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THE CHEMISTRY OF DIBORANE

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CONTENTS

Introduction 207

I. Structure and physical properties of diborane 208

II. Methods for preparing diborane and its alkyl and aryl derivatives 208

1. Preparation of diborane 208
2. Preparation of alkyldiboranes 209
3. Preparation of aryldiboranes 209

III. Chemical properties of diborane and its alkyl and aryl derivatives 210

1. Reactions of diborane and its alkyl and aryl derivatives with nitrogen compounds 210
2. Reactions of diborane with phosphorus, arsenic, and antimony compounds 216
3. Reactions of diborane with oxygen compounds 216
4. Reactions of diborane with sulphur compounds 217
5. Halogenated borines 218
6. Reactions of diborane and tetramethyldiborane with metals 219
7. Reactions of diborane and alkyldiboranes with alkoxy- and alkylthio-derivatives of boron 219
8. Reactions of diborane and its alkyl and aryl derivatives with unsaturated compounds 220

INTRODUCTION

The chemistry of diborane and of the higher hydrides of boron was discussed in Stock's monograph [1] published in 1933, and subsequently reviews [2-11] and monographs [12-14] have appeared dealing with certain stages in the development and individual aspects of the chemistry of the boron hydrides. During recent years the chemistry of diborane has been developing very rapidly, and therefore a brief account of the progress made in this field is opportune.

The great theoretical achievement is the formulation of general quantum-chemical principles underlying the so-called "three-centre bonds" which have provided an explanation of the peculiarities of structure of the boron hydrides. The application of physical methods had led to the establishment of the geometrical structure of many interesting functional derivatives of diborane.

Considerable success was achieved in working out methods for obtaining diborane, alkyl- and aryl-diboranes, amine complexes of diborane and its chlorine derivatives, which formed the basis for a more thorough study of the chemical properties both of diborane itself and of its compounds.

Interesting work was carried out in establishing the structure of "diborane diammine", which increased our knowledge about compounds of the boronium type. Further work on the reactions of diborane with phosphorus compounds and especially sulphur compounds revealed new types of derivatives of borine and diborane.

Research on the catalytic effect of alkyldiboranes on the interconversion of organoboron compounds is noteworthy from both theoretical and preparative points of view. During recent years an intensive study has been made of the addition of diborane to unsaturated compounds, which has acquired great importance in the chemistry of organoboron compounds, and also in organic chemistry as a method for the stereospecific hydration of olefines contrary to Markovnikov's rule.

The reactions of diborane and its alkyl, aryl, and alkylthio-derivatives with diene hydrocarbons have been used to develop promising new methods for the synthesis of heterocyclic compounds containing boron in the ring.

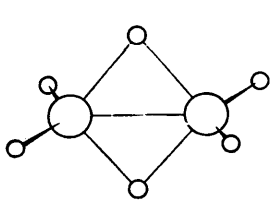
Progress in the chemistry of diborane, by clearing up the urgent problems of complex formation, dimerisation, and disproportionation in electron-deficient compounds, is extremely valuable for the development of the theory of chemical combination and molecular structure.

Diborane and its compounds are also of practical interest. Both diborane itself and several of its derivatives are used as reducing agents, and many compounds of diborane, primarily its nitrogen and phosphorus derivatives, form heat-resistant polymers. Diborane is also of interest in view of its genetic relationship to the higher boron hydrides, which have prospects of employment as rocket fuels.

I. STRUCTURE AND PHYSICAL PROPERTIES OF DIBORANE

The structure of diborane and the higher boron hydrides became the subject of prolonged discussion. The problem arises because they do not fit the usual ideas of the nature of the chemical bond. It is only recently, by careful examination of the experimental data and the development of the concept of a new type of bond, the so-called "three-centre bond", that the problem of the structure of the boron hydrides has been solved.

According to modern views, the 1*s* orbital of hydrogen and four $2sp^3$ orbitals of boron are utilised in diborane. Each of the boron atoms forms two covalent B–H bonds, both the boron atoms and four hydrogen atoms being in the same plane. The two remaining hydrogen atoms are situated at equal distances from this plane on a line perpendicular to it and bisecting the B–B line (see diagram). Each of these two "bridge" hydrogen atoms is joined to both boron atoms by three-centre bonds. Each B–H–B bridge is regarded as a filled three-centre localised bonding orbital, which utilises one hydrogen orbital and one hybrid orbital from each of the boron atoms. The hydrogen atom contributes one electron to this orbital, and each boron atom contributes half an electron [15,16].



Structure of B_2H_6.

Electron-diffraction studies [17] show that the length of a terminal B–H bond in diborane is 1.19 Å, that of a bridge B–H bond 1.33 Å, the distance between the boron atoms 1.77 Å, and the H–B–H angle 121.5°. The frequencies of the stretching vibrations of the terminal B–H bonds lie in the range 2500–2600 cm^{-1} in the infra-red absorption spectra and the Raman spectra, while the vibrational frequencies of the B–H bridge bonds are situated at ~1600 cm^{-1} and ~1800–2000 cm^{-1} (the latter are less intense) in the infra-red absorption spectra, and ~2100 cm^{-1} in the Raman spectra [18-22].

The energy of a terminal boron–hydrogen bond is 93.1 kcal $mole^{-1}$, that of a B–H–B bond 107.2 kcal $mole^{-1}$, and the energy of dissociation of diborane into two borine molecules is 28.5 kcal $mole^{-1}$.[23] The mass spectra of diborane have been investigated [24].

II. METHODS FOR PREPARING DIBORANE AND ITS ALKYL AND ARYL DERIVATIVES

1. Preparation of Diborane

New methods have recently been discovered for obtaining diborane, several of which are very convenient in view of the availability of the starting materials, the rapidity of the process, and the consistently high yields.

One such method, discovered by Schlesinger *et al.* is based on the reaction of boron trichloride with lithium aluminium hydride in ether [25]. It is more convenient to use the ether addition compound of boron trifluoride [26] when the yield of diborane is 70–80%.

$$3LiAlH_4 + 4BX_3 = 3LiX + 3AlX_3 + 2B_2H_6,$$

where X = F, Cl.

Another convenient method for preparing diborane, proposed by Schlesinger and Brown [27,28] is the reaction of the addition complex of ether and boron trifluoride with lithium or sodium borohydride (tetrahydroborate);

$$3MBH_4 + 4BF_3 = 2B_2H_6 + 3MBF_4,$$

where M = Li, Na.

The reaction with lithium borohydride can conveniently be carried out in ethyl ether [29]; when sodium borohydride is used, it is advisable to carry out the process in "diglyme" (the methyl ether of diethylene glycol) [30], when the yield of diborane is 90% based on the above equation. Ethyl ether can be used as solvent instead of diglyme, but the yield of diborane is then ~70% [31]. Boron trichloride also reacts with $NaBH_4$ in diglyme to form diborane, but the yield is decreased in the presence of an excess of BCl_3, and when the reactants are in equimolar proportions diborane is not obtained at all because diborane and BCl_3 are able to form relatively stable addition compounds of ether and chloroborine [30].

Diborane contaminated with SO_2 is obtained by the action of sulphuric acid on sodium borohydride; when the sulphuric acid is replaced by methanesulphonic acid, diborane is obtained in 76% yield free from SO_2.[32]

Another group of methods for obtaining diborane is based on the use of metal hydrides. Lithium hydride as a fine powder suspended in ether reacts on heating with the ether addition compound of boron trifluoride with the evolution of diborane[29]. The process represented by the equation below takes place very slowly and gives low and variable yields of diborane:

$$6LiH + 8BF_3 = B_2H_6 + 6LiBF_4.$$

The influence of temperature[33] and of activators[34] (bromine, iodine) on the course of this reaction has been investigated. The assessment of this method as the simplest and the most economical for obtaining diborane[35] is incorrect.

The reaction between sodium hydride and the ether compound of boron trifluoride in ethyl ether is still less suitable for the preparation of diborane[36]. In diglyme, however, this reaction takes place smoothly[30], and can be recommended as a laboratory preparation.

The photochemical preparation of diborane from BCl_3 and silane in the presence of azomethane has been described[37], and also the reduction of boron halides with calcium hydride[38-40].

2. Preparation of Alkyldiboranes

Schlesinger and his collaborators found that alkyl derivatives of diborane are formed when the latter reacts with trialkylborines. If a mixture of trimethylborine and diborane is left for several hours at room temperature, four methyl derivatives of diborane — methyldiborane, unsymmetrical dimethyldiborane, trimethyldiborane, and tetramethyldiborane — are obtained[41]. When less substituted methyldiboranes are treated with trimethylborine, they are methylated, but even with a considerable excess of trimethylborine no pentamethyldiborane is obtained. Ethyldiborane and unsymmetrical diethyldiborane are obtained by the reaction of triethylborine with diborane in the proportions 1 : 5; excess of triethylborine yields a mixture of tri- and tetra-ethyldiborane[42]. Interaction of diborane and tri-n-propylborine in the proportions 8 : 1 gives n-propyldiborane and unsymmetrical di-n-propyldiborane[42].

Symmetrical dimethyldiborane is not formed directly from trimethylborine and diborane. It can be obtained from monomethyldiborane by treating it with methyl ether[43] or tetrahydrofuran[44] at low temperatures: the methyldiborane is converted into the ether complex of borine and into methylborine, which does not give an ether complex but dimerises:

$$2CH_3B_2H_5 + 2(CH_3)_2O \rightarrow 2(CH_3)_2O \cdot BH_3 + (CH_3BH_2)_2.$$

Symmetrical dimethyldiborane is unstable, being converted on standing into the unsymmetrical isomer.

Solomon *et al.*[45] in a detailed investigation of the properties of ethyldiborane, found that after an hour at 25° half of it has been converted to diborane and symmetrical diethyldiborane. The mechanism of this disproportionation, consisting in the reversible dissociation of diborane and alkyldiboranes, is represented by the following scheme:

$$2C_2H_5B_2H_5 \rightleftharpoons 2C_2H_5BH_2 + 2BH_3$$
$$sym\text{-}(C_2H_5)_2B_2H_4 \quad B_2H_6$$

As usually prepared, unsymmetrical diethyldiborane contains the symmetrical isomer as impurity, from which it cannot be freed by distillation. The pure unsymmetrical diethyldiborane has been isolated using the ability of the symmetrical isomer to react rapidly with diborane. When the latter reacts with a mixture of the diethyldiboranes, the symmetrical isomer is converted into ethyldiborane, which can now be separated by fractionation. Symmetrical diethyldiborane is comparatively stable to heat: it remains unchanged after 24 h at 25°; unsymmetrical diethyldiborane after 16 h at 25° is 30% converted into diborane and different ethyldiboranes, but it does not yield the symmetrical diethyldiborane[45]. These alkyldiboranes were obtained in millimole amounts by a high-vacuum technique, and did not have sufficiently complete physical characterisation. Mikhailov *et al.*[46] synthesised alkyldiboranes in larger amounts by the usual procedures of organic synthesis. By passing diborane into ethereal solutions of tri-n-propylborine and tri-n-butylborine they obtained the comparatively thermally stable tetraalkyldiboranes

$$4BR_3 + B_2H_6 = 3R_2BH \cdot BHR_2,$$

and unsymmetrical di-n-propyldiborane, which is unstable to heating. Determination of the physical constants of these alkyldiboranes enabled the refractions of the terminal and the bridge boron–hydrogen bonds to be calculated as 2.76 and 1.72 cm^3.

Tetrakis(-2-methylpentyl)diborane was obtained by the action of a trialkylamine–borine on tris(-2-methylpentyl). .borine[47].

Alkyldiboranes can be obtained by the action of metal borohydrides (tetrahydroborates) or lithium aluminium hydride on trialkylborines in the presence of hydrogen chloride[48]. Alkyldiboranes of different degrees of substitution can be obtained depending on the proportions of the reactants. The reaction with sodium borohydride takes place at 150°–175° and is represented by the equation

$$NaBH_4 + HCl + 3BR_3 \rightarrow 2R_4B_2H_2 + NaCl + RH.$$

With lithium borohydride the reaction takes place at a lower temperature and has a diff(rent mechanism:

$$2LiBH_4 + 2HCl + 4BR_3 \rightarrow 3R_4B_2H_2 + 2LiCl + 2H_2.$$

Boron trichloride can be used instead of hydrogen chloride, the reaction then being represented by the equation

$$3LiBH_4 + BCl_3 + 2B(CH_3)_3 \rightarrow 3B_2H_4(CH_3)_2 + 3LiCl.$$

Tetraalkyldiboranes can be obtained by the action of lithium aluminium hydride on the dialkylboron chloride in ethereal solution[48]:

$$LiAlH_4 + 4(C_3H_7)_2BCl = 2(C_3H_7)_4B_2H_2 + LiCl + AlCl_3.$$

Diethyldiborane and di-n-propyldiborane are obtained by the action of sodium borohydride on vinyl and allyl bromide respectively[49].

Alkyldiboranes are also obtained by the action of hydrogen under pressure on trialkylborines[50,51].

The vibrational frequencies of the terminal B–H bonds in alkyldiboranes lie within the range 2500–2600 cm^{-1} in the infra-red absorption and Raman spectra, while those of the bridge B–H bonds are in the range 1500–1600 cm^{-1} in the infra-red spectra[52-57].

3. Preparation of Aryldiboranes

In 1929 Pace[58] reported the preparation of phenyldiborane from $C_6H_5BI_2.2HI$ and alcohol, but it proved impossible to repeat his results[59]. Later Hurd[60] showed that hydrolysis of the reaction products obtained from benzene

TABLE 1. Alkyldiboranes and aryldiboranes.

Compound	M.p., °C	B.p., °C	Vapour pressure, mm/°C	References
$CH_3B_2H_5$			55/—78.5	41
$(CH_3)_2BH \cdot BH_3$	—150.2	—2.6	10/—78.5	41,51
$(CH_3BH_2)_2$	—124.9	+4.9	7/—78.5	43
$(CH_3)_2BH \cdot BH_2CH_3$	—122.9	45.5	123/0	41
$[(CH_3)_2BH]_2$	— 72.5	68.6	48/0	41,48,49
$C_2H_5B_2H_5$			7/—78.5	42
$(C_2H_5)_2BH \cdot BH_3$			46/0	42,45
$(C_2H_5BH_2)_2$			36/0	45
$(C_2H_5)_2BH \cdot BH_2C_2H_5$			4/0	42
$[(C_2H_5)_2BH]_2$			0.5/0	42
$n\text{-}C_3H_7B_2H_5$			6.2/—60	42
$(n\text{-}C_3H_7)_2BH \cdot BH_3$		34/32[a]	2.8/0	46
$[(n\text{-}C_3H_7)_2BH]_2$		34/1[b]	21/6	46,48
$[(n\text{-}C_4H_9)_2BH]_2$		41/0.25[c]		46
$(C_6H_5BH_2)_2$	85			53,62
$(p\text{-}ClC_6H_4BH_2)_2$	117			62
$(\alpha\text{-}C_{10}H_7BH_2)_2$	119			62

[a] n_D^{20} 1.4088;

[b] d_4^{20} 0.7388; n_D^{20} 1.4327;

[c] d_4^{20} 0.7647; n_D^{20} 1.4375.

and diborane at 120° and 12 atm yielded phenylboronic acid, but the phenyl derivative of diborane itself was not isolated. Nielsen *et al.*[61] were unsuccessful in preparing phenyldiborane from phenylboron chloride and lithium aluminium hydride in boiling dioxane, since at the given temperature 1,2-diphenyldiborane is converted into triphenylborine and diborane.

It was only in 1958 that Wiberg and his coworkers[59] first obtained an aryl derivative of diborane (1,2-diphenyldiborane) by heating triphenylborine with diborane at 40°–100° and 2–4 atm:

$$2\,(C_6H_5)_3B + 2B_2H_6 \longrightarrow 3\,(C_6H_5BH_2)_2.$$

The same compound was obtained by the reduction of phenylboron dichloride with sodium borohydride in ether.

Mikhailov and Dorokhov[62] showed that 1,2-diaryldiboranes are obtained in high yields by the action of diborane on esters of diarylborinic acids in ether:

$$3Ar_2BOR + 2B_2H_6 = 3\,(ArBH_2)_2 + B\,(OR)_3.$$

This method was used to obtain the 1,2-diphenyl, 1,2-di-*p*-chlorophenyl, and 1,2-di-α-naphthyl derivatives of diborane. 1,2-Diaryldiboranes are obtained in lower but still quite good yields by the action of diborane on arylboronic esters[62]. The properties of the alkyl- and aryl-diboranes are set out in Table 1.

III. CHEMICAL PROPERTIES OF DIBORANE AND ITS ALKYL AND ARYL DERIVATIVES

1. Reactions of Diborane and Its Alkyl and Aryl Derivatives with Nitrogen Compounds

Even at comparatively high temperatures the degree of dissociation of diborane into borine (BH_3) molecules is so low[63] that it cannot be detected experimentally. In chemical reactions, however, diborane behaves as a compound which is easily decomposed into two BH_3 groups. It reacts at low temperatures with substances having lone pairs of electrons, such as amines, ethers, etc. to form coordination compounds of borine.

(a) Reactions of diborane with tertiary amines. Trialkylamine–borines†. Tertiary amines convert diborane into trialkylamine complexes of borine. With trimethylamine the reaction is rapid and quantitative at -110°.[64] The energy of dissociation of trimethylamine–borine $(CH_3)_3N.BH_3$ into its components in the gaseous state is 31.5 kcal mole^{-1},[23] so that formation of the complex involves an increase in energy of 17.3 kcal × × mole^{-1}:

$$(CH_3)_3N + {}^1/_2B_2H_6 = (CH_3)_3N \cdot BH_3.$$

Trialkylamine–borines are prepared by passing diborane into an ethereal solution of the trialkylamine[65]. They can also be conveniently obtained by Schaeffer and Anderson's method[66], based on the reaction in ethereal medium between lithium borohydride and a salt of the tertiary amine. Trimethylamine–borine was obtained in 85% yield in this way. Salts of higher trialkylamines also react smoothly[67]. The primary reaction product is evidently the trialkylammonium borohydride, which evolves hydrogen and is converted to the borine complex:

$$R_3N.HCl + LiBH_4 = [R_3NH]\,BH_4 + LiCl,$$

$$[R_3NH]\,BH_4 = R_3N \cdot BH_3 + H_2.$$

Köster in a short note pointed out the possibility of obtaining trialkylamine–borines by heating a mixture of a trialkylborine and a tertiary amine in the presence of hydrogen under pressure at 220° [68]:

$$R_3N + BR'_3 + 3H_2 = R_3N \cdot BH_3 + 3R'H.$$

Diborane forms complex compounds with pyridine, its homologues, and quinoline. Pyridine–borine is obtained by the action of diborane on pyridine at room temperature[69]. The heat of reaction in nitrobenzene solution was 17.9 kcal × × mole^{-1}:[70]

$${}^1/_2\,B_2H_6 + C_5H_5N\ \text{(in nitrobenzene)} = C_5H_5N \cdot BH_3\ \text{(in nitrobenzene)}.$$

Allowing for the dissociation energy of diborane[23] the change in enthalpy accompanying the reaction

$$BH_3\,(\text{gas}) + C_5H_5N\ \text{(in nitrobenzene)} = C_5H_5N \cdot BH_3\ \text{(in nitrobenzene)},$$

is thus 32.15 kcal. This is very close to the heat of reaction of boron trifluoride with pyridine in nitrobenzene (32.9 kcal) and considerably larger than that of trimethylborine with pyridine (21.4 kcal).[71] Pyridine–borine can be prepared in 80–90% yield by the action of sodium borohydride on pyridine hydrochloride in pyridine solution[72]:

$$C_5H_5N \cdot HCl + NaBH_4 = C_5H_5N \cdot BH_3 + NaCl + H_2.$$

Brown and Domash[70] prepared a series of complex compounds of diborane with homologues of pyridine and measured the heats of reaction. The increased heat of reaction of diborane with 3- and 4-picolines compared with pyridine is consistent with the increase in basicity of these homologues due to the inductive effect of the methyl groups.

† In the naming of the complex compounds of borine and its derivatives with nitrogenous bases, the nomenclature adopted in the American literature should be adhered to. Wiberg's nomenclature, according to which this type of compound is termed a "borazan", cannot be accepted as suitable, since, being based on the purely formal analogy with the alkanes, it does not reflect the complex nature of the B — N bond in such compounds, and it makes the terminology extremely complicated in several cases. Thus the complex of borine with pyridine (pyridine—borine) would be called "*N*-cyclopentatrienylborazan" according to this nomenclature.

The decreased heats of reaction of diborane with 2-alkylpyridines is explained by the effect of steric hindrance, which weakens the donor–acceptor interaction. Steric factors are less evident in complex compounds or borine than in those of trialkylborines or of boron trifluoride [73].

Diborane does not form a complex with trisilylamine [74], which is a weak base.

The properties of the complexes which have been obtained are given in Table 2. For the vapour pressure of trimethylamine–borine see Ref. 75; its dipole moment is 4.62 D, [76,77] while that of pyridine–borine is 5.86 D.[76]

Trialkylamine – alkylborines and trialkylamine – arylborines. Alkyldiboranes react with tertiary amines to form complex compounds of alkylborines. Symmetrical dimethyldiborane and trimethylamine yield trimethylamine–methylborine [43], while tetramethyldiborane with trimethylamine gives trimethylamine–dimethylborine $(CH_3)_3N.BH(CH_3)_2$.[43] Mono- and tri-methyldiborane are converted by trimethylamine into mixtures of the corresponding adducts, which are difficult to separate into their components [43]. The action of trimethylamine and pyridine on solid 1,2-diphenyldiborane in a high vacuum yields the corresponding complex compounds of phenylborine [59].

Hawthorne [79] discovered a very convenient method for preparing trialkylamine–alkylborines, which consists in reducing alkylboronic acid anhydrides with lithium aluminium hydride in the presence of tertiary amines in ether:

$$(RBO)_3 + 3R'_3N \xrightarrow{LiAlH_4} 3R'_3N \cdot BH_2R.$$

By reducing arylboronic esters or the acid anhydrides with lithium aluminium hydride in the presence of pyridine or a tertiary amine in ether Hawthorne [80,81] obtained 24–78% yields of the pyridine and trialkylamine complexes of arylborines:

$$ArB(OR)_2 \xrightarrow[C_5H_5N]{LiAlH_4} ArBH_2 \cdot C_5H_5N.$$

By a similar procedure diarylborinic esters yield the pyridine complexes of diarylborines [82]:

$$Ar_2BOR \xrightarrow[C_5H_5N]{LiAlH_4} Ar_2BH \cdot C_5H_5N.$$

TABLE 2. Complexes of borine with tertiary amines.

Compound	M.p., °C	B.p., °C or °C/mm vapour pressure, mm/°C	References
$(CH_3)_3N \cdot BH_3$	95	171	64,66,67,75,77
$(C_2H_5)_3N \cdot BH_3$	— 2	42 /10^{-4}	65,67,68
$(n\text{-}C_3H_7)_3N \cdot BH_3$	18	101 /12	67
$(CH_3)_2C_6H_5N \cdot BH_3$	17.7		65
$CH_3(C_2H_5)_2N \cdot BH_3$	—38		65
$(n\text{-}C_4H_9)_3N \cdot BH_3$	—12	80 /10^{-5}	65,67,68
$(C_2H_5)_2C_4H_9N \cdot BH_3$	—32	125 /14	68
$C_6H_5(CH_3)_2N \cdot BH_3$	35		109
		Vapour pressure	
Pyridine.BH_3[a]	11	2.5/100	69,70,72,78
4-Picoline.BH_3	74	1.2/105	70
3-Picoline.BH_3	10.5	1.1/100	70
2-Picoline.BH_3	51	1.7/100	70
2-Ethylpyridine.BH_3	50	8.6/100	70
2-Isopropylpyridine.BH_3	19	8/80	70
2-t-Butylpyridine.BH_3	25	22/50	70
2,6-Lutidine.BH_3	111	4.9/100	70
Quinoline.BH_3	96		78

[a] n_D^{25} 1.5280.[72]

TABLE 3. Trialkylamine and pyridine complexes of alkyl- and aryl-borines.

Compound	M.p., °C	B.p., °C (extrapolated)	References
$(CH_3)_3N \cdot BH_2CH_3$	0.8	176.4	43
$(CH_3)_3N \cdot BH_2C_3H_7$-n			79
$(CH_3)_3N \cdot BH_2C_3H_7$-iso			79
$(CH_3)_3N \cdot BH_2C_4H_9$-n			79
$(CH_3)_3N \cdot BH_2C_4H_9$-2			79
$(CH_3)_3N \cdot BH(CH_3)_2$	—18	171.4	43
$(CH_3)_3N \cdot BH_2C_6H_5$	69		59,81
$(C_6H_5)_3N \cdot BH_2CH_2C_6H_5$	65		81
$C_5H_5N \cdot BH_2C_3H_7$-iso			80
$C_5H_5N \cdot BH_2C_4H_9$-n			80
$C_5H_5N \cdot BH_2C_6H_5$	83		59,80,81
$C_5H_5N \cdot BH_2C_6H_4Cl$-p	62		80,81
$C_5H_5N \cdot BH_2C_6H_4OCH_3$-p	79		80,81
$C_5H_5N \cdot BH_2C_6H_4OCH_3$-o	56		81
$C_5H_5N \cdot BH_2C_6H_4CH_3$-p	65		80,81
$C_5H_5N \cdot BH_2C_{10}H_7$-α	141		80,81
$C_5H_5N \cdot BH_2CH_2C_6H_5$	106		80
$C_5H_5N \cdot BH(C_6H_5)_2$	109		80,82
$C_5H_5N \cdot BH(C_6H_4Cl\text{-}p)_2$	104		80,82
$C_5H_5N \cdot BH(C_6H_4CH_3\text{-}p)_2$	113		80,82
$C_5H_5N \cdot BH(C_6H_4OCH_3\text{-}p)_2$	110		80,82
$C_5H_5N \cdot BH(C_6H_4Br\text{-}p)_2$	124		80,82

The physical properties of the complexes of the alkyl- and aryl-borines are listed in Table 3.

Properties of trialkylamine – borines and trialkylamine – alkylborines. Trimethylamine–borine reacts slowly with moist air; in the absence of air it is quite stable and withstands being heated at 125° for several hours without appreciable decomposition [43]. Dry hydrogen chloride produces stepwise replacement of hydrogen by chlorine atoms [43]. Hydrolysis of trimethylamine–borine with hydrogen chloride in aqueous and aqueous–dioxane solutions is a first-order reaction with respect to the complex [83], its activation energy being 25.7 kcal mole^{-1}.

The energy of dissociation of trimethylamine–dimethylborine is 23.4 kcal mole^{-1}, whereas the value for the trimethylamine complex of trimethylborine [23] is 17.6 kcal × × mole^{-1}. Thus successive replacement of the hydrogen atoms in borine by methyl groups is accompanied by a decrease in the electron-acceptor properties of the molecule, which is associated with the positive inductive effect of the methyl groups. In conformity with this, the trimethylamine complexes of the methylborines differ in thermal stability [43]. Trimethylamine–methylborine is stable at 100°, but at 200° it undergoes disproportionation according to the equation

$$3(CH_3)_3N \cdot BH_2CH_3 \rightarrow 2(CH_3)_3N \cdot BH_3 + (CH_3)_3N.B(CH_3)_3.$$

Trimethylamine–dimethylborine disproportionates at an appreciable rate even at 70°:

$$2(CH_3)_3N \cdot BH(CH_3)_2 \rightarrow (CH_3)_3N \cdot BH_2CH_3 + (CH_3)_3N + B(CH_3)_3.$$

Trialkylamine–alkylborines react with ammonia in diglyme at 100°–150°, in the presence of aluminium chloride as catalyst, to form *B*-trialkylborazoles [79]:

$$3NH_3 + 3R_3N.BH_2R \xrightarrow{NH_3} (RBNH)_3 + 3R_3N + 6H_2.$$

With phenylenediamine they are smoothly converted into heterocyclic compounds, the dihydrobenzoboradiazoles [79]. Trimethylamine–borine [84] and pyridine–borine [85,86] have been investigated as reducing agents for carbonyl compounds.

The trimethylamine complexes of methylborine and dimethylborine react with dry hydrogen chloride in a similar manner to trimethylamine–borine, but at a greater rate[43].

Hawthorne and Lewis[87] investigated the kinetics of the hydrolysis of pyridine–diphenylborine in acetonitrile solution.

(b) Reactions of diborane with secondary amines. In 1948 Wiberg *et al.*[88] obtained dimethylamine–borine by mixing diborane with the amine:

$$^1/_2B_2H_6 + (CH_3)_2NH = (CH_3)_2NH \cdot BH_3.$$

Dialkylamine–borines are more conveniently obtained by passing diborane into an ether solution of the secondary amine, as did Mikhailov and Dorokhov[89] in the synthesis of diethylamine–borine.

A second method for obtaining dialkylamine–borines is based on the reaction between alkylammonium salts and lithium borohydride discovered by Schaeffer and Anderson[66]. Nöth and Beyer[67] obtained a high yield of dimethylamine–borine by the reaction of dimethylammonium chloride with this reducing agent in ethereal medium at room temperature, in spite of Schaeffer and Anderson's results indicating the formation of dimethylaminoborine by this reaction[66]:

$$(CH_3)_2NH \cdot HCl + LiBH_4 = (CH_3)_2NH \cdot BH_3 + LiCl + H_2.$$

Several other dialkylamine–borines were obtained in yields of 82–98% by this method[67].

At 120°–150° dialkylamine–borines split off hydrogen and are converted into dialkylaminoborines. Wiberg *et al.*[88,90] obtained dimethylaminoborine by heating a mixture of diborane and dimethylamine (1 : 2) at 180°–200°:

$$^1/_2B_2H_6 + (CH_3)_2NH = (CH_3)_2N{-}BH_2 + H_2.$$

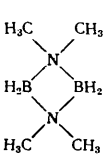
However, the process goes quite smoothly under less severe conditions. Burg and Randolph[91] prepared the same compound in almost quantitative yield by passing diborane into dimethylamine at -42° and then heating the resulting complex in a vacuum at 130°.

At room temperature dimethylaminoborine exists in the form of a dimer, which is 90% dissociated at 105°, the energy of dissocation being 20.7 kcal mole^{-1}. Dimethylaminoborine is comparatively stable to heat: on being heated in a sealed tube at 106° for a week, it undergoes very slight disproportionation into both bisdimethylaminoborine and dimethylaminodiborane[91]:

$$3\,(CH_3)_2NBH_2 \rightleftarrows [(CH_3)_2N]_2BH + (CH_3)_2NB_2H_5.$$

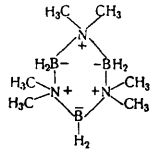
This is a reversible process: when an equimolar mixture of these products is heated at 90° for 12 h, dimethylaminoborine is formed in 90% yield.

The exact structure of the dimer of dimethylaminoborine has not been established, but by analogy with amino- and dimethylamino-diborane it is apparently similar to that of diborane but the bridge hydrogen atoms replaced by dialkylamino-groups combined with the boron atoms by three-centre bonds:



The dimer is stable towards water and hydrogen bromide, with both of which it reacts only on heating[88].

Dimethylaminoborine is able to exist not only as a dimer but also as a trimer, the latter being formed when the dimer is heated with pentaborane–9, B_5H_9, at 110°.[92] Burg, having obtained the trimer in this way, erroneously assigned the formula $[(CH_3)_2N]_3B_3H_4$ to it[93]. X-Ray analysis shows it to have a cyclic structure[94], which is confirmed by nuclear magnetic resonance measurements[92]:



It is stable in moist air, and is not appreciably hydrolysed in moist acetone at room temperature; when heated with methanol at 85° for 26 h it evolves the theoretical quantity of hydrogen.

Dimethylaminodeuteroborine is obtained by heating deuteroborine with $(CH_3)_2ND$.[95]

Not very pure[97] bisdimethylaminoborine[96] is formed when dimethylaminoborine is heated with an equal quantity of dimethylamine (200° for 10 h). To obtain the pure disubstituted derivative[97], it is advisable to heat dimethylaminoborine with a slightly greater quantity of dimethylamine than is required by the equation

$$(CH_3)_2NBH_2 + (CH_3)_2NH = [(CH_3)_2N]_2BH + H_2,$$

at 150° for 12 h.

Dimethylaminoborine is converted into bisdimethylaminoborine also when it is heated with trimethylamine at 140° for 19 h:[97]

$$2\,(CH_3)_2NBH_2 + (CH_3)_3N \rightleftarrows [(CH_3)_2N]_2BH + (CH_3)_3N \cdot BH_3.$$

Formation of an unstable complex of dimethylaminoborine and trimethylamine, $(CH_3)_2NBH_2 \cdot N(CH_3)_3$, was observed in this reaction. Bisdimethylaminoborine was also obtained by the reduction of chlorobisdimethylaminoborine with lithium aluminium hydride[98]:

$$[(CH_3)_2N]_2BCl \xrightarrow{LiAlH_4} [(CH_3)_2N]_2BH,$$

and also by heating dimethylaminoborine with sodium hydride at 100°[97]:

$$2\,(CH_3)_2NBH_2 + NaH \rightarrow [(CH_3)_2N]_2BH + NaBH_4.$$

Bisdimethylaminoborine can be converted to dimethylaminoborine by heating with diborane at 100°:

$$2[(CH_3)_2N]_2BH + B_2H_6 \rightarrow 4\,(CH_3)_2NBH_2.$$

On prolonged heating of diborane with an excess of dimethylamine (1 : 5) at 205°, trisdimethylaminoborine is formed[97], and this reacts with an equimolar quantity of diborane at elevated temperatures to form dimethylaminoborine[97]:

$$2\,[(CH_3)_2N]_3B + 2B_2H_6 \rightarrow 6\,(CH_3)_2NBH_2.$$

With diborane, dimethylaminoborine forms dimethylaminodiborane[91]:

$$2\,(CH_3)_2NBH_2 + B_2H_6 = 2\,(CH_3)_2NB_2H_5.$$

The reaction is carried out either in a sealed tube or in a flow system at 135°, the yield being almost quantitative in both cases. In order to obtain dimethylaminodiborane in greater amounts, diborane is allowed to react with dimethylamine at -42°, the reaction mixture is heated, and diborane is then passed into the resulting crude dimethylaminoborine at 135°. The yield is 75–85%.

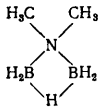
Another method for obtaining dimethylaminodiborane is to heat a mixture of dimethylaminoborine and boron trifluoride at 90°.[91] It is formed just as smoothly, together with a small amount of dimethylaminoborine, when diborane is heated with bisdimethylaminoborine at temperatures close to 100°:

$$2[(CH_3)_2N]_2BH + 3B_2H_6 = 4(CH_3)_2NB_2H_5,$$

or when it is heated with trisdimethylaminoborine[97]:

$$2[(CH_3)_2N]_3B + 5B_2H_6 = 6(CH_3)_2NB_2H_5.$$

The structure of dimethylaminodiborane has been established by electron diffraction[99]. It is equivalent to diborane in which one bridge hydrogen has been replaced by a dimethylamino-group:



The nitrogen atom is at an identical distance of 1.55 Å from each boron atom, while the distance between the boron atoms is 1.92 Å, the B–N–B angle being 76.4 ± 5.5°. For the Raman and infra-red spectra of dimethylaminodiborane, see Ref. 100.

Dimethylaminodiborane reacts with BF_3 at 100° with the formation of diborane and $(CH_3)_2N.BH_2.BF_3$; reaction with BCl_3 yields $(CH_3)_2NB_2H_4Cl$.[91]

There are indications that diethylaminoborine is formed when diethylamine is heated (at 200°–230°) with diborane[88], but the properties of this compound are not stated. Mikhailov and Dorokhov[89] obtained dimeric diethylaminoborine by the pyrolysis of diethylamine–borine at 130°–150° for 7 h, the yield being 89%:

$$2(C_2H_5)_2NH.BH_3 = [(C_2H_5)_2NBH_2]_2 + 2H_2.$$

Bisdiethylaminodiborane is stable at room temperature towards water and alcohols, but it reacts with them at 60° It is capable of adding on to olefinic hydrocarbons in the presence of pyridine at 130° [89]:

$$\tfrac{1}{2}[(C_2H_5)_2NBH_2]_2 + 2R{-}CH{=}CH_2 \rightarrow (R{-}CH_2{-}CH_2)_2B{-}N(C_2H_5)_2,$$

where R = C_2H_5, C_6H_{13}.

Burg and Good[101] investigated the reactions of diborane with cyclic secondary amines. Piperidine forms an unstable piperidine–borine, which changes at 110°–145° into piperidinoborine $C_5H_{10}NBH_2$, and this on heating with diborane (at 85°–110°) gives piperidinodiborane. Pyrrolidine and azetidine behave similarly towards diborane. Aziridine (ethyleneimine) reacts with diborane to form the complex $C_2H_4NH.BH_3$, which is partly converted to ethylaminodiborane with opening of the ring on heating (at 100°) in a current of diborane.

1,2-Dimethyldiborane reacts with dimethylamine in a manner similar to that of diborane. When the components are mixed at -78° a non-volatile methylborine complex is obtained, which on heating is converted to methyl(dimethylamino)borine $(CH_3)_2N.BHCH_3$. In the liquid state this substance is dimeric, but in the gas phase it is almost completely monomeric. Conversion of one form to the other is slow, which enables them both to be isolated in the pure form and their physical properties to be determined.

Methyl(dimethylamino)borine exhibits no tendency to exchange its dimethylamino-group, but at room temperature it disproportionates by exchanging methyl groups for hydrogen atoms, yielding dimethylaminoborine and tetramethylaminoborine:

$$2(CH_3)_2NBHCH_3 \rightleftarrows (CH_3)_2NBH_2 + (CH_3)_2NB(CH_3)_2.$$

The reaction of diethylamine with a solution of 1,2-diphenyldiborane in ether yields diethylamine–phenylborine[89]:

$$(C_6H_5BH_2)_2 + 2(C_2H_5)_2NH \rightarrow 2(C_2H_5)_2NH.BH_2C_6H_5,$$

which on being heated in a vacuum (to 150°) evolves hydrogen and is converted to a mixture of diphenyldiethylaminoborine and diethylaminoborine. The latter is collected, in a trap cooled to -70°, as a mobile liquid which is converted with rise in temperature to crystalline bisdiethylaminodiborane. If the pyrolysis of diethylamine–phenylborine is carried out at atmospheric pressure, it is possible to isolate the intermediate reaction product phenyldiethylaminoborine, which can be reversibly converted to a mixture of diphenyldiethylaminoborine and diethylaminoborine[89]:

$$2(C_2H_5)_2NH.BH_2C_6H_5 \xrightarrow{-H_2} 2C_6H_5B\begin{matrix}H\\ N(C_2H_5)_2\end{matrix} \rightleftarrows (C_6H_5)_2BN(C_2H_5)_2 + (C_2H_5)_2NBH_2.$$

The physical properties of the dialkylamine–borines, dialkylaminoborines, alkyl(dialkylamino)borines, and dialkylaminodiboranes are given in Table 4.

The dialkylamine–borines are associated in benzene solution[67]. The dipole moments of the dialkylamine–borines have values of 4.55–4.87 D.[76] For the vapour pressure of dimethylamine–borine, see Ref. 74 and for the infra-red spectra of dimethylaminoborine, see Ref. 102.

TABLE 4. Dialkylamine-borines, dialkylaminoborines, and dialkylamino-*B*-alkylborines.

Compound	M.p., °C	B.p., °C (calc.)	References
$(CH_3)_2NH.BH_3$	37	49/10-2[b]	67,88
$(C_2H_5)_2NH.BH_3$[a]	—20	77/2,5[b]	67,89
$(n\text{-}C_3H_7)_2NH.BH_3$	30	—	67
$(iso\text{-}C_3H_7)_2NH.BH_3$	23	88/1[6]	67
$(n\text{-}C_4H_9)_2NH.BH_3$	15		67
$(iso\text{-}C_4H_9)_2NH.BH_3$	19		67
$C_5H_4NH.BH_3$	42		101
	Vapour pressure, mm/°C		
$[(CH_3)_2NBH_2]_2$	75	9.1/23	88,91
$[(CH_3)_2NBH_2]_3$	97.8		92,93
$(CH_3)_2N.BD_2$	74.5		95
$[(C_2H_5)_2NBH_2]_2$	44		89
$[(C_5H_8N.BH_2]_2$	51.8	186	101
$C_4H_8NBH_2$	34.2	194	101
$C_5H_{10}NBH_2$	110	202	101
$(CH_3)_2NBHCH_3$	—136.2	42	44
		Vapour pressure, mm/°C	
$[(CH_3)_2N.BHCH_3]_2$	melts at room temperature	1.2/0	44
$(H_3Si)_2NBH_2$	—78	7/—78	73
$[(H_3Si)_2NBH]_2$		10/25	73
$(CH_3)_2NB_3H_8$	—54.4	50.3	91,103,104
$(CH_3)_2NB_3D_8$	—57		95
$C_5H_8NB_2H_5$	—45.3	87	101
$C_6H_8NB_2H_5$	—63.6	121.8	101
$C_8H_{10}NB_2H_5$		148	101
		Vapour pressure, mm/°C	
$(H_3Si)_2NB_2H_5$	—68.8	74.5/0	73
$(CH_3NSiH_3)B_2H_5$	—39	81.5/0	73
$[(CH_3)_2N]_2BH$	—57	105.7	96,97

[a] d_4^{20} 0.7568; n_D^{20} 1.4358.

[b] experimental.

(c) Reactions of diborane and of alkyldiboranes with primary amines. Methylamine–borine has been obtained by mixing diborane with methylamine at low temperatures [105,106]. The corresponding ethylamine and n-propylamine compounds are obtained similarly [101].

Nöth and Beyer [67] used Schaeffer and Anderson's reaction [66] for the synthesis of alkylamine–borines, *i.e.* the interaction of alkylammonium salts and lithium borohydride in ether:

$$[RNH_3]Cl + LiBH_4 = RNH_2 \cdot BH_3 + LiCl + H_2.$$

The alkylamine–borines obtained earlier by this method were not isolated, but were heated in the crude form to give *N*-alkylborazoles [106,107]. The alkylamine–borines which have been synthesised [67] are solids with the exception of n-butylamine–borine: methylamine–borine actually has a melting point of 56°, not 10° as stated previously [106]. The stability of the alkylamine–borines to heat varies greatly with the nature of the alkylamine [67]. Thus n-butylamine–borine evolves hydrogen at 10°–15°, whereas t-butylamine–borine decomposes only at 120°–140°.

Several workers [66,105,106] have studied the pyrolysis of methylamine–borine (at ~200°) into *N*-trimethylborazole without isolating the intermediate product, methylaminoborine. Bissot and Parry [108] found that on moderate heating (to 100°) methylamine–borine is smoothly converted to methylaminoborine, which exists as the trimer:

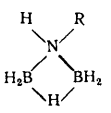
$$3CH_3NH_2 \cdot BH_3 \xrightarrow{100^\circ} (CH_3NHBH_2)_3 + 3H_2.$$

This substance possesses considerable stability, being hydrolysed very slowly by water, and it can be recrystallised from methyl or ethyl alcohol. At 200° the trimer is converted to *N*-trimethylborazole with a yield of 78%. The compound evidently has a cyclic structure with alternating boron and nitrogen atoms, similar to that of trimeric dimethylaminoborine. When diborane is passed into aniline, a crystalline substance is formed, which may perhaps have the structure of diphenylaminoborine [bis(phenylamino)borine ? (Ed. of Translation)] [109].

Alkylamine–borines react with diborane at 90°–100° with the formation of alkylaminodiboranes. The first stage of the reaction is obviously the conversion of the initial complexes to alkylaminoborines, which then add on a borine molecule:

$$RNH_2 \cdot BH_3 \xrightarrow{-H_2} RNH{-}BH_2 \xrightarrow{BH_3} RNH \cdot B_2H_5.$$

Methylamino- [91], ethylamino-, and n-propylamino-diborane [101], have been prepared in this way. Like dimethylaminodiborane and aminodiborane, alkylaminodiboranes evidently have the structure of diborane in which a bridge hydrogen atom has been replaced by an alkylamino-group:



Alkylaminodiboranes are intermediate in stability between aminodiborane (see below) and dimethylaminodiborane. Thus methylaminodiborane is 39% decomposed after 5 h at 90°, and n-propylaminodiborane undergoes a 1.2% change during 4 days at 25°.

With aniline tetraalkyldiboranes form complex compounds which evolve hydrogen at room temperature and are converted into compounds of the phenylaminodialkylborine type [46]:

$$R_4B_2H_2 + 2C_6H_5NH_2 = 2R_2BNHC_6H_5 + 2H_2.$$

The physical properties of the alkylamine–borines and the alkylaminodiboranes are given in Table 5. For the vapour pressure of methylamine–borine, see Ref. 74; the dipole moments of the alkylamine–borines have values of 4.62–5.19 D. [76]

(d) Reactions of diborane with ammonia. In 1923 Stock and Kuss [110] obtained from diborane and ammonia at low temperatures a non-volatile compound, stable at 80°, which had the composition $B_2H_6.2NH_3$. "Diborane diammine" has been assigned the structures (I), [111,112] (II), [113] and (III) [114]:

$$(NH_4)_2B_2H_4 \quad NH_4[H_3B{:}\ddot{N}{:}BH_3]\ (H \text{ above } N) \quad [NH_4]^+[H_2BNH_2[BH_4]]^-$$

(I) (II) (III)

It has recently been ascertained that the actual structure is (IV): *i.e.* the compound contains a tetrahydroborate (borohydride) anion and a diammineboronium cation:

$$[H_2B(NH_3)_2]^+BH_4^-. \quad (IV)$$

Cationic complexes are quite uncharacteristic of boron, and therefore structure (IV) seems unusual. However, compounds of the boronium type have been known for a long time: they were described as early as 1905 by Dilthey [115], who obtained bisacetylacetone and bisbenzoylacetone complexes of boron from the β-diketones and BCl_3.

Schultz and Parry [116] demonstrated the presence of the cation $[H_2B(NH_3)_2]^+$ in "diborane diammine" by preparing diammineboronium salts $[H_2B(NH_3)_2]X$ by the action of ammonium chloride or bromide on the "diammine" in liquid ammonia:

$$[H_2B(NH_3)_2]BH_4 + 2NH_4X = 2[H_2B(NH_3)_2]X + 2H_2,$$

where X = Cl, Br.

X-Ray analysis showed the ionic structure of the salt $[H_2B(NH_3)_2]Cl$; the B–N bonds in it are 1.58 Å in length, and form an almost tetrahedral angle at the boron atom [117].

The salt $[H_2B(NH_3)_2]Br$ reacts with sodium in liquid ammonia with the evolution of one equivalent of hydrogen, as does the "diammine". In both cases the hydrogen comes

TABLE 5. Alkylamine-borines and alkylaminodiboranes.

Compound	M.p., °C	B.p., °C (calc.)	References
$CH_3NH_2 \cdot BH_3$	56		67, 105, 106
$C_2H_5NH_2 \cdot BH_3$	19		67, 91
$n\text{-}C_3H_7NH_2 \cdot BH_3$	45		67, 91
$iso\text{-}C_3H_7NH_2 \cdot BH_3$	65		67
$n\text{-}C_4H_9NH_2 \cdot BH_3$	−48		67
$t\text{-}C_4H_9NH_2 \cdot BH_3$	96		67
$CH_3NH \cdot B_2H_5$		Vapour pressure 47.5 mm/0°C	91
$C_2H_5BHB_2H_5$	−96.4	86.6	101
$n\text{-}C_3H_7NHB_2H_5$	−143*	121	101

* Softening temperature of vitreous mass.

from the ammonia molecules of the boronium cation, which possesses acid properties, as with the ammines and aquo--salts of platinum, cobalt, aluminium, and other metals. The correctness of this conclusion was confirmed by a study of the reaction between sodium and various deutero--derivatives of "diborane diammine" in liquid ammonia[118]. Thus the reaction of a diammineboronium salt and of (IV) with sodium can be represented by the scheme

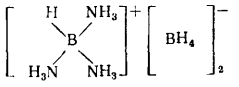
$$[H_2B(NH_3)_2]X + Na \rightarrow NaX + {}^1/_2H_2 + NH_3 + H_2BNH_2,$$

where X = Br, BH_4.

The absence of an ammonium cation from "diborane diammine" is proved by the fact that, unlike ammonium bromide (which reacts rapidly), it does not evolve hydrogen on treatment with sodium borohydride.

The presence of a borohydride ion is confirmed by the formation of sodium borohydride when the "diammine" reacts with sodium, and also by a study of the Raman spectra[119]

The preparation of "diborane diammine" necessitates strict adherence to the reaction conditions: the reactants must be mixed slowly and the excess of ammonia removed at -78°. If, however, the reaction is carried out rapidly or the reaction product is kept at -45° for a long time, a different substance is obtained[120,121], which is apparently the compound (V).[122]



(V)

The behaviour of "diborane diammine" towards ammonium salts in ether is quite different from its behaviour in liquid ammonia, as Shore and Parry[123,124] have shown. Hydrogen is formed in this case too, but a complex, ammine–borine ($H_3N.BH_3$), is obtained instead of a diammineboronium salt. The reaction is accelerated by the presence of a small quantity of ammonia. Hydrogen and ammine–borine are also evolved slowly on the addition of lithium salts to a suspension of "diborane diammine" in ether[125].

A simple method for obtaining ammine–borine, with a yield of ~45%, is based on the reaction between lithium borohydride and ammonium chloride in ether[123,124], the prototype of which is Schaeffer and Anderson's reaction[66] between alkylammonium chlorides and lithium borohydride. "Ammonium borohydride" is obviously formed at first, and then decomposes into hydrogen and ammine–borine:

$$LiBH_4 + NH_4Cl \rightarrow NH_4BH_4 + LiCl,$$
$$NH_4BH_4 \rightarrow H_3N{\cdot}BH_3 + H_2.$$

It is interesting that thermal decomposition of solid ammonium borohydride yields "diborane diammine"[119,126].

Ammine–borine is formed also by the action of ammonia on an ethereal solution of the complex of borine and methyl ether[124]:

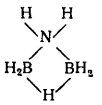
$$(CH_3)_2O{\cdot}BH_3 + NH_3 \rightarrow H_3N{\cdot}BH_3 + (CH_3)_2O.$$

Ammine–borine is a crystalline substance which is slowly hydrolysed by cold water.

Results of X-ray diffraction analysis show the length of the B–N bond in ammine–borine to be 1.56[127] or 1.60 Å[128], close to the B–N length in trimethylamine–borine[129]. The dipole moment of ammine–borine is 4.88 D.[130]

The preparation and properties of ammine–borine provided a direct proof that "diborane diammine" cannot be regarded as a dimer of ammine–borine[131].

Aminodiborane is a byproduct in the preparation of borazole from diborane and ammonia[105]. It is formed in 33% yield when a current of diborane is passed over "diborane diammine" at 88° and atmospheric pressure[132]. It can be stored at room temperature for several days without appreciable decomposition. It melts at -66.5° and boils at 75.2°. The structure of aminodiborane has been established by electron diffraction[99]: it is like that of diborane, with one bridge hydrogen replaced by an amino-group:



(e) Reactions of diborane with hydroxylamine and its methyl derivatives. Diborane and solid hydroxylamine either do not react at temperatures between -186° and -96° or else they do so explosively. In the presence of ethyl ether and with strong cooling the process takes place approximately in conformity with the equation

$$nB_2H_6 + 2\,nNH_2OH \xrightarrow{-112°} 2(H_3B{\cdot}NH_2OH)_n.$$

The reaction product could not be isolated in a pure form, since it was unstable, decomposing with the evolution of hydrogen when the temperature was raised[133]. The product of the addition of *N*-methylhydroxylamine to diborane is also unstable, and was not isolated in a pure form[133]. *NN*-Dimethylhydroxylamine, on the other hand, forms with a borine molecule a molecular compound which withstands being heated to 25°[133].

O-Methyl derivatives of hydroxylamine form still more stable compounds with borine. Thus methoxyamine–borine decomposes explosively on being rapidly heated to 90°, but with slow heating decomposition occurs quietly with the evolution of hydrogen. The use of ether is desirable but not necessary in the preparation of *ON*-dimethylhydroxylamine–borine; this substance decomposes without explosion at 65°. *ONN*-Trimethylhydroxylamine forms an adduct with borine in the absence of solvent; this adduct does not explode on being rapidly heated at 100°, but decomposes slowly at this temperature[134] with the evolution of hydrogen.

(f) Reactions of diborane with nitriles. Diborane and acetonitrile form a solid adduct $CH_3CN.BH_3$[2] having a vapour pressure of 40 mm at 20°; when kept at this temperature for several days, it is converted in 50% yield, to *N*-triethylborazole[135].

The complex of propionitrile with borine $C_2H_5CN.BH_3$ is less stable: it dissociates reversibly at -30°. The heat of dissociation of the solid complex into C_2H_5CN and diborane is 9.8 kcal mole^{-1}, the value for dissociation into the nitrile and BH_3 being 24 kcal mole^{-1}. The compound decomposes at 20° into hydrogen and an unidentified solid. At -10° or 0° the complex is converted to *N*-tri-n-propylborazole in good yield. The formation of *N*-trialkyl derivatives of borazole from complexes of nitriles with borine is represented by the following scheme:

$$RC{\equiv}N{\cdot}BH_3 \rightarrow [RCH{=}NBH_2] \rightarrow [RCH_2N{=}BH] \rightarrow (RCH_2N{-}BH)_3.$$

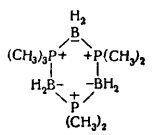
Acrylonitrile and diborane give the addition compound $CH_2:CHCN.BH_3$ at -132°; this decomposes rapidly at 0° without forming a borazole compound. Benzonitrile gives the adduct $C_6H_5CN.BH_3$ with diborane [135].

Diborane forms complexes with silyl cyanides [136]. Trimethylsilyl cyanide–borine decomposes at 100° forming trimethylsilane. It is slowly hydrolysed by water, and reacts with HCl with the evolution of hydrogen; trimethylamine displaces the trimethylsilyl cyanide from the complex.

2. Reactions of Diborane with Phosphorus, Arsenic, and Antimony Compounds

Diborane and phosphine react at 110° to form an unstable compound having the composition $BH_3.PH_3$.[137] The kinetics of this reaction have been studied [138]. Burg and Wagner [139] found greater thermal stability in compounds of borine with methylphosphines, which were obtained by mixing the components at a low temperature. Methylphosphine–borine $CH_3PH_2.BH_3$ loses hydrogen at 100° and is converted to a viscous oil. Dimethylphosphine–borine $(CH_3)_2PH.BH_3$ evolves hydrogen at 150°, the main product being trimeric dimethylphosphinoborine $[(CH_3)_2PBH_2]_3$ together with some tetramer and a polymer. The trimer and the tetramer are chemically inert and heat resistant substances, which are slowly hydrolysed at 300°; [139] the dimer decomposes very slowly at 250°.[140]

According to X-ray studies [141], the trimer of dimethylphosphinoborine has a cyclic structure with alternating BH_2 and $(CH_3)_2P$ groups linked together in the form of a "chair". The P–B bond length is 1.935 Å, and P–C length 1.837 Å:



When dimethylphosphine–borine and ethylmethylphosphine–borine are heated with triethylamine in a vacuum at 200°, polymers are obtained in which the recurrent groups are R_2PBH_2.[142]

Bis(trifluoromethyl)fluorophosphine reacts with diborane forming $[(CF_3)_2PBH_2]_3$, which is also obtained, together with a small amount of the tetramer $[(CF_3)_2PBH_2]_4$, by the interaction of $(CF_3)_2PH$ and diborane. The trimer reacts with hydrochloric acid only at 150°.[143] The cyclic phosphine C_4H_8PH (phospholan) reacts similarly to dialkylphosphines with diborane, forming the complex $C_4H_8PH.BH_3$, which is converted at 200° to $(C_4H_8PBH_2)_3$.[144]

Diborane and phosphorus trifluoride at high pressures give the unstable complex $F_3P.BH_3$.[145]

Recently Burg and Slota [146] have suggested obtaining dialkylphosphinoborines from more readily available phosphorus compounds than dialkylphosphines: heating dimethyl- and diethyl-chlorophosphines with sodium borohydride gave 50–70% yields of the corresponding trimeric dialkylphosphinoborines:

$$(C_2H_5)_2PCl + NaBH_4 \xrightarrow{-NaCl} [(C_2H_5)_2PH\cdot BH_3] \xrightarrow{-H_2} 1/3\,[(C_2H_5)_2PBH_2]_3.$$

The dimethyl trimer was obtained also by the pyrolysis of the complex of borine and dimethylaminodimethylphosphine [146].

TABLE 6. Boron–phosphorus and boron–arsenic compounds.

Compound	M.p., °C	B.p., °C (calc.)	References
	Strongly dissociated at 0°		
$BH_3\cdot PH_3$			137,138
$CH_3PH_2\cdot BH_3$	—49.3	150	139
$(CH_3)_2PH\cdot BH_3$	—22.6	85.5	139,142
$CH_3(C_2H_5)PH\cdot BH_3$	—	—	142
$(CH_3)_3P\cdot BH_3$	103.5	—	139
$(CH_3)_2NP(CH_3)_2\cdot BH_3$	12	—	144
$(CF_3)_2BF\cdot BH_3$	—	—	143
$(CH_3PHBH_3)_x$	—	—	139
$[(CH_3)_2P\cdot BH_2]_3$	86	235	139,144,148
$[(CH_3)_2PBH_2]_4$	161	310	139,148
$[(C_2H_5)_2P\cdot BH_2]_3$		134/1.5	144
$[(CH_3)_2PBH_2]_x$	164—168	—	142
$[CH_3(C_2H_5)PBH_2]_x$	118—126	—	142
$[(CF_3)_2PBH_2]_3$	30.5	177	143
$[(CF_3)_2PBH_2]_4$	—	—	143
$C_4H_8PH\cdot BH_3$	—	—	144
$(C_4H_8P\cdot BH_2)_3$	—	—	144
$F_3P\cdot BH_3$	—116	—61.8	145
$F_3P\cdot BD_3$	—115	—59.8	145
$(C_6H_5)_3PCH_2.BH_3$	192	—	149
$(C_6H_5)_3P\cdot CHCH_3\cdot BH_3$	172	—	149
$(C_6H_5)_3PCHC_6H_5.BH_3$	144	—	149
$CH_3AsH_2\cdot BH_3$	—80	—	150
	Completely dissociated at room temp.		
$(CH_3)_2AsH\cdot BH_3$	—21.5	85.5	150
$(CH_3)_3As\cdot BH_3$	74.5	154	150
$[(CH_3)_2AsBH_2]_x$			
$[(CH_3)_2AsBH_2]_3$	50.6	250	150
$[(CH_3)_2AsBH_2]_4$	150.5	352	150

At -78° diphosphine forms with diborane the complex $P_2H_4.B_2H_6$; at room temperature P_2H_4 and B_2H_6 react slowly with the formation of PH_3, H_2, and a solid having the composition $BPH_{3.5}$.[147] Tetramethyldiphosphine with diborane yields the complex $P_2(CH_3)_4.B_2H_6$, which at 170°–200° is converted to the trimer and the tetramer of dimethylphosphinoborine [148].

Diborane reacts in ethereal solutions with methylenetriphenylphosphorane and its analogues forming methylenetriphenylphosphorane–borine $(C_6H_5)_3PCH_2.BH_3$ and analogous compounds [149].

Arsine and alkylarsines behave similarly to phosphorus compounds towards diborane [150].

The action of sodium borohydride on dimethylantimony bromide yields dimethylstibinoborine, which above 78° decomposes with the evolution of hydrogen [151].

It is interesting that trimethylphosphine forms less stable complexes than does trimethylamine with trimethylborine or boron trifluoride, whereas it acts as a stronger complexing agent than trimethylamine towards borine [143]: $(CH_3)_3N > (CH_3)_3P > (CH_3)_3As$ in relation to $B(CH_3)_3$ and BF_3; $(CH_3)_3P > (CH_3)_3N > (CH_3)_3As > (CH_3)_3Sb$ in relation to BH_3‡. The physical properties of the boron–phosphorus and boron–arsenic compounds are given in Table 6.

3. Reactions of Diborane with Oxygen Compounds

(a) Reactions with ethers, alcohols, etc. Diborane reacts with ethers to form ether complexes of borine $R_2O.BH_3$. The complexes with methyl ether [120,152]

‡ *cf.* F.G.A.Stone, Chem.Rev., 58, 101 (1958) (Ed. of Translation).

(dissociation pressure 18 mm at -78.5°) and with tetrahydrofuran[152,153] (1.6 mm at -78°) have been isolated and described; the existence of a complex of borine with ethyl ether has been demonstrated spectroscopically[154]. The order of stability of these complexes is as follows:

$$\begin{matrix}CH_2{-}CH_2\\ |\quad\quad\\ CH_2{-}CH_2\end{matrix}\!\!>O\cdot BH_3 > (CH_3)_2O\cdot BH_3 > (C_2H_5)_2O\cdot BH_3.$$

The dissociation pressure of the complex of deuteroborine with methyl ether is 32 mm at -78.5° [155].

Alcohols convert diborane into boric esters, but dialkoxyborines are formed when an excess of diborane is used. Only dimethoxyborine[156] (calc. b.p. 26°, m.p. -130.6°) has been studied in detail. In the gas phase this substance is monomeric, its rate of decomposition,

$$6\,(CH_3O)_2BH \rightleftarrows B_2H_6 + 4\,(CH_3O)_3B,$$

being comparatively low and dependent on the vapour pressure; in the liquid state at 0° reaction occurs rapidly. A study has been made of the alcoholysis of diborane and deuteroborine with ordinary and with labelled ethanol[157]. The infra-red spectra of dimethoxyborine[158], diethoxyborine[159], and diisopropoxyborine[160] have been determined. For the reducing properties of diborane, see Refs. 161 and 162.

The mechanism of the hydrolysis of diborane in the gas phase has been investigated[163] and the heat of the reaction determined[164].

The action of n-butyl alcohol on 1,1-di-n-propyldiborane yields n-butyl di-n-propylborinate and n-butyl borate[46].

Mikhailov *et al.*[46] found that the reaction of tetraalkyldiboranes with alcohols is accompanied by disproportionation, so that alkylboronic esters and trialkylborines are obtained in addition to dialkylborinic esters. An analogous disproportionation obviously took place in the experiments of Brown *et al.*[165,166] on the methanolysis of the products obtained by the action of 1 mole of diborane on 4 moles of pent-1-ene in ethereal solution, when the n-pentylboronic ester and tri-n-pentylborine were obtained in addition to the expected ester of di-n-pentylborinic acid. These workers assume that the formation of the above compounds in their experiments is a consequence of equilibrium between tri-n-pentylborine and diborane.

(b) Borine carbonyl $H_3B.CO$. This borine complex, which has been known for a long time, is obtained by the action of an excess of carbon monoxide on diborane under pressure[64]. At room temperature borine carbonyl dissociates into carbon monoxide and diborane. Burg[167] supposed that the equilibrium

$$H_3B\cdot CO \rightleftarrows BH_3 + CO, \qquad (1)$$

is established rapidly, and that the rate-determining stage of the whole process is

$$H_3B\cdot CO + BH_3 \rightarrow B_2H_6 + CO. \qquad (2)$$

Bauer regards this mechanism as incorrect[168]. In his opinion, the kinetics of the process can be satisfactorily interpreted on the assumption that the rate-determining stage is the formation of borine [stage (1)], which is followed by the relatively rapid stages (2) and (3):

$$BH_3 + BH_3 \rightleftarrows B_2H_6. \qquad (3)$$

The energy of the dissociation of borine carbonyl into its components is 18.8 kcal mole^{-1}.[23,169] The carbonyl is also formed, together with B_4H_8CO, by the action of carbon monoxide on pentaborane[170]:

$$B_5H_{11} + 2CO \rightarrow H_3B\cdot CO + B_4H_8CO.$$

4. Reactions of Diborane with Sulphur Compounds

Burg and Wagner[171] showed that at -78° diborane and dimethyl sulphide form the borine complex $(CH_3)_2S.BH_3$. This compound is also obtained by the thermal decomposition of trimethylsulphonium borohydride (tetrahydroborate)[172].

In the dialkyl sulphides the tendency to coordinate increases in the sequence[173]

$$(CH_3)_2S \simeq (C_2H_5)_2S > (CH_2)_4S.$$

It is very interesting that dimethyl sulphide behaves as a stronger base than dimethyl selenide and methyl ether towards borine and trimethylborine[174]:

$$(CH_3)_2S\cdot BH_3 > (CH_3)_2Se\cdot BH_3,\ (CH_3)_2O\cdot BH_3,$$

whereas with boron trifluoride the ether is a stronger complex-forming agent than dimethyl sulphide. With respect to dimethyl sulphide and trimethylphosphine, the acidity of boron compounds falls in the following sequence:

$$BH_3 > BF_3 > B(CH_3)_3.$$

According to Burg and Wagner[171], diborane reacts with methanethiol forming a solid product, which on being heated in a vacuum to about 100° is converted to a complicated mixture of liquid and solid products which are considered to be polymers, $(CH_3SBH_2)_x$, of various degrees of polymerisation. With an excess of trimethylamine the polymer yields the adduct $CH_3SBH_2.N(CH_3)_3$; when a current of diborane is passed over the polymer at 90°, a small yield of unstable methyldithiodiborane, $CH_3SB_2H_5$, is obtained.

Mikhailov *et al.*[175-177] found that diborane reacts smoothly with thiols in ether, various alkylthio-derivatives of borine being formed depending on the proportions of the reactants and the nature of the thiols. With methanethiol and ethanethiol the polymeric alkylthioborines are formed independently of the proportions of the reactants. With n-butanethiol diborane gives poly-n-butylthioborine only when the reactants are in the proportions 1 : 2:

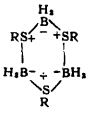
$$xB_2H_6 + 2xRSH \rightarrow 2\,(RSBH_2)_x + 2xH_2.$$

Polyethylthioborine and poly-n-butylthioborine are very thick syrupy liquids, which on standing at room temperature for a day are converted to the trimeric alkylthioborines. The solid polymer of methylthioborine does not undergo such a change spontaneously, but is converted to the trimer in tetrahydrofuran solution:

$$3\,(RSBH_2)_x \rightarrow x\,(RSBH_2)_3,$$

where R = CH_3, C_2H_5, n-C_4H_9.

The trimeric alkylthioborines are very stable towards water, and are difficult to oxidise with hydrogen peroxide, but they are completely destroyed on being heated with alcohols. They probably have a cyclic structure similar to those of the trimers of alkylaminoborines and dimethylphosphinoborine:



Reaction of diborane with an excess of propanethiol and n-butanethiol yields the dialkylthioborines, which are largely dimerised to the tetraalkylthiodiboranes:

$$B_2H_6+4RSH\rightarrow[(RS)_2BH]_2+4H_2.$$

At 100°–150° the alkylthioborine trimers and the tetraalkylthiodiboranes react with thiols forming trialkylthioborates[176,178]:

$$(RSBH_2)_3+6RSH\rightarrow 3B(SR)_3+6H_2.$$

Alkylthioborine polymers react in ether with olefines forming dialkylthioborinic esters:

$$(RSBH_2)_x+2x RCH=CH_2\rightarrow x(RCH_2—CH_2)_2BSR.$$

The reaction is complicated by disproportionation, so that trialkylborines and tetraalkylthiodiboranes are also formed.

In ether solution alkylthioborine polymers readily add on to diene hydrocarbons, forming cyclic compounds containing boron in the ring[179]. 1,3-Dienes yield alkylthio-derivatives of borocyclopentane:

$$(RSBH_2)_x+xC_4H_6\rightarrow xRS—B\begin{matrix}CH_2—CH_2\\ |\\ CH_2—CH_2\end{matrix}$$

while boracyclohexane derivatives can be synthesised from 1,4-dienes:

$$(RSBH_2)_x+xCH_2=CH—CH_2—CH=CH_2\rightarrow xRS—B\begin{matrix}CH_2—CH_2\\ \diagdown\quad\diagup\ CH_2\\ CH_2—CH_2\end{matrix}$$

Since the alkylthio-group attached to the boron atom is highly reactive, 1-alkylthioboracycloalkanes can be sucessfully used for the synthesis of various functional derivatives of cyclic compounds of boron.

Tetrabutylthiodiborane is also able to react with unsaturated compounds[180]. Its addition to hex-1-ene, oct-1-ene, styrene, cyclohexene, and diethylmethylvinylsilane was effected by heating the components in the presence of pyridine at 70°–80°, high yields of n-butyl alkylthioboronates being obtained in all cases other than that of styrene:

$$(n\text{-}C_4H_9S)_2BH+RCH=CH_2\rightarrow RCH_2CH_2B(SC_4H_{9}\text{-}n)_2.$$

The reactions between tetra-n-butylthiodiborane and propene or isobutene are complicated. When the mixture containing propene is heated in the presence of pyridine in an autoclave at 70°–80° and 5–15 atm, n-butyl n-propylthioboronate is formed, together with n-butyl di-n-propylthioborinate and tri-n-butyl thioborate. Isobutene reacts similarly, being converted to a mixture of the isobutylthioboronic and diisobutylthioborinic esters and the thioborate. The formation of dialkylthioborinic esters is explained by the partial conversion under these conditions of tetra-n-butylthiodiborane to the thioborate and n-butylthioborine; it is the latter which forms the corresponding dialkylthioborinic esters with the olefines.

Tetra-n-butylthiodiborane reacts with primary amines (ethylamine, n-butylamine) giving high yields of *N*-trialkylborazoles[180]. A complex of the dialkylthioborine with the amine is evidently formed in the first stage of the process, and this splits off a thiol, being converted to an alkylamino(alkylthio)borine; the latter gives the borazole derivative with the elimination of a further thiol molecule:

$$(n\text{-}C_4H_9S)_2BH+RNH_2\rightarrow(n\text{-}C_4H_9S)_2BH\cdot NH_2R\xrightarrow{-C_4H_9SH}$$

$$\rightarrow(n\text{-}C_4H_9S—BH—NHR]\xrightarrow{-C_4H_9SH}{}^1/_3(HB—NR)_3.$$

Thiols act on tetraalkyldiboranes at room temperature to give 60–83% yields of dialkylthioborinic esters[46,171]:

$$R_4B_2H_2+2R'SH=2R_2BSR'+2H_2.$$

Hawthorne[181] has shown that trimethylamine–borine on being heated with the higher thiols is converted to thioboric esters, while trimethylamine–alkylborines react with thiols at 60°–110° to form alkylthioboronic esters.

With dimethyl disulphide, diborane forms a solid product having the composition $(CH_3SBH_2)_x$;[171] with hydrogen sulphide it gives a vitreous polymer $(HBS)_x$.[171]

Mikhailov and Dorokhov[89] found that dialkylamine–borines and bis(dialkylamino)diboranes react with thiols at 80°–120° to form an interesting new type of compound, the alkylthiodialkylaminoborines, which exist in the monomeric form:

$$R_2NH\cdot BH_3+R'SH=R_2N—BH—SR'+2H_2,$$

$$[R_2NBH_2]_2+2R'SH=2R_2N—BH—SR'+2H_2.$$

When these compounds are heated (60°–70°) with primary amines, they exchange the R_2N and RS groups for alkylamino-groups, thus being converted to the previously unknown bisalkylaminoborines[182]:

$$R_2N—BH—SR'+2R''NH_2=(R''NH)_2BH+R'SH+R_2NH.$$

When these latter compounds are hated above 150°, they eliminate alkylamines and form *N*-trialkylborazoles:

$$3(RNH)_2BH=(HB—NR)_3+3RNH_2.$$

Thiols act on alkylamine–borines giving unstable alkylaminoalkylthioborines, which at 100° eliminate the thiol and condense into *N*-trialkylborazoles[183]:

$$RNH_2\cdot BH_3+R'SH\xrightarrow{-H_2}[RNH—BH—SR']\xrightarrow{-R'SH}(HB—NR)_3.$$

Since the thiol is regenerated during the reaction, *N*-trialkylborazoles can be synthesised from alkylamine–borines with moderate heating (100°) using a small amount of the thiol, which acts as a catalyst for the reaction. The thermal conversion of alkylamine–borines to *N*-trialkylborazoles requires a temperature of 200°–300°.

5. Halogenated Borines

In the synthesis of diborane from BCl_3 and H_2 in an electric discharge, chloroborines are obtained which rapidly disproportionate to B_2H_6 and BCl_3. One of these compounds — chlorodiborane — has been isolated[184]. Dichloroborine, formed in high yield from H_2 and BCl_3 at 400°–450°, can be preserved from further spontaneous changes by cooling to -135°.[185]

Ether complexes of chloroborine, which are quite stable at room temperature, are obtained by the interaction of diborane and boron trichloride in ether[30,186,187]; methyl ether, ethyl ether, diglyme, tetrahydropyran, and tetrahydrofuran can be used as solvents[187]:

$$B_2H_6+BCl_3+3O\langle=3BH_2Cl\cdot O\langle.$$

Equimolar proportions of the reactants yield ether complexes of chloroborine[187] which are liquid at room temperature; proportions of 1 : 4 give ether complexes of dichloroborines[187].

Nöth and Beyer[188] recommend the preparation of ether complexes of chloroborine by the action of lithium borohydride on an ether solution of BCl_3 or by the action of hydrogen chloride on an ether solution of diborane:

$$BCl_3 + LiBH_4 + 2R_2O = 2BH_2Cl \cdot OR_2 + LiCl,$$

$$2HCl + B_2H_6 + 2R_2O = 2BH_2Cl \cdot OR_2 + 2H_2.$$

Crystalline amine complexes of halogenoborines are also stable, and have recently been obtained by Nöth and Beyer[188] by four methods. The first method consists in the action of a hydrogen halide on an ether solution of an alkylamine complex of borine:

$$R_nNH_{3-n} \cdot BH_3 + HX = R_nNH_{3-n} \cdot BH_2X + H_2,$$

where X = Cl, Br, I. In the second method boron tribromide (or trichloride) acts on trialkylamine–borines:

$$3R_3N \cdot BH_3 + BBr_3 = 3R_3N \cdot BH_2Br + {}^1/_2B_2H_6.$$

By using two moles of BBr_3 in this way, we can also obtain the amine complexes of dibromoborine. The third method is to add a tertiary amine to an ether solution of chloroborine:

$$R_3N + BH_2Cl \cdot OR_2 = R_3N \cdot BH_2Cl + R_2O.$$

Finally, amine complexes of iodoborine can be obtained by the action of iodine on trialkylamine–borines:

$$2(CH_3)_3N \cdot BH_3 + I_2 = 2(CH_3)_3N \cdot BH_2I + H_2.$$

Lynds and Stern found that dichloroborine adds to alkenes at 10°–30° in accordance with Markovnikov's rule, with the formation of alkylboron dichlorides[185], although it had previously been stated that in the presence of ether the reaction results in the production of trialkylborines[187]:

$$BHCl_2 + CH_3CH = CH_2 \rightarrow (CH_3)_2CH - BCl_2.$$

Dichloroborine is capable also of addition to acetylene and butadiene[184].

6. Reactions of Diborane and Tetramethyldiborane with Metals

Diborane does not react with solid alkali metals, but is absorbed by sodium amalgam at room temperature. Stock and his collaborators supposed[110,189,190] that reaction stops after 2–3 days, the compound $Na_2B_2H_6$ being formed. It was later found that sodium is able to absorb a greater amount of diborane than is required to form $Na_2B_2H_6$.[191]

Reaction between diborane and the amalgam is considerably more rapid in the presence of ethyl or n-butyl ether, and is complete in 1–2 days with the absorption of one mole of diborane by one g-atom of sodium[192,193]. The final products of the reaction, which have the empirical composition NaB_2H_6, represent an equimolecular mixture of sodium borohydride and the previously unknown compound NaB_3H_8. The latter substance is stable at 200° and is readily soluble in ether, so that it can be separated from the sodium borohydride:

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

Tetramethyldiborane reacts with sodium in liquid ammonia at -78° to form the salt-like compound $Na_2HB(CH_3)_2$.[194] The reaction with calcium in liquid ammonia leads to the formation of $CaHB(CH_3)_3 \cdot NH_3$.[195]

7. Reactions of Diborane and Alkyldiboranes with Alkoxy- and Alkylthio-Derivatives of Boron

Mikhailov and Vasil'ev investigated the reactions of diborane and tetraalkyldiboranes with boric and organoboric esters[196,197]. In contrast to the reaction of diarylborinic esters with diborane, which yields 1,2-diaryldiboranes and orthoborates[62], dialkylborinic esters react with diborane (2 : 1) to form alkylboronic esters and dialkyldiboranes:

$$2R_2BOR' + B_2H_6 = RB(OR')_2 + 1.5R_2B_2H_4.$$

Since the dialkyldiboranes can equilibrate with dialkylborinic esters, resulting in the formation of alkylboronic esters and tetraalkyldiboranes,

$$4R_2BOR' + R_2B_2H_4 = 2RB(OR')_2 + 2R_4B_2H_2,$$

the action of one mole of diborane on eight moles of the dialkylborinic ester is represented by the equation

$$8R_2BOR' + B_2H_6 = 4RB(OR')_2 + 3R_4B_2H_2.$$

Tetraalkyldiboranes undergo alkyl transfer reactions with borates, slowly at room temperature and rapidly on moderate heating (60°–100°), with the formation of alkylboronic esters and dialkyldiboranes:

$$R_4B_2H_2 + 2B(OR')_3 = 3RB(OR')_2 + {}^1/_2R_2B_2H_4.$$

The process is complicated by the formation of diborane by the partial symmetrical redistribution of the dialkyldiborane and its interaction with the original borate. If the reaction is carried out with the mixture heated to boiling, the diborane being removed from the reaction zone, the reaction between the tetraalkyldiborane and the borate is represented by the equation

$$3R_4B_2H_2 + 8B(OR')_3 = 12RB(OR')_2 + B_2H_6.$$

The ability of alkyldiboranes to undergo alkyl interchange reactions enables them to be used as catalysts for reactions between different boron compounds. Thus in the presence of a catalytic quantity of a tetraalkyldiborane, trialkylborines and borates are smoothly converted at 60°–100° to alkylboronic esters:

$$BR_3 + 2B(OR')_3 \xrightarrow{R_4B_2H_2} 3RB(OR')_2.$$

In the presence of tetraalkyldiboranes good yields of alkylboronic esters are obtained by heating mixtures of a dialkylborinic ester and a borate:

$$R_2BOR' + B(OR')_3 \xrightarrow{R_4B_2H_2} 2RB(OR')_2.$$

An equimolar mixture of a trialkylborine and an alkylboronic ester can be converted to a dialkylborinic ester using a small quantity of a tetraalkyldiborane:

$$BR_3 + RB(OR')_2 \xrightarrow{R_4B_2H_2} 2R_2BOR'.$$

The thio-analogues behave similarly to the borates and alkylboronic and dialkylborinic esters. Thus heating a mixture of a trialkyl thioborate and a trialkylborine in the presence of tetra-n-butyldiborane produces a high yield of an alkylthioboronic ester:

$$BR_3 + 2B(SR')_3 \xrightarrow{R_4B_2H_2} 3RB(SR')_2.$$

8. Reactions of Diborane and Its Alkyl and Aryl Derivatives with Unsaturated Compounds

In 1948 Hurd established that diborane reacts with alkenes to form trialkylborines[60]. By heating ethylene with 2% of diborane in a sealed tube at 100° for 4 h, he obtained a small quantity of triethylborine, which he identified in the mass spectrograph. Diborane adds rather more rapidly to isobutene[60]. In later work a mixture of ethylene and diborane (4.4 : 1) was heated at 60° for 10 days to form triethylborine and a small amount of diethyldiborane[198].

Diborane adds smoothly to alkenes in a circulatory flow system at 230°–250° if its concentration in the gas phase is 3.5–3.8%.[199] The kinetics of the reaction between ethylene and diborane were studied over the range 130°–177° by Whatley and Pease[200]. The kinetics of the reactions of alkenes with aluminium borohydride, as a source of diborane, have also been studied[201,202].

The reactions of diborane with derivatives of ethylene are complicated. The interaction of diborane and fluorinated alkenes involves the formation of boron trifluoride and alkyl fluoroborates; a mixture of diborane and tetrafluoroethylene in certain proportions explodes at 80°–100°;[198,203] the reactions of diborane with acrylonitrile and methyl methacrylate give boron compounds of undetermined structure[204].

In 1957 Brown and Rao[205] discovered that in ethers the addition of diborane to alkenes is very rapid and almost quantitative. "Hydroboronation", as Brown termed the addition of diborane to unsaturated compounds, is carried out by passing a current of diborane into an ether solution of the alkene, the resulting trialkylborine being separated by distillation (or it is oxidised, without separation, to the corresponding alcohol and boric acid). The hydroboronation of ethylene, pent-1-ene, hex-1-ene, hex-2-ene, oct-1-ene, cyclopentene, cyclohexene, and other alkenes, has been accomplished in this way[205,206]. Another procedure is to prepare diborane *in situ* in the reaction vessel containing the alkene in solution. For this purpose, the ether complex of boron trifluoride is added to a solution of the alkene and sodium borohydride in diglyme[206] or to an ether solution of the alkene and lithium borohydride[207]. Alternatively, a suspension of sodium borohydride in tetrahydrofuran or diglyme can be treated with hydrogen chloride, and then the alkene added to the resulting diborane solution[207]. Finally, diborane can be obtained from lithium aluminium hydride and the ether complex of boron trifluoride in ethyl ether[207,208]. The different methods of hydroboronation are described in a review paper by Brown *et al.*[209]

Brown and Rao[210,211] found also that trialkylborines are obtained smoothly by the action on alkenes of a mixture of sodium borohydride and aluminium chloride in diglyme solution:

$$9RCH=CH_2 + 3NaBH_4 + AlCl_3 \rightarrow 3\,(R-CH_2-CH_2)_3B + 3NaCl + AlH_3.$$

The addition of diborane to α-olefines takes place mainly contrary to Markovnikov's rule:

$$3R-CH=CH_2 + {}^1/_2B_2H_6 \rightarrow (R-CH_2-CH_2)_3B,$$

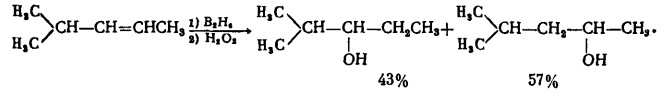
the isomeric compound being formed to only a slight extent. Thus hydroboronation of hex-1-ene with subsequent oxidation of the reaction products yields 94% of hexan-1-ol and 6% of hexan-2-ol:[212]

$$6C_4H_9CH=CH_2 + B_2H_6 \rightarrow (C_4H_9CH_2-CH_2-)_3B + \left(\begin{matrix}C_4H_9\\CH_3\end{matrix}\!\!>\!CH\right)_3B.$$

94% 6%

Branched α-olefines, such as 3-methylbut-1-ene and 3,3-dimethylbut-1-ene, form the corresponding isomeric trialkylborines in the same ratio[212,213]. Phenyl groups adjacent to a double bond change the proportions of the isomers, styrene for example giving 20% of the α- and 80% of the β-isomer. The presence of electronegative substituents in the aromatic ring favours Markovnikov addition still more: *p*-chlorostyrene yields 35% of the α- and 65% of the β-isomer[212,213].

Alkenes with non-terminal double bonds yield almost equal quantities of isomers on hydroboronation. Thus 4-methylpent-2-ene forms a mixture of trialkylborines, oxidation of which yields 43% of 2-methylpentan-3-ol and 57% of 4-methylpentan-2-ol [212,213]:



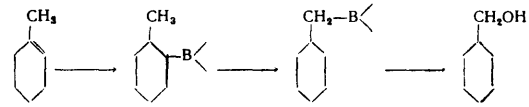
Hex-2-ene gives after oxidation equal quantities of hexan-2-ol and hexan-3-ol [213,214].

Compounds containing a semicyclic double bond are converted to primary alcohols on hydroboronation with subsequent oxidation of the addition products. In this way myrtanol has been obtained fron norpinene, and camphanol from camphenone[215,216].

In spite of its great velocity, hydroboronation is an extremely selective reaction. Treatment of equimolar mixtures of pent-1-ene and pent-2-ene and of hex-1-ene and hex-2-ene with insufficient diborane results in selective conversion of the α-olefines to tri-n-pentylborine and tri-n-hexylborine respectively, while the β-olefines remain unchanged[217].

Brown and Zweifel[218] showed the stereospecificity of hydroboronation in a series of cyclic alkenes, by obtaining the *trans*-2-methylcycloalkanols from 1-methylcyclopentene and 1-methylcyclohexene, and *cis*-1,2-dimethylcyclopentanol from 1,2-dimethylcyclopentene. The hydration of steroids is also stereospecific[208,219]. Cholesterol on hydroboronation followed by oxidation yields as the main product cholestane-3β, 6α-diol and only a small amount of the product of frontal *cis*-addition, coprostane-3β, 6β-diol. Stereospecific *cis*-addition of diborane takes place also with acyclic systems. Thus *trans*-(2-*p*-methoxyphenyl)but-2-ene can be converted to *erythro*-(3-*p*-methoxyphenyl)butan-2-ol, while the *cis*-isomer gives the compound with the *threo*-configuration[220].

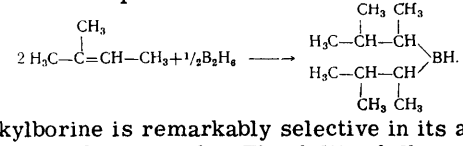
Since trialkylborines with secondary or tertiary alkyl radicals can isomerise on heating to trialkylborines having primary radicals[221], hydroboronation enables alkenes with non-terminal double bonds to be converted to primary alcohols[217,222]. This method also allows cycloalkenes to be converted to alcohols containing the hydroxyl group in the side-chain, so that, for example, cyclohexylmethanol can be prepared from 1-methylcyclohexene[222]:



On the other hand, hydroboronation can be used as a convenient synthetic route for obtaining the thermodynamically less stable alkenes with terminal double bonds from the more stable branched alkenes. This method of "contrathermodynamic" isomerisation of alkenes is based on the fact that trialkylborines on being heated with higher alkenes

undergo transalkylation with the removal of the lower alkene[217,223,224]. The process is thus essentially hydroboronation of an alkene containing the double bond in the middle of the chain, thermal isomerisation of the resulting trialkylborine to a trialkylborine having primary hydrocarbon radicals, and finally displacement of a lower by a higher alkene. For example, 3-ethylpent-2-ene may be hydroboronated, and the reaction product boiled for an hour and then heated with dec-1-ene, the resulting 3-ethylpent--1-ene being distilled off[225].

Not all alkenes are converted by diborane to trialkylborines. In several cases the reaction stops at the dialkylborine stage owing to steric hindrance. Thus Brown and Zweifel[212] found that hydroboronation of 2-methylbut-2-ene at 0° leads to bis(1,2-dimethylpropyl)borine even when an excess of alkene is present:

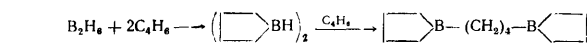


This dialkylborine is remarkably selective in its addition to other unsaturated compounds. The ability of alkenes of different structures to add bis-1,2-dimethylpropylborine diminishes in the following order: hex-1-ene > 3-methylbut-1--ene > 2-methylbut-1-ene > *cis*-hex-2-ene > cyclopentene > *trans*-hex-2-ene > *trans*-4-methylpent-2-ene > > cyclohexene > 1-methylcyclopentene > 2-methylbut-2--ene > 1-methylcyclohexene ≥ 2,3-dimethylbut-2-ene. In many cases the difference in reactivity is so great that bis(1,2--dimethylpropyl)borine can be utilised for the selective hydroboronation of more reactive alkenes mixed with less reactive compounds. In this way pent-1-ene can be practically quantitatively removed from its mixtures with pent-2-ene. Similarly hex-1-ene is quantitatively hydroboronated in the presence of cyclohexene.

A still more marked difference in reactivity towards bis(1,2-dimethylpropyl)borine is observed with *cis-trans*--isomers, which enables the isomers to be separated. Thus treatment with this dialkylborine of commercial pent-2-ene, containing 18% of the *cis*-form, enables *trans*-pent-2-ene of 97% purity to be obtained[226].

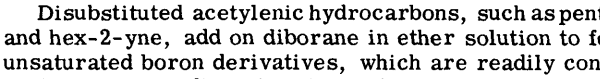
In some cases steric hindrance is so great that the reaction between diborane and the alkene stops at the alkylborine stage. Thus 2,2,5,5-tetramethylhex-3-ene with diborane gives 1-t-butyl-3,3-dimethylbutylborine, $C_{10}H_{21}BH_2$.[227]

Köster found that diborane adds to butadiene with the formation of a bisboracyclopentane, which is converted by an excess of butadiene to 1,4-bisboracyclopentylbutane[228,229]:

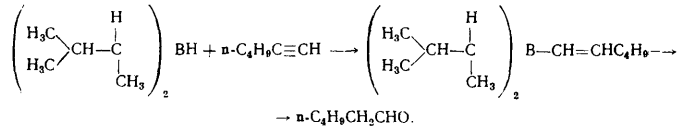


Oxidation of the addition product of diborane and butadiene produces mainly butane-1,4-diol[230]; oxidation of the reaction product from diborane and hexa-1,5-diene gives hexane-1,6-diol[230]. On hydroboronation of cyclopentadiene with subsequent oxidation, a 30% yield of cyclopent-3-enol is obtained[220].

Disubstituted acetylenic hydrocarbons, such as pent-2-yne and hex-2-yne, add on diborane in ether solution to form unsaturated boron derivatives, which are readily converted to the corresponding *cis*-alkenes by glacial acetic acid[231]:



Direct hydroboronation of hex-1-yne cannot be achieved, for about half of the hydrocarbon taken in an experiment does not react with the diborane, while the remainder forms a dialkenyl derivative of borine. However, hex-1-yne does add on bis(1,2-dimethylpropyl)borine; when the addition product is oxidised with hydrogen peroxide, n-hexanal is obtained[231]:



Hydroboronation of 2,2,5,5-tetramethylhex-3-yne with subsequent oxidation of the addition products led to the isolation of 2,2,5,5-tetramethylhexan-3-ol and 2,2,5,5-tetramethylhexane-3,4-diol[227].

Very little work has yet been done on the reactions of alkene derivatives with diborane. The reaction of vinyl chloride with diborane in methyl ether is complex; a small quantity of a crystalline substance was isolated from the reaction products, and assigned the structure of an ether complex of 2-chloroethylboron dichloride[232]. With allyl chloride, diborane gives a 36% yield of tris(3-chloropropyl)borine and a little bis(3-chloropropyl)boron chloride; hydrolysis of 3-chloropropyl derivatives of boron[233] is accompanied by the formation of cyclopropane.

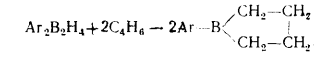
Seyferth[234,235] investigated the hydroboronation of trimethylvinylsilane with a mixture of sodium borohydride and aluminium chloride, and found that oxidation of the reaction products yielded 1- and 2-trimethylsilylethanol in the ratio 1 : 2.

Tetraalkyldiboranes in ether solution readily add to alkenes forming trialkylborines. Unsymmetrical trialkylborines can be obtained in this way[46].

1,2-Diphenyldiborane reacts with alkenes forming phenyldialkylborines, which undergo redistribution even at room temperature into triphenylborine and a trialkylborine[31]:

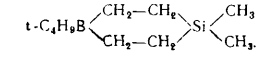


1,2-Diaryldiboranes add to diene hydrocarbons in benzene solution at -40° with the formation of 1-arylboracyclopentanes[31]:



Hawthorne[236] showed that pyridine–borine adds to alkenes in the presence of diglyme under pressure at 100°. Ashby[237] synthesised trialkylborines by heating alkenes with trialkylamine–borines at 200°. Triethylamine–borine has been used for the hydroboronation of trimethylvinylsilane[235]. A trialkylamine–borine reacts at 100° with butadiene, forming a bisboracyclopentane[229].

Trimethylamine-t-butylborine at 50°–60° adds rapidly to alkenes (ethylene, propene, butene, isobutene) forming unsymmetrical trialkylborines. With butadiene and isoprene it forms 1-t-butylboracyclopentane and 3-methyl--1-t-butylboracyclopentane respectively; reaction between the complex and dimethyldivinylsilane yields 1,1-dimethyl--4-t-butyl-1-sila-4-boracyclohexane[238].



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POLYMERS OF CARBONYL COMPOUNDS

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CONTENTS

I. Introduction 225

II. Preparation and properties of polymers of carbonyl compounds 225

1. Polyformaldehyde 225
2. Polyacetaldehyde 225
3. Polymers of higher aldehydes 229
4. Polymers of halogenated aldehydes 229
5. Polyacroleins 230
6. Polymers of ketones 231

III. Molecular structure of carbonyl polymers 231