H_7$, respectively (*73*).

It was learned long ago that boranes and methanol release hydrogen rapidly when mixed. Moreover, if the borane is in excess an unstable polymeric species CH_3OBH_2 appears which subsequently disproportionates to di- and trimethoxyboranes and diborane (*38*). Dimethoxyborane, $(CH_3O)_2BH$, the oxygen analog of $[(CH_3)_2N]_2BH$, is the first member of a series of monomeric[3] dialkoxyboranes. These are formed when diborane or some of the higher boranes are treated with aldehydes, ketones (*16*, *156*), or alkene oxides (*135*). The dialkoxyboranes disproportionate more readily than do the aminoboranes.

E. REACTIONS LEADING TO FORMATION OF BORON-SULFUR OR BORON-SELENIUM BONDS

The effect of diborane on several sulfur compounds and one selenium compound has been studied. No compounds from higher boranes and sulfur compounds have yet been reported apart from an adduct $(CH_3)_2S \cdot B_3H_7$ derived from B_4H_{10} (*73*, *74*). The complex $CH_3SH \cdot BH_3$ may be prepared from its components at −78°, but even at this temperature it begins to lose hydrogen to make $(CH_3SBH_2)_n$ polymer (*44*). In contrast to compounds like $(R_2PBH_2)_3$ and $[(CH_3)_2AsBH_2]_3$, polymer bonding in $(CH_3SBH_2)_n$ is weak. This is shown by the readiness with which $(CH_3SBH_2)_n$ yields a series of low polymers when heated over its melting range of 65–80°, and more especially by removal of CH_3SBH_2 groups, with formation of a complex $(CH_3)_3N \cdot BH_2SCH_3$, when $(CH_3SBH_2)_n$ is treated with trimethylamine. The adduct $(CH_3)_3N \cdot BH_2SCH_3$ reacts with a stream of diborane at elevated temperatures to form $(CH_3)_3N \cdot BH_3$ and the interesting derivative $CH_3SB_2H_5$. The latter very probably has a sulfur-bridge structure analogous to the nitrogen-bridged aminodiboranes, but it is much less stable than these compounds, easily reverting to diborane and $(CH_3SBH_2)_x$.

With dimethyl sulfide and dimethyl selenide, diborane forms well-defined BH_3 complexes (Table II). The compound $(CH_3)_2S \cdot BH_3$ is unusual in being more stable than either $(CH_3)_2S \cdot BF_3$ or $(CH_3)_2O \cdot BH_3$. Similarly $(CH_2)_4S \cdot BH_3$ is more stable than $(CH_2)_4S \cdot BF_3$ or $(CH_2)_4O \cdot BH_3$, and $(C_2H_5)_2S \cdot BH_3$ is more stable than $(C_2H_5)_2S \cdot BF_3$ or $(C_2H_5)_2O \cdot BH_3$ (*49, 58*). In forming more stable complexes with oxygen donors than with sulfur donors, boron trifluoride parallels the behavior of trimethylaluminum (*50*) and trimethylgallium (*48*). By exhibiting the reverse behavior, borane differs from most of those Group III acceptor molecules which have been studied. Furthermore, on the basis of electronegativity effects alone it would be expected that boron trifluoride would always form more stable complexes than borane. However, there is considerable evidence suggesting that the acceptor power of boron trifluoride is reduced by F—B dative π-bonding. Thus heats of formation of the trimethylamine adducts of boron trifluoride and borane, and of the pyridine adducts of these two acids are very similar (*58*). Nevertheless, with heavier donor atoms (P, As, Sb, S, and Se) borane forms much stabler complexes than does boron trifluoride, even though it is necessary to supply considerable energy to diborane to break its bridge bonds to supply borane groups. These observations have been interpreted in terms of there being something unusual about the borane group. Perhaps the atomic orbitals of the three hydrogen atoms of borane can combine, thereby forming a p_π-like orbital which can then overlap with an empty orbital of a ligand. There would thus be a π-bond strengthening the σ-bond in certain borane complexes, but not in those involving oxygen or nitrogen since these elements possess no low-lying vacant orbitals (*58*). The effect with BH_3 would be something like the hyperconjugation of organic chemistry except that with borane the effect would be greater due to the charge separation in the dative σ-bond. Some support for this idea comes from a study of the infrared spectrum of $(CH_3)_2S \cdot BH_3$ (*94*). The boron-hydrogen stretching frequencies in $(CH_3)_2S \cdot BH_3$ are higher than the corresponding frequencies in the borane-etherates, indicating greater charge transfer to boron in the latter, yet these are much weaker complexes than their sulfur analogs. However, supplementary π-bonding is in the reverse direction to the donor σ-bond, so the total effect in dimethylsulfide-borane could be less negative charge on boron resulting in a higher B—H stretching frequency.

F. Reactions Leading to Formation of Boron-Carbon Bonds

A number of reactions of the boranes lead to synthesis of boron-carbon bonds. With boron alkyls the boron hydrides undergo important alkylation reactions, but only in the case of diborane have these reactions been described in detail. When diborane is mixed with trimethylborane at room temperature, a mixture of methyldiboranes is obtained (*116*). These methyldiboranes readily exchange methyl groups with each other, and the interconversions have recently been studied kinetically using gas partition fractometry (*138*). Unlike its isomer 1,1-dimethyldiborane, the compound 1,2-dimethyldiborane is hardly present at all in an equilibrium mixture of methyldiboranes. It may be prepared by removal of a borane group from $CH_3B_2H_5$ with tetrahydrofuran (*30*),

$$CH_3B_2H_5 + (CH_2)_4O \rightarrow (CH_2)_4O \cdot BH_3 + \frac{1}{2}\, CH_3HB(H_2)BHCH_3.$$

1,2-Dimethyldiborane has been used to prepare a number of compounds wherein boron is bonded to one methyl group; for example, $(CH_3)_2NBHCH_3$ (*30*) and $(CH_3O)_2BCH_3$ (*25*).

Besides the methyl compounds a number of other alkyldiboranes have been prepared from diborane and trialkylboranes (*111*, *128*). The alkylated diboranes can also be obtained by treating at elevated temperatures $NaBH_4$, $LiBH_4$, or $LiAlH_4$ with R_3B, and either a hydrogen halide or a boron trihalide (*83b*).

Even when trimethylborane is taken in great excess for reaction with diborane, only four hydrogen atoms of the hydride are replaced by methyl groups. Tetramethyldiborane is fairly easily removed by fractional condensation from the reaction mixture. Since it behaves chemically as a source of $(CH_3)_2BH$ fragments, it has been used to develop a considerable chemistry of the $(CH_3)_2B$-group, for example,

$$CH_3SH + \frac{1}{2}[(CH_3)_2BH]_2 \rightarrow CH_3SH \cdot BH(CH_3)_2 \rightarrow CH_3SB(CH_3)_2 + H_2, \qquad (\mathit{44})$$

$$(CH_3)_2NH + \frac{1}{2}[(CH_3)_2BH]_2 \rightarrow (CH_3)_2NH \cdot BH(CH_3)_2 \rightarrow (CH_3)_2NB(CH_3)_2 + H_2, \qquad (\mathit{29})$$

With sodium in liquid ammonia the two halves of a molecule of tetramethyldiborane behave differently. One half forms $H_3N \cdot BH(CH_3)_2$, which is converted to $(CH_3)_2BNH_2$ and H_2, and the other half forms a salt $Na_2HB(CH_3)_2$ (*32*). The latter when treated with trimethylborane in liquid ammonia forms $Na_2HB_2(CH_3)_5$ which very likely contains a boron-boron bond. When pure, both $Na_2HB(CH_3)_2$ and $Na_2HB_2(CH_3)_5$ are stable in *vacuo* to about 100°. A calcium compound $CaHB(CH_3)_2 \cdot NH_3$ has also been prepared (*46*), but in contrast to its sodium analog it does not act as a Lewis base towards trimethylborane.

Few boron-carbon bonded derivatives of the higher boranes have been reported, but well-authenticated alkyl- and benzyl-decaboranes have been prepared from the remarkable "Decaborane" Grignard (*54*, *126*).

$$B_{10}H_{14} + CH_3MgI \xrightarrow{\text{ether}} B_{10}H_{13}MgI + CH_4$$

$$B_{10}H_{13}MgI + 2C_6H_5CH_2Cl \longrightarrow C_6H_5CH_2B_{10}H_{13} + MgCl_2 + C_6H_5CH_2I.$$

Best yields of alkyl-substituted decaboranes are obtained from reactions between the decaborane Grignard and alkyl fluorides rather than from decaborane Grignard and other alkyl halides.

The compound borane-carbonyl occupies a special position in any discussion of molecules derived from boron hydrides with boron-carbon bonds. Carbon monoxide reacts with diborane (20 atm/room temperature) to give an adduct of the borane group which does not rearrange or lose hydrogen (*39*). The adduct $OC \cdot BH_3$ does, however, dissociate into carbon monoxide and diborane at ordinary temperatures. No carbonyls of other Group III acceptor molecules have been prepared so far (*133*), and it has been suggested (*27*, *58*) that borane-carbonyl owes its existence to the ability of the hydrogen atoms of borane to transfer electrons to a vacant p_π-orbital in carbon monoxide.

The behavior of carbon monoxide toward borane would, therefore, be similar to its behavior towards metals in the metal carbonyls in which multiple bonding between the metal and carbon monoxide groups has long been postulated. The carbon monoxide groups of metal carbonyls may sometimes be replaced by phosphorus trifluoride groups. It has been suggested (*47*) that this is possible because phosphorus trifluoride functions as a ligand like carbon monoxide, that is, PF_3 can donate electrons in a dative σ-bond, as well as accept them in a π-bond, since phosphorus has vacant $3d$-orbitals. It is therefore, interesting that the phosphorus trifluoride complex of borane has been prepared (*85*) (see above). Its existence could be due to phosphorus-boron multiple bonding,[9] although it should be recognized that there is no general agreement on this idea. Nevertheless, the concept of the H_3B group being able to release electron density to a ligand with vacant orbitals as well as to accept it in a classical σ-dative bond accords well with many experimental facts (*58*).

Diborane is not unique among the boron hydrides in its ability to form a carbonyl. High pressure reaction of either pentaborane-*11* or tetraborane-*10* with carbon monoxide forms a substance which behaves like borane-carbonyl in its manner of decomposition. The formula of this polyborane-carbonyl has recently been established as $OC \cdot B_4H_8$ (mp, $-114.5°$; bp, $59.6°$) (*41a*). It reacts with trimethylamine without release of carbon monoxide.

A different approach to the synthesis of boron-carbon bonds from the boranes involves addition of B—H bonds to carbon-carbon double bonds.

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[9] Boron trifluoride does not form a PF_3 adduct. However, even though PF_3 is a very weak electron pair donor, by using a strong enough acceptor atom (boron is rather weak in this respect compared with aluminum or gallium) it might well be possible to make a PF_3 adduct of a Group III acceptor molecule in which the dative bonding could be described in terms of a classical σ–bond.

The reaction

$$6CH_2{:}CH_2 + B_2H_6 \rightarrow 2(C_2H_5)_3B$$

proceeds slowly in the gas phase at ordinary temperatures, but more rapidly at 80° (*76*).

Recently it has been found that the speed of addition of diborane to olefins is remarkably increased if an ether is present (*21*). In spite of its great speed this hydroboration reaction in ether is fairly selective. Thus treatment of an equimolar mixture of 1- and 2-hexene with a deficiency of diborane, followed by refluxing, yielded tri-*n*-hexylborane. Under the influence of heat the organoborane from 2-hexene isomerized into tri-*n*-hexylborane (*22*). Similarly a mixture of 2-, 3-, 4-, and 5-decenes treated with diborane in ether, heated and then subsequently oxidized gave an 80% yield of 1-decanol. Diborane may thus be used to transform olefins into alcohols.

A logical extension of the ether-catalyzed diborane-olefin reaction was the discovery that amineboranes, for example, $(CH_3)_3N \cdot BH_3$ or $C_5H_5N \cdot BH_3$, and olefins react to yield triorganoboranes (*1a, 66, 81, 118*).

Reactions between diborane and molecules containing carbon-carbon p_π-p_π bonds do not always involve simple addition of B—H to the double bond. Thus the principal volatile products of the gas-phase diborane-vinylsilane reaction are silane and hydrogen. In the presence of an ether, however, the silyl group is not cleaved from vinylsilane by borane and addition of B—H to the carbon-carbon bond does take place. Similarly in Pyrex bulbs at 80° the volatile products of the reaction between diborane and perfluoropropene are CF_4 and SiF_4, the latter formed presumably by hydrogen fluoride attack on the reaction vessel (*129*). How varied the effect of diborane on an organic molecule can be is illustrated by the action of the hydride on fluoroethylenes such as vinyl fluoride. See Fig. 1. In the absence of ether, all fluoroethylenes with diborane give the same mixture of products (*4*). The main reaction products are boron trifluoride, ethyldifluoroborane, diethylfluoroborane, and triethylborane. Composition of the mixture, however, depends markedly on the fluoroethylene taken for reaction. With tetrafluoroethylene distribution of boron in the volatile products is in the order: $BF_3 > C_2H_5BF_2 \gg (C_2H_5)_2BF > (C_2H_5)_3B$, while with vinyl fluoride it is: $C_2H_5BF_2 > (C_2H_5)_2BF \gg BF_3 > (C_2H_5)_3B$. The products may be accounted for by the reaction scheme outlined (Fig. 1) (*4*). In the presence of ether, however, preliminary results indicate that borane adds to the double bond of vinyl fluoride to some extent without rupture of the carbon-fluorine bond (*129*). In this manner organoboranes with fluorine atoms in the side chain may be obtained in small quantity. In the absence of ether, in a manner similar to the reaction between diborane and vinyl fluoride, treatment of vinyl chloride with diborane yields ethyldichloroborane, diethylchloroborane, triethylborane, and boron trichloride (*129*). In this reaction, however, significant quantities of chloroethylboranes are also formed, demonstrating that addition of borane to the double bond of the vinyl halide is almost as important a process as reduction of the vinyl halide to ethylene.

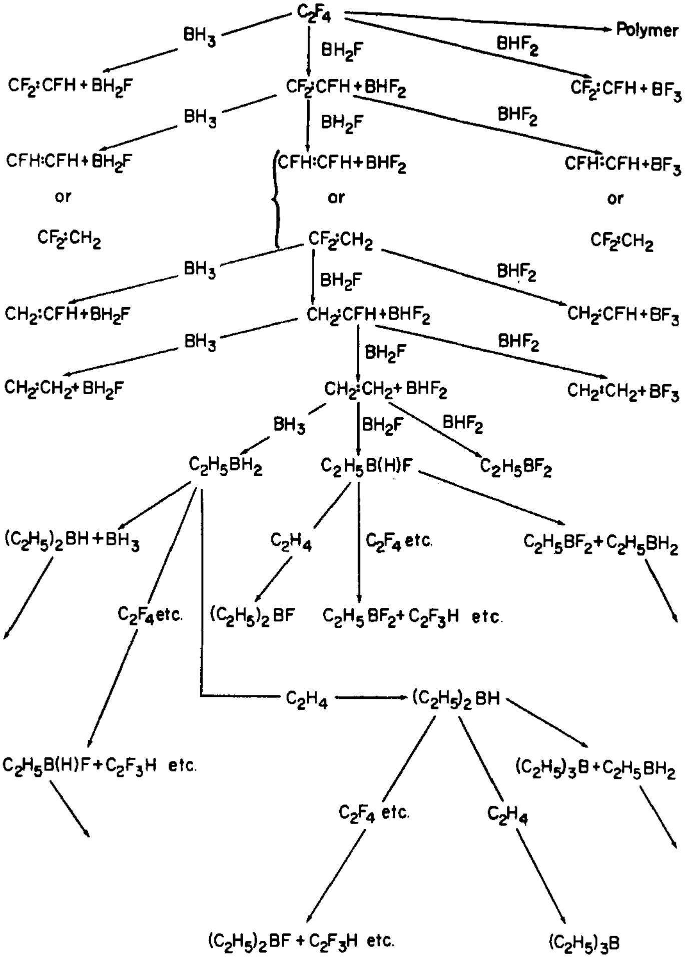

FIG. 1. The effect of diborane on fluoroethylenes.

When diborane is led into vinyl chloride in ethereal solvents like diglyme, tetrahydrofuran, and diethyl ether, thermally unstable mixtures are obtained which defy separation (*67*). In an attempt to simplify this behavior, vinyl chloride in dimethyl ether was treated with diborane at

−80°. Again, however, in working up the products exothermic decomposition often occurred, but it was possible to isolate in low yield β-chloroethylboron dichloride as its crystalline dimethyl etherate. In a similar manner, diborane and allyl chloride in diethyl ether afford a mixture of tri-γ-(chloropropyl)-borane and di-γ-(chloropropyl)-boron chloride. Hydrolysis of these chloropropyl boranes yields cyclopropane.

It is probable that a whole new area of boron chemistry will result from compounds obtained from reactions between the higher boranes and compounds containing carbon-carbon double bonds. In this respect discovery of the new compound dimethylenetetraborane, $C_2H_4B_4H_8$, is particularly intriguing (*64*). This compound, which may be formed in 70% yield from tetraborane and ethylene, appears to have a cyclic bridged structure in which one hydrogen atom of each of the two BH_2 groups in the tetraborane structure has been lost, the two boron atoms then being bonded to each other by a $—CH_2CH_2—$ group.

G. REACTIONS LEADING TO FORMATION OF BORON-HALOGEN BONDS

This section of this article would not be complete without some mention of reactions of the boranes and their derivatives which lead to boron-halogen bond synthesis. It was noted above that reactions between diborane and halogen-substituted ethylenes led to boron-halogen as well as boron-carbon bond synthesis. In addition to these reactions, and preceding them chronologically, it was observed that several of the more stable boranes (B_2H_6, B_5H_9, $B_{10}H_{14}$) under carefully controlled conditions undergo substitution reactions with halogens, hydrogen halides, or boron halides. Usually only one or two of the hydrogen atoms of the borane can be replaced by halogen without breakdown of the hydride structure. Compounds prepared directly from the boranes and having both boron-hydrogen and boron-halogen bonds include B_2H_5Br, B_2H_5Cl, B_5H_8Cl, B_5H_8Br, B_5H_8I, $B_{10}H_{13}I$ (two isomers), $B_{10}H_{13}Br$, and $B_{10}H_{12}I_2$ (two isomers). The structures of several of these compounds have been reviewed by Lipscomb (*83*).

The compound B_2H_5Cl can only be isolated with difficulty since it is transformed into BCl_3 and B_2H_6 rapidly at room temperature, disproportionating much more readily than does B_2H_5Br. Indeed, mixtures of boron trichloride and diborane at ambient temperatures exhibit pressures which are additive for the two components. In the presence of ethers, however, diborane and boron trichloride react readily at room temperature to form chloroborane etherates (*24*);

$$B_2H_6 + BCl_3 + 3R_2O \rightarrow 3R_2O \cdot BH_2Cl,$$
$$B_2H_6 + 4BCl_3 + 6R_2O \rightarrow 6R_2O \cdot BHCl_2.$$

These chloroborane etherates can also be prepared from alkali metal borohydrides (Section III).

For the preparation of unusual boron compounds the hydrogen atoms of certain derivatives of borane can also be replaced by halogen; for example,

$$[(CH_3)_2PBH_2]_3 + \underset{\text{anhydrous}}{6HF} \longrightarrow [(CH_3)_2PBF_2]_3 + 6H_2, \qquad (140)$$

$$[(CH_3)_2PBH_2]_3 + 6CH_3X \xrightarrow{AlX_3} \underset{(X = Cl, Br, I)}{[(CH_3)_2PBX_2]_3 + 6CH_4,} \qquad (140)$$

$$(CH_3)_3N \cdot BH_3 + \underset{\text{anhydrous}}{HCl} \longrightarrow (CH_3)_3N \cdot BH_2Cl + H_2. \qquad (25)$$

III. Recent Advances in the Chemistry of the Borohydrides

Preparation of the first borohydrides, those of aluminum, beryllium, and lithium, by Schlesinger, H. C. Brown, Burg, and Sanderson (*40, 106, 114, 115*), suggested the existence of similar compounds of other elements. This field was rapidly extended by studies related to the search for solid sources of hydrogen gas, volatile uranium compounds, and new methods for preparing diborane (*107*).

Further stimulus came on the discovery that the borohydrides were very useful reducing agents in inorganic and organic chemistry. Borohydrides of some 35 metals have now been reported in the literature, including those of elements of Groups I, II, and III, those of several subgroup elements (for example, Zn, Cu, Ti, Cr, Mn, etc.), those of several lanthanide elements, and those of a few of the transuranic elements. A still more recent development has been a report of triple hydrides (for example, $NaAl(BH_4)_4$, $Ca[Al(BH_4)_4]_2$) by Wiberg and co-workers (*147*).

Borohydrides vary greatly in volatility, and in such properties as thermal stability, ease of oxidation or hydrolysis. Decreasing thermal stability and ease of oxidation correlate roughly with increasing electronegativity of the metal. Thus sodium borohydride is stable to 300° in dry air, and to 400° in *vacuo*, whereas titanium(III) borohydride decomposes completely within a few days at ordinary temperatures. Some borohydrides, such as those of copper and silver, have been observed only at low temperatures. Potassium and sodium borohydrides can be crystallized from cold water, whereas aluminum borohydride is hydrolyzed explosively. Sodium borohydride, having a face-centered cubic structure (*127*), is essentially ionic, but volatile borohydrides like $Al(BH_4)_3$, $(CH_3)_2GaBH_4$, and $U(BH_4)_4$ represent fairly nonpolar situations, with varying degrees of covalent bonding of metal ion to BH_4^- groups *via* three center bonds like those in diborane.

Sodium borohydride, now commercially available, may be prepared without recourse to diborane by the reaction *(108)*:

$$4\text{NaH} + \text{B(OCH}_3)_3 \xrightarrow{225\text{–}275^\circ} \text{NaBH}_4 + 3\text{NaOCH}_3.$$

Although alternative synthetic routes are available for some of the borohydrides, most can be prepared from sodium or lithium borohydrides by metathesis; for example,

$$\text{FeCl}_3 + 3\text{LiBH}_4 \xrightarrow[\text{ether}]{-45^\circ} 3\text{LiCl} + \frac{1}{2}\text{H}_2 + \frac{1}{2}\text{B}_2\text{H}_6 + \underset{\substack{\text{decomposes}\\ \text{at } 0^\circ}}{\text{Fe(BH}_4)_2}, \qquad (103)$$

$$\text{AlCl}_3 + 3\text{NaBH}_4 \xrightarrow{\text{heat}} 3\text{NaCl} + \underset{\text{bp } 44.5^\circ}{\text{Al(BH}_4)_3}, \qquad (109)$$

$$\text{LiCl} + \text{NaBH}_4 \longrightarrow \text{NaCl} + \text{LiBH}_4, \qquad (109)$$

$$\text{CH}_3\text{OCs} + \text{NaBH}_4 \xrightarrow{\text{CH}_3\text{OH}} \text{CH}_3\text{ONa} + \text{CsBH}_4, \qquad (3)$$

$$[\text{Cr(NH}_3)_6]\text{F}_3 + 3\text{NaBH}_4 \xrightarrow[-45^\circ]{\text{liq. NH}_3} 3\text{NaF} + [\text{Cr(NH}_3)_6](\text{BH}_4)_3 \cdot \frac{1}{2}\text{NH}_3. \qquad (87)$$

Under suitable conditions boron trifluoride will liberate diborane from lithium or sodium borohydrides according to the equation *(18)*:

$$3\text{MBH}_4 + 4\text{BF}_3 \rightarrow 3\text{MBF}_4 + 2\text{B}_2\text{H}_6.$$

Although several other methods for preparing the simplest borane are known *(132)*, this method represents a convenient laboratory route to the hydride. However, when sodium borohydride is used, the above equation does not completely represent the course of reaction unless sodium borohydride is added in increments to boron trifluoride, both reagents being dissolved in diglyme.[10] If a deficiency of boron trifluoride is added to sodium borohydride dissolved in diglyme, the reaction,

$$\text{NaBH}_4 + \frac{1}{2}\text{B}_2\text{H}_6 \xrightarrow{\text{diglyme}} \text{NaBH}_4 \cdot \text{BH}_3$$

occurs *(23)*, yielding the interesting new substance NaB_2H_7. Only on addition of excess of boron trifluoride are considerable amounts of diborane liberated. Similarly if boron trichloride is used to form diborane from sodium borohydride, only stoichiometric quantities of reagents ($\text{BCl}_3 : \text{NaBH}_4$, 1:3) give quantitative yields. As in the analogous boron trifluoride reaction a deficiency of the Lewis acid gives low yields of diborane. Furthermore,

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[10] Sodium borohydride is insoluble in the ordinary ethers but is soluble in diglyme, the dimethyl ether of diethylene glycol.

unlike the boron trifluoride situation, use of an excess of boron trichloride also decreases the yield. This is because ether solutions of boron trichloride absorb diborane to form a new class of compound, the mono- and dichloroborane etherates (*24*) (See Section II,G). The boron trichloride-sodium borohydride system can be represented by the equations,

$$7NaBH_4 + BCl_3 \rightarrow 3NaCl + NaB_2H_7,$$
$$3NaBH_4 + BCl_3 \rightarrow 3NaCl + 2B_2H_6,$$
$$NaBH_4 + BCl_3 + R_2O \rightarrow NaCl + 2R_2O \cdot BH_2Cl.$$

Sodium borohydride is useful in the preparation of hydrides of several elements, for example,

$$Sn^{++} \xrightarrow[H^+]{NaBH_4} SnH_4, \qquad (102)$$

$$GeO_2 \xrightarrow[H^+]{NaBH_4} GeH_4. \qquad (153)$$

Lithium borohydride has also found some use in this respect, for example, (*152*)

$$C_6H_5MCl_2 + 2LiBH_4 \rightarrow C_6H_5MH_2 + B_2H_6 + 2LiCl$$
$$(M = P, As, Sb)$$

In aqueous solution many metal ions are reduced by sodium borohydride to borides [for example, Ni(II) and Co(II)], to the metal [for example, Ag(I)], or to a lower oxidation state [for example, Ce(IV) converted to Ce(III)]. Some of these reactions have found analytical application; for example, analysis of iron, wherein $NaBH_4$ replaces $SnCl_2$ or the Jones Reductor.

The borohydrides have found their greatest use as reducing agents in organic chemistry (*56*). Reduction products are obtained in nearly quantitative yield and the reactions are highly selective. Reducing power of the borohydride group depends on the nature of the associated cation, on the solvent, and on the presence or absence of other substances (*19*). Thus sodium borohydride does not normally reduce olefinic double bonds, but in diglyme solution in the presence of aluminum chloride reduction readily takes place, thereby providing a route to triorganoboranes, or even alcohols by subsequent oxidation of the borane, followed by hydrolysis of the boron ester (*20*). Aluminum borohydride may be an intermediate in this reaction, but if so it is not present in the sodium borohydride-aluminum chloride reagent in more than trace amounts. Table IV illustrates the selectivity of sodium borohydride and related substances as reducing agents in organic chemistry. In the construction of Table IV no attempt has been made to take solvent effects into account. Choice of solvent sometimes determines whether reduction takes place or not. Suitable solvents for sodium borohydride are diglyme, isopropyl alcohol, or even water or methanol. Lithium borohydride and lithium aluminum hydride may be used in a variety of ethers, but not in water or alcohols since they react vigorously with these substances.

Finally mention should be made of the existence of a variety of substituted borohydrides, as well as of the existence of aluminohydrides. Many of these substances, especially lithium aluminum hydride, have, like the parent borohydrides, revolutionized the preparative techniques of organic and inorganic chemistry. Examples of substituted borohydrides include trialkoxyborohydrides, $NaBH(OR)_3$ (*14, 15*), sodium triphenylborohydride, $NaBH(C_6H_5)_3$ (*155*), lithium phenylborohydride, $LiB(C_6H_5)H_3$ (*150*), and sodium triformatoborohydride, $NaBH(O_2CH)_3$ (*141, 142*).

TABLE IV

SODIUM BOROHYDRIDE AND RELATED COMPOUNDS AS SELECTIVE REDUCING AGENTS IN ORGANIC CHEMISTRY

at 25–100°

++ Reacts rapidly, + Reacts at a moderate rate, − Reacts slowly or negligibly.

	$NaBH_4$	$LiBH_4$	$NaBH_4$ + $AlCl_3$	$NaBH_4$ + LiBr	B_2H_6	$LiAlH_4$
RCHO	++	++	++	++	++	++
RR'CO	++	++	++	++	++	++
RCOCl	++	++	++	++	−	++
RCOOR'	−	+	++	+	+	++
RCOOH	−	+	++	−	++	++
RCOOM	−	−	−	−	−	++
RCH_2Cl	−	−	++	−	−	−
RCN	−	−	++	−	++	++
RNO_2	−	−	−	−	−	+
$RCH{=}CH_2$	−	−	++	−	++	−

IV. Conclusion

This review, concerned with reactivity of the boranes with no attempt to make the references exhaustive, has demonstrated the current and intense activity in this area of chemistry. The reader may already have recognized that nearly 60% of the references quoted refer to work published in this field during the last five years. With the application of new methods of preparation and separation, it is evident that boron compounds will be described in increasing numbers. Meanwhile, it is hoped that the subject matter reviewed here will be of help to research workers and teachers alike.

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