THE REACTION CHEMISTRY OF DIBORANE

L. H. Long

Department of Chemistry, University of Exeter, Exeter, England

I. Introduction

The preparative chemistry of diborane, together with its physical and molecular properties, have been reviewed recently (*1*), as have its interconversion reactions to other boranes (*2*). Because of the high reactivity of diborane, the types of reaction which it undergoes are unusually numerous and varied, but during the last decade there has been a surprising lack of reviews on its general reaction chemistry. The most useful compilation of information covering the published data to 1962 or early 1963 is to be found in a chapter on the boron hydrides by Adams (*3*). Earlier accounts of certain aspects of diborane chemistry are due to

Mikhailov (*4*) and Schenker (*5*). Since subsequent developments have been numerous, a reappraisal of the state of knowledge is long overdue. The present chapter attempts to cover in sufficient detail all the main types of reaction known, without going to the length of being fully comprehensive.

Diborane is a mildly endothermic compound that is only on the verge of stability at room temperature, since it slowly decomposes during prolonged storage. This circumstance and the fact that diborane is electron deficient have very important chemical consequences, one of which is that the compound is associated with numerous reactions that have unusually low activation energies. This state of affairs, in turn, confers upon diborane a truly rare kind of chemical versatility that enables it to react readily with the majority of substances. Indeed, diborane must be numbered among the most reactive compounds known, and certainly one of the most chemically versatile. Most reactions in which it participates occur readily at room temperature, and often well below; that is to say, at reaction temperatures vastly lower than those usually required by the paraffins, for example. For the most part the reactions of diborane are not violent, and can be readily controlled. One result of the lower temperatures required is that the reactions have a greater tendency to be pure and display a minimum of side reactions.

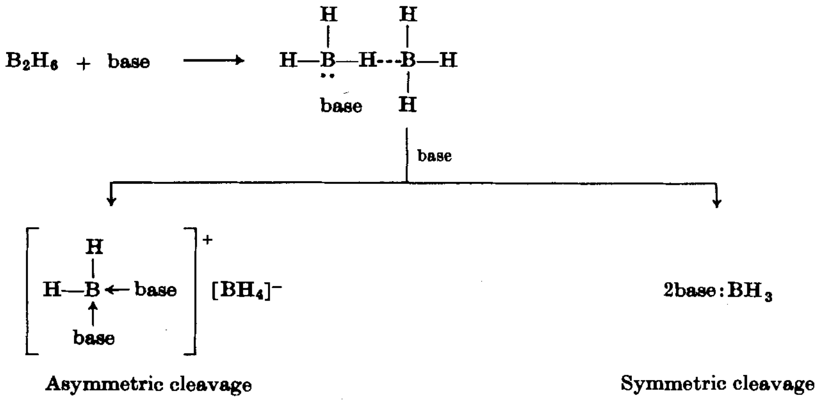
Another factor which has a profound influence on the chemistry of diborane, and which indeed dominates the chemistry of boron in general, is the exceptionally high affinity that this element displays for fluorine, oxygen, and, to a lesser extent, nitrogen. The boron atoms will therefore often shed attached hydrogen atoms or organic groups if, for instance, they can be replaced by oxygen in the form of, e.g., a hydroxy or alkoxy group. This is a factor which frequently governs the direction of a reaction in a predictable manner, and results in such changes as alkyl-transfer reactions, for example.

Because of the complexity of the situation, the reactions of diborane are somewhat difficult to classify conveniently. True, except for a relatively few substitution reactions they can be divided into three main types, namely, reactions in which the B_2H_6 molecule undergoes (*a*) symmetric cleavage to $2BH_3$ (which may be followed by further cleavage of the BH_3 to $-BH_2$ plus $-H$), (*b*) asymmetric cleavage to BH_2^+ (coordinated) plus BH_4^-, and (*c*) complete disruption. Such a broad classification is of comparatively little practical use, however, and for the purpose of this review it is more practical to consider first, addition; second, substitution; and third other reactions; the last group being classified according to the second reactant.

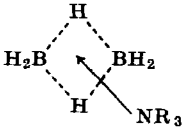
II. Addition Reactions

A. ADDITION REACTIONS WITH NEUTRAL MOLECULES

Because of its electron-deficient nature, diborane possesses strong acceptor properties and reacts with Lewis bases generally, including some rather weak donors such as carbon monoxide. It is a stronger acceptor than pentaborane(9) (*6*). In such acceptor reactions the diborane molecule may be preserved as an integral unit, but it is much more usual for it to be cleaved by a second molecule of the base. Such cleavage may be symmetric or, less commonly, asymmetric, according to whether the second base molecule attacks the second or first boron atom:



In the first stage the base attacks one of the boron atoms of the diborane molecule nucleophilically. The first product, the singly bridged adduct $B_2H_6\cdot$base, is however not always isolable, even under the most carefully controlled conditions, although there are good reasons for expecting it to occur as an unstable intermediate. Thus, the original claim (*7*) for the existence of the intermediates $B_2H_6\cdot NC_5H_5$ and $B_2H_6\cdot NEt_3$ soon found support from chemical evidence for a corresponding intermediate with ammonia, $B_2H_6\cdot NH_3$ (*8*), and confirmation for the existence of the latter, as well as of $B_2H_6\cdot NH_2Me$ and $B_2H_6\cdot NMe_3$, was obtained by tensiometric titration (*9*). Diborane is thus a Lewis acid per se. Even with bases so weak that the reaction shows only slight tendency to proceed further, such adducts may have transitory existence; as has apparently, for example, the species $B_2H_6\cdot OEt_2$, which is proposed by Gaines (*10*) to account for the very rapid proton exchange of B_2H_6 when dissolved in ether. The chemical and thermodynamic evidence for molecules of the type $B_2H_6 \cdot NR_3$, including the lack of boron isotope exchange between B_2H_6 and $H_3B \cdot NMe_3$, is in strong support of the single bridged structure given above (*9, 11*) rather than the alternative doubly bridged structure



once suggested (*12*).

The $B_2H_6 \cdot$base adducts may also be formed by the action of diborane on the borane adduct $BH_3 \cdot$base:

$$2BH_3 \cdot \text{base} + B_2H_6 \rightarrow 2B_2H_6 \cdot \text{base}$$

In the case of the trimethylamine adduct $Me_3N \cdot BH_3$, at least, it has been demonstrated by isotope studies that this reaction takes place without the rupture of the B–N bond (*11*).

Instances of symmetric cleavage are very common. In such reactions diborane reacts in effect as $2BH_3$, which latter species, with its vacant orbital, is unquestionably to be regarded as a Lewis acid. The cleavage of the diborane is normally symmetric when either (*a*) the base is sufficiently bulky to hinder the attack of a second molecule on the same boron atom, or (*b*) is more electropositive than hydrogen. If the base is strong, a relatively stable solid complex with only a low dissociation pressure is likely to result; e.g., trimethylamine gives $H_3B \cdot NMe_3$, which at 25°C has a vapor pressure of less than 1 Torr and a B–N bond dissociation energy equal to $\frac{1}{2}D(H_3B \cdots BH_3) + 18.7$ kcal mole^{-1} [as calculated from thermochemical data (*13, 14*)]. But the corresponding compound with the much weaker base dimethyl ether, i.e., $H_3B \cdot OMe_2$, already exerts a pressure of 18 Torr at $-78.5°C$ and is completely dissociated in the vapor phase (*15*). With donors such as NMe_3, the acceptor power decreases in the order $BBr_3 > BCl_3 > BF_3 > \frac{1}{2}B_2H_6$ (*16*), but it must be remembered that the apparent acceptor power of BH_3 is lower than the true acceptor power by an amount equal to one-half the bridge-bond dissociation energy of diborane.

The compounds $H_3B \cdot PMe_3$, $H_3B \cdot AsMe_3$, $H_3B \cdot SMe_2$, and $H_3B \cdot SeMe_2$ are much more stable than $H_3B \cdot OMe_2$. This has led to the observation (*17, 18*) that, although with BF_3 the strength of coordination falls in the sequences $NMe_3 > PMe_3 > AsMe_3$ and $OMe_2 > SMe_2 > SeMe_2$, with BH_3 the orders are different and follow the sequences $PMe_3 > NMe_3 > AsMe_3$ and $SMe_2 > SeMe_2 > OMe_2$, respectively. The explanation originally advanced, that hyperconjugation of the BH_3 group permitted

π bonding with vacant *d* orbitals of the donor atom in the case of atoms other than nitrogen and oxygen, may not be the correct one. Rather, evidence from other systems containing B–H bonds indicates that the relative strength of a Lewis base with respect to a reference acid depends principally on the strength of the acid, so that as the acid becomes increasingly stronger the σ bond formed between the donor and the boron atoms also increases in strength, eventually tending to reverse the sequence more usually observed (*19*) (see also Section VII, E). At all events, BH_3 is a much stronger Lewis acid than BF_3 (in which the acceptor powers of the boron atom may be assumed to be reduced by π bonding through back coordination from the fluorine atoms), and the order of adduct stability with phosphorus, sulfur, or selenium compounds is $\frac{1}{2}B_2H_6 > BF_3$. Even so, the extreme instability of the monoborane complexes with many ethers is striking, and arises essentially from the circumstance that on dissociation the complex is in equilibrium not with borane but with diborane, the energy recovered by the formation of the bridge bond being almost sufficient to dissociate the complex. Thus, the existence of $H_3B \cdot OEt_2$, for example, is barely demonstrable, and then only at low temperatures. However, diborane is much more soluble in tetrahydrofuran than in diethyl ether, and $H_3B \cdot OC_4H_8$ has a considerably more definite existence, the established order of adduct stability being $C_4H_8O > Me_2O > Et_2O$ (*20*). The species $H_3B \cdot OH_2$ is not isolable because of the rapid hydrolysis of diborane, but it has been postulated as an intermediate in the hydrolysis of diborane (*21*).

Since the useful reviews of Stone (*22*, *23*), a large number of additional borane adducts have been described. The complex between diborane and phosphine has been shown on the basis of its high-resolution NMR spectrum to be $H_3B \cdot PH_3$ (*24*), and not $B_2H_6 \cdot 2PH_3$ as originally thought. Surprisingly, the complex $H_3B \cdot PHF_2$ has been found to be much more stable (*25*) than $H_3B \cdot PH_3$ or $H_3B \cdot PF_3$, the suggested explanation being based on hydrogen–fluorine interaction within the PHF_2 moiety. It is not yet known whether this is reflected in an increased $B \leftarrow P$ bond order, which has been calculated (*26*) at 0.78 for $H_3B \cdot PH_3$ and 0.92 for $H_3B \cdot PF_3$. For the latter molecule the parameters are particularly well known, the $B \leftarrow P$ bond having a length of 1.836 Å and a dissociation energy at 25°C equal to $\frac{1}{2}D(H_3B \cdots BH_3) + 10.99$ kcal $mole^{-1}$ (*27*). Borane forms an adduct with the cyclic compound tetramethylenephosphine, $H_3B \cdot PH(CH_2)_4$ (*28*). Other simple complexes of borane include $H_3B \cdot PF_2(CF_3)$ (*29*), $H_3B \cdot PF(CF_3)_2$ (*29*), $H_3B \cdot PH_2Me$ (*30*), $H_3B \cdot PHR_2$ (*31*), $H_3B \cdot PMe_3$ (*32*), $H_3B \cdot PH_2Ph$ (*33*), $H_3B \cdot PHPh_2$ (*33*), $H_3B \cdot PPh_3$ (*34*), $H_3B \cdot P(OR)_3$ (*35*), $H_3B \cdot P(NH_2)_3$ (*36*), $H_3B \cdot P(NR_2)_3$ (*37*), $H_3B \cdot P(SiMe_3)_3$ (*38*), $H_3B \cdot PH_2(SiH_3)$ (*39*), $H_3B \cdot PH_2(GeH_3)$ (*40*),

$H_3B \cdot AsMe_3$ (*41*), $H_3B \cdot AsPh_3$ (*42*), $H_3B \cdot SMe_2$ (*43*), $H_3B \cdot S(CH_2)_4$ (*44*), and $H_3B \cdot S(NMe_2)_2$ (*45*). In the last compound it is believed that the sulfur atom is the donor. Subject to the restrictions mentioned above, borane can form simple complexes in which the nitrogen atom is the donor if the nitrogen base is sufficiently bulky, e.g., $H_3B \cdot NMe_3$ (*46*), $H_3B \cdot N_2R_2$ (*47*), $H_3B \cdot NC_5H_5$ (*48*), or $H_3B \cdot NC_5H_4R$ (*49*).

Of interest is the manner in which the frequencies of the B–H valency vibrations of the borane complexes shift with change in the nature of the base, and this phenomenon has been investigated for some complexes with substituted phosphines and amines (*50*). Constitutive changes in NMR spectra have been studied (*51*), as have also the changes in magnetic rotatory power and molecular refraction (*52–55*). The chromatographic behavior of many borane adducts has been investigated (*56, 57*).

Carbon monoxide and the electronically related organic isocyanides react with diborane. Of particular interest is borane carbonyl, $H_3B \cdot CO$, first discovered by Burg and Schlesinger (*46*) and since the object of much study. Its molecular parameters are accurately known (*58*). Since carbon monoxide is usually reckoned as a weak donor, it is of some surprise to find that the $B \leftarrow C$ bond length is 1.540 Å, virtually identical with the C–C distance in ethane. The reason for this is not known, although hyperconjugation associated with π bonding has been suggested. It is readily prepared from diborane and excess carbon monoxide under pressure at 90°–100°C (*46*). At room temperature equilibration is slow.

$$B_2H_6 + 2CO \rightleftharpoons 2H_3BCO$$

The product is readily isolable, but decomposes progressively unless it is stored at low temperatures. The carbon monoxide is completely displaced by trimethylamine (although there is evidence for the existence of an adduct $H_3BC(O)NMe_3$ isolable at low temperatures), but not by dimethylamine, methylamine, or ammonia, which react differently (*59*) (see later). With NMe_3 the reaction is exothermic, but proceeds with an activation energy of 8.60 ± 0.30 kcal mole^{-1} (*60*). Hydrolysis is less simple than once supposed and involves a temperature-dependent competition between two reactions (*61*). The proportion of dihydroxy-

$$H_3BCO + 3H_2O \rightarrow B(OH)_3 + 3H_2 + CO$$
$$H_3BCO + 2H_2O \rightarrow (HO)_2BCH_2OH + H_2$$

(hydroxymethyl)borane, which arises through reduction of the carbonyl group, increases as the temperature is reduced. The reaction of H_3BCO with oxygen under controlled conditions has received study (*62*).

It has been noted that the BH_3 group is isoelectronic with the oxygen atom, so that H_3BCO may be compared with CO_2. On this view it should give rise to salts of the boranocarbonate ion $H_3BCO_2^{2-}$ and the boranobicarbonate ion H_3BCOOH^-, analogous to the carbonates, and even to boranocarbonic acid $H_3BC(OH)_2$, as is, in fact, observed (*61, 63*). For example,

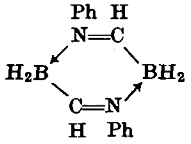
$$CaO + H_3BCO \xrightarrow{\text{trace } H_2O} Ca[H_3BCO_2]$$

$$NaOH + H_3BCO \longrightarrow Na[H_3BCOOH]$$

Similarly the compound formed with ammonia, $H_3BCO \cdot 2NH_3$ (*46*), might be likened to a carbamate, and the boranocarbamate structure $NH_4^+[H_3BCONH_2]^-$ has indeed received support from chemical, infrared, and X-ray diffraction studies, as have the structures of analogous compounds with mono- and dimethylamines (*59, 64*). Likewise the compound which $H_3B \cdot PH_3$ forms with ammonia, $B_2H_6 \cdot PH_3 \cdot NH_3$, is correctly formulated $NH_4^+[H_2P(BH_3)_2]^-$, analogous to ammonium hypophosphite $NH_4^+[H_2PO_2]^-$ (*65*). $Na[H_2P(BH_3)_2]$ and its deuterated analogs have also been studied (*66*). With P_4O_6, BH_3 can also act as an oxygen atom to give compounds (*67–69*) that bear a formal resemblance to P_4O_{10}, namely, $P_4O_6 \cdot BH_3$, $P_4O_6 \cdot 2BH_3$, $P_4O_6 \cdot 3BH_3$, and $P_4O_6 \cdot 4BH_3$, although the last two compounds have low stabilities (and at 1 atm the last is only known in solution in equilibrium with the other species) (*69*).

The compound $(ON)_3Co \cdot BH_3$ has recently been prepared from trinitrosylcobalt and diborane (*70*).

Many simple borane adducts undergo changes on heating other than reversible dissociation (*15*). There are two principal ways in which this may occur. One is polymerization, usually accompanied by the shifting of hydrogen from the boron to another atom. Thus, with phenyl isocyanide PhNC, the simple adduct (which is not isolated) apparently immediately dimerizes (*71*) to

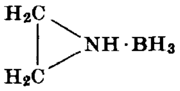


and with methyl cyanide the isolable adduct $MeCN \cdot BH_3$ trimerizes above 20°C to 1,3,5-triethylborazine $(MeCH_2NBH)_3$ (*72*). The other manner in which decomposition may occur is to split off hydrogen or some more complex molecule irreversibly, which presupposes that the donor atom has a hydrogen atom or some suitable group attached to it. Burg has discussed some cases for which the rates of hydrogen evolution have been observed to differ widely (*15*). We mention here that methylamine borane (which slowly liberates hydrogen at room temperature) rapidly decomposes on heating to form trimeric *N*-methylaminoborane (1,3,5-trimethylcycloborazane) and ultimately 1,3,5-trimethylborazine (*73*, *74*).

$$3H_3B\cdot NH_2Me \xrightarrow[-3H_2]{100°C} (H_2BNHMe)_3 \xrightarrow[-3H_2]{190°C} (HBNMe)_3$$

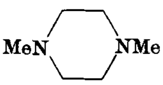
[The first stage occurs via identifiable intermediates (*73*)]. Similarly, the diphenylketimine adduct $Ph_2C{:}NH\cdot BH_3$ loses H_2 at 120°C to form $(Ph_2CHNBH)_3$ (*75*). On the other hand, $H_3B\cdot N(SiH_3)Me_2$ and $H_3B\cdot N(SiH_3)_2Me$ split off silane, SiH_4, at 0°C (*76*), while $H_3SiCN\cdot BH_3$ and $Me_3SiCN\cdot BH_3$ lose SiH_4 and $SiHMe_3$, respectively, on heating to give a solid of empirical formula BH_2CN (*77*); $H_3B\cdot P(SiMe_3)_3$ likewise eliminates $SiHMe_3$ on heating (*78*).

Other reactions of BH_3 adducts have been studied, and it is clear that the hydridic nature of the B–H bonds is considerably modified on coordination. Thus, although B_2H_6 is immediately hydrolyzed by water, $Me_3N\cdot BH_3$ is so slowly hydrolyzed, that it is possible to deuterate it by exchange over several hours with acidified D_2O (*79*). Whereas monohalogenated diboranes such as B_2H_5Cl are very labile and disproportionate rapidly at room temperature, the monohalogen derivatives of amine boranes, e.g., $Me_3N\cdot BH_2Cl$ and $Me_3N\cdot BH_2Br$, are preparable from the amine borane by a mild halogen-exchange reaction with the appropriate *N*-halogenosuccinimide and are stable solids with definite melting points (*80*). Monochloroborane complexes of phosphines are prepared similarly (*81*). [With $H_3P\cdot BH_3$, halogen substitution on the boron is also readily effected by HCl or HBr (*82*)]. Another way in which $Me_3N\cdot BH_3$ can react is in hydride ion abstraction reactions, as with iodine and amines (*83*) or with Ph_3CBF_4 in donor solvents (*84*) to give $[H_2B(base)_2]^+$ salts. Aziridine borane has been recently described and studied (*85*–*87*).

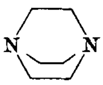


Symmetrical cleavage of diborane may also occur with bidentate and polydentate donors. Substituted diphosphines react differently, in that P_2Me_4 gives the bisborane adduct $P_2Me_4\cdot 2BH_3$ (*88*, *89*), whereas P_2F_4

gives no sign of the bis adduct, only $P_2F_4 \cdot BH_3$ (*90*). The phosphorus methylimide $P_4(NMe)_6$ forms adducts containing 1, 2, 3, or 4 borane groups $P_4(NMe)_6(BH_3)_n$, in which, as indicated by NMR studies, the boron atoms are linked to the phosphorus atoms (*91*), as is also the case with adducts such as $P_2(NMe_2)_4 \cdot 2BH_3$ (*92*). Likewise, in adducts of formula $MeSNR_2 \cdot BH_3$ the boron atom is in all probability linked to the sulfur atom, since rearrangement to $MeSBH_2 \cdot NHR_2$ readily occurs and, on heating, $MeSBHNR_2$ is formed with the loss of hydrogen (*93*). Bisdimethylaminomethane and -silane give the bisborane adducts $CH_2(NMe_2)_2 \cdot 2BH_3$ and $SiH_2(NMe_2)_2 \cdot 2BH_3$, in which the boron is linked to the nitrogen, but probably for steric reasons, $SiH(NMe_2)_3$ and $Si(NMe_2)_4$ give only the 1:2 and 1:1 borane adducts, respectively (*94*). On the other hand, with methylated polyamines such as pentamethyldiethylenetriamine, diborane adds quantitatively one BH_3 group per N atom (*95*). However, controlled conditions with polyamines can lead to adducts with less than the maximum proportion of borane, as with



and



which give both the 1:1 and 1:2 adducts with borane (*96*). Hydrazine also forms a 1:1 (*97*, *98*) and a 1:2 (*98*, *99*) adduct, as do also methylhydrazines (*88*, *99*, *100*). Whereas for a long time it was not known whether hydrazine behaved like ammonia to give dimeric adducts based on asymmetric cleavage (*vide infra*), the recent proof (*101*) that hydrazine borane $H_3B \cdot N_2H_4$ is isosteric with $C_2H_5NH_2$ establishes that it does not and that the cleavage of diborane by hydrazine is symmetric.

Another group of compounds which cleaves diborane symmetrically to give borane adducts are the ylides such as $Ph_3\overset{+}{P}-\overset{-}{C}H_2$ (*102*, *103*). The boron becomes linked to the carbon. Ylides containing arsenic instead of phosphorus also react (*104*), as do those containing sulfur (*105*), but in the latter case rearrangement occurs.

Asymmetric cleavage of diborane is effected by a number of Lewis bases, including ammonia, although it was a long time before this was understood. The solid of low volatility obtained with ammonia originally in 1923 by Stock and Kuss (*106*) was demonstrated by molecular weight determination in liquid ammonia not to be the monomeric species $H_3B \cdot NH_3$, but to be dimeric (*107*). After abortive attempts to explain the structure as ammonium salts of formulas $(NH_4)_2[B_2H_4]$ (*108*) and $NH_4[H_2N(BH_3)_2]$ (*15*), Parry and his collaborators at first reported (*109*) and then in a series of papers (*8*, *110–113*) amply demonstrated that the compound is, in fact, a tetrahydroborate of formula $[H_2B(NH_3)_2][BH_4]$. A second compound of formula $[HB(NH_3)_3][BH_4]_2$ can also be formed (*113*). However, it is further possible to prepare the monomeric compound $H_3N \cdot BH_3$ by indirect means from alkali metal tetrahydroborates (*109*, *111*) or tetrahydrofuran borane $C_4H_8O \cdot BH_3$ (*114*). More recently it has been prepared directly by passing B_2H_6 into a solution of ammonia in an ether, alcohol, or even water (*115*) (for $H_3N \cdot BH_3$ is hydrolytically stable toward cold water). By contrast, ammonia borane shows appreciable volatility and can be sublimed in a vacuum (*111*). In addition, it is soluble in ether and dioxane. in both of which it is monomeric (*109*), as is also the case in liquid ammonia (*111*). The structure is known (*116*, *117*), and has also been treated theoretically (*118*). Probably methylamine also forms both kinds of adducts, in that with diborane it gives an imperfectly characterized nonvolatile product (m.p. 5°–10°C) (*119*) showing an NMR spectrum (*120*) and X-ray diffraction pattern (*121*) consistent with the formulation $[H_2B(NH_2Me)_2][BH_4]$ (*120*), whereas with sodium borohydride a volatile solid (m.p. 56°C) identified as $H_3B \cdot NH_2Me$ results (*122*). But $[H_2B(NH_2Me)_2][BH_4]$, in any case, slowly rearranges to $H_3B \cdot NH_2Me$ (*121*), which may indicate that even in many cases where symmetric cleavage appears to be the mode of reaction the initial cleavage is, in fact, asymmetric, the product actually isolated depending on the relative stability of the species $[H_2B(\text{base})_2][BH_4]$ first formed. It would however be rash to assume that this is invariably the reaction path.

Dimethylamine also shares the power to cleave diborane asymmetrically (*120*) and also symmetrically to give the simple adduct $HMe_2N \cdot BH_3$. With the latter compound there is evidence that the coordinated BH_3 group can participate (as a proton acceptor) in hydrogen bonding with hydroxy compounds such as methanol or phenol (*123*). $HMe_2N \cdot BH_3$ also possesses a certain acidity in its amino hydrogen atom and will react to form salts of the dimethylamidotrihydroborate ion $[Me_2NBH_3]^-$ (*124*, *125*). $HMe_2P \cdot BH_3$ reacts similarly (*125*).

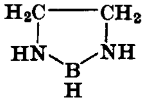
$$2HMe_2N \cdot BH_3 + 2Na \xrightarrow[-40^\circ C]{\text{liq. } NH_3} 2Na[Me_2NBH_3] + H_2$$

$$HMe_2N \cdot BH_3 + NaH \xrightarrow[45^\circ C]{\text{glyme}} Na[Me_2NBH_3] + H_2$$

$$HMe_2P \cdot BH_3 + NaH \xrightarrow{\text{glyme}} Na[Me_2PBH_3] + H_2$$

Trimethylamine apparently lacks the capacity to cleave diborane asymmetrically, and gives only the monomeric adduct by symmetric cleavage. This is not to say that the cation $[H_2B(NMe_3)_2]^+$ does not exist, for it can be prepared in other ways (*126, 127*), as can cations of the type $[H_2B(PR_3)_2]^+$, $[H_2B(AsR_3)_2]^+$, and $[H_2B(SR_2)_2]^+$ (*127*). With B_2H_6 in tetrahydrofuran LiHS reacts directly to form two compounds which give rise to the ions $[H_2B(SH)_2]^-$ and $[H_3BSH]^-$, respectively, showing that in this case asymmetric and symmetric cleavage processes of diborane occur simultaneously (*128*). Asymmetric cleavage is also effected by dimethyl sulfoxide to give $[H_2B(OSMe_2)_2]^+[BH_4]^-$ (*129*). In the presence of iodine, ether will cleave diborane asymmetrically to give the cation $[H_2B(OEt_2)_2]^+$ (*130*). Even on their own some ethers can apparently cause a slight measure of asymmetric cleavage, presumably to $[H_2B(OR_2)_2]^+$ and $[BH_4]^-$, since diborane dissolved in them causes them to conduct an electric current (*131*).

Bidentate donors may also effect asymmetric cleavage of diborane. At least, Goubeau and Schneider (*132*) have prepared both the borane and diborane adducts of ethylenediamine, $en \cdot BH_3$ and $en \cdot B_2H_6$, by using an indirect method of preparation. From their infrared spectra it was concluded that $en \cdot BH_3$ has the simple chain structure and $en \cdot B_2H_6$ an ionic structure with a cyclic cation $[H_2B(NH_2CH_2)_2]^+[BH_4]^-$. This, however, has been disputed by Kelly and Edwards (*133*), who found that, irrespective of whether the latter compound was prepared by the indirect or direct method, its ^{11}B NMR spectrum indicates the open-chain structure of a bisborane adduct, corresponding to symmetric cleavage of the diborane. The evidence is clearly conflicting. More recently, Russian workers (*134*) have claimed that even the monoborane adduct is cyclic and at 20°C loses hydrogen vigorously to give the cyclic compound



The position requires further study, for the monoborane adduct handled by Goubeau was apparently much more stable. Also the Russian workers found it impossible to prepare the compound $en \cdot B_2H_6$, even with excess diborane, whereas the other workers report no difficulty in preparing it and noted that it can be heated to 89°C before it begins to decompose (*135*).

B. Addition Reactions with Charged Species

It was discovered by Brown and co-workers (*7, 136*) that alkali metal tetrahydroborates dissolved in diglyme absorb diborane. The explanation given is that the latter reacts additively (with symmetric cleavage) with the BH_4^- ion:

$$2BH_4^- + B_2H_6 \rightarrow 2B_2H_7^-$$

It is possible to isolate the sodium salt NaB_2H_7 as a solvate from solutions in various polyethers, but attempts to remove the last molecule of solvent invariably lead to its decomposition (*137*). Attempts to demonstrate the existence of the potassium salt in solution failed (*138*, *139*). Solutions of sodium heptahydrodiborate in polyethers were found to be better conductors than those of $NaBH_4$ (*139*, *140*). In tetrahydrofuran, but not in diethyl ether, the conductivity of $LiBH_4$ increases with the introduction of B_2H_6 and reaches a maximum when the concentration of the latter has risen to a point corresponding with the formation of LiB_2H_7 in solution (*141*, *142*). Evaporation of the solvent gives only the starting materials. In solution, the ^{11}B NMR spectrum of the $B_2H_7^-$ ion shows the boron atoms to be equivalent (*10*, *143*), and the structure of the ion is doubtless to be written with a single hydrogen bridge. It exchanges rapidly with B_2H_6 and more slowly with excess BH_4^- ion (*10*). When associated with bulky tetraalkylammonium cations, the $B_2H_7^-$ anion appears to show a greater stability, as in the salts $[Bu_4N]^+[B_2H_7]^-$ (*144*) and $[Et_4N]^+[B_2H_7]^-$ (*145*), which have recently been prepared. Possible structures for the $B_2H_7^-$ ion have been calculated (*146*), but calorimetric studies have suggested that the lone pair of electrons usually thought necessary for hydrogen-bond formation may, in fact, be antibonding in character (*145*).

With the thiolotrihydroborate ion $HSBH_3^-$ diborane apparently gives a new unstable ion of formula $HS(BH_3)_2^-$ by simple addition of BH_3 (*147*).

$$HSBH_3^- + \tfrac{1}{2}B_2H_6 \xrightarrow{-78°C} HS(BH_3)_2^-$$

Diborane reacts similarly with salts containing the AlH_4^- ion to produce, first, salts of the $AlBH_7^-$ anion (*141*). This ion is presumably similar in structure to $B_2H_7^-$, and is said to rearrange to the more stable $[AlH_3(BH_4)]^-$ ion. Other ionic double hydrides react similarly with diborane to give triple hydrides (*148*). With the silyl anion SiH_3^- diborane apparently gives the adduct ion $[SiH_3 \cdot BH_3]^-$, which is unstable and decomposes into BH_4^-, SiH_4, and condensed species (*149*). Likewise, with GeH_3^- $[GeH_3 \cdot BH_3]^-$ is formed (*150*). Addition of BH_3 also occurs with the ions $RCOO^-$ (*151*), CNO^-, R_2NCS^-, $C(CN)_3^-$, and $N(CN)_2^-$ (*152*). The thiocyanate ion SCN^- reacts similarly (*125*), as apparently does the N_3^- ion in the first instance (at least, in the case of LiN_3) (*153*), although the product is unstable. The fluoride ion gives $[BH_3F]^-$ (*125*). The cyanide ion is exceptional in adding on two BH_3 groups to give $[BH_3CN \cdot BH_3]^-$ (*125*). However, the monoadduct $[BH_3CN]^-$, first isolated as a dioxanate of the lithium salt (*154*, *155*), is also obtainable, and this has been studied from the standpoint of hydrolysis (*156*, *157*), hydrogen exchange (*156*), reducing powers (*157–159*), and spectrum (*157*), as well as from the standpoint of the complexes it forms. Thus, with nickel the nitrogen atoms coordinate to the metal atom in the complex $en_2Ni(NCBH_3)_2$ (*160*), while with nitrogen donors such as trimethylamine the boron acts as an acceptor in the ultimate complex $Me_3N \cdot BH_2CN$, a negatively charged hydride ion having been displaced (*161*).

In its reactions with some ions, B_2H_6 provides further evidence of the relationship between BH_3 and the isoelectronic oxygen atom. Thus, it reacts with the anion of the salt $(NaNO)_x$ to give the boranonitrite $Na^+[NO(BH_3)]^-$ (*162*).

That B_2H_6 can even react with certain metal carbonyl anions to give compounds in which BH_3 acts as a ligand, has been noted by Parshall (*163*), who reports the manganese and rhenium anions $[H_3BMn(CO)_5]^-$, $[H_3BMn(CO)_4(PPh_3)]^-$, $[H_3BRe(CO)_5]^-$, and $[(H_3B)_2Re(CO)_5]^-$. There is evidence that the cobalt anion $[Co(CO)_4]^-$ forms a similar borane complex at low temperatures, but this is very unstable and was not isolated. Compounds formed with the carbonyls of metals in Group VII and of cobalt, rhodium, and iridium have been patented (*164*). For such transition metal species to be stable, the metal atom probably needs to have a high complement of electrons (as in these instances). In $[(H_3B)_2Re(CO)_5]^-$ the second BH_3 is not necessarily linked to the rhenium atom to give a 7-coordinated structure. It could be linked to the first BH_3 group via a single hydrogen bridge, in which case this is the first example known in which undissociated B_2H_6 acts as a ligand. Alternatively it might be linked in some surprising and unpredictable way, as is the case with $(H_3B)_2Mn_3H(CO)_{10}$ (*165*). A structural determination of the $[(H_3B)_2Re(CO)_5]^-$ ion is therefore an interesting prospect.

III. Substitution

A. SUBSTITUTION BY ORGANIC GROUPS

The simplest form of substitution undergone by diborane is the replacement of hydrogen by deuterium, but this has already been discussed elsewhere (*1*, *2*). With boranes that exchange BH_3 units, diborane and its derivatives will also exchange alkyl groups, presumably by the transference of BH_2R units; thus, this occurs with B_4H_{10} (*166, 167*) and B_5H_{11} (*166, 168*), but not with B_5H_9 or $B_{10}H_{14}$ (*168*). Only the terminal hydrogen atoms of B_2H_6 can be substituted by organic groups, so that no penta- or hexasubstituted derivatives are known. If attempts are made to prepare these, disproportionation with bridge rupture occurs and a trisubstituted borane is one of the products. Substitution of any or all of the terminal hydrogen atoms does not normally break the bridge, so that the report that $H_2BCH(CMe_3)CH_2CMe_3$ is a monomer (*169*) is an oddity. Trisubstituted boranes readily exchange their ligands with diborane, usually at room temperature, and the kinetics of the B_2H_6–

$$(6-n)B_2H_6 + 2nBR_3 \rightleftharpoons 6B_2H_{6-n}R_n \qquad (n = 1\text{–}4)$$

BMe_3 reaction have received study (*170*). Such equilibrium reactions provide a convenient way of preparing many organic derivatives, as was first observed for the methyl compounds (*171*). It follows, however, that disproportionation reactions such as

$$2B_2H_3R_3 \rightleftharpoons B_2H_4R_2 + B_2H_2R_4$$

will occur and lead to the establishment of redistribution equilibria involving all the possible species. For the methyldiboranes such equilibria are established within hours in the gas phase (*172*), but the activation energies are such that the pure compounds can be isolated by fractionation at low temperatures and can be stored at −78.5°C. For the disubstituted derivatives both 1,1- and 1,2-isomers are known (*173*); the latter are capable of existing in cis and trans forms (*174*). Equilibrium reactions involving various alkyldiboranes have received study (*170, 172, 175, 176*).

A number of other methods for preparing alkyldiboranes are available. Instead of reacting trialkylboranes with B_2H_6, they can be made to react with molecular hydrogen either by the application of temperature and high pressures (*177, 178*) or by the use of a silent discharge (*179*). When reacted with B_4H_{10}, trialkylboranes will also give diborane derivatives $B_2H_2R_4$ along with a B_2H_4 polymer (*180*). The interaction of olefins with diborane to give alkylated diboranes is an application of hydroboration, which is discussed more fully in Section IV, B. Thus, B_2H_6 and C_2H_4 will give B_2H_5Et, $B_2H_2Et_4$, etc. (*181, 182*). The same method will also produce mixed alkylated boranes, e.g., BMe_2Et from $B_2H_2Me_4$ and C_2H_4 (*183*). Brown and Klender have used the method to produce derivatives containing bulkier alkyl groups (*184*).

With organometallic compounds the transference of organic ligands to boron sometimes takes place, as, for example, with tetramethyllead. This

$$B_2H_6 + PbMe_4 \rightarrow B_2H_5Me + PbHMe_3$$

reaction occurs at room temperature in 1,2-dimethoxyethane and proceeds further (*185*). Vinyl groups can similarly be transferred from $Pb(C_2H_3)_4$ (*186*). Tetraalkyldiboranes are one of the products of interaction of diborane with alkoxydialkylboranes R_2BOR' (*187*). Likewise chlorodiphenylborane Ph_2BCl is converted to 1,2-diphenyldiborane by B_2H_6 in hexane (*188*). Other methods depend on reduction. Thus, alkyldiboranes are formed on the reduction of trialkylboroxines $(BRO)_3$ by $AlHR_2$ (*189*), of BEt_2Cl by NaH (*190*), and of BCl_3 by Al and H_2 in the presence of methyl iodide as a methylating agent (*191*).

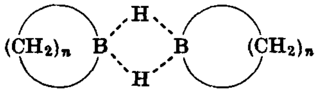
Alternatively alkali metal tetrahydroborates may be used as starting material. Thus, alkyldiboranes are produced from the reaction of trialkylboranes with $NaBH_4$ and BF_3 in tetrahydrofuran (*192*), but it is more convenient to dispense with the solvent and to heat the tetrahydroborate with BR_3 plus anhydrous HCl in an autoclave (*172, 193, 194*).

$$NaBH_4 + 3BR_3 + HCl \rightarrow 2B_2H_2R_4 + NaCl + RH$$
$$2LiBH_4 + 4BR_3 + 2HCl \rightarrow 3B_2H_2R_4 + 2LiCl + 2H_2$$

Anhydrous $AlCl_3$ improves the yield. Alternatively the BR_3 may be replaced by AlR_3 (*195, 196*).

$$6LiBH_4 + 4AlR_3 + 18HCl \rightarrow 3B_2H_2R_4 + 6LiCl + 4AlCl_3 + 18H_2$$

Alicyclic and aromatic derivatives of diborane have received little study, but preparations of the cyclohexyl (*178*), phenyl (*178, 197*), *p*-chlorophenyl (*198*), and naphthyl (*198*) compounds have been reported. An interesting development has been the preparation of cyclic alkyldiboranes, namely 1,1:2,2-bis(polymethylene)diboranes



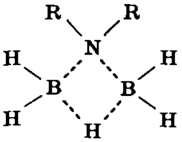
(where $n = 4, 5, \ldots$) and their derivatives (*199*). These are also known as bisboracycloalkanes. They are prepared by the reaction of the appropriate diolefin with diborane followed by thermal rearrangement, or by reacting, e.g., the B-substituted derivatives (*200*, *201*) of boracycloalkanes with diborane. The ring structures are associated with particularly stable bridge bonding between the boron atoms (*199*), and, unlike the tetraalkyldiboranes, the bis(polymethylene)diboranes are stable at room temperature toward hydrolysis, alcoholysis, and atmospheric oxidation (*202*). Compounds with 7-membered and larger rings are changed by thermal action into compounds with more stable 6-membered rings (*199*).

Trifluoromethyl-substituted diboranes have been reported (*203*).

Physical studies of organo derivatives of diborane are still sparse. The NMR spectra of alkyldiboranes have been examined (*204*). Electron diffraction experiments on $B_2H_2Me_4$ have resulted in an accurate set of molecular parameters and demonstrated that the methyl groups are not freely rotating (*205*). Infrared spectra of methyl- (*206–211*) and ethyldiboranes (*207–209*, *212*) have been measured and vibrational assignments made, as have also Raman spectra in the case of four of the methyl compounds (*213–215*).

B. SUBSTITUTION BY OTHER GROUPS OR ATOMS

Reactions leading to the formation of B–N, B–P, B–As, B–Sb, B–O, B–S, B–Se, and B–halogen bonds have been reviewed in 1960 by Stone (*23*). Although aminodiborane $H_2NB_2H_5$ is a stable monomeric compound readily prepared by the action of diborane on its diammine (*216*), its structure is not comparable with that of methyldiborane. In accordance with the original suggestion of Burg and Randolph (*217*), the amino group occupies a bridge position, as has since been demonstrated not only for μ-$H_2NB_2H_5$ and μ-$Me_2NB_2H_5$ by electron-diffraction studies (*218*), but also for μ-$Et_2NB_2H_5$ from its infrared spectrum (*219*). The dimethylamino bridge is stronger than the hydrogen bridge, as demonstrated by the ^{11}B NMR spectrum of the *B*-methyl-substituted compound μ-$Me_2NB_2H_4Me$. At lower temperatures the cyclic doubly bridged structure is clearly indicated, but as the temperature is raised the hydrogen bridge undergoes progressive rupture to give predominantly $H_3B \cdot NMe_2BHMe$. The bridging nitrogen apparently enhances the



stability with respect to disproportionation, since the compound has a definite vapor pressure (31.0 Torr) at 0°C, whereas the measured vapor pressure for B_2H_5Me undergoes rapid change through disproportionation even at –78.5°C (*220*).

In the bis(dialkylamino)diboranes, both dialkylamino groups presumably occupy bridge positions (*221*), but this is not clear from a study of the crystal structure of the bis(dimethylamino) compound (*222*). Nevertheless, a $(BN)_2$ 4-membered ring structure has been established for the chlorinated analog $(Me_2N)_2B_2Cl_4$ (*223*).

Various other methods are now available for preparing the μ-aminodiboranes, including the action of diborane on (dimethylamino)boranes (*224*), tetrakis(dimethylamino)diborane(4) (*225*), tetramethylhydrazinebisborane (*88*), sodium dimethylamidotrihydroborate (*226*), and bis(dimethylamino)sulfide (*45*), the action of $Al(BH_4)_3$ on (dimethylamino)borane (*224*), and the reversible disproportionation of the latter compound on heating (*224*).

$$3Me_2NBH_2 \rightleftharpoons (Me_2N)_2BH + Me_2NB_2H_5$$

As is to be expected, $Me_2NB_2H_5$ is a much weaker Lewis acid (*227*) than B_2H_6 because of the bonding to the boron atoms of an atom with a lone pair of electrons. Nevertheless, adducts with pyridines, trimethylamine, and substituted phosphines have been prepared (*227*). NMR studies have demonstrated that μ-aminodiboranes undergo an intramolecular bridge and terminal hydrogen exchange that is accelerated by ethers (*228*). The kinetics of the process have now been elucidated (*229*).

It is not possible to replace more than two hydrogen atoms of B_2H_6 by amino or substituted amino groups, since the bridge bond is weakened and the molecule splits up into substituted boranes. This is also generally true when other atoms from Groups V, VI, or VII are linked to boron. Even the bis(dialkylamino)diboranes are in equilibrium, at least in the liquid and vapor phases, with the monomeric species (Section VII, D).

$$(Me_2N)_2B_2H_4 \rightleftharpoons 2Me_2NBH_2$$

The enthalpy change (about 20 kcal $mole^{-1}$) (*221*) has been calculated from dissociation-pressure data, but this has since been corrected to allow for the accompanying disproportionation reaction, and a new free-energy equation has been derived (*224*). The enthalpies of dissociation in the liquid phase have been determined for a number of analogs by means of NMR techniques (*230*).

Other methods of preparing the (dialkylamino)boranes are known, such as heating the dialkylamine with diborane at about 190°C (*221*), the removal of BH_3 from $R_2NB_2H_5$ by certain Lewis bases (*227*), the thermal decomposition of the bisborane adduct of the corresponding tetraalkylhydrazine at 100°C (*88*), the reduction of the corresponding *B*-chloro-

$$R_4N_2 \cdot 2BH_3 \xrightarrow{100°C} 2R_2NBH_2 + H_2$$

borane with tributyltin hydride (*231*), and the simple fission of hydrogen at 180°–200°C from the dialkylamine borane (*221*). The properties of

$$R_2NH \cdot BH_3 \xrightarrow{190°C} R_2NBH_2 + H_2$$

these and similar compounds have been described (*232*). The degree of polymerization varies with the nature of R. Nor can it be assumed that it is always the dimer that is formed in the case of analogs. We have met with a trimer in the case of *N*-methylaminoborane (Section II, A); and for the parent compound $(H_2NBH_2)_n$, which is formed by the action of Na (*233*) or $NaNH_2$ (*234*) on $[BH_2(NH_3)_2]BH_4$ in liquid ammonia, or of B_2H_6 on $LiNH_2$ in ether (*235*, *236*), a number of cyclic compounds are formed. Here *n* may equal 2, 3, and 5, and possibly 4 (*234*), the mean value of *n* being about 4 (*236*). On the other hand, some analogs are strictly monomeric, as, for example, Me_2NBMe_2 (*119*) and $HMeNBMe_2$ (*237*).

Burg and co-workers have studied the disproportionation reactions of (dimethylamino)boranes (*224*), and their conversion by means of Lewis bases to $(Me_2N)_2BH$ and $(Me_2N)_3B$ (*227*), which di- and trisubstituted borane derivatives exhibit no tendency to polymerize. As substitution increases, the acidic properties decrease in accordance with expectation; only the monosubstituted derivative Me_2NBH_2 forms an adduct with trimethylamine that is sufficiently stable to be isolated (*224*).

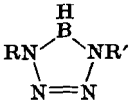
There appears to be partial double-bond character of the B–N bonds in aminoboranes, because NMR studies with (methylphenylamino)dimethylborane (*238*) and various other dialkylaminoboranes (*239*) have revealed that the activation energy of rotation about the B–N bond is in the region of 50–100 kJ $mole^{-1}$.

When the hydrogen on the boron is substituted by alkyl groups, it is possible to obtain related compounds in which two dialkylboryl groups are attached to the same nitrogen atom. Thus, Nöth and Vahrenkamp have reported reactive compounds of the type $(R_2B)_2NH$ and $(R_2B)_2NMe$ prepared from the halogeno compound R_2BX and either a disilazane or an N-metalated aminoborane; or alternatively from the appropriate methylthio compound R_2BSMe and ammonia (*240*).

$$(Me_3Si)_2NH + 2R_2BCl \rightarrow (R_2B)_2NH + 2Me_3SiCl$$
$$LiNMeBR_2 + R_2BCl \rightarrow (R_2B)_2NMe + LiCl$$
$$2Me_2BSMe + NH_3 \rightarrow (R_2B)_2NH + 2MeSH$$

Disilylaminodiborane $(H_3Si)_2NB_2H_5$ and disilylaminoborane $(H_3Si)_2NBH_2$ are known, the latter as monomer and dimer (*241*).

Azidoboranes are also preparable, and are formed, for example, by the interaction of NaN_3 and B_2H_6 in diethyl ether (*153*). They have been the subject of a detailed review by Paetzold (*242*). H_2BN_3 is not monomeric, the degree of association depending on the concentration. Cryoscopic measurements in benzene extrapolated to infinite dilution yield a molecular weight lying between that of the dimer and trimer. Et_2BN_3 has also been described, but ^{11}B NMR studies indicate that this disproportionates to an equilibrium mixture of Et_3B, Et_2BN_3, $EtB(N_3)_2$, and $B(N_3)_3$ (*153*). By the action of methyl azide MeN_3 on $H_2MeN \cdot BH_3$ and $H_2PhN \cdot BH_3$, Morris and Perkins have prepared the 2,5-dimethyl and the 2-methyl-5-phenyl derivatives of the unknown cyclotetrazenoborane (*243*)



Dimethylphosphinoborane, unlike the corresponding dimethylamino compound, does not occur as a dimer, but as a trimer and tetramer, $(Me_2PBH_2)_3$ and $(Me_2PBH_2)_4$, mainly the former (*32*). A little higher polymer is formed at the same time (*32*, *244*). Other alkyl homologs are also known. They are prepared by the thermal degradation of dialkylphosphine boranes.

$$HMe_2P \cdot BH_3 \xrightarrow{150°C} \frac{1}{n}(Me_2PBH_2)_n + H_2 \quad (n = 3, 4)$$

Both the trimer and tetramer are exceedingly stable toward heat and hydrolysis, and even with concentrated hydrochloric acid a temperature of about 310°C is required before a slow reaction occurs. X-Ray diffraction studies have confirmed the formation of a $(BP)_3$ ring structure for the trimer (*245*). The same compounds are obtained from heating tetramethyldiphosphine bisborane (*88*, *246*). The compounds are slightly

$$Me_4P_2 \cdot 2BH_3 \xrightarrow[16\ hr]{220°C} \frac{2}{n}(Me_2PBH_2)_n + H_2$$

volatile solids, but the corresponding compound obtained from heating methylphosphine borane is a nonvolatile oil $(HMePBH_2)_n$ and that from phosphine borane a refractory solid (*32*). On analysis one preparation of the latter proved not to have the exact formulation $(H_2PBH_2)_n$, but was deficient in hydrogen and corresponded to the formula $(PBH_{3.75})_n$. Certain analogs in which the hydrogen atoms attached to boron are substituted by methyl groups have also been prepared. The strength of the B–P bonds in all these compounds has been explained by π bonding involving the B–H bonding electrons and the vacant *d* orbitals of the phosphorus atoms (*32*), but proof of this is lacking. The 6-membered ring of $(Me_2PBH_2)_3$ is not planar and the B–H bonds are not suitably oriented for π bonding (*245*). Whether or not some sort of π bonding is involved, if it is reflected that the σ bonding between the B and P atoms is only partial, a conceivable alternative is that the boron atoms act as acceptors for the hybridized lone pairs on the phosphorus atoms (but see Section VII, E).

The analogous bis(trifluoromethyl)phosphinoboranes have been prepared from $PF(CF_3)_2$ or $PH(CF_3)_2$ and B_2H_6 (*247*). Like the methyl compounds they exist as the trimer and tetramer, $[(F_3C)_2PBH_2]_3$ and $[(F_3C)_2PBH_2]_4$, but are thermally a little less stable.

Dimethylarsinoboranes, $(Me_2AsBH_2)_3$ and $(Me_2AsBH_2)_4$, resemble their phosphino analogs and are prepared along with a higher polymer by analogous methods (*41*), but are both formed and decomposed at lower

$$HMe_2As\cdot BH_3 \xrightarrow[36\text{ hr}]{130°C} \frac{1}{n}(Me_2AsBH_2)_n + H_2$$

temperatures. The tetramer is partly converted to the trimer at 180°C, and decomposition of the trimer sets in above 200°C. They have lower melting points but higher (extrapolated) boiling points than the corresponding phosphorus compounds. The monomethylarsino compound $(HMeAsBH_2)_n$ is nonvolatile and, as prepared, slightly hydrogen-deficient, as is also to a more marked degree the unsubstituted arsino compound, the formula of which reportedly approximates to $(BAsH_{3.7})_n$ (*41*). On heating more hydrogen is lost.

Quite different is the antimony analog dimethylstibinoborane prepared from dimethylstibine or, better, tetramethyldistibine and

$$Sb_2Me_4 + B_2H_6 \xrightarrow[1.75\text{ hr}]{100°C} 2Me_2SbBH_2 + H_2$$

diborane (*248*). This compound is strictly monomeric (boiling around 70°C), is relatively unreactive, and has virtually no Lewis acid or

Lewis base properties. It is stable up to 200°C, and π bonding, possibly involving an antimony hybridized $5p5d$ orbital, is clearly indicated, since almost all known substituted monoboranes with BH_2 groups are at least dimers in their most stable forms.

Among the diboranes and boranes substituted with a Group VI element, a close parallel has been observed with those substituted with a Group V element only in the cases of derivatives containing sulfur and nitrogen, respectively. The derivatives containing oxygen ligands, which will next be considered, exhibit only a very restricted similarity to those involving nitrogen ligands. Thus, unlike the NH_2 derivatives, simple OH derivatives of diborane and borane (other than boric acid) appear to be incapable of isolation. Nevertheless, there is mass spectral evidence for the existence of H_2BOH and $HB(OH)_2$ in the presence of B_2H_6 and H_3BO_3 when these are allowed to stand in contact; also, it has even been possible to estimate the enthalpies of formation of both hydroxyborane species in the vapor phase from their equilibrium concentrations (*249*). The nonisolation of the hydroxyboranes is doubtless to be attributed to their thermodynamic and kinetic instability with respect to B_2H_6 and $B(OH)_3$. On the other hand, if the hydrogen atoms are replaced by alkyl groups, both the R_2BOH and the $RB(OH)_2$ series of compounds are isolable. The former are usually volatile liquids that react immediately with air, whereas the latter are volatile crystalline solids that show a fair stability toward oxygen. The alkoxy compounds H_2BOR and $HB(OR)_2$ are again thermodynamically unstable with respect to B_2H_6 and $B(OR)_3$, and the former cannot be isolated, but can apparently be stabilized by coordination, e.g., with ether (*130*). Dialkoxyboranes, on the other hand, are isolable, as was first shown for $HB(OMe)_2$ by controlled alcoholysis of B_2H_6 (*250*), but they readily disproportionate.

$$B_2H_6 + 4MeOH \rightarrow 2HB(OMe)_2 + 4H_2$$
$$6HB(OMe)_2 \rightleftharpoons B_2H_6 + 4B(OMe)_3$$

Lehmann and co-workers have reported the infrared spectra of $HB(OMe)_2$ (*251*), $HB(OEt)_2$ (*252*), and $HB(OCHMe_2)_2$ (*253*). Particular interest is attached to the vibrational frequencies of the B–O bonds, which have recently been studied for a number of related molecules (*254*). Some strengthening of the bond by π bonding might be expected, and rather persuasive evidence for this is found in the low-temperature NMR spectra of Me_2BOMe and $(Me_2B)_2O$, which indicate an energy barrier to free rotation about the B–O bonds in these molecules of about 8.5 kcal mole^{-1} (*255*), a value about three times that found for the energy barriers to free rotation about the C–O bonds in methyl ethers.

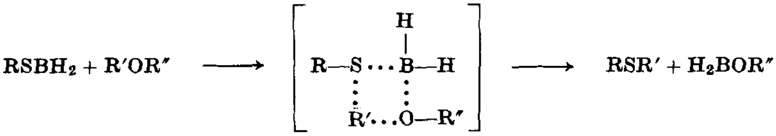
In accordance with the high affinity of boron for oxygen, diborane will slowly cleave some ethers to produce alkoxyboranes and ultimately trialkylborates. Thus, with excess tetrahydrofuran at 60°C, the diborane is completely converted within 64 hours to tri-*n*-butylborate (*256*), while with diglyme a similar reaction occurs in which methyl groups are displaced as methane (*257*). But it is not certain that these reactions occur with BF_3-free diborane (see Sections IV, A and VII, F).

Compounds containing ligands linked to boron by a sulfur atom show a much greater resemblance to those containing ligands linked by a nitrogen atom. Like the NR_2 group, the SH group occupies a bridge position in monosubstituted diborane, as has been demonstrated for the recently prepared and rather unstable μ-mercaptodiborane HSB_2H_5 (*258*, *259*). It has been prepared by treating the salt $[NR_4]^+[HS(BH_3)_2]^-$—from NR_4HS and B_2H_6—with HCl, and has an extrapolated boiling point of 27°C. It cleaves ether at room temperature (*258*). The structure of methylthiodiborane is likewise μ-$MeSB_2H_5$ (*260*). It also is unstable and volatile (boiling point about 60°C), and is monomeric (*43*). The alkylthioboranes, however, are trimeric $(RSBH_2)_3$ in the condensed phase with 6-membered $(BS)_3$ rings (*260*), but the methyl derivative, at least, is approximately dimeric in the vapor phase (*43*). Bis(alkylthio)-boranes $(RS)_2BH$ and trialkyl thioborates $(RS)_3B$ are also known (*261*). The latter, like trialkyl borates $(RO)_3B$, undergo reversible redistribution with diborane, whereas with trialkylboranes they give alkylbis(alkylthio)boranes $(RS)_2BR'$ (*187*). Mixed dialkylaminoalkylthioboranes such as $Et_2NBH(SPr)$ have also been prepared (*262*). Similar compounds can be prepared by thermal degradation of the dialkylamine adducts of

$$MeSBH_2\cdot NHEt_2 \xrightarrow{280°C} MeSBH(NEt_2) + H_2$$

alkylthioboranes (*93*). By treating ethanedithiol with diborane, the compounds $H_2BSCH_2CH_2SBH_2$ and $(CH_2S)_2BH$ have been obtained (*263*). The latter compound, 1,3,2-dithiaborolane, has a 5-membered ring structure. In the vapor phase it is monomeric, whereas in the condensed state association through weak intermolecular boron–sulfur coordinate bonds occurs without any evidence for hydrogen bridging between the boron atoms. For this reason and for other considerations it is highly unlikely that compounds such as $[(PrS)_2BH]_2$ (*264*), if indeed they are dimeric, can be rightly regarded as tetrasubstituted diboranes with hydrogen bridges.

Alkylthioboranes will cleave ethers to give thioethers, apparently via a 4-center reaction step (*265*).



This is evidence that the relative strength of the B–O bond is enhanced above that of the B–S bond to a greater extent that the strength of the C–O bond exceeds that of the C–S bond.

The only simple selenium derivatives of diborane so far reported are trialkyl selenoborates $(RSe)_3B$ (*266*). Other selenium-containing borane derivatives as have been prepared are ring compounds (*267, 268*). Trimethyl telluroborate $(MeTe)_3B$ has recently been reported (*642*). It would be interesting to attempt to prepare $MeTeBH_2$ and discover whether it is monomeric like Me_2SbBH_2.

With halogen substitution, it is not possible to substitute more than one hydrogen atom of B_2H_6 without rupturing the hydrogen bridge, and even the monofluoro derivative B_2H_5F is unknown. A recent attempt to detect it in infrared absorption of B_2H_6–BF_3 mixtures after treatment over a large range of pressures and temperatures up to 110°C failed (*269*), and the only intermediate detected was HBF_2. On the other hand, B_2H_5Cl, B_2H_5Br, and B_2H_5I have all been isolated although they rather readily disproportionate to B_2H_6 and, ultimately, the corresponding boron trihalide. The chloro compound has an extrapolated boiling point of -11°C, and at atmospheric pressure the gas-phase disproportionation equilibrium requires about 70 hours to reach equilibrium at 35°C (*270*). It can also be prepared by the action of excess H_2 on BCl_3 vapor in an electric discharge (*271*), or by treating B_2H_6 with BCl_3 (*269, 271, 272*). As this last equilibration reaction has been shown to proceed without any change in the number of molecules (*273*), it is most correctly written (*274*)

$$B_2H_6 + BCl_3 \rightleftharpoons B_2H_5Cl + BHCl_2$$

B_2H_5Br is similarly produced from BBr_3 (*271, 275*), and B_2H_5I from BI_3 (*276*). Alternatively, B_2H_6 may be reacted with the hydrogen halide (*275*), preferably in the case of HBr in the presence of aluminum bromide (*272*), but only B_2H_5Br can conveniently be prepared from B_2H_6 and the free halogen (*272*), chlorine reacting too violently and iodine only very slowly, even on heating (*276*). In all cases, the halogenodiborane needs to be separated from the reaction mixture by low-temperature fractionation or vapor chromatography. B_2H_5Br has been identified as a product of reacting boron atoms with HBr (*277*).

It is rather surprising that no structural determinations have been carried out on B_2H_5Cl. From analogy with μ-B_2H_5SMe one might expect that the chlorine atom occupies a bridge position. The evidence, however, points the other way. It is claimed by Cornwell that the microwave spectrum of B_2H_5Br can be explained only by assuming that the bromine atom is in a terminal position (*278*, *279*). The ^1H and ^{11}B NMR spectra have also been reported (*280*), while the infrared spectrum has been compared with those of B_2H_5Cl and B_2H_5Me (*281*). The infrared spectrum of B_2H_5I also shows close similarities to those of B_2H_5Cl and B_2H_5Br (*276*). In their properties the chloro compound is the least stable thermally and the most reactive, being spontaneously inflammable in air. All are however very reactive, and even B_2H_5I, which shows no tendency to inflame in air, hydrolyzes more rapidly than B_2H_6 (*276*).

It is rather surprising that the existence of BHF_2 was not reported before 1964; indeed, the isolation of no halogen derivative of BH_3 was reported before 1959. BHF_2 can be prepared by the pyrolysis of B_2H_6 in the presence of BF_3 or an organoboron fluoride, or preferably by reacting BF_3 with $HB(OMe)_2$ (*282*) or even B_2H_6 (*269*). It disproportionates over a period of weeks to BF_3 and B_2H_6 (*283*). Infrared (*282–285*) and NMR (*282*, *286*) data have been reported for BHF_2 and isotopic species. The molecule has also recently been the subject of theoretical studies (*287*, *288*). That $BHCl_2$ was missed by a number of expert workers in the field over several decades is probably to be attributed to the exceedingly difficult separation from BCl_3 and B_2H_5Cl by conventional vacuum fractionation. Its first isolation was effected from the products of heating BCl_3 with H_2 (*289*), and it is also a principal product of heating BCl_3 with CH_4 (*290*) or of equilibrating BCl_3 with B_2H_6 (*269*, *273*). The spectra of $BHCl_2$ and its isotopic species have been reported (*270*, *289–293*), as have also the thermodynamics of disproportionation (*294*), which reaction requires a few weeks for completion in a closed cell at room temperature. In the B_2H_6-BCl_3 distribution equilibrium the concentration of the intermediate B_2H_5Cl is favored at room temperature, but that of $BHCl_2$ is favored at 100°C (*274*). It has been claimed that the species BH_2Cl has been detected in the gas phase from its infrared bands (*281*). The dibromo compound $BHBr_2$ is similarly formed when BBr_3 is heated with H_2 (*295*) or equilibrated with B_2H_6 (*269*). Its spectrum (*296*, *297*) and that of $BDBr_2$ (*298*) have been reported. On the other hand, BHI_2 is unknown and, unlike B_2H_5I, did not appear in a recent study of the B_2H_6–BI_3 system (*276*).

Although monohalogenoboranes BH_2X may occur as intermediates in B_2H_6–BX_3 redistribution reactions and spectroscopic evidence has been found for BH_2Cl, they are otherwise unknown either as monomers or dimers. Presumably they disproportionate too rapidly to isolate. On the other hand, like the dihalogeno compounds BHX_2, they are stabilized by coordination. Thus, ethers give complexes such as $R_2O \cdot BH_2Cl$ (*299*, *300*) and $Et_2O \cdot BH_2I$ (*130*), while with amines such complexes as $R_3N \cdot BH_2X$ (*301*) and $C_5H_5N \cdot BH_2I$ (*302*) possess well characterized infrared and NMR spectra.

In contrast to the lack of stability of the monohalogenoboranes, alkylhalogenoboranes BR_2X and BRX_2 [X = F, Cl, Br, I] are readily isolable. In general, these disproportionate only slowly at room temperature and more rapidly on heating.

IV. Reactions Effecting Reduction

A. GENERAL USE AS A REDUCING AGENT

Diborane is a very extensive and useful reducing agent, on the whole more powerful than $NaBH_4$, but less so than $LiAlH_4$; however, in its mode of attack it differs from $NaBH_4$. This invests it with a certain selectivity. Thus, whereas $NaBH_4$ reacts principally by nucleophilic attack on an electron-deficient center, because it is already electron-deficient B_2H_6 preferentially attacks a molecule at a position of high electron density. Thus, it will reduce azo compounds but (in the absence of a coordinating agent) not chloral (whose C=O bond is adjacent to the strongly electron-withdrawing CCl_3 group), whereas with $NaBH_4$ the reverse is true. Again, B_2H_6 will reduce both COOH and COOR groups, whereas $LiBH_4$ only reduces the latter. This fact has been utilized in the study of compounds of biochemical origin as the basis of a diagnostic test for nonesterified carboxyl groups, but the test must be applied with care (*303*).

Another matter of great importance for selective reductions and reductions in general is the catalytic effect of BF_3, even in traces, in enhancing the reducing powers of B_2H_6. This has, on occasion, even led to the formation of different products, depending on the method of generating the B_2H_6 (*304*, *305*). Many methods of preparation (*1*) [e.g., Shapiro's method (*306*)] use boron trifluoride etherate $F_3B \cdot OEt_2$ as the starting material, and this inevitably means that the B_2H_6 is contaminated with traces of BF_3, which cannot readily be removed even by passing the gas through a solution of $NaBH_4$ in diglyme. If instead, the B_2H_6 is prepared by the newer method which uses $NaBH_4$ and I_2 (*307*), no contamination by BF_3 is possible, and reproducible results are obtained in reduction experiments (*305*). The effect of the BF_3 when present is possibly to promote reaction by forming a coordination complex with the reactant, which then has an enhanced reactivity toward diborane or its borane adduct; alternatively a fluoroborane species such as BHF_2 or BH_2F etherate $R_2O \cdot BH_2F$ may be involved. Because of this effect, the reducing properties of pure diborane need a general reinvestigation, and this should be borne in mind when reading the rest of this Section (see also Section VII, F).

In many cases of reduction with diborane, the conversion is not completed in a single step and the product may need working up with water or some hydroxyl-containing medium for the final stage. Because of its high reactivity, diborane can effect reduction in several different ways. For example, the net effect may be simply to supply hydrogen, the molecule that undergoes reduction receiving either two or four hydrogen atoms, with or without bond rupture; alternatively no hydrogen is transferred, but an atom of oxygen is removed. In other cases the net effect is both to supply two or four hydrogen atoms and remove one oxygen atom; or, less commonly, at least three atoms of hydrogen are supplied while a univalent atom or group is removed. It will suffice here to give some examples of each kind of reduction. Precise knowledge concerning the mechanisms is still largely lacking.

In reductions of the first class hydrogen addition from diborane either reduces a multiple bond to a single bond, or effects the complete rupture of a bond, whether multiple or single. (Ordinary aromatic rings are however not attacked.) The addition of hydrogen across a double or triple bond never occurs in a single step, but as the result of subsequent protonolysis of the initial product, normally by means of a hydroxyl-containing medium. The first step is the provision of borane BH_3, which adds as $-H$ and $-BH_2$, respectively, to the two atoms participating in the multiple bond. Such an addition is known as *hydroboration*. This is of sufficient importance to deal with separately (Section IV, B) for the case of $C{=}C$ and $C{\equiv}C$ bonds, but the effect on multiple bonds involving atoms other than carbon will be considered here. The boryl group BH_2 is most likely to add to the electron-richer atom, i.e., oxygen in the case of the $C{=}O$ bond and nitrogen in the cases of the $C{\equiv}N$ and $C{=}N$ bonds. After protonolysis, the ultimate effect is to convert, e.g., the $C{=}O$ group to CHOH, so that aldehydes (*308*) and ketones (*308–311*) become primary and secondary alcohols, respectively. These changes occur via compounds of the type $(RCH_2O)_2BH$ (*312*) in the former case and $(R_2CHO)_2BH$ (*308*, *312*) in the latter. The yields are usually good. The kinetics of the vapor-phase reaction with acetone have been studied (*313*), as have the stereochemistry and path of the reaction with 4-*t*-butylcyclohexanone (*314*). Diborane alone similarly converts the $>C{=}O$ group of lactones to the hydroxy compound (isolated as the hemiacetal), but in the presence of boron trifluoride etherate further reduction to $>CH_2$ occurs (*315*).

Other cases where reduction by diborane of $>C{=}O$ all the way to $>CH_2$ was achieved (*316*, *317*) were later recognized (*305*) to be due to the presence of BF_3. With *p*-benzoquinone the product of reduction with diborane is not a $>CHOH$ compound, but hydroquinone in almost quantitative yield (*318*).

The C=N bond behaves like the C=O bond, so that oximes RR′C=NOH are reduced to *N*-alkylhydroxylamines RR′CH–NHOH (*319*–*322*) [which may be reduced further to amines (*322*)]. Likewise, Schiff bases $RC_6H_4CH{=}NC_6H_4R'$ are reduced to $RC_6H_4CH_2{-}NHC_6H_4R'$ (*323*). Phenyl isocyanate is also reduced (*318*), but the products are not reported. The C≡N bond takes up twice the quantity of hydrogen, so that nitriles RCN are reduced to amines RCH_2NH_2 (*151*). The reaction is said to proceed via RCH_2NBH (*308*), which is incidentally probably trimeric. Phenyl isocyanate also consumes more than two atoms of hydrogen (*318*).

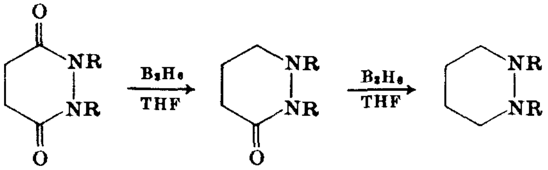
Bond cleavage occurs of necessity when the reduction takes place at a single bond. C–C bonds are not normally affected, but an exception is provided by cyclopropanes (*324*), in which the bonds are weakened through steric strain. With cyclohexane, cleavage only occurs under extreme conditions and in the presence of a catalyst (*325*). C–O bonds may also be cleaved at varying rates. Again strain may be largely responsible for the rapid reductive cleavage of a C–O bond in epoxides (*308*, *318*, *326*, *327*), which is catalyzed by small amounts of tetrahydroborate (*328*) or BF_3 (*329*). Tetrahydrofuran (*256*) and other cyclic ethers (*330*) are cleaved very much more slowly or require higher temperatures. With the former, diborane is said to react completely in 16 weeks at room temperature or 64 hours at 60°C. At 80°C diisopropyl ether is also cleaved (*331*). But generally speaking dialkyl ethers show considerable resistance to reductive cleavage at room temperature, which enables them to be classed as useful solvents for diborane. However, some caution must be exercised, because a slow reaction is feasible, and such has been noted even with diglyme (*257*, *332*) which, although one of the most commonly used solvents for diborane, has been observed slowly to liberate CH_4 as one of the products. Nevertheless, in accordance with a recent suggestion (*305*), all these cases of slow ether cleavage may be attributable to the catalytic effect of traces of boron trifluoride. There is still uncertainty concerning this point, but in no case has it been definitely established that BF_3-free B_2H_6 reacts in this way.

Reductive cleavage is readily effected of one of the C–O bonds in acetals and ketals, which are thereby converted by diborane to ethers (*333*).

$$RR'C(OR'')_2 \xrightarrow[(B_2H_6)]{[2H]} RR'CHOR'' + R''OH$$

Most C–S bonds are not attacked, but reductive cleavage occurs in the cases of the mercaptan Ph_3CSH and disulfide $Ph_3CSSCPh_3$ to produce triphenylmethane (*334*). The presence of the aryl groups seems to be necessary. Again, although C–Cl and C–Br bonds are not normally attacked, aralkyl halides are reduced by reductive cleavage of the carbon–halogen bond, at least in nitromethane as solvent (*335*). B_2H_6 has also been observed to cleave Si–C, Si–O, and Si–P bonds with the production of silanes in the cases of silyl cyanide H_3SiCN (*336*), disiloxane (disilyl ether) $H_3SiOSiH_3$ (*337*), and dialkylphosphinosilanes R'_3SiPR_2 (*338*), respectively. Likewise stannanes have been produced with the cleavage of Sn–N (*339*) and Sn–O (*340*) bonds. The N–N bond, though normally not attacked, can be cleaved in benzoylhydrazines with the formation of amines by diborane in tetrahydrofuran (*341*). The N=N double bond in azo compounds is similarly ruptured by diborane (*151*), as is the N–O bond in hydroxylamines (*322*); azoxybenzene, however, is not attacked (*318*).

Reductions of the second class, in which an oxygen atom is extracted, have received very little study as yet; but a few clear cases are known in the almost quantitative conversion by diborane of triphenylphosphine oxide Ph_3PO and tris(dimethylamino)phosphine oxide $(Me_2N)_3PO$ to the corresponding phosphines Ph_3P (*342*) and $(Me_2N)_3P$ (*343*), respectively, and in the conversion of 1,2-substituted perhydropyridazine-3,6-diones to the corresponding perhydropyridazin-3-ones and eventually to the completely reduced perhydropyridazines by diborane in tetrahydrofuran (*341*).



An oxygen atom is formally lost in the conversion by diborane of a *tert*-cyclopropylcarbinol $RCMe(C_3H_5)OH$ to the hydrocarbon $RCHMeC_3H_5$ (*304*), but this is better regarded as a rare replacement of –OH by –H. Normally alcohols are not reduced by diborane, and even in this case catalysis by BF_3 is required.

In reductions of the third class, features of both of the first two classes appear. We have seen that ordinary aldehydes and ketones are reduced to alcohols; but if the compound is aromatic and exceptionally electron-rich, the ultimate product is the substituted hydrocarbon (*316*, *317*). Likewise fluoroacetamides are reduced to fluoroethylamines (*344*), although here the effect of the fluorine substituent is electron-withdrawing. The overall effect is the loss of an oxygen atom and the gain of two hydrogen atoms (although again this does not occur at a single step). Xanthones (*345*) behave like ordinary ketones toward diborane, as do cyclopropylketones (*304*) and lactones (*315*) in the presence of BF_3. With coumarins both hydrogenolysis of the carbonyl group and cleavage of the heterocyclic ring occur, so that coumarin itself gives *o*-allylphenol (*305*), this being an example of the gain of four hydrogen atoms and loss of one oxygen atom. With analogs, however, the degree of reduction sometimes varies (*305, 346*).

Carboxylic acids and their esters (but not their salts) react in stages to produce alcohols, the acids more rapidly and the esters more sluggishly than do ketones, so that under controlled conditions reduction of compounds with more than one functional group can be selective (*151, 303, 347, 348*). The reduction of the free acids can proceed via a triacylborane $(RCOO)_3B$ (*308, 349*), more than one subsequent pathway being conceivable (*350*). Steric hindrance by the attached group may affect the reducibility of the carboxyl function, as has been observed, for example, with polycarbonate esters (*351*). Treatment with diborane is an effective method for reducing carbohydrate carboxylic acids (*352*) and compounds of high molecular weight, such as carboxyl-terminated polysiloxanes (*353*), or peptides and proteins (*354*), where again a very valuable high selectivity is achieved by working at −10°C. An exactly comparable reaction occurs with certain substituted amides, so that, for example, *N,N*-dimethylformamide is reduced to trimethylamine (*355*). However,

$$HCONMe_2 \xrightarrow[0^\circ C]{B_2H_6} Me_3N\cdot BH_3$$

with a limited quantity of B_2H_6 at −30°C, what is apparently the adduct $HCOMe_2N\cdot BH_3$ can be isolated, which explodes on warming to room temperature. *N,N*-Dimethylacetamide is similarly reduced to $Me_2EtN\cdot BH_3$.

In their behavior toward diborane, N=O bonds are sometimes completely reduced. Thus, aromatic nitroso compounds (*356*) are reduced to amines. Alkyl nitro compounds, however, do not react as such (*318*), but their salts (nitronates) (*357*) are reduced to *N*-monosubstituted hydroxylamines. The last reaction may be more correctly regarded as a combination of classes 1 and 2, in that the incoming hydrogen atoms do not take the place of the oxygen atom removed, the loss of the latter being associated with the reduction in valency of the nitrogen atom, while the remaining nitrogen–oxygen bond is reduced and gives the NHOH group. When pyridine *N*-oxide is reduced by diborane, the nitrogen is likewise brought to the trivalent state (*318*).

In the fourth class of reduction by diborane, the outgoing atom or group is univalent, but something more complex than reductive cleavage is involved. Thus, three atoms of hydrogen are taken up in the reduction of oxime ethers RR′C=NOR″ (*322*), when the observed products are amines plus alcohols. Still more hydrogen is required in the reduction of oxime esters RR′C=NOCOR‴ (*322*, *358*, *359*), to give the same products, but this is perhaps best regarded as a combination of classes 3 and 4, in that the acyl group is reduced to an alkoxy group during the process in a typically class-3 manner. Formally, at least, the conversion by diborane of benzoyl chloride and other acid chlorides (*360*, *361*) to the corresponding alcohol may be regarded as another example of a class-4 reduction, but it may also be regarded as a combination of classes 1 and 3. The versatility of diborane as a reducing agent is thus amply demonstrated.

H. C. Brown and his collaborators have published a useful comparison of the rates of reduction of a large number of functional groups by diborane under standard conditions (*318*).

B. HYDROBORATION

Although early experiments (*362*) showed that excess ethylene would react with B_2H_6 to give triethylborane, because of the inconvenience and slowness of the reaction (4 days at 100°C) its importance remained unrecognized for several years. It was later found that this

$$B_2H_6 + 3C_2H_4 \rightarrow 2B(C_2H_5)_3$$

reaction is highly exothermic, can be catalyzed by active carbon or oxides such as Al_2O_3 (*363*), and (with higher proportions of B_2H_6) can proceed explosively. The kinetics and mechanism of the B_2H_6–C_2H_4 reaction are complex, although attempts have been made to interpret them (*364*, *365*). The last stage of the reaction, at least, is reversible, with an activation energy which is high (33.7 ± 1.2 kcal mole^{-1}) (*366*), but still much less than one-third of the energy required for complete dissociation to $B_2H_6 + 3C_2H_4$, namely, 172.5 ± 2.1 kcal mole^{-1} (*367*).

$$BEt_3 \rightleftharpoons BHEt_2 + C_2H_4$$

The observation in 1956 by Brown that olefins are readily converted into organoboranes at room temperature by the combined action of $NaBH_4$ and $AlCl_3$ (*368*) soon led him to reinvestigate the action of B_2H_6 (*369*) and discover that in the presence of ethers diborane adds very smoothly and rapidly to olefins at room temperature to produce organoboranes in near quantitative yield in an easily controllable reaction, for which he coined the name "hydroboration." Subsequently, protonolysis by a carboxylic acid yields the saturated hydrocarbons (*370*).

$$6RCH{=}CH_2 + B_2H_6 \longrightarrow 2(RCH_2CH_2)_3B$$

$$(RCH_2CH_2)_3B \xrightarrow{EtCOOH} 3RCH_2CH_3$$

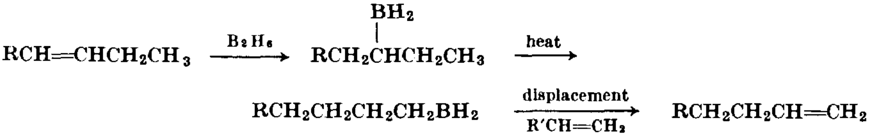
The last stage is completed by refluxing in a high-boiling polyether solvent. Alternatively the saturated alcohol may be obtained as the final product (without necessarily isolating the intermediate) on oxidation by alkaline hydrogen peroxide (*371*, *372*). Addition across the double bond

$$(RCH_2CH_2)_3B \xrightarrow{NaOH,\ H_2O_2} 3RCH_2CH_2OH$$

is cis and anti-Markownikoff, and is generally highly stereospecific. Although, in general, a stream of gaseous diborane gives the best yields, it is frequently adequate to prepare the latter reagent *in situ* (*372*, *373*), e.g., from $NaBH_4$ and BF_3 etherate or $AlCl_3$.

$$12RCH{=}CH_2 + 3NaBH_4 + 4BF_3{\cdot}OEt_2 \rightarrow 4(RCH_2{-}CH_2)_3B + 3NaBF_4 + 4Et_2O$$
$$9RCH{=}CH_2 + 3NaBH_4 + AlCl_3 \rightarrow 3(RCH_2{-}CH_2)_3B + 3NaCl + AlH_3$$

Quick recognition of the importance of the hydroboration reaction as a synthetic tool resulted in its intensive study. The reaction is general, but proceeds less rapidly with internal than with terminal double bonds. With the latter the boryl group attaches itself predominantly to the terminal carbon atom, and with the former the less sterically hindered position is favored. Induction effects also play a role; thus, boryl addition to styrene is 80% terminal, which figure rises to 93% with *p*-methoxystyrene, but drops to 65% with the *p*-chloro compound. By using partially substituted boranes in place of B_2H_6 these percentages may be modified, usually enhancing the directive effect, especially when the substituent is bulky. Such bulky groups may prevent the hydroboration from proceeding beyond the disubstituted or even monosubstituted borane stage. These latter compounds are normally dimers and, hence, derivatives of diborane. When the boron is not linked to a terminal carbon atom, isomerization occurs on heating, in which the boron migrates to the least sterically hindered position. Since the olefin is subject to displacement by another olefin of greater reactivity, this effectively shifts the double bond and even enables olefins to be isomerized in a direction opposed to the order of increasing thermodynamic stability.



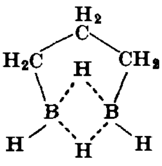
$$\text{RCH}{=}\text{CHCH}_2\text{CH}_3 \xrightarrow{\text{B}_2\text{H}_6} \text{RCH}_2\overset{\text{BH}_2}{\overset{|}{\text{C}}}\text{HCH}_2\text{CH}_3 \xrightarrow{\text{heat}}$$

$$\text{RCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{BH}_2 \xrightarrow[\text{R}'\text{CH}=\text{CH}_2]{\text{displacement}} \text{RCH}_2\text{CH}_2\text{CH}{=}\text{CH}_2$$

Chain doubling through coupling occurs on application of $AgNO_3$ and alkali, whereas ring closure occurs when chloroolefins are hydroborated. Thus, allyl chloride gives cyclopropane [which however may itself be attacked by diborane (*324*)].

The extreme versatility and serviceability of the hydroboration reaction, its stereochemistry and the influence of steric hindrance, isomerization, displacement, directive effects, selectivity, and relative stabilities of functional groups toward reduction during hydroboration were all well understood by the latter part of 1961, when Brown summarized the earlier work in a book (*374*), to which the interested reader is referred for further detail.

Dienes normally give diols after treatment of the initial products, which (as produced in ether solution) are not simple but polymeric and of low volatility. If the diene is conjugated, it is less reactive, while aromatic rings are completely unreactive. With conjugated dienes the unsaturated monohydric alcohol is not produced by partial hydroboration, because the second double bond is attacked much faster than the first. At higher temperatures and in the absence of ether, or after thermal rearrangement, the products may be simple, so that a bora- and a bisboracycloalkane can be obtained as volatile liquids from butadiene and diborane (*199*, *375*). The mechanism of the butadiene reaction has received study (*376*). Allene is peculiar in giving initially the cyclic compound 1,2-trimethylenediborane (*377*), which undergoes a rapid and



reversible polymerization.

Acetylenes hydroborate very rapidly and also initially give nonvolatile products. The C≡C triple bond is capable of bishydroboration. Thus, 1-hexyne gives a polymeric diborylhexane containing the two boryl groups for the most part attached to the same terminal carbon atom, i.e., mainly $H_3C(CH_2)_4CH(BH_2)_2$ (*378*). This on further treatment gives largely 1-hexanol, a fact attributed to the rapid hydrolysis of one of the boron–carbon bonds. (However, it must be remembered that if the aldehyde were formed it would be immediately reduced to the alcohol by the boranes still present.) Under other conditions terminal acetylenes give mainly aldehydes, while internal acetylenes give ketones (*379*). Monohydroboration of the triple bond is also feasible, when vinylboranes and then *cis*-olefins are produced (*379*). Treatment of the vinylboranes with I_2 can lead to interesting transfer reactions (*380*). Acetylene itself is unusual and gives with diborane a polymer of formula $[B_2(C_2H_4)_3]_n$ (*381*); this yields mainly C_2H_6 on hydrolysis with propionic acid.

Recent advances in hydroboration applications include the use of carbon monoxide. At or above 100°C with the organoborane in diglyme this will give rise to a product which, upon the usual oxidation, yields a tertiary alcohol (*382*). In the presence of water the product is a ketone (*383*).

$$R_3B + CO \xrightarrow[\text{diglyme}]{100°\text{–}125°\text{C}} [R_3CBO] \xrightarrow{\text{NaOH, } H_2O_2} R_3COH$$

$$R_3B + CO \xrightarrow[H_2O]{100°\text{C}} RB(OH)CR_2OH \xrightarrow{\text{NaOH, } H_2O_2} R_2CO$$

In these examples the chain length is more than doubled by the transfer of alkyl groups to the carbon of the CO. Under different conditions, by using CO in conjunction with $NaBH_4$ or $LiAlH(OMe)_3$ at lower temperatures, primary alcohols (*384*) or aldehydes (*385*) are produced and the chain length is increased by one carbon atom only. Carbon monoxide in the presence of other reagents will also give carboxylic acids (*386*) with the products of hydroboration.

$$R_3B + CO \xrightarrow[NaBH_4\text{, diglyme}]{45°\text{C}} \xrightarrow{\text{KOH}} RCH_2OH$$

$$R_3B + CO \xrightarrow[LiAlH(OMe)_3\text{, THF}]{25°\text{C}} \xrightarrow[\text{buffer}]{H_2O_2} 2ROH + RCHO$$

The chain length has been increased by more than one carbon atom at a time in a hydroboration procedure which uses unsaturated ketones and aldehydes to prepare higher saturated ketones (*387*) and alcohols

(*388*), and in other methods which use ethyl bromoacetate or chloroacetonitrile to produce an ester (*389*) or a nitrile (*390*), respectively. Such procedures have considerable potential synthetic value. Instead of diborane, many of its derivatives and also some of its adducts have been used in hydroboration procedures, including, recently, $R_3N \cdot BH_3$ and $R_3N \cdot BH_2Cl$ (*391*).

Concerning the hydroboration of multiple bonds involving elements other than carbon, see Section IV, A.

V. Reaction with Hydrogen and Hydrogen Compounds

Diborane does not react with elementary hydrogen, except to undergo hydrogen exchange (*1*, *2*). Indeed, hydrogen tends to stabilize diborane, apparently because of the reversibility of the decomposition step (*2*)

$$B_3H_9 \rightleftharpoons B_3H_7 + H_2$$

With metal hydrides such as LiH, NaH, or KH hydroborates are formed, but such reactions will, in general, only proceed satisfactorily, if at all, in the presence of a solvent suitable for the product (*392–394*).

$$NaH \xrightarrow[\text{diglyme}]{\frac{1}{2}B_2H_6} NaBH_4 \xrightarrow[\text{diglyme}]{\frac{1}{2}B_2H_6} NaB_2H_7\ (\text{solvated}) \xrightarrow[100°\text{C}]{\frac{1}{2}B_2H_6} NaB_3H_8 + H_2$$

The NaB_2H_7 cannot be freed from solvent without decomposition. The conditions under which the reaction with NaH proceeds further to give salts of the $B_3H_8^-$ and $B_{12}H_{12}^{2-}$ anions have been studied (*395*). The reaction with BeH_2 gives BeB_2H_8 and requires warming (*396*), but those with MgH_2 (*397*, *398*) and CaH_2 (*399*) require the presence of an ether (tetrahydrofuran) and, with advantage, pressure.

$$MgH_2 \xrightarrow[C_4H_8O \text{ or } Et_2O]{B_2H_6} Mg(BH_4)_2 \xrightarrow[100°\text{C}]{2B_2H_6} Mg(B_3H_8)_2 + 2H_2 \longrightarrow \text{higher hydroborates}$$

Diborane reacts with a number of other hydrides of boron. B_2H_4 is not isolable, but the isolable adduct $B_2H_4(PF_3)_2$ is converted almost quantitatively into tetraborane (*400*, *401*). With other boron hydrides,

$$B_2H_4(PF_3)_2 + B_2H_6 \rightarrow B_4H_{10} + 2PF_3$$

diborane may undergo BH_3 exchange at a measurable rate (*402*) if the second borane is hydrogen-rich, i.e., contains a BH_2 terminal group.

These include B_4H_{10} and B_5H_{11}, but not B_5H_9, B_6H_{10}, or $B_{10}H_{14}$, with which species only hydrogen exchange can occur (*402*). Otherwise, more particularly on heating, chemical reaction leading to higher boranes takes place. Thus, B_4H_{10} is largely converted initially into B_5H_{11} (*403–405*), while B_5H_{11} is converted to n-B_9H_{15} (*406*) and other products (*407*). On the other hand, diborane converts B_5H_9 mainly to $B_{10}H_{14}$ and a solid polymer, though probably not by direct action (*2*), it having been shown that just one-half of the boron of $B_{10}H_{14}$ comes from the B_2H_6 (*408*). It has recently been reported that this reaction is complex and that smaller amounts of many other products occur (*409*). Diborane will convert $B_{10}H_{14}$ to a nonvolatile polymeric boron hydride (*410*), but the reaction is slow and again probably does not occur directly but by the interaction of $B_{10}H_{14}$ with pyrolysis products of B_2H_6 (*2*). With B_4H_8CO or $B_4H_8PF_3$, diborane will give B_4H_{10} and B_5H_{11}, which may thus be prepared in an isotopically labeled form (*411*). With ionic species B_2H_6 may undergo boron exchange, as with $NaB_{10}H_{13}$ (*412*), or effect complete chemical change. Thus, according to the conditions, the BH_4^- ion is converted either to $B_2H_7^-$ (*7*, *136*) or via $B_3H_8^-$ to the $B_{11}H_{14}^-$ and $B_{12}H_{12}^{2-}$ ions (*413*). The presence of an ether as solvent appears to be necessary. The conversion of $NaBH_4$ in diglyme at 100°C to NaB_3H_8 by I_2 (*414*) is doubtless best regarded as the result of action by B_2H_6 prepared *in situ*, for diborane is first liberated by the action of I_2 on $NaBH_4$ (*307*).

$$2NaBH_4 + I_2 \rightarrow 2NaI + B_2H_6 + H_2$$
$$BH_4^- + B_2H_6 \rightarrow B_3H_8^- + H_2$$

In ether solution AlH_3 (*415*) and $LiAlH_4$ (or $NaAlH_4$) (*416*) are converted by diborane via AlH_2BH_4 and $AlH(BH_4)_2$ to $Al(BH_4)_3$. Possibly species of the type $Li[AlH_{4-n}(BH_4)_n]$ are intermediates (*417*, *418*). The final result may even be salts of the anion $[Al(BH_4)_4]^-$, as has been observed with the tetraalkylammonium aluminum hydrides at 20°–60°C (*419*).

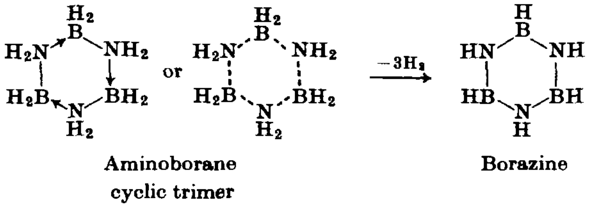
$$[NR_4]AlH_4 + 2B_2H_6 \rightarrow [NR_4][Al(BH_4)_4]$$

Alkoxyaluminum hydrides $[(RO)_nAlH_{3-n}]_x$ are, however, converted by diborane to alkoxyaluminum tetrahydroborates (*420*). Uranium hydride UH_3 on heating in diborane yields uranium boride (*421*).

With saturated hydrocarbons, B_2H_6 reacts to a negligible extent below 100°C, but at temperatures at which its pyrolysis becomes rapid (180°C) significant carbon–carbon bond rupture and boron–carbon bond formation occurs (*362*). In the presence of a Friedel–Crafts catalyst, other reactions may occur (*325*). With cyclopropanes the cleavage of a

C–C bond occurs more readily and leads to the formation of primary alkylboranes (*324*, *422*). Because of the general inertness of C–H bonds toward diborane at room temperature, however, B_2H_6 can be used for the manometric determination of active hydrogen in organic compounds (*423*). Unsaturated hydrocarbons are immediately attacked at the multiple bond in an addition reaction which involves the cleavage of one or more B–H bonds on each boron atom of the diborane. This important reaction (hydroboration) is considered separately in Section IV, B. Diborane would not be expected to react readily with the simple hydrides of other Group IV elements, but detailed studies do not appear to have been undertaken.

With the hydrides of Group V elements, the initial reaction is addition or substitution, as already described in Sections II, A and III, B, respectively. Especially at higher temperatures, borazine is formed with ammonia by condensation, hydrogen elimination, and ring closure reactions (*272*).



Aminoborane cyclic trimer

Borazine

In its formation, the trimeric aminoborane (cycloborazane), known from other reactions, is a likely intermediate. With excess ammonia and at progressively higher temperatures, borimide $B_2(NH)_3$ and boron nitride BN are among the products (*424*). Apart from giving adducts (Section II, A), hydrazine reacts with diborane with the liberation of H_2 (*425*). The B_2H_6–P_2H_4 reaction does not appear to have been studied.

Of the reactions with the hydrides of Group VI elements, that with water is a special case, in that it leads to complete decomposition without the formation of isolable intermediates (see Section VII, F). With liquid H_2S, diborane furnishes no evidence for adduct formation or thiohydrolysis, and has not more than a slight tendency to form ions under neutral conditions; but in the presence of base analogs such as $Me_4N^+SH^-$ diborane first forms the ion $[HS(BH_3)_2]^-$ (*426*). The resultant solution is unstable and readily loses H_2 to give unidentified products, which could feasibly include the more recently discovered μ-mercaptodiborane (*258*) (Section VII, G). With gaseous H_2S at room temperature B_2H_6 slowly gives a polymer of composition $(HBS)_x$ (*43*). Its reactions with higher hydrides of sulfur and with H_2Se and H_2Te appear not to have received study.

Likewise the reaction of B_2H_6 with HF appears not to have been investigated, but because of the unusually high affinity of boron for fluorine one would expect hydrogen to be ejected rather readily with the formation of BHF_2 or BF_3. With the other hydrogen halides the product is B_2H_5X, but in the cases of HCl and HBr the reaction is inconveniently slow, though that with HBr can be catalyzed by aluminum bromide (*272*) (Section III, B).

VI. Reaction with Metals and Metal Compounds

It is surprising that, of the more active metals, only sodium, potassium, and calcium have been investigated in their reactions with diborane. Diborane is slowly absorbed, but reaction requires days, even if the metal is amalgamated. At the time of the earliest studies (*427–429*), tetrahydroborates were not known, and the products were assumed to be $Na_2[B_2H_6]$, $K_2[B_2H_6]$, and $Ca[B_2H_6]$, in which there was supposed to be a $B_2H_6^{2-}$ ion isostructural with ethane. After sublimation, the product from the potassium reaction was observed to be cubic with a single refractive index (*430*). Had it been noted that this implied either an incorrect formula or that the substance underwent change on sublimation, the BH_4^- ion might have been identified about a decade earlier than eventuated. It was not until 1949 that the X-ray powder diffraction pattern of the product from the sodium–diborane reaction was shown to be identical with that of $NaBH_4$ (*431*), which had meanwhile been prepared by other methods. Although this is generally assumed to settle the matter, it must be pointed out that here again the product had been heated, so that there is still no rigid proof that the earlier conclusions were wrong and that $Na_2[B_2H_6]$ or some comparable intermediate is not first formed at room temperature. Unlike KBH_4 (*432*), the original product of the potassium–diborane reaction is reported to be insoluble in liquid NH_3 (*428*) and only partly sublimable (*429*), so that the reaction in the absence of solvent needs further study. In any case some rearrangement must have occurred to account for the transfer of a fourth hydrogen atom to the boron atom.

In the presence of an ether as solvent such rearrangement is favored at room temperature and the whole reaction speeded up. The overall reaction with sodium amalgam has been demonstrated to involve the simultaneous formation of the octahydrotriborate (*433*, *434*).

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

Even here, however, there is evidence for intermediates, kinetic data being consistent with the initial formation of $Na_2B_2H_6$, which reacts further with diborane to give NaB_2H_6 as a second intermediate with its own characteristic X-ray diffraction pattern distinct from those of $NaBH_4$ and NaB_3H_8, into which compounds it disproportionates with time.

The reaction of B_2H_6 with lithium, either in the presence or absence of a solvent, remains unreported. This omission would be worth rectifying, since with compounds of the lighter elements the reactions of lithium often differ from those of sodium and potassium.

In place of sodium amalgam, the addition compounds of sodium with naphthalene or triphenylborane react with B_2H_6 in ether to give the same products (*435*). The much higher speed of reaction is a major advantage. Dissolved in liquid ammonia, sodium apparently does not react in an identical way, but gives a variety of products in a complex reaction (*8*).

It has been claimed (*436*) that if a cyclic ether is used as solvent, alkaline earth metals and aluminum in their amalgams will react with diborane in a manner comparable to alkali metals. So far as is known, transition metals do not react with B_2H_6, but finely divided metals such as nickel or platinum will catalyze its decomposition at room temperature (*437*).

The reaction of diborane with metal compounds has received but limited study. However, its action on carbonyls of metals in the manganese and cobalt vertical groups has been investigated (see Section II, B). With $Co(NO)_3$ it gives $(ON)_3Co \cdot BH_3$ (*70*). Its behavior with metal cyclopentadienyls has not yet been reported, but there is no reason why such compounds as ferrocenylborane should not be obtainable, since other starting materials provide derivatives (*438*, *439*). Reaction with many metal hydrides (see Section V) and several metal alkyls has received attention, but, surprisingly, not with the alkyls of Na, K, Ca, Sr, or Ba. Ethyllithium gives the tetrahydroborate and alkyldiboranes (*440*), e.g.,

$$2LiEt + 2B_2H_6 \rightarrow 2LiBH_4 + B_2H_4Et_2$$

Methyllithium behaves in a like manner (*441*), but phenyllithium may react differently. One group of workers states that it gives the phenyltrihydroborate (*442*),

$$2LiPh + B_2H_6 \rightarrow 2LiBH_3Ph$$

but elsewhere it is stated to give first phenyldiborane, which reacts further (*441*):

$$B_2H_6 \xrightarrow{LiPh} B_2H_5Ph \overset{LiPh}{\rightleftarrows} PhBH_2$$

Dimethylberyllium and trimethylaluminum resemble the former and give (ultimately) BeB_2H_8 (*443*, *444*) and $Al(BH_4)_3$ (*445*), respectively, which, however, unlike $LiBH_4$, are covalent. The $BeMe_2$ reaction occurs in at least four stages, giving first, a glassy material; second, a still methyl-rich nonvolatile mobile liquid; and third, the volatile and fully characterized intermediate $MeBeBH_4$ (*443*, *444*), the BeB_2H_8 only appearing at a subsequent final stage. Diethylmagnesium will give $Mg(BH_4)_2$, but the reaction is complex unless a trialkylaluminum is present in catalytic amounts (*446*); in its absence a variety of products result, including $EtMgBH_3Et$, $Mg(BH_3Et)_2$, and MgH_2 (*447–449*). Grignard reagents RMgX in tetrahydrofuran were originally reported to give $HMgX \cdot 2THF$ with diborane (*450*), but recent workers were unable to repeat this and obtained $XMgBH_4 \cdot 2THF$ with traces of BH_3R^- and $BH_2R_2^-$ instead (*451*, *452*). Trimethylgallium gives $Ga(BH_4)_3$ at reduced temperatures (*453*), but at room temperature this is liable to decompose to the metal by an autocatalytic reaction. The product with $InMe_3$ is even less stable (*454*). B_2H_6 does not react with $SnMe_3H$ except to catalyze its decomposition to Sn_2Me_6 and $(SnMe_2)_n$ (*455*). Organolead compounds such as the tetramethyl (*185*) and tetravinyl (*186*), on the other hand, do react, but in a manner differing from the foregoing cases—the end products are metallic lead and the organoborane.

$$3PbR_4 + 2B_2H_6 \rightarrow 3Pb + 4BR_3 + 6H_2$$

Diborane reacts with certain alkoxides in ether solution to form tetrahydroborates, with the transference of alkoxy groups to boron atoms. Potassium methoxide does not react, but alkoxides of lithium and sodium such as LiOEt or NaOMe do so readily (*392*, *456*).

$$3NaOMe + 2B_2H_6 \rightarrow 3NaBH_4 + B(OMe)_3$$

Alkaline earth metal ethoxides also react (*457*). Such reactions may produce new kinds of tetrahydroborates, even at low temperatures, as occurs with alkoxy derivatives of Al (*458*), Sn(II) (*459*), and Pb(IV)

$$4Al(OCHMe_2)_3 + 2B_2H_6 \rightarrow Al(BH_4)_3 \cdot 3Al(OCHMe_2)_3 + B(OCHMe_2)_3$$
$$2Sn(OMe)_2 + 3B_2H_6 \rightarrow 2Sn(BH_4)_2 + 2BH(OMe)_2$$
$$4R_3PbOMe + 3B_2H_6 \rightarrow 4R_3PbBH_4 + 2BH(OMe)_2$$

(*460*). The stability of the products varies: $Sn(BH_4)_2$ decomposes to the metal above −65°C. Sn(IV) alkoxides react differently and give the corresponding hydrides (*461*).

$$Sn(OMe)_4 + B_2H_6 \rightarrow SnH_4 + 2BH(OMe)_2$$
$$4R_3SnOMe + B_2H_6 \rightarrow 4R_3SnH + 2BH(OMe)_2$$

$Ti(OBu)_4$ and $Zr(OCHMe_2)_4$ in tetrahydrofuran, however, give the tetrahydroborates $Ti(BH_4)_3$ and $Zr(BH_4)_4$, respectively (*462*), as would be expected of transition metals. With metal dialkylamides the dialkylamino group is likewise transferred to boron, at least in the case of Sn(IV) compounds, but again the tin hydrides and not the tetrahydroborates result (*339*).

$$2R_{4-n}Sn(NEt_2)_n + nB_2H_6 \rightarrow 2R_{4-n}SnH_n + 2nH_2BNEt_2$$

With metal salts, two possibilities of reaction arise, in that either the cation or the anion may be attacked by the diborane. The cation may be involved when the metal is noble in character, so that acidified cupric sulfate is reduced at 0°C mainly to CuH with some crystalline Cu (*463*); or, presumably, when a metal of variable valency can be reduced to a lower valence state. Surprisingly, further evidence on the latter point is still lacking, both for crystalline salts and their solutions [the case mentioned above of the Ti(IV) compound $Ti(OBu)_4$ being converted to a Ti(III) compound hardly refers to a salt]. For salts of strongly electropositive metals such as sodium, or even magnesium, the only possibility of reaction is with the anion, and such is liable to occur when, for example, the free ion can add on BH_3. Several examples of this are cited in Section II, B. The reaction does not always stop there, however. Thus, $NaBH_4$ dissolved in diglyme is converted to NaB_2H_7 (*136*), but at higher temperatures the product is NaB_3H_8 (*464*), hydrogen being liberated. The reaction with B_2H_6 proceeds differently with $Na[B(OMe)_4]$ (*465*), $Mg[B(OR)_4]_2$ (*466*), $Na[BH(OMe)_3]$ (*392*), or $K[H_2NBMe_3]$ (*467*), group replacement being observed.

$$3NaB(OMe)_4 + 2B_2H_6 \rightarrow 3NaBH_4 + 4B(OMe)_3$$
$$2NaBH(OMe)_3 + B_2H_6 \rightarrow 2NaBH_4 + 2B(OMe)_3$$
$$2K[H_2NBMe_3] + 3B_2H_6 \rightarrow 2K[H_2N \cdot B_2H_6] + 2B_2H_3Me_3$$

[It is however probably more correct to regard the $K[H_2N \cdot B_2H_6]$ as a mixture of KBH_4 and polymeric $H_2N \cdot BH_2$ (*467*).] With NaN_3 in ether B_2H_6 gives $NaBH_4$ and H_2BN_3 (*153*). With aqueous NaOH the product is likewise mainly $NaBH_4$ (*468*). That the last reaction is to be regarded as a reaction of the OH^- ion is clear from the fact that $[Me_4N]OH$ reacts in a similar way in solution to give Me_4NBH_4. With phosphomolybdic acid a blue coloration of unknown origin is obtained and this may be used as the basis of a method for determining diborane (*469*).

The reaction of B_2H_6 with metal complexes is a field which (if one discounts the carbonyls mentioned above) remains virtually unstudied to date. However, it has been briefly reported that the bis-1,10-phenanthroline complex of ferrous cyanide $Fe(phen)_2(CN)_2$ forms the adduct $Fe(phen)_2(CN)_2 \cdot 2BH_3$, in which it is believed that BH_3 groups are linked to the nitrogen atoms of the cyano groups (*470*).

VII. Reaction with Nonmetals, Metalloids, and Their Compounds

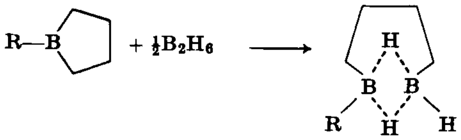
A. REACTION WITH OTHER BORON COMPOUNDS

Many reactions of diborane with boron compounds have already received mention, namely, those with other boranes and the tetrahydroborate ion (Section V), and the reversible redistribution reactions with trialkylboranes (Section III, A), borate esters, thioborates, and boron trihalides (Section III, B). Relatively few additional reactions with other classes of boron compounds have been studied.

With substituted diboranes, diborane may undergo isotope-exchange reactions, as with μ-(dimethylamino)diborane $B_2H_5NMe_2$ (*471*). It reacts more radically with substituted tetrahydroborates, when one of the products is normally the unsubstituted tetrahydroborate (*392*, *466*) (which may, of course, react further).

$$2NaBH(OMe)_3 + B_2H_6 \rightarrow 2NaBH_4 + 2B(OMe)_3$$
$$3Mg[B(OMe)_4]_2 + 4B_2H_6 \rightarrow 3Mg(BH_4)_2 + 8B(OMe)_3$$

Disodium dimethylhydroborate(2-) Na_2HBMe_2 also reacts with diborane, but in this case about 1.4 BH_3 groups per mole are added to give a product stable *in vacuo* at 25°C that apparently does not contain $NaBH_4$ (*472*). With some cyclic organic boranes, diborane effects ring opening with the entry of BH_3 (*473*), e.g.,



B-Alkylborolane 1-Alkyl-1,2-tetramethylenediborane

With aminoborazines diborane reacts with cleavage of the exocyclic B–N bonds to give the corresponding borazines plus polymeric boron–nitrogen compounds and hydrogen (*474*). Diborane reacts with the gaseous species $H_2B_2O_3$ to give boroxine $H_3B_3O_3$ by a reaction which is photochemically accelerated (*475*).

$$H_2B_2O_3 + \tfrac{1}{2}B_2H_6 \rightarrow H_3B_3O_3 + H_2$$

The borane adducts of organic sulfides, when heated with diborane, react with the loss of hydrogen and yield polyboron compounds of unusual stability (*476*). Diborane reacts with B_2Cl_4 in a complex reaction producing BCl_3 and viscous liquid products (*477*), but B_2H_5Cl, $BHCl_2$, an unidentified solid, and some H_2 have also been reported (*281*). In ether solution at −23°C the reaction is less complex, and apparently follows the course:

$$B_2Cl_4 \xrightarrow[Et_2O]{B_2H_6} \underset{\text{(in } Et_2O \text{ solution)}}{B_2Cl_4 \cdot B_2H_6} \xrightarrow[\text{excess } Et_2O]{\text{removal of}} B_3H_3Cl_4 \cdot 2Et_2O$$

B. Reaction with Carbon Compounds

We need concern ourselves here only with reactions in which diborane forms boron–carbon bonds. The number of carbon compounds which form adducts with diborane that have carbon directly linked to boron is small and confined to CO and isocyanides (see Section II, A), and to certain ylides. A boron–carbon bond is also present in the borane adduct (*157*) and bisborane adduct (*148*) formed by the cyanide ion. With ylides a boron–carbon bond is formed if the ylide bond is from carbon to phosphorus, arsenic, or sulfur, as in $Ph_3\overset{+}{P}–\overset{-}{C}H_2$ or $Me_3\overset{+}{As}–\overset{-}{C}HSiMe_3$ (Section VII, E), or $Me_2\overset{+}{S}–\overset{-}{C}HSiMe_3$ (Section VII, G). However, if the ylide bond is to nitrogen, as in $Me_3\overset{+}{N}–\overset{-}{C}H_2$, no comparable reaction occurs (Section VII, D).

Organically substituted boranes may be formed by reacting diborane with certain organometallic compounds (Sections III, A and VI) and organic compounds containing multiple carbon–carbon bonds (Section IV, B). Only in the case of cyclopropanes are single carbon–carbon bonds known to react comparatively readily (*224*, *422*). These reactions need no further description here, while other reactions dealing with the formation of carboranes are conveniently deferred until Section VIII. In other cases of reduction of organic compounds the products do not contain boron–carbon bonds (Section IV, A); this is in line with the preference of boron to attach itself to elements possessing lone pairs of electrons.

Because of the general inertness of C–H bonds toward diborane, there are virtually no reactions involving carbon which do not fall into one of the above classes. Excited molecules may react, as illustrated by the photolysis of hexafluoroacetone in the presence of diborane (*478*), but the products are ill-defined.

C. Reaction with Compounds of Silicon and Germanium

Although compounds containing boron–silicon bonds are readily preparable from halogenated boranes (*479*), only in the cases of the ionic compounds $KSiH_3$ (*149*) and $KGeH_3$ (*150*) have there been reports of diborane giving products in which the boron is directly linked to silicon or germanium, and even these products are very unstable. The ultimate products with $KSiH_3$, for example, are mainly KBH_4, SiH_4, and an SiH_2 polymer (*149, 167*). In other cases where reaction occurs under controlled conditions—as with the silyl cyanides H_3SiCN and Me_3SiCN (*77*), the silylamines H_3SiNMe_2, $(H_3Si)_2NMe$ and $(H_3Si)_3N$ (*76*), the silylphosphines H_3SiPH_2 (*39*) and $(H_3Si)_3P$ (*38*, *78*), silylarsine H_3SiAsH_2 (*480*), disilyl ether $(H_3Si)_2O$ (*337*), and the germyl compounds H_3GePH_2 (*40*) and H_3GeAsH_2 (*481*)—the first product, although not everywhere identified, appears invariably to be a borane adduct in which (as would be expected) the boron is linked as acceptor to the Group V or VI element, even though both arsine adducts are too unstable to isolate. The position is not always so simple, however, as redistribution of the silyl and germyl ligands about the Group V atoms may be promoted by the B_2H_6, so that, for example, H_3SiAsH_2 is converted partly to $(H_3Si)_3As$ (*480*). Also, isotope studies have shown that proton exchange occurs between the boron and silicon or germanium in silyl compounds (*482*) and germyl compounds (*40*, *481*). Under more vigorous conditions each of the above-mentioned silyl cyanides is reduced to the appropriate silane with the rupture of the silicon–cyanide bond (*336*).

Attempts to react B_2H_6 with H_3SiNCO failed (*483*).

D. Reaction with Nitrogen and Its Compounds

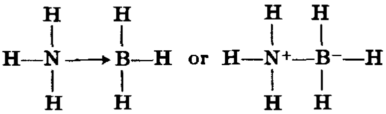
Diborane is attacked by atomic nitrogen; the products have not been identified, but the wavelength and distribution of the light emitted have received study (*484*). Diborane does not, however, interact chemically with molecular N_2. No appreciable BN formation is to be expected or is observed even when B_2H_6 is burnt in air under fuel-rich conditions (*485*), in contrast to what is observed if the nitrogen is initially present as N_2H_4.

The chemical behavior of diborane with nitrogen compounds is strongly bound up with the fact that boron forms rather strong bonds with nitrogen, which bonds are moreover of several different kinds and bond orders. First to be encountered are the dative bonds which can arise by virtue of the donor powers of a trivalent nitrogen atom and the acceptor powers of a boron atom, although the acceptor powers are much weaker in diborane than in free BH_3 (a thing to be associated with the reorganization that the B_2H_6 unit must undergo to provide a vacant orbital to accept a lone pair of electrons). Except where steric or other effects interfere, such bonds are very readily formed, and at low temperatures. If both boron atoms in B_2H_6 act as acceptors the bridge bond between the boron atoms is dissolved (and symmetrically at that), but if only one boron atom becomes linked to a nitrogen atom a weakened form of the bridge bonding involving only one hydrogen atom may be preserved (as we have seen in Section II, A), while a third possibility arises when two nitrogen atoms link up with the same boron atom and give rise to an ionic compound through asymmetric cleavage of the diborane.

Thus, the reaction of diborane with ammonia is complex, giving rise under controlled conditions to $H_3N \cdot B_2H_6$, $H_3N \cdot BH_3$, or $[H_2B(NH_3)_2]^+[BH_4]^-$ (see Section II, A), but when hydrogen is lost, yet other products are formed (see later). With primary, secondary, and tertiary amines the picture tends to become progressively less complex (*120*) and is simplest in the case of tertiary amines NR_3, which readily give only $R_3N \cdot BH_3$, although the rather precarious existence of $Me_3N \cdot B_2H_6$ (*9*) and $Et_3N \cdot B_2H_6$ (*7*) has been demonstrated. Indeed, the kinetics of formation of $Me_3N \cdot BH_3$ from B_2H_6 and NMe_3 indicate that $Me_3N \cdot B_2H_6$ is an essential intermediate (*486*).

Instead of using gaseous diborane, amine boranes may be rapidly and efficiently prepared by treating the amine with $NaBH_4 + I_2$ in monoglyme (*487*). This is tantamount to preparing diborane *in situ*, because B_2H_6 is known to be liberated almost quantitatively from $NaBH_4$ by I_2 dissolved in a glyme (*307*).

Although the amine boranes $R_3N \cdot BH_3$ are so easily prepared, it is only comparatively recently that the simplest member of the series, ammonia borane $H_3N \cdot BH_3$, has become readily available (*114*). A recent theoretical approach has predicted its structure with considerable accuracy (*118*). The bonding is a matter of considerable interest. Although the photoelectron spectrum appears to indicate σ bonding (*488*), the electron distribution is very poorly depicted by the representation in which the nitrogen has a formal charge of +1.

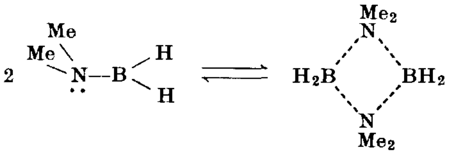


$$H_3N \rightarrow BH_3 \quad \text{or} \quad H_3N^+ - B^-H_3$$

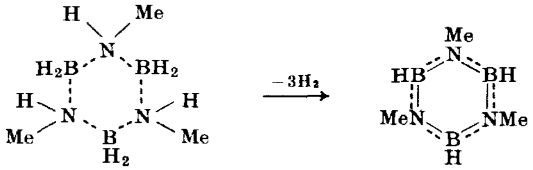
Rather, another theoretical study based on a nonempirical SCF-LCAO method using Gaussian orbitals has predicted a negative charge (−0.822) for the N atom and an almost zero charge for the B atom (*489*). The picture obtained from an extended Hückel LCAO-MO method (*490*) is qualitatively similar. Deuteron magnetic resonance of $Me_3N \cdot BD_3$ demonstrates that there is free rotation about the B–N bond even at low temperatures (*491*). Proton magnetic resonance experiments reveal that $Me_3N \cdot BH_3$ undergoes intermolecular exchange with excess NMe_3 at room temperature (*492*). The B–N stretching force constant has been calculated and is higher for $H_3N \cdot BH_3$ than for $Me_3N \cdot BH_3$ (*493*).

Several different types of compound are formed when hydrogen is lost, including aminoboranes, borazines, and even salts of polyhedral borane cations (see below). Normally, heating is required, as in the preparation of deuterated Me_2NBH_2 (*494*), but under the influence of tetrahydrofuran as solvent hydrogen evolution can occur even at reduced temperatures, and the product of reacting ammonia with diborane below −10°C may be a polyaminoborane of formula $H_3N(BH_2NH_2)_nBH_3$ (*495*). At elevated temperatures, B_2H_6 and ammonia or amines will give monomeric and polymeric aminoboranes and borazines; and these products may also be formed successively when the simple adducts such as $H_3N \cdot BH_3$ or $R_3N \cdot BH_3$ are heated to lose H_2 (or alkane), as in the already cited case of $H_2MeN \cdot BH_3$ (Section II, A). [The elimination of H_2 from $HMe_2N \cdot BH_3$ has been shown not to be a unimolecular step (*496*). With the first step, at least, the B–N bond order is increased, the stretching force constant rising to about 7.0 mdyne $Å^{-1}$ in aminoboranes, which is about double that for amine boranes, but dropping back somewhat in borazines (*497*). Accordingly, the calculated bond order of less than 0.7 obtained for the B–N bond in the analog Me_2NBH_2 by a simple LCAO-MO Hückel treatment (*498*) is almost certainly very wide of the mark: because of π bonding the true value is likely to be well in excess of unity. For H_2NBH_2 the bond polarity is $^-N–B^+$ and the energy barrier to rotation about the bond as calculated by the use of extended basis sets of Gaussian-type orbitals is 40.7 kcal $mole^{-1}$ (*499*), compared with a mere 2.47 kcal $mole^{-1}$ for $H_3N \cdot BH_3$ (*500*). It would follow that the boron–nitrogen bond in aminoborane has appreciable double-bond character, and that with substituted aminoboranes $R^1R^2NBR^1R^3$ cis and trans isomers should exist, as has indeed been demonstrated by NMR studies (*501*).

The presence of donor and acceptor sites in the same molecule conveys to the aminoboranes a more or less pronounced tendency to dimerize or oligomerize. (This doubles the number of B–N bonds, but presumably weakens them.) Thus, in the vapor phase, Me_2NBH_2 exists in equilibrium with its dimer, which has a $(BN)_2$ ring (*221*, *224*). However, steric and



other factors play an important role. Thus, many more highly substituted aminoboranes exist only as monomers, whereas the unsubstituted aminoborane H_2NBH_2 prefers to exist as cyclic oligomers or polymers. Indeed, knowledge of the monomer as a transitory species rested on evidence obtained from the pyrolysis of the dimer (*234*) and from a mass spectrometric study of the vapor of subliming $H_3N \cdot BH_3$ (*502*) until the monomeric species was successfully trapped by cryochemical means (*503*). The monomer begins to polymerize even below −155°C. The isolable forms of aminoborane include a number of oligomers $(H_2NBH_2)_n$, where n may equal 2, 3, (4), 5, ... (*234*). The structure and dissociation energy of the dimer have been calculated *ab initio* using Gaussian orbital basis sets (*504*). Methylaminoborane $HMeNBH_2$, however, appears to prefer to exist as the cyclic trimer $(BH_2NHMe)_3$, and the reaction path by which the latter is formed has been clarified, at least in part (*73*). In such a case there need be no disruption of the ring on further thermal decomposition to the borazine. This change will take place at a more moderate temperature when catalyzed by thiols (*505*). Unlike the latter



1,3,5-Trimethylcycloborazane 1,3,5-Trimethylborazine

compound, $(BH_2NHMe)_3$ has a nonplanar skeleton, and the existence of two conformational isomers has been demonstrated (*506*). Even Me_2NBH_2 can be catalytically condensed to the trimer (*507*), although the condensed phase normally consists of the dimer. Once formed, the trimer, whose molecular structure has been determined (*508*), shows exceptional thermal stability against dissociation. The monomer–dimer equilibria of a number of substituted aminoboranes have been extensively studied by NMR techniques and their enthalpies and entropies of dimerization determined (*230*). But in the case of dimethylaminoborane there is an important competing equilibrium in which dismutation to

$$3Me_2NBH_2 \rightleftharpoons (Me_2N)_2BH + \mu\text{-}Me_2NB_2H_5$$

$(Me_2N)_2BH$ occurs (*224*). $(Me_2N)_2BH$ is therefore a further product which may be obtained from the interaction of B_2H_6 and $NHMe_2$.

The other major factor which affects oligomerization is additional back coordination (π bonding). Thus, compounds in which two or more nitrogen atoms are attached to the same boron atom, such as $(Me_2N)_2BH$ or $(Me_2N)_3B$, show little or no tendency to accept lone electron pairs from donors and, hence, do not oligomerize.

At rather higher temperatures in the range 100°–180°C, and preferably in sealed vessels, salts of polyhedral borane anions such as $B_{12}H_{12}^{2-}$ may be obtained from diborane and either an amine or an amine borane (*413, 509*).

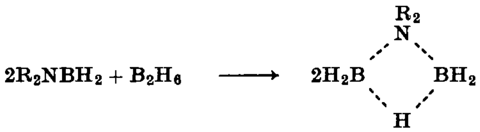
$$2NR_3 + 6B_2H_6 \xrightarrow{100°\text{–}180°C} (NHR_3)_2[B_{12}H_{12}] + 11H_2$$

$$2NR_3 \cdot BH_3 + 5B_2H_6 \longrightarrow (NHR_3)_2[B_{12}H_{12}] + 11H_2$$

The yield is very dependent on the nature of the amine. Under certain conditions the amine may, in part, end up in the anion, e.g., as the $B_{12}H_{11}NR_3^-$ anion, or in a nonionic compound of the $B_{12}H_{10}(\text{base})_2$ type. It may also end up in the cation as $[H_2B(NR_3)_2]^+$. The complete picture of the possible reactions of diborane with amines is thus a very complex one.

The reaction of B_2H_6 with ethylenediamine to give compounds which may or may not be cyclic has already received discussion (Section II, A). With dimethylaminoethanol $Me_2NC_2H_4OH$ both addition and alcoholysis occur, and the final product is the borate ester $[Me_2N(BH_3)C_2H_4O]_3B$ (*510*). With the cation $[Me_3PCH_2NMe_2]^+$ diborane forms a simple borane adduct $[Me_3PCH_2NMe_2BH_3]^+$ (*511*), the first cation of this type known.

With amines substituted by inorganic groups, different types of reactions may occur. Compounds with boron already linked to the nitrogen are not excluded. Thus, further diborane will convert the above-mentioned aminoboranes into μ-aminodiboranes (*217*).



With $B_2(NMe_2)_4$, μ-$Me_2NB_2H_5$ may likewise be formed, but the adduct $B_2(NMe_2)_4 \cdot (BH_3)_2$ is also produced, and this is thought to have a

B_4H_{10}-like structure (*225*). μ-$Me_2NB_2H_5$ will undergo isotope exchange with further diborane (*471*). In the presence of μ-$Me_2NB_2H_5$, diborane will convert piperazine $C_4H_8(NH)_2$ at 100°C to piperazinobisdiborane $C_4H_8(NB_2H_5)_2$ (*512*). With silylamines such as H_3SiNMe_2 and $(H_3Si)_2NMe$ diborane gives the BH_3 adducts, but these are decomposed irreversibly at 0°C (*76*). Trisilylamine $(H_3Si)_3N$ forms no adduct (*241*, *513*).

With hydrazine N_2H_4, reaction may lead to ignition or explosion, but even here studies of the flame have shown (*514*, *515*) that there is initially a relatively low-temperature reaction to produce a hydrazine–diborane adduct which changes by polymerization and dehydrogenation into largely uncharacterized solid products, including boron nitride (*516*), whereas radical mechanisms occur in the high-temperature region. At reduced temperatures the reaction can be made to proceed without ignition, and the original suggestion (arising from the variable composition) that a mixture of the mono- and bisborane adducts, $N_2H_4 \cdot BH_3$ and $H_3B \cdot NH_2NH_2 \cdot BH_3$, is formed (*425*), has found confirmation in the subsequent isolation of both (*97*, *99*). From the crystal structure of $N_2H_4 \cdot BH_3$, the length of the B–N bond is 1.56 Å (*101*). Although it has been claimed that $N_2H_4 \cdot (BH_3)_2$ loses hydrogen at higher temperatures without appreciable rupture of the N–N bond (*97*), the latter is not preserved when the tetramethylhydrazine analog $N_2Me_4 \cdot (BH_3)_2$ is heated (*88*). In the latter case dimethylaminoborane Me_2NBH_2 (or its dimer) and hydrogen are formed. With acylhydrazines, the reaction of diborane is normally reduction to the corresponding alkylhydrazines, but with 1,2-dibenzoylhydrazine considerable cleavage of the N–N bond has been observed (*341*). With certain salts of hydrazine, such as N_2H_5Cl in ether solution at room temperature, diborane will give a polymeric material whose infrared spectrum points to the $[N_2H_4 \cdot BH_2^+]_x$ grouping (*517*).

Diborane can react explosively with hydroxylamine and its derivatives, but forms borane adducts at low temperatures, although reaction is not always stoichiometric. The adducts of NH_2OH and $NHMeOH$ are particularly unstable and lose hydrogen below room temperature, apparently undergoing internal oxidation to give inadequately characterized products; but $Me_2N(OH) \cdot BH_3$ is much more stable thermally and can be distilled under reduced pressure at 25°C (*518*). However, it reacts destructively with additional diborane, and the boron–nitrogen bond is not strong enough to prevent the NMe_2OH from being replaced by NMe_3. The *O*-methyl derivatives of the abovementioned hydroxylamine, NH_2OMe, $NHMeOMe$, and NMe_2OMe, all give borane adducts of enhanced stability. The stoichiometry of the reactions with diborane is excellent, but on controlled heating internal oxidation again occurs to give products in which the oxygen in the form of a methoxy group is attached to the boron (*519*) (rapid heating results in explosion). The transfer of oxygen in this way is compatible with what is known of the high affinity of boron for oxygen.

Of the halogen-substituted amines, only Me_2NCl has been examined in reference to its reaction with diborane (*520*), which is reported to be complicated. Although the reaction has not been elucidated, in the light of the reactions of this amine with other boron compounds it is probable that transference of the chlorine from the nitrogen to the boron is one of the changes that occur.

Almost no information is available concerning the behavior toward diborane of ionic species derived from ammonia or the ammonium ion, and this is a considerable gap in our knowledge. However, it has recently been shown that the ionic species $Me_2NBH_3^-$ (*226*) and $Me_2N(BH_3)_2^-$ (*521*) are both converted to μ-dimethylaminodiborane.

$$Me_2NBH_3^- + B_2H_6 \rightarrow \mu\text{-}Me_2NB_2H_5 + BH_4^-$$
$$Me_2N(BH_3)_2^- + B_2H_6 \rightarrow \mu\text{-}Me_2NB_2H_5 + B_2H_7^-$$

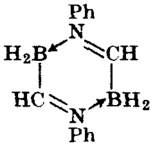
Aromatic nitrogen also forms stable links with the BH_3 group, but the aromatic ring is not attacked. The first effect of diborane on pyridine is therefore normally to form $C_5H_5N \cdot BH_3$, which is a substance of low volatility and m.p. 10°–11°C (*48*). It is rather less stable with respect to dissociation than $Me_3N \cdot BH_3$, so that the boron–nitrogen bonding is not so strong. A peculiar feature is that in diglyme solution excess diborane effects the formation not only of $C_5H_5N \cdot B_2H_6$ at 0°C, but also of $C_5H_5N \cdot B_3H_9$ at −64°C (*7*). The heats of reaction of diborane with many substituted pyridines have been measured (*522, 523*). The NMR spectra of the borane adducts have been studied (*49, 524*), and the merits of using the ^{11}B chemical shifts as a measure of donor–acceptor interaction discussed (*49*). Borazines are not usually attacked by diborane (*525*), but aminoborazines react to give borane adducts which decompose with cleavage of the exocyclic B–N bonds (*474*). Pyridine *N*-oxide C_5H_5NO is reduced by diborane (*318*), but the ultimate products have not been identified.

Diazomethane reacts with diborane at room temperature, but the reaction is unusual, in that the product is a highly linear CH_2 polymer (*526*).

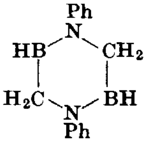
When the nitrogen is doubly bonded to carbon, the normal reaction with diborane is reduction of $>C=N-$ to $>CH-NH-$, as in the case of oximes, oxime ethers, oxime esters, and Schiff bases (Section IV, A), but additional reductions may also occur. With the ylide trimethylammonium methylide $Me_3\overset{+}{N}-\overset{-}{C}H_2$, neither adduct formation nor reduction appears to result with diborane in tetrahydrofuran, and only a limited evolution of trimethylamine occurs (*527*). This is in contrast to the reaction with ylides of phosphorus (Section VII, E) and sulfur (Section VII, G).

The triple bond $-C{\equiv}N$ is readily reduced to $-CH_2NH_2$ by diborane in ether solvents (*151*). In the absence of a donor solvent, however, the reaction proceeds differently, in that acetonitrile MeCN first gives an isolable adduct $MeCN \cdot BH_3$, which has a rather weak boron–nitrogen bond and dissociates reversibly, and which on heating decomposes by hydrogen transfer to give a number of products including 1,3,5-triethylborazine ($B_3H_3N_3Et_3$) and μ-$B_2H_5NEt_2$ (*72*, *528*). It is doubtful whether the observed reactions with HCN and $(CN)_2$ are comparable, as the products have not been characterized (*72*). With inorganic cyanides a comparable reaction has not been observed: silyl cyanides such as H_3SiCN and Me_3SiCN give the simple adducts $H_3SiCN \cdot BH_3$ and $Me_3SiCN \cdot BH_3$ (*336*) (which on heating lose SiH_4 or $SiHMe_3$, respectively, to leave polymeric BH_2CN as a glassy solid), whereas the salt NaCN gives $Na[H_3BCNBH_3]$ (*125*). For other similar reactions with ions incorporating the CN grouping, see Section II, B.

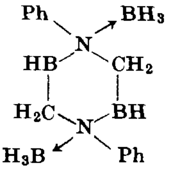
Isocyanides react differently from cyanides. With diborane at low temperatures phenylisocyanide gives, apparently, an adduct which is not isolated, but which immediately dimerizes with hydrogen migration to give a compound containing the 6-membered $(NCB)_2$ ring. Provided this is carried out in a nonpolar solvent such as anhydrous petroleum ether, the first product isolated (I) still retains two hydridic hydrogen atoms per boron atom (*71*), but in dimethyl or diethyl ether as solvent further migration of the hydrogen atoms from the boron to the carbon occurs, and the product obtained (II) retains only one hydridic hydrogen atom per boron atom (*529*), being capable of forming a bisborane adduct (III) with further diborane.



(I)



(II)



(III)

With metal cyanates in an ether, diborane gives borane adducts (*152*). With organic isocyanates (at least with phenyl isocyanate) reduction occurs (*318*), but the products have not been specified. Diborane does not react chemically with silyl isocyanate (not even to form an adduct), and is recovered unchanged; however, it catalyzes the polymerization of the silyl isocyanate (*483*).

With inorganic thiocyanates diborane gives a borane adduct, but the infrared spectrum accords better with a structure in which the BH_3 is linked to the sulfur rather than the nitrogen (*125*). There appear to be no reports of the behavior of diborane with organic thiocyanates or isothiocyanates.

It would be expected that diborane reacts with most compounds containing multiple bonds between nitrogen atoms. There is however no information published regarding its behavior with N_2F_2, while N_2O is reported to be inert (*530*). With azobenzene reduction accompanied by rupture of the N=N bond occurs (*151*), but not in the case of azoxybenzene (*318*). With hydrogen azide in ether solution diborane reacts at –20°C essentially according to the equation (*531*)

$$B_2H_6 + 6HN_3 \xrightarrow[-20°C]{Et_2O} 2B(N_3)_3 + 6H_2$$

but $BH(N_3)_2$ and $BH_2(N_3)$ are formed at the same time. The reaction is completed at room temperature. With excess HN_3 an oil having the composition $HB(N_3)_4$ is obtained. With inorganic azides azidoborane $H_2B(N_3)$ is formed (*153*), but only in the case of the lithium salt has the simple borane adduct $LiN_3 \cdot BH_3$ been shown to occur as an intermediate.

With compounds containing nitrogen linked to phosphorus, diborane forms adducts in which the boron is preferentially linked to the phosphorus (Section VII, E). An exception is the ylide $Ph_3\overset{+}{P}–\overset{-}{N}Ph$, which apparently gives the adduct $Ph_3PN(BH_3)Ph$ (*103*). No information is available regarding the behavior of diborane with nitrogen linked to arsenic or antimony.

Our knowledge about the reactions of diborane with nitrogen compounds containing oxygen is incomplete, but it has been shown that N_2O (*530*) does not react. Likewise NO is inert at room temperature, but gives H_2, N_2O, and H_3BO_3 at 90°C (*530*). When sparked, B_2H_6–NO mixtures give N_2 and either H_2 plus B_2O_3 or H_3BO_3 (*532*). The absence of OH lines in the spectrum obtained from the reaction of diborane-rich mixtures would indicate that the boron of the diborane reacts with the nitric oxide so rapidly as to be completely oxidized before the hydrogen can react. However, with other procedures there is evidence that the adduct $BH_3 \cdot NO$ can be formed as a transitory species (*530, 533*). No information is available for the behavior of diborane with the other oxides of nitrogen. With "$(NaNO)_x$"—actually *cis*-$Na_2N_2O_2$—the adduct $Na^+[ON \cdot BH_3]^-$ is formed (*162*).

With organic compounds containing nitrogen linked to oxygen, the general rule is that reduction occurs if the nitrogen is in the trivalent state, but not if it is in the pentavalent state. This suggests that reaction occurs by way of an addition complex, for the formation of which the presence of a lone electron pair on the nitrogen atom is required (an observation which also accords with the inertness of N_2O cited above). Thus, nitroso compounds are attacked and converted to amines (*356*), while this is not true of nitro compounds (*318*). It is even possible to conduct reactions involving B_2H_6 in nitrobenzene solution without interference from the solvent (*523*, *534*). This inertness toward diborane is shared by azoxybenzene (*318*). That nitronates (*357*) are however reduced, although the nitrogen is in its maximal valency state, implies that the mechanism here is different and doubtless associated with the negative charge on the anion. Pyridine *N*-oxide constitutes another exception, its nitrogen being reduced to the trivalent state (*318*). With compounds containing the =N–OH or =N–OR grouping, such as oximes, oxime ethers, and oxime esters (*322*), reaction occurs reductively to produce amines via the corresponding N-substituted (or presumably N,O-disubstituted) hydroxylamines, which may be isolable. Indeed, for certain oximes (e.g., that of benzophenone) the hydroxylamine actually constitutes the stage at which the reaction terminates. It thus follows that diborane reacts reductively with some but not all nitrogen compounds containing the NHOH group. The available evidence indicates that reaction with the NHOR grouping occurs more readily, and that the product is invariably the amine.

Diborane gives borane adducts with compounds containing nitrogen linked to sulfur, but the boron is preferentially attached to the sulfur (Section VIII, G). Evidence is very limited, however, and not even N_4S_4 has been investigated in this respect. There are no reports of studies with compounds containing nitrogen linked to selenium or tellurium.

Diborane reacts with gaseous NF_3 on warming to give an uncharacterized yellow solid, but no new volatile products (*535*). With tetrafluorohydrazine N_2F_4 at about 150°C a complex reaction occurs producing a mixture of fluoroborazines, BF_3, $H_3N \cdot BF_3$, B_5H_9, H_2, and N_2 (*536*). Clearly the high affinity of boron for fluorine promotes hydrogen–fluorine exchange with the nitrogen. Presumably reaction would also occur with difluorodiazine N_2F_2, but this has not been put to experimental test. Compounds containing nitrogen linked to other halogens would also be expected to react with diborane, but only in the case of dimethylchloramine Me_2NCl (*520*) is experimental confirmation available, and even here the products have not been identified. The reaction is stated to be complicated.

E. Reaction with Compounds of Phosphorus, Arsenic, Antimony, and Bismuth

No reports are available concerning the behavior of diborane with elementary phosphorus, arsenic, antimony, or bismuth. Although diborane may on occasions be cleaved asymmetrically by compounds of phosphorus and arsenic (see below), such cases are much rarer than with nitrogen compounds, and the interest here is focused mainly on the formation and properties of adducts of substituted phosphines and arsines. Information regarding the behavior with antimony compounds is scant, and totally lacking in the case of bismuth compounds.

The existence of phosphine adducts of undissociated diborane has not been established, although numerous borane adducts of phosphines have become known since the first of these, phosphine borane $H_3P \cdot BH_3$, was reported in 1940 (*537*). It has since been shown to be monomeric (*24*, *538*), and does not exchange hydrogen as shown by a study of its partly deuterated derivatives (*539*). From kinetic data for the B_2H_6–PH_3 reaction the following mechanism of formation has been proposed as possible (*540*).

$$B_2H_6 + PH_3 \rightleftharpoons PH_3 \cdot BH_3 + BH_3$$
$$BH_3 + PH_3 \rightleftharpoons PH_3 \cdot BH_3$$

However, it must be stated that the kinetic evidence does not exclude the formation of the diborane adduct $H_3P \cdot B_2H_6$ as the initial product. The same is true for the faster reactions of the methylphosphines (*541*). As reported for the amine boranes (Section VII, D), boranes of the substituted phosphines may be prepared by reacting the phosphine with gaseous diborane direct, or with diborane prepared *in situ* in monoglyme solution from $NaBH_4$ plus I_2 (*307*, *487*).

One of the unexpected features about the borane adducts $R'R''R'''P \cdot BH_3$ is their enhanced stability relative to that of the borane adducts of the corresponding amines. Although the heats of reaction of a number of phosphines with diborane have been measured (*542*), because of lack of information concerning the heats of sublimation and solution of the products no precise numerical comparison of the strengths of boron–phosphorus and boron–nitrogen bonds can be given at present, but in every case so far studied the phosphorus compound has the lower dissociation pressure. Solid $H_3P \cdot BH_3$ is formed from PH_3 and B_2H_6 at

0°C (*540*), at which temperature its saturation pressure is 200 Torr (*537*). Its vapor is extensively dissociated at room temperature (*540*), but $Me_3P \cdot BH_3$ is reported to be essentially undissociated in the vapor phase at 200°C (*18*). Also the equilibrium

$$Me_3N \cdot BH_3\ (s) + Me_3P\ (g) \rightleftharpoons Me_3P \cdot BH_3\ (s) + Me_3N\ (g)$$

is stated to lie well over to the right (*18*). Although the amine is displaced by the corresponding phosphine (*543*), it is thus not feasible to displace the phosphine completely by the amine, and if this is attempted other compounds are liable to be formed in which the boron still remains linked to the phosphorus (*65*).

$$2H_3P \cdot BH_3 + NH_3 \rightarrow NH_4[PH_2(BH_3)_2] + PH_3$$

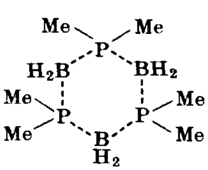
Because the B–P bonding in the simple phosphine boranes is stronger than would be expected for σ bonding alone (*33*), it has frequently been suggested that additional π bonding involving the 3*d* orbitals of the phosphorus is present (*32*). However, there is no unambiguous evidence for this suggestion. Rather, recent theoretical considerations imply that if there is π bonding in $H_3P \cdot BH_3$, the effect must be small (*544*). Moreover, π bonding would effect shortening of the P–B bond, but in $Me_4P_2 \cdot 2BH_3$ its length is 1.951 Å, which is actually 0.124 Å *longer* than the single P–C bond in the same compound (*89*). Also the barrier to internal rotation about the B–P bond in $F_3P \cdot BH_3$ is only 3.24 kcal mole^{-1} (*27*), which is hardly compatible with appreciable π bonding [that for the B–N bond in $H_3N \cdot BH_3$ has been calculated as 2.47 kcal mole^{-1} (*500*)]. Different arguments against π bonding have been voiced by others (*19*). A clue to the true state of affairs doubtless lies in the observation of Burg, who noted that the P–H stretching frequencies in the phosphines increase when the phosphines are coordinated to borane (*545*), which is the opposite effect to that observed with the N–H stretching frequencies of amines. This implies that additional energy is liberated by the three phosphine bonds on coordination of the phosphorus atom, hence increasing the reaction energy, whereas with amines it will be depressed. These effects will account for a large part, if not all, of the enhancement in coordination energy observed with phosphines. In other words, the anomalous trend in the dissociation energies of the B–N and B–P bonds could be compatible with a normal trend in the true bond energies as reflected by other bond properties. The stretching force constants do, in fact, show the normal trend, having been calculated as 2.948 mdyne Å^{-1} for the B–N bond in $H_3N \cdot BH_3$ (*546*) and 1.958 mdyne

Å^{-1} for the B–P bond in $H_3P \cdot BH_3$ (*26*). The point warrants further investigation, but it is already apparent that there is no clear case for supplementary π bonding in the phosphine boranes. [The B–H stretching frequencies are only slightly lower in $Et_3P \cdot BH_3$ than in $Et_3N \cdot BH_3$ (*50*).] As would be expected, diborane exhibits a progressively decreasing tendency to form stable borane adducts with arsines and stibines, so that there is no anomaly here. Already in the case of arsenic, arsine borane $H_3As \cdot BH_3$ is not isolable, but as the arsine is progressively methylated adducts of increasing stability are formed (*41*).

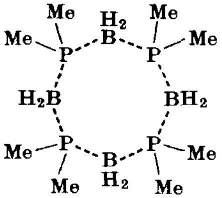
In confirmation of the above considerations, a further example of the importance of changes in the phosphine molecule itself is provided by the exceptional stability of $HF_2P \cdot BH_3$ relative to $H_3P \cdot BH_3$ and $F_3P \cdot BH_3$ (*25*), which has been ascribed to F···H···F interactions. And here we remark that such interactions would be expected to increase and thus liberate energy on coordination of the phosphorus atom, which change would doubtless be associated with a reduction in the F···H distances.

In general, the stability of the borane complex with phosphines is exceptionally sensitive to the nature of the substituents attached to the phosphorus, since these affect not only the Lewis base strength but also the steric requirements of the phosphine. Any change which increases the *p* character of the phosphorus lone pair or permits a closer approach of the boron atom to the phosphorus atom will tend to strengthen the interaction. A case in point is the stabilization of the complex of tricyclopropylphosphine $(c\text{-}C_3H_5)_3P \cdot BH_3$ relative to that of triisopropylphosphine $(i\text{-}C_3H_7)_3P \cdot BH_3$ (*547*).

NMR techniques have been applied to the study of the B–P bond (*31*, *548*) and have confirmed that it is a true coordination bond. Moreover they reveal that in benzene solution at room temperature $Me_3P \cdot BH_3$ does not undergo intermolecular exchange reactions with excess of the starting materials. This is in contrast to the behavior of $Me_3N \cdot BH_3$ (*492*). Phosphine boranes have also been studied with regard to other physical properties, including their magnetooptical properties, magnetic susceptibilities, and molecular refractions (*53–55*, *549*). The temperatures of decomposition (as distinct from dissociation) have been studied for the borane adducts of the trialkyl compounds of phosphorus, arsenic, and antimony (*550*). Phosphine boranes with hydrogen linked to the phosphorus, such as $HMe_2P \cdot BH_3$, lose molecular hydrogen around 150°C to give phosphinoboranes of the type $(Me_2PBH_2)_n$ (*32*), analogous to the aminoboranes (Section VII, D), except that here *n* is usually 3 or 4 or a high number. In the latter case the product has the properties of a nonvolatile polymer, and is probably chainlike, but the trimer and tetramer are known to be cyclic (*245*, *551*). In neither case are the rings



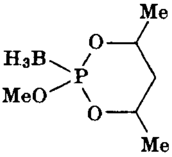
Trimer



Tetramer

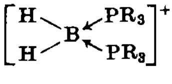
planar. Arsine boranes lose H_2 even more readily to form similar ring compounds (*41*). The exact nature of the P–B and As–B bonding is not known, but the P–B bond lengths are appreciably greater than those of the single P–C bonds, i.e., respectively, 1.935 and 2.08 Å as against 1.84 Å, suggesting an order of less than unity. Nevertheless, these compounds, which can also be prepared by interacting B_2H_6 with the appropriate phosphine or arsine at elevated temperatures, are surprisingly stable, both chemically and thermodynamically. The B–H bonds have virtually lost their hydridic character and have become very resistant to hydrolysis [even toward 4 M HCl at 100°C (*32*)], yet within experimental error retaining the same HBH bond angle (*245*) as in diborane; while in the absence of air the compounds will withstand prolonged heating to 250°C or more (200°C in the case of the arsenic compounds) without appreciable decomposition. The results of heating B_2H_6 with PH_3 or AsH_3 is a nonvolatile solid, $(BPH_x)_n$ or $(BAsH_x)_n$, respectively, where $x < 4$ (*32*, *41*), and the loss of more than one molecule of hydrogen from the simple adduct suggests a parallel with the B_2H_6–NH_3 system, which gives $(BNH_2)_n$ as well as $(BNH_4)_n$. Some observations (*550*) suggest that adducts of the type $R_3P \cdot BH_3$ can lose alkane RH on heating, which, if established, would be a further parallel with the nitrogen analogs. Certainly the silane $SiMe_3H$ is split off >80°C from $(Me_3Si)Et_2P \cdot BH_3$ to leave $(Et_2PBH_2)_3$ (*338*). Moreover, the Si–P bond of Me_3SiPEt_2 is cleaved by B_2H_6. The same is true of $(Me_3Si)_3P$ (*78*), in contrast to $(Me_3Si)_3N$ (*513*), which does not react. The silylphosphine boranes are typical adducts, and even the simplest of them, $H_3SiPH_2 \cdot BH_3$, is not ionic (*39*, *552*). The germyl compound $H_3GePH_2 \cdot BH_3$ is similar (*40*). They, however, exchange hydrogen between the boron sites and the silicon or germanium sites, respectively (*40*, *482*). The adducts $Si_2H_5PH_2 \cdot BH_3$ and $(H_3Si)_2PH \cdot BH_3$ also exist and give, respectively, $(PH_2BH_2)_n$ and $(PHBH)_n$ on heating (*553*).

Phosphines with more electronegative substituents may also form borane adducts with B_2H_6. Foremost among these is PF_3 which, in spite of its poor basic powers, gives $F_3P \cdot BH_3$ (*554*). The adduct, which is formed at room temperature under pressure, has a stability similar to that of borane carbonyl H_3BCO, which it also resembles in other ways. Its reaction with oxygen has been studied (*555*). Here again, theoretical calculations show that the P–B bond is essentially σ with little contribution from π bonding (*556*). The much higher stability of $HF_2P\cdot BH_3$ (*25*) has already been commented upon (see also Section II, A). The highly volatile complex $(CF_3)_2FP\cdot BH_3$ also exists in spite of the weak basic powers of $(CF_3)_2PF$, in which the fluorine atom attached to the phosphorus has an enhanced reactivity. Accordingly, in addition to adduct formation, $(CF_3)_2PF$ undergoes other reactions on treatment with B_2H_6 at elevated temperatures or even at 0°C, whereby fluorine is transferred to the boron with the formation of BHF_2, BF_3, $(CF_3)_2PH$, $[(CF_3)_2PBH_2]_3$, and $[(CF_3)_2PBH_2]_4$ (*557*). Trialkylphosphites $(RO)_3P$ and trisdialkylaminophosphines $(R_2N)_3P$ also readily give the adducts $(RO)_3P\cdot BH_3$ and $(R_2N)_3P\cdot BH_3$, for which it has been shown that the boron is everywhere linked to the phosphorus and not to oxygen or nitrogen (*35*, *53*, *55*, *548*, *558–560*). The same is true for the adducts formed with alkoxychlorophosphines, namely, $Cl(RO)_2P\cdot BH_3$ and $Cl_2(RO)P\cdot BH_3$ (*561*). The precise geometry of the adduct schematically represented as

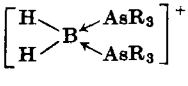


and involving the cyclic phosphite 2-methoxy-*cis*-4,6-dimethyl-1,3,2,-dioxaphosphorinane has been established (*562*). The boron is also linked to phosphorus in the BH_3 adducts with $Me(Et_2N)P(OCHMe_2)$ (*563*) and $Me_2PCH_2NMe_2$ (*511*), although the latter compound can also form a stable diadduct, a power apparently not shared by bases in which the phosphorus and nitrogen atoms are adjacent. For borane adducts of compounds containing both phosphorus and sulfur, such as Me_2PCH_2SMe (*511*), the boron is linked to the phosphorus rather than to the sulfur.

Other less simple reactions which diborane may undergo with substituted phosphines and arsines at elevated temperatures to a large extent have their parallel with reactions with the amines. Thus, cations of the type



and



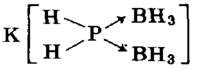
are readily formed (*127, 413, 509*). At the same time some of the diborane condenses to form anions such as $B_{12}H_{12}^{2-}$, $B_{12}H_{11}(PR_3)^-$, and $B_{12}H_{11}(AsR_3)^-$, as well as the neutral species $B_{12}H_{10}(AsR_3)_2$. Compounds such as $[H_2B(PMe_3)_2]_2[B_{12}H_{12}]$ and $[H_2B(AsMe_3)_2][B_{12}H_{11}AsMe_3]$ have been proposed as pyrotechnics (*564*). No such compounds have been reported for substituted stibines. In fact, even under conditions sufficiently mild for Ph_3As to form $Ph_3As \cdot BH_3$ as an isolable adduct, both Ph_3Sb and Ph_3Bi are reduced by B_2H_6 (*42*).

Bisphosphines of the type HPhP–R–PHPh (*565*) form bisborane adducts, while the sublimable bisborane adduct which $Me_2PC_2H_4PMe_2$ forms with diborane decomposes on stronger heating to $(Me_2PBH_2)_3$ and $(Me_2PBH_2)_4$ (*566*). In contrast to compounds of the type $R_2PNR'_2$ incorporating a P–N bond, diphosphines containing the P–P bond give diadducts. That from P_2H_4 is probably $P_2H_4 \cdot 2BH_3$, although cited as $P_2H_4 \cdot B_2H_6$ (*567*). $Me_4P_2 \cdot 2BH_3$ is much better characterized and has three conformational isomers of known structure (*89*). Like the corresponding adduct of tetramethylhydrazine it decomposes on heating. The

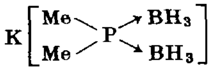
$$Me_4P_2 \cdot 2BH_3 \xrightarrow{220°C} 2Me_2PBH_2 + H_2$$

Me_2PBH_2 is obtained as a mixture of the trimer and tetramer (*88*). The fluoride P_2F_4 appears to give only $F_4P_2 \cdot BH_3$ with diborane, no evidence for a diadduct having been found (*90*), while the chloride P_2Cl_4 is reduced by diborane to unidentified yellow-orange solids (*568*). Tetrakis(dimethylamino)biphosphine $(Me_2N)_4P_2$ forms a bisborane adduct with diborane, which can be recrystallized from petroleum ether and on heating first begins to decompose at 132°C (*92*).

When the hydrogen of a phosphine has been partly replaced by a metal, as in potassium phosphinide and dimethylphosphinide, KPH_2 and $KPMe_2$, a facile reaction with diborane results in a bisborane ionic product in which the phosphorus in the anion is 4-coordinate (*569*).



$K[H_2P(BH_3)_2]$



$K[Me_2P(BH_3)_2]$

The products are very reactive, and react with HCl or O_2 at room temperature. Diborane will also effect the coordination of up to four borane molecules to the P_4O_6 molecule, but each successive BH_3 group is held less tenaciously, and the existence of the tetraadduct is only demonstrable by equilibrium measurements in solution (*69*).

Because of their stability, there is little tendency, in general, for diborane to react with compounds of pentavalent phosphorus. But the reduction of phosphine oxides (*342, 343*) to phosphines constitutes an exception, and a further exception is provided by the ylides such as alkylidene triphenylphosphoranes, of which the simplest is $Ph_3P=CH_2$ or $Ph_3\overset{+}{P}-\overset{-}{C}H_2$. This compound, unlike the nitrogen analog $Me_3\overset{+}{N}-\overset{-}{C}H_2$ (Section VII, D), gives a borane adduct which may be written $Ph_3P\rightarrow CH_2\rightarrow BH_3$ or $Ph_3\overset{+}{P}-CH_2-\overset{-}{B}H_3$ (*102*). The product is stable toward water, but is a strong reducing agent. On refluxing in nonpolar solvents it rearranges first to $Ph_3\overset{+}{P}-\overset{-}{B}H_2-CH_3$ and then to $Ph_3P\cdot BH_3$ with the evolution of PPh_3 and BMe_3 (*570*). Adducts from derivatives of the type $Ph_3\overset{+}{P}-\overset{-}{C}HR$ have also been prepared (*103*), while the ylide $Me_3SiCPMe_2PMe_3$ forms a bisborane adduct (*571*). The arsenic-containing ylide $Me_3\overset{+}{As}-\overset{-}{C}HSiMe_3$ also gives a borane adduct with B_2H_6 (*104*).

Diborane gives a blue coloration with phosphomolybdic acid, which has been proposed as the basis of a microanalytical method for the determination of diborane and its derivatives (*469*).

F. Reaction with Oxygen and Its Compounds

Diborane burns in oxygen or air liberating 517.6 kcal $mole^{-1}$ on conversion to boric oxide and water, or 531.6 kcal $mole^{-1}$ on conversion to boric acid, as calculated from heats of formation (*572*). The heat of combustion, viewed in terms of heat per unit weight of fuel, is extraordinarily high and is exceeded only by the corresponding heats per unit weight for H_2, BeH_2, and BeB_2H_8. Consequently, diborane and its derivatives have been much investigated as potential high-energy fuels and propellants; but to obtain the maximum energy the boric oxide formed needs to be in the condensed phase, and because of this and other technical limitations and difficulties, neither diborane nor any other boron compound has found any large-scale use for either purpose. In a welding torch diborane will give a flame temperature of over 3000°C.

In contrast to higher boranes, pure B_2H_6 is stable toward oxygen at room temperature. The flash point (for B_2H_6 of 99% purity) is stated to be 130°–135°C and a little higher in air (145°–150°C) (*573*), and is moreover not lowered by packing the reaction vessel with glass tubes. A slow reaction is however observable at temperatures as low as 110°C (*574*). Kinetic studies of the B_2H_6–O_2 reaction above 120°C have been carried out (*575*). No direct action is observed below 110°C, so that it is to be suspected that occasional reports of detonation of mixtures at room temperature after prolonged standing arise from other causes such as the accumulation of oxygen-sensitive products from a slow spontaneous decomposition of the diborane. This explanation is the more likely because the presence of hydrogen both inhibits these explosions (*573*) and inhibits the decomposition of B_2H_6 (*2*, *576*).

The reaction with oxygen in both explosion and combustion has been much studied. Of the two conceivable reactions with excess O_2, the

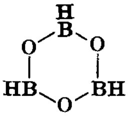
$$B_2H_6 + 3O_2 \rightarrow B_2O_3 + 3H_2O$$
$$B_2H_6 + 3O_2 \rightarrow 2H_3BO_3$$

former is favored by the bulk of the evidence.

Mixtures of B_2H_6 and O_2 containing between 2.0 and 27.6% of the former can be detonated on sparking (*577*). Detonation velocities up to 2.6 km sec^{-1} have been observed (*578*), a very high value. In early work on the explosion reaction, Price (*573*) recognized first, second, and third explosion limits, the third limit being sensitive to the diameter of the reaction vessel. He also reported the inhibiting effects of H_2, N_2, and excess O_2, respectively. The effect of many other inhibitors has since been studied, butadiene and toluene having been found very effective (*579*), as is iron pentacarbonyl (*580*). Small proportions of nitrogen dioxide (1.2%) actually reduce the explosion temperature to as low as 74°C, but larger amounts increase it again (*581*). Nitric oxide even effects immediate explosion at room temperature. The reaction mechanism of the B_2H_6–O_2 reaction is imperfectly understood, but it is generally agreed to be typical of a branching-chain free-radical mechanism. The evidence with additives implies that the chain-branching step is bimolecular and the chain-breaking step termolecular. The radical involved in the chain-branching–chain-breaking competition may be BH_3O_2, as suggested by Gobbett and Linnett (*575*), or B_3H_7O, as put forward by Skinner and Snyder (*579*), both species having previously been proposed by other workers to be present as intermediates (*582*). The species BH_3O_2 has a parallel in compounds of the type $R_3B \cdot O_2$ found by Bamford and Newitt to be the initial products in the reaction of oxygen with trialkylboranes (*583*). If B_3H_7O is responsible for the above-mentioned competition, then the suggested mode of formation (*579*) is less likely than the step

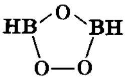
$$B_3H_9 + O_2 \rightarrow B_3H_7O_2 + H_2$$

since the slow oxidation reaction is of order 1.5 with respect to the diborane concentration (*582*), while the floating concentration of B_3H_9 is also proportional to $[B_2H_6]^{1.5}$ (*2*). This, surely, is more than coincidence. The low value of $[B_3H_9]$ would also explain why the rate is independent of $[O_2]$ for measurable oxygen concentrations (*582*). Of the incompletely oxidized boron products, one which has been definitely identified by mass spectroscopy in the explosion reaction is boroxine $H_3B_3O_3$ (*584*).



Boroxine

Both in the explosion reaction (*582*) and in mixtures subjected to an electric discharge (*585*) the species $H_2B_2O_3$ has been demonstrated to be present. This has been ascribed the structure:



Both species occur in the photochemical oxidation of diborane by oxygen (*586*), $H_2B_2O_3$ arising from a slow initial reaction and $H_3B_3O_3$ from an explosive reaction. A proposed intermediate in their formation is B_2H_4O, but positive evidence for this is lacking. In fuel-rich explosions, H_2 is a major product and may account for virtually all the hydrogen present, except that in very rich mixtures a significant proportion may remain in the solid reaction products (*587*). The appearance of molecular hydrogen rather than H_2O is indicative of the much higher affinity for oxygen displayed by the boron. For this reason, no doubt, OH radicals have not been detected spectroscopically in chemical detonations, although they appear in the flash-photolyzed reaction (*588*). Other studies of the explosion reaction include the variation of the detonation rate (*577*), which is predictable from thermodynamic data for mixtures containing up to 12% B_2H_6, but becomes unpredictably high for richer mixtures, possibly because of condensation of products just behind the wavefront.

Diborane flames have also received study, and as the information is not easily accessible, it will be necessary to summarize the chief information gained. Early work showed that B_2H_6–O_2 mixtures containing 0.9–98% B_2H_6 will support a flame, so that the flammability limits are exceedingly wide (*578*). The corresponding range for B_2H_6–air mixtures is 0.8–87.5% by volume, according to a particularly valuable study by

Berl and Renich (*589*). However, the nondetonating region of flammability on the fuel-lean side is seen to be narrow, being restricted to the range 0.9–2.0% diborane. Flame speeds are exceedingly high, the highest so far measured, the quenching diameter falling to a small fraction of 1 mm (*590*). In the early work speeds of 100 m sec^{-1} were reported (*578*), namely, 20 to 100 times those of hydrocarbon flames, but these may refer to mixtures just inside the detonating region, since detonations sometimes occurred after the flame had travelled a limited distance. For B_2H_6–air mixtures at 25°C, the maximum burning velocity observed is about 5 m sec^{-1} (*589*), more than a power of 10 above the rate for C_3H_8–air mixtures. Although small quantities inhibit slightly (*591*), the addition of about 6% B_2H_6 to propane or isobutane effects a marked increase in the burning velocity of the gas (*592*). For larger additions, a selective burning of the diborane becomes apparent. With propane containing 15% admixed B_2H_6, burning velocities show two maxima, one where the proportion of air is close to stoichiometric for the B_2H_6 alone, and one where it is about stoichiometric for the total fuel (*589*). At the first maximum the propane is behaving mainly as a diluent reducing the temperature of the flame, although it undergoes some cracking. But as the proportion of oxygen rises, increasing oxidation of the propane is accompanied by a reduction in the flame velocity until the minimum between the two maxima is reached. This may be regarded as *prima facie* evidence that at least one oxidation product of the hydrocarbon is acting as an inhibitor of the B_2H_6–O_2 reaction. Such mixtures do not follow the Spalding rule (*593*) concerning flame speeds for mixtures. That the diborane is burnt before much oxygen is consumed by the hydrocarbon is doubtless a reflection of the higher affinity for oxygen possessed by boron relative to carbon, and is also manifest in the structure of flames of B_2H_6–C_3H_8 mixtures (*589*). These manifest three zones, a lower sky-blue luminous cone or region of diborane oxidation (emitting the α bands of BO) superposed by a nonluminous zone, above which is situated the luminous hydrocarbon-combustion mantle. The latter emits the green so-called "fluctuation" bands of B_2O_3. Even though some cracking and partial oxidation of the hydrocarbon must occur in the first zone, it is clear from this that the organic species present burn much more slowly than the diborane. Similar distinct zones are apparent when B_2H_6 is burnt without added hydrocarbon, save that with flames near the fuel-lean limit the temperature of the final zone may not be hot enough to effect the emission of the green fluctuation bands. In these flames the boron is burning before the hydrogen. Further, experimental evidence of a variety of kinds indicates that the combustion of the boron is virtually complete before any water

$$B_2H_6 + 1\tfrac{1}{2}O_2 \rightarrow B_2O_3 + 3H_2$$

is formed. Indeed, with flames near their B_2H_6-lean limit, even in spite of the large excess of oxygen, a considerable proportion of molecular hydrogen is present just downstream of the luminous reaction zone and is only oxidized subsequently (*589*). Consequently, there is no evidence that any water is formed soon enough to hydrolyze unburnt diborane.

The sum of the evidence is still to leave even the nature of the products of diborane flames inadequately known, especially on the diborane-rich side. Consequently, no convincing oxidation mechanism covering the reaction within the flame is known to science. Berl (*485*) has made the most useful review to date of the available knowledge and tentatively suggested possible mechanistic pathways. The gaseous products present in the flame include BH, B, BO, B_2O_2, B_2O_3, BO_2, HBO_2, H_3BO_3, H_2, OH, and H_2O, of which only OH has not been observed. Some of these may also be present as condensed species. There is reason to believe that the following additional gaseous species are probably present in the flame: BH_3, B_3H_9, BH_3O_2, $B_3H_7O_2$, BHO, and $(BHO)_3$. For these, confirmation is at present lacking. Yet other species are not excluded. The reaction system is therefore much more complex than the hydrocarbon–oxygen reaction system. The intrusion of the formerly unsuspected species BO_2(g) is to a considerable degree responsible for reducing the temperature of the flame (*485*) and, hence, the impulse achievable from diborane and other borane fuels, though this is not the only reason that these fuels have fallen below the expected performance.

The light emitted in the chemiluminescent reaction between B_2H_6 and both molecular and atomic oxygen has been studied (*594*). The products of the reaction with atomic O have also been investigated (*595*). This reaction occurs at room temperature and probably well below. The photochemical decomposition of N_2O was used as a source of oxygen atoms. The initial products are confined to H_2, B_4H_{10}, B_5H_9, and a white solid of formula $(BHO)_n$. The initial step is apparently

$$B_2H_6 + O \rightarrow BH_3O + BH_3$$

but there is a faster reaction which competes for the oxygen atoms and

$$B_4H_{10} + O \rightarrow BH_3O + B_3H_7$$

keeps down the concentration of B_4H_{10}.

There is no information regarding the reaction of diborane with ozone.

Turning now to reactions with oxygen compounds, the first observation which must be made is that, notwithstanding the two lone pairs of electrons normally present on the oxygen atom, the formation of stable borane adducts by diborane does not dominate the overall picture here as it does with nitrogen and phosphorus compounds (or even to some extent with sulfur compounds). There are two main reasons for this. First, in most cases other more extensive reactions usually occur, even at room temperature. Second, even with compounds which undergo such reactions either not at all or only slowly (e.g., ethers), the donor powers toward borane of oxygen are so far depressed relative to those of nitrogen, that the borane adducts are too unstable to be isolated at room temperature, although frequently they can be shown to be present in solution. [But if the borane is already part of an adduct, as in $Me_3N \cdot BH_3$, $C_5H_5N \cdot BH_3$, or $Et_3P \cdot BH_3$, there is spectroscopic evidence that hydroxy compounds such as alcohols and phenols will form hydrogen bonds with the borane moiety, the latter acting as proton acceptor (*596*).]

In its reaction with H_2O, diborane is very rapidly hydrolyzed completely in a highly exothermic reaction, the heat of which has been accurately measured (*597*). A sixfold volume of hydrogen is liberated according to the equation

$$B_2H_6 + 6H_2O \rightarrow 2H_3BO_3 + 6H_2$$

and until very recently all attempts to identify any intermediates in the reaction proved fruitless. The initial step is probably the formation of an adduct, and $H_3B \cdot OH_2$ was proposed (*21*). But definite evidence is now claimed for the existence at –130°C of $B_2H_6 \cdot 2H_2O$ (*598*), which one suspects to be of the form $[BH_2(OH_2)_2]^+[BH_4]^-$, although it could be $H_3B \cdot OH_2$. It is difficult to avoid the assumption that in the hydrolysis reaction the hydrogen is liberated through successive replacement of hydrogen atoms by hydroxyl groups, yet no partially hydroxylated derivatives have been isolated in the reaction of a small amount of water with a large excess of diborane (*21*), where the products are only H_3BO_3 and H_2 with unchanged B_2H_6. It follows that any partially hydroxylated derivatives formed must disproportionate very rapidly into boric acid and diborane. Nevertheless, hydrolysis of B_2H_6 with ice at –80°C does not proceed to completion, but yields only $4H_2$. The B_2H_6–H_2O reaction is first order with respect to $[H_2O]$ and order 0.5 with respect to $[B_2H_6]$ (*21*).

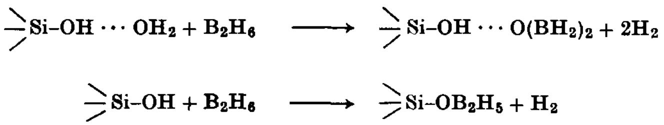
Under strongly acid conditions (8 *M* HCl) hydrolysis yields only $2H_2$ at –75°C, the remaining $4H_2$ being liberated on warming to above –20°C (*599*, *600*). This has been interpreted in terms of the formation and subsequent decomposition of aquated BH_2^+, the ionic species $[BH_2(OH_2)_2]^+$ being the most probable. Under strongly alkaline conditions hydrolysis yields only a limited amount of hydrogen, and the principal product is a tetrahydroborate, together with some metaborate

(*468, 600*). A combination of the following equations may explain the products.

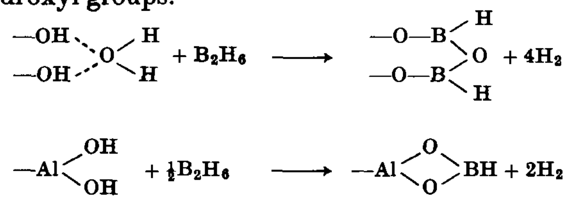
$$2B_2H_6 + 4OH^- \rightarrow 3BH_4^- + B(OH)_4^-$$
$$B_2H_6 + 2OH^- + 2H_2O \rightarrow BH_4^- + B(OH)_4^- + 2H_2$$

The ion $BH(OH)_3^-$ has been considered as another product of this reaction, but attempts to detect it from the ^{11}B NMR spectrum failed (*600*). The reaction of B_2H_6 with alkaline D_2O has also been studied (*601*). The H_2 liberated is not significantly contaminated with HD. Of the two possible mechanisms, the results favor that involving asymmetric cleavage through coordination, as originally suggested by Parry and Edwards (*602*).

After earlier studies with "bound water" of silica gel (*603*) and silica–alumina catalysts (*604*), the reaction of diborane with the water of constitution of various hydrated inorganic solids was studied on a quantitative basis (*605*). For every molecule of B_2H_6 consumed, H_2O of crystallization was considered to liberate two molecules of H_2 and OH groups only one (complete hydrolysis would have liberated six). This is explained for the example of silica gel by the changes:



The concentration of OH groups on the surface has been measured by means of the B_2H_6 hydrolysis effected (*606*). It has moreover been claimed that the spectroscopic properties of the surface in the infrared region differ according to whether BH_2 or BH_3 groups are on the surface (*607*). Later workers have however concluded that the above reaction does not permit the making of a distinction between H_2O molecules and silanol groups in silica gel (*608*). Still later, other workers found that frequently more than two molecules of H_2 were liberated for every molecule of B_2H_6 consumed, and concluded that the figure was >2 for hydration water and $\leqslant 2$ for silanol groups (*609, 610*). According to this view, terminal B_2H_5 groups are not formed, only $>O:BH_3$, $-BH_2$, and $>BH$ terminal groups, the latter arising from hydration water or from adjacent hydroxyl groups.



From what is known of the chemistry of diborane, it must be admitted that OB_2H_5 groups are rather unlikely; and still more difficult to accept is the more recent suggestion that the surface of γ-alumina contains O^{2-} ions which coordinate weakly with diborane to produce linear polyboranes (*611*). But it cannot be claimed that the differences between the various opinions have been finally resolved. However, three different $\gt BH$ surface structures prepared by another method have now been spectroscopically recognized (*612*). Certainly treatment with diborane enhances the catalytic activity of surfaces of silica–aluminas through partial hydrolysis of the B_2H_6, and a useful procedure has been published (*613*).

With alcohols adducts of formula $B_2H_6 \cdot 2ROH$ are formed at low temperatures (*598*), as apparently with water. Diborane undergoes alcoholysis at ordinary temperatures, but the release of hydrogen is much less violent than in hydrolysis. By comparison with water, the reaction may be rather sluggish, especially in the later stages. With methanol, for example, the ultimate product is trimethylborate, but otherwise than in the reaction with water a rather stable intermediate, dimethoxyborane $BH(OMe)_2$, can be isolated (*250*). A total of $6H_2$ is liberated, the last

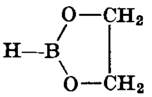
$$4MeOH + B_2H_6 \rightarrow 2BH(OMe)_2 + 4H_2$$
$$2MeOH + 2BH(OMe)_2 \rightarrow 2B(OMe)_3 + 2H_2$$

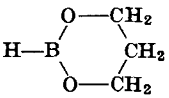
stage being much slower than the first. A white solid by-product is observed, apparently polymeric methoxyborane $(BH_2OMe)_x$, since it disproportionates into diborane and $BH(OMe)_2$ or $B(OMe)_3$. The intermediate $BH(OMe)_2$ has a boiling point of 26°C, and even in the absence of excess methanol is slowly converted to $B(OMe)_3$ by disproportionation.

$$6BH(OMe)_2 \rightleftharpoons 4B(OMe)_3 + B_2H_6$$

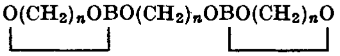
Its infrared spectrum is known (*251*), as are those of other dialkoxyboranes (*252, 253*). A study of the ethanolysis of B_2H_6 and B_2D_6 with ordinary and labeled ethanol has been described (*614*). In the presence of a third substance such as iodine, aliphatic alcohols undergo a much more rapid low-temperature reaction with diborane (*130*). As this reaction is comparable with that undergone by aliphatic ethers in like circumstances, to avoid repetition it will be discussed below in considering the behavior of ethers.

Alcoholysis of diborane by the dihydric alcohols $HO(CH_2)_nOH$ ($n = 2, 3$) leads to the cyclic compounds (*615, 616*):





These disproportionate reversibly into diborane and bicyclic compounds of the type



$$O(CH_2)_nOBO(CH_2)_nOBO(CH_2)_nO$$

The alcoholysis of B_2H_6 can be used as a means of determining the hydroxyl groups in organic compounds (*617*, *618*). This method depends on the fact that only $>$C–OH groups and not simple alkoxy or other $>$C–OR groups are attacked at ordinary temperatures.

Accordingly ethers would be expected to be stable in contact with diborane, and within the limitations mentioned below this is borne out by observation. This provides opportunity for adduct formation, but in spite of the high solubility of B_2H_6 in ethers no adducts are stable at room temperature. Accordingly it must be concluded that coordinate bonds from oxygen to borane or diborane are very much weaker than those from nitrogen. This is in harmony with the observation that simple borane adducts with amino acid esters contain the borane linked to the nitrogen atom and not to the oxygen atom of the carbonyl group: $ROCOCH_2NH_2 \cdot BH_3$ (*619*).

However, evidence for loose adduct formation with simple ethers at low temperatures is well documented. Thus, the NMR evidence with ether solutions of B_2H_6 is quite convincing in the case of dimethyl ether and tetrahydrofuran (*620*), and only rather less so in the case of diethyl ether (*10*, *620*), where even at temperatures as low as –80°C the adduct is apparently still undergoing fast equilibration. In the latter case Gaines has claimed that the very transient adduct is $Et_2O \cdot B_2H_6$ (*10*), and there is independent kinetic confirmation that this is first formed (*313*), although the adduct is frequently assumed by other workers to be $Et_2O \cdot BH_3$. At all events the latter also appears to have existence, since the internal chemical shift of the alkyl protons of the complex is observed to be the same within the limits of measurement as for the complex $Et_2O \cdot BMe_3$ (*621*). Phase studies suggest two very weak complexes of formulas $Et_2O \cdot BH_3$ and $Et_2O \cdot B_3H_9$ (*622*), but the variation in melting point over a very wide range of concentration is sufficiently small to leave room for doubt. Methyl ethyl ether quite definitely forms a single complex of formula $MeEtO \cdot B_2H_6$ (*622*).

Dimethyl ether, on the other hand, is a somewhat stronger base and definitely forms the adduct $Me_2O \cdot BH_3$, since this can be isolated at –80°C (*15*, *622*), albeit with an appreciable dissociation pressure. The still more basic tetrahydrofuran gives the adduct $(CH_2)_4O \cdot BH_3$, which can be isolated below its melting point of −34°C (*622, 623*). These adducts are probably not formed in one step, there being kinetic evidence in the latter case implying that $(CH_2)_4O \cdot B_2H_6$ first occurs (*313*). Both adducts are completely dissociated in the vapor phase (*15*, *44*). The fully fluorinated ethers $(C_2F_5)_2O$ and cyclo-C_4F_8O form no adducts with diborane (*622*).

In the liquid phase some ethers show signs of reacting in other ways than that of simple adduct formation, since B_2H_6 dissolved in them causes them to exhibit some powers of conducting an electric current (*131*). Provided this is not due to impurities such as BF_3 in the diborane, this would seem to imply the existence of an ionization equilibrium such as

$$2R_2O + B_2H_6 \rightleftharpoons [BH_2(OR_2)_2]^+ + BH_4^-$$

The point merits further investigation.

Again, as discussed in Section IV, A, the possible catalytic role of traces of BF_3 in the reported slow reductive cleavage of the polyether diglyme by B_2H_6 at room temperature (*332*, *624*) requires study, as it is not certain that this occurs with BF_3-free diborane. This change appears to be an irreversible one producing methane and a borate ester, since diethylene glycol monomethyl ether is formed on subsequent treatment with alkaline hydrogen peroxide.

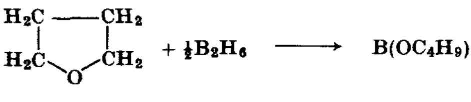
$$3(MeOC_2H_4)_2O + \tfrac{1}{2}B_2H_6 \xrightarrow{(?BF_3)} B(OC_2H_4OC_2H_4OMe)_3 + 3CH_4$$

Biswas and Jackson have concluded that the instability of solutions of diborane in ethers may be due to the presence of traces of BF_3 (*305*). This conclusion seems all the more likely because diborane stated to be pure reacts with diisopropyl ether at elevated temperatures (80°C) in quite a different sense, liberating not propane but hydrogen (*331*).

$$3(i\text{-Pr})_2O + B_2H_6 \xrightarrow[6\ \text{hr}]{80°\text{C}} PrB(O\text{—}i\text{-Pr})_2 + Pr_2BO\text{—}i\text{-Pr} + 3H_2$$

Propylboroxine is a by-product.

Similar considerations regarding catalysis by BF_3 may apply to the slow ring cleavage by B_2H_6 of cyclic ethers such as tetrahydrofuran at 60°C (*256*).



Certainly it has been observed that BF_3 catalyzes the ring cleavage of epoxides (*329*). Epoxide rings are, however, apparently also cleaved without a catalyst (*308*, *318*, *326*). The mechanism has been studied (*327*).

In the presence of a third substance, diborane will sometimes cleave aliphatic ethers and alicyclic ethers in a most interesting low-temperature reaction (*625*). Aliphatic alcohols react similarly. Thus, in the presence (without a solvent) of iodine (*626*) or bromine (*627*) (chlorine is inconveniently reactive) and with excess of the ether (or alcohol), the oxygen atom of the cleaved C–O bond attaches itself to boron, while the carbon atom becomes linked to halogen.

$$\begin{aligned} B_2H_6 + 6R_2O + 3I_2 &\rightarrow 2B(OR)_3 + 6RI + 3H_2 \\ B_2H_6 + 6ROH + 3I_2 &\rightarrow 2H_3BO_3 + 6RI + 3H_2 \\ B_2H_6 + 6(CH_2)_nO + 3I_2 &\rightarrow 2B[O(CH_2)_nI]_3 + 3H_2 \end{aligned}$$

This is a very efficient way (*628*) of converting alkyl ethers or aliphatic alcohols to alkyl iodides, and cyclic ethers to ω-iodo alcohols (on subsequent hydrolysis of the boric ester first formed). No iodine is lost, but when bromine is used some HBr is formed in a side reaction, presumably by direct action with the diborane. The main reaction proceeds via intermediates such as $R_2O \cdot BH_2I$, as is clear from a study of the kinetics of the reaction in an inert solvent (cyclohexane) at low temperatures (*130*, *629*); but these intermediates are not generally isolable except that (when the ether is diethyl ether) the ionic substance $[BH_2(OEt)_2]^+I^-$ has been observed to be thrown out of solution and subsequently to redissolve as it reacted further. Although the nature of the dealkoxyhalogenation reaction of the carbon atom of the cleaved C–O bond has not been definitely established, it is probably S_N2 since the comparable dehydroxyhalogenation reaction at the asymmetric carbon atom of an optically active alcohol proceeds with inversion of configuration (*630*). (However, in a similar dealkylation reaction involving $NaBH_4$ in place of B_2H_6 retention of configuration has been reported (*631*).) In the former reaction an alkyl group is transferred from oxygen to halogen. (Here it may be interposed that other oxygen-containing organic compounds undergo comparable reactions, including epoxides, aldehydes, and ketones (*628*), though in the case of epoxides hydrolysis of the boric ester initially formed is required to obtain an organic halide, while with the carbonyl compounds additional reduction by the diborane occurs; and with organic esters (*632*) the reaction is associated with both additional reduction and the need to hydrolyze the first product.) Ethers also undergo a rather similar reaction in which the third substance is a mercaptan instead of free halogen, when the diborane effects the transfer of an alkyl group from oxygen to sulfur (*265*). The yield of sulfide is likewise good. By analogy, the expected reaction is

$$B_2H_6 + 6R_2O + 6R'SH \rightarrow 2B(OR)_3 + 6RSR' + 3H_2$$

Diborane thus has much promise in alkyl-transfer reactions.

The action of diborane on almost all other oxygen-containing organic compounds such as aldehydes, ketones, carboxylic acids and esters, lactones, acetals, ketals, *p*-benzoquinone, and amides is to reduce them (see Section IV, A). Little is known about the precise mechanisms of these reactions, except in the case of that with acetone, where the kinetics

$$4Me_2CO + B_2H_6 \rightarrow 2(Me_2CHO)_2BH$$

are first-order in diborane and first-order in acetone (*313*). Alkoxyl and aroxyl groups are not affected by diborane, but oxygen bound in other ways (as in the carbonyl group) is normally reduced to hydroxyl, though subsequent hydrolysis of an intermediate boron ester may be required; only by exception does reduction proceed further leading to replacement of the hydroxyl group by hydrogen, as when a coordinating (acceptor) substance such as BF_3 is present as catalyst, or when strongly electron-withdrawing systems are attached to the carbon atom [as with substituted perhydropyridazine-3,6-diones (*341*)].

Reduction also frequently occurs with compounds in which the oxygen is directly attached to some element other than carbon, as with the alcoholates of some alkali (*392*, *456*) and alkaline earth (*457*) metals, which are converted to tetrahydroborates (Section VI). Boron compounds such as dialkoxyalkylboranes $R'B(OR)_2$ (*187*) and alkoxydiphenylboranes Ph_2BOR (*188*) are also reduced, although here the substitution of OR by H is reversible and accompanied by disproportionation. With aluminum triisopropoxide partial reduction occurs with the formation of a complex of formula $Al(BH_4)_3 \cdot 3Al(O\text{-}i\text{-}Pr)_3$, which can be distilled unchanged at low pressures (*458*). In all these reactions the

$$4Al(O\text{-}i\text{-}Pr)_3 + 2B_2H_6 \rightarrow Al(BH_4)_3 \cdot 3Al(O\text{-}i\text{-}Pr)_3 + B(O\text{-}i\text{-}Pr)_3$$

boron attaches itself to the oxygen, displacing another element, as it also does with oxygen compounds of silicon, tin, and lead, as exemplified by disilyl ether (*337*), diethyldimethoxytin (*340*), and triethylmethoxylead (*460*). In these cases the product is a hydride or sometimes a tetrahydroborate (as in the case of the lead compound, which is surprising).

$$4(H_3Si)_2O + B_2H_6 \rightarrow 4SiH_4 + 2BH(OSiH_3)_2$$
$$2Et_2Sn(OMe)_2 + B_2H_6 \rightarrow 2Et_2SnH_2 + 2BH(OMe)_2$$
$$4Et_3PbOMe + 3B_2H_6 \rightarrow 4Et_3PbBH_4 + 2BH(OMe)_2$$

If the oxygen is linked to nitrogen, diborane usually effects reduction, the oxygen being removed and an amine or a substituted hydroxylamine left (see Section VII, D for further details). That nitrous oxide (*530*), azoxybenzene (*318*), and nitrobenzenes (*318*) do not react under ordinary conditions must surely be due to high activation energies, that is, to kinetic rather than thermodynamic factors. When oxygen is singly linked to phosphorus, as in dialkylphosphonates $PH(O)(OR)_2$ (*633*) and trialkylphosphites $P(OR)_3$ (*559*), no reduction occurs with diborane at ordinary temperatures, but in the latter case there is evidence that reduction sets in at elevated temperatures to form compounds of type $(RO)_2PBH_2$. Phosphine oxides $R_3P{=}O$ lose their oxygen and yield phosphines (*342*, *343*). Phosphoric acid and its derivatives are resistant to such reduction, and it is possible to prepare diborane in the presence of H_2O-free phosphoric (*634*) and fluorophosphoric acids (*635*). Information is lacking concerning the behavior of B_2H_6 with oxygen compounds in which the oxygen is linked to arsenic, antimony, or bismuth.

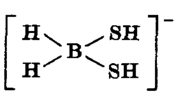
There is very little published data concerning the behavior of diborane with compounds containing oxygen linked to sulfur, and none at all in which it is linked to selenium or tellurium. Diborane is destroyed by sulfur dioxide in about 24 hours at room temperature, boric acid being one of the products (*636*). With dimethyl sulfoxide, on the other hand, no reduction occurs and the diborane is cleaved asymmetrically to give $[BH_2(Me_2SO)_2]^+[BH_4]^-$ (*129*). Sulfones $RR'SO_2$ do not react (*151*).

Except in the case of F_2O (Section VII, H), there is no information regarding the way diborane reacts with compounds containing oxygen linked to halogen.

G. REACTION WITH COMPOUNDS OF SULFUR, SELENIUM, AND TELLURIUM

There are still no reports of any studies concerning the behavior of diborane with elementary sulfur, selenium, or tellurium.

With H_2S diborane forms no adduct even at −78°C, but a very slow reaction produces a glassy polymer deviating somewhat from the formula $(HBS)_x$ (*43*). Since thiohydrolysis does not occur, the behavior is quite unlike that with water. But under anhydrous conditions in tetrahydrofuran, lithium hydrogen sulfide reacts with diborane below 0°C to produce two ionic species (*128*), $HSBH_3^-$ and



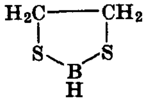
Other base analogs which give rise to the SH^- ion in liquid H_2S produce yet a third ionic species, the adduct $HS(BH_3)_2^-$ (*258, 259, 426*). The latter has a low stability in solution, losing hydrogen to give products which have not been fully characterized. One would, however, expect the rather unstable μ-mercaptodiborane HSB_2H_5 to be one of them, since this compound is certainly produced on the introduction of hydrogen chloride (*258, 259*).

In a study of sulfur–boron bonding (*43*) it has been shown that methyl groups attached to the sulfur increase the power of the latter to form coordinate links with borane, so that the bare existence of $HMeS \cdot BH_3$ at −78°C is demonstrable, while $Me_2S \cdot BH_3$ is an isolable solid below its melting point of −38°C. In general, the borane adducts of organic sulfides are much more stable than those of their oxygen analogs (*44*), and this is reflected in a much greater solubility of diborane in sulfides than in ethers (*637*). Sulfur is thus more effective than oxygen in forming dative bonds with borane, an anomalous trend paralleled in Group V by phosphorus and nitrogen (Section VII, E). Even so, the strengths of the bonds formed by sulfur do not attain to those formed by either phosphorus or nitrogen.

There is some resemblance between the borane adducts formed by thiols and amines, respectively. Thus, the species $HMeS \cdot BH_3$ readily loses H_2 to give a white, ether-insoluble polymer of formula $(MeSBH_2)_x$, which on heating *in vacuo* undergoes partial depolymerization to volatile oligomers, at least temporarily (*43*). The most stable form of the ethyl analog appears to be the spontaneously formed trimer $(EtSBH_2)_3$ with a 6-membered ring (*260*), and the trimer of the methyl compound can also be prepared (*638*). Near 140°C the vapor of the methyl compound corresponds approximately to the dimer (*43*), but decomposes further to give $(MeS)_3B$ as one of the products. At about 90°C, the $MeSBH_2$ oligomers react with more diborane to give an unstable liquid of formula $MeSB_2H_5$ (*43*), which is now known from its structure to be μ-methylmercaptodiborane (*260*). Under other conditions polyboron–sulfur compounds of unforeseen stability result (*476*). More fully substituted boranes have been obtained from the action of diborane on *n*-propyl and *n*-butyl thiols (*261*) and ascribed the dimeric formulas $[(RS)_2BH]_2$ (*264*); but, as in other boron–sulfur compounds (*263*), these substances, if truly dimeric, would be expected to contain boron–sulfur coordinate bonds rather than hydrogen bridges, so may not rightly be regarded as tetrasubstituted diboranes.

Intermolecular boron–sulfur coordinate bonding has been found for the products of reaction of diborane and 1,2-ethanedithiol $HSCH_2CH_2SH$. Hydrogen is liberated and, according to the ratio of the reactants,

$H_2BSCH_2CH_2SBH_2$, $(CH_2S)_2BH$, and $(CH_2S)_2BSCH_2CH_2SB(SCH_2)_2$ are obtained in varying proportions; but because of the said coordinate bonding these substances are not monomeric in the condensed state (*263*). The second of these is, however, monomeric in the vapor phase.



Disulfanes also react with B_2H_6. Thus, MeSSMe gives the same product as MeSH, namely, $(MeSBH_2)_x$ (*43*). The preservation of the C–S bond is, however, not invariably observed, either with disulfanes or thiols, since with $Ph_3CSSCPh_3$ and Ph_3CSH C–S bond cleavage occurs to give Ph_3CH and $(HBS)_x$ (*334*). But generally speaking thioethers possess a stability toward diborane (*374*), forming at most weak adducts from which the reactant can be recovered unchanged. Nevertheless, C–S bonds are frequently ruptured when the sulfur is attached to an unsaturated organic residue, as with certain thioketals (*639*), but even this is not a reliable guide, as the C–S bonds in allyl methyl sulfide and allyl phenyl sulfide are reported to be left intact by diborane (*370*, *640*). It appears that C–S bond rupture only occurs when the steric conditions permit $B \leftarrow S$ coordination and a subsequent hydride shift, but the matter cannot be said to be fully understood (*639*).

In the presence of an ether, diborane reacts in a different way with a thiol, transferring an alkyl group from the ether to the sulfur, thus forming a new C–S bond (*265*).

Organic sulfides containing other donor atoms such as nitrogen or phosphorus, e.g., Me_2NCH_2SMe or Me_2PCH_2SMe, form borane adducts with B_2H_6, but in the monoadducts the BH_3 group appears not to be linked to the sulfur. No diadduct is reported for the phosphorus compound, but boron–sulfur bonding occurs in the diadduct of the nitrogen compound (*511*). This is an unstable liquid which decomposes spontaneously at room temperature by a hydride shift.

$$H_3B \cdot NMe_2CH_2S(Me) \cdot BH_3 \rightarrow H_3B \cdot NMe_3 + \frac{1}{n}(MeSBH_2)_n$$

The substituted sulfonium ylide $Me_3SiCH{=}SMe_2$ or $Me_3Si\overset{-}{C}H{-}\overset{+}{S}Me_2$ readily forms a borane adduct with B_2H_6 in ether solution, but the adduct is unstable and liberates dimethyl sulfide even at low temperatures to leave an unidentified mixture of boron compounds (*105*).

Knowledge regarding the behavior of B_2H_6 with compounds containing sulfur attached to elements other than carbon is limited. When it is attached to boron, as in $(RS)_3B$ or $(RS)_2BR'$, reversible exchange of RS for H occurs, presumably to give compounds such as $BH(SR)_2$ (*187*). In this there is a parallel with the alkoxyboranes $(RO)_3B$ and $(RO)_2BR'$. It is to be expected that the selenium and tellurium analogs $(RSe)_3B$ and $(RTe)_3B$—which have recently been prepared (*266*, *641*, *642*)—will behave similarly to give the unknown compounds of types $(RSe)_xBH_{3-x}$ and $(RTe)_xBH_{3-x}$ ($x = 1, 2$), but the matter has not been put to experimental test, nor is it known whether such compounds would be monomers.

When the sulfur is linked to nitrogen, diborane effects the formation of a monoadduct only, with the boron here apparently linked to the sulfur, as when a methylthiodialkylamine $MeSNR_2$ is converted initially to $Me(R_2N)S \cdot BH_3$ (*93*). The adducts are however unstable and undergo a hydride shift spontaneously at room temperature to give dialkylamine methylthioboranes $HR_2N \cdot BH_2SMe$. Bisdimethylaminosulfide $(Me_2N)_2S$ again only forms the monoadduct $(Me_2N)_2S \cdot BH_3$, which, though slightly more stable, undergoes a similar hydride shift to $HMe_2N \cdot BH_2SNMe_2$ (*45*). Clearly the effect of the adjacent nitrogen is to increase the donor power of the sulfur toward borane, and this has been ascribed to stabilization through sulfur–nitrogen d_π–p_π interaction (*45*).

The behavior of diborane toward certain compounds in which sulfur is linked to oxygen has been examined, in all of which the two elements are doubly bonded. Dimethyl sulfoxide Me_2SO does not give a simple borane adduct, but cleaves the B_2H_6 asymmetrically to $[BH_2(OSMe_2)_2]^+ BH_4^-$ even at low temperatures (*129*). The solid product is soluble in dichloromethane. It has not been determined whether the sulfur or oxygen is linked to boron, but since sulfones $RR'SO_2$, on the other hand, do not react with diborane (*151*), this would suggest that in the case of Me_2SO the lone pair of electrons on the sulfur atom is responsible for the bonding. Diborane is decomposed slowly at room temperature when mixed with SO_2, giving H_2S, sulfur, and boric acid (*636*); about 24 hours are required (but in the presence of certain solvents such as ether the reaction is much more rapid and occurs at low temperatures). In flash photolysis of the mixture, however, H_2, B_2S_3, and a polymer of formula $(HBS)_x$ have also been identified among the products (*643*).

No information is available concerning the reaction of B_2H_6 with compounds containing sulfur–halogen bonds.

H. REACTION WITH HALOGENS AND HALOGEN COMPOUNDS

A key to the behavior of diborane with the halogens is provided by the strengths of the boron–halogen bonds, which are given for the boron trihalides in Table I. Not only are these everywhere stronger than the corresponding carbon–halogen bonds, but the overall spread is much greater. Thus, the B–F bond with a bond energy of 154.3 kcal mole^{-1} (compared with a C–F bond energy in CF_4 of 117.0 kcal mole^{-1}) is the strongest usually written as a single bond that is known to chemistry, though its order doubtless exceeds unity through a measure of back coordination, which effect becomes progressively less important as the atomic number of the halogen increases. The overall effect is that B–F bonds show the greatest stability and B–I bonds the greatest reactivity in the series: Indeed boron shows a very exceptional affinity for the first-row element fluorine, which is greater even than the exceptional affinity which we have noted it to have for oxygen, this, in turn, being greater than its marked affinity for nitrogen. Its affinity for iodine is, however, distinctly low, and BI_3 is an endothermic compound (*572*).

TABLE I

BORON–HALOGEN BOND ENERGIES IN THE BORON TRIHALIDES

Halide BX_3	B–X bond energy[a] kcal mole^{-1}	kJ mole^{-1}
BF_3	154.3	645.6
BCl_3	106.1	443.9
BBr_3	88.0	368.2
BI_3	63.7	266.5

[a] Calculated from Refs. *572* and *644*.

Although the open literature is silent on the subject, there is scarcely room for doubt that elementary fluorine will react spontaneously with diborane down to exceedingly low temperatures, as it does with hydrogen and many hydrides. Diborane certainly ignites in "flox" (a mixture of O_2 and F_2) at −195°C (*645*), and the combination has been tested as a rocket propellant. It has long been known that at ordinary temperatures chlorine reacts explosively with diborane, with the separation of some elementary boron, but that the reaction can be moderated by reducing the temperature, when with chlorine in excess it proceeds quantitatively according to the equation (*646*):

$$B_2H_6 + 3Cl_2 \rightarrow 2BCl_3 + 6HCl$$

Even with diborane in excess the products are essentially the same and most of the excess is recovered unchanged with only a little of the partially halogenated product B_2H_5Cl. By contrast, bromine attacks diborane only very slowly at room temperature, even in the presence of light, and several hours at 100°C are required to complete the reaction (*646*). The main product is BBr_3, but in this case B_2H_5Br can be isolated in appreciable amounts. Iodine does not react with pure B_2H_6 at room temperature, even after several days (*647*), but B_2H_5I is very slowly formed on heating (*276*). The BI_3 and unidentified oily products reported by Stock and Pohland (*648*) probably arise secondarily by interaction with the decomposition products of diborane on very prolonged standing or on heating. In the presence of a trialkylamine or an ether, however, iodine reacts with diborane to produce iodoborane adducts such as $Me_3N{\cdot}BH_2I$ (*649*) and $Et_2O{\cdot}BH_2I$ (*130*), and reaction may proceed further.

Turning to halogen compounds, the interaction of anhydrous HF with diborane has not been reported. With gaseous HCl no reaction with B_2H_6 is observed at room temperature, even in the presence of $AlCl_3$ (*106*). However, Schlesinger and Burg observed that if B_2H_6 containing HCl is allowed to stand for 3 months the HCl is used up with the formation of a variety of products, and not only B_2H_5Cl; but that if the mixture is heated to 120°–130°C much of the diborane is converted to B_5H_9 (*650*). By contrast, diborane readily reacts at 80°–90°C with HBr in the presence of $AlBr_3$ as a catalyst, giving B_2H_5Br (*106*), whereas with HI a corresponding reaction occurs at 50°C without a catalyst (*276, 648*).

$$B_2H_6 + HI \rightarrow B_2H_5I + H_2$$

However, in the presence of an ether or an amine, hydrogen halides give adducts of halogenoboranes, e.g., $R_2O{\cdot}BH_2Cl$ or $R_nH_{3-n}N{\cdot}BH_2Br$ (*649*). The halogen-substituted diboranes B_2H_5X very readily disproportionate to B_2H_6 and BX_3, although the stability increases from the chloro to the iodo compound. The reaction is reversible, so that diborane will also react with the boron trihalides.

With boron trifluoride, there is only one isolable intermediate, namely, BHF_2 (*269, 282*).

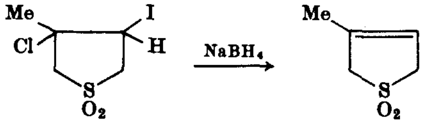
$$B_2H_6 + 4BF_3 \rightleftharpoons 6BHF_2$$

The reaction is catalyzed by ether, methanol, and BCl_3, respectively (*651*). With BCl_3 diborane gives two intermediates, B_2H_5Cl and $BHCl_2$ (*273, 274, 294*), and possibly BH_2Cl as well (*281*), although the latter has not been isolated and is known only (from spectral bands) in gaseous mixtures. With BBr_3 diborane gives B_2H_5Br and $BHBr_2$ (*275*), but with BI_3 the overall equilibrium is to be written

$$5B_2H_6 + 2BI_3 \rightleftharpoons 6B_2H_5I$$

and B_2H_5I is the only isolable intermediate (*276*). The subject is discussed in more detail in Section III, B. In the presence of a trialkylamine, the product may be the amine halogenoborane, e.g., $R_3N \cdot BH_2Br$ or $R_3N \cdot BHBr_2$ (*649*). The only other boron halide which has been studied in this respect is diboron tetrachloride B_2Cl_4, which at 0°C and below undergoes (at least partially) rupture of the B–B bond with the formation of a complex variety of products (*281*, *477*).

Our knowledge of the behavior of diborane with other halogen compounds is sparse indeed. Although it is commonly assumed, at least tacitly, that halogen linked to carbon is inert toward B_2H_6, no systematic study of the matter has been undertaken, and it is certainly not universally true. Thus, it is definitely known that the chlorine in acid chlorides is reactive toward diborane and is eliminated, since the products are simply alcohols (*360*, *361*). Still more to the point is the conversion (in nitromethane solvent at 15°C) of aralkyl chlorides and bromides to the corresponding hydrocarbon (*335*). Certainly the conversion of halides to hydrocarbons by diborane is generally thermodynamically favorable, especially in the case of the fluorides, and future studies should be directed toward determining the heights of kinetic barriers. The field is wide open. Other cases of such reactions will doubtless be found, because alkali tetrahydroborates, which are, in general, to be regarded as weaker hydrogenating reagents than diborane, are known to remove halogen from a number of organic substances, including bromoketopregnanes (*652*), bromo- and chloroketosteroids (*653*, *654*), α-bromonitrocycloalkanes (*655*), aliphatic perbromo nitro compounds (*656*), substituted 3-bromo-1,2,4,5-tetrazines (*657*), 14-bromocodeine (*658*), 2-bromo-2-nitropentane (*659*), bischloromethylbenzimidazolone (*660*), vinyl and allyl bromides (*661*), vinylic fluorides and chlorides (*662*), and halogenated hydrocarbons (*663*). Also effected is the dehalogenation (*664*)



whereas dehalogenation of CBr_4 and CHI_3 by $NaBH_4$ is only partial (*665*). Although one would suspect that many of these dehalogenation reactions would also occur with diborane, the reaction paths and even the products may not necessarily be the same in all cases, and frequently fluorine compounds would be expected to react differently from those of the other halogens.

Concerning the behavior of diborane with halogen covalently bound to nitrogen, information (and that limited) is available only for NF_3, N_2F_4, and Me_2NCl (see Section VII, D). In the case of compounds containing halogen linked to a Group VI element, only the compound OF_2 appears to have been put to the test. Here reaction sets in slowly at −195°C and becomes violent at higher temperatures (*645*, *666*). The B_2H_6–OF_2 system has been seriously considered recently as a propellant suitable for future unmanned long-distance interplanetary spacecraft (*667–671*). The kinetics of the reaction have been studied (*672*, *673*). The products are BF_3, B_2O_3, and H_2, but in the reaction conducted at 300°–330°K small quantities of BHF_2, B_2F_4, and unidentified boron-containing solids occur.

VIII. Reactions Forming Carboranes

Unlike the higher boranes, diborane has to date found comparatively little use in the production of carboranes, probably because the latter normally contain more than two boron atoms per molecule, so that a preformed boron skeleton is helpful in obtaining appreciable yields. However, the first evidence for the existence of carboranes was provided in 1953 from experiments in which Landesman (*674*) used a hot wire to flash B_2H_6 admixed with acetylene. Very small yields of volatile compounds containing two carbon atoms and, respectively, three, four, and five boron atoms suggested the existence of molecules of formulas $C_2B_3H_x$, $C_2B_4H_y$, and $C_2B_5H_z$, as well as a number of other new compounds. Better yields of products since identified as the *closo*-carboranes 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$ have been formed by passing an electric discharge through B_2H_6–C_2H_2 mixtures at reduced pressure, with or without dilution by an inert gas such as helium (*675*, *676*). Methylated derivatives are formed at the same time.

Substituted carboranes can also be formed from alkyldiboranes. Thus, 1,5-dimethyl-2,3,4-triethyl-1,5-dicarba-*closo*-pentaborane appears (with derivatives of other carboranes) in 10–15% yield when ethyldiboranes are heated with C_2H_2 (*677*, *678*). Alternatively, ethyldiboranes may be heated with alkynylboranes, when the yield of substituted 1,5-dicarba-*closo*-pentaboranes may exceed 50% (*679*). A rather similar mixture of substituted carboranes is formed in about 15% yield when ethyldiboranes are heated with metallic sodium (*680*) (lithium gives a lower yield); and even when pyrolyzed alone at 200°–230°C ethyldiboranes give detectable quantities of substituted carboranes, including various alkylated dicarba-*closo*-heptaboranes. Although the mechanisms of such reactions are not clear, it has been assumed that they are dependent on the initial formation of $R_2B\cdot$ radicals (*680, 681*). Since alkyldiboranes are directly preparable *in situ* from diborane and trialkylboranes, these reactions may be regarded as indirect reactions of diborane itself.

One further synthetic use of B_2H_6 is in the conversion of one carborane into a second carborane containing a greater number of boron atoms. Thus [adopting the nomenclature of Williams (*682*)], *C,C'*-dimethyl-*arachno*-dicarbanonaborane $C_2B_7H_{11}Me_2$ is converted at 200°C in diphenyl ether solvent by B_2H_6 into the *C,C'*-dimethyl-*closo*-carboranes 1,6-$C_2B_8H_8Me_2$ (41% yield) and 1,7-$C_2B_{10}H_{10}Me_2$ (8% yield) (*683*). It is to be noted that these are pyrolyzing conditions.

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