CHEMISTRY OF THE BORON HYDRIDES

By F. G. A. Stone, M.A., Ph.D.

(Mallinckrodt Laboratory, Harvard University,
Cambridge 38, Massachusetts, U.S.A.)

Review articles[1-4] have periodically drawn attention to the boron hydrides and their derivatives, but rapid progress in this field necessitates another survey of this branch of chemistry. Moreover, until recently the hydrides have been of interest mainly because of the structural problems they present, but now a fuller recognition of the consequences of the reactivity of diborane, the simplest boron hydride, towards electron-donor reagents has led to extensive new developments. Furthermore, certain compounds of salt-like type, related to diborane, have attracted attention to this field through their rapidly growing importance as reducing agents.

Systematic investigation of the boron hydrides was first undertaken by Stock [5] and his collaborators, who were also responsible for early work on the silicon hydrides. The volatility of the hydrides, together with their sensitivity towards oxidation, led Stock to develop the high-vacuum techniques essential for the manipulation of these compounds.

The Characterised Boron Hydrides and Their General Properties

The melting and boiling points of the volatile boron hydrides are summarised in Table 1. Only the hydrides listed have been definitely characterised, but this does not preclude the existence of other hydrides, and indeed there have been reports (varying in degree of clarity) of another hexaborane,[5] an octaborane,[6] an enneaborane,[6] and a dodecaborane.[5]

Diborane has received such extensive study that a later section of this Review is devoted to a discussion of this aspect of boron hydride chemistry. In comparison, the chemistry of the other hydrides has received little attention, but there are a number of properties applicable to the group as a whole, supporting the general assumption that the chemistry of the higher hydrides will, when more thoroughly investigated, parallel closely that of diborane.

Pyrolysis of the volatile hydrides leads to non-volatile solids of the variable composition $(BH_x)_n$, some of them colourless but progressing through yellow and brown towards black as hydrogen is lost at higher and higher temperatures. Their structural and chemical characteristics are virtually unknown.[5] At about 700° all the hydrides are quantitatively

[1] H. I. Schlesinger and A. B. Burg, *Chem. Rev.*, 1942, **31**, 1.

[2] S. H. Bauer, *ibid.*, p. 43.

[3] R. P. Bell and H. J. Emeléus, *Quart. Rev.*, 1948, **2**, 132.

[4] Gmelin's " Handbuch der Anorganischen Chemie ", Bor, 1954, **13**, pp. 97—123, 161—167, 235—253.

[5] A. Stock, " Hydrides of Boron and Silicon ", Oxford, 1933.

[6] I. Shapiro and B. Keilen, *J. Amer. Chem. Soc.*, 1954, **76**, 3864 ; F. J. Norton, *ibid.*, 1950, **72**, 1849.

TABLE 1.   *Physical constants of the volatile boron hydrides*

Molecular formula .	B_2H_6	B_4H_{10}	B_5H_9	B_5H_{11}	B_6H_{10}	$B_{10}H_{14}$
Name . .	Diborane [7]	Tetraborane	Stable pentaborane [7]	Unstable pentaborane	Hexaborane	Decaborane
M.p. . B.p. .	$-165\cdot5°$ $-92\cdot5$	$-120°$ 18	$-46\cdot6°$ 48	$-123°$ 63	$-65°$ (V.p. at 0°, 7·2 mm.)	99·7° 213

decomposed into boron and hydrogen, a property utilised to prepare pure boron and to form coatings of the element on ferrous metals.[8]   However, limited exposure of a boron hydride to less than red heat yields a mixture of the other volatile hydrides, as well as the solid boron–hydrogen-containing materials and hydrogen.   Eventually, however, at a rate dependent on the reaction conditions, all the volatile boron hydrides are converted into non-volatile materials and hydrogen.   Compared with that of some of the other boranes, the stability of diborane is high.   At ordinary temperatures its decomposition usually amounts to less than 10% in a year, but at 100° it rapidly decomposes.   Both tetraborane and unstable pentaborane readily decompose at room temperature.   Even at $-80°$ unstable pentaborane very slowly changes into other hydrides.   Hexaborane is also unstable at room temperature, but stable pentaborane and decaborane show little sign of decomposition below 150°.   It is interesting that the interconversion of the hydrides is a process somewhat analogous to hydrocarbon cracking, differing chiefly in that it takes place at lower temperatures.

Since the hydrogen in a boron hydride has a hydridic as opposed to protonic character, the hydrides all evolve hydrogen on treatment with water although their susceptibility to hydrolysis varies markedly among the members of the group.   Diborane is very rapidly decomposed by cold water ; stable pentaborane, however, is more resistant to protonic attack, requiring prolonged heating at elevated temperatures for complete hydrolysis to boric acid and hydrogen.   The instability of the B–H bond in aqueous solution has important analytical application throughout this branch of chemistry.

Boron hydride vapours have a pronounced odour and are highly poisonous.   Clinical observations on the toxicology [9] of the compounds and detection [10] of their vapours in low concentrations have been described. The hydrides react with atmospheric oxygen giving brown solids of variable composition, but their sensitivity towards oxygen varies.[1]   The pentaboranes are spontaneously inflammable in air at ordinary temperatures, but diborane usually mixes with air without explosion although the resulting

[7] For other physical constants of B_2H_6 and B_5H_9 see S. H. Smith and R. R. Miller, *J. Amer. Chem. Soc.*, p. 1452 ; A. E. Newkirk, *ibid.*, 1948, **70**, 1978.

[8] H. I. Schlesinger and G. W. Schaeffer, U.S.P. 2,494,267, 2,528,454.

[9] H. M. Rozendaal, *Arch. Ind. Hyg. Occup. Med.*, 1951, **4**, 257.

[10] T. L. Etherington and L. V. McCarty, *ibid.*, 1952, **5**, 447.

mixture may detonate later. Price [11] has studied the pressure limits of explosion of diborane or stable pentaborane with oxygen, and the results indicate a branching-chain mechanism.

Under carefully controlled conditions the hydrides react with ammonia to give materials with empirical designations like $B_2H_6,2NH_3$ or $B_4H_{10},4NH_3$. Such ammoniates are salt-like solids which decompose on heating to yield borazole (see p. 186), hydrogen, and non-volatile boron–nitrogen-containing materials. Reaction between ammonia and a boron hydride at elevated temperatures is complex. Reference should be made to the diborane–ammonia reaction described on p. 186.

It is possible to substitute some, but not all, of the hydrogen atoms in a boron hydride with halogen atoms or alkyl groups. Free halogens usually react vigorously with the hydrides, but with hydrogen halides a smoother substitution of hydrogen atoms often takes place. These reactions have received close study only in the case of diborane which, on treatment with a deficiency of halogen or hydrogen halide, forms halogenodiboranes. An interesting characteristic of the latter is their instability with respect to disproportionation (e.g., $6B_2H_5Br \rightleftharpoons 5B_2H_6 + 2BBr_3$), the reverse of which offers a better way of preparing chloro- or bromo-diboranes. Substitution reactions also occur when diborane is mixed with trimethylboron at room temperature.[12] The four methyl derivatives obtained in this way are similar to the halogenodiboranes in that they disproportionate. Hydrolysis gives methylboric acids. A number of other alkyldiboranes have been prepared.[13]

During investigation of these substitution reactions, it was found that, no matter how much trimethylboron was employed, it was not possible to replace more than four hydrogen atoms in diborane with methyl groups, or to have more than two methyl groups attached to each boron atom in a diborane derivative. Furthermore, compounds of molecular formula BH_2R or BHR_2 are known only as dimers. From this it has been inferred that two of the hydrogen atoms in diborane are bound differently from the others. However, such an inference does not necessarily follow, since the substitution of alkyl groups for hydrogen distinctly alters the bonding powers of the boron atom. The strictly monomeric character of a trialkyl-boron may be due to steric factors, as suggested by Rundle,[14] or to a use of C–H bonding electrons from the alkyl groups to increase the electron density on boron, thus relieving any tendency to polymerise, or to combine with less methylated borine groups. Hence a real difference of hydrogen atoms in diborane must be argued from many recent physical evidences and more subtle chemical facts.

Structure of the Boron Hydrides

It is well known that the boron hydrides and some of their derivatives are examples of *electron-deficient* compounds and as such present interesting

[11] F. P. Price, *J. Amer. Chem. Soc.*, 1950, **72**, 5361 ; 1951, **73**, 2141.
[12] H. I. Schlesinger and A. O. Walker, *ibid.*, 1935, **57**, 621.
[13] H. I. Schlesinger, L. Horvitz, and A. B. Burg, *ibid.*, 1936, **58**, 407.
[14] R. E. Rundle, *ibid.*, 1947, **69**, 1327, 2075.

problems concerning structures and bond types. An electron-deficient compound is one containing too few valency electrons to permit all the adjacent atoms to be held together by two-atom electron-pair bonds. Besides boron, a number of other elements form covalent compounds in which some of the bonds have an order of less than unity. Thus electron-deficiency is also exemplified in the dimeric aluminium alkyls like Al_2Me_6, tetrameric platinum tetra-alkyls like $(PtMe_4)_4$, and associated forms of dimethylberyllium and ethyl-lithium.

Electron-deficient compounds are most easily recognisable among the Group IIIB elements which, although possessing only three valency electrons, can form a stable sp^3 set of tetrahedral orbitals. It must be emphasised, however, that this does not give rise to electron-deficiency in all compounds of these elements, since donor groups can bestow four-covalency by formation of co-ordinate bonds. Nevertheless, the hydrides are all electron-deficient since no compounds of the expected molecular formulæ BH_3 or AlH_3 have any stable existence ; only the dimer B_2H_6 and polymeric $(AlH_3)_n$ are found as the simplest compounds.

Assignment of suitable structures to the boron hydrides has been difficult. The major portion of the published work has been concerned with diborane on the reasonable assumption that allocation of a satisfactory structure to the simplest hydride would establish principles from which the structures of the higher hydrides could be deduced. Determination of the configuration of diborane had to await the introduction of physical methods of structure determination since in its chemical reactions the hydride readily passes over into materials with normal electron-pair bonds, offering no genuine evidence as to the structure of the original molecule.

There is now available an overwhelming amount of physical evidence in favour of a bridge structure (I) for diborane. It is interesting that a bridge structure was first suggested by Dilthey [15] as long ago as 1921, but it was not at first accepted, preference being given to an ethane-like configuration, $H_3B \cdot BH_3$, or to an ionic arrangement $(H^+)_2(B_2H_4)^{-2}$. Of these formulations the ionic structure was the least favoured. It was proposed mainly to account for the nature of the product obtained in the low-temperature reaction between diborane and ammonia. However, this interpretation of diborane–ammonia chemistry was later shown to be incorrect. The suggestion by many workers of an ethane-like arrangement for diborane was more difficult to dispose of since it received support from interpretations by Bauer [16] of electron-diffraction data. Nevertheless, a reconsideration [17, 18] of the electron-diffraction results showed that the data were equally in accordance with a bridge structure for the hydride. Thus application of the electron-diffraction method of structure determination to this problem was at first inconclusive. More recently, Hedberg

[15] W. Dilthey, *Z. angew. Chem.*, 1921, **34,** 596.

[16] S. H. Bauer, *J. Amer. Chem. Soc.*, 1937, **59,** 1096.

[17] H. C. Longuet-Higgins and R. P. Bell, *J.*, 1943, 250.

[18] M. E. Dyatkina and Y. K. Syrkin, *Compt. rend. Acad. Sci. U.R.S.S.*, 1942, **35,** 180.

and Schomaker [19] have made more precise comparative electron-diffraction studies on ethane and on diborane, and the results strongly favour the bridge model with the bridge hydrogens lying in a plane perpendicular to a plane containing the remaining atoms. The dimensions of the diborane molecule are: B–B distance 1·77 Å, B–H distance 1·19 Å, B–H$_b$ (bridge) 1·33 Å, < HBH = 121·5°, and < H$_b$BH$_b$ = 100°.
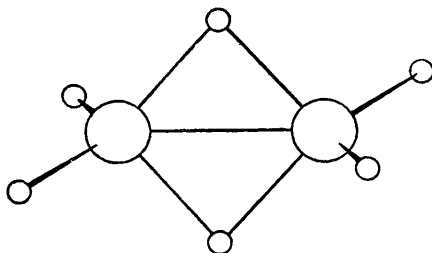
(I) *The structure of diborane*

(Reproduced, by permission, from Lipscomb, *J. Chem. Phys.*, 1954, **22**, 985)

Other evidence in favour of the hydrogen-bridge configuration may be summarised as follows.

The observed infrared spectrum [20-23] resembles that of ethylene rather than that of ethane. This is to be expected if diborane has a bridge configuration. The hydrogen atoms are then not all equivalent and the diborane molecule has the symmetry of ethylene. Furthermore, investigation of the Raman spectrum [23, 24] of diborane revealed frequencies attributable to two types of B–H linkage, supplying more evidence for the idea of the non-equivalence of all the hydrogen atoms. Attempts to make the results consistent with those to be expected for an ethane model, with its equivalent hydrogen atoms, require assumptions which are difficult to substantiate.

The Raman [25] and infrared [26] spectra of tetramethyldiborane show no bands corresponding to terminal B–H linkages, a result also in accordance with a bridge model for both tetramethyldiborane and diborane. Furthermore, electron-diffraction studies on tetramethyldiborane show that the four methyl groups and the two boron atoms are coplanar.[27]

Comparison of the microwave spectrum of bromodiborane with that of vinyl bromide has been made by Cornwell.[28] The results can only be satisfactorily explained by assuming a bridge structure for diborane.

Specific-heat measurements also favour the bridge structure for diborane.

[19] K. Hedberg and V. Schomaker, *J. Amer. Chem. Soc.*, 1951, **73**, 1482.
[20] W. C. Price, *J. Chem. Phys.*, 1947, **15**, 614 ; 1948, **16**, 894.
[21] F. Stitt, *ibid.*, 1940, **8**, 981 ; 1941, **9**, 780.
[22] W. E. Anderson and E. F. Barker, *ibid.*, 1950, **18**, 698.
[23] R. C. Lord and E. Nielsen, *ibid.*, 1951, **19**, 1.
[24] T. F. Anderson and A. B. Burg, *ibid.*, 1938, **6**, 586.
[25] B. Rice, J. M. G. Barredo, and T. F. Young, *J. Amer. Chem. Soc.*, 1951, **73**, 2306.
[26] R. D. Cowan, *J. Chem. Phys.*, 1949, **17**, 218.
[27] L. Pauling, *Ind. Eng. Chem.*, 1947, **25**, 2970.
[28] C. D. Cornwell, *J. Chem. Phys.*, 1950, **18**, 1118.

The data indicate a degree of hindered rotation between the boron atoms of a greater value than that expected for an ethane-like structure and more like that to be expected if diborane has the symmetry of ethylene.[21]

Thus the hydrogen-bridge configuration of diborane must now be regarded as established but assignment of an electronic structure is more difficult since, as in the valency-bond theory of metals, more orbitals are available than there are electrons to fill them. In the case of diborane, however, the electron-deficiency can be confined to the " bridge system ". Electron-diffraction and spectrum results reviewed by Bell and Emeléus [3] show that the terminal B–H bonds are at least equivalent to the electron-pair type and the " bridge system " is, therefore, bonded by means of only four electrons.

The character of this bridge bonding does not seem amenable to simple description, and accordingly has been treated from diverse viewpoints. These viewpoints, involving such concepts as hydrogen bonding, donor bonding, resonance, etc., have been adequately discussed and criticised elsewhere.[3, 29]   Solution of this and related problems must await development of a more refined theory of chemical valency, but here as a basis for argument one may consider first the double bond in ethylene.   It was once thought that this might be formed by simple overlapping of two pairs of sp^3 orbitals, but on energetic grounds this idea was discarded in favour of a direct carbon–carbon σ-bond surrounded by a π-bond.   Before this point was resolved by Penney,[30] Wiberg [31] had described diborane as having two protons buried in a double bond, and afterwards, this concept was sharpened by Pitzer [32] whose reference to a " protonated double bond " could only mean attachment of protons to the upper and lower portions of the π-bond. But diborane offers no protons for attachment to bases,[33] so that the idea of a protonated double bond of the $\sigma\pi$-ethylenic type is at least misleading and possibly wrong.

A different approach is to consider the sp^3-overlap idea of a boron–boron double bond, discarded though it be for ethylene, and then note that this becomes energetically far more appropriate if protons are buried in the

(A)   (B)
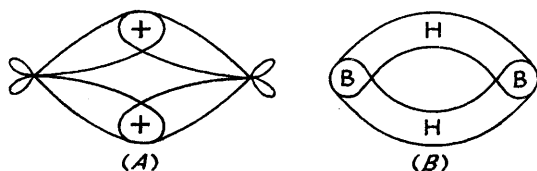
two parts,[29, 34] (A) resulting in (B).   This situation has been described by Rundle [14] as a set of four B–H " half-bonds ".   Now the actual boron–boron distance corresponds to half the strength of a σ-bond and accordingly

[29] C. A. Coulson, " Valence ", Oxford University Press, 1952, p. 322.
[30] W. G. Penney, *Proc. Roy. Soc.*, 1934, A, **144**, 166.
[31] E. Wiberg, *Ber.*, 1936, **69**, 2816.
[32] K. S. Pitzer, *J. Amer. Chem. Soc.*, 1945, **67**, 1126.
[33] A. B. Burg, *ibid.*, 1947, **69**, 747.
[34] H. C. Longuet-Higgins, *J. Chim. phys.*, 1949, **46**, 275.

one must assign some electron density to the space directly between the boron atoms. To do so is to effect a compromise between the " half-bond "
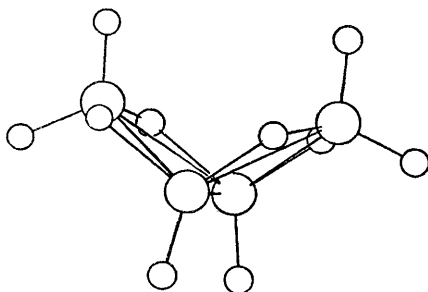

FIG. 1

The structure of B_4H_{10}.

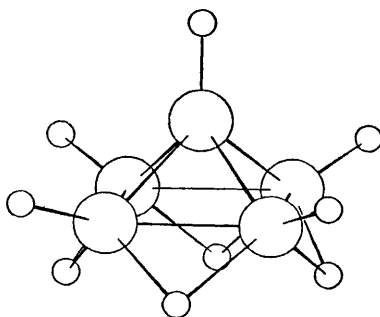(Reproduced, by permission, from Lipscomb, *J. Chem. Phys.*, 1954, **22**, 985)

FIG. 2

The structure of B_5H_9.

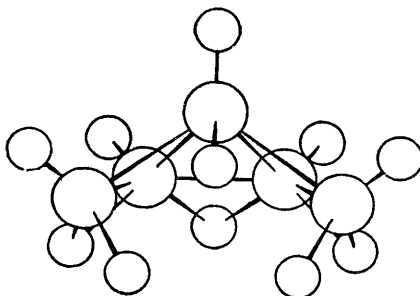(Reproduced, by permission, from Lipscomb, *J. Chem. Phys.*, 1954, **22**, 985)

FIG. 3

The structure of B_5H_{11}.

(Reproduced, by permission, from Lipscomb, *J. Chem. Phys.*, 1954, **22**, 985)

idea and the protonated double bond concept, so that the reality could be regarded as a resonance hybrid state, representing a lower energy level than

either specific pattern would imply.   Thus the protons are not free as such for chemical action, nor is the direct boron–boron σ-bond wholly neglected.

The higher boranes are also electron-deficient, and are presumed to contain hydrogen-bridge linkages much like those attributed to diborane. However, as in the simplest hydride, some of the bonds are of the normal electron-pair type.   A number of physical studies on the configurations of the higher hydrides have recently been made and the results have been reviewed by Lipscomb.[35]   Only the structure of B_6H_{10} appears to remain unresolved and this hydride is under investigation.   Electron-diffraction and X-ray work on tetraborane [36] and stable pentaborane [37] show that these molecules have the structures indicated by Figs. 1 and 2, respectively. Microwave spectra studies [38] on stable pentaborane also support the structure shown in Fig. 2. X-Ray observations [39] on the very reactive unstable pentaborane suggest that it has the more open structure shown in Fig. 3. Electron-diffraction and X-ray [40] studies on decaborane show that this hydride has a configuration with the boron atoms arranged in two regular pentagonal pyramids with an edge in common.   Four hydrogen atoms form bridges, while the other ten are linked to single boron atoms.

Discussion of the structures of many derivatives of the hydrides is made at appropriate points in the Review.

Preparation of the Boron Hydrides

Old Methods.—The boranes were originally obtained by adding magnesium boride to hydrochloric acid.[5]   The yields were low (4%) and separation from impurities such as carbon dioxide, hydrogen sulphide, phosphine, and the silanes was difficult.   Yields were slightly improved (11%) by using phosphoric instead of hydrochloric acid.[41]   The majority of the boron in the volatile products appeared as tetraborane, and the rest as traces of stable pentaborane, hexaborane, and decaborane.   Diborane was not obtained by this aqueous method because of its high reactivity towards water. Stock [5] was able to obtain diborane, however, by the pyrolysis of tetraborane.

A more direct method of preparing diborane was achieved by Schlesinger and Burg [42] in 1931.   Boron trichloride vapour and hydrogen were passed at low pressures through an electric discharge, giving a mixture of hydrogen chloride, the chloro-derivatives of diborane, unchanged hydrogen, and boron trichloride.   The chlorodiboranes were then allowed to disproportionate

[35] W. N. Lipscomb, *J. Chem. Phys.*, 1954, **22**, 985.

[36] M. E. Jones, K. Hedberg, and V. Schomaker, *J. Amer. Chem. Soc.*, 1953, **75**, 4116 ; C. E. Nordman and W. N. Lipscomb, *ibid.*, p. 4116 ; *J. Chem. Phys.*, 1953, **21**, 1856.

[37] K. Hedberg, M. E. Jones, and V. Schomaker, *Proc. Nat. Acad. Sci.*, 1952, **38**, 679 ; W. J. Dulmage and W. N. Lipscomb, *Acta Cryst.*, 1952, **5**, 260.

[38] H. J. Hrostowski and R. J. Myers, *J. Chem. Phys.*, 1954, **22**, 262.

[39] L. R. Lavine and W. N. Lipscomb, *ibid.*, 1953, **21**, 2087 ; 1954, **22**, 614.

[40] C. M. Lucht, *J. Amer. Chem. Soc.*, 1951, **73**, 2373 ; J. S. Kaspar, C. M. Lucht, and D. Harker, *Acta Cryst.*, 1950, **3**, 436.

[41] B. D. Steele and J. E. Mills, *J.*, 1930, 74.

[42] H. I. Schlesinger and A. B. Burg, *J. Amer. Chem. Soc.*, 1931, **53**, 4321.

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at $0°$ and 2 atm. into boron trichloride and diborane. The disproportionation reaction was made irreversible by removal of the diborane through a fractionating column. Boron tribromide may be used instead of boron trichloride.[43] From either boron halide about an 80% conversion into diborane could be effected.

Modern Methods.—Finholt, Bond, and Schlesinger's [44] discovery of lithium aluminium hydride, which has the ability to reduce covalent halides to the hydrides, remarkably simplified the preparation of diborane and many other covalent hydrides. A solution of lithium aluminium hydride, in diethyl ether when treated with the diethyl ether complex of either boron trichloride or boron trifluoride, gives diborane in almost quantitative yield : [44, 45]

$$3LiAlH_4 + 4BX_3 \longrightarrow 3LiX + 3AlX_3 + 2B_2H_6 \quad (X = Cl \text{ or } F)$$
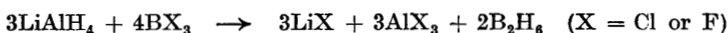
Boron trifluoride is commercially more readily available than the trichloride, so its use is more common.

Diborane may also be obtained by slowly adding the boron trifluoride–ether complex to an ether suspension of lithium hydride.[46] The mixture is then gently refluxed and the reaction

$$6LiH + 8Et_2O,BF_3 \longrightarrow 6LiBF_4 + B_2H_6 + 8Et_2O$$
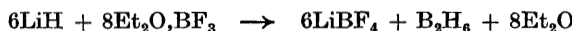
can be made to give an 87% yield of the hydride. Sodium hydride may be substituted for the lithium compound. In order to obtain high yields of diborane in these reactions it is essential that the alkali-metal hydrides be used in a finely divided state.

Another method of obtaining diborane involves the compound sodium trimethoxyborohydride, $NaBH(OMe)_3$, prepared by heating sodium hydride with methyl borate.[47] When suspended in ether, sodium trimethoxyborohydride also reacts with the boron trifluoride–ether complex to give diborane. Particularly good yields (94%) of hydride result if the ether complex is in excess, and as much as 20 litres (S.T.P.) of diborane have been obtained in a single preparation :

$$6NaBH(OMe)_3 + 8Et_2O,BF_3 \longrightarrow B_2H_6 + 6NaBF_4 + 6B(OMe)_3 + 8Et_2O$$

Diborane can also be prepared by treating lithium or sodium borohydrides with boron trifluoride–diethyl ether complex.[48] When the lithium compound is used the yield is theoretical :

$$3LiBH_4 + 4Et_2O,BF_3 \longrightarrow 3LiBF_4 + 2B_2H_6 + 4Et_2O$$

As a result, therefore, of the work of Schlesinger and his collaborators, there are now available several convenient methods for preparing diborane.

[43] A. Stock and W. Sutterlin, *Ber.*, 1934, **67**, 407.

[44] A. E. Finholt, A. C. Bond, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1947, **69**, 1199 ; Finholt, Bond, K. E. Wilzbach, and Schlesinger, *ibid.*, p. 2692.

[45] I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik, and G. B. L. Smith, *ibid.*, 1952, **74, 901.**

[46] H. I. Schlesinger, H. C. Brown, J. R. Gilbreath, and J. J. Katz, *ibid.*, 1953, **75,** 195 ; J. R. Elliott, E. M. Boldebuck, and G. F. Roedel, *ibid.*, 1952, **74, 5047.**

[47] H. C. Brown, H. I. Schlesinger, I. Sheft, and D. M. Ritter, *ibid.*, 1953, **75**, 192.

[48] H. I. Schlesinger, H. C. Brown, *et al.*, *ibid.*, pp. 186, 199.

For small-scale work the methods involving lithium aluminium hydride, sodium borohydride, or lithium borohydride are probably the most satisfactory, while for preparation on a larger scale it is well to use lithium hydride. Experimental procedures for these reactions are simple, and diborane can be obtained in large amount and high yield. The classic method, discovered by Stock,[5] of obtaining diborane from tetraborane, and the discharge method due to Schlesinger and Burg [42] have thus been superseded.

Diborane produced by methods involving the boron trifluoride–ether complex may contain small amounts of ethane. If the sample is not too large and very pure diborane is required, the ethane can be removed by preparing the dimethyl ether complex of diborane (see later) and pumping away the hydrocarbon from the solid complex. The latter is then allowed to dissociate, and the diborane is separated by high-vacuum fractional condensation.[49] The pyridine complex of diborane may also be used for purification of the hydride.[50]

It has been reported [51] that diborane can be obtained by passing boron halides mixed with hydrogen over certain metals or metal hydrides at high temperatures. Sodium, aluminium, magnesium, zinc, sodium hydride, or calcium hydride has been used. The yield of diborane in these reactions is low.

The Higher Boranes.—When a boron hydride is heated at moderate temperatures a mixture of the other hydrides results ; this is the only satisfactory means of preparing higher volatile hydrides. It was Burg and Schlesinger [52] who first recognised that such interconversions proceeded *via* a series of complex reactions some of which, involving hydrogen, were reversible. Addition, therefore, of molecular hydrogen to the reaction mixture had a marked effect on the equilibria. Furthermore, the presence of excess of hydrogen inhibited the formation of solid non-volatile materials, thus preventing loss of volatile boron hydrides. By using these principles it was possible to obtain a satisfactory yield of any particular higher hydride with the exception of hexaborane which is apparently not involved in the complex reactions to any appreciable extent, and is, therefore, still best obtained by hydrolysis of magnesium boride. Thus Burg and Schlesinger devised methods of obtaining unstable pentaborane by passing diborane through a U-tube at 115°, and tetraborane by heating together hydrogen and unstable pentaborane at 100° ($B_5H_{11} + H_2 \rightleftharpoons B_4H_{10} + \frac{1}{2}B_2H_6$). The optimum conditions for converting diborane into stable pentaborane have been studied by McCarty and Di Giorgio.[53] Good yields of pentaborane were obtained by circulating mixtures of diborane and hydrogen through a glass tube heated to 200—250°. It is interesting that kinetic studies [54]

[49] A. B. Burg, *J. Amer. Chem. Soc.*, 1952, **74,** 1340.

[50] H. I. Schlesinger, H. C. Brown, *et al., ibid.,* 1953, **75,** 191.

[51] D. T. Hurd, *ibid.,* 1949, **71,** 20.

[52] A. B. Burg and H. I. Schlesinger, *ibid.,* 1933, **55,** 4009.

[53] L. V. McCarty and P. A. Di Giorgio, *ibid.,* 1951, **73,** 3138.

[54] R. P. Clarke and R. N. Pease, *ibid.,* p. 2132 ; J. K. Bragg, L. V. McCarty, and F. J. Norton, *ibid.,* p. 2134.

indicate that the interconversion of the hydrides proceeds through a radical mechanism with borine, BH_3, as an intermediate.

The Chemistry of Diborane and some Borine Derivatives

Although the presence of borine in diborane cannot be detected by physical methods,[55] it is probable that BH_3 is an intermediate in the reactions of the hydride, since diborane behaves as though it were two loosely held BH_3 fragments capable of easy separation on treatment with suitable reagents. This behaviour has been of assistance since it allows the hydride and many of its derivatives to be discussed in terms of Lewis's generalised acid–base theory.[56] Borine, like any BX_3 type compound, has an incomplete electron octet around the boron atom, giving rise to a strong tendency towards electron-acceptor bonding. Borine, therefore, is a Lewis acid. Thus the well-characterised compound borine–trimethylamine, $Me_3\overset{+}{N}\cdot\overset{-}{BH_3}$,[57] where four sp^3-type bonds originate from boron, is the classic example of a compound in which the boron atoms in diborane have adjusted themselves to give more normal bonding when a base supplies electrons for the purpose. Application of Lewis's acid–base theory to diborane chemistry has been especially useful in collating much information which would otherwise be unrelated, but undoubtedly the chemistry of the borine radical must also be considered in terms of the energy cycle of formation of borine complexes : vaporisation of reactants, dissociation and shaping of the BH_3 group, shaping of the base, falling together for bonding, and condensation of the product to a liquid or a solid. Finally, there is the important question as to whether the energy of the final state is above or below that of the reactants. Thus each reaction must be examined individually, and it is important to note that many potential electron-donors do not offer enough bonding power to promote the dissociation of diborane.

The ultimate product of a reaction between diborane and a compound having electron-donor properties does not necessarily contain the BH_3 group, since the borine co-ordination complex initially formed often undergoes further reaction. Such behaviour takes place if the electron-donor has an available proton, in which case release of hydrogen from the complex always occurs under appropriate conditions. The hydridic character of the B–H bond is promoted by the base, and a proton–hydride combination reaction results. This principle is illustrated in the reaction between diborane and dimethylamine. At $-42°$ the complex NN-dimethylamine–borine, which may tentatively be designated as Me_2NH,BH_3, is first formed. This borine adduct readily evolves hydrogen when heated, producing NN-dimethylaminoborine, $Me_2N\cdot BH_2$.[58-60] Another important way in which a borine complex can decompose is

[55] S. H. Bauer, A. Shepp, and R. E. McCoy, *J. Amer. Chem. Soc.*, 1953, **75**, 1003.
[56] G. N. Lewis, *J. Franklin Inst.*, 1938, **226**, 293.
[57] A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1937, **59**, 780.
[58] E. Wiberg and A. Bolz, *Ber.*, 1940, **73**, 209.
[59] E. Wiberg, A. Bolz, and P. Buchheit, *Z. anorg. Chem.*, 1948, **256**, 285.
[60] A. B. Burg and C. L. Randolph, *J. Amer. Chem. Soc.*, 1949, **71**, 3451.

in a hydride-transfer reaction. This happens in the addition of B–H units into carbonyl or cyanide groups or olefinic double bonds, to form C–H and B–O, B–N or B–C linkages. In this type of reaction the borine complex usually undergoes rearrangement so rapidly that it is not isolated. Thus, the reaction between diborane and acetaldehyde [61] can be interpreted by assuming a reaction step $CH_3 \cdot \overset{+}{C}HO \cdot \overset{-}{B}H_3 \rightarrow CH_3 \cdot CH_2 \cdot O \cdot BH_2$. These intermediates are not isolated, and the products are diethoxyborine, $(C_2H_5O)_2BH$, and triethyl borate, the formation of which can be understood by supposing that the monoalkoxyborine either disproportionates or reacts with other molecules of acetaldehyde. A further example of hydride transfer occurs in the reaction between diborane and methyl cyanide.[1] In this case it is possible to isolate the intermediate $CH_3 \cdot CN, BH_3$.

The chemistry of diborane and related compounds will now be reviewed. This survey can conveniently be made in terms of the types of bond formed between boron and other elements when diborane or some of its derivatives react with compounds having electron-donor properties. Since the strongest of donor atoms are those of the Group VB elements, it is not surprising that they form a large number of borine derivatives. These compounds will be considered first.

Compounds with Boron bonded to Group VB Elements.—Diborane has proved to be a useful starting material for the synthesis of compounds containing boron bound to nitrogen, phosphorus, or arsenic. Stock made some progress in this direction, thereby discovering the diammoniate of diborane and the cyclic compound borazole, but this aspect of boron chemistry has now been considerably extended, principally by Burg and his collaborators. As is well known, tercovalent compounds of the Group VB elements tend to react with BX_3-type compounds—a tendency derived from the ability of the elements to act as electron-pair donors when in this valency state. Basic power, however, decreases with increasing atomic size and is, therefore, most pronounced in the case of nitrogen, the most electronegative element of the Group. This property is demonstrated in boron hydride chemistry by comparing the complexing ability of ammonia, phosphine, or arsine towards the reference acid diborane. At $-120°$ diborane and ammonia give a solid which is stable up to $80°$. Diborane and phosphine, however, form an adduct at low temperatures which is largely dissociated at $0°$, while diborane and arsine do not form a borine complex even at $-80°$.

The behaviour of ammonia towards diborane is extremely complex : reaction between the two hydrides can lead to a variety of products and several of these products have numerous derivatives. The salt-like *diammoniate*, $B_2H_6, 2NH_3$, is prepared by a low-temperature reaction between excess of ammonia and diborane.[5] Once thought to have the ionic structure $(NH_4)_2{}^+(B_2H_4)^{-2}$,[62] the solid is now formulated as the salt $(NH_4)^+(H_3B \cdot NH_2 \cdot BH_3)^-$,[63] on the basis of its reaction with one equivalent

[61] H. C. Brown, H. I. Schlesinger, and A. B. Burg, *J. Amer. Chem. Soc.*, 1939, **61**, 673.

[62] E. Wiberg, *Ber.*, 1936, **69**, 2816.

[63] H. I. Schlesinger and A. B. Burg, *J. Amer. Chem. Soc.*, 1938, **60**, 290.

of sodium in liquid ammonia to give one equivalent of hydrogen, its ready conversion into compounds having B–N–B linkages, and its ability to exchange only N-bonded hydrogen with ND_3.[33] Interpretation of the *diammoniate* as a *monoammonium* salt enables the ion $(H_3B \cdot NH_2 \cdot BH_3)^-$ to be regarded as a complex formed between two borine groups and an amide ion.

At elevated temperatures diborane and excess of ammonia form boron imide, and ultimately on prolonged heating boron nitride. However, when the proportions of the two hydrides are those of the diammoniate, or when the latter substance itself is heated above 200°, the volatile compound borazole, $B_3N_3H_6$ (b.p. 53°), is produced in yields as high as 45%. These high-temperature reactions have been explained by assuming as the initial step formation of $H_3\overset{-}{B} \cdot \overset{+}{N}H_3$ which subsequently decomposes with release of hydrogen : [1]

$$H_3B,NH_3 \xrightarrow{-H_2} H_2B \cdot NH_2 \xrightarrow{-H_2} HB:NH \longrightarrow \tfrac{1}{3}B_3N_3H_6$$
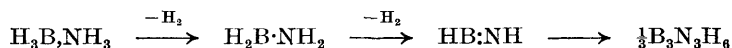
Successive release of hydrogen in this way should be noted. It can always occur from borine adducts where more than one hydrogen is bonded to the donor atom, and it usually leads to the production of polymeric materials. The cyclic structure (II) for borazole was suggested by its discoverers [64] and confirmed by electron-diffraction studies.[2, 5]

In addition to the methods described above, borazole can also be produced (35% yield) by heating lithium borohydride with ammonium chloride at 200°, diborane being formed as a by-product.[65] Another new and potentially very useful method of obtaining borazole involves reducing the compound $BB'B''$-trichloroborazole [58] with lithium borohydride in n-butyl ether at room temperature. The yield of borazole in this reaction can be as high as 90% : [66]

$$2B_3N_3H_3Cl_3 + 6LiBH_4 \longrightarrow 2B_3N_3H_6 + 6LiCl + 3B_2H_6$$

$BB'B''$-Trichloroborazole can be obtained by adding boron trichloride to a suspension of ammonium chloride in chlorobenzene at 140—150°.[67] Methyl derivatives of borazole have been prepared with methyl groups attached either to boron atoms or to nitrogen atoms or to both. Thus thermal decomposition of the diammoniates of the mono-, di-, or tri-methyl-diboranes at 200° gives borazole, the three B-methyl derivatives of borazole and the compound BB-dimethylaminoborine, $Me_2B \cdot NH_2$.[68] The B-methyl-borazoles can also be obtained by treating borazole with trimethylboron but this method is less satisfactory.[69] It has also been reported that pyro-

[64] A. Stock and E. Pohland, *Ber.*, 1926, **59**, 2215.

[65] G. W. Schaeffer, R. Schaeffer, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1951, **73**, 1612.

[66] R. Schaeffer, M. Steindler, L. Hohnstedt, H. S. Smith, L. B. Eddy, and H. I. Schlesinger, *ibid.*, 1954, **76**, 3303.

[67] A. W. Laubengayer and C. A. Brown, private communication.

[68] H. I. Schlesinger, L. Horvitz, and A. B. Burg, *J. Amer. Chem. Soc.*, 1936, **58**, 409.

[69] H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *ibid.*, 1938, **60**, 1296.

lysis of the addition compound Me_3B,NH_3 at $330°/20$ atm. gives $BB'B''$-trimethylborazole and methane.[70] Thermal decomposition of trimethyl-boron ammoniate at lower temperatures yields $Me_2B \cdot NH_2$. The three N-methyl derivatives of borazole may be prepared by heating diborane either with methylamine or with mixtures of ammonia and methylamine.[69] $NN'N''$-Trimethylborazole can also be prepared by reducing monomethyl-ammonium chloride with lithium borohydride : [71]

$$3MeNH_3Cl + 3LiBH_4 \longrightarrow B_3N_3H_3Me_3 + 3LiCl + 9H_2$$
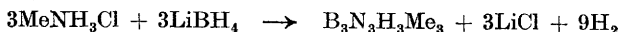
These N-methyl derivatives can be further methylated by heating them with trimethylboron at $100°$, giving compounds containing methyl groups bonded to both boron and nitrogen.[69] Hexamethylborazole can be obtained by heating Me_3B,NH_2Me at $450°/20$ atm.[70]

(II)   (III)   (IV)
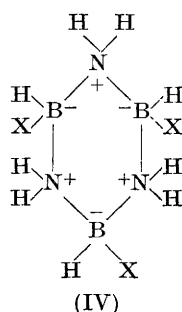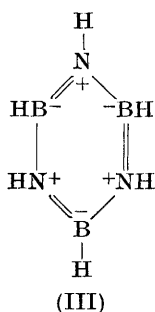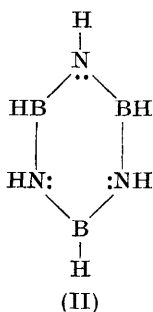
The structural similarity between borazole and benzene is now well known. The nitrogen atoms in (II) have unshared electron-pairs which are able to complete the octets of adjacent boron atoms, giving a pseudo-aromatic system with π-bonding between the nitrogen and boron atoms (III). Kekulé-like resonance would occur. Electron-diffraction results support this concept. The B–N bond distance (1.44 Å) is intermediate between that expected for a B–N single bond (1.48 Å) and a B–N double bond (1.30 Å). The terms borazole and inorganic benzene were suggested by Wiberg [58] in order to emphasise the structural analogy with the aromatic hydrocarbon, an analogy which is somewhat supported by similarities in infrared and Raman spectra.[72]

Resemblance between some substances having boron–nitrogen bonds and certain others with carbon–carbon bonds is to be expected, since the two bond types are of similar size and are isoelectronic. Indeed, Wiberg [70, 73] has drawn considerable attention to the fact that there are several boron-nitrogen compounds analogous to aliphatic or aromatic substances. For instance, besides the borazole–benzene situation we may note that BB-dimethylaminoborine, $Me_2B \cdot NH_2$, is isoelectronic and isosteric with isobutene. Other examples can be found in Wiberg's review,[73] but comparisons between

[70] E. Wiberg, K. Hertwig, and A. Bolz, Z. anorg. Chem., 1947, **255**, 141 ; 1948, **256**, 177.
[71] G. W. Schaeffer and E. R. Anderson, J. Amer. Chem. Soc., 1949, **71**, 2143.
[72] B. L. Crawford and J. T. Edsall, J. Chem. Phys., 1939, **7**, 223.
[73] E. Wiberg, Naturwiss., 1948, **35**, 182, 212.

boron–nitrogen compounds and their carbon–carbon analogues should not be carried too far because of the basic difference between the B–N and C–C linkage. The latter involves atoms of the same element while the former involves atoms of differing electronegativity and, therefore, the electron-cloud representing the bond is not symmetrical. Consequently, boron–nitrogen bonds should be broken more readily than their carbon–carbon analogues. Borazole, for example, although chemically similar to its isosteric analogue benzene in undergoing a number of addition and substitution reactions, is considerably more reactive, behaving more like a triborine–triamine (II) than an inorganic analogue of benzene (III). One mole of borazole will add three moles of cold water, methanol, methyl iodide, or hydrogen halide, HX (X = Cl, Br), the negative group in the adding molecule usually attaching itself to the boron atoms (IV).[5] These addition compounds are not volatile without decomposition, ordinarily giving substituted borazoles. Thus $B_3N_3H_6,3HCl$, formed at low temperatures, releases hydrogen at 100° giving $B_3N_3H_3Cl_3$. Borazole is hydrolysed at high temperatures to ammonia and boric acid. Simple substitution reactions are less common. Chlorine or bromine forms derivatives of the type $B_3N_3H_5X$ and the corresponding hydrogen halide. Treatment of borazole with bromine can also give a dibromo-addition compound.[58] As described above, trimethylboron with borazole yields a mixture of B-methylborazoles and non-volatile material, $(BNH)_x$.[69] The comparable reaction with boron trichloride or tribromide yields B-mono- and B-di-halogenoborazoles.[65] This reaction, however, is accompanied by side reactions giving diborane, hydrogen, and polymeric materials. At room temperature borazole slowly decomposes in the liquid phase and even more slowly in the gas phase, producing hydrogen, small quantities of diborane, and non-volatile solids.

In addition to the diammoniate and borazole, another interesting compound may be obtained from diborane and ammonia. During the preparation of borazole by heating mixtures of ammonia and diborane, a volatile liquid of composition B_2H_7N is produced together with non-volatile material.[69] The compound B_2H_7N was found to be monomeric and was obtained in better yield by passing diborane over the diammoniate at 88° and at a pressure of about 1 atm.[74] It slowly decomposes over a period of days into diborane and a polymeric residue $(H_2B\cdot NH_2)_x$.

Until recently, assignment of a satisfactory structure to this nitrogen derivative of diborane was difficult,[1] but the problem has now been resolved by the preparation of N-methyl derivatives and electron-diffraction studies. As described earlier, pyrolysis of the adduct Me_2NH,BH_3 gives hydrogen and the compound NN-dimethylaminoborine, $Me_2N\cdot BH_2$.[58–60] The latter readily adds a borine group by reacting rapidly with diborane in a flow system at 135°, forming NN-dimethylaminodiborane, $Me_2NB_2H_5$.[60] Heating the complex $MeNH_2,BH_3$ in the presence of diborane gives another new compound, N-methylaminodiborane, $(MeNH)B_2H_5$. Electron-diffraction [75]

[74] H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *J. Amer. Chem. Soc.*, 1938, **60**, 2297.

[75] K. Hedberg and A. J. Stosick, *ibid.*, 1952, **74**, 954.

studies show that these aminodiboranes have bridge configurations with a hydride unit in a position suitable for sharing its electrons with both boron atoms (V). Like the parent compound aminodiborane, $H_2N \cdot B_2H_5$, both N-methyl derivatives form 1 : 1 addition compounds with trimethylamine. Such base-addition would occur by suppression of one side of the B–H–B bridge in (V). It is interesting that the volatility (Table 2, p. 193) and the stability of the aminodiboranes increase in the order $H_2N \cdot B_2H_5$, $(MeNH)B_2H_5$, $Me_2N \cdot B_2H_5$; the last can be stored permanently at ordinary temperatures. Burg has extended the chemistry of aminodiborane by characterising the rather unstable silylamino-compounds $(SiH_3)_2NB_2H_5$ and $(Me \cdot NSiH_3)B_2H_5$.[76.] It is likely that these substances also have nitrogen-bridge structures. Their preparation required a route different from that which gave the aminodiboranes since there are no primary or secondary amines with the silyl group linked to nitrogen. The method used depended on the lability of the silyl groups in trisilylamine :

$$2(SiH_3)_3N + 2B_2H_5Br \xrightarrow{-80°} 2(SiH_3)_2N \cdot BH_2 + 2SiH_3Br + B_2H_6$$
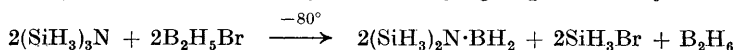
The compound $(SiH_3)_2N \cdot BH_2$ was then treated with diborane at low temperatures, yielding NN-disilylaminodiborane, $(SiH_3)_2NB_2H_5$. Like a typical aminodiborane the latter compound decomposes at ordinary temperatures into diborane and in this case monomeric $(SiH_3)_2N \cdot BH_2$. Polymerisation of $(SiH_3)_2N \cdot BH_2$ makes the decomposition irreversible. The interaction of the Lewis acid bromodiborane with $MeN(SiH_3)_2$ at $-78°$ is very complex, producing SiH_3Br, B_2H_6, SiH_4, $NN'N''$-trimethylborazole, a non-volatile solid, and $(MeNSiH_3)B_2H_5$. Unlike the methylaminodiboranes, both silyl compounds are spontaneously inflammable in air. During this work the very weak basic character of trisilylamine was demonstrated by its inability to react with diborane, and although it formed a complex with the much stronger acid boron trifluoride, the addition compound decomposed above $-40°$. The weakness of $(SiH_3)_3N$ as a base is attributable to wandering of the lone-pair on nitrogen into the $3d$-orbitals of silicon.[76] This idea of π-bonding involving the nitrogen electron-pair is supported by the observation that trisilylamine is planar, and accounts for the weakness of the N–B bonds in the silylaminodiboranes, resulting in the instability of these compounds compared with their methyl analogues.
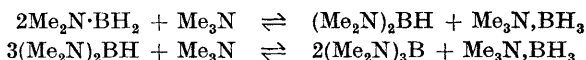
The volatile solid NN-dimethylaminoborine, $Me_2N \cdot BH_2$, from which NN-dimethylaminodiborane is derived, was discovered by Wiberg and his co-workers.[58, 59] Its preparation by pyrolysis of the complex Me_2NH,BH_3 at 130° is nearly quantitative except for the formation of a small amount of bisdimethylaminoborine, $(Me_2N)_2BH$. Since molecules containing a BH_2 group tend to polymerise, it is to be expected that NN-dimethylaminoborine would be associated to some extent. Indeed, a study of its vapour density[59] showed that at room temperature it was dimeric. However, as the temperature was raised, the apparent molecular weight approached that
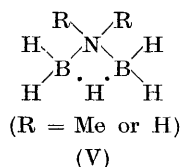
[76] A. B. Burg and E. S. Kuljian, J. Amer. Chem. Soc., 1950, 72, 3103.

value demanded by the monomeric formula $Me_2N \cdot BH_2$. These results were interpreted in terms of a vapour-phase monomer–dimer equilibrium, $(Me_2N \cdot BH_2)_2 \rightleftharpoons 2Me_2N \cdot BH_2$. Burg and Randolph,[77] however, have made a more exact study of this problem and have found that above 80° the reversible disproportionation $3Me_2N \cdot BH_2 \rightleftharpoons (Me_2N)_2BH + Me_2NB_2H_5$ is itself sufficiently rapid and extensive as to cause errors in any study of the vapour-phase association which neglects to take into account this decomposition reaction. If allowance is made for disproportionation, the corrected equilibrium data agree very well with the idea that $Me_2N \cdot BH_2$ associates to a dimer in the gas phase as proposed, but not made certain, by the early results.[59] The dimerisation of NN-dimethylaminoborine is an example of a change from internal dative-bonding, or p_π–p_π overlap, in the monomer (VI) to external use of the nitrogen electrons in the dimer (VII). It is interesting to compare structure (VII) with that suggested for the aminodiboranes (V) and with the bridge structure of diborane (I). It will be observed that the structure of the aminodiboranes is intermediate in character between that of diborane and that proposed for dimeric NN-dimethylaminoborine.

Decomposition of $Me_2N \cdot BH_2$ at high temperatures may be made more extensive by removal of borine groups with trimethylamine : [77]

$$2Me_2N \cdot BH_2 + Me_3N \rightleftharpoons (Me_2N)_2BH + Me_3N,BH_3$$
$$3(Me_2N)_2BH + Me_3N \rightleftharpoons 2(Me_2N)_3B + Me_3N,BH_3$$

Bisdimethylaminoborine and trisdimethylaminoborine are both liquids at ordinary temperatures (Table 2).

Development of aminoboron chemistry prompted the question of the possible existence of phosphino- and arsino-boron compounds. A start was made in this direction by a study of the reaction between diborane and phosphine at $-110°$.[78] Although the product had the composition $B_2H_6,2PH_3$, it was not stable (decomposition pressure 200 mm. at 0°) like the diborane diammoniate. Furthermore, the phosphine–diborane compound could not be formulated as $(PH_4)^+(H_3B \cdot PH_2 \cdot BH_3)^-$ since no phosphine was liberated when the compound was mixed with ammonia at $-77°$, and even at $-60°$ the liberation of phosphine was slow. Normal phosphonium salts rapidly evolve phosphine under comparable conditions. Trimethylamine, however, displaced phosphine quantitatively at $-40°$:

$$B_2H_6,2PH_3 + 2Me_3N \longrightarrow 2PH_3 + 2Me_3N,BH_3$$
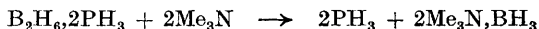
This suggests the structure $H_3\overset{+}{P} \cdot \overset{-}{B}H_3$ for the diborane–phosphine compound since trimethylamine usually displaces BH_3 groups from compounds containing them, forming trimethylamine–borine. However, this idea is by no means established.

A comprehensive study of boron–phosphorus and boron–arsenic bonding has recently been made by Burg, Wagner, and Stone.[79, 80] At ordinary

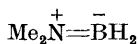[77] A. B. Burg and C. L. Randolph, *J. Amer. Chem. Soc.*, 1951, **73**, 953.
[78] E. L. Gamble and P. Gilmont, *ibid.*, 1940, **62**, 717.
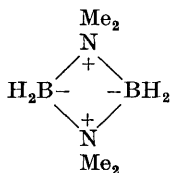[79] A. B. Burg and R. I. Wagner, *ibid.*, 1953, **75**, 3872.
[80] F. G. A. Stone and A. B. Burg, *ibid.*, 1954, **76**, 386.

temperatures diborane and phosphine react slowly, giving hydrogen and a non-volatile polymeric white solid of the approximate composition $(H_2P \cdot BH_2)_x$. Diborane and arsine interact similarly but rather more rapidly, yielding hydrogen and $(H_2As \cdot BH_2)_x$. The latter darkens on exposure to air and, like its phosphorus analogue, is insoluble in organic solvents, is hydrolysed with difficulty, and slowly releases hydrogen on further heating. There are no phosphorus or arsenic analogues of borazole. The latter situation apparently arises through the proper combination of donor-acceptor properties and steric factors.
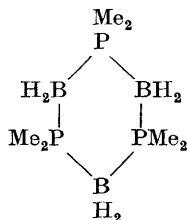
Both dimethylphosphine and dimethylarsine form the expected addition compounds Me_2PH,BH_3 and Me_2AsH,BH_3 with diborane below room temperature. The vapour density of Me_2PH,BH_3 indicates a normal molecular weight for this compound, but the corresponding measurement on Me_2AsH,BH_3, together with its abnormally high Trouton constant, shows that dimethylarsine–borine is largely dissociated into dimethylarsine and diborane in the vapour phase. This is as expected in terms of the rule that the electron-donor bonding power of a heavier element is less than that of a lighter element in the same group provided little or no supplementary π-bonding is involved. Both dimethylphosphine–borine and dimethylarsine–borine release hydrogen on heating. The presence of only

<div align="center">

$$Me_2\overset{+}{N}=\overset{-}{B}H_2$$

(VI)

$$H_2B^- \underset{\overset{+}{N}}{\overset{\overset{+}{N}}{\diamond}} BH_2 \quad \overset{Me_2}{N},\ \overset{Me_2}{N}$$

(VII)

(VIII)

</div>

one P–H or As–H linkage per molecule prevents the reactions from becoming too complex. Prolonged heating of Me_2PH,BH_3 at 150° yields very stable and extraordinarily chemically resistant polymers of $Me_2P \cdot BH_2$, produced in the form of trimer, tetramer, and a trace of high polymer. A similar result is found with the arsenic compound Me_2AsH,BH_3, which begins to liberate hydrogen at 50°, forming $(Me_2As \cdot BH_2)_3$, $(Me_2As \cdot BH_2)_4$, and $(Me_2As \cdot BH_2)_n$. These dimethylphosphino- and dimethylarsino-borine trimers and tetramers are volatile, crystalline solids which may be separated by fractional sublimation under high vacuum. Their melting points and calculated boiling points are recorded in Table 2. Although they contain B–H bonds, the stability of these compounds towards acid or base hydrolysis is exceedingly high, and they can be recrystallised from organic solvents in the open air. Dimethylphosphinoborine trimer and tetramer are hydrolysed but slowly with concentrated hydrochloric acid at 300°, forming H_3BO_3, Me_2PO_2H, and $4H_2$ per $Me_2P \cdot BH_2$ unit. The compound $(Me_2As \cdot BH_2)_3$ is a little less stable; nevertheless, it requires treatment with 12M-hydrochloric acid at 250° for 96 hours to effect complete hydrolysis. The stability of the bonding in these compounds was further shown

by an experiment in which $(Me_2P \cdot BH_2)_3$ was treated with sodium in liquid ammonia for 62 days at room temperature. Subsequently, nearly 50% of the original trimer was recovered, most of the remainder being converted into methane and $Me_5NH_2P_3(BH_2)_3$ (m.p. 35°). The latter is apparently a compound with one methyl group of the trimer replaced by an amide group. The phosphorus and the arsenic tetramers are converted into their corresponding trimers when heated.

Burg and Wagner [79] suggested that these substances were ring compounds, the structure of $(Me_2P \cdot BH_2)_3$, for example, being based on a $(P-B)_3$ hexa-atomic ring (VIII), while the tetramers would have an octa-atomic ring. X-Ray diffraction studies [81] have confirmed that dimethyl-phosphinoborine trimer does have a ring structure like the chair form of *cyclo*hexane. An electron structure with equivalent P–B or As–B bonds and alternating B^- and P^+ or As^+ formal charges may be written for these cyclic compounds. This does not account for the extraordinarily inert character, however, which has been explained in terms of weak but multiplex $B \rightarrow P$ or $B \rightarrow As$ π-bonding using hybridised d-orbitals of phosphorus or arsenic and a contribution of electron density from the B–H linkages.[79, 80] In this way the electron density on hydrogen would be reduced, rendering the B–H bonds less susceptible to attack by protonic reagents. Use of B–H bonding electrons would tend to compensate the formal charge distribution brought about by the $P \rightarrow B$ or $As \rightarrow B$ σ-bonding, and the bonding systems would be much stronger than in the more reactive $Me_2N \cdot BH_2$, nitrogen having no such abundance of orbitals available for bonding as phosphorus or arsenic. The compound $(Me_2P \cdot BMe_2)_3$ (m.p. 334°) has also been prepared and it is interesting that it is nearly as stable as $(Me_2P \cdot BH_2)_3$. In $(Me_2P \cdot BMe_2)_3$ the B–P π-bonding would be more important than in $(Me_2P \cdot BH_2)_3$ since a larger contribution of electron density would be made by the Me_2B system than by the BH_2 arrangement. Attachment of methyl groups, however, reduces the acceptor power of boron so the $P \rightarrow B$ σ-bonding would be weakened. The two effects apparently compensate each other, since the two trimers are almost equally inert.

Both methylphosphine and methylarsine form BH_3 adducts, but $MeAsH_2,BH_3$ is stable only at low temperatures. Pyrolysis of $MePH_2,BH_3$ or the slow reaction between methylarsine and diborane at ordinary temperatures gives non-volatile polymeric materials. This is as expected, since more than one reactive hydrogen atom is attached to the donor atom in the BH_3 addition compound.

Reference has already been made to the very stable volatile complex borine–trimethylamine, Me_3N,BH_3, obtained from diborane and trimethylamine at $-110°$.[57] Its stability is demonstrated by its quantitative formation from reactions occurring at temperatures as high as 200°. The addition compounds Me_3P,BH_3 [79] and Me_3As,BH_3 [80] have now also been prepared, and in agreement with our ideas on donor–acceptor bonding the stability decreases in the order Me_3N,BH_3, Me_3P,BH_3, Me_3As,BH_3. Trimethylamine

[81] W. C. Hamilton, *Acta Cryst.*, in the press.

undergoes similar reactions with trimethylboron and the methylboranes producing Me_3N,BMe_3, $Me_3N,BHMe_2$, and Me_3N,BH_2Me.[82] Methylation of BH_3 lowers the acidity of the boron atom, so in this series of compounds the stability decreases from Me_3N,BH_3 to Me_3N,BMe_3. Trimethylamine

TABLE 2. *Physical constants of some diborane derivatives of Group VB elements*

Common name	Formula	M.p.	B.p.*
Diammoniate of diborane . .	$B_2H_6,2NH_3$	Solid stable to 80	
Diphosphinate of diborane . .	$B_2H_6,2PH_3$	Largely dissociated at 0	
Methylamine–borine	$MeNH_2,BH_3$	5 to 10	—
Methylphosphine–borine . . .	$MePH_2,BH_3$	−49·3	150°
Methylarsine–borine	$MeAsH_2,BH_3$	Solid at −80° ; completely dissociated at ordinary temperatures	
Dimethylamine–borine . . .	Me_2NH,BH_3	11	—
Dimethylphosphine–borine . .	Me_2PH,BH_3	−22·6	174
Dimethylarsine–borine . . .	Me_2AsH,BH_3	−21·5	85·5
Trimethylamine–borine . . .	Me_3N,BH_3	94	171
Trimethylphosphine–borine . .	Me_3P,BH_3	103·5	—
Trimethylarsine–borine . . .	Me_3As,BH_3	74·5	154
Aminoborine	$(H_2N \cdot BH_2)_n$	Polymeric solids (approximate compositions shown) which release hydrogen on further heating	
Phosphinoborine	$(H_2P \cdot BH_2)_n$	,,	
Arsinoborine	$(H_2As \cdot BH_2)_n$	,,	
Methylaminoborine polymer . .	$(MeNH \cdot BH_2)_n$	,,	
Methylphosphinoborine polymer	$(MePH \cdot BH_2)_n$	,,	
Methylarsinoborine polymer . .	$(MeAsH \cdot BH_2)_n$	,,	
NN-Dimethylaminoborine . .	$(Me_2N \cdot BH_2)_2$	75·0	—
Dimethylphosphinoborine trimer	$(Me_2P \cdot BH_2)_3$	86·0	235
,, tetramer	$(Me_2P \cdot BH_2)_4$	161·0	310
Dimethylarsinoborine trimer .	$(Me_2As \cdot BH_2)_3$	50·6	250
,, tetramer .	$(Me_2As \cdot BH_2)_4$	150·5	352
Bisdimethylaminoborine . . .	$(Me_2N)_2BH$	−57	105·7
Trisdimethylaminoborine . .	$(Me_2N)_3B$	−16·1	152
Aminodiborane	$H_2NB_2H_5$	−66·4	76·2
N-Methylaminodiborane . .	$(MeNH)B_2H_5$	−33	66·8
NN-Methylsilylaminodiborane .	$(SiH_3 \cdot NMe)B_2H_t$	−39·0	51
NN-Dimethylaminodiborane .	$Me_2NB_2H_5$	−54·4	50·3
NN-Disilylaminodiborane . .	$(SiH_3)_2NB_2H_5$	−68·8	54

* Usually obtained by extrapolation of vapour-tension data.

will also remove borine groups from the higher boron hydrides ; hence three moles of Me_3N,BH_3 are formed when excess of trimethylamine, dissolved in tetrahydrofuran, is treated with one mole of B_4H_{10}.[83]

Use of diborane to prepare compounds with B–N linkages and interesting properties continues to receive attention. Burg and Good [84] have begun

[82] H. I. Schlesinger, N. W. Flodin, and A. B. Burg, *J. Amer. Chem. Soc.*, 1939, **61**, 1078.
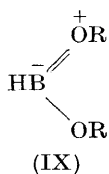[83] A. B. Burg and F. G. A. Stone, *ibid.*, 1953, **75**, 228.
[84] Private communication.

an investigation of aminoboron compounds based on cyclic amines, such as piperidine, pyrrolidine, and azetidine, leading to compounds of the type $R\rangle NHBH_3$, $R\rangle NBH_2$, and $R\rangle NB_2H_5$. A new branch of boron chemistry is likely to develop from treatment of diborane with compounds containing more than one tercovalent nitrogen atom. In the absence of a solvent the reaction between hydrazine and diborane [85] is complex, since the initially formed borine complex releases hydrogen in a series of proton–hydride combination processes, being similar in this respect to the hypothetical borine–ammine, H_3B,NH_3, mentioned earlier. Schlesinger and Steindler [86] have studied the hydrazine–diborane reaction in the presence of ether as solvent and have in this way isolated the complex N_2H_4,B_2H_6.

Compounds with Boron bonded to Group VIB Elements.—A number of oxygen and sulphur compounds are sufficiently powerful electron-pair donors to form adducts with BH_3 derived from diborane. Thus at $-80°$ dimethyl ether and diborane form the solid dimethyl ether–borine, $Me_2\overset{+}{O}{\cdot}\overset{-}{B}H_3$.[63] This complex is among the least stable of the demonstrable BH_3 derivatives, having a dissociation pressure of 18 mm. at $-78.5°$.

Alcohols with excess of diborane yield hydrogen and dialkoxyborines, $(RO)_2BH$.[87] It has been suggested that this reaction and the hydrolysis [88] of diborane proceed through the intermediates $R(H)\overset{+}{O}{\cdot}\overset{-}{B}H_3$ and $H_2\overset{+}{O}{\cdot}\overset{-}{B}H_3$, respectively, which instantly decompose with release of hydrogen. Dialkoxyborines are also produced on treatment of diborane with certain compounds containing a carbonyl group ; [61] e.g., diborane reacts rapidly with acetaldehyde or acetone at $-80°$, giving diethoxy- and diisopropoxy-borine respectively. As described earlier, reaction with the carbonyl group occurs through co-ordination of borine followed by hydride transfer. A similar mechanism of hydride wandering accounts for yet another process yielding dialkoxyborines. The reaction between ethylene oxide and diborane gives $(C_2H_5O)_2BH$ and a polymer of the type $H{\cdot}[CH_2{\cdot}CH_2{\cdot}O]_n{\cdot}BH_2$, while propylene oxide and diborane form $(Me_2CH{\cdot}O)_2BH$ and $H{\cdot}[CHMe{\cdot}CH_2{\cdot}O]_n{\cdot}BH_2$.[89] These alkene oxide reactions probably occur through the intermediates $(CHR{\cdot}CH_2)O,BH_3$, where $R = H$ or Me, which decompose with hydride transfer and opening of the ring. Dialkoxyborines are of interest on account of the fact that they disproportionate, $6BH(OR)_2 \rightleftharpoons B_2H_6 + 4B(OR)_3$, and are monomeric. The electron-deficiency of the boron atom is probably relieved by assumption of a structure like (IX) : one resonance hybrid shown. This would explain the non-occurrence of dimerisation. It is interesting to compare (IX) with the structure of monomeric dimethylaminoborine (VI), the disproportionation of which has been mentioned.

$$HB\overset{\displaystyle\overset{+}{O}R}{\underset{\displaystyle O R}{\diagdown}}$$

(IX)

[85] H. J. Eméleus and F. G. A. Stone, *J.*, 1951, 840.
[86] M. J. Steindler and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1953, **75,** 756.
[87] A. B. Burg and H. I. Schlesinger, *ibid.*, 1933, **55,** 4020.
[88] H. G. Weiss and I. Shapiro, *ibid.*, 1953, **75,** 1221.
[89] F. G. A. Stone and H. J. Eméleus, *J.*, 1950, 2755.

On account of its weak electron-donor power, hydrogen sulphide does not form a recognisable borine adduct even at low temperatures. Burg and Wagner,[90] however, have found that a slow reaction occurs over a period of months at room temperature, producing hydrogen and polymeric material of approximate composition $(HBS)_x$. The stronger sulphur base dimethyl sulphide forms the complex Me_2S,BH_3 (m.p. $-39°$; b.p. $97°$) with diborane at $-80°$. It is interesting that this borine adduct, only 63% dissociated at $53°$, is considerably more stable than Me_2O,BH_3. Thus towards borine the bonding power of sulphur in dimethyl sulphide is greater than that of oxygen in dimethyl ether. This is a reversal of the more usual behaviour found in complexes formed between a reference Lewis acid and a series of ligand atoms from the same periodic group, $viz.$, decreasing donor power with increasing atomic size. Other examples of the breakdown of this rule are found in co-ordination chemistry, and the results have been reviewed.[91] These anomalies have been interpreted in terms of supplementary bonding involving d-orbitals, and in dimethyl sulphide–borine, sulphur probably uses its $3d$-orbitals with a contribution of electron density from the C–H and B–H bonding electrons. Oxygen cannot offer any orbitals above the $2sp^3$ octet suitable for chemical bonding, so in Me_2O,BH_3 additional π-bonding with increased stability is not possible.

Unlike dimethyl sulphide, dimethyl disulphide shows no sign of compound formation with diborane at $-80°$. This is not unexpected since the presence in a compound of two adjacent sulphur atoms would result in each sulphur atom's weakening the electron-donor power of the other. At room temperature, however, the sulphur–sulphur bond is cleaved, and polymeric $(MeS \cdot BH_2)_x$ and hydrogen are formed. The non-volatile solid $(MeS \cdot BH_2)_x$ is also obtained by release of hydrogen from the adduct $MeSH,BH_3$. When heated past its melting range (65—80°), $(MeS \cdot BH_2)_x$ yields a labile series of low polymers of $MeS \cdot BH_2$. At 140° these polymers disproportionate giving $(MeS)_3B$ (m.p. 3·0°). With trimethylamine, the $MeS \cdot BH_2$ polymers form the liquid Me_3N,BH_2SMe. If a stream of diborane at 90° is passed over $(MeS \cdot BH_2)_x$, or better over the trimethylamine complex, a very unstable liquid $MeS \cdot B_2H_5$, methylthiodiborane, is produced, in which the sulphur atom probably bridges the two boron atoms just as the nitrogen atom bridges two boron atoms in the aminodiboranes (V).

Burg and Wagner [90] have also found that, despite the presence of methyl groups bonded to boron, tetramethyldiborane is sufficiently acidic to form the adduct $Me_2BH,HSMe$ with methanethiol at $-50°$. Pyrolysis liberates hydrogen and forms $MeS \cdot BMe_2$ (b.p. 70·8°). Unlike the parent compound $MeS \cdot BH_2$, $MeS \cdot BMe_2$ does not polymerise, perhaps owing to internal dative bonding, $Me\overset{+}{S}{=}\overset{-}{B}Me_2$. However, both internal and external dative bonding to a BMe_2 group would be weak since alkyl groups attached to boron greatly

[90] A. B. Burg and R. I. Wagner, *J. Amer. Chem. Soc.*, 1954, **76,** 3307.
[91] D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel, and L. E. Sutton, *J.*, 1954, 332 ; R. S. Nyholm, *Rev. Pure Appl. Chem.*, 1954, **4,** 1.

reduce its acceptor power. So the inability of Me_2BX type compounds to polymerise could be due to insufficient $\overset{+}{X}$—$\overset{-}{B}$ dative bonding to hold together a dimer.

Compounds with Boron bonded to Carbon.—A survey of compounds derived from diborane containing B–C linkages should discuss the alkyl-diboranes, but since the latter have received attention in an earlier section, they will not be described at this point except to record the discovery of an interesting boron base derived from tetramethyldiborane.[92] If this compound is brought into contact with a solution of sodium in liquid ammonia at $-78°$, it forms Me_2BH,NH_3 (which decomposes into $Me_2B\cdot NH_2 + H_2$) and the white solid Na_2HBMe_2 which is stable *in vacuo* to $90°$. The ion Me_2BH^{2-} is a strong base, since Na_2HBMe_2 reacts with BMe_3 in liquid ammonia to give Na_2HBMe_2,BMe_3, a compound stable to $100°$ which probably contains a B–B bond.

Among the earliest of borine complexes to be recognised was borine carbonyl,[57] H_3B,CO (b.p. $-64°$), prepared by establishing the equilibrium $2CO + B_2H_6 \rightleftharpoons 2H_3B,CO$, by use of excess of carbon monoxide and a pressure of 20 atm., with the temperature near $20°$. At ordinary temperatures borine carbonyl dissociates into carbon monoxide and diborane. The mechanism of this decomposition has recently received attention.[93] The kinetics can satisfactorily be interpreted by assuming as the initial step establishment of the equilibrium $H_3B,CO \rightleftharpoons BH_3 + CO$, followed by a rate-determining step $BH_3 + H_3B,CO \longrightarrow B_2H_6 + CO$.

Hurd[94] has studied the reaction between diborane and hydrocarbons. With olefins the main product is a trialkylboron, while with paraffins, like methane, carbon-chain synthesis and B–C bond synthesis take place. Diborane and benzene give phenylboron compounds.

Borohydrides and Related Compounds

Borohydrides may be regarded as metal derivatives of the boron hydrides formed by bonding the Lewis base H^- with the acid BH_3. Many salts of the methane-like structure BH_4^- are now known, but the earliest characterised compounds of this type were $Al(BH_4)_3$, $Be(BH_4)_2$, and $LiBH_4$.[95] These three compounds were obtained by treatment of the appropriate metal alkyl with diborane. Schlesinger and Brown and their co-workers[48] have made an extensive study of borohydride chemistry during recent years, discovering the borohydrides of Na,[48] K,[48] Mg,[96] Zn,[96] Me_2Ga,[97] and

[92] A. B. Burg and G. W. Campbell, *J. Amer. Chem. Soc.*, 1952, **74**, 3744.

[93] A. B. Burg, *ibid.*, p. 3482.

[94] D. T. Hurd, *ibid.*, 1948, **70**, 2053.

[95] H. I. Schlesinger, R. T. Sanderson, and A. B. Burg, *ibid.*, 1939, **61**, 536 ; 1940, **62**, 3421 ; A. B. Burg and H. I. Schlesinger, *ibid.*, p. 3425 ; H. I. Schlesinger and H. C. Brown, *ibid.*, p. 3429.

[96] A. E. Finholt, H. I. Schlesinger, G. D. Barbaras, C. Dillard, T. Wartik, and K. E. Wilzbach, *ibid.*, 1951, **73**, 4585.

[97] H. I. Schlesinger, H. C. Brown, and G. W. Schaeffer, *ibid.*, 1943, **65**, 1786.

U(IV).[98]   In addition, more efficient methods of preparing Al, Be, and Li borohydrides were developed.[99]   The compounds $RbBH_4$ and $CsBH_4$ have also been prepared.[100]

Alkali-metal borohydrides are white solids, and, as described on p. 182, may be used to prepare diborane. This approach to the problem of obtaining diborane in high yield was of little value as long as the borohydrides themselves could be synthesised only from diborane. However, sodium borohydride can now be prepared in yields as high as 94% by a method not involving diborane but utilising the reaction

$$4NaH + B(OMe)_3 \longrightarrow NaBH_4 + 3NaOMe$$
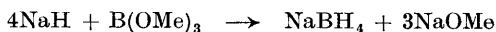
which proceeds rapidly at 225—275°.[101]   *iso*Propylamine is used to extract the borohydride from the reaction mixture. Lithium borohydride can be similarly prepared but in lower yield (70%), and separation from the reaction product is more difficult.

An excellent method for preparing lithium borohydride involves treating lithium hydride with diborane in the presence of diethyl ether : [48]

$$2LiH + (BH_3)_2 \longrightarrow 2LiBH_4$$
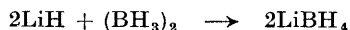
Sodium borohydride cannot be obtained by the analogous reaction involving sodium hydride, and it has been suggested [48] that this may be due to differences in the solvation tendencies of the two metal ions and to the fact that, unlike lithium borohydride, sodium borohydride is insoluble in ether.   The compound sodium trimethoxyborohydride, however, is a useful source of hydride ion and may be used to prepare sodium borohydride by treatment with diborane :

$$B_2H_6 + 2NaBH(OMe)_3 \longrightarrow 2NaBH_4 + 2B(OMe)_3$$
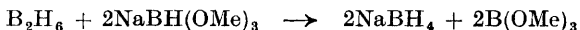
This method yields sodium borohydride in almost quantitative yield, and proceeds so rapidly that diborane, taken from a generator, can be passed directly through a column of solid sodium trimethoxyhydride, thus avoiding the necessity of storing large amounts of diborane.   Other reactions suitable for preparing sodium borohydride are :

$$2B_2H_6 + 3NaB(OMe)_4 \longrightarrow 3NaBH_4 + 4B(OMe)_3$$
$$2B_2H_6 + 3NaOMe \longrightarrow 3NaBH_4 + B(OMe)_3$$
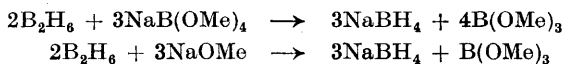
Potassium methoxide does not react with diborane, and so potassium borohydride was prepared through the reactions :

$$KOMe + B(OMe)_3 \longrightarrow KB(OMe)_4$$
$$3KB(OMe)_4 + 2B_2H_6 \longrightarrow 3KBH_4 + 4B(OMe)_3$$
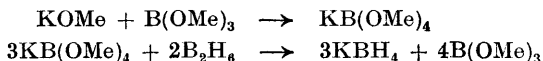
Aluminium borohydride may be prepared by heating mixtures of

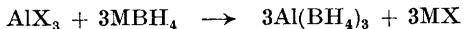[98] H. I. Schlesinger and H. C. Brown, *J. Amer. Chem. Soc.*, 1953, **75**, 219.
[99] H. I. Schlesinger, H. C. Brown, and E. K. Hyde, *ibid.*, p. 209.
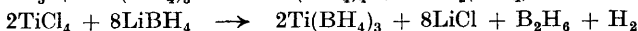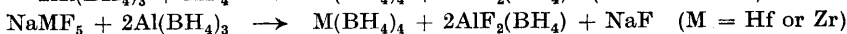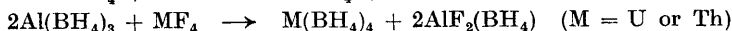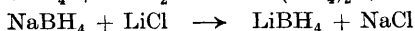[100] M. D. Banus, R. W. Bragdon, and A. A. Hinckley, *ibid.*, 1954, **76**, 3848.
[101] H. I. Schlesinger, H. C. Brown, and A. E. Finholt, *ibid.*, 1953, **75**, 205.

N

aluminium chloride or bromide with sodium or lithium borohydride at moderate temperatures : [99]

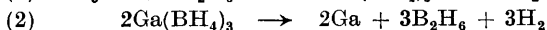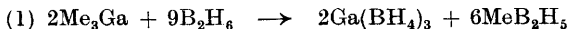$$AlX_3 + 3MBH_4 \longrightarrow 3Al(BH_4)_3 + 3MX$$

Higher yields of aluminium borohydride can be obtained by passing diborane over lithium aluminium hydride but the conditions are critical.

Several borohydrides have the useful ability of producing other borohydrides by metathetical reactions, a property which has found wide application in this branch of chemistry as a preparative method : [98, 99, 102]

$$2LiBH_4 + BeBr_2 \longrightarrow Be(BH_4)_2 + 2LiBr$$
$$NaBH_4 + LiCl \longrightarrow LiBH_4 + NaCl$$
$$2Al(BH_4)_3 + MF_4 \longrightarrow M(BH_4)_4 + 2AlF_2(BH_4) \quad (M = U \text{ or } Th)$$
$$NaMF_5 + 2Al(BH_4)_3 \longrightarrow M(BH_4)_4 + 2AlF_2(BH_4) + NaF \quad (M = Hf \text{ or } Zr)$$
$$2TiCl_4 + 8LiBH_4 \longrightarrow 2Ti(BH_4)_3 + 8LiCl + B_2H_6 + H_2$$

Gallium borohydride is apparently unstable, since mixtures of diborane and trimethylgallium at room temperature yield only gallium metal, diborane, and hydrogen. This behaviour may be interpreted in terms of the steps : [97]

$$(1) \; 2Me_3Ga + 9B_2H_6 \longrightarrow 2Ga(BH_4)_3 + 6MeB_2H_5$$
$$(2) \quad\quad 2Ga(BH_4)_3 \longrightarrow 2Ga + 3B_2H_6 + 3H_2$$

At $-45°$, however, treatment of trimethylgallium with diborane gives the very unstable dimethylgallium borohydride :

$$2Me_3Ga + 3B_2H_6 \longrightarrow 2Me_2GaBH_4 + 2MeB_2H_5$$
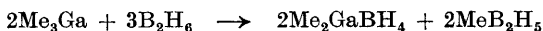
Magnesium borohydride [96, 103] can be obtained from diborane and a magnesium alkyl, and zinc borohydride [96] from diborane and zinc hydride in diethyl ether.

The borohydrides vary from compounds of salt-like character to compounds of essentially covalent character. As would be expected, covalent character becomes greater with increasing electronegativity of the metal present. The alkali-metal borohydrides and thorium borohydride are crystalline salt-like compounds stable in dry air. Potassium borohydride begins to decompose *in vacuo* at about 500°, sodium borohydride may be heated to 400° without decomposition, lithium borohydride is stable to 275°, and thorium borohydride decomposes but little below 204°. The borohydrides of beryllium, aluminium, hafnium, and zirconium, on the other hand, are covalent substances which react with air and are the most volatile known compounds of these elements. Uranium(IV) borohydride and its monomethyl derivative are the most volatile compounds of quadrivalent uranium. Aluminium borohydride is used whenever a liquid source of BH_4^- groups is required. It must be handled with care, however, since its vapour detonates violently on contact with air containing only traces of moisture. The volatile borohydrides are unstable, decomposing at variable rates into hydrogen and non-volatile materials. Aluminium and

[102] H. R. Hoekstra and J. J. Katz, *J. Amer. Chem. Soc.*, 1949, **71**, 2488.
[103] E. Wiberg and R. Bauer, *Z. Naturforsch.*, 1950, **5**, *B*, 397.

uranium borohydrides decompose but slowly at room temperature, but titanium borohydride decomposes completely within a few days. All borohydrides react with water, giving borates and hydrogen. The reducing strength of a borohydride depends very much on the character of the metal ion associated with the borohydride group, increasing as the electronegativity of the metal increases. This behaviour is attributed to a tendency towards $BH_3 + H^-$ character as opposed to BH_4^- character in the more ionic compounds. Thus trimethylamine will remove BH_3 groups from the volatile borohydrides whereas ionic borohydrides are unaffected by this reagent.

The hydrolysis of sodium borohydride is very dependent upon the temperature and the pH of the solution.[104] It can be partially recovered from cold water as $NaBH_4,2H_2O$, but with water at 100° hydrolysis is complete within a few minutes. At ordinary temperatures evolution of hydrogen is at first rapid but subsequently decreases. This decrease in rate is due to a rise in pH of the solution caused by formation of the strongly basic metaborate ion ($BH_4^- + 2H_2O \rightarrow BO_2^- + 4H_2$). Indeed, the initial hydrolysis of sodium borohydride in cold water may be prevented by dissolving the compound in a basic solution rather than in pure water ; on the other hand, complete reaction can be brought about by addition of acid. Sodium borohydride is a useful source of hydrogen when use of compressed gas is inconvenient, being in this respect superior to calcium or lithium hydrides since it yields more hydrogen per gram and has a lower heat of hydrolysis. When it is used for this purpose hydrogen evolution is made rapid by incorporating acidic or catalytic accelerators in pellets of sodium borohydride. Boric acid was found to be a suitable acidic accelerator and certain metal salts such as cobalt(II) chloride were even more effective. The hydrolysis of lithium borohydride resembles that of the sodium compound except that initial evolution of gas is more rapid, and the hydrogen sometimes ignites. It may be conveniently handled as a dioxan complex since this is less hygroscopic than lithium borohydride itself. Evaporation of an ethereal solution of lithium borohydride gives a compound $LiBH_4,Et_2O$. The ether may be removed *in vacuo* by raising the temperature. Sodium borohydride, although insoluble in ether, is soluble in liquid ammonia and in a number of lower aliphatic amines. Alkali-metal borohydrides react with hydrogen chloride and with methanol thus :

$$2MBH_4 + 2HCl \longrightarrow 2MCl + 2H_2 + B_2H_6$$
$$MBH_4 + 4MeOH \longrightarrow MB(OMe)_4 + 4H_2$$
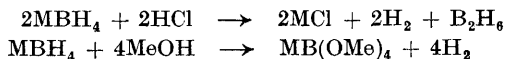
The behaviour of other borohydrides towards hydrogen chloride or methanol is similar.

The very important compound, lithium aluminium hydride,[44] is prepared by adding slowly an ethereal solution of aluminium chloride to an ether suspension of extremely finely divided lithium hydride :
$4LiH + AlCl_3 \rightarrow LiAlH_4 + 3LiCl$. Removal of lithium chloride by filtration, and evaporation of the solvent yields the double hydride as a white

[104] H. I. Schlesinger, H. C. Brown, *et al.*, *J. Amer. Chem. Soc.*, 1953, **75**, 215 ; M. Kilpatrick and C. D. McKinney, *ibid.*, 1950, **72**, 5474.

solid.   Lithium aluminium hydride is similar to its analogue lithium boro-hydride in that it is stable in dry air and reacts vigorously with water. Its decomposition, however, occurs at a lower temperature (125—150°). Schlesinger and his co-workers have also prepared the compounds, $LiGaH_4$, $NaAlH_4$, and $Ca(AlH_4)_2$.

Wiberg and his collaborators [105] have described the preparation of a number of other AlH_4^- compounds by treatment of metal chlorides with lithium aluminium hydride: $MCl_n + nLiAlH_4 \rightarrow M(AlH_4)_n + nLiCl$.   In this way mixed hydrides, which Wiberg has termed " alanates ", of Be, Mg, Al, Ga, In, Tl(III), Ti(IV), and Sn(IV) have been reported.   The stabilities of these compounds in each periodic group decrease with increasing radius of the metal associated with the AlH_4^- group.   Thus $Tl(AlH_4)_3$ decomposes below $- 115°$; while $Al(AlH_4)_3$, which is probably aluminium hydride, is stable above 100°.   The aluminohydrides appear to be somewhat less ionic than their borohydride analogues.

Lithium aluminium hydride is a powerful reducing agent and as such has found wide use in inorganic and organic chemistry.   The results obtained must be regarded as among the most important in recent years.   In general, a solution of lithium aluminium hydride in an organic solvent, usually diethyl ether, reduces the covalent halides of many elements to their hydrides at room temperature and in high yield.[44]   Besides the preparation of diborane from BF_3,Et_2O, already described, silanes, alkyl-silanes, stan-nanes, monogermane, phosphine, arsine, and stibine have been obtained through use of lithium aluminium hydride.   Usually the chlorides of these elements are reduced, but the hydrides of beryllium, magnesium, zinc, and cadmium have been prepared by treating the metal alkyls with lithium aluminium hydride.[96]   These new hydrides are non-volatile white powders. The cadmium compound is unstable above 0° whereas zinc hydride decom-poses only slowly at room temperature.   Beryllium and magnesium hydride are more stable.

Lithium aluminium hydride as a reducing agent in organic chemistry has received particularly wide study.[106]   The carbonyl groups in aldehydes, ketones, acids, esters, acid chlorides, and anhydrides are converted into hydroxyl groups in yields usually as high as 70—100%.   Nitro-compounds, amides, nitriles, and oximes are reduced to amines, and halogen atoms in organic molecules are in general replaced by hydrogen.   Lithium aluminium hydride may also be used for determining active hydrogen in organic com-pounds.   As a reagent, the double hydride possesses the further advantage of not attacking unsaturated carbon–carbon bonds unless the latter are activated by being adjacent to a phenyl group and substituted on the other side by a reducible group (e.g., carbonyl or nitro).

Sodium and lithium borohydrides are also being used in organic chemistry.[106]   Sodium borohydride may be used in aqueous or methanolic

[105] E. Wiberg, *Angew. Chem.*, 1951, **63**, 485.

[106] *Ann. Reports*, 1948, **45**, 122 ; 1949, **46**, 140 ; 1950, **47**, 154 ; 1951, **48**, 143 ; 1952, **49**, 139 ; 1953, **50**, 167.   See also W. G. Brown, " Organic Reactions ", 1951, **6**, 469.

solution and is a milder reducing agent than lithium aluminium hydride. For the latter reason, it may be employed in selective reductions since, although it will reduce carbonyl groups in aldehydes and ketones to alcohols, it has no effect on acids, esters, nitriles, anhydrides, or nitro-compounds. For example, sodium borohydride will convert m-nitrobenzaldehyde into m-nitrobenzyl alcohol, whereas lithium aluminium hydride attacks the nitro-group also. The reducing power of lithium borohydride is intermediate between that of lithium aluminium hydride and that of sodium borohydride. Hitherto the high cost of the borohydrides has restricted their use, but new methods of preparation should obviate this. Sodium borohydride is also a useful analytical reagent, reducing iron(III) to iron(II), vanadium(V) to vanadium(IV), thallium(III) to thallium(I), and silver(I) to silver metal.[48]

X-Ray diffraction studies [107] show that sodium borohydride has a face-centred cubic structure consisting of discrete Na^+ and tetrahedral BH_4^- ions. Lithium borohydride has an orthorhombic lattice with the BH_4^- ions slightly distorted from tetrahedral arrangement.[108] X-Ray studies on sodium borohydride have been important in prompting a re-investigation of some metal boron hydride derivatives reported by Stock,[109] who found that treatment of sodium, potassium, or calcium amalgam with diborane gave solid non-volatile addition compounds of composition $M_2B_2H_6$ or CaB_2H_6. This work, however, is now in doubt because an investigation [110] of disodium diborane, $Na_2B_2H_6$, shows that its X-ray diffraction pattern is identical with that of $NaBH_4$. Existence of the materials $M_2B_2H_6$ as a class of compound separate from the borohydrides is thus questioned.

Increase in salt-like character along the series B_2H_6, $Al(BH_4)_3$, $Be(BH_4)_2$, $LiBH_4$, $NaBH_4$ suggests that the volatile borohydrides might have hydrogen-bridge structures like the boron hydrides. Electron-diffraction studies by Bauer [111] seemed at first not to support M–H–B bridges, but re-examination [112] of the results indicates that the data are not inconsistent with unsymmetrical bridges with tetrahedral BH_4 arrangements (X). Infrared spectrum studies [113] also support the idea of bridge structures for the volatile borohydrides.

(X)

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[107] A. M. Soldate, *J. Amer. Chem. Soc.*, 1947, **69**, 987.
[108] P. M. Harris and E. P. Meibolm, *ibid.*, p. 1231.
[109] A. Stock, W. Sütterlin, and F. Kurzen, *Z. anorg. Chem.*, 1935, **225**, 225.
[110] J. S. Kaspar, L. V. McCarty and A. E. Newkirk, *J. Amer. Chem. Soc.*, 1949, **71**, 2583.
[111] J. Y. Beach and S. H. Bauer, *ibid.*, 1940, **62**, 3440 ; G. Silbiger and S. H. Bauer, *ibid.*, 1946, **68**, 312.
[112] S. H. Bauer, *ibid.*, 1950, **72**, 622.
[113] W. C. Price, H. C. Longuet-Higgins, B. Rice, and T. F. Young, *J. Chem. Phys.*, 1949, **17**, 217 ; W. C. Price, *ibid.*, p. 1044.