ORGANIC COMPOUNDS OF BORON

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CONTENTS

I. INTRODUCTION

For the purpose of this review, the compounds considered to be within its scope are those boron-containing substances which have one or more organic radicals. These are broadly divisible into the following classes: (*1*) organic derivatives of borine (BH_3) and polymers of these; (*2*) organic derivatives of diborane (symmetrical di, tetra, and hexa derivatives are clearly within class 1); (*3*) coordination compounds of inorganic boron derivatives with organic ligands; and (*4*) subcompounds. Because of the very extensive literature, only the first of these classes, which is by far the largest, is dealt with herein. This decision is made because reviews are available for compounds of classes 2 and 3, albeit some of not very recent date, and with regard to class 4 only two papers (on derivatives of B_2Cl_4) have so far been published (340, 341). Class 3 is comprehensively covered by reviews on the coordination compounds of boron trifluoride (143) in 1954, of boron trichloride (222) in 1944, of boron tribromide and triiodide (223) in 1948, and of borine (68) in 1954, whereas data on compounds of class 2 were last summarized in 1942 (306).

The definition "derivatives of borine" is intended to include not merely substitution derivatives (i.e., in general, compounds having the empirical formula Babc, wherein a, b, and c are univalent atoms or groups and at least one of these contains an organic radical) but also their addition compounds. The latter may be of three types: (*1*) d:Babc; (*2*) [abBde]Y; and (*3*) M[Babcf]; in these formulas a, b, and c are as above defined, d and e are donor molecules, f is similar to a, b, and c, Y is a univalent anion, and M is a univalent cation (derivatives where M is bivalent, i.e., $M[abBcf]_2$ are also known, but none with higher valency),

Of the substitution derivatives of borine, those containing oxygen are numerically the greatest; hence division of the review into four classes has been made, depending on the extent of oxygen substitution. The contents of these are mentioned in detail, in order to demonstrate the nomenclature subsequently employed, because even today this is not uniformly standardized. Section II deals with the following: orthoborates (trialkyl, trialkenyl, and triaryl borates, $B(OR)_3$; also mixed and chelated orthoborates); triacyl borates, $B(OOCR)_3$; tetraacyl diborates, $(RCOO)_2BOB(OOCR)_2$; metaborates, ROBO. Section III is concerned with the dialkoxyborines, the alkyl(and aryl)boronic acids, and the boronates, all being derivatives of $HB(OH)_2$; and with the boroxoles, which are derivatives of HBO. Section IV deals with the dialkyl(and diaryl)boronous acids and the boronites, these being derivatives of $HOBH_2$, and with the dialkyl(and diaryl)boronous anhydrides, $(R_2B)_2O$. Section V concerns compounds wherein none of the three groups is oxygen-containing. The term "borine" is used exclusively for those compounds which have one or two hydrogen atoms in BH_3 unsubstituted; the others are named "borons," e.g., BR_3 represents the trialkylborons, $B(NR_2)_3$ represents the tris(dialkylamino)borons, and the compounds having the structure R_2BCl are called the dialkylboron chlorides. Compounds in which substitution is by sulfur-containing groups are discussed as thio analogs of the corresponding oxygen compounds in Sections II to IV.

The names "boroxoles," "borsulfoles," "borazoles," "borazenes," and "borazynes" have come into usage to stress isosteric relationships with carbon compounds. The first three represent compounds of the formulas $(XBO)_3$, $(XBS)_3$, and $(XBNX')_3$ (where X and X′ are univalent atoms or groups) and are six-membered ring compounds, displaying aromatic character as found in benzene. The borazenes, RR′NBXX′, are isosteric with the alkenes (due to nitrogen–boron back-coordination); the borazene nomenclature has not been employed because monomeric and dimeric forms are frequently known and only the former are related to the olefins. The borazynes, $RN{=}BX$, are isosteric with the alkynes and are the unstable precursors of their trimers, the borazoles; neither of these are discussed because of recent reviews (325, 350).

In order to avoid duplication, the quadrivalent boron compounds are discussed within subsections on chemical properties concerning the corresponding trivalent boron compounds; e.g., $[BO(CH_3)_3]_3 \cdot NH_3$ and $Li[B(C_6H_5)_4]$ are dealt with under the chemical properties of orthoborates and of alkyl- and arylborons, respectively.

For each class of compound the discussion is divided into preparation, physical properties, and chemical properties. In the preparative section the methods are described, and their yields, their range of application, and their limitations are discussed. In the sections on physical properties, reference is made to all published data, and these are very briefly discussed where relevant to structural problems. In addition, for each class a table is given listing all the known members (together with references) and also showing their characterizing constants (boiling point, melting point, refractive index, and density), where available; however, only values which are considered the most reliable are given, unless very wide discrepancies exist. The chemical properties are described and, where published data permit, reaction mechanisms are reproduced. As a very large number of the compounds considered are electron-deficient molecules, a high electrophilic reactivity is general and is widely prominent in such reactions as oxidation, hydrolysis, alcoholysis, and solvolysis (involving reaction with solvents containing donor atoms) and in reactions forming coordination compounds, particularly with nitrogen bases. Other reactions which are widely met are disproportionation and mutual replacement reactions. By the former is meant the very general tendency for unsymmetrical boron compounds to decompose to afford symmetrical products, e.g.,

$$3RBR'_2 \rightarrow BR_3 + 2BR'_3$$

and by the latter the reverse reaction, e.g.,

$$B(OR)_3 + 2BCl_3 \rightarrow 3ROBCl_2$$

or more generally the ease of interaction of two boron compounds with one another, resulting in mutual replacement of groups.

The literature is reviewed to the end of 1955 (some of the December issues of journals were not yet available when the manuscript was completed).

II. Derivatives of Boric Acid

A. INTRODUCTION

The best-known and most stable of the organic derivatives of boric acid are the trialkyl and triaryl orthoborates, $B(OR)_3$. Unsymmetrical esters, $ROB(OR')_2$, are known but tend to disproportionate to the symmetrical forms. The acid ester derivatives of boric acid, $HOB(OR)_2$ and $ROB(OH)_2$, have never with certainty been isolated, although they have been postulated as intermediates in both the hydrolysis (293) and the dealkylation (123) by hydrogen halides of trialkyl borates. However, chelate compounds of this type are known (see Section II,E). Recently, mono-*l*-menthyl borate (m.p. 132–135°C.) has been obtained by the controlled hydrolysis of *l*-menthyl metaborate (261).

$$ROBO + H_2O \rightarrow ROB(OH)_2$$

The alkyl metaborates, ROBO, are not nearly as well known as the orthoborates; indeed, until recently their existence had not been definitely established. This is in marked contrast to the relative stabilities of the inorganic borates, the meta salts being better known than the ortho.

Triacyl borates are known, but the most stable forms of acyloxyboron compounds appear to be the tetraacyl diborates, $[(RCOO)_2B]_2O$, which have also been named "pyroborates."

Esters of pyroboric acid do not appear to have been recorded, but the menthyl (m.p. -24°C.) and ethyl (vapor pressure = 1 mm. at 25.9°C.) esters of subboric acid, $(HO)_4B_2$, have been reported. The original preparation, due to Wiberg and Ruschmann (366), involved the reaction of sodium with dimethyl or diethyl chloroboronate:

$$2ClB(OR)_2 + 2Na \rightarrow 2NaCl + (RO)_2BB(OR)_2$$

The ethyl ester was also obtained by the ethanolysis of boron subchloride (341).

$$B_2Cl_4 + 4C_2H_5OH \rightarrow [(C_2H_5O)_2B]_2 + 4HCl$$

B. PREPARATION OF ORTHOBORATES

1. Introduction

The principal starting materials that have been used for the preparation of orthoborates are boron trichloride, boron trioxide, boron acetate, orthoboric acid, metallic borates, and other orthoborates. These will be considered individually. The esters which have proved the most troublesome to prepare in good yield are the methyl, ethyl, and tertiary alkyl borates.

2. *Boron trichloride*

Ebelmen and Bouquet (104) in 1846 were the first workers to mention orthoborates. They prepared trimethyl, triethyl, and triamyl borates by heating the appropriate alcohol with the trichloride in a sealed tube. The same method was used for triallyl borate, but poor yields were reported and the attempted preparation of tribenzyl borate was unsuccessful, benzyl chloride and bibenzyl being the major products (93). Michaelis and Hillringhaus (242) in 1901 prepared the first triaryl borates when they obtained the borates of phenol, *m*-cresol, and *β*-naphthol by employing the sealed-tube method at 100°C.; chlorinated by-products were also isolated. More recently (89, 90), it has been shown that heating is unnecessary, triaryl borates being obtained in nearly quantitative yield at −80°C. by the addition of 1 mole of boron trichloride to 3 moles of the phenol in methylene dichloride. Wiberg and Sütterlin (372) investigated the reaction sequences in the boron trichloride–methanol and boron trichloride–ethanol systems, employing a high-vacuum apparatus at −80°C., and showed that quantitative yields of the orthoborates were obtained in both systems when the correct proportion of reagents was used.

$$3ROH + BCl_3 \rightarrow B(OR)_3 + 3HCl$$

Later work confirmed that triborates may be obtained instantaneously and in nearly quantitative yields by the same method, or more suitably for larger scale preparations, by addition in an inert solvent such as *n*-pentane. The method was applicable to all the primary alcohols used [*n*-C_3H_7OH (126); *n*-C_4H_9OH, *i*-C_4H_9OH (123); $(CH_3)_3CCH_2OH$, *n*-$C_8H_{17}OH$ (126); $ClCH_2CH_2OH$, $Cl(CH_2)_4OH$ (105); CCl_3CH_2OH (40); $C_2H_5OOCCH_2OH$, $C_2H_5OOCCH_2CH_2OH$ (114)] and to secondary alcohols [$CH_3CH_2CHOHCH_3$ (123); *i*-$C_3H_7CHOHCH_3$, $(CH_3)_3CCHOHCH_3$ (126); *n*-$C_6H_{13}CHOHCH_3$ (122); $C_2H_5OOCCHOHCH_3$, $C_2H_5OOCCH_2CHOHCOOC_2H_5$ (114); $(CCl_3)_2CHOH$ (121)], except those which had a powerfully electron-releasing group, such as a phenyl group attached to the alcoholic carbon atom, when the major product was the alkyl chloride. An example of such a case was 1-phenylethanol (122). An alkyl chloride was the only product if the method was applied to a tertiary alcohol, e.g., tertiary butyl alcohol (123). Boron trichloride has been used for the preparation of tertiary alkyl borates, as well as of many other types, in almost quantitative yields by the addition of boron trichloride (1 mole) to a mixture of the alcohol and pyridine (3 moles of each) in an inert solvent at low temperature (122, 204). The reaction was again rapid.

$$BCl_3 + 3ROH + 3C_5H_5N \rightarrow 3C_5H_5N\cdot HCl + B(OR)_3$$

A method which gave nearly quantitative results for a wide variety of trialkyl borates (including tertiary) employed pyridinoboron trichloride as the starting material and heated this under reflux with the alcohol and pyridine in chloroform (125).

$$C_5H_5N\cdot BCl_3 + 3ROH + 2C_5H_5N \rightarrow 3C_5H_5N\cdot HCl + B(OR)_3$$

This method has the advantage of avoiding the use of easily hydrolyzable and highly volatile (b.p. 12°C.) boron trichloride.

Dichloroboronites (Section IV,F,3) and chloroboronates (Section III,G,3) also afford orthoborates by the alcoholysis, disproportionation, or decomposition of their amine complexes.

3. Boron trioxide

Schiff (297) introduced the use of boron trioxide for the preparation of methyl, ethyl, and *n*-amyl borates, by heating with the appropriate alcohol in a digestor. Later, *n*-propyl, isopropyl, isobutyl, and allyl borates were prepared by heating the oxide with the alcohols in an autoclave at 110–170°C. (94). For the preparation of very pure methyl and ethyl borates a pressure bottle has been used, which was constantly agitated to avoid caking of the hygroscopic boron trioxide. A 68 per cent yield of crude trimethyl borate was obtained, but this was an azeotrope of the borate (70 per cent) and methanol (30 per cent), from which the alcohol was removed by treatment with calcium chloride (107). The formation of an azeotrope, which has only been observed in the case of the methyl compound, has proved a constant source of difficulty. The yields of trimethyl (42 per cent) and triethyl (31 per cent) borates were improved by avoiding the use of a pressure vessel and instead introducing a device for the gradual addition of the trioxide to the alcohol (346). A further modification, particularly for borates of high molecular weight, comprised heating boron trioxide and the alcohol with an inert solvent (e.g., toluene) and allowing the condensed vapors to percolate through anhydrous copper sulfate in a Soxhlet extractor, thus removing the water formed in the reaction (103). The method has been considered to be the most convenient for the preparation of trialkyl borates, when about 20–100 g. was required, and was also extended in its range of application (331). The method was unsuccessful for the borates of tertiary alcohols (173, 331). Recently, an almost quantitative yield of trimethyl borate on a large scale has been achieved (305); the best results were obtained when the oxide (1 mole) and methanol (4 moles) were used.

$$B_2O_3 + 4CH_3OH \rightarrow B(OCH_3)_3 \cdot CH_3OH + H_3BO_3$$

The borate could be recovered from the azeotrope by any one of the following methods: extraction of a ligroin solution with concentrated sulfuric acid; addition of carbon disulfide and removal of the alcohol as an azeotrope with the solvent; addition of zinc chloride or preferably lithium chloride. The most recent method employing boron trioxide recommends adding it (2 moles) to methanol (3 moles) at 35–60°C. and digesting the mixture for 1 hr. at 25°C.; this procedure afforded trimethyl borate (77 per cent pure) in 92 per cent yield (296).

$$2B_2O_3 + 3CH_3OH \rightarrow 3HBO_2 + B(OCH_3)_3$$

4. Boron acetate

The preparation and structure of boron acetate are discussed later (Section II,G), Pictet and Geleznoff (269) prepared a number of trialkyl and triaryl borates by warming alcohols or phenols with the acetate and separating, by fractional distillation, the mixture of the ester and acetic acid. Later attempts (107) to repeat the method for trimethyl borate were unsuccessful, as a ternary azeotrope of methanol, the borate, and methyl acetate was obtained, and also for triethyl borate, as separation of the ester, b.p. 117°C., and acetic acid, b.p. 118°C., was impracticable. Tri-*tert*-butyl borate was claimed to have been prepared by this method and, indeed, the ester was well characterized (173), but later work has failed to confirm this (2, 7, 91, 147), although it has been shown that the method is of wide application (1, 2, 7, 91, 147, 229).

5. *Orthoboric acid*

Cohn (88) was the first to use boric acid for the preparation of orthoborates (methyl, ethyl, *n*-propyl, and isobutyl).

$$B(OH)_3 + 3ROH \rightarrow B(OR)_3 + 3H_2O$$

Esterification with alcohols was carried out in the presence of either hydrogen chloride or concentrated sulfuric acid. Later, it was suggested that the water of esterification be removed as an azeotrope with excess alcohol, which could later be recovered (16). Subsequent workers (13, 147, 167, 293, 384) have shown that the method gives excellent yields for a wide range of trialkyl borates and for triphenyl borate (89), but is unsuccessful in the case of those borates whose parent alcohols do not form azeotropes with water and for the tertiary alkyl borates (147, 293), although impure samples of these have been obtained (2). It has been suggested that the method is in general the most suitable if large quantities of a borate are required, and a further modification, the incorporation of an inert solvent, such as benzene, toluene, or carbon tetrachloride, has been recommended, the water being thus removed as a ternary azeotrope (331). This modification was particularly successful for a number of triaryl borates (271, 272, 273, 274, 275) and for tertiary alkyl borates (120, 219). For trimethyl borate the method has been modified still further; the lowest boiling constituent in this system is the borate–methanol azeotrope and careful fractionation permits esterification to proceed (8).

6. *Metallic borates*

Rose (286) prepared trimethyl borate by the dry distillation of potassium methyl sulfite and borax, a method later also adopted by Frankland (111). Triethyl borate has been obtained by the interaction of the alcohol with sodium pyroborate in the presence of hydrogen chloride gas (176). The method was recommended for small-scale purposes.

$$3Na_2B_4O_7 + 6HCl + 15C_2H_5OH \rightarrow 6NaCl + 5B(OC_2H_5)_3 + 7B(OH)_3$$

More recently (305), yields of up to 92 per cent of trimethyl borate have been obtained by the same method, but using concentrated sulfuric acid instead of hydrogen chloride and employing a large excess of methanol.

$$Na_2B_4O_7 \cdot 10H_2O + 2H_2SO_4 + 16CH_3OH \rightarrow 2NaHSO_4 + 4B(OCH_3)_3 + 4CH_3OH + 17H_2O$$

The methanol–trimethyl borate azeotrope was separated in the manner described previously (Section II,B,3). Attempts to employ silver borate and ethyl iodide have failed (252, 297).

7. Orthoborates

Easily obtainable trialkyl borates, e.g., *n*-butyl or *n*-propyl, have been used to obtain borates which are less readily prepared by other methods.

$$B(OR)_3 + 3R'OH \rightarrow B(OR')_3 + 3ROH$$

The method was first used by Schiff (297). Trimethyl borate has been prepared by heating under reflux a mixture of methanol and tributyl borate and subsequently separating the methyl ester from the azeotrope by washing with concentrated sulfuric acid (342). A wide range of trialkyl borates and also triphenyl borate were obtained by heating under reflux the appropriate alcohol or phenol with tri-*n*-propyl borate, using benzene as solvent (384). Triphenyl borate has also been used as a starting material (e.g., for trimethyl borate), but with tertiary butyl alcohol, isobutylene and diisobutylene were isolated and no tri-*tert*-butyl borate (89) was obtained. This borate has, however, been obtained from triethyl borate and tertiary butyl alcohol in the presence of a trace of sodium, a fractionating column of high efficiency being used (120). From trimethyl borate, the ethyl, isopropyl, and *tert*-butyl esters have been made (227).

8. Other methods

Alkylation of orthoboric acid using an ester (e.g., a tetraalkoxysilane) instead of an alcohol has been mentioned (196). Trimethyl and triethyl borates have been obtained by the action of boron tribromide on tetraalkoxysilanes at −80°C. (364).

$$Si(OR)_4 + BBr_3 \rightarrow B(OR)_3 + ROSiBr_3$$

In their preparations of the valuable reducing agent sodium borohydride, Schlesinger and Brown have used diborane and either sodium methoxide (300) or sodium trimethoxyborohydride (299) as starting materials; in each case trimethyl borate (80 per cent yield) was obtained as a by-product.

$$3NaOCH_3 + 2B_2H_6 \rightarrow 3NaBH_4 + B(OCH_3)_3$$

$$2NaBH(OCH_3)_3 + B_2H_6 \rightarrow 2NaBH_4 + 2B(OCH_3)_3$$

Trimethyl borate has also been obtained from sodium trimethoxyborohydride, either by the action of boron trifluoride (58) or by the action of heat (301), as a by-product in the preparation of sodium borohydride. It has also been obtained by heating lithium tetramethoxyboron, which was in turn obtained from lithium borohydride and methanol (298).

$$NaBH(OCH_3)_3 \xrightarrow{BF_3} B(OCH_3)_3$$

$$4NaBH(OCH_3)_3 \xrightleftharpoons{230°C.} NaBH_4 + 3B(OCH_3)_3 + 3NaOCH_3$$

$$LiBH_4 + 4CH_3OH \xrightarrow{-4H_2} LiB(OCH_3)_4 \xrightarrow{\Delta H} LiOCH_3 + B(OCH_3)_3$$

The action of diborane on lithium ethoxide, sodium methoxide, or lithium tetramethoxyboron gave ethyl and methyl borates as well as lithium or sodium borohydrides, whilst the action of sodium trimethoxyborohydride on either diborane or dimethoxyborine gave trimethyl borate as well as sodium borohydride (303).

$$2B_2H_6 + 3MOR \rightarrow 3MBH_4^* + B(OR)_3^*$$

$$2B_2H_6 + 3LiB(OCH_3)_4 \rightarrow 3LiBH_4 + 4B(OCH_3)_3\dagger$$

$$B_2H_6 + 2NaBH(OCH_3)_3 \rightarrow 2NaBH_4 + 2B(OCH_3)_3$$

$$3HB(OCH_3)_2 + NaBH(OCH_3)_3 \rightarrow NaBH_4 + 3B(OCH_3)_3$$

* M = lithium or sodium; R = methyl or ethyl (see also reference 358).

† See also reference 365.

The action of boron trifluoride dimethyl etherate on tetramethylammonium chloride gave trimethyl borate as a by-product (349).

$$4(CH_3)_2O\cdot BF_3 + 3(CH_3)_4NCl \rightarrow 3(CH_3)_4NBF_4 + 3CH_3Cl + B(OCH_3)_3 + (CH_3)_2O$$

A mixed sulfuric-boric anhydride on alcoholysis (with methanol, ethanol, or *n*-amyl alcohol) gave trialkyl borates (270).

$$(SO_3)_2B_2O_3 + 6ROH \rightarrow 2B(OR)_3 + 2H_2SO_4 + H_2O$$

Tris(1-ethoxy-2-chloroethyl) borate was obtained from epichlorohydrin and boron trifluoride diethyl etherate (229),

C, PHYSICAL PROPERTIES OF ORTHOBORATES

Viscosities of borates [*n*-propyl, *n*-butyl, *n*-amyl, allyl (147); $Cl(CH_2)_2$— and $(ClCH_2)_2CH$— (171)] have been measured. The Trouton constants for methyl and ethyl borates showed them to be monomeric (372); a similar conclusion was arrived at for tri-*n*-butyl borate as the result of molecular-weight measurement (116). Parachor measurements on methyl and ethyl borates (107, 208), on *n*-propyl, *n*-butyl, *n*-heptyl, *n*-octyl, and *n*-decyl borates (9), and on 2-chloroethyl and 2,2′-dichloroisopropyl (171) borates were considered to be evidence of their planar structure. Similar conclusions had been arrived at by dipole moment investigations on ethyl (96), *n*-propyl (217), *n*-butyl (263), isobutyl (248), *sec*-butyl (217), *n*-amyl (263), and isoamyl (96) borates. The paper by Lewis and Smyth (217), especially, should be consulted on this point; these authors concluded that the three B—O bonds make angles of 120° with one another and have sufficient double-bond character to prevent rotation about the bonds. Raman spectra frequencies on the methyl (6, 172, 247, 248), ethyl (6, 172, 247, 248), *n*-propyl and isopropyl (172), *n*-butyl (164, 172, 173, 248), isobutyl (173), *sec*-butyl (173), and *tert*-butyl (173) esters have been determined. Investigations of x-ray spectra (174) have been carried out on methyl, ethyl, and isobutyl borates. Electron diffraction measurements (17) on trimethyl borate showed that the BO_3 configuration is planar, with angles of 120°; bond distances were measured.

TABLE 1

Physical constants of orthoborates

Borate	Boiling Point	Melting Point	d_4^{20}	n_D^{20}	References
	°*C.*	°*C.*			
CH_3—	68.7	−29.2	0.9547	1.3610	(6, 8, 20, 58, 77, 78, 81, 93, 104, 107, 125, 133, 137, 163, 172, 174, 208, 230, 247, 248, 269, 270, 286, 296, 297, 298, 299, 300, 301, 303, 342, 346, 347, 349, 372)
C_2H_5—	117.3	−84.8	0.8635	1.3741	(6, 78, 88, 91, 93, 95, 96, 104, 107, 111, 120, 125, 163, 172, 174, 208, 227, 247, 248, 269, 270, 297, 303, 331, 342, 372)
n-C_3H_7—	177		0.8545*	1.3945	(9, 38, 76, 78, 81, 88, 91, 93, 126, 147, 172, 217, 293, 347, 384)
i-C_3H_7—	140			1.4057	(9, 91, 172, 201, 227, 269)
n-C_4H_9—	115/15 mm.		0.8560	1.4085	(9, 81, 116, 123, 125, 147, 164, 167, 172, 173, 204, 248, 261, 263, 293)
i-C_4H_9—	212		0.8403*	1.4035	(88, 93, 123, 125, 173, 174, 201, 204, 217, 245, 269, 293)
s-C_4H_9—	194		0.8290*	1.3968	(96, 123, 125, 173, 204, 293, 347)
t-C_4H_9—	55/10 mm.	12	0.814	1.3883	(7, 120, 123, 125, 173, 204, 217, 219)
n-C_5H_{11}—	147/16 mm.		0.8549	1.4190	(125, 147, 167, 263, 270, 293, 297, 347)
i-C_5H_{11}—	132/12 mm.		0.8514	1.4156	(96, 147, 172, 182, 230, 269, 384)
t-C_5H_{11}—	92/8 mm.		0.853	1.4020	(7, 125, 219, 227)
				1.4124	(219)
$C_3H_7CH(CH_3)$—	110/12 mm.		0.8375	1.4075	(293, 384)
$(C_2H_5)_2CH$—	105/8 mm.		0.8337†	1.4100	(125, 293)
s-$C_4H_9CH_2$—	260		0.8470†	1.4170	(293)
i-$C_3H_7CH(CH_3)$—	59–61/0.4 mm.		0.8339†	1.4080	(126, 293)
Cyclohexyl	203/17 mm.	54			(91, 347, 384)
n-Hexyl	183		0.8471†	1.4250	(293)
n-$C_3H_7(CH_3)_2C$—	74–95/1 mm.				(219)
t-$C_4H_9CH(CH_3)$—	122/9 mm.		0.841	1.4151	(126)
n-$C_5H_{11}CH(CH_3)$—	128/5 mm.		0.7693†	1.4160	(293)
i-C_6H_{13}—	140/5 mm.				(293)
i-$C_4H_9CH(CH_3)$—	120/10 mm.		0.7575†	1.4115	(125, 293, 331)
s-$C_4H_9CH_2$—	169/15 mm.		0.8572†	1.4283	(293)
n-C_7H_{15}—	185/2 mm.		0.8398	1.4280	(9)
n-$C_3H_7CH(i$-$C_3H_7)$—	288				(293)
n-C_8H_{17}—	174/0.4 mm.		0.8548	1.4377	(9, 125, 126, 204)
n-$C_6H_{13}CH(CH_3)$—	148/0.5 mm.		0.8642	1.4290	(122, 125, 347)
n-$C_{10}H_{21}$—	275/0.15 mm.		0.8581	1.4440	(9)
n-$C_{12}H_{25}$—	185/23 mm.				(142)
Allyl	181			1.4278	(13, 93, 147, 201)
2-Methylallyl	120/19 mm.	28–29			(13, 293, 331, 332)
2-Methoxyethyl	135/15 mm.		1.0096	1.4059	(293)
2-Fluoroethyl	173				(91)
2-Chloroethyl	70/0.1 mm.		1.2780	1.4556	(105, 125, 171)
2-Aminoethyl	126/8 mm.	95–98			(331)
		74			(284)
2,2,2-Trichloroethyl	112/0.05 mm.	97–98			(40)
$C_2H_5OOCCH_2$—	124/0.01 mm.		1.160	1.4290	(114)

* At 25°C.
† At 6°C.

TABLE 1—*Concluded*

Borate	Boiling Point	Melting Point	d_4^{20}	n_D^{20}	References
	°*C.*	°*C.*			
$C_2H_5OOCCH(CH_3)$—	110/0.01 mm.		1.070	1.4215	(114, 125)
$C_2H_5OOCCH_2CH_2$—	134/0.01 mm.		1.108	1.4331	(114)
$CH_3CH(COOC_3H_7)$—	169-175/5 mm.				(331)
$C_2H_5OOCCH_2CH(COOC_2H_5)$—	180/0.01 mm.		1.167	1.4408	(114)
$(CH_2Cl)_2CH$—	198/5 mm.		1.4028	1.4883	(171)
$(CCl_3)_2CH$—		325			(121)
2,3-Dibromopropyl					(94)
$C_2H_5OCH_2CH(CH_2Cl)$—	145-150/0.05 mm.				(229)
$Cl(CH_2)_4$—	136-140/0.1 mm.		1.350	1.4623	(105)
$C_6H_5CH_2$—	180/3 mm.				(230, 384)
$C_6H_5(CH_3)CH$—	174/0.2 mm.		1.064	1.5347	(122, 125)
C_6H_5—					(1, 89, 124, 230, 242, 269, 271, 347, 384)
	142/0.5 mm.	92-93			(89)
		38-40			(384)
α-Naphthyl					(1, 90, 269, 271)
		108			(90)
		84-85			(1, 269)
β-Naphthyl					(1, 90, 242, 269)
		120			(90)
		115.5-116			(1)
m-$CH_3C_6H_4$—		40			(93)
o-$CH_3C_6H_4$—	198/2.5 mm.				(272)
p-$CH_3C_6H_4$—	249/5 mm.	58-61			(331)
p-*t*-$C_4H_9C_6H_4$—	275-280/2.5 mm.				(271, 272, 273)
p-$C_3H_{17}C_6H_4$—		82			(90)
p-ClC_6H_4—	259/5 mm.	60-64			(271, 272, 331)
o-ClC_6H_4—	242/6 mm.	48			(331)
o-IC_6H_4—		90			(90)
o-$CH_3OC_6H_4$—	230/2.5 mm.				(271, 272)
p-$CH_3OC_6H_4$—	288/7 mm.	44			(331)
o-$O_2NC_6H_4$—		90			(90)
o-$C_6H_{11}C_6H_4$—	280-285/2.5 mm.				(271, 274)
p-$C_6H_{11}C_6H_4$—	275-280/2.5 mm.				(271, 274)
o-$HOOCC_6H_4$—		258-259			(1)
o-$C_6H_5C_6H_4$—	320-330/7.5 mm.				(271, 275, 283)
2,6-$(CH_3)_2C_6H_3$—		135			(90)
2,6-$Cl_2C_6H_3$—		106			(90)
2,6-$(CH_3O)_2C_6H_3$—		134			(90)
2-C_6H_5-4-ClC_6H_3—	342-348/3.8 mm.				(271, 275, 283)
2,4,6-$Cl_3C_6H_2$—		173			(90)
l-Menthyl		150-152			(261)
Bornyl		226			(384)

The heats of hydrolysis (81) for methyl, ethyl, *n*-propyl, and *n*-butyl borates were ascertained and from this data the mean bond dissociation energies of the B—O links were calculated as 110 ± 5 kcal./mole. From infrared and Raman spectra data it was concluded that trimethyl borate is planar and, although there is restricted rotation about the B—O bonds, the valency force constants support single-bond character for these bonds (20). Infrared spectra for a series of orthoborates (methyl, *n*-propyl, *n*-butyl, *n*-amyl, *sec*-butyl, phenyl, 1-methylheptyl, cresyl, cyclohexyl) in each case showed a strong characteristic absorption band at 1340 ± 10 cm.$^{-1}$, which was attributed to the asymmetric stretching frequency of the BO_3 group (347), The infrared spectra of ethyl and *tert*-butyl borates have also been noted (120).

D, CHEMICAL PROPERTIES OF ORTHOBORATES

1. Thermal stability

Orthoborates are generally very stable and may be heated to quite high temperatures without significant decomposition. Boric acid has been used as a catalyst for the conversion of alcohols to olefins, and the suggestion has been made that its activity is due to the initial formation of the orthoborate, which then decomposes (36).

$$3RCH_2CH_2OH + B(OH)_3 \rightarrow B(OCH_2CH_2R)_3 \rightarrow 3RCH{=}CH_2 + B(OH)_3$$

This suggestion requires modification, however, as later work indicated that the function of the orthoboric acid is twofold: (*1*) in forming the orthoborate and (*2*) in converting this to the metaborate which was then thermally unstable (see Section II,H) (261). Thus *l*-menthyl orthoborate was unchanged after being heated for several hours at 300°C., but reacted with boric acid at 270°C, to give a mixture of menthenes. Dodecyl borate on pyrolysis afforded the α-olefin (10),

2, Solvolysis reactions and reactions with acids

The orthoborates are generally very readily hydrolyzed, even on exposure to the atmosphere. Hydrolysis may be a stepwise reaction, but intermediates [$HOB(OR)_2$ and $ROB(OH)_2$] have not been isolated.

$$B(OR)_3 + 3H_2O \rightarrow 3ROH + B(OH)_3$$

Orthoborates which are not so readily hydrolyzed are the diisopropylcarbinyl and neopentyl esters (293), cyclohexyl borate (91), and bis(trichloromethyl)-methyl borate (121); these results may be explained on the basis of steric hindrance. This view would be in agreement with the qualitative observation that secondary alkyl borates hydrolyze less readily than the straight-chain primary esters (293). Tendency for hydrolysis was not apparently reduced in 1 *N* hydrochloric acid and it was considered unlikely, therefore, that hydroxide-ion addition was the rate-determining step (293). Hydrolysis would appear normally to involve boron–oxygen fission rather than alkyl–oxygen fission, because hydrolysis of optically active orthoborates (1-methylheptyl and 1-phenylethyl) gave the configurationally retained alcohols (122) and because neopentyl alcohol and not a rearranged alcohol was obtained from the neopentyl ester (293),

Alcoholysis reactions of orthoborates have been discussed (Section II,B,7). The orthoborates do not react with ethers (89, 372).

Triethyl borate has been reacted with a number of acids (84, 297) to give products indicated by the following equations (for its reaction with boron trioxide see Section II,H):

$$B(OC_2H_5)_3 + 2B(OH)_3 \xrightarrow{160\text{–}180°C.} 3C_2H_5OH + 3HOBO$$

$$B(OC_2H_5)_3 + H_2SO_4 \xrightarrow{\text{heat}} C_2H_5HSO_4 + 2C_2H_4 + HOBO + H_2O$$

$$B(OC_2H_5)_3 + H_2SO_4 + H_2O \xrightarrow[\text{(2) addition of } H_2O]{\text{(1) heat to 140–150°C. (anh.)}} C_2H_5HSO_4 + B(OH)_3 + (C_2H_5)_2O$$

$$B(OC_2H_5)_3 + H_2SO_4 + 2RCOOH \rightarrow C_2H_5HSO_4 + B(OH)_3 + 2RCOOC_2H_5$$

$R = CH_3$, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, and C_6H_5.

$$B(OC_2H_5)_3 + 3HNO_3 \rightarrow 3C_2H_5ONO_2 + B(OH)_3$$

$$B(OC_2H_5)_3 + H_3PO_4 \rightarrow PO_4B + 3C_2H_5OH$$

Triethyl borate when heated with carboxylic acids (acetic, benzoic, succinic, and oxalic) afforded the ethyl esters (297). Borates have been formed from alcohols (ethyl, *n*-butyl, isoamyl, menthyl, terpineyl, linalyl) or phenols (phenol, cresols, thymol) and boric acid, employing the ternary azeotrope method (see Section II,B,5) and, without isolation, have been used to esterify glacial acetic acid by boiling the mixture for 3–4 hr., an excess of the acid being used (253). Yields of 52–90 per cent were achieved; *tert*-butyl alcohol gave a 30 per cent yield of *tert*-butyl acetate.

$$B(OH)_3 + 3ROH \xrightarrow{ArH} B(OR)_3 \xrightarrow{3CH_3COOH} 3CH_3COOR + B(OH)_3$$

Trimethyl borate did not react with *p*-hydroxybenzoic acid; when reacted with salicylic acid it ultimately gave methyl salicylate, but initially it formed tris(*o*-carboxyphenyl) borate, $B(OC_6H_4COOH)_3$, which decomposed on melting (88).

3. *Halogenation reactions*

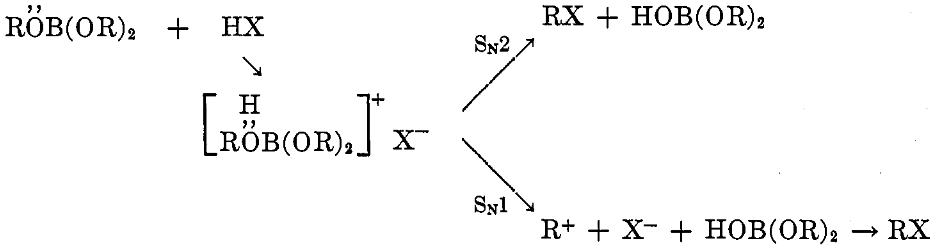
Hydrogen chloride did not react with primary alkyl orthoborates or with the majority of secondary alkyl orthoborates [ethyl (297); isoamyl (182); *n*-butyl, isobutyl, *sec*-butyl (123); 1-methylheptyl (122)] even at 120°C., but with borates having powerfully electron-releasing alkyl groups [1-phenylethyl (122); *tert*-butyl (123)] rapid dealkylation took place, giving the alkyl chloride and boric acid. Hydrogen bromide and hydrogen iodide were progressively more reactive, and dealkylation was general also with primary and secondary alkyl esters (122, 123).

$$B(OR)_3 + 3HX \rightarrow 3RX + B(OH)_3$$

X = halogen.

These results were interpreted in terms of an S_N2 reaction for borates having alkyl groups normally responsive to "in-line" replacement, and in terms of an

S_N1 mechanism for those having powerfully electron-releasing groups. Evidence of optical activity was given (122).



Both phosphorus pentachloride and antimony trichloride reacted with triethyl borate to give ethyl chloride (297); neither the former reagent nor thionyl chloride reacted with triisoamyl borate (182). The reactions of borates with the boron halides are dealt with later (Section III,G,1 and Section IV,F,1).

The halogens ($Cl_2 > Br_2 > I_2$) reacted with triethyl borate to give substitution products of uncertain composition (95), but one of the products of the reaction with chlorine appeared to be 1,2,2-trichloroethyl ethyl ether.

4. Reaction with ammonia and amines

Ammonia showed little tendency to react with triethyl borate, but some ethylamine has been claimed as a product (297). There was no interaction between isobutyl borate and ammonia, aniline, or dimethylaniline (88, 94), or between pyridine and tri-*n*-butyl borate (51),

The only trialkyl borate to react (coordinate) with ammonia and amines appears to be the methyl homolog, although with triethyl borate and amines heat of mixing has been observed (343). The action of excess ammonia on trimethyl borate produced a 1:1 complex, whilst when ammonia was treated with an excess of the borate, a 1:4 complex was obtained, which sublimed to give a 1:2 complex (133). Trimethyl borate gave 1:1 complexes with methylamine (m.p. 42°C.), dimethylamine (m.p. 9°C.), and trimethylamine (m.p. −50°C.); with the first of these an excess of the base was required in order to prevent polymerization (137). 1:1 Complexes of trimethyl borate have also been obtained with other bases (diethylamine; di-*n*-propylamine; di-*n*-butylamine; di-*n*-amylamine; triethylamine; tri-*n*-butylamine; ethylenediamine, m.p. 81–82°C.; *tert*-butylamine, m.p. 67–80°C.; piperidine, m.p. 75°C.), but no reaction was observed with either pyridine or quinoline (343).

In contrast to the alkyl orthoborates, the aryl compounds do generally form coordination complexes with ammonia and amines (89, 90). This difference was attributed to the fact that the "back-coordination" from oxygen to boron, which is present in trialkyl borates (see Section II,C), is largely offset in the triaryl borates by the resonance interaction of the oxygen lone pairs with the π-electrons of the aromatic rings. Therefore, the result is that the aryl borates are more powerful Lewis acids than their alkyl counterparts. However, it was shown that also steric factors are important in coordination reactions of aryl borates. Thus, 1:1 complexes with pyridine of the following borates were obtained (the melting points are shown in parentheses): C_6H_5— (148°C.); 4-ClC_6H_4— (68–70°C.); 2,5-$Cl_2C_6H_3$— (146–148°C.); 2-IC_6H_4— (52–55°C.); 4-n-$C_8H_{17}C_6H_4$— (112°C.); 2-$O_2NC_6H_4$— (167°C.); α-$C_{10}H_7$— (175°C.); β-$C_{10}H_7$— (57–60°C.); but only slight or no complex formation was observed with 2,4,6-trichlorophenyl-, 2,6-dimethylphenyl-, or 2,6-dimethoxyphenyl borate. α-Picoline gave complexes with the following borates: C_6H_5— (104°C.); β-$C_{10}H_7$— (66–68°C.); 2-IC_6H_4— (110°C.), whilst 2,4,6-collidine gave a 1:1 complex with tri-α-naphthyl borate (m.p. 110°C.), but showed only incomplete reaction with triphenyl borate. Similar incomplete reaction was observed in the following systems: triphenyl borate with diethylamine, triethylamine, and tri-n-butylamine; 2,5-dichlorophenyl borate with di- and triethylamine; 4-chlorophenyl borate with triethylamine; 2-iodophenyl borate with diethylamine. 1:1 Complexes of triphenyl borate were formed with quinoline (m.p. 93–94°C.) and also with ethylamine. When ammonia was reacted with triphenyl borate a complex, $B(OC_6H_5)_3 \cdot 2NH_3$ (m.p. 125°C.), was obtained, whilst 2,4,6-trichlorophenyl borate gave the complex $B(OCl_3C_6H_2)_3 \cdot 3NH_3$ (m.p. 150°C.). Both these compounds increased the conductivity of an acetone solution.

5. *Borate complexes with metal salts*

Copaux (95) observed the reaction of triethyl borate with sodium ethoxide to give a 1:1 complex, $Na[B(OC_2H_5)_4]$. This reaction was confirmed and a number of other metal tetraalkoxyboron compounds of the type $M[B(OR)_4]$ (where M = Na or K and R = CH_3, C_2H_5, or n-C_3H_7; M = Li or Ca and R = CH_3; M = Tl and R = C_2H_5 or n-C_3H_7) were obtained by the same method (78). Other compounds of this type, which have been prepared by a similar procedure (i.e., the interaction of a metal alkoxide with an orthoborate), are the following: $Zn[B(OCH_3)_4]_2$; $Na[B(OC_5H_{11}\text{-}i)_4]$; $K[B(OCH_2C_6H_5)_4]$; $Na[B(OC_6H_5)_4]$ (230); also $Na[B(OC_3H_7(i))_4]$ (227). In these cases a solvent was employed: either the appropriate alcohol, xylene (230), or tetrahydrofuran (227). Sodium tetra-*tert*-butoxyboron could not be obtained by this method (227). It has been stated that the reactivity of borates with respect to alkoxides is in the order: CCl_3CH_2— > $C_2H_5OCH_2CH_2$— > $CH_3OCH_2CH_2$— > $C_6H_5CH_2$ > $CH_2{=}CHCH_2$— > CH_3 > C_2H_5 > i-C_3H_7 (228).

The alkoxide–orthoborate method has been modified by preparing the metal alkoxide *in situ* (356, 357).

$$M + 2ROH + 2B(OR)_3 \rightarrow M[B(OR)_4]_2 + H_2$$

R = CH_3 or C_2H_5; M = Mg, Ca, Sr, or Ba.

The corresponding tetramethoxyberyllium compound could not be obtained in this way, nor from beryllium chloride and sodium tetramethoxyboron, nor from beryllium borohydride and methanol; this was attributed to its facile disproportionation to beryllium methoxide and trimethyl borate (356).

Lithium tetramethoxyboron (298, 303) and the sodium analog (303) have in addition been obtained from lithium or sodium borohydride and methanol (298).

$$MBH_4 + 4CH_3OH \rightarrow M[B(OCH_3)_4] + 4H_2$$

Sodium tetramethoxyboron could be isolated as a decompositon product from the pyrolysis of sodium trimethoxyborohydride (58, 301) and also from the methanolysis of this compound (58),

$$4Na[HB(OCH_3)_3] \rightarrow NaBH_4 + 3Na[B(OCH_3)_4]$$

$$Na[HB(OCH_3)_3] \rightarrow Na[B(OCH_3)_4] + H_2$$

The metal tetraalkoxyborons are crystalline solids, soluble in alcohols or tetrahydrofuran but sparingly soluble in other common organic solvents, They are generally thermally stable, but on strong heating decompose to the appropriate metal alkoxide and orthoborate. The ethyl compounds of the Group IIA metals are less stable than their methyl analogs (357).

Novel complexes, $Li[C_6H_5B(OC_4H_9\text{-}i)_3]$ and $Li[(C_6H_5)_2B(OC_4H_9\text{-}i)_2]$ have recently been reported (245) as a result of interaction of phenyllithium and diisobutyl phenylboronate. The former compound was also obtained by the addition of butyllithium, in benzene and isobutyl alcohol, to the boronate and also, together with lithium tetraisobutoxyboron, from phenyllithium and triisobutyl borate,

Orthoborates (methyl, ethyl, *n*-butyl), when employed in slight excess, reacted with sodium hydride (and in the case of *n*-butyl orthoborate in dioxane as solvent to moderate the reaction) under reflux to afford sodium trialkoxyborohydrides (58).

$$NaH + B(OR)_3 \rightarrow Na[HB(OR)_3]$$

With lithium hydride the reaction was not so clean (58). Sodium trimethoxyborohydride was also obtained by the reaction of sodium metal with trimethyl borate and hydrogen at 250°C. under pressure (301),

$$2Na + H_2 + 2B(OCH_3)_3 \rightarrow 2Na[HB(OCH_3)_3]$$

The metal hydride–orthoborate method has also been used with tetrahydrofuran as a solvent for the sodium and lithium trialkoxyborohydrides (methyl, ethyl, isopropyl) (54, 227).

The alkoxyborohydrides are stable white solids and have powerful reducing properties (54, 58, 227). Sodium trimethoxyborohydride could be recrystallized (m.p. 230°C.) from liquid ammonia or isopropylamine (58). It reacted with hydrogen chloride and carbon dioxide (58) in the manner indicated in the following equations. The pyrolysis (see also this section, above) and the reactions with diborane, boron trifluoride, and dimethoxyborine have already been discussed (Section II,B,8).

$$Na[HB(OCH_3)_3] + HCl \rightarrow NaCl + CH_3OH + HB(OCH_3)_2$$

$$Na[HB(OCH_3)_3] + CO_2 \rightarrow HCOONa + B(OCH_3)_3$$

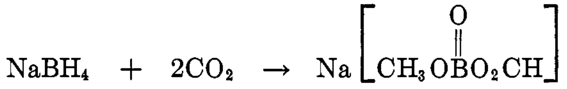
Probably the most important reaction of sodium trimethoxyborohydride is that with boron trifluoride diethyl etherate (58, 301), which until recently was the best method for preparing diborane.

$$6Na[HB(OCH_3)_3] + 8(C_2H_5)_2O \cdot BF_3 \rightarrow B_2H_6 + 6NaBF_4 + 6B(OCH_3)_3 + 8(C_2H_5)_2O$$

It was observed that metal trialkoxyborohydrides disproportionate readily to afford mixtures of alkoxyborohydrides (227). In the case of the sodium compounds, the same equilibrium mixture could be obtained from sodium borohydride and sodium tetraalkoxyborons. Sodium triisopropyloxyborohydride was a more powerful reducing agent than sodium borohydride, as shown in its reaction towards acetone. Sodium trimethoxyborohydride reduced benzoyl chloride to a mixture of benzaldehyde (47 per cent) and benzyl alcohol (227) and in general reduced aldehyde, ketone, acid chloride, and anhydride groups; ester and nitrile groups reacted only slowly at elevated temperature, whereas the carbonyl group and the olefinic double bond were unreactive (54).

It has been suggested that the ethoxides of the Group IIA metals react with diborane in ether to give corresponding monoethoxyborohydrides, $M[C_2H_5OBH_3]_2$ (358).

Carbon dioxide with sodium borohydride under varying conditions gave either a formatoborohydride (dimethyl ether as solvent at room temperature) or a carbonatoborohydride (at 125°C. in a sealed tube), as indicated by the hydrolysis products (344).



$$NaBH_4 + 2CO_2 \rightarrow Na\left[CH_3O\overset{\overset{\displaystyle O}{\|}}{B}O_2CH\right]$$

$$NaBH_4 + 3CO_2 \rightarrow Na[HB(O_2CH)_3]$$

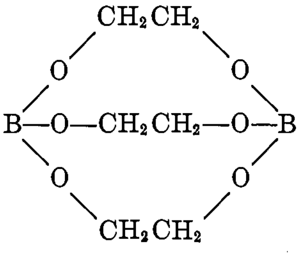
6. Other reactions

Despite an early statement (231) that orthoborates are not reducing agents, certain orthoborates (isopropyl, isobutyl, allyl) were later shown to be successful in converting aldehydes (aromatic more easily than aliphatic) to alcohols, but lower yields were obtained and higher temperatures were required than with aluminum alkoxides (201).

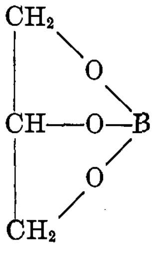
Orthoborates have been used instead of alkyl halides in Friedel–Crafts alkylation reactions (175, 338, 342), as fluxes in welding (342), as plasticizers for natural and synthetic resins (37, 142), as catalysts for the preparation of alkylidene polymers from diazomethane and its derivatives (228, 278), and as antiseptic preparations (162). Trimethyl borate showed slight inhibitor action in the benzoyl peroxide–dimethylaniline system (156). Reactions with organometallic compounds are discussed later (Sections III,C,3; IV,B,1; IV,D,3; IV,C,1; V,B).

E. CHELATED ORTHOBORATES AND BORATES OF POLYHYDRIC ALCOHOLS

Councler (93) obtained the compound $B(OC_2H_4OH)_3$, m.p. 161.7°C., by the interaction of boron trichloride and ethylene glycol. The same glycol with boron acetate gave the borate shown in formula I, m.p. 100°C., b.p. 100°C. (269); a similar compound was obtained earlier by the boron trioxide method (297). Glyceryl borate has been obtained in crude state by employing the boron acetate method (269) and more recently (2) in a pure state, m.p. 150–151°C., by this and also the boric acid (azeotropic removal of water) method; formula II was proposed as the probable structure.

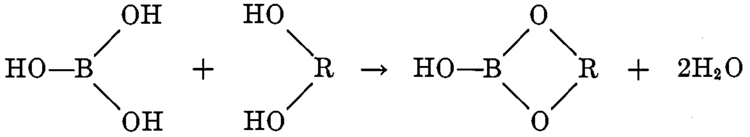


I

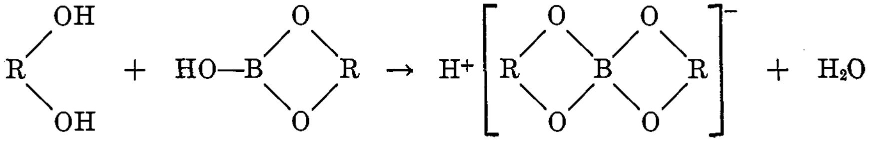


II

The increase in the acidity of boric acid which is observed on addition of polyhydric alcohols, a property of which use is made in the acidimetric estimation of boric acid (mannitol or glycerol is usually employed), has been ascribed by Boeseken (31) to the formation of complex acids of the type shown in formula III, which were said to form through the intermediate esters of the type shown in formula IV.



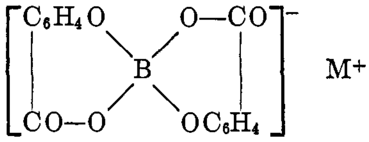
IV



III

Esters of type IV have been isolated by mixing boric acid and the appropriate alcohol in equimolecular proportions. These, with their physical constants, are shown in table 2.

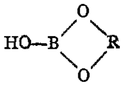
Salts of an acid of the type shown in formula III have been obtained in the case of the salicylic acid derivatives (V) (32), wherein M was potassium, ammonium, phenylammonium, sodium, silver, pyridinium, or strychninium and analogous salts of bivalent metals (calcium, strontium, barium, lead, zinc, copper, cobalt, maganese, nickel, magnesium).



V

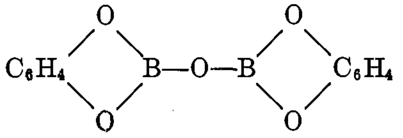
TABLE 2

Physical constants of chelated orthoborates

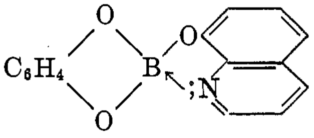
R in 	Boiling Point	Melting Point	References
	°C.	*°C.*	
$—CH_2CH_2—$	176–187/1 mm.		(283)
$—CH(CH_3)CH_2—$	155–158/15 mm.		(283)
$—CH_2CH_2CH_2—$	147–151/3 mm.		(283)
$—CH(CH_3)CH(CH_3)—$	112–117/3 mm.		(283)
$—CH(C_2H_5)CH_2—$	107–109/1 mm.		(283)
$—C(CH_3)_2CH_2—$	76–79/<1 mm.		(283)
$—CH_2CH(OCH_3)CH_2—$	145–150/1 mm.		(283)
$—CH_2CH(OC_4H_9(n))CH_2—$	162–165/<1 mm.		(283)
$—C(CH_3)_2CH_2C(CH_3)_2—$	228	102	(150)
$—C(CH_3)_2CHOHC(CH_3)_2—$		118	(268)
$—C(CH_3)_2CHClC(CH_3)_2—$		132	(268)
$—C(CH_3)_2CH(CH_3)C(CH_3)_2—$		72	(268)
$—C(CH_3)(C_2H_5)CHClC(CH_3)_2—$		58	(268)
$—C(C_2H_5)_2CHClC(CH_3)_2—$		55	(268)

The *l*-strychnine compound was particularly interesting, as it was separable into diastereoisomers by fractional crystallization, indicating that optical activity was possible in V, owing to the asymmetry of the boron atom in a spiran compound.

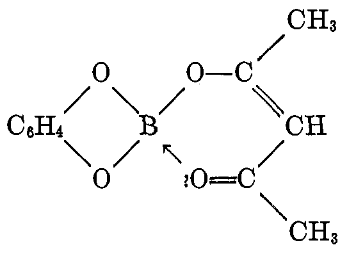
When catechol and boron trioxide were melted together, a borate (VI) was obtained. This borate formed 1;2 complexes with both quinoline and piperidine, and reacted with 8-hydroxyquinoline and acetylacetone to give the compounds VII and VIII, respectively (295).



VI



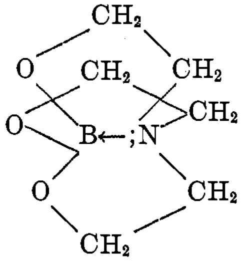
VII



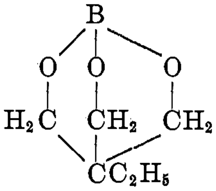
VIII

The borate of diethanolamine (an oil) and that of triethanolamine (m.p. 230°C.) were obtained by the boric acid method (284). This result was confirmed for triethanolamine borate (IX) (51, 148), but a borate of formula X could not be obtained from 1,1,1-tris(hydroxymethyl)propane and boric acid; a polymer,

$[C_2H_5C(CH_2O)_3B]_x$, was produced instead. This result was explained in terms of steric strains (51),



IX



X

Compound IX is unimolecular (cryoscopic in nitrobenzene); it gave addition compounds with many acids and salts (148) and with methyl iodide (51).

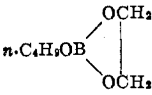
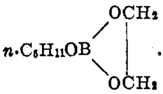
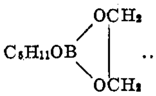
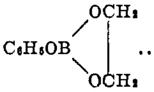
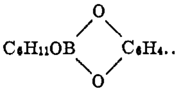
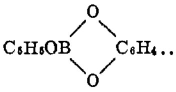
Other chelate orthoborates are discussed in Section F.

F, MIXED ORTHOBORATES

An early claim for the preparation of diethyl amyl borate, $(C_2H_5O)_2BOC_5H_{11}(n)$, and diamyl ethyl borate, $(n\text{-}C_5H_{11}O)_2BOC_2H_5$, by heating triethyl

TABLE 3

Physical constants of mixed orthoborates

Mixed Borate	Boiling Point	Melting Point	n_D^{25}	d_4^{25}	References
	°C.	°C.			
	108/35 mm.		1.4280	0.9976	(212)
	106/12 mm.		1.4343		(212, 332)
	119/10 mm.				(332)
	123-127/5 mm.				(332)
	168/20 mm.	55-59			(332)
	166-167/12 mm.	40-44			(332)

borate with amyl alcohol or triamyl borate with ethyl alcohol (297) was later questioned, when it was noted that such mixed esters were not stable but easily underwent disproportionation to the symmetrical ones (332). Attempted preparation of diphenyl *n*-butyl borate by addition of 1 mole of *n*-butyl dichloroboronite, $n\text{-}C_4H_9OBCl_2$, to 2 moles of phenol at −80°C. afforded no mixed ester, but instead gave tri-*n*-butyl and triphenyl borates (89). Diethyl *o*-nitrophenyl borate, however, was remarkably stable, although with pyridine it gave triethyl borate and $(o\text{-}O_2NC_6H_4O)_3B \cdot py$ (90).

Mixed esters from polyhydric sources, however, have been prepared either from boron trioxide, the two hydroxy compounds, and an inert solvent (benzene or toluene) (332), or from borates (*n*-butyl, *n*-amyl) (1 mole), by heating with ethylene glycol (1 mole), when 75 per cent yields of mixed borates were obtained (212). The physical constants are recorded in table 3.

These borates are easily hydrolyzed; their reactions with organometallic compounds are discussed later (Section III,C,3; Section III,C,6; Section IV,C,1),

G. ACYL BORATES

Schützenberger (310) in 1861 observed that a compound was formed between boric oxide and acetic anhydride. Pictet and Geleznoff (269) showed this to be triacetyl borate, $B(OCOCH_3)_3$. It was prepared either from the anhydride and oxide by prolonged heating, or by warming boric acid in acetic anhydride,

$$B_2O_3 + 3(CH_3CO)_2O \rightarrow 2B(OCOCH_3)_3 \tag{1}$$

$$B(OH)_3 + 3(CH_3CO)_2O \rightarrow B(OCOCH_3)_3 + 3CH_3COOH \tag{2}$$

Triacetyl borate was used for the preparation of other acyl borates (*n*-butyryl, isovaleryl, stearyl, trichloroacetyl, benzoyl, succinyl, phthaloyl, and salicyl) (269) by reaction with the appropriate acid or acid chloride.

$$B(OCOCH_3)_3 + 3RCOOH \rightarrow B(OOCR)_3 + 3CH_3COOH \tag{3}$$

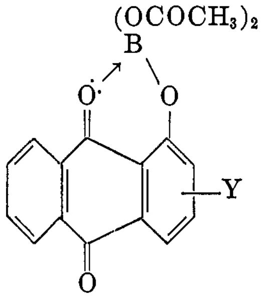
$$B(OCOCH_3)_3 + 3RCOCl \rightarrow B(OOCR)_3 + 3CH_3COCl \tag{4}$$

The action of an acid chloride on boric acid has also been used for the acetyl, benzoyl, and phthaloyl compounds (269).

$$B(OH)_3 + 3RCOCl \rightarrow B(OOCR)_3 + 3HCl \tag{5}$$

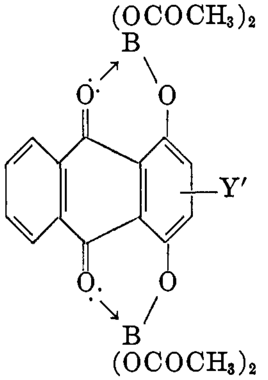
Methods 4 and 5 were modified into one-stage processes: the former by reacting boric acid or oxide with the organic acid (stearic, benzoic, or lauric) and acetic anhydride, the acetyl borate being prepared *in situ*; the latter by reacting boric acid and the organic acid (stearic or cinnamic) with thionyl chloride (or other non-metallic chloride), thus preparing the acyl chloride *in situ* (149).

On repeating reaction 1 Dimroth (99) concluded that the product was the tetraacetyl diborate, $[(CH_3COO)_2B]_2O$, and not the triacetyl borate, although acetoxyboron derivatives of anthraquinones were prepared of the types XI to XIV (100).



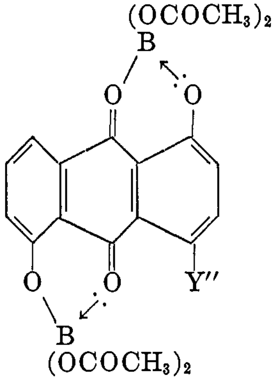
XI

(Y = H, or OH in the 2- or 8-position, or CH_3COO in the 8-position (m.p. 178°C.))



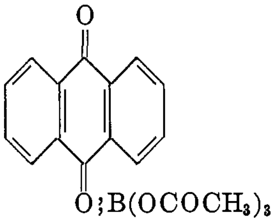
XII

(Y′ = H, or OH in the 2-position, or CH_3COO in the 5-position)



XIII

(Y″ = H or CH_3COO (m.p. 165°C.))



XIV

Both the tetraacetyl diborate (127, 233) and the triacetyl borate (1, 2) structures have received support; it has been suggested that under certain conditions the triacetate may eliminate acetic anhydride and form the tetraacetyl diborate (2).

$$2B(OCOCH_3)_3 \rightarrow [(CH_3COO)_2B]_2O + (CH_3CO)_2O$$

In view of the doubt that still exists regarding this compound it is referred to here non-committally as boron acetate and its homologs as acyl borates.

Boron acetate has also been obtained by the action of boron trichloride on

TABLE 4

Physical constants of acyl borates

Acyl Borate	Melting Point	Density	References
	°C.		
Acetyl			(1, 2, 23, 91, 99, 127, 147, 173, 233, 269)
	121		(269)
	147–148		(91)
	150–152		(99)
Trichloroacetyl	165		(269)
n-Butyryl		1.064 (23°C.)	(269)
Isovaleryl		1.024 (21.5°C.)	(269)
Neovaleryl	193–196		(219)
Cinnamyl	125–130		(149)
Stearyl	73		(149, 269)
Succinyl	164		(269)
Benzoyl			(149, 269)
	145		(269)
	166		(149)
Phthaloyl	165		(269)
Salicyl	258–259		(1, 269)
Lauryl			(149)

either acetic anhydride (233) or glacial acetic acid (127), although an earlier report (146) on the latter reaction did not mention this.

The Raman spectrum of boron acetate showed little resemblance to the spectra of the trialkyl borates (173). Melting points of acyl borates are recorded in table 4.

The acyl borates behave chemically as mixed anhydrides. Thus, on hydrolysis, which is easily accomplished, boric acid and a carboxylic acid are obtained, Tetraacetyl diborate on heating afforded acetyl metaborate and acetic anhydride (99). Alcoholysis reactions have already been mentioned (Section II,B,4), and those with carboxylic acids and with acyl chlorides have been mentioned previously in this section.

H. METABORATES

Schiff (297) observed that the primary reaction between ethanol and boron trioxide was the formation of ethyl metaborate, C_2H_5OBO, a compound that was also obtained from ethanol and triethyl borate.

$$C_2H_5OH + B_2O_3 \rightarrow HOBO + C_2H_5OBO$$

$$B(OC_2H_5)_3 + B_2O_3 \rightarrow 3C_2H_5OBO$$

Ethyl metaborate was a syrupy, hygroscopic liquid; it decomposed on heating and for that reason was not distilled. Little mention of metaborates has since been made. When trialkyl borates (methyl, ethyl) were prepared from boron trioxide and the appropriate alcohols, residual oils remained after distillation of the orthoborates; it has been suggested that these were metaborates (107, 305). Acetyl metaborate has been claimed as a product of the pyrolysis of tetraacetyl diborate, but no details were given (99). Boron trioxide and trimethyl borate, when heated in a sealed tube in equimolecular proportions, afforded methyl metaborate, which was trimeric (cryoscopic) and therefore formulated as a boroxole (see Section III,H,5); it decomposed at 170–220°C. (135), By oxidation of the trimeric *n*-butylboronic anhydride with dry air, *n*-butyl metaborate was obtained, which was monomeric (cryoscopic in benzene) (145).

$$2(C_4H_9BO)_3 + 3O_2 \rightarrow 6C_4H_9OBO$$

l-Menthyl (m.p. 113–115°C.) and cyclohexyl (m.p. 165–167°C.) metaborates were prepared by interaction of the appropriate alcohol and orthoboric acid (261); the water formed in the esterification was removed by azeotropic distillation with toluene.

$$ROH + B(OH)_3 \rightarrow ROBO + 2H_2O$$

These compounds were trimeric and infrared examination showed absence of B=O; hence a boroxole structure was indicated.

The metaborates hydrolyze readily with water to give the parent alcohol and orthoboric acid, probably through a monoalkyl orthoborate intermediate, which, however, has been isolated only in the case of the *l*-menthyl compound (261).

$$ROBO \xrightarrow{H_2O} ROB(OH)_2 \xrightarrow{H_2O} ROH + B(OH)_3$$

With ethanol, ethyl metaborate was converted to the orthoborate (297). The decomposition of *l*-menthyl and cyclohexyl metaborates at 270°C. afforded the corresponding olefins; in the former case the olefin had the *cis* configuration.

I, THIOÖRTHOBORATES

Goubeau and Wittmeier (140) have prepared trimethyl thioörthoborate (m.p. 3.2°C., b.p. 218.2°C.) by refluxing boron tribromide for several hours with an excess of silver or lead mercaptide in benzene,

$$3AgSCH_3 + BBr_3 \rightarrow 3AgBr + B(SCH_3)_3$$

The method was not successful if alkali metal mercaptides were used, but trimethyl thioörthoborate has since been obtained from sodium mercaptide and boron tribromide by dispensing with solvent (75). It has also been obtained by heating the polymeric thiomethoxyborine, $(CH_3SBH_2)_x$.

Methyl thioörthoborate is monomeric (Trouton constant) and its Raman spectrum has been recorded. With water it hydrolyzes rapidly to give methyl mercaptan and orthoboric acid; the alcoholysis reaction is similar (140).

Thioörthoborates, unlike orthoborates from oxygen analogs, cannot be obtained by the action of excess mercaptan (methyl) on boron trichloride (374) or tribromide (140), nor by the action of excess sulfide on boron trichloride (*n*-butyl) (205) or boron tribromide (methyl) (140),

III, DERIVATIVES OF $HB(OH)_2$ AND HBO

A, INTRODUCTION

Neither dihydroxyborine, $HB(OH)_2$, nor its anhydride, HBO, exists, but the dialkoxyborines, $HB(OR)_2$, and the boronic acids, $RB(OH)_2$, with their anhydrides, RBO, are well-known and stable compounds. Derivatives of the boronic acids—the boronates—comprise the esters, $RB(OR')_2$, the halogenoboronates, $XB(OR)_2$, and one isolated example of an aminoboronate, $H_2NB(OCH_3)_2$. This compound was believed to be formed by the dissociation of its trimethyl borate complex, which resulted from the action of trimethyl borate on the 1:1 complex between this borate and ammonia (134).

$$B(OCH_3)_3 \cdot NH_3 + B(OCH_3)_3 \rightleftharpoons B(OCH_3)_3 \cdot H_2NB(OCH_3)_2 + CH_3OH$$

$$B(OCH_3)_3 \cdot H_2NB(OCH_3)_2 \rightleftharpoons B(OCH_3)_3 + H_2NB(OCH_3)_2$$

The boronic acid anhydrides, RBO, and other derivatives of HBO appear to be invariably trimeric; these are discussed collectively under the heading 'boroxoles," following Wiberg's suggestion (350). Their sulfur analogs, the "borsulfoles," are not dealt with here, as they have recently been the subject of a review (371).

B. THE DIALKOXYBORINES

The first compound in this class to be prepared was dimethoxyborine, obtained by Burg and Schlesinger (73) by the action of methanol on diborane,

$$B_2H_6 + 4CH_3OH \rightarrow 2HB(OCH_3)_2 + 4H_2$$

Later, other dialkoxyborines were prepared by the action of diborane on aldehydes (acetaldehyde or trimethylacetaldehyde), acetone (56), epoxides (ethylene oxide or propylene oxide) (326), or less successfully on esters (methyl formate or ethyl acetate) (56), but they were not produced if acid chlorides were used (acetyl chloride or phosgene) (56). It has been suggested that dimethoxyborine is one of the products both in the thermal decomposition of sodium trimethoxyborohydride (301) and in the reaction of this compound with hydrogen chloride (58) (Section II,D,5). The attempted preparation of monomethoxyborine yielded a polymeric product, $(CH_3OBH_2)_x$, which on decomposition gave dimethoxyborine.

The dialkoxyborines were shown to be unassociated in the vapor state (73), Their physical constants are recorded in table 5. The relative partial charges on the combined hydrogen in the methyl, ethyl, and *n*-propyl homologs have been calculated (292).

Dimethoxyborine undergoes disproportionation when heated; the action of

TABLE 5

Physical constants of the dialkoxyborines

R in $HB(OR)_2$	Boiling Point	Melting Point	Vapor Pressure	References
	°C.	*°C.*	*mm.*	
Methyl	25.9	−130.6		(58, 73, 301, 303)
Ethyl			36.5 (0°C.)	(56, 326)
Isopropyl			10 (0°C.)	(56, 326)
Neoamyl			3 (25°C.)	(56)

water afforded boric acid and methanol (73). The reaction (303) with sodium trimethoxyborohydride has been mentioned (Section II,B,8).

C. PREPARATION OF BORONIC ACIDS AND ESTERS

1. Introduction

The boronic acids and esters are conveniently considered together, because the acids have frequently been obtained as a result of hydrolysis of the intermediate esters. The acids have received far more attention in the literature than the esters; in fact, reference to the latter compounds has, until very recently, been largely in their role of precursors to the acids. In this section, therefore, attention will be concentrated on the acids, and special methods designed for esters only will be considered in a final subsection.

The more important methods for the preparation of boronic acids and esters have depended on one of the following procedures: (*1*) the oxidation of a trialkylboron to a boronic ester and the hydrolysis of the latter; (*2*) the addition of a metallic alkyl or aryl to a trialkyl borate and the hydrolysis of the boronic ester thus formed; (*3*) the addition of a metallic alkyl or aryl to a boron trihalide to obtain the alkyl- or arylboron dihalide, which on hydrolysis gives the boronic acid or on alcoholysis the ester. These methods will be considered separately.

2. Oxidation of trialkylborons

The mechanism of these oxidation reactions will be discussed later (Section V,D,2). This section is concerned with the topic only in so far as it is a method of preparing boronic acids or esters. Frankland and Duppa (113), in 1859, obtained diethyl ethylboronate by the controlled oxidation of the spontaneously flammable triethylboron; hydrolysis of the ester afforded ethylboronic acid.

$$B(C_2H_5)_3 + O_2 \rightarrow C_2H_5B(OC_2H_5)_2 \xrightarrow{2H_2O} C_2H_5B(OH)_2 + 2C_2H_5OH$$

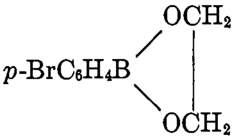
Subsequently it was pointed out that it is difficult to obtain the boronate in a pure state; ethyl diethylboronite and triethyl borate were also formed (235). However, using absolutely dry air it was later possible to convert tri-*n*-butylboron quantitatively to the boronate (168). Several alkylboronic acids have been prepared by allowing trialkylborons to stand in loosely stoppered vessels and then hydrolyzing the products (190).

3. Metal alkyls or aryls on trialkyl borates

Khotinsky and Melamed (177) obtained phenyl- and *m*-tolylboronic acids and some of their alkyl esters by adding ethereal solutions of trialkyl borates (methyl, ethyl, *n*-propyl, isobutyl, isoamyl) to the arylmagnesium bromides at 0°C,

$$B(OR)_3 + ArMgBr \rightarrow ArB(OR)_2 \xrightarrow{2H_2O} ArB(OH)_2$$

and by like procedure a number of alkylboronic acids were prepared. Their claim that the addition of trimethyl borate to phenylmagnesium bromide afforded toluene was not confirmed and indeed an 86 per cent yield of phenylboronic acid by this method has been claimed (130). However, other workers could obtain no better than a 30 per cent yield from the same reaction and this only when reversing the order of addition (311). The method was further improved by Bean and Johnson (19), who recommended using tri-*n*-butyl borate [instead of $B(OCH_3)_3$] to which the Grignard reagent was added; the best yields (50–60 per cent) were obtained by operating at −60°C. The method has been extensively employed in the aromatic (28, 29, 35, 38, 85, 183, 191, 197–200, 202, 203, 237, 321, 322, 335, 385–387) as well as in the aliphatic (primary, secondary, and tertiary alkyl) (169, 320) field. Using triphenyl borate and *n*-butylmagnesium bromide, *n*-butylboronic acid could not be obtained and instead phenol and tri-*n*-butylboron were isolated (130). To prepare 2-methyl-1-propene-1-boronic acid, the lithium alkenyl and trimethyl borate have been employed (211), but only a small yield was obtained (22 per cent crude; 7 per cent pure). For di-*n*-butyl *n*-butylboronate it was shown (38) that employing *n*-butyllithium instead of the Grignard reagent improved the yield by some 50 per cent, but using phenyllithium in place of phenylmagnesium bromide decreased the yield, only about 36 per cent of phenylboronic acid being obtained. Di-*n*-butyl *n*-octylboronate could not be prepared by either the Grignard or the lithium method, *n*-butyl di-*n*-octylboronite, $C_4H_9OB(C_8H_{17})_2$, being obtained instead (38). A by-product in the reaction between *p*-bromophenylmagnesium bromide and the compound $n\text{-}C_4H_9OB(OCH_2)_2$ was the ethylene glycol ester of *p*-bromophenylboronic acid,



which on hydrolysis gave the acid (213).

4, Hydrolysis or alcoholysis of alkyl- or arylboron dihalides (produced by the action of metal alkyls or aryls on boron halides)

Michaelis and Becker (239) heated boron trichloride and diphenylmercury in a sealed tube for 1 hr. at 180–200°C. and thus obtained phenylboron dichloride, which hydrolyzed (240) or alcoholyzed (C_2H_5OH) with vigor to give phenylboronic acid and diethyl phenylboronate, respectively. Other arylboronic acids were similarly prepared (238, 241). The same method has recently been used to obtain 2-chlorovinylboronic acid (34), but better yields were obtained if the antimony alkyl was used.

$$Hg(C_6H_5)_2 \quad + \quad 2BCl_3 \quad \rightarrow \quad 2C_6H_5BCl_2 \quad \xrightarrow{4H_2O} \quad 2C_6H_5B(OH)_2$$

Boron tribromide had advantages over the trichloride in that reflux conditions could be used, instead of the pressure vessel, and the reaction was more rapid (244). An ethereal solution of 3 moles of phenylmagnesium bromide [which is more reactive than the dialkylmercury (129)] has been employed, into which

1 mole of boron trichloride was distilled; the resulting mixture was hydrolyzed (328). Probably the most successful modification involved using excess boron trifluoride, or its diethyl etherate, which was added to the Grignard reagent [alkyl Grignard reagent (191); aryl Grignard reagent (186, 191)] in diethyl ether at 0°C. The alkyl- or arylboron difluorides were then hydrolyzed with excess water to afford the boronic acids.

5. *Other methods for boronic acids*

Boronic anhydrides, $(RBO)_3$ (see Section III,H,2), are usually obtained by dehydration of the corresponding acids; therefore the fact that on hydrolysis they give the reverse reaction is of little preparative value. However, the methylboronic acid is dehydrated so readily that to obtain the pure acid it has been suggested that one start with the anhydride, use an excess of it, add water, and then remove the excess anhydride *in vacuo* (66),

$$(CH_3BO)_3 + 3H_2O \rightarrow 3CH_3B(OH)_2$$

A method that has been used only for methylboronic acid is the hydrolysis of symmetrical dimethyldiborane (307).

$$(CH_3BH_2)_2 + 2H_2O \rightarrow 2CH_3B(OH)_2 + 2H_2$$

The identity of certain uranium-boron compounds was established by showing that the products of their hydrolysis included methylboronic acid (304).

Methylboronic acid has also been obtained by the hydrolysis of *B*,*B′*,*B″*-trimethylborazole (361). Ethyl- and *n*-propylboronic acids were formed when monoalkyldiboranes, RB_2H_5, were hydrolyzed (308). Phenylboronic acid has been obtained by hydrolysis of the product of heating benzene and 5 per cent of diborane (157). The same acid has also been claimed as the product of reaction when treating phenol with boric acid in the presence of phosphorus oxychloride (265),

A number of nuclear-substituted arylboronic acids have been prepared by conventional aromatic techniques. Thus, *m*-nitrophenylboronic acid has been obtained by nitration of phenylboronic acid, using a mixture of concentrated nitric and sulfuric acids (3) at −20°C. or fuming nitric acid (311), whilst *o*-nitrophenylboronic acid was obtained by nitration when acetic anhydride was used as solvent (311). *p*-Tolylboronic acid and *p*-bromophenylboronic acid gave 4-methyl-3-nitrophenylboronic acid and 4-bromo-3-nitrophenylboronic acid, respectively, when nitrated with fuming nitric acid (119). Aminoboronic acids have been obtained by reduction of the corresponding nitro acids, using either hydrogenation in the presence of platinum (19, 311) or freshly precipitated ferrous hydroxide (311). The *m*-hydroxyphenylboronic acid has been obtained from the *m*-aminophenylboronic acid by diazotization and hydrolysis (19), whilst carboxy-substituted phenylboronic acids have been obtained from the corresponding tolyl compounds by oxidation with a saturated solution of potassium permanganate (28, 29, 183). Alkaline permanganate caused ring fission (Section III,E,2). Carbethoxy-substituted phenylboronic acids have been prepared by esterifying the carboxy-substituted phenylboronic acids with ethanol, the water formed being eliminated as a ternary azeotrope ($H_2O/C_2H_5OH/C_6H_6$); the diethyl carbethoxyphenylboronates were then hydrolyzed to give the carbethoxyboronic acids (199).

By oxidation of di-*n*-propylboronous acid, formed by the hydrolysis of di-*n*-propylboron iodide, some *n*-propylboronic acid was obtained (220). The oxidation of diarylboronous acids by halogens (chlorine, bromine) afforded the corresponding boronic acids (236).

$$Ar_2BOH + H_2O + X_2 \rightarrow 2ArB(OH)_2 + HX + ArX$$

The action of a 6 *N* ethereal solution of hydrogen chloride upon 2-aminoethyl α-naphthylphenylboronate produced phenylboronic acid and naphthalene, after subsequent hydrolysis (210).

6. Special methods for boronic esters

Dimethyl β-naphthylboronate has been obtained by the action of sodium methoxide on β-naphthylboron dichloride (238).

$$ArBCl_2 + 2NaOCH_3 \rightarrow ArB(OCH_3)_2 + 2NaCl$$

Alcoholysis of phenylboron dichloride gave esters (*n*-butyl, isobutyl, *sec*-butyl, and 1-methylheptyl) when primary or secondary alcohols were used, but was poor for the preparation of *tert*-alkyl (*tert*-butyl) esters (40). Di-*tert*-butyl phenylboronate has, however, been obtained by a method analogous to that which has been recommended for *tert*-alkyl borates (Section II,B,2), by the addition of 1 mole of phenylboron dichloride to a mixture of 2 moles of *tert*-butyl alcohol and 2 moles of pyridine (38). By heating a mixture of 1-butanol, pyridine, and the 1:1 complex between pyridine and phenylboron dichloride, di-*n*-butyl phenylboronate was obtained (40).

$$C_6H_5BCl_2 + 2t\text{-}C_4H_9OH + 2C_5H_5N \rightarrow 2C_5H_5N\cdot HCl + C_6H_5B[OC_4H_9(t)]_2$$

$$C_6H_5BCl_2\cdot C_5H_5N + 2n\text{-}C_4H_9OH + C_5H_5N \rightarrow 2C_5H_5N\cdot HCl + C_6H_5B(OC_4H_9\text{-}n)_2$$

Methyl, ethyl, *n*-propyl, and *n*-butyl esters of a number of arylboronic acids (C_6H_5—; *o*-, *m*-, *p*-$CH_3C_6H_4$—) have been prepared in nearly quantitative yields from the appropriate boronic acid and alcohol, the water of esterification being removed by refluxing through a Soxhlet of anhydrous copper sulfate (methyl esters), or by azeotropic distillation with excess of the alcohol (*n*-propyl and *n*-butyl esters), or by azeotropic distillation with excess of the alcohol and benzene (ethyl esters) (335). These results have been confirmed for the phenylboronates, and other esters of phenylboronic acid (isobutyl, *sec*-butyl, 2,2-dimethylpropyl, 1-methylheptyl, 2,2,2-trichloroethyl) have also been prepared by the same method; the procedure was not satisfactory for di-*tert*-butyl phenylboronate (38). The method was also successful for the diethanolamine esters of certain arylboronic acids (C_6H_5—, *p*-$CH_3C_6H_4$—, *p*-$CH_3OC_6H_4$—, *p*-BrC_6H_4—,

m-$O_2NC_6H_4$—) (251). A modification was to use phenylboronic anhydride instead of the acid (38).

$$ArB(OH)_2 + 2ROH \rightleftharpoons ArB(OR)_2 + 2H_2O$$

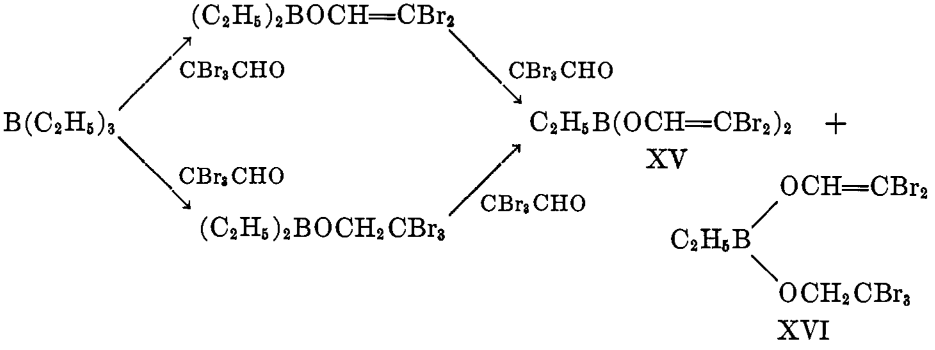
$$(C_6H_5BO)_3 + 6ROH \rightleftharpoons 3C_6H_5B(OR)_2 + 3H_2O$$

Esterification of an acid had been mentioned previously (199), but in that investigation the ester was merely an intermediate and was not characterized. Good yields (60–90 per cent) of esters of some arylboronic acids with certain polyhydric alcohols have been prepared by simply mixing the two components, whereupon the esters precipitated (200). This method is limited in its application to those compounds where the esters are less soluble than either of their parent acids or alcohols. By heating 2-aminoethanol and an arylboronic acid (C_6H_5—, p-BrC_6H_4—, p-$CH_3OC_6H_4$—, α-$C_{10}H_7$—) in toluene and then cooling, crystals of the di-2-aminoethyl arylboronates were obtained (213).

Alcoholysis of boronates was a good method for preparing esters of higher molecular weight from those of lower molecular weight. Thus, the *n*-butyl, *sec*-butyl, isobutyl, and octan-2-yl esters of phenylboronic acid were prepared from diethyl phenylboronate by reaction with the appropriate alcohol (40).

$$ArB(OR)_2 + 2R'OH \rightleftharpoons ArB(OR')_2 + 2ROH$$

The boronates XV and XVI were prepared by interaction of bromal and triethylboron, but this does not appear to be a method of general application, as other aldehydes studied did not behave in the same manner (232).

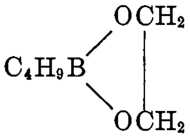


$$(C_2H_5)_2BOCH_2CBr_3 \xrightarrow{CBr_3CHO} XVI + C_2H_5B(OCH_2CBr_3)_2$$

Dimethyl methylboronate has been obtained from tetramethoxysilane and methylboron dibromide (364).

$$Si(OCH_3)_4 + CH_3BBr_2 \rightarrow CH_3B(OCH_3)_2 + (CH_3O)_2SiBr_2$$

The ethylene glycol ester of *n*-butylboronic acid



has been prepared in 46 per cent yield by the addition of ethylene glycol and toluene to a concentrated aqueous solution of methylboronic acid, followed by removal of the water as a ternary azeotrope (212).

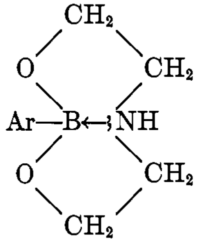
D. PHYSICAL PROPERTIES OF BORONIC ACIDS AND ESTERS

The melting points given in the literature for particular boronic acids often differ widely from one another. This is probably due to their dehydration to boronic anhydrides, the melting points of which are more reliable as characterizing constants for the acids.

Molecular-weight determinations (cryoscopic in nitrobenzene) revealed no dimerization nor association with solvent for arylboronic acids (116, 180) or alkylboronic acids (116). Similar results were obtained with dioxane as solvent, but in benzene some association appeared probable (116). Dipole moment data, on the other hand, revealed no such association for the acids (phenyl, *n*-butyl, and *n*-amyl), either in benzene or in dioxane (263). The heat of solution of *n*-butylboronic acid in water has been measured (102),

Branch, Yabroff, Almquist, Bettman, and Clear (28, 29, 35, 85, 386, 387) measured the dissociation constants of many boronic acids (thirty-one acids, mainly aromatic, were considered). Phenylboronic acid is three times as strong as boric acid (386). *n*-Butylboronic and 2-phenylethylboronic acids are approximately one-tenth as strong as phenylboronic acid, whilst benzylboronic acid is of comparable strength (387). Nuclear substitution of an alkyl or phenyl group in the ortho position decreases the acid strength, whilst meta and para substitution only slightly decreases the acid strength (387). Electronegative groups ($NO_2 > F > Cl > Br > COOH$) in the ring considerably increase acid strength (29, 35), but the effect is least pronounced with the *o*-nitro group. Theoretical discussion of these results was provided by these authors as well as by other workers (161, 282).

Infrared examination of diethanolamine arylboronates (p-$CH_3C_6H_4$—, p-$CH_3OC_6H_4$—, p-BrC_6H_4—, m-$O_2NC_6H_4$—, and C_6H_5—) supported the view that these compounds exhibited transannular cyclization, as shown in formula XVII (251).



XVII

Physical constants for boronic acids, boronic esters, and boronic esters of polyhydric alcohols and phenols are shown in tables 6 to 8,

TABLE 6

Physical constants of boronic acids

Boronic Acid	Melting Point	References
	°C.	
CH_3—*		(66, 361)
C_2H_5—		(111, 112, 113, 308)
n-C_3H_7—	107	(80, 177, 190, 220, 308, 320)
n-C_4H_9—	92–94	(12, 116, 168, 263, 320)
i-C_4H_9—	112	(157, 177, 190, 320)
t-C_4H_9—	113	(157, 169, 193)
n-C_5H_{11}—	93–94	(116, 263, 320)
i-C_5H_{11}—	101	(177)
	169	(190)
n-C_6H_{13}—	88–90	(320)
$C_6H_5CH{=}CH$—	138–141	(236, 237)
$ClCH{=}CH$—	129	(34)
$C_6H_5CH_2CH_2$—		(387)
C_6H_5—	216	(3, 19, 38, 80, 116, 130, 154, 155, 157, 177, 180, 186, 191, 197, 198, 199, 200, 210, 236, 240, 241, 244, 251, 263, 265, 311, 328, 335)
o-$CH_3C_6H_4$—	168	(180, 183, 241, 335)
m-$CH_3C_6H_4$—		(177, 183, 199, 335)
	137–140	(177)
	157	(183)
p-$CH_3C_6H_4$—	240	(19, 80, 183, 186, 199, 200, 236, 240, 244, 251, 335)
	245	(183)
1,2,4-$(CH_3)_2C_6H_3$—	211	(244)
p-$C_2H_5C_6H_4$—	108–111	(236)
$C_6H_5CH_2$—	161	(169, 177, 192, 387)
o-ClC_6H_4—	97–98	(35)
	149	(183)
m-ClC_6H_4—	189–190	(29, 35, 180, 191, 202)
p-ClC_6H_4—	149	(29, 35, 180, 183, 186, 191, 200, 236)
	275	(186)
m-BrC_6H_4—	170	(29)
p-BrC_6H_4—		(19, 29, 80, 180, 183, 186, 199, 200, 213, 236, 251)
	312–315	(29)
	276–281	(19)
	191	(186)
	254–256	(213)
m-FC_6H_4—	220–221	(29)
p-FC_6H_4—	289–290	(29)
p-$ClC_6H_4CH_2$—	140	(236)
o-$CH_3OC_6H_4$—	165	(241)
	105	(183)
m-$CH_3OC_6H_4$—	147	(183, 241)
p-$CH_3OC_6H_4$—	209–210	(19, 183, 199, 203, 236, 241, 251)
o-$C_2H_5OC_6H_4$—		(35, 180, 241)
	171	(241)
	102–103	(35)
m-$C_2H_5OC_6H_4$—	130	(35)
p-$C_2H_5OC_6H_4$—	159	(241)
	150	(35)
p-$C_6H_5OC_6H_4$—	123–124	(29, 180)
o-$O_2NC_6H_4$—	139–140	(29, 311)
m-$O_2NC_6H_4$—	275–277	(29, 80, 199, 251, 311)
p-$O_2NC_6H_4$—	305	(29, 311)
o-$H_2NC_6H_4$—	179–180	(19, 311)
o-$C_6H_5CONHC_6H_4$—	283	(85)
m-$H_2NC_6H_4$—	93–94	(19, 311)
m-$(C_2H_5)_2NC_6H_4$—		(321)

* Vapor pressure given by $\log_{10} P = 11.813 - 3404/T$.

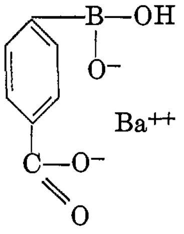
TABLE 6—*Concluded*

Boronic Acid	Melting Point	References
	°C.	
m-$C_6H_5CONHC_6H_4$—	290	(85, 311)
m-$CH_3CONHC_6H_4$—	274-275	(311)
m-HOC_6H_4—	225	(19, 321)
o-$HOOCC_6H_4$—	152	(183)
m-$HOOCC_6H_4$—	240	(183)
	253	(29)
p-$HOOCC_6H_4$—	225	(29, 183, 244)
	240	(29)
m-$C_2H_5OOCC_6H_4$—		(199)
p-$C_2H_5OOCC_6H_4$—		(199)
2-CH_3-5-ClC_6H_3—	184-186	(236)
4-CH_3-5-ClC_6H_3—	242-247	(236)
4-CH_3-2-BrC_6H_3—	157	(236)
4-CH_3-3-$O_2NC_6H_3$—	260-264	(19)
4-CH_3-3-$H_2NC_6H_3$—	209-212	(19)
4-CH_3-3-HOC_6H_3—	266-268	(19)
4-Br-3-$O_2NC_6H_3$—	300-301	(19)
2,4-$(CH_3)_2C_6H_3$—		(238)
2,4-$(CH_3)_2$-5-ClC_6H_2—	155-157	(236, 237)
2,4-$(CH_3)_2$-5-BrC_6H_2—	206-211	(236, 237)
3,4-$(CH_3)_2C_6H_3$—	190.5	(238)
2,5-$(CH_3)_2C_6H_3$—	186	(238)
o-$C_6H_5C_6H_4$—	129	(387)
m-$C_6H_5C_6H_4$—	207-208	(387)
p-$C_6H_5C_6H_4$—	232-234	(387)
	185-190	(237)
α-$C_{10}H_7$—		(180, 183, 241, 387)
	259	(241)
	202	(183)
β-$C_{10}H_7$	248	(183, 241, 387)
2-Furyl	110	(169)
2-Thienyl	134-135	(169)
4-$(CH_3)_2N$-1-$C_{10}H_6$—	82-85	(322)
4-CH_3O-1-$C_{10}H_6$—	195	(321)

E. CHEMICAL PROPERTIES OF BORONIC ACIDS

1. *Acid properties*

The boronic acids display characteristic acid properties. Thus, they dissociate (see Section III,D) and they readily form anhydrides (see Section III,H,2), esters (see Section III,C,6), and salts, although not many examples of this last class have been described. Phenylboronic acid formed both a sodium and a calcium salt when treated with the appropriate hydroxide (240). The barium salt of p-carboxyphenylboronic acid was said to have the structure shown in formula XVIII. n-Butylboronic acid formed a hydrated sodium salt when treated with very concentrated sodium hydroxide (320).



XVIII

TABLE 7

Physical constants of boronic esters

R' in R'B(OR)$_2$	R in R'B(OR)$_2$	Boiling Point	n_D^{20}	d_4^{20}	References
		°C.			
CH_3—	CH_3—	53.5			(364)
C_2H_5—	C_2H_5—	125			(112, 113)
C_2H_5—	CBr_3CH_2—				(232)
C_2H_5—	CBr_2=CH—	140/3 mm.			(232)
n-C_4H_9—	n-C_4H_9—	105/10 mm.	1.4169	0.8300	(38, 39, 40)
ClCH=CH—	CH_3—	132			(209)
$CH_3OCH_2CH_2CH_2$—	n-C_4H_9—	140-150/41 mm.			(166)
$C_6H_5CH_2$—	i-C_4H_9—	189-196/36 mm.			(177)
C_6H_5—	CH_3—	74-75/11 mm.	1.4926*	1.0024*	(335)
C_6H_5—	C_2H_5—	90-91/11 mm.	1.4785	0.954	(38, 39, 40, 335)
C_6H_5—	n-C_3H_7—	112-113/10 mm.	1.4738*	0.9279*	(335)
C_6H_5—	n-C_4H_9—	139-140/10 mm.	1.4751	0.9245	(38, 39, 40, 335)
C_6H_5—	i-C_4H_9—	55/0.2 mm.	1.4711	0.9163	(38, 39, 40, 245)
C_6H_5—	s-C_4H_9—	49/0.2 mm.	1.4658	0.9073	(38, 39, 40)
C_6H_5—	$C_6H_{13}CH(CH_3)$—	119/0.01 mm.	1.4666	0.8847	(38, 39, 40)
C_6H_5—	$(CH_3)_3CCH_2$—	74/0.2 mm.	1.4678	0.9903	(38)
C_6H_5—	CCl_3CH_2—	118/0.01 mm.	1.5333		(38, 40)
C_6H_5—	$H_2NCH_2CH_2$—	214-215 (m.p.)			(213)
o-$CH_3C_6H_4$—	CH_3—	74-75/9 mm.	1.4870*	0.9798*	(335)
o-$CH_3C_6H_4$—	C_2H_5—	91-92/10 mm.	1.4737*	0.9351*	(335)
o-$CH_3C_6H_4$—	n-C_3H_7—	116-117/9 mm.	1.4721*	0.9206*	(335)
o-$CH_3C_6H_4$—	n-C_4H_9—	139-140/9 mm.	1.4706*	0.9099*	(335)
m-$CH_3C_6H_4$—	CH_3—	85-86/10 mm.	1.4926*	0.9846*	(335)
m-$CH_3C_6H_4$—	C_2H_5—	101-102/11 mm.	1.4796*	0.9388*	(335)
m-$CH_3C_6H_4$—	n-C_3H_7—	128-129/11 mm.	1.4757*	0.9226*	(335)
m-$CH_3C_6H_4$—	n-C_4H_9—	146-147/8 mm.	1.4744*	0.9126*	(335)
m-$CH_3C_6H_4$—	i-C_4H_9—	195-207/66 mm.			(177)
p-$CH_3C_6H_4$—	CH_3—	89-90/10 mm.	1.4948*	0.9860*	(335)
p-$CH_3C_6H_4$—	C_2H_5—	106-107/12 mm.	1.4793*	0.9389*	(335)
p-$CH_3C_6H_4$—	n-C_3H_7	128-129/11 mm.	1.4770*	0.9225*	(335)
p-$CH_3C_6H_4$—	n-C_4H_9—	159-160/13 mm.	1.4758*	0.9127*	(335)
p-ClC_6H_4—	n-C_4H_9—				(151)
p-ClC_6H_4—	Lauryl				(151)
p-BrC_6H_4—	$H_2NCH_2CH_2$—	255-256 (m.p.)			(213)
p-$CH_3OC_6H_4$—	$H_2NCH_2CH_2$—	216-218 (m.p.)			(213)
2,4-$(CH_3)_2C_6H_3$—	C_2H_5—	160			(238)
α-$C_{10}H_7$—	$H_2NCH_2CH_2$—	242-243 (m.p.)			(213)
β-$C_{10}H_7$—	CH_3—	160-180/50 mm.			(241)
α-$C_{10}H_7$—	n-C_4H_9—	170-174/1 mm.	1.5322		(210)

* At 25°C.

TABLE 8

Physical constants of boronic esters of polyhydric alcohols and phenols

Ester Formed From		Boiling Point	Melting Point	Reference
Boronic acid	Alcohol or phenol			
		°C.	*°C.*	
n-Butyl*	Ethylene glycol*	78-79/66 mm.		(212)
Phenyl	Diethanolamine		209.5-210	(215)
Phenyl	Sorbitol		187-190	(200)
Phenyl	Mannitol		134-135	(200)
Phenyl	Pinacol		29-30	(200)
Phenyl	*cis*-Indan-1,2-diol		107.5-108.5	(200)
Phenyl	Diethyl *d*-tartrate		46-48	(200)
Phenyl	Catechol		111-112	(200)
Phenyl	Pentaerythritol		207-208	(200)
p-Methylphenyl	Diethanolamine		232-233	(215)
p-Methylphenyl	Mannitol		162-164	(200)
p-Methoxyphenyl	Diethanolamine		223-223.5	(215)
m-Nitrophenyl	Diethanolamine		222.5-223	(215)
p-Chlorophenyl	Mannitol		184-185	(200)
p-Bromophenyl	Ethylene glycol	150-153/15 mm.	72-80	(213)
p-Bromophenyl	Diethanolamine		272.5-273	(215)
p-Bromophenyl	Mannitol		204-205	(200)

* d_4^{25} = 0.9141; n_D^{25} = 1.4129.

Deboronation (*cf.* decarboxylation) of arylboronic acids is a facile process, It may be accomplished by treatment with water at elevated temperatures, or more rapidly with acids, or preferably with bases. Heating phenylboronic acid with 50 per cent sodium hydroxide produced benzene; the same reaction was effected by heating with water under pressure or with concentrated hydrochloric acid (3),

$$C_6H_5B(OH)_2 + H_2O \rightarrow C_6H_6 + B(OH)_3$$

p-Bromophenyl- and *p*-tolylboronic acids were recovered unchanged after 28 hr. in water at 100°C., but 6 hr. at 130–150°C. effected complete deboronation (80). Both 4-dimethylamino- and 4-methoxy-α-naphthylboronic acids were easily deboronated by mild hydrolysis or under the influence of either dilute acids or bases (322).

By contrast, the deboronation of alkylboronic acids is far more difficult (*cf*, the decarboxylation of aromatic and aliphatic carboxylic acids). The *n*-propyl acid was quite stable when heated with water for 7 hr. at 140°C, (3). Prolonged heating of alkylboronic (*n*-propyl, *n*-butyl, isobutyl, *n*-amyl, *n*-hexyl) acids with (*1*) strong aqueous solutions of bases, (*2*) 40 per cent hydrobromic acid, or (*3*) 40 per cent hydriodic acid effected no boron–carbon cleavage (320), although heating the hydrated sodium salt of *n*-butylboronic acid afforded *n*-butane. Benzylboronic acid resembled the aromatic acids. Thus, although there was no appreciable decomposition when reacting with either hot water or hot 5 per cent sulfuric acid, treatment with a hot 5 per cent sodium hydroxide solution quantitatively afforded toluene (169).

Other boron–carbon cleavage reactions are well known, but these involve interaction of boronic acids with either oxidizing agents or metal salts (which may also in some cases function as oxidizing agents). These reactions are more suitably considered separately; in general, cleavage of arylboronic acids is far easier than of alkylboronic acids, except with respect to atmospheric oxidation,

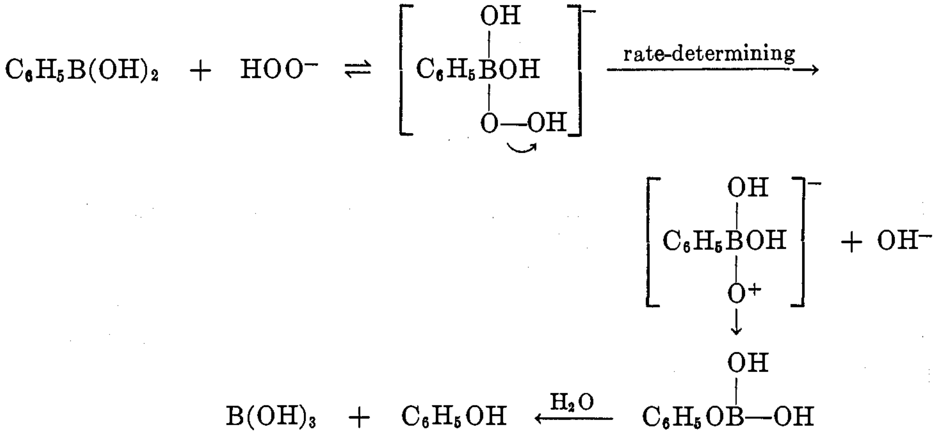
2, Boron–carbon cleavage reactions (oxidizing agents)

The sodium salt of *n*-butylboronic acid was not susceptible to atmospheric oxidation (320). Free alkylboronic acids, however, were readily autoxidized in dry air to orthoboric acid, but were quite stable when moist (169, 320), The ease of such autoxidation appears to be related to the degree of electron release of the alkyl group. Despite a report that *tert*-butylboronic acid was stable in air (193), it was later demonstrated that this acid (like benzylboronic acid) was oxidized even in moist air and was more reactive than isobutylboronic acid, which in turn was more reactive than either the *n*-butyl- or the *n*-hexylboronic acid (169). The conversion of boronic acids to orthoboric acid was thought to involve the following reaction sequence:

$$RB(OH)_2 + \tfrac{1}{2}O_2 \rightarrow ROB(OH)_2 \xrightarrow{H_2O} ROH + B(OH)_3$$

In contrast, neither the arylboronic acids nor the 1-furyl- or 1-thienylboronic acids are oxidized in the atmosphere (169),

Hydrogen peroxide quantitatively oxidized alkylboronic acids to orthoboric acid; use has been made of this in estimating the boron content of such compounds (320). Phenylboronic acid reacted with hydrogen peroxide in like manner, affording orthoboric acid and phenol (3). The kinetics of this reaction has been studied, and the following mechanism was proposed (197):



$$C_6H_5B(OH)_2 + HOO^- \rightleftharpoons \left[C_6H_5\overset{OH}{\underset{O-OH}{B}}OH\right]^- \xrightarrow{\text{rate-determining}} \left[C_6H_5\overset{OH}{\underset{O^+}{B}}OH\right]^- + OH^-$$

$$\downarrow$$

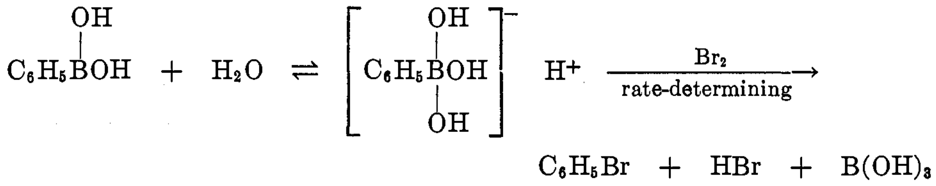
$$B(OH)_3 + C_6H_5OH \xleftarrow{H_2O} C_6H_5O\overset{OH}{B}-OH$$

The alkaline permanganate oxidation of arylboronic acids has revealed that many of these rapidly react at room temperature, affording fission of the ring; although the reactions were dependent on the other groups attached to the benzene ring, it appears that the —$B(OH)_2$ group sensitizes the nucleus towards oxidation (387). Phenyl-, *m*-phenetyl-, *m*-tolyl-, and *p*-tolylboronic acids were not appreciably affected by the reagent. *n*-Butyl- and 2-phenylethylboronic acids were oxidized to the respective alcohols and orthoboric acid.

The action of the halogens on boronic acids has received attention. Whereas alkylboronic acids do not react (320), the action of chlorine water, of bromine water, or of a solution of iodine in potassium iodide on phenylboronic acid afforded in each case the appropriate halogenobenzene (3). 1-Furyl- and 1-thienylboronic acids behaved similarly with iodine in potassium iodide (169).

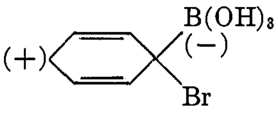
$$ArB(OH)_2 + X_2 + H_2O \rightarrow ArX + HX + B(OH)_3$$

The bromine reaction has been utilized as a volumetric method for the estimation of boron in arylboronous and arylboronic acids (237). The kinetics of the bromonolysis of phenylboronic acid in aqueous acetic acid has been studied (198). The reaction showed a positive salt effect, and was catalyzed by bases and retarded by acids. This was considered to be an example of an electrophilic displacement reaction, and it was suggested that in general the reactions of the boronic acids which involve replacement of the —$B(OH)_2$ group proceed by such a mechanism,



$$C_6H_5\overset{OH}{B}OH + H_2O \rightleftharpoons \left[C_6H_5\overset{OH}{\underset{OH}{B}}OH\right]^- H^+ \xrightarrow[\text{rate-determining}]{Br_2} C_6H_5Br + HBr + B(OH)_3$$

The rate constants for the brominolysis of ten arylboronic acids in 20 per cent acetic acid at 25°C. were evaluated. A Hammett plot for the reaction of phenylboronic acid indicated the presence of an intermediate of the type shown in formula XIX (199).



XIX

The rate of iodinolysis of *p*-methoxyphenylboronic acid was proportional to the product of the concentrations of the reactants, when the iodide-ion and proton concentrations were constant (203). The reaction was not subject to general acid or base catalysis, but sodium fluoride and chelating agents were specific catalysts. These results were interpreted by a mechanism similar to that proposed for brominolysis.

3, Boron–carbon cleavage reactions (metal salts)

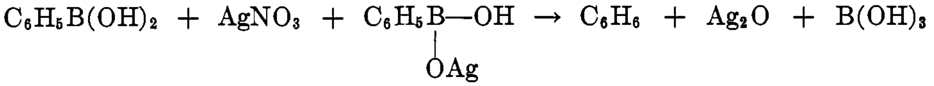
The arylboronic acids have been shown to react with aqueous solutions of copper, silver, zinc, cadmium, mercury, and thallium salts. It may be significant that these elements are all members of B subgroups of the periodic system. In contrast, beryllium chloride, magnesium chloride, magnesium bromide, calcium chloride, or calcium bromide did not react with phenylboronic acid (3).

Cupric chloride and cupric bromide reacted with phenylboronic acid to give the appropriate halogenobenzenes, whilst copper sulfate gave benzene, biphenyl, and a trace of phenol (3).

$$C_6H_5B(OH)_2 + 2CuX_2 + H_2O \rightarrow C_6H_5X + Cu_2X_2 + HX + B(OH)_3$$

Cupric acetate reacted to give cuprous oxide and the appropriate binuclear hydrocarbon from phenylboronic acid, *o*-nitrophenylboronic acid, or *m*-nitrophenylboronic acid (154). Alkylboronic acids, by contrast, did not react with cupric salts (320), whereas 2-furyl- and 2-thienylboronic acids behaved like phenylboronic acid, affording with cupric chloride the appropriate 2-chloro heterocycle (169).

Phenylboronic acid and silver nitrate gave benzene and silver oxide, the silver salt being an intermediate (240).



$$C_6H_5B(OH)_2 + AgNO_3 + C_6H_5\underset{\displaystyle|\atop\displaystyle OAg}{B}\text{—}OH \rightarrow C_6H_6 + Ag_2O + B(OH)_3$$

Similarly, an ammoniacal solution of silver nitrate converted *o*-tolylboronic acid to toluene (241), and the 2-furyl- and 2-thienylboronic acids to their parent heterocycles (169). Alkylboronic acids, $RB(OH)_2$, also reacted with silver compounds and showed themselves to be reducing agents (177), affording in each case the appropriate paraffin (RR) (169, 320). The aromatic reaction was visualized as a hydrolytic cleavage (169).

$$ArB(OH)_2 + H_2O \xrightarrow{[Ag(NH_3)]^+} C_6H_6 + B(OH)_3$$

Both cadmium bromide and zinc chloride converted phenylboronic acid to benzene; an organometallic intermediate was considered probable (3). Alkylboronic acids did not react (320).

$$C_6H_5B(OH)_2 + MX_2 + H_2O \rightarrow C_6H_5MX + HX + B(OH)_3$$

$$C_6H_5MX \xrightarrow{H_2O} C_6H_6$$

Phenylboronic acid when reacted with aqueous mercuric chloride gave phenylmercuric chloride (240). *o*-Tolylboronic (241), 2-furylboronic (169), and 2-thienylboronic (169) acids behaved similarly.

$$C_6H_5B(OH)_2 + HgCl_2 \rightarrow C_6H_5HgCl + HCl + B(OH)_3$$

Mercuric bromide gave an analogous product (3). *n*-Propylboronic acid was said to react with aqueous mercuric chloride at 140–150°C. (20 hr.) to give a comparable reaction (80). This could not be confirmed, however; in general, alkylboronic acids do not react with mercuric salts (320), although benzylboronic acid does (177).

Phenylboronic acid was also shown to give diphenylmercury when reacted with solutions containing mercuric ions (240); this was used as an analytical method for mercury. Thus, mercuric nitrate was quantitatively converted to diphenylmercury when treated with phenylboronic acid (154). When phenylboronic acid was boiled for 1 hr. with yellow mercuric oxide, in an aqueous medium, phenylmercuric hydroxide and diphenylmercury were obtained (80). After only 30 min. the product was exclusively diphenylmercury. *p*-Tolyl-, *p*-bromophenyl-, and *m*-nitrophenylboronic acids were similarly converted to the appropriate mercury diaryl with mercuric oxide in water.

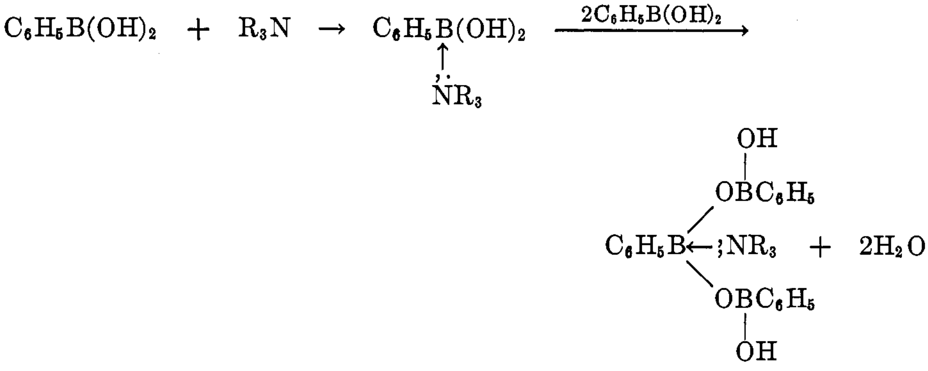
A number of arylboronic acids were converted to either diarylthallium halides, or arylthallium dihalides, by reaction with aqueous thallic chloride or bromide in appropriate proportions (237).

$$2ArB(OH)_2 \xrightarrow{TlX_3,\ H_2O} Ar_2TlX \xrightarrow{TlX_3,\ H_2O} ArTlX_2$$

Thallic chloride did not react, however, with *n*-propylboronic acid, even after heating the mixture for 4 hr. at 100°C. in water (80).

4. Other reactions

Phenylboronic acid was observed to react with nitrogen bases to give complexes (XX) which were thought to form by the following reaction sequence (385):



$$C_6H_5B(OH)_2 + R_3N \rightarrow \underset{\underset{NR_3}{\uparrow}}{C_6H_5B(OH)_2} \xrightarrow{2C_6H_5B(OH)_2}$$

XX

The complexes with diethylamine, trimethylamine, and pyridine had melting points of −85°C., 39°C., and 148–149°C., respectively.

The benzene-nuclear reactions of the arylboronic acids have already been discussed (Section III,C,5). The reaction with boron trifluoride will be considered later (Section V,H,4).

Both *m*-hydroxyphenylboronic acid and *m*-diethylaminophenylboronic acid coupled with diazonium salts, yielding azo dyes containing the —$B(OH)_2$ group (321).

Polyisocyanates and polyisothiocyanates were said to react with boronic acids to give linear polymers (339).

Phenylboronic acid was shown to be toxic towards microörganisms (240); this effect was later attributed to the presence of free phenol in the earlier sample (19). Nevertheless, many arylboronic acids have marked bacteriostatic properties. It has been suggested that compounds possessing a boron–carbon linkage have insecticidal properties (27), while phenylboronic acid has been said to enhance the efficiency of a number of hypnotics (79).

The general similarity between alkylboronic acids and aliphatic aldehydes has been remarked upon (320).

F. CHEMICAL PROPERTIES OF BORONIC ESTERS

The lower alkyl esters of phenylboronic acid and of the three tolylboronic acids hydrolyzed readily (335), although not as readily as the trialkyl borates (38).

$$ArB(OR)_2 + 2H_2O \rightarrow ArB(OH)_2 + 2ROH$$

Diethanolamine esters of arylboronic acids were much more resistant towards such hydrolysis, and this has been interpreted by reference to their structure (Section III,D) (251). Di-*n*-butyl *n*-butylboronate, $C_4H_9B(OC_4H_9)_2$, was much more stable towards hydrolysis than the majority of arylboronic esters (38, 168) and also than trialkyl borates, e.g., $B(OC_4H_9\text{-}n)_3$; this fact was utilized in its preparation (38). The mechanism of boronate hydrolysis probably involves boron–oxygen rather than alkyl–oxygen fission, because hydrolysis of di(*d*-(+)-1-methylheptyl) phenylboronate afforded *d*-(+)-2-octanol, with no loss of activity, and hydrolysis of dineopentyl phenylboronate gave neopentyl alcohol and not a rearranged alcohol (40). Similar conclusions, also based on evidence derived from optical activity, were reached for the mechanism of alcoholysis of diethyl phenylboronate (40); alcoholysis reactions have been discussed previously (Section III,C,6). Dimethyl β-naphthylboronate was converted to the anhydride and methanol on exposure to moist air (241).

Di-*n*-propyl *n*-propylboronate was thought to be an intermediate in the oxidation of tri-*n*-propylboron (15).

Neither di-*n*-propyl nor di-*n*-butyl phenylboronate formed complexes with ammonia (213). Likewise, there was no evidence for coordination between pyridine and either di-*n*-butyl *n*-butylboronate or di-*n*-butyl phenylboronate, but in contrast di(2,2,2-trichloroethyl) phenylboronate did form a stable 1:1 complex (m.p. 111–116°C.) with pyridine (40).

Chlorine, bromine, and iodine were without effect on any of the lower alkyl esters of phenylboronic acid or of the three tolylboronic acids (335), contrary to an earlier report (3). The reaction of hydrogen halides with boronates (39) was analogous to that with orthoborates (Section II,D,3). Thus, hydrogen chloride gave no reaction, even after 7 hr. at 120°C., with the *n*-butyl, isobutyl, and *sec*-butyl esters of phenylboronic acid or with di-*n*-butyl *n*-butylboronate, Hydrogen bromide, however, slowly dealkylated all these esters and also di(*d*-(+)-1-methylheptyl phenylboronate at 120°C.; the *l*-(−)-2-bromoöctane obtained from the last-named ester was almost completely optically inverted. Di-*tert*-butyl phenylboronate reacted rapidly at 20°C. with hydrogen chloride to give *tert*-butyl chloride.

$$\mathrm{RB(OR')_2 + 2HX \rightarrow RB(OH)_2 + 2R'X}$$

The mechanism proposed for these reactions was analogous to that suggested for the dealkylation reactions of orthoborates.

The reactions of boronic esters with organometallic compounds (Section II,D,5; Section IV,D,3; Section V,B) and with the boron halides (Section IV,G; Section V,H,4) will be discussed later. The general similarity between orthoborates and boronates has been stressed (39, 40).

G. THE HALOGENOBORONATES

1. Preparation

Gasselin (118) prepared dimethyl fluoroboronate, $\mathrm{FB(OCH_3)_2}$, by the action of boron trifluoride on either trimethyl borate or sodium methoxide.

$$\mathrm{2B(OCH_3)_3 + BF_3 \rightarrow 3FB(OCH_3)_2}$$

$$\mathrm{2NaOCH_3 + BF_3 \rightarrow FB(OCH_3)_2 + 2NaF}$$

The latter reaction, however, has been stated to give not the fluoroboronate but a coordination compound, $\mathrm{BF_3 \cdot NaOCH_3}$ (234). The former reaction has been repeated (138). Attempts to prepare di-*n*-butyl fluoroboronate from tri-*n*-butyl borate and boron trifluoride (206), boron trifluoride diethyl etherate (91), or *n*-butyl difluoroboronite (206), or by the disproportionation of *n*-butyl difluoroboronite have all failed.

Dimethyl fluoroboronate, as well as dimethyl chloroboronate, dimethyl bromoboronate, and diethyl bromoboronate, was prepared by the addition of a boron halide to a trimethylalkoxysilane (364). However, no experimental details were given.

$$2ROSi(CH_3)_3 + BX_3 \rightarrow 2(CH_3)_3SiX + XB(OR)_2$$

Chloroboronates were first prepared by Wiberg and Sütterlin by the action of boron trichloride on either alcohols (methanol, ethanol) (372) or ethers (dimethyl and diethyl ethers) (373) in the correct proportions at −60°C. to −80°C. in a high-vacuum apparatus.

$$2ROH + BCl_3 \rightarrow ClB(OR)_2 + 2HCl$$

$$2ROR + BCl_3 \rightarrow ClB(OR)_2 + 2RCl$$

In the latter reaction heating was required to effect the decomposition of the addition products first formed. The reaction sequence between boron trichloride and the two ethers was represented by the following scheme (277, 373):

$$ROR + BCl_3 \rightarrow ROR{\cdot}BCl_3 \xrightarrow{\text{heat}} RCl + ROBCl_2$$

$$ROBCl_2 \xrightarrow{ROR} ROR{\cdot}(ROBCl_2)_2 \rightarrow ClB(OR)_2 + ROR{\cdot}BCl_3$$

These intermediate addition compounds were not isolated with ethers of higher molecular weights, the overall reaction then being rapidly complete even at −80°C. (124).

Dimethyl chloroboronate was obtained by the action of boron trichloride on trimethyl borate (370). This type of mutual replacement reaction, as well as the boron trichloride alcoholysis reaction, has been used for the isolation in quantitative yield of chloroboronates having various types of branching in the alkyl group (105, 123, 207), the reactions being carried out in *n*-pentane or in the absence of solvent at a low temperature.

$$2B(OR)_3 + BCl_3 \rightarrow 3ClB(OR)_2$$

Alkyl dichloroboronites have also been used to prepare chloroboronates by alcoholysis (123, 207, 372), by reaction with trialkyl borates (207), or by disproportionation (105, 126, 207).

$$ROBCl_2 + ROH \rightarrow ClB(OR)_2 + HCl$$

$$ROBCl_2 + B(OR)_3 \rightarrow 2ClB(OR)_2$$

$$2ROBCl_2 \rightleftharpoons ClB(OR)_2 + BCl_3$$

All the methods for preparing chloroboronates, except the disproportionation reaction, are quantitative and complete at low temperature. Probably the most

TABLE 9

Physical constants of chloroboronates

R in $ClB(OR)_2$	Melting Point	Boiling Point	n_D^{20}	d_4^{20}	References
	°C.	*°C.*			
CH_3—	−87.7	74.7			(366, 370, 372, 373, 376)
C_2H_5—		112.3			(317, 366, 370, 372, 373)
n-C_3H_7—		36/6 mm.	1.4028	0.959	(207)
n-C_4H_9—		40/0.25 mm.	1.4132	0.941	(123, 126, 207)
i-C_4H_9—		32/0.2 mm.	1.4055	0.938	(123, 207)
s-C_4H_9—			1.4017	0.924	(207)
i-C_5H_{11}—		110-113/14 mm.			(182)
$(CH_3)_3CCH_2$—		30/0.2 mm.	1.4102	0.906	(126, 207)
t-$C_4H_9(CH_3)CH$—		35/0.015 mm.	1.4165	0.901	(207)
n-C_8H_{17}—			1.4380	0.906	(207)
n-$C_6H_{13}CH(CH_3)$—			1.4277	0.897	(207)
$Cl(CH_2)_2$—			1.4551	1.1320*	(105)
C_6H_5—					(89)
p-$O_2NC_6H_4$—	187-190				(90)

* At 18°C.

convenient methods are the trialkyl borate reactions with either boron trichloride or alkyl dichloroboronites; both of these have the advantage that the required chloroboronate is the sole product of the reaction. Owing to the difficulty of accurately weighing boron trichloride (it boils at 12.5°C.), the latter method is probably superior, but it is limited to primary alkyl esters, as only primary alkyl dichloroboronites are stable.

Diphenyl (89) and di-*p*-nitrophenyl (90) chloroboronates are so far the only known aryl members. They were prepared by the boron trichloride–phenol (analogous to BCl_3 and ROH) method and by disproportionation of the nitrophenyl dichloroboronite.

Iodoboronates have not been reported. With regard to bromoboronates, only the isolated experiment already mentioned (364) has been published.

2. Physical properties

Dimethyl fluoroboronate boils at 52.7°C. and could not be crystallized; its Raman spectrum has been investigated (138).

Dimethyl and diethyl chloroboronates were shown to be unimolecular (372). The Trouton constants, determined for dimethyl (372), diethyl (372), and di-2-chloroethyl (224) chloroboronates, showed no association. The heat of hydrolysis of diethyl chloroboronate was measured as -206.3 ± 1.2 kcal./mole, a value which was 4.0 kcal./mole greater than expected from a value calculated from the bond energies for B—Cl and B—OC_2H_5 bonds in boron trichloride and triethyl borate, respectively (317). The calculated and observed (based on density and refractive index measurements) molecular refractivities of eight dialkyl chloroboronates showed good agreement (207). Physical constants are shown in table 9.

3. *Chemical properties*

Attempts to crystallize dimethyl fluoroboronate were unsuccessful, because in this process the products of disproportionation were obtained (138),

$$2FB(OCH_3)_2 \rightarrow B(OCH_3)_3 + CH_3OBF_2$$

The inability to obtain the *n*-butyl analog has also been attributed to similar disproportionation (91, 206).

Dimethyl and diethyl chloroboronates were reported to be stable compounds (372). The stability of their higher homologs, however, has been shown to be dependent on the nature of the alkyl group (105, 123, 207) and on the rigorous absence of impurities (207). Decomposition involved the following reactions (207):

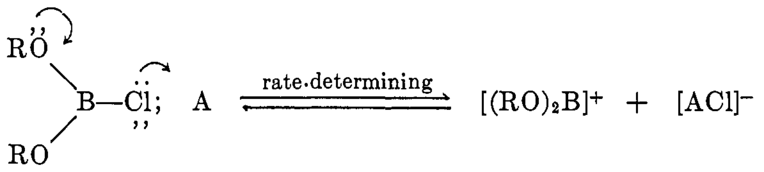
$$3ClB(OR)_2 \rightarrow B_2O_3 + B(OR)_3 + 3RCl \qquad (1)$$

$$3ClB(OR)_2 \rightarrow B_2O_3 + B(OR)_3 + 3HCl + 3(\text{olefin}) \qquad (2)$$

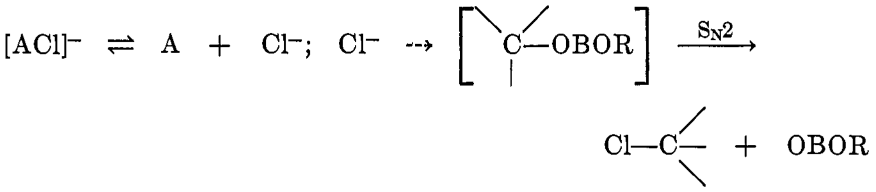
$$\left.\begin{array}{l} 2ClB(OR)_2 \rightleftharpoons B(OR)_3 + ROBCl_2 \\ 2ROBCl_2 \rightleftharpoons BCl_3 + ClB(OR)_2 \end{array}\right\} \quad (3)$$

The isolation of far less than quantitative yields of chloroboronates in certain experiments (182, 224) is probably due to their having been carried out under such conditions of temperature and pressure that considerable decomposition had set in.

Depending on experimental conditions either reaction 3, or 1 and 2 together, was observed (207). At pressures equal to or greater than atmospheric and under reflux or sealed-tube conditions, reactions 1 and 2 were observed. Under reflux, by reduction of pressure, reaction 3 was the principal one. This reaction was reversible and so was reaction 1, but in this case only when the alkyl group was primary and straight-chain. For di-2-chloroethyl chloroboronate the characteristic reaction was reaction 3 (105). The inability to obtain di-*tert*-butyl chloroboronate, even at low temperature, was attributed to reaction 1 (123, 207). The stability, with respect to reaction 1, increased with both length of chain and extended branching (except at the α-carbon atom) (207). Rearrangements of the Wagner–Meerwein type were demonstrated in the conversion of isobutyl (123), neopentyl, and α-methylneopentyl (207) chloroboronates to *tert*-butyl, *tert*-amyl, and *tert*-hexyl chlorides, respectively, by reaction 1. *d*-(+)-1-Methylheptyl chloroboronate afforded *l*-(−)-2-chloroöctane (207). Reaction 1 was remarkably catalyzed by traces of Lewis acids (ferric chloride, aluminum chloride, or $ROBCl_2$) and retarded by Lewis bases (ether). For example, di-*n*-butyl chloroboronate showed no significant decomposition after 3 hr. at 100°C. when pure, but in the presence of 0.05 per cent ferric chloride, decomposition was almost instantaneous at 20°C. These results were interpreted in terms of the following mechanism, wherein A designates the Lewis acid or a second molecule of the chloroboronate:



(4)



(5)

$$[(RO)_2B]^+ \rightarrow R^+ + OBOR \xrightarrow[S_N1]{[ACl]^-} RCl + A \qquad (6)$$

The usual mechanism was considered to be reaction 4 with reaction 5, but if the group R was hindered with respect to "in-line" approach of the attacking reagent, then it was reaction 4 with reaction 6. The importance of steric as well as polar considerations was emphasized.

Diphenyl chloroboronate was unstable, undergoing disproportionation by reaction 3 (89); inability to decompose (reaction 1) was attributed to the general difficulty of nucleophilic substitution in the benzene ring. The *p*-nitrophenyl analog was considerably more stable (90).

The dialkyl chloroboronates are liquids; the two diaryl compounds are solids. All fume in air; this is due to rapid and quantitative hydrolysis, originally demonstrated for the methyl and ethyl chloroboronates (372),

$$ClB(OR)_2 + 3H_2O \rightarrow B(OH)_3 + 2ROH + 3HCl$$

Alcoholysis, likewise, is rapid (372), but with ethers there is no reaction (124, 372).

$$ClB(OR)_2 + ROH \rightarrow B(OR)_3 + HCl$$

Trimethylamine afforded a 1;1 complex (m.p. 34°C.) with dimethyl chloroboronate, which on heating disproportionated (376). With di-2-chloroethyl chloroboronate and pyridine, similar but no so clean-cut results were obtained (105).

$$2ClB(OCH_3)_2 + 2N(CH_3)_3 \rightarrow 2(1{:}1 \text{ complex}) \xrightarrow[100°C.]{4 \text{ hr.}} CH_3OBCl_2 \cdot N(CH_3)_3 + B(OCH_3)_3 + N(CH_3)_3$$

The reaction of chloroboronates with metallic sodium has already been discussed (Section II,A); that with boron trichloride will be mentioned later (Section IV,F,1),

H. BOROXOLES

1. *Introduction*

The organic boroxoles are compounds having the general formula $(BOX)_3$, where X is an alkyl, an aryl, or an alkoxyl group (these compounds, the metaborates, have, for convenience, already been discussed in Section II,H) or a substituted amino group. They are so called because they are structurally similar to the borazoles [derivatives of $(BH_2N)_3$], which were given this name in order to emphasize their similarity to aromatic compounds. The boroxoles have been shown to be six-membered ring compounds, with alternate boron and oxygen atoms. The most important group of compounds in this category is that of the boronic anhydrides, and these will therefore be considered separately,

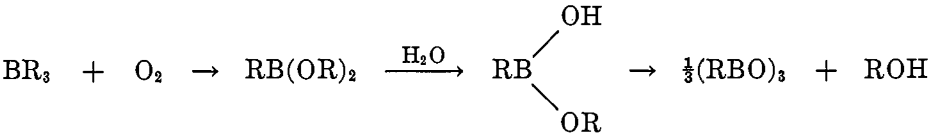
2. *Preparation of boronic anhydrides*

Phenylboronic anhydride, $(C_6H_5BO)_3$, was the first member of this class to be prepared by Michaelis and Becker in 1882 (240) either by allowing phenylboronic acid to stand in a desiccator for a considerable time or by heating it. A large number of boronic anhydrides have since been prepared; all of them are available by dehydration of the corresponding acids.

$$3RB(OH)_2 \rightarrow (RBO)_3 + 3H_2O$$

The dehydration is invariably carried out by one of the two above methods, As desiccating agents, concentrated sulfuric acid (320), phosphorus pentoxide (320), thionyl chloride (320), and calcium sulfate (for the methyl derivative only) (66) have been used.

Alkylboronic anhydrides (*n*-propyl, isobutyl, isoamyl) were originally obtained by the controlled oxidation of trialkylborons (190). Later it was considered that in this oxidation dialkyl alkylboronates were first formed and that hydrolysis of these gave the anhydrides (168).



$$BR_3 + O_2 \rightarrow RB(OR)_2 \xrightarrow{H_2O} RB\begin{matrix} OH \\ \\ OR \end{matrix} \rightarrow \tfrac{1}{3}(RBO)_3 + ROH$$

Such a hydrolysis had afforded β-napththylboronic anhydride from dimethyl β-naphthylboronate (241).

Methylboronic anhydride was prepared by heating boron trioxide and trimethylboron at 300–330°C. for 6 hr. (135), and also by the hydrolysis of hexamethylborazole with a limited amount of water (359).

3. *Physical properties and structure of boronic anhydrides*

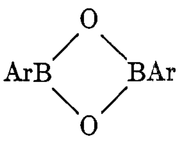
The first hints regarding the structures of the boroxoles were the molecular-weight measurements of Kinney and Pontz (181) on a number of arylboronic anhydrides, cryoscopically in nitrobenzene, which showed them to have molecu-

TABLE 10

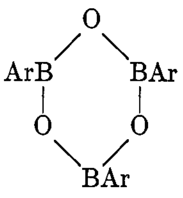
Physical constants of boronic anhydrides

R in $(RBO)_3$	n_D^{20}	d_4^{20}	Melting Point	Boiling Point	References
			°C.	°C.	
CH_3—			−38	79	(66, 135, 136, 361)
n-C_3H_7—					(191, 320)
n-C_4H_9—	1.4208			138/18 mm.	(40, 102, 145, 168, 226, 320)
i-C_4H_9—					(190, 320)
t-C_4H_9—				66-68/5 mm.	(169)
n-C_5H_{11}—					(226, 320)
i-C_5H_{11}—					(190)
n-C_6H_{13}—	1.4323	0.8876		149/5 mm.	(226, 320)
C_6H_{11}—					(226)
C_6H_5—			214–216		(38, 181, 191, 193, 240)
o-$CH_3C_6H_4$—			160–161		(241)
m-$CH_3C_6H_4$—			160–161.5		(199)
p-$CH_3C_3H_4$—			259–260		(181, 183, 199)
$C_6H_5CH_2$—			140		(387)
o-ClC_6H_4—			167–169		(35)
m-ClC_6H_4—			178–179		(181, 199)
p-ClC_6H_4—			261–262.5		(181, 199)
p-BrC_6H_4—					(19, 181, 183, 199)
			280		(183)
			301–302		(19)
p-$CH_3OC_6H_4$—			204–207		(193, 199)
m-$CH_3OC_6H_4$—			159		(183)
m-$C_2H_5OC_6H_4$—			152–153		(35)
p-$C_2H_3OC_6H_4$—			171		(35)
o-$C_2H_5OC_6H_4$—					(181)
o-$O_2NC_6H_4$—			280–281		((29)
m-$O_2NC_6H_4$—			285–286		(199)
m-$C_2H_5OOCC_6H_4$—			136–138		(199)
p-$C_2H_5OOCC_6H_4$—			198–200		(199)
o-$C_6H_5C_6H_4$—			195		(387)
2,4-$(CH_3)_2C_6H_3$—			202		(238)
3,4-$(CH_3)_2C_6H_3$—			226		(238)
2,5-$(CH_3)_2C_6H_3$—			176		(238)
p-$C_6H_5OC_6H_4$—					(181)
α-$C_{10}H_7$—			207		(181, 183, 241)
β-$C_{10}H_7$—			266		(241)

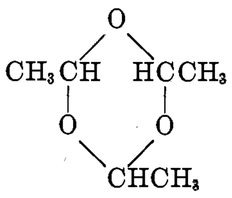
lar weights corresponding to two to three times the equivalent weights. It was suggested that the anhydrides were mixtures of XXI and XXII, Evidence of later workers has pointed exclusively to structure XXII. The trimeric nature of the alkylboronic anhydrides (n-propyl, n-butyl, isobutyl, n-amyl, n-hexyl) was demonstrated by determining their molecular weights; the similarity in boiling points and chemical properties between these compounds and paraldehyde (XXIII) and its homologs was stressed (320).



XXI



XXII



XXIII

The molecular weight (66, 135) of the methyl member corresponded to a trimeric formula, as did the Trouton constant (66) also. The results obtained from the electron diffraction measurements on methylboronic anhydride vapor were concordant with a planar six-membered ring with alternating boron and oxygen atoms, the methyl groups being bonded to the boron atoms and in the plane of the ring (17). Bond distances and bond angles were determined. Raman spectra investigation of this anhydride has confirmed its ring structure (136). The heats of vaporization (66) of methylboronic anhydride and of solution in water (102) of *n*-butylboronic anhydride have been measured. Physical constants are shown in table 10.

4. Chemical properties of boronic anhydrides

The oxidation of *n*-butylboronic anhydride (145) has already been mentioned (Section II,H); it is inhibited by phenyl-β-naphthylamine, but not by hydroquinone. There is no evidence for the formation of a peroxidic substance.

The anhydride properties are demonstrated by the ease of hydrolysis to the corresponding acid (66, 183, 361) and by the alcoholysis (Section III,C,6).

$$(RBO)_3 + 3H_2O \rightarrow 3RB(OH)_2$$

Methylboronic anhydride formed both a 1:1 and a 1:2 complex with ammonia, $(CH_3BO)_3 \cdot NH_3$ and $(CH_3BO)_3 \cdot 2NH_3$, and also a 1:1 complex (m.p. 67°C.) with trimethylamine (66).

Aluminum chloride reacted with *n*-butylboronic anhydride to give a mixture of di-*n*-butylboron chloride and *n*-butylboron dichloride (226). The reactions of anhydrides with boron trifluoride (Section V,H,4) and with organometallic compounds (Section V,B) will be discussed later.

5. Other boroxoles

Metaboranilide was prepared by heating orthoboric acid with aniline and zinc chloride (83).

$$B(OH)_3 + C_6H_5NH_2 \rightarrow C_6H_5NHBO + 2H_2O$$

A number of its salts were also prepared. No physical measurements were made, but it seems possible that metaboranilide is trimeric and hence a boroxole.

Two other boroxoles, $[(CH_3)_2NBO]_3$ and $(CH_3OBO)_3$ (see Section II,H), were prepared by heating boron trioxide with either tris(dimethylamino)boron or trimethyl borate, respectively (135).

$$B_2O_3 + B[N(CH_3)_2]_3 \rightarrow [(CH_3)_2NBO]_3$$

$$B_2O_3 + B(OCH_3)_3 \rightarrow (CH_3OBO)_3$$

Molecular-weight [Dumas method (135)] and Raman spectra investigations (136) on these methylboroxoles supported the ring structures. *B,B′,B″*-Tris(dimethylamino)boroxole was a solid, m.p. 64°C., b.p. 221°C./752 mm.; its heat of vaporization was determined (135). *B,B′,B″*-Trimethoxyboroxole decomposed at 170–220°C.

By heating metaboranilide with an excess of sulfur for 10 min. metathioboranilide, C_6H_5NHBS, m.p. 109–110°C., was obtained (83). This may prove to be trimeric and hence a borsulfole.

I. THIO COMPOUNDS

Apart from the borsulfoles, only two sulfur compounds have been prepared which might properly be described as sulfur analogs of dihydroxyborine derivatives.

Di-*n*-dodecyl chlorovinylthioboronate was obtained by heating *n*-dodecanethiol and dimethyl chlorovinylboronate at 100°C. (209),

$$CHCl{=}CHB(OCH_3)_2 + 2C_{12}H_{25}SH \rightarrow CHCl{=}CHB(SC_{12}H_{25})_2 + 2CH_3OH$$

The existence of dimethyl bromothioboronate, $BrB(SCH_3)_2$, has been postulated, but it was too unstable to be characterized (140). It was believed to be an intermediate in the preparation of trimethyl thioborate by the interaction of boron tribromide and methyl mercaptan (Section II,I).

IV, DERIVATIVES OF $HOBH_2$ AND H_2BOBH_2

A. INTRODUCTION

Compounds in this section have on the whole had less attention devoted to them than those described so far. In the case of the boronous acids, R_2BOH, and boronous esters, R_2BOR', this may be due to their considerable ease of oxidation to boronic derivatives. The boronous acids, and particularly those of the aliphatic series, are dehydrated very readily, affording anhydrides, $(R_2B)_2O$.

Unlike the dialkoxyborines (Section III,B), the alkoxyborines, $ROBH_2$, are not well established, only polymeric compounds being known. Thus, a polymeric methoxyborine, $(CH_3OBH_2)_x$, a white solid, was formed by the interaction of trimethyl borate and diborane, but it readily disproportionated (73). A similar polymeric sulfur compound, $(CH_3SBH_2)_x$, m.p. 65–80°C., has been prepared from an unstable methylmercaptan 1:1 complex of borine.

$$xCH_3SH \cdot BH_3 \rightarrow (CH_3SBH_2)_x + xH_2$$

This compound hydrolyzed with water to give boric acid, methyl mercaptan, and hydrogen; pyrolysis afforded trimethyl thioborate, hydrogen, and a mixture of boron hydrides (75).

More stable polymers of the type $H(CHRCH_2O)_nBH_2$ (where $n = 6$ or 8) have been prepared in conjunction with dialkoxyborines (ethyl, isopropyl) by the interaction of diborane and epoxides (ethylene or propylene oxides) at −80°C. (326).

B. THE BORONOUS ACIDS

1. *Preparation*

The boronous acids have been prepared essentially by hydrolysis methods, using the corresponding halides, esters, or borines.

Michaelis and Behrens (241) in 1894 obtained diphenylboronous acid, which was the first boronous acid to be prepared, by the hydrolysis of diphenylboron chloride, which in turn was obtained in low yield by the interaction of diphenylmercury and phenylboron dichloride.

$$Hg(C_6H_5)_2 + C_6H_5BCl_2 \rightarrow (C_6H_5)_2BCl \xrightarrow{H_2O} (C_6H_5)_2BOH$$

Better results were obtained when boron tribromide was used together with two equivalents of diphenylmercury (244), *p*-Tolylboronous acid could not be obtained, as it was readily dehydrated to give the anhydride. Di-*n*-propylboronous acid was obtained by the hydrolysis of di-*n*-propylboron iodide (220), di-*n*-butylboronous acid by the hydrolysis of the bromide (166), and di-2-chlorovinylboronous acid by the hydrolysis of the chloride (34).

A number of diarylboronous acids were prepared by the addition of 1 mole of triisobutyl borate in ethereal solution to 2 moles of arylmagnesium bromide at room temperature (183, 236, 237) and hydrolysis of the products (isobutyl diarylboronites), which were not isolated.

$$2ArMgBr + B(OC_4H_9\text{-}i)_3 \rightarrow Ar_2BOC_4H_9\text{-}i \xrightarrow{H_2O} Ar_2BOH$$

This method has been repeated ($Ar = C_6H_5$) in all essentials, except that the order of addition was reversed; only 23 per cent of isobutyl diphenylboronite (isolated as an ammonia complex) was obtained, although the yield was improved to 49 per cent when the addition was carried out at −60°C. and tri-*n*-butyl borate was used (210). In this investigation the ester was required *per se* and not for the preparation of the boronous acid. The hydrolysis of boronous esters obtained by various methods (Section IV,D,1–4) has been used for the preparation of both diarylboronous (210, 213) and dialkylboronous (232) acids and also for a mixed alkylarylboronous acid, $C_6H_5(CH_3)BOH$ (337).

The hydrolysis of suitable methyldiboranes (di-, tri-, and tetra-), such that two methyl groups were attached to the boron atom, gave dimethylboronous acid (309), and similar postulates have been made regarding their ethyl and *n*-propyl analogs (308). Bis(dimethylamino)boronous acid, $[(CH_3)_2N]_2BOH$, was obtained by the hydrolysis of bis(dimethylamino)borine, $[(CH_3)_2N]_2BH$, but no details about the compound were given (351).

2. Properties

The only physical properties of the boronous acids which have so far been determined are the characterizing constants, which are shown in table 11. The boiling points which have been recorded may actually be those of the anhydrides.

Diphenylboronous acid was said not to form salts with alkalis (241). Boronous acids may be esterified to afford the corresponding esters (Section IV,D,4) and are easily dehydrated to give anhydrides (Section IV,C,1).

Chlorine, bromine, or hydrogen peroxide quantitatively oxidized several di-

TABLE 11

Physical constants of boronous acids

R in R_2BOH	Melting Point	Boiling Point	d_4^{20}	Vapor Pressure	References
	°C.	*°C.*		*mm.*	
CH_3—				36 (0°C.)	(66, 86, 309)
C_2H_5—	−51 to −48	35–37/75 mm.	0.7921		(232, 235, 308)
n-C_3H_7—					(220, 308)
CHCl═CH—		66–68/3 mm.			(34)
C_6H_5—					(183, 236, 237, 238, 241, 244)
	264–267				(237)
	57.5	150–155/20 mm.			(183)
		215–235/17 mm.			(241)
p-ClC_6H_4—	75				(236, 237)
p-BrC_6H_4—					(183, 213)
	113				(183)
	82–84				(213)
p-$CH_3OC_6H_4$—	107				(183)
p-$C_6H_5C_6H_4$—	>300				(236, 237)
2-CH_3-5-ClC_6H_3—	81				(236, 237)
β-$C_{10}H_7$—	172				(183)
α-$C_{10}H_7$—	105–106				(210)
C_6H_5—, α-$C_{10}H_7$—					(210)

arylboronous acids, first to boronic acids and subsequently to orthoboric acid (236, 237).

$$Ar_2BOH + Y_2 + H_2O \rightarrow ArB(OH)_2 + ArY + HY$$

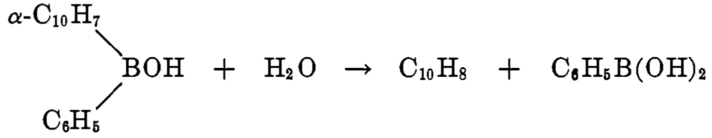
$$ArB(OH)_2 + Y_2 + H_2O \rightarrow B(OH)_3 + ArY + HY$$

Y = Cl, Br, or OH.

Bromination of α-naphthylphenylboronous acid in aqueous acetic acid gave α-bromonaphthalene, 1,4-dibromonaphthalene, and bromobenzene (210).

When di-α-naphthylboronous acid was heated for 6 hr. at 120–130°C., naphthalene was obtained as a sublimate and a residue of α-naphthylboronic anhydride remained (210). Similar cleavage was effected by heating the acid with an aqueous ethanolic solution of 2-(dimethylamino)ethanol (210).

$$3(\alpha\text{-}C_{10}H_7)_2BOH \rightarrow 3C_{10}H_8 + (\alpha\text{-}C_{10}H_7BO)_3$$



$$(\alpha\text{-}C_{10}H_7)(C_6H_5)BOH + H_2O \rightarrow C_{10}H_8 + C_6H_5B(OH)_2$$

C. THE BORONOUS ANHYDRIDES

1. Preparation

The methods for obtaining boronous anhydrides have invariably depended upon the dehydration of the appropriate acid as a final step. In many of the preparations the acids were not actually isolated; hence these methods are described fully, As a result of interaction between *p*-tolylmercury and boron tribromide and subsequent hydrolysis, Michaelis and Richter (244) obtained di-*p*-tolylboronous anhydride. A number of other diarylboronous acids were said to form anhydrides in the presence of dehydrating agents (237).

$$2Ar_2BOH \rightarrow (Ar_2B)_2O + H_2O$$

Attempts to distil diethylboronous acid afforded the anhydride (235). Dimethylboronous acid was converted into its anhydride by the action of phosphorus pentoxide (66).

When methyl diallylboronite was hydrolyzed and the product repeatedly distilled, diallylboronous anhydride was obtained (289). The same compound was also produced by repeated distillation of the product obtained from boron trifluoride (or its diethyl etherate) and allylmagnesium bromide, the product being first decomposed by ammonium chloride.

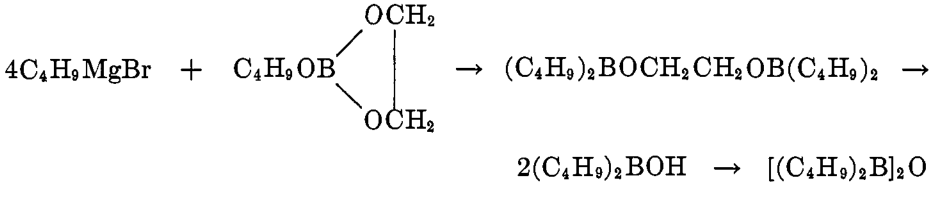
$$\begin{tikzcd}
BF_3 + 2C_3H_5MgBr \arrow[r] & {[(C_3H_5)_2BF]} \arrow[dr] & & \\
 & & {[(C_3H_5)_2BOH]} \arrow[r] & \tfrac{1}{2}[(C_3H_5)_2B]_2O \\
 & (C_3H_5)_2BOCH_3 \arrow[ur] & &
\end{tikzcd}$$

Tri-*n*-butylboron and aqueous hydrobromic acid gave a quantitative yield of di-*n*-butylboronous anhydride (166),

$$(n\text{-}C_4H_9)_3B \rightarrow [(n\text{-}C_4H_9)_2BBr] \rightarrow [(n\text{-}C_4H_9)_2BOH] \rightarrow \tfrac{1}{2}[(n\text{-}C_4H_9)_2B]_2O$$

When the hydrolysis products obtained from 2-aminoethyl diarylboronites were dried, the corresponding anhydrides were produced (213, 214).

By the action of 2 moles of *n*-butylmagnesium bromide on 1 mole of a chelate orthoborate Letsinger and Skoog (212) obtained a novel type of ester, $(C_4H_9)_2BOCH_2CH_2OB(C_4H_9)_2$, b.p. 133–144°C./1 mm., $n_D^{27°} = 1.4340$, $d_{4°}^{25°} = 0.8266$ (an *n*-amyl analog had the following properties: b.p. 147°C./0.48 mm., $n_D^{25°} = 1.4378$, $d_{4°}^{25°} = 0.8276$), which on hydrolysis and subsequent distillation afforded di-*n*-butylboronous anhydride.



$$4C_4H_9MgBr + C_4H_9OB\!\left\langle\begin{matrix}OCH_2\\ |\\ OCH_2\end{matrix}\right. \rightarrow (C_4H_9)_2BOCH_2CH_2OB(C_4H_9)_2 \rightarrow 2(C_4H_9)_2BOH \rightarrow [(C_4H_9)_2B]_2O$$

In a similar manner, the addition of 1 mole of tri-*n*-butyl borate to 2 moles of an arylmagnesium bromide (C_6H_5—, *p*-$CH_3C_6H_4$—) and subsequent hydrolysis afforded the appropriate diarylboronous anhydride (259). Diphenylboronous anhydride was also obtained, together with biphenyl, by the hydrolysis of sodium tetraphenylboron (256).

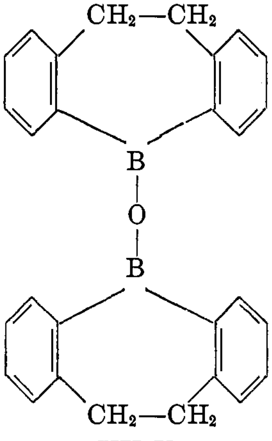
TABLE 12

Physical constants of boronous anhydrides

R in $(R_2B)_2O$	n_D^{25}	d_4^{25}	Melting Point	Boiling Point	References
			°C.	°C.	
CH_3—				21	(66, 74)
C_2H_5—				142–144	(235)
n-C_4H_9—	1.4254	0.7933		136/12 mm.	(166, 212)
CH_2=$CHCH_2$—				118–120/12 mm.	(289)
C_6H_5—				210–213/1 mm.	(213, 256–260)
			116–118		(256)
			104–105		(213)
p-$CH_3C_6H_4$—			105–106		(259)

2. Properties

Of the physical properties, only the characterizing constants are available and these are shown in table 12. The anhydride (XXIV) melted at 131–136°C, (214); when this was heated with either palladium, or zinc chloride and water, bibenzyl was obtained.



XXIV

Diphenylboronous anhydride has been used for various analytical purposes (257, 258, 260).

Reactions of anhydrides with boron trifluoride (Section V,H,4) and with alcohols (Section IV,D,4) are discussed later.

D. PREPARATION OF BORONOUS ESTERS

1. Introduction

The three principal methods for obtaining boronous esters utilize (*1*) trialkyl- or triarylborons, (*2*) the interaction of orthoborates or boronic esters with organometallic compounds, or (*3*) the esterification of boronous acids, anhydrides, or dialkylboron chlorides. In this last method the intermediates were in some cases not isolated, but were prepared *in situ*.

Other methods which have produced boronous esters are the methanolysis of $H_2PB(CH_3)_2$ (74), the action of hydrogen chloride upon the 1:1 complex between methanol and (methylamino)dimethylboron (86), and preparation from the 1:1 complex between ammonia and isobutyl diphenylboronite, either by addition of ethanolamine and distillation of the formed 1-butanol as an azeotrope with toluene, or by adding ethanolamine to an aqueous ethanolic solution of the complex to give 2-aminoethyl diphenylboronite (213).

$$H_2PB(CH_3)_2 + CH_3OH \rightarrow (CH_3)_2BOCH_3 + PH_3$$

$$(CH_3)_2NB(CH_3)_2 \cdot CH_3OH + HCl \rightarrow (CH_3)_2BOCH_3 + (CH_3)_2NH \cdot HCl$$

$$(C_6H_5)_2BOC_4H_9(i) \cdot NH_3 + H_2NCH_2CH_2OH \rightarrow (C_6H_5)_2BOCH_2CH_2NH_2 + n\text{-}C_4H_9OH + NH_3$$

2. Trialkylborons and triarylborons

Meerwein, Hinz, Majert, and Sönke (232) were the first to prepare boronous esters, by reacting triethylboron with certain aldehydes (CCl_3CHO, C_6H_5CHO, p-ClC_6H_4CHO) or with the corresponding alcohols.

$$B(C_2H_5)_3 + RCHO \rightarrow (C_2H_5)_2BOCH_2R + C_2H_4$$

$$B(C_2H_5)_3 + RCH_2OH \rightarrow (C_2H_5)_2BOCH_2R + C_2H_6$$

With bromal the reaction was more complex, both 2,2-dibromovinyl diethylboronite and 2,2,2-tribromoethyl diethylboronite being obtained (232).

The 2-aminoethyl esters of both diphenylboronous and di-α-naphthylboronous acids were prepared in an analogous manner, from the appropriate triarylboron and ethanolamine, by heating in boiling benzene (285), However, with methanol and the triarylboron the reaction was more complex; the α-naphthyl compound afforded naphthalene and trimethyl borate, whilst with triphenylboron and a large excess of methanol phenyl diphenylboronite, $(C_6H_5)_2BOC_6H_5$, was isolated as an ammonia complex,

Triethylboron reacted with carboxylic acids (acetic, *p*-chlorobenzoic) to give acyl diethylboronites (235).

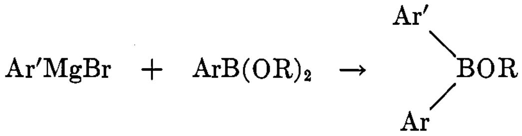
$$B(C_2H_5)_3 + RCOOH \rightarrow (C_2H_5)_2BOOCR + C_2H_6$$

Tri-*n*-butylboron reacted with oxygen in the presence of moisture to give *n*-butyl di-*n*-butylboronite (168), and with *tert*-butyl hypochlorite at −80°C. to give a mixture of products, including *n*-butyl dibutenylboronite (166).

3. Organometallic compounds

The addition of 2 moles of allylmagnesium bromide to 1 mole of trimethyl borate afforded methyl diallylboronite (289); by similar reaction *n*-butyl di-*n*-octylboronite was obtained (38). The preparation of butyl esters of diphenylboronous acid by use of the Grignard reagent has already been mentioned (Section IV,B,1).

The reaction of arylmagnesium bromides with dialkyl arylboronates has been used for the preparation of mixed boronites (210, 215, 336, 337).

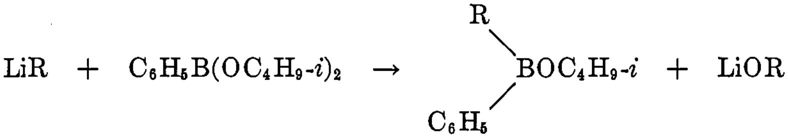


$$\mathrm{Ar'MgBr} + \mathrm{ArB(OR)_2} \rightarrow \underset{\mathrm{Ar}}{\overset{\mathrm{Ar'}}{\diagdown\!\!\diagup}}\mathrm{BOR}$$

When orthoborates (allyl or methallyl) and diethylzinc were reacted in tetralin as solvent, esters of diethylboronous acid were obtained (289).

$$\mathrm{Zn(C_2H_5)_2 + B(OR)_3 \rightarrow (C_2H_5)_2BOR + Zn(OR)_2}$$

n-Octyllithium and tri-*n*-butyl borate gave *n*-butyl di-*n*-octylboronite (38). Both *n*-butyl- and *n*-propyllithium with diisobutyl phenylboronate gave mixed boronites (246).



$$\mathrm{LiR} + \mathrm{C_6H_5B(OC_4H_9\text{-}\mathit{i})_2} \rightarrow \underset{\mathrm{C_6H_5}}{\overset{\mathrm{R}}{\diagdown\!\!\diagup}}\mathrm{BOC_4H_9\text{-}\mathit{i}} + \mathrm{LiOR}$$

4. Esterification methods

In those experiments where an intermediate ester or acid was not isolated, the entire preparation is described.

Heating 1-butanol with di-*n*-butylboronous anhydride yielded the ester (166).

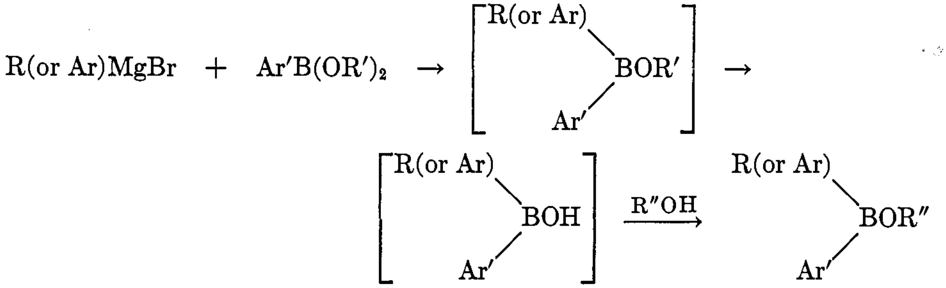
$$\mathrm{[(C_4H_9)_2B]_2O + 2C_4H_9OH \rightarrow 2(C_4H_9)_2BOC_4H_9 + H_2O}$$

Addition of aqueous ethanolic ethanolamine to di-α-naphthylboronous acid precipitated the 2-aminoethyl ester (210). Similarly, the addition of 2-amino-2-methyl-1-propanol to an aqueous ethanolic solution of the mixed α-naphthylphenylboronous acid, which was itself obtained by hydrolysis of the 2-aminoethyl ester with a concentrated ethereal solution of hydrogen chloride, gave the appropriate ester.

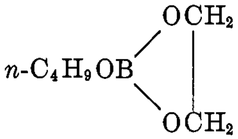
2-Aminoethyl di-α-naphthylboronite and also the corresponding phenyl compound were prepared from the appropriate diarylboronous acid obtained *in situ* from the Grignard reagent (2 moles) which was added to tri-*n*-butyl borate (1 mole) at about −60°C., whereupon the product was hydrolyzed with dilute hydrochloric acid and converted to the 2-aminoethyl ester by addition of ethanolic ethanolamine (210). Likewise, *o*,*o*′-dibenzyldilithium and tri-*n*-butyl borate gave a product which on hydrolysis and esterification afforded the ester (XXVI) (214). Mixed *n*-butyl boronites were prepared similarly, using di-*n*-butyl phenyl-(or α-naphthyl)boronate and α-naphthyl(or phenyl)magnesium bromide (210, 215). Mixed *n*-propyl diarylboronites were also prepared from mixed diarylboronous acids, obtained *in situ*, by esterification with 1-propanol, the water produced being removed as an azeotrope with excess of the alcohol (336). This same method of esterification was employed for preparing alkyl (*n*-propyl, *n*-

butyl) esters of mixed phenylalkylboronous acids, which in turn were prepared from dialkyl phenylboronates and the appropriate alkylmagnesium bromide (337).

$$2\text{ArMgBr} + \text{B(OR)}_3 \rightarrow [\text{Ar}_2\text{BOR}] \rightarrow [\text{Ar}_2\text{BOH}] \xrightarrow{\text{R'OH}} \text{Ar}_2\text{BOR'}$$



A modification of this process for 2-aminoethyl di(*p*-bromophenyl)boronite employed a chelated orthoborate



and the Grignard reagent; only a small yield of the ester was obtained (213),

TABLE 13

Physical constants of simple boronous esters

R' in $R_2'BOR$	R in $R_2'BOR$	Melting Point	Boiling Point	References
		°C.	°C.	
CH_3—	CH_3—		21	(74, 86)
C_2H_5—	CCl_3CH_2—		78-79/12 mm.	(232)
C_2H_5—	CBr_3CH_2—		117-119/12 mm.	(232)
C_2H_5—	$Br_2C{=}CH$—		98-99/11 mm.	(232)
C_2H_5—	Allyl		130-140	(289)
C_2H_5—	Methallyl		52-54/17 mm.	(289)
C_2H_5—	$C_6H_5CH_2$—		114-115/16 mm.	(232)
C_2H_5—	p-ClC_6H_4—		141.5-142/16 mm.	(232)
C_2H_5—	CH_3CO—	86-87		(235)
C_2H_5—	o-ClC_6H_4CO—	50-52	96-97/1 mm.	(235)
n-C_4H_9—	n-C_4H_9—		120-121/24 mm.	(166, 168)
$C_2H_5CH{=}CH$—	n-C_4H_9—		70-71/5 mm.	(166)
$ClCH{=}CH$—	C_2H_5—		74/8 mm.	(34)
Allyl	C_2H_5—		115-120	(289)
Allyl	CH_3—		82/15 mm.	(289)
CH_2ClCH_2—	Lauryl			(152)
$Cl(CH_2)_6$—	Cyclohexyl			(152)
n-C_8H_{17}—*	n-C_4H_9—		84/0.005 mm.	(38)
C_6H_5—	$H_2NCH_2CH_2$—	190-192		(210, 213, 285)
p-BrC_6H_4—	$H_2NCH_2CH_2$—	236-237		(213)
α-$C_{10}H_7$—	$H_2NCH_2CH_2$—	205-206		(210, 285)
α-$C_{10}H_7$—	$H_2N(CH_3)_2CCH_2$—	208-210		(210)

* $n_D^{20} = 1.4312$; $d_4^{20} = 0.8036$.

TABLE 14

Physical constants of mixed boronous esters

R' in R'R"BOR	R" in R'R"BOR	R in R'R"BOR	Boiling Point	Melting Point	n_D^{25}	d_4^{25}	References
			°C.	°C.			
CH_3—	C_6H_5—	n-C_3H_7—	87–89/9 mm.		1.4880	0.8985	(337)
C_2H_5—	C_6H_5—	n-C_4H_9—	110–111/9 mm.		1.4864	0.8940	(337)
n-C_3H_7—	C_6H_5—	i-C_4H_9—	86–87/3 mm.			0.8943*	(246)
n-C_4H_9—	C_6H_5—	i-C_4H_9—	96–97/3 mm.			0.8894*	(246)
C_6H_5—	o-$CH_3C_6H_4$—	n-C_3H_7—	156–159/9 mm.		1.5440	0.9748	(336)
C_6H_5—	α-$C_{10}H_7$—	$H_2NCH_2CH_2$—		228–229			(210, 215)
C_6H_5—	α-$C_{10}H_7$—	$(CH_3)_2(NH_2)CCH_2$—		199–200			(210)
o-$CH_3C_6H_4$—	m-$CH_3C_6H_4$—	n-C_6H_7—	173–175/11 mm.		1.5407	0.9646	(336)
o-$CH_3C_6H_4$—	p-$CH_3C_6H_4$—	n-C_3H_7—	173–175/10 mm.		1.5420	0.9648	(336)
o-$CH_3C_6H_4$—	p-ClC_6H_4—	n-C_3H_7—	176–177/10 mm.		1.5522		(336)

* At 20°C.

Ethanolysis of bis(2-chlorovinyl)boron chloride afforded the ethyl ester (34),

$$(CH_2{=}CH)_2BCl + C_2H_5OH \rightarrow (CH_2{=}CH)_2BOC_2H_5 + HCl$$

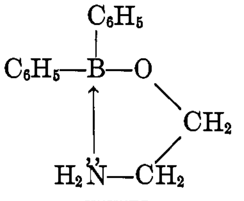
E. PROPERTIES OF BORONOUS ESTERS

1. Physical properties

The values for the latent heat of vaporization and Trouton's constant for methyl dimethylboronite have been obtained (74, 86). The molecular weight of the same ester showed it to be monomeric (74). Diphenylboronous acid was also shown to be monomeric (cryoscopic in camphor) (213). The only other physical data available are the characterizing constants shown in tables 13 and 14.

2. Chemical properties

The comparative ease of oxidation of boronous esters has necessitated operations involving their preparation or reactions to be carried out under nitrogen. The hydrolysis of boronous esters has already been mentioned (Section IV,B,1). The relative stability of 2-aminoethyl diphenylboronite towards both oxidation and hydrolysis (it can be recrystallized from water) has led to the suggestion that its structure is as shown in formula XXV (213).



XXV

Such chelation has also been suggested to account for the inability of both this ester and its α-naphthyl analog to undergo alcoholysis reactions (285).

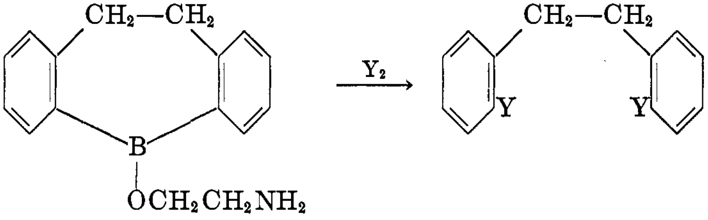
2-Aminoethyl α-naphthylphenylboronite reacted with ethanolic hydrogen peroxide and with aqueous zinc chloride to give α-naphthol and naphthalene, respectively (210).

Methyl dimethylboronite formed a 1:1 complex (m.p. 51–52°C.) with dimethylamine (86). Similarly, isobutyl diphenylboronite formed a 1;1 complex (m.p. 64–67°C.) with ammonia, which slowly evolved ammonia (213, 215). Phenyl diphenylboronite also formed such a complex with ammonia (285). n-Propyl mixed diarylboronites were not isolated directly when prepared from an arylmagnesium bromide and a propyl arylboronate, because the alkoxymagnesium bromide which formed was said to give a 1:1 complex with the boronite (336).

$$\mathrm{ArAr'BOR + ROMgBr \rightarrow [ArAr'B(OR)_2]^{-}MgBr^{+}}$$

The reaction of bromal with certain diethylboronites has already been described (Section III,C,5).

The structure of a cyclic 2-aminoethyl boronite (XXVI) was verified by its reactions with bromine and hydrogen peroxide (214).



XXVI

Y = Br or OH.

F. THE DIHALOGENOBORONITES

1. Preparation

Methyl difluoroboronite, CH_3OBF_2, was first prepared by Gasselin (118) by methods similar to those used for dimethyl fluoroboronate (Section III,G,1).

$$BF_3 + NaOCH_3 \rightarrow CH_3OBF_2 + NaF$$

$$2BF_3 + B(OCH_3)_3 \rightarrow 3CH_3OBF_2$$

The sodium methoxide reaction has not been confirmed (234), but the other method was successfully repeated (138). The only other simple difluoroboronite to have been characterized is the n-butyl compound, which was prepared by the action of boron trifluoride on either tri-n-butyl borate or the borate–1-butanol–boron trifluoride complex (206).

$$2BF_3\cdot B(OC_4H_9)_3\cdot C_4H_9OH + 3BF_3 \rightarrow 6C_4H_9OBF_2 + BF_3\cdot 2C_4H_9OH$$

It has been suggested that trialkyl borates initially form 1:2 complexes with the trifluoride, which then disproportionate to difluoroboronites (229). With unsubstituted alkyl orthoborates these complexes were said to be extremely unstable, but the tri-2-chloroethyl borate complex was stable. No evidence for these suggestions has appeared.

$$B(OR)_3\cdot 2BF_3 \rightleftharpoons 3ROBF_2$$

The action of boron trifluoride on benzene solutions of diketones (acetylacetone, benzoylacetone, and dibenzoylmethane) afforded chelated difluoroboronites (XXIX) (249). It is interesting to note that the corresponding boron trichloride reactions (and also that with ethyl acetoacetate) were different, in that compounds of uncertain structure were produced [e.g., with acetylacetone the product was thought to be either $(CH_3COCHCOCH_3)_2BCl$ or $(CH_3COCHCOCH_3)_2BCl\cdot 2HCl$] (98, 288).

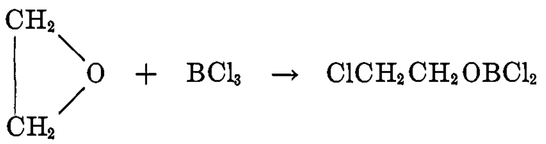
The preparation of both *n*-butyl difluoroboronite and dichloroboronite from boronic esters is discussed later (Section IV,G).

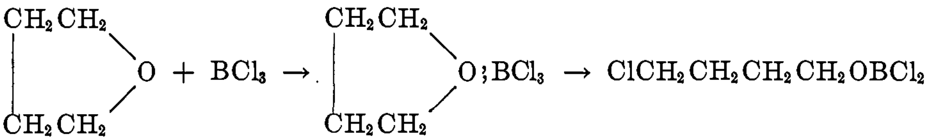
The first dichloroboronite to be prepared was the ethyl homolog by Ramser and Wiberg (277), by gently warming boron trichloride diethyl etherate, formed by the interaction of boron trichloride and diethyl ether in equimolecular proportions, in a high-vacuum apparatus at low temperature; methyl dichloroboronite was similarly prepared (373).

$$R_2O + BCl_3 \rightarrow R_2O\cdot BCl_3 \rightarrow ROBCl_2 + RCl$$

The method has since been further investigated. Diphenyl ether was exceptional in that it did not react with boron trichloride (89). For a wide range of mixed ethers the method was successful, but the intermediate complexes, except in *O*-alkylphenols (124), could not be isolated, the overall reaction being quantitatively complete at low temperature. Moreover in mixed ethers of the formula ROR′, pure RCl and $R'OBCl_2$ were obtained and not mixtures of all four possible components, the groups R and R′ being such that the former was the more electron-releasing (122, 124).

Ethylene oxide and boron trichloride gave 2-chloroethyl dichloroboronite as the sole product at −80°C., but with tetrahydrofuran heating was required to decompose the fairly stable 1:1 complex (105).





Earlier results had indicated that 1;1 coordination complexes were formed in both reactions (and also with propylene oxide and tetrahydropyran), which on heating reversibly dissociated in the former instance and irreversibly in the latter to give an unsaturated alcohol and boron trichloride, which could then react further (144).

Methyl and ethyl dichloroboronites were prepared in quantitative yield by reacting the alcohols with boron trichloride in equimolecular proportions at −80°C. in a high-vacuum apparatus (372).

$$ROH + BCl_3 \rightarrow ROBCl_2 + HCl$$

Even more convenient was the mutual replacement reaction between 2 moles of boron trichloride and 1 mole of trimethyl borate, which also gave a quantitative yield (370).

$$(CH_3O)_3B + 2BCl_3 \rightarrow 3CH_3OBCl_2$$

Both the alcohol and the borate methods have been investigated further for the preparation of various types of alkyl and aryl dichloroboronites (89, 90, 105, 123, 126).

Alkyl dichloroboronites were also obtained by the mutual replacement reaction between boron trichloride and dialkyl chloroboronates (126).

$$BCl_3 + ClB(OR)_2 \rightarrow 2ROBCl_2$$

Owing to the difficulty of accurately weighing boron trichloride, probably the most convenient method is the borate–boron trichloride process, employing a slight excess of the latter, the excess being easily removed under reduced pressure (126). *tert*-Alkyl dichloroboronites could not be obtained, and the *sec*-alkyl compounds were unstable at room temperature (Section IV,F,3).

Carbalkoxyalkyl dichloroboronites could not be obtained by any of the above methods; this was probably due to carbalkoxy fission (114). This view received support from the observation that carboxylic esters ($CH_3COOC_2H_5$, $CH_3COOC_6H_5$) reacted with boron trichloride to form 1:1 complexes, which decomposed on heating and afforded dichloroboronites; this, however, is not a suitable method for preparing dichloroboronites, because the heating required to decompose the complexes also causes appreciable decomposition of the dichloroboronites.

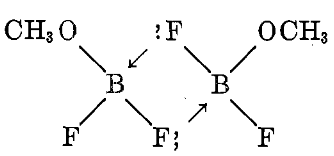
$$ROCOCH_3 + BCl_3 \rightarrow [ROCOCH_3 \cdot BCl_3] \rightarrow CH_3COCl + [ROBCl_2]$$

Neither dibromo- nor diiodoboronites have as yet been prepared.

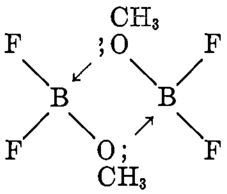
2. Physical properties

Raman spectra investigations (138) on methyl difluoroboronite confirm the earlier statement (4), based on parachor measurements, that it is dimeric in the liquid state; in the gas phase it is unimolecular (138). Structures XXVII (4) and XXVIII (138) have been proposed. The evidence for the latter is much stronger.

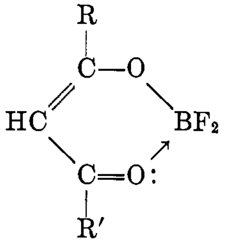
n-Butyl difluoroboronite was also bimolecular (cryoscopic in cyclohexane) (206). The melting points of the chelated difluoroboronites are shown below formula XXIX; these compounds were all unimolecular (249).



XXVII



XXVIII



XXIX

$R = CH_3 = R'$; m.p. 43°C.
$R = C_6H_5 = R'$; m.p. 191°C.
$R = CH_3, R' = C_6H_5$; m.p. 155°C,

Dimethyl and diethyl chloroboronites were shown to be unimolecular (372), a result confirmed by calculation of their Trouton constants. The heat of hydrolysis of ethyl dichloroboronite was measured as -158.3 ± 1.2 kcal./mole, a value which was 4.8 kcal./mole greater than expected from the bond energies for B—Cl and B—OC_2H_5 bonds in boron trichloride and triethyl borate, respectively (317).

Available physical constants are shown in table 15.

3. Chemical properties

The difluoroboronite (XXIX: $R = CH_3 = R'$) obtained from acetylacetone hydrolyzed in moist air; hydrogen fluoride was evolved and acetylacetone was recovered (249).

TABLE 15

Physical constants of dihalogenoboronites

R in $ROBX_2$	X in $ROBX_2$	Melting Point	Boiling Point	n_D^{20}	d_4^{20}	References
		°C.	°C.			
CH_3—	F	41.9	85.2		1.417 (35.4°C.)	(4, 118, 138, 234)
n-C_4H_9—	F		43/11 mm.	1.3858 (22°C.)	1.112	(206)
CH_3—	Cl	−15	58			(370, 372, 373)
C_2H_5—	Cl		77.9			(124, 277, 372, 373)
n-C_3H_7—	Cl			1.4094	1.138	(126, 207)
n-C_4H_9—	Cl		42/20 mm.	1.4162	1.079	(123, 124, 126, 204, 207)
i-C_4H_9—	Cl		34/20 mm.	1.4088	1.047	(123, 124, 126, 207)
$(CH_3)_3CCH_2$—	Cl			1.4097	1.032	(126)
n-C_8H_{17}—	Cl			1.4315	1.015	(126, 207)
$ClCH_2CH_2$—	Cl			1.4432	1.358 (18°C.)	(105)
$Cl(CH_2)_4$—	Cl			1.4522	1.254	(105)
C_6H_5—	Cl					(89)
o-$O_2NC_6H_4$—	Cl	63				(90)

n-Butyl difluoroboronite reacted with water to give a 1:2 boron trifluoride complex with 1-butanol; this compound was also obtained, as well as a 1:1:1 complex between the trifluoride, 1-butanol, and tri-*n*-butyl borate, on 1-butanolysis (206). Heating with solid sodium hydroxide afforded 1-butanol; heating alone caused disproportionation, which was also induced by the addition of pyridine.

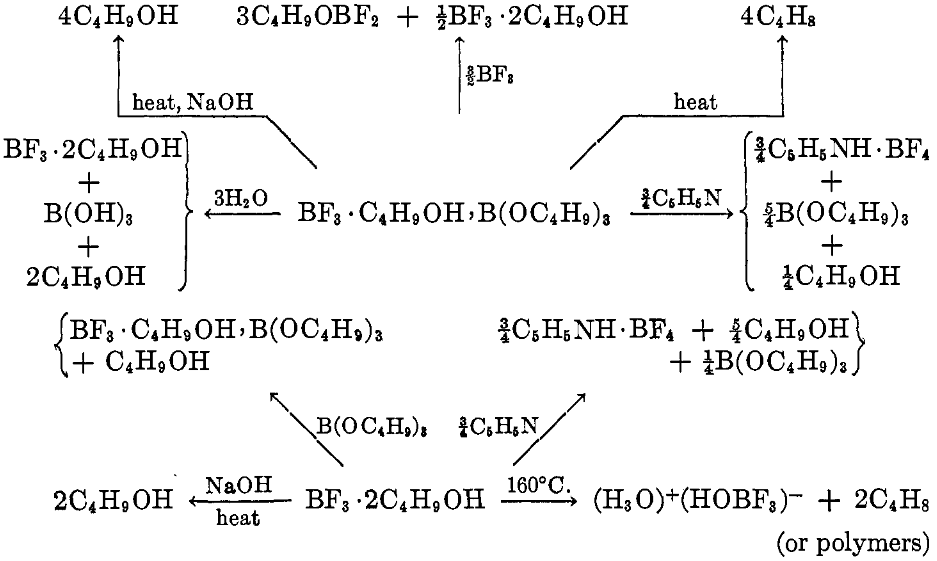
$$2C_4H_9OBF_2 + 3H_2O \rightarrow BF_3\cdot 2C_4H_9OH + B(OH)_3 + HF$$

$$3C_4H_9OBF_2 + 3C_4H_9OH \rightarrow BF_3\cdot C_4H_9OH\cdot B(OC_4H_9)_3 + BF_3\cdot 2C_4H_9OH$$

$$3C_4H_9OBF_2 \rightarrow 2BF_3 + B(OC_4H_9)_3$$

$$3C_4H_9OBF_2 + 2C_5H_5N \rightarrow 2BF_3\cdot C_5H_5N + B(OC_4H_9)_3$$

The composition of the complexes was demonstrated by syntheses and also by the reactions shown in the following schemes:



The reactions of *n*-butyl difluoroboronite and *n*-butyl dichloroboronite with boronic esters are discussed later (Section IV,G).

Ethyl dichloroboronite decomposed giving ethyl chloride, boron trioxide, and boron trichloride when heated at 50–70°C. (277, 372); the same reaction was observed with the methyl homolog (372). The stability of the higher members has been shown to depend on the nature of the alkyl group (105, 123, 126) and on the rigorous absence of impurities (126). Decomposition involved one of the following reactions (126):

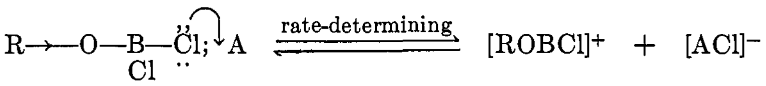
$$3ROBCl_2 \rightarrow B_2O_3 + BCl_3 + 3RCl \tag{1}$$

$$3ROBCl_2 \rightarrow B_2O_3 + BCl_3 + 3HCl + 3\ (\text{olefin}) \tag{2}$$

$$2ROBCl_2 \rightleftharpoons BCl_3 + ClB(OR)_2 \tag{3}$$

Depending on experimental conditions, either reaction 3 or reactions 1 and 2 together were observed. Under reflux, without heating in some cases and upon reduction of pressure, reaction 3 predominated; at atmospheric or higher pressures, under reflux or in a sealed tube, reactions 1 and 2 were observed. Only reaction 3 was reversible and the high volatility of boron trichloride was considered to be the reason for the dominance of this reaction when the pressure was reduced.

The stability of dichloroboronites with respect to reaction 1 decreased with increasing electron release of the alkyl group (126). Thus, the tertiary members could not be isolated; the secondary were unstable at room temperature, but evidence for their existence at −80°C. was obtained both analytically and also by means of isolation of stable 1:1 complexes with pyridine (123, 126). Primary alkyl dichloroboronites were relatively stable to heat. Rearrangement of the Wagner–Meerwein type was demonstrated by the conversion of isobutyl, neopentyl, 3-methylbutan-2-yl and α-methylneopentyl dichloroboronites to *tert*-butyl, *tert*-amyl, *tert*-amyl, and a *tert*-hexyl chloride, respectively. *d*-(+)-1-Methylheptyl dichloroboronite afforded much racemized *l*-(−)-2-chlorooötane (122, 126). Reaction 1 was very responsive to the presence of traces of a Lewis acid (ferric chloride, aluminum chloride) as an impurity (126). For example, pure *n*-butyl dichloroboronite was unchanged after 9 hr. at 100°C., whereas in the presence of ferric or aluminum chloride (1 per cent) decomposition was complete after half a minute at room temperature. These results were interpreted in terms of the following mechanism, wherein A designates the Lewis acid or a second molecule of the dichloroboronite.



$$R{\rightarrow}\!-O-\underset{Cl}{B}-\ddot{Cl}\!:\;A \xrightleftharpoons{\text{rate-determining}} [ROBCl]^+ + [ACl]^-$$

$$[ROBCl]^+ \rightarrow R^+ + OBCl \xrightarrow{[ACl]^-} A + RCl$$

An alternative mechanism, involving synchronous carbonium cation formation and B—Cl heterolysis, was recognized as a possibility. Boron oxychloride, although unknown (222), has been obtained as a pyridine complex (204) and was thought to decompose to boron trichloride and boron trioxide as a final step (126, 277).

The characteristic decomposition reaction of both aryl (89, 90) and 2-chloroethyl (105) dichloroboronites (reaction 3) was probably due to the difficulty of carbonium cation formation. Of the aryl dichloroboronites, the *o*-nitrophenyl compound was particularly stable (heating for 6 hr. at 100°C. effected no change) and this was attributed to intramolecular association between the nitro group and the boron atom (90).

The dichloroboronites fume in air; this is due to rapid and quantitative hydrolysis, which was originally demonstrated with the ethyl homolog (277).

$$ROBCl_2 + 3H_2O \rightarrow B(OH)_3 + ROH + 2HCl$$

Alcoholysis also involves evolution of hydrogen chloride and is stepwise (123, 126, 372).

$$ROBCl_2 \xrightarrow{ROH} ClB(OR)_2 \xrightarrow{ROH} B(OR)_3$$

The reaction of dichloroboronites with ethers and orthoborates has already been described (Section III,G,1).

Methyl dichloroboronite formed a stable 1:1 complex (m.p. 120°C.) with trimethylamine, which disproportionated when heated at 180°C. for 4 hr.

$$3CH_3OBCl_2 + 3(CH_3)_3N \rightarrow 3(1;1 \text{ complex}) \rightarrow B(OCH_3)_3 + (CH_3)_3N + 2BCl_3 \cdot (CH_3)_3N$$

Similar stable 1:1 complexes with pyridine have been obtained with *n*-butyl (204), 2-chloroethyl, 4-chlorobutyl (105), 1-methylheptyl (126), phenyl (89), and *o*-nitrophenyl (m.p. 172°C.) (90) dichloroboronites, and a 1:2 complex, $Cl(CH_2)_2OBCl_2 \cdot 2C_5H_5N$ (105), has also been reported. The 1:1 complex between pyridine and *n*-butyl dichloroboronite was also obtained from the 1;1 complex between pyridine and boron trichloride by 1-butanolysis; this complex and others were shown to decompose in two stages, depending on the extent of heating (204). In the case of *d*-(+)-1-methylheptyl, *l*-(−)-2-chlorooöctane was obtained without significant loss of activity.

$$BCl_3 \cdot C_5H_5N + ROH \rightarrow ROBCl_2 \cdot C_5H_5N + HCl$$

$$3ROBCl_2 \cdot C_5H_5N \rightarrow B(OR)_3 + 2BCl_3 \cdot C_5H_5N + C_5H_5N \rightarrow 3RCl + 3BOCl \cdot C_5H_5N$$

G, ALKYL(AND ARYL) HALOGENOBORONITES

These are compounds of the formulas RO(R′)BX and RO(Ar)BX. A number of these compounds were recently prepared by Brindley, Gerrard, and Lappert (39, 40) and their properties were investigated.

n-Butyl *n*-butylfluoroboronite was obtained from di-*n*-butyl *n*-butylboronate, either by passing boron trifluoride into it at 0°C. until ⅓ mole of the gas was absorbed or by addition of *n*-butyl difluoroboronite (39).

$$3C_4H_9B(OC_4H_9)_2 + BF_3 \rightarrow 3C_4H_9O(C_4H_9)BF + B(OC_4H_9)_3$$

$$2C_4H_9B(OC_4H_9)_2 + C_4H_9OBF_2 \rightarrow C_4H_9O(C_4H_9)BF + B(OC_4H_9)_3$$

The phenyl analog was obtained by equimolecular interaction between boron trifluoride and di-*n*-butyl phenylboronate.

$$C_6H_5B(OC_4H_9)_2 + BF_3 \rightarrow C_4H_9O(C_6H_5)BF + C_4H_9OBF_2$$

An analogous method using boron trichloride was suitable for the preparation of both *n*-butyl *n*-butylchloroboronite and *n*-butyl phenylchloroboronite. The former was also obtained from the dichloroboronite, either by equimolecular interaction with di-*n*-butyl *n*-butylboronate or by a reaction analogous to that shown above for the corresponding fluorine compound.

TABLE 16

Physical constants of alkyl(and aryl) halogenoboronites

Compound	Boiling Point	n_D^{20}	d_4^{20}	References
	°C.			
n-$C_4H_9O(n$-$C_4H_9)BF$	(Volatile at 0.01 mm.)	1.3900	0.888	(39, 40)
n-$C_4H_9O(C_6H_5)BF$	27/0.005 mm.	1.4565	0.972	(39, 40)
n-$C_4H_9O(n$-$C_4H_9)BCl$	50/1.5 mm.	1.4170	0.898	(39, 40)
n-$C_4H_9O(C_6H_5)BCl$	65/0.4 mm. (m.p., −32)	1.4996	1.021	(39, 40)
n-$C_6H_{13}CH(CH_3)O(C_6H_5)BCl$	94/0.1 mm.	1.4865	0.965	(39, 40)

$$C_4H_9B(OC_4H_9)_2 + C_4H_9OBCl_2 \rightarrow C_4H_9O(C_4H_9)BCl + ClB(OC_4H_9)_2$$

Phenylchloroboronites were also obtained from phenylboron dichloride, either by controlled alcoholysis (*n*-butyl, 1-methylheptyl) (40) or by the action of boronic esters (*n*-butyl) (39). The latter method was probably the most convenient of all.

$$C_6H_5BCl_2 + ROH \rightarrow RO(C_6H_5)BCl + HCl$$

$$C_6H_5B(OC_4H_9)_2 + C_6H_5BCl_2 \rightarrow 2C_4H_9O(C_6H_5)BCl$$

The alkyl(and aryl) halogenoboronites were unimolecular (cryoscopic in cyclohexane) (39); physical constants are shown in table 16.

There was considerable similarity between these compounds and alkyl dihalogenoboronites and (in the case of the chlorine compounds) the dialkyl chloroboronates (40).

The fluoroboronites underwent hydrolysis in excess water in such a way that all the fluorine and boron were quantitatively converted to hydrogen fluoride and orthoboric acid, respectively; this was indicated by analysis. Addition of pyridine to the esters induced disproportionation, which also resulted when heating in the absence of addenda.

$$2C_4H_9O(R)BF \rightarrow RBF_2 + RB(OC_4H_9)_2$$

The chloroboronites were thermally stable, but traces of Lewis acids (ferric chloride) catalyzed decomposition and a rapid reaction at 20°C. was then observed. *d*-(+)-1-Methylheptyl phenylchloroboronite gave *l*-(−)-2-chloroöctane, with little loss of activity. A mechanism similar to that proposed for dichloroboronite (Section IV,F,3) and chloroboronate (Section III,G,3) decomposition was suggested.

$$3RO(C_4H_9 \text{ or } C_6H_5)BCl \rightarrow [C_4H_9(\text{or } C_6H_5)BO]_3 + 3RCl$$

Hydrolysis as well as 1-butanolysis of *n*-butyl *n*-butylchloroboronite afforded di-*n*-butyl *n*-butylboronate.

$$2C_4H_9O(C_4H_9)BCl + 2H_2O \rightarrow C_4H_9B(OC_4H_9)_2 + C_4H_9B(OH)_2 + 2HCl$$

$$C_4H_9O(C_4H_9)BCl + C_4H_9OH \rightarrow C_4H_9B(OC_4H_9)_2 + HCl$$

Whereas addition of *n*-butyl phenylchloroboronite to an excess of pyridine afforded an unstable 1:2 complex, the addition of pyridine to *n*-butyl *n*-butylchloroboronite induced disproportionation.

$$2C_4H_9O(C_4H_9)BCl + C_5H_5N \rightarrow C_4H_9BCl_2 \cdot C_5H_5N + C_4H_9B(OC_4H_9)_2$$

H. THIO COMPOUNDS

The only known thioboronous acid derivative is methyl dimethylthioboronate (m.p. −84°C.), which was prepared by the interaction of methyl mercaptan and tetramethyldiborane (75).

$$2CH_3SH + B_2H_2(CH_3)_4 \rightarrow 2(CH_3)_2BSCH_3 + 2H_2$$

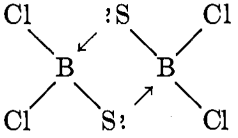
Methyl dibromothioboronate was prepared by the action of boron tribromide on methyl mercaptan (374); a 1:1 addition product was postulated as an intermediate.

$$CH_3SH + BBr_3 \rightarrow BBr_3 \cdot CH_3SH \rightarrow CH_3SBBr_2 + HBr$$

A similar method, using boron trichloride, afforded methyl dichlorothioboronite, CH_3SBCl_2, m.p. 72.7°C.; the intermediate addition product melted at −20°C. (140),

Attempted preparations using boron halides on dialkyl sulfides [dimethyl sulfide and boron tribromide (140); dibutyl sulfide and boron trichloride (205)] were unsuccessful.

Methyl dichlorothioboronite was shown to be dimeric (cryoscopic in benzene) and formula XXX was suggested as the probable structure; it hydrolyzed only slowly in water, yielding methyl mercaptan. The corresponding bromo derivative (m.p. −112.3°C.) was 85 per cent dimeric. Raman spectra were investigated (140).



XXX

The reaction between octanethiol and chlorovinylboron dichloride at 100°C. produced *n*-octyl chlorovinylchlorothioboronite (209).

$$C_8H_{17}SH + ClCH{=}CHBCl_2 \rightarrow C_8H_{17}S(ClCH{=}CH)BCl + HCl$$

V. DERIVATIVES OF BORINE

A. INTRODUCTION

Derivatives of the unknown compound borine, BH_3, may be considered under six headings:

(1) The compounds in which the hydrogen atoms are replaced by alkyl, aryl, or alkenyl groups (with one exception, $C_6H_5BH_2$, these compounds are such that all three hydrogen atoms are replaced, i.e., they are of the type BRR′R″).

(2) The compounds in which one or more hydrogen atoms are replaced by one or more amino or alkyl(or aryl)-substituted amino groups, with or without simultaneous replacement by one or more alkyl groups; i.e., compounds of the type $(RR'N)_nBR''_{3-n}$ (where $n = 1, 2,$ or 3 and R, R′, and R″ are either the same or different and each is hydrogen or an alkyl or an aryl group).

(3) The compounds in which one or two hydrogen atoms are replaced by alkyl(or aryl)-substituted amino groups and the remaining two or one hydrogen atom is replaced by halogen; i.e., compounds of the type $(RR'N)BX_2$ and $(RR'N)_2BX$ (where R and R′ are as defined in paragraph 2).

(4) The compounds in which each of the hydrogen atoms is replaced by an alkyl group, a substituted amino group, and a halogen atom, respectively (only three members of this class have been reported to date).

(5) The compounds in which one or two hydrogen atoms are replaced by alkyl or aryl groups and the remaining two or one hydrogen atom is replaced by halogen; i.e., compounds of the type RBX_2 and R_2BX.

(6) Organoboron compounds containing other metalloidal elements (in practice only very few examples of these are known and they are derivatives of silicon, arsenic, or phosphorus).

The compounds of the sixth class will not be discussed here because they have very recently been reviewed (325).

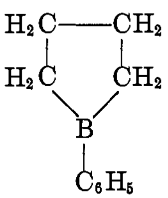
B. PREPARATION OF ALKYLBORONS AND ARYLBORONS

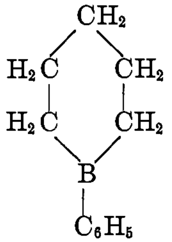
The large majority of compounds in this section are of type BR_3, i.e., trialkyl- or triarylborons.

Phenylborine, $C_6H_5BNH_2$, was prepared by Pace (264), by treating a phenylboron diiodide–hydrogen iodide complex with hydrogen in ethanol.

$$C_6H_5BI_2 \cdot 2HI + 2C_2H_5OH + 2H_2 \rightarrow C_6H_5BH_2 + 2C_2H_5I + 2HI$$

Apart from two cyclic members (XXXI and XXXII), obtained from phenylboron difluoride and either 1,4-dilithiobutane or 1,5-dilithiopentane, respectively (335), the only reasonably stable mixed borons are phenyldi(*o*-tolyl)boron (335), obtained from phenylboron difluoride and *o*-tolylmagnesium bromide, and alkenylalkylborons (266, 267). Vinyl compounds were prepared from vinylsodium and dimethylboron bromide, whilst propenyl compounds were obtained


XXXI


XXXII

from propenyllithium and the same bromide. A further preparation is mentioned later (Section V,D, 4).

$$C_6H_5BF_2 + 2o\text{-}CH_3C_6H_4MgBr \rightarrow (o\text{-}CH_3C_6H_4)_2BC_6H_5$$

$$RCH{=}CHNa(Li) + (CH_3)_2BBr \rightarrow (CH_3)_2BCH{=}CHR \xrightarrow{\text{slow}} \tfrac{1}{2}CH_3B(CH{=}CHR)_2 + \tfrac{1}{2}B(CH_3)_3$$

The first trialkylborons to be prepared were the ethyl (113) and methyl (112) homologs, obtained by Frankland and Duppa in 1859 by the action of excess dialkylzinc on triethyl borate.

$$3ZnR_2 + 2B(OC_2H_5)_3 \rightarrow 2BR_3 + 3Zn(OC_2H_5)_2$$

The method has not been used by later workers and indeed a trialkyl borate has only been employed as starting material in one other investigation (166), the preparation of tri-*n*-butylboron (50 per cent yield) from *n*-butylmagnesium bromide and trimethyl borate, a result which was contrary to an earlier report (177) that only one methoxyl group in trimethyl borate was replaceable. A small quantity of triphenylboron was obtained as a by-product in the preparation of isobutyl diphenylboronite from phenylmagnesium bromide and triisobutyl borate (213).

Both esters (*n*-propyl, *n*-butyl) (337) and the anhydride (193) of phenylboronic acid gave, with alkylmagnesium bromides (*n*-propyl, ethyl), mixtures of triphenylboron and the appropriate trialkylboron; a mixture was also obtained from *n*-propyl phenylmethylboronite and methylmagnesium bromide (337). In these preparations the mixed borons, which were presumably formed initially, disproportionated.

$$C_6H_5B(OR)_2 + 2R'MgBr \rightarrow [C_6H_5BR'_2] \xleftarrow{6R'MgBr} (C_6H_5BO)_3$$

$$C_6H_5(CH_3)BOC_3H_7 \xrightarrow{CH_3MgBr} [C_6H_5B(CH_3)_2]$$

$$3[C_6H_5BR'_2] \rightarrow B(C_6H_5)_3 + 2BR'_3$$

Most of the other preparations have depended upon the reaction of organometallic compounds, in particular Grignard reagents, on boron halides. The attempted preparation of triphenylboron from diphenylmercury and boron trichloride (or phenylboron dichloride) was unsuccessful, substitution taking place no further than the formation of diphenylboron chloride (238). Quantitative yields of trialkylborons (methyl, ethyl) were obtained by interaction of zinc alkyls with boron trichloride (324, 355, 367) or boron trifluoride (355).

$$2BX_3 + 3ZnR_2 \rightarrow 2BR_3 + 3ZnX_2$$

Krause and Nitsche (190) introduced the method that in various modifications has remained the most widely used in this field, the action of boron trifluoride on an ethereal solution of a Grignard reagent (*n*-propyl, isobutyl, isoamyl).

$$BF_3 + 3RMgX \rightarrow BR_3 + 3MgXF$$

The first triarylborons to be reported were also successfully prepared by this method [C_6H_5— (191); *p*-$CH_3C_6H_4$— (194, 377); *o*- and *m*-$CH_3C_6H_4$— (377); 1,4-$(CH_3)_2C_6H_3$— (192); *p*-$CH_3OC_6H_4$— (193); α-$C_{10}H_7$— (192)] and other trialkylborons also [isopropyl (193); *tert*-butyl (193); *n*-hexyl (226); cyclohexyl (195); $C_6H_5CH_2$— (192)]. The same method for tri-*n*-butylboron gave an 80 per cent yield (166). The use of the diethyl ether complex of boron trifluoride, in preference to the gas itself, was later recommended; with this modification triisopropyl- and tri-*tert*-butylborons have been obtained in 60–65 per cent yields (47) and tri-*n*-propylboron in 50–60 per cent yield (220). Boron trifluoride with methylmagnesium bromide gave only a 10 per cent yield of trimethylboron (355). This was improved (47) by using the Grignard reagent, which was added to boron trifluoride di-*n*-butyl etherate; triethylboron was similarly obtained from this etherate by adding it to ethylmagnesium bromide in *n*-butyl ether. The use of this ether had previously been mentioned for trimethylboron, but in this procedure without the reversal of addition (50).

Phenyllithium with boron trifluoride gave a 74 per cent yield of triphenylboron (379); tri-*o*-phenylphenylboron and tri-*p*-dimethylaminophenylboron were similarly obtained (377).

Methylmagnesium bromide and boron trichloride (CH_3MgBr;$(C_2H_5)_2O$;BCl_3 = 3:2:1) gave trimethylboron (87 per cent) (367).

Methylmagnesium iodide has similarly been used (319). Methylmagnesium bromide with boron tribromide in the absence of ether gave a 45 per cent yield of trimethylboron, but an 87 per cent yield was obtained if the tribromide in benzene was added to a benzene solution of the Grignard reagent from which the bulk of the ether used in its preparation had been removed (355). Tri-*n*-butylboron (70 per cent) was obtained from *n*-butylmagnesium bromide and boron trichloride (319).

Allylmagnesium bromide and di-*n*-butylboron bromide afforded some tri-*n*-butylboron (289). Other reactions which afforded trialkylborons, from either dialkylboron halides or alkylboron dihalides, are mentioned elsewhere (Section V,I,2).

From a mixture of 2-methylpropene and diborane (2–10 per cent), maintained for 24 hr. at 100°C., triisobutyl- and tri-*tert*-butylborons were obtained; from ethylene and diborane (2 per cent), evidence (mass spectrometer) was given for the formation of triethylboron after maintaining the mixture for 4 days at 100°C.; and from benzene and diborane (3 per cent), a product was obtained after 12 hr. at 100°C. which on hydrolysis gave triphenylboron as one of the products (157). The kinetics of the diborane–ethylene reaction has been studied (348). Aluminum borohydride with ethylene at 140°C. gave triethylboron; the reaction was catalyzed by traces of oxygen (42, 43).

Mixtures of alkyl chlorides (methyl, ethyl) and boron halides (fluoride, chloride, bromide) when passed over aluminum at 350°C., or zinc at 325–350°C., gave trialkylborons (159).

C. PHYSICAL PROPERTIES OF ALKYLBORONS AND ARYLBORONS

The molecular weights (cryoscopic in benzene) of triarylborons (C_6H_5—, p-$CH_3C_6H_4$—, α-$C_{10}H_7$—) showed them to be unimolecular (189); the tricyclohexyl (189), methyl (324), and ethyl (324) homologs were likewise unimolecular (vapor density). Similar conclusions had been arrived at by the evaluation of Trouton's constant (methyl, n-propyl, isopropyl) (14). Raman (132, 314) and ultraviolet (132) spectra investigations on trimethylboron have been carried out and force constants calculated from the data (132); the high values obtained suggested that resonance of the type found in the boron halides was unlikely (314). Nuclear quadrupole spectra for B^{10} and B^{11} were determined, using trialkylborons (methyl, ethyl) as reference compounds (97). The parachor for triethylboron was calculated and also the boron–carbon distances (208), These last data have also been obtained for trimethylboron (216) by the electron diffraction method and the covalent radius for boron was calculated; it was concluded that the molecule was planar. The heat of combustion for trimethylboron

TABLE 17

Physical constants of trialkylborons and triarylborons

R in BR_3	Boiling Point	Melting Point	$n_D^{22.6}$	Density	References
	°C.	*°C.*			
CH_3—	−21.8	−161.5			(14, 45, 46, 47, 48, 49, 50, 52, 53, 55, 57, 60, 61, 62, 63, 64, 97, 112, 113, 132, 159, 216, 221, 250, 298, 304, 314, 319, 324, 355, 367)
C_2H_5—	95	−92.9		d_4^{23} = 0.6931	(41. 43, 47, 97, 113, 157, 158, 159, 208, 232, 235, 324)
n-C_3H_7—	60/20 mm.	−65.5	1.41352	$d_4^{22.6}$ = 0.7225	(14, 15, 128, 190, 220)
i-C_6H_7—	33-35/12 mm.	−54 to −53			(14, 47, 193)
n-C_4H_9—	90–91/9 mm.				(33, 166, 168, 319)
i-C_4H_9—	86/20 mm.		1.42445	$d_4^{22.6}$ = 0.7400	(157, 190)
t-C_4H_9—	71/12 mm.				(45, 47, 157, 193)
i-C_5H_{11}—	119/14 mm.		1.43207	$d_4^{22.6}$ = 0.7607	(190)
n-C_6H_{13}—	97/0.002 mm.				(226)
C_6H_{11}—	194/15 mm.	98-100			(189, 195)
CH_2=CH—	Vapor pressure = 65 mm. at 0°C.				(267)
$C_6H_5CH_2$—	229-232/13 mm.	47			(191, 194)
C_6H_5—	203/15 mm.	137			(5, 25, 26, 106, 108, 109, 110, 119, 128, 153, 156, 157, 184, 185, 189, 191, 193, 213, 256, 279, 280, 290, 291, 333, 334, 337, 377-383)
p-$CH_3C_6H_4$—	233-234/12 mm.	142–144			(189, 195, 377)
o-$CH_3C_6H_4$—	208/12 mm.	67-69			(377)
m-$CH_3C_6H_4$—	218-222/12 mm.	59-60			(377)
p-$CH_3OC_6H_4$—		128			(193)
o-$C_6H_5C_6H_4$—		201-203			(377)
2, 5-$(CH_3)_2C_6H_3$—	221/12 mm.	146–147			(189, 192, 194)
p-$(CH_3)_2NC_6H_4$—		209-212			(377)
α-$C_{10}H_7$—		206–207			(24, 25, 59, 189, 192, 194)
$B(\alpha$-$C_{10}H_7)_3 \cdot 2C_6H_6$.					(24, 25, 59, 189, 192, 194)
		170			(192)

was measured and this value, together with the known heat of atomization, was used to calculate the binding energy of the boron–carbon bond and the energies required for removal of the alkyl radical (221). Potential barrier values for trimethylboron have been calculated (115) and a theoretical paper on the same compound has appeared (312). The relative partial charges on combined hydrogen in trimethylboron and also in phenylborine have been calculated (292). The absence of dimerization in trimethylboron has been attributed to stabilization by trigonal hyperconjugation (250). Tri-α-naphthylboron crystallized solvated from benzene [1;2 (189, 192); 1;1 (59)]. It has been suggested that this compound may exist in two rotationally isomeric forms (59). Available physical constants for symmetrical compounds are shown in table 17.

Phenylborine had a boiling point of 193°C. (264). Phenyldi(*o*-tolyl)boron boiled at 203–205°C./12 mm.; the cyclic compounds XXXI and XXXII had boiling points of 85–87°C./11 mm., and 105–107°C./11 mm., respectively (335), The known alkenylalkylborons, which are all unimolecular, are (the vapor pressures in millimeters at 0°C. are shown in parentheses): dimethylvinyl- (126); methyldivinyl (109.5); dimethylpropenyl- (76.5); methyldipropenyl- (12.5) (266).

D. CHEMICAL PROPERTIES OF ALKYLBORONS AND ARYLBORONS

1. *Introduction*

Phenylborine was shown to undergo hydrolysis in water to give phenylboronic acid, and to react with phenylboron dichloride to afford a novel type of organoboron compound, $C_6H_5B{=}BC_6H_5$, m.p. 155°C. (264).

The chemical characteristics of the trialkyl- and triarylborons are due to their very powerful Lewis acid properties. This makes them highly reactive as electrophiles and the majority of their reactions, at least in the initial steps, involve coordination. On the basis of the Michler's ketone test, tri-*n*-propylboron was described as more reactive than triphenylboron and both were considered to be less reactive than the corresponding aluminum compounds (128).

The properties which, owing to the considerable information available, warrant separate discussion are (*1*) the oxidation reactions, (*2*) the formation of coordination compounds with ammonia and amines, and (*3*) the formation of metal, or quaternary ammonium, tetracovalent boron complexes. For convenience, other reactions are considered in this introduction.

The trialkyl- and triarylborons are thermally stable; tri-*n*-butylboron, when heated under reflux for 2 days at 90–100°C. and a pressure of 5 mm. afforded butylene, whilst heating for 10 days at 125–130°C. and 10 mm. pressure produced *trans*-isobutylene and di-*n*-butyldiborane (287). Triethylboron decomposed at 100°C. (324).

Triethylboron was insoluble in cold water (113); with water at 90–100°C. a reaction took place, but the products were not identified (232). The reactions with alcohols, aldehydes, and carboxylic acids have already been mentioned (Section III,C,6; Section IV,D,2); these demonstrated their reducing properties, which were considered to be less than those of their aluminum analogs, because triethylboron did not (in contrast to triethylaluminum) reduce trichloroacetone or benzil (232).

Triethylboron reacted with neither triethyl borate nor orthoboric acid (235), There was no compound formation between trimethylboron and xenon (363), Trimethylboron did not associate with ethylene in the liquid phase, but the lattice compound was the 2;3 complex (82).

Krause discovered the remarkable property of the triarylborons [C_6H_5— (25, 187, 194); *p*-$CH_3C_6H_4$— (194); *p*-$CH_3OC_6H_4$— (193); tribenzylboron (192)] of forming 1;1 addition compounds with the alkali metals (particularly sodium) by reaction in ether; this was in contrast to the trialkylborons (*n*-propyl, *tert*-butyl, cyclohexyl), which did not react (193, 194). Tri-α-naphthylboron with sodium amalgam in ether gave a 1;2 compound, $B(\alpha\text{-}C_{10}H_7)_3 \cdot 2Na$ (24); the free energy of this reaction was −11.2 kcal., compared with −11,5 kcal. for the formation of $B(C_6H_5)_3 \cdot Na$ (25). The specific resistance in ether of these complexes was measured (26). The entropy of ionization of the tri-α-naphthylboron 1:1 complex with sodium was evaluated (92). By reacting triphenylboron with an excess of sodium amalgam (40 per cent) in tetrahydrofuran, a disodium triphenylboron complex was formed (334).

Trialkylborons have been mentioned in connection with the decomposition of diazomethane to give polymethylene (156, 228). Reactions with halogens, hydrogen halides, and boron halides are discussed later (Section V,H,3),

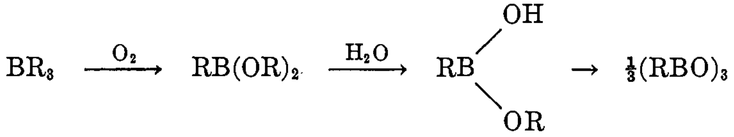
2. Oxidation

Trialkyl- and triarylborons are in general very readily oxidized and experiments involving their preparation or properties are, therefore, usually carried out under nitrogen. The applications of some of these oxidation reactions have already been described (Section III,C,2; Section III,H,2; Section IV,D,2), Tri-*n*-butylboron was completely oxidized in aqueous solution to orthoboric acid by hydrogen peroxide, benzoyl peroxide, or perbenzoic acid (168).

$$BR_3 \xrightarrow{[O]} B(OR)_3 \xrightarrow{H_2O} B(OH)_3$$

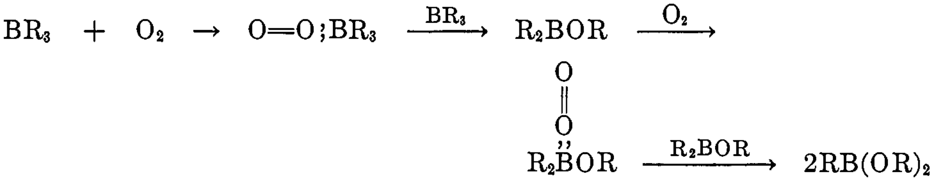
Frankland and Duppa observed that trimethyl- and triethylborons were spontaneously combustible, and that in pure oxygen the reaction was explosive (112, 113). Increase in molecular weight apparently reduces the tendency of trialkylborons to undergo oxidation, since the *n*-butyl and higher homologs were not spontaneously flammable (168). The autoxidation of other trialkylborons (benzyl, *n*-propyl, *tert*-butyl, cyclohexyl) has also been reported (192, 193, 195). Triarylborons (C_6H_5—, *p*-$CH_3C_6H_4$—, *p*-$CH_3OC_6H_4$—) fumed in air and were easily oxidized thereby (191, 193, 195). Tri-α-naphthylboron, however, was stable in air, probably owing to steric hindrance (192); a sample which had been in contact with the atmosphere for one year was unchanged (59).

The controlled oxidation (by slow diffusion of air) of triethylboron afforded diethyl ethylboronate (113), although a more complex mixture (borate, boronate, and boronite) was obtained by later workers (235). The first stage in the autoxidation of trialkylborons was said to be the formation of the appropriate boronic anhydride (190), but this was later considered to be formed through ester intermediates (168).



$$BR_3 \xrightarrow{O_2} RB(OR)_2 \xrightarrow{H_2O} RB\begin{matrix}OH\\ OR\end{matrix} \rightarrow \tfrac{1}{3}(RBO)_3$$

This view received support from the observation that oxidation of tri-*n*-butylboron with dry air gave di-*n*-butyl *n*-butylboronate, whereas moist air gave only *n*-butyl di-*n*-butylboronite (168). The proposed reaction sequence was;



$$BR_3 + O_2 \rightarrow O{=}O;BR_3 \xrightarrow{BR_3} R_2BOR \xrightarrow{O_2}$$

$$R_2\overset{\begin{array}{c}O\\ \|\\ O\end{array}}{B}OR \xrightarrow{R_2BOR} 2RB(OR)_2$$

The inhibitor effect was explained as due to the formation of a reasonably stable hydrate of the alkyl dialkylboronite, which therefore prevented coordination with oxygen. The cessation of atmospheric oxidation at the boronate stage, even in the absence of moisture, was considered to be due to the increasing oxygen–boron back-coordination, which so weakened the electrophilic character of the boron atom in the boronate that coordination with oxygen would not take place.

The kinetics of the homogeneous oxidation of trimethyl- and tri-*n*-propylborons was investigated (15). The rate was too fast to be measured in the latter case. The less ready oxidation of trimethylboron, compared with some of its higher homologs, was attributed to the strengthening of the carbon–boron bond due to hyperconjugation. The proposed mechanism for oxidation was a free-radical chain reaction, or an energy chain reaction, being initiated and terminated on the walls of the reaction vessel. The reaction was inhibited by mixtures of boron trifluoride and water.

Triethylboron ignited spontaneously when in contact with oxygen in a Pyrex bulb at 0°C. at a partial pressure less than 1 mm. (41). The reaction chains were thought to be initiated in the gas phase and terminated on the walls; when these were coated with the reaction products, the minimum pressure was even lower.

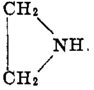
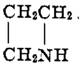
3. Coordination compounds

A large number of 1:1 compounds of ammonia and amines with trialkyl- and triarylborons have been prepared by interaction usually at low temperature, either in equimolecular proportions or using an excess of the base, and subsequently removing the excess under vacuum. These are listed in tables 18 and 19, with their characterizing constants. Coordination compounds involving oxygen or other donor elements are not known.

No compound formation was observed between the following: trimethylboron

TABLE 18

Physical constants of nitrogen complexes of trimethylboron

R'_3N in $BR_3 \cdot NR'_3$	Melting Point	Saturation Vapor Pressure at 0°C.	References
	°C.	*mm.*	
NH_3	56	1.0	(45, 47, 112, 324, 330)
	73.2–73.7		(50)
CH_3NH_2	26.9–27.2	0.16	(45, 330, 359)
$(CH_3)_2NH$	35.0–35.5	0.20	(45)
$(CH_3)_3N$	128	0.24	(44, 45, 47, 57, 63, 307, 329)
$C_2H_5NH_2$	24.0–24.5	0.1	(46, 62, 330)
$(C_2H_5)_2NH$	26–28	0.3	(46, 62)
$(C_2H_5)_3N$	−18 to −14	238	(62)
$n\text{-}C_3H_7NH_2$	6.0–6.4	0.1	(61, 64, 330)
$(n\text{-}C_3H_7)_2NH$		0.1	(55)
$i\text{-}C_3H_7NH_2$	8.7	0.26	(49, 55)
$(i\text{-}C_3H_7)_2NH$	−28 to −24	>165	(55)
$n\text{-}C_4H_9NH_2$	3.4–3.7		(61, 64, 330)
$s\text{-}C_4H_9NH_2$	−7		(49)
$t\text{-}C_4H_9NH_2$	16.7–19.5		(49)
$(t\text{-}C_4H_9)_3N$		1.3	(55)
$n\text{-}C_5H_{11}NH_2$			(61, 64)
$n\text{-}C_6H_{13}NH_2$			(64)
$(CH_3)_2NC_4H_9$	16.4–19	0.24	(53)
$(CH_3)_2NCH_2C(CH_3)_3$	13–16.5	31.3	(53)
$C_6H_5NH_2$	21		(360)
C_5H_5N	53.8–55.1	0.03	(48, 57)
$2\text{-}CH_3C_5H_4N$	28–33	3.2	(48)
$3\text{-}CH_3C_5H_4N$	72.5–73	0.02	(48)
$4\text{-}CH_3C_5H_4N$	78.5–80	0.00	(48)
Quinuclidine			(60)
	10–12		(52)
 $\begin{matrix} CH_2CH_2 \\ \vert \quad \vert \\ CH_2NH \end{matrix}$	−9 to −6		(52)
C_4H_9N	43–44		(52)
$C_5H_{11}N$	81.5–82.5		(52)

and diisopropylamine (vapor pressure > 165 mm. at 0°C.) (55), 2-*tert*-butylpyridine and 2,2-dimethylpyridine (53); triisopropylboron and trimethylamine (47); tri-*tert*-butylboron and trimethylamine (47), diethylamine, or triethylamine (46); tri-α-naphthylboron and trimethylamine (59) [a complex was reported earlier (see table 19), but the conflicting results were attributed to the existence of two rotationally isomeric forms of tri-α-naphthylboron (59)]. These results were explained in terms of "face to face" steric hindrance (F-strain).

The formation of the trimethylboron–trimethylamine complex from a dimethylaminoboron dichloride complex has been indicated from investigations of infrared spectra (44).

$$B(CH_3)_3 + (CH_3)_2NBCl_2 \cdot (CH_3)_3N \rightarrow B(CH_3)_3 \cdot (CH_3)_3N + (CH_3)_2NBCl_2$$

Trimethylboron formed 2:1 complexes with ethylenediamine (m.p. 139°C.)

TABLE 19

Physical constants of nitrogen complexes of other trialkyl- and triarylborons

R in $BR_3 \cdot NR_3$	NR'_3 in $BR_3 \cdot NR'_3$	Vapor Pressure at 0°C.	Melting Point	References
		mm.	°*C.*	
C_2H_5—	NH_3		−11 to −10	(47, 112)
C_2H_5—	$(CH_3)_3N$		−46 to −45	(47)
i-C_3H_7—	NH_3		−27 to −26	(47)
t-C_4H_9—	CH_3NH_2	1.5		(45)
t-C_4H_9—	$(CH_3)_2NH$	44.5		(45)
t-C_4H_9—	$C_2H_5NH_2$	5.3		(45)
Cyclohexyl	NH_3		105–106	(57)
Cyclohexyl	$C_6H_{11}N$		135–136	(57)
$C_6H_5CH_2$—	NH_3		194–196	(45)
$C_6H_5CH_2$—	CH_3NH_2		105–112	(45)
$C_6H_5CH_2$—	$(CH_3)_3N$		128	(45)
$C_6H_5CH_2$—	$C_5H_{11}N$		104–106	(45)
C_6H_5—	NH_3		212	(110, 137, 188, 280, 343, 381)
C_6H_5—	CH_3NH_2		208–209	(188)
C_6H_5—	$(CH_3)_2NH$		186–187	(188)
C_6H_5—	$(CH_3)_3N$		135–137	(188)
C_6H_5—	$C_2H_5NH_2$		166–168	(188)
C_6H_5—	*n*-$C_3H_7NH_2$		101–102	(188)
C_6H_5—	$C_6H_5NH_2$		138–140	(188)
C_6H_5—	C_5H_5N		214 (decomp.)	(188)
C_6H_5—	Quinoline			(188)
p-$CH_3C_6H_4$—	NH_3		225–226	(195)
p-$CH_3C_6H_4$—	C_5H_5N		201–202	(195)
p-$CH_3C_6H_4$—	$C_6H_{11}N$		202	(195)
p-$CH_3OC_6H_4$—	NH_3		191 (decomp.)	(193)
$(CH_3)_2C_6H_3$—	NH_3		181–182	(192)
$(CH_3)_2C_6H_3$—	CH_3NH_2		155–156	(192)
$(CH_3)_2C_6H_3$—	C_5H_5N		146–148	(192)
$(CH_3)_2C_6H_3$—	$C_6H_{11}N$		109–110	(192)
α-$C_{10}H_7$—	NH_3		193–194	(59, 112)
α-$C_{10}H_7$—	CH_3NH_2		192–193	(59, 112)
α-$C_{10}H_7$—	$(CH_3)_2NH$			(59)
α-$C_{10}H_7$—	$(CH_3)_3N$		178–180	(192)
α-$C_{10}H_7$—	C_5H_5N		202–206	(192)
α-$C_{10}H_7$—	$C_6H_{11}N$		160	(192)

and 1,3-diaminopropane (m.p. 104°C.) (141). The former compound (1 mole) reacted with hydrogen chloride (4 moles) at room temperature. When heated to 250°C. in a bomb, methane was eliminated and a novel type of organoboron compound, $(CH_3)_2BNHCH_2CH_2NHB(CH_3)_2$ (extrapolated boiling point = 149°C.; Trouton's constant = 24.2) was produced.

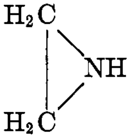
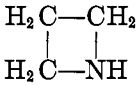
Although trimethylboron formed complexes with both trimethylamine and $(SiH_3)(CH_3)_2N$ (the former being the more stable), no complexes were observed with either $(SiH_3)_2NCH_3$ or $(SiH_3)_3N$, This was attributed to steric factors (329),

The heats of dissociation of complexes of trimethylboron with ammonia, methylamine, ethylamine, *n*-propylamine, and *n*-butylamine were all of the same order (−7.26 ± 0.21 kcal./mole) (330).

The study of these coordination compounds has played an important part in the development of the steric strain theories of H. C. Brown and his collaborators. A brief summary of the work, insofar as it is relevant to the present discussion, is given below. The general aim was to establish experimentally the relative stability of coordination compounds of varying structural types and to correlate the data in terms of steric and polar explanations. The important point is that the relative strength of bases is dependent on the nature of the reference acid and the steric and polar requirements of both the acid and the base can be widely varied. The experimental methods of investigation involved competition reactions, measurements of saturation vapor pressures of complexes, or thermodynamic measurements.

The relative strength of certain acids when trimethylamine was the reference base was $B(CH_3)_3 < HB(CH_3)_2 < CH_3BH_2 < BH_3$ (307).

The relative strength of certain bases, when trimethylboron was the reference acid, for various series was: $NH_3 < (CH_3)_3N < CH_3NH_2 < (CH_3)_2NH$ (the same order as for proton acids, which have negligible steric requirements; hence the result was explained in terms of B-strain) (45); $(CH_3)_3N < C_5H_5N$ (the converse of proton acids, borine, and boron trifluoride; hence explained in terms of F-strain) (57); $NH_3 \ll C_2H_5NH_2 <$ n-$C_3H_7NH_2 <$ n-$C_4H_9NH_2 <$ n-$C_5H_{11}NH_2 <$ n-$C_6H_{13}NH_2 < CH_3NH_2$ (61, 64); $(C_2H_5)_3N < NH_3 < (C_2H_5)_2NH < C_2H_5NH_2$ (*cf.* $NH_3 < (C_2H_5)_3N < C_2H_5NH_2 < (C_2H_5)_2NH$ for proton acids; hence F-strain) (46, 62); $(i\text{-}C_3H_7)_3N < (i\text{-}C_3H_7)_2NH < NH_3 <$ i-$C_3H_7NH_2$ and $(t\text{-}C_4H_9)_3N < (t\text{-}C_4H_9)_2NH <$ t-$C_4H_9NH_2 < NH_3$ (i.e., in the latter case a total reversal of polar predictions, but a complete agreement with steric requirements) (55); $(i\text{-}C_3H_7)_2NH < (n\text{-}C_3H_7)_2NH$ (in agreement with F-strain prediction) (55); 2-methylpyridine < pyridine < 3(= 4)-methylpyridine (*cf.* $C_5H_5N <$ 3(=4)-methylpyridine < 2-methylpyridine for hydrogen acids) (48); $(C_2H_5)_3N <$ quinuclidine (60);

 $\ll$ piperidine < pyrrolidine < 

(the low stability of the first member was attributed to I-strain and the greater stability of the pyrrolidine complex compared with the piperidine complex to F-strain) (52); t-$C_4H_9NH_2 < NH_3 \ll$ s-$C_4H_9NH_2 <$ i-$C_3H_7NH_2$ (49); $(CH_3)_2NCH_2C(CH_3)_3 \ll (CH_3)_2NC_4H_9$-$n$ (53).

The relative strength of certain bases when tri-*tert*-butylboron was the reference acid was: $(CH_3)_3N < (CH_3)_2NH < NH_3 < CH_3NH_2$ (45); $(C_2H_5)_3N < (C_2H_5)_2NH < C_2H_5NH_2 < NH_3$ (46). With tri-α-naphthylboron the order was $(CH_3)_3N < (CH_3)_2NH < CH_3NH_2 < NH_3$ (59). All these results were interpreted in terms of the theory of F-strain.

For higher trialkylborons (ethyl, isopropyl, *tert*-butyl) the stability of the ammonia complexes was greater than that of the trimethylamine complexes (i.e., a reversal compared with trimethylboron) (47).

The pyrolysis of amine complexes is discussed later (Section V,E,1 and 3).

4. Tetracovalent boron complexes

The complexes which are the subject of this subsection have the general formula M[BRR′R″R‴], where M is a univalent metal, quaternary ammonium or phosphonium group, or some other univalent cation, and R, R′, R″, R‴ are the same or different and each is hydrogen, an alkyl, alkenyl, alkynyl, or aryl group, or a univalent anionic radical.

Krause was the first to prepare a compound of this class, when he observed that triphenylboron readily formed an addition compound with sodium ethoxide (188). Similar complexes with sodium amide and tetra-*n*-butylammonium hydroxide were later reported, and the electrical conductivity and dissociation constant of the former and the polarization curve of the latter were measured (184, 185). 1:1 Complexes of triphenylboron and tetramethyl- and tetra-*n*-butylammonium hydroxides and fluorides were obtained from the appropriate quaternary salt and the 1:1 complex between triphenylboron and ammonia (110); their conductivities were measured. 1:1 Metal amide complexes of trimethyl- and tri-*n*-butylborons were formed by interaction of the trialkylboron and the metal (sodium, potassium) in liquid ammonia; lithium with trimethylboron in ethylamine afforded hydrogen and an unstable product, which decomposed evolving methane (319).

The observation that neither trimethyl- nor triphenylboron reacted with lithium or sodium alkyls or aryls, in ligroin at 120°C. (333), was later attributed to the use in that work of a hydrocarbon solvent (166), because tri-*n*-butylboron formed complexes with phenylmagnesium bromide, diphenylmagnesium, phenyllithium, *n*-butyllithium, and *n*-butylmagnesium bromide, but not with dimethylzinc, when reacted in diethyl ether. These complexes were recognized as ionic, e.g.:

$$[\mathrm{MgBr}]^+(\mathrm{C_6H_5B(C_4H_9)_3})^- \text{ and } [\mathrm{C_6H_5Mg}\cdot((\mathrm{C_2H_5})_2\mathrm{O})_n]^+(\mathrm{C_6H_5B(C_4H_9)_3})^-$$

Lithium tetraphenylboron was obtained by Wittig and Keicher (378) from triphenylboron and phenyllithium. An improved procedure was to prepare the triphenylboron *in situ*, i.e., to react 1 mole of boron trifluoride diethyl etherate with 4 moles of phenyllithium (381). Similarly, boron trifluoride etherate and an excess of phenylmagnesium bromide afforded the complex $[\mathrm{MgBr}][\mathrm{B(C_6H_5)_4}]$.

Lithium tetraphenylboron was monomeric in diethyl ether over a wide range of concentrations (380). With potassium chloride cationic exchange was effected (379). It was faintly acid in water and, in acetic acid solution, could be used for the gravimetric estimation of rubidium, cesium, and ammonium compounds, owing to the quantitative precipitation of the appropriate (insoluble) tetraphenylboron by cation exchange (381). Other tetraphenylborons were also obtained from the lithium compound. The reaction schemes are shown below, together with some of the properties of the compounds,

$$\mathrm{Li[B(C_6H_5)_4]} + \mathrm{(CH_3)_3N\cdot HCl} \xrightarrow{\mathrm{H_2O}} \mathrm{[(CH_3)_3NH][B(C_6H_5)_4]} \xrightarrow{200^\circ\mathrm{C.}}$$
$$\mathrm{B(C_6H_5)_3} + \mathrm{(CH_3)_3N} + \mathrm{C_6H_6}$$

$$\mathrm{Li[B(C_6H_5)_4]} + \mathrm{(C_6H_5)_4PI} \xrightarrow{\mathrm{CH_3OH}} \underset{\text{m. p. 309–311°C.}}{\mathrm{[(C_6H_5)_4P][B(C_6H_5)_4]}} \xleftarrow{\text{2 weeks}}$$

$$\mathrm{B(C_6H_5)_3} + \mathrm{P(C_6H_5)_5}$$

$$\mathrm{Ag[B(C_6H_5)_4]} \xleftarrow[\mathrm{CH_3OH}]{\mathrm{AgNO_3}} \mathrm{Li[B(C_6H_5)_4]} \xrightarrow[\text{several weeks}]{\mathrm{CuBr_2}} \mathrm{[Cu^{(I)}][B(C_6H_5)_4]}$$

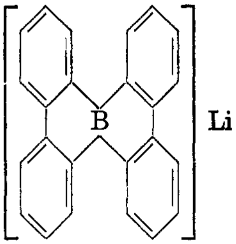
$$\mathrm{Li[B(C_6H_5)_4]} + \mathrm{C_6H_5N_2Cl} \xrightarrow{\mathrm{CH_3OH}} \underset{\text{(explodes when dry)}}{\mathrm{[C_6H_5N_2][B(C_6H_5)_4]}} \xrightarrow[\text{under } \mathrm{H_2O}]{\text{55°C.}}$$

$$\mathrm{C_6H_5C_6H_5} + \mathrm{C_6H_5N{=}NC_6H_5}$$

Sodium tetraphenylboron was obtained from its ammonium analog by reaction with sodium methoxide by heating in methanol under reflux (381). It was also prepared either by the addition of a saturated solution of sodium chloride to the product obtained by the action of boron trifluoride etherate on an excess of phenylmagnesium bromide (153), or (62–68 per cent yield) by the interaction of the latter and sodium fluoroborate (254) [a similar method had been used for $\mathrm{K[B(C_6H_5)_4]}$ (255)]. It is becoming increasingly important as an analytical reagent, particularly for the estimation of potassium, ammonium, rubidium, and cesium (5, 108, 119, 153, 160, 291). Its hydrolysis has already been mentioned (Section IV,C,1).

The specific conductance of potassium tetraphenylboron at 25°C. was 3.3×10^{-8} ohm^{-1} cm.$^{-1}$ (290). Although potassium and ammonium tetraphenylborons were insoluble in water, cyclohexane, and benzene, they were soluble in chloroform (unlike the lithium compound) and the addition of mercury to these solutions afforded diphenylmercury and triphenylboron (279). This was considered to be a free-radical reaction, involving the phenyl radical, particularly because mercury reacted neither with triphenylboron nor with lithium tetraphenylboron in a polar solvent such as water. However, with lithium chloride also present, phenylmercuric chloride was obtained in the latter instance (280).

Aryl (*o*-, *m*-, and *p*-$\mathrm{CH_3C_6H_4}$—, *p*-$\mathrm{(CH_3)_2NC_6H_4}$—) analogs of lithium tetraphenylboron have been obtained from the appropriate aryllithium and triarylboron (377); lithium was replaceable by the tetramethylammonium and sodium ions in the *p*-dimethylaminophenyl example. The lithium tetratolylborons were insoluble in non-polar solvents such as benzene, but were soluble in acetone, ethanol, and water. The compound XXXIII was obtained from *o*,*o*′-dilithio-



XXXIII

biphenyl and boron trifluoride etherate. It very slowly hydrolyzed to give di(*o*-phenylphenyl)boronous acid. The corresponding tetramethylammonium compound melted at 370°C.

The magnetic moment of nickelcyclopentadienyl tetraphenylboron, $[Ni(C_5H_5)_2][B(C_6H_5)_4]$, has been determined (106). A complex cobalt–indene derivative, $[Co(C_9H_7)_2][B(C_6H_5)_4]$, is also known (109).

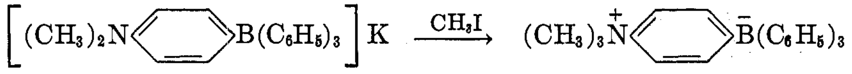
Mixed complexes are also well established. Triphenylboron and lithium phenylacetylide, when warmed in ether and cooled to −80°C., gave the complex $Li[C_6H_5C{\equiv}CB(C_6H_5)_3]$ (381), which with acids generated phenylacetylene and with aqueous iodine gave phenylacetylyl iodide. α-Naphthyllithium and triphenylboron afforded the complex $Li[\alpha\text{-}C_{10}H_7 \cdot B(C_6H_5)_3]$, which with ammonium or potassium salts gave cationic exchange (280). The lithium and ammonium compounds, $M[C_6H_5B(\alpha\text{-}C_{10}H_7)_3]$ and $M[p\text{-}CH_3C_6H_4B(C_6H_5)_3]$, were similarly obtained. Mercury caused fission of the ammonium compounds.

$$NH_4[\alpha\text{-}C_{10}H_7B(C_6H_5)_3] \rightarrow C_{10}H_8 + B(C_6H_5)_3 \cdot NH_3$$

$$NH_4[C_6H_5B(\alpha\text{-}C_{10}H_7)_3] \rightarrow 2C_{10}H_8 + (\alpha\text{-}C_{10}H_7)_2C_6H_5B \cdot NH_3$$

$$NH_4[p\text{-}CH_3C_6H_4B(C_6H_5)_3] \rightarrow CH_3C_6H_5 + B(C_6H_5)_3 \cdot NH_3$$

Triphenylboron and *p*-dimethylaminophenyllithium gave a complex which was converted to the potassium salt, and this on heating with methyl iodide in acetone afforded the "zwitterion" XXXIV, melting at 337–339°C. (377).



XXXIV

Prolonged heating of complexes in aqueous cellosolve resulted in decomposition (281). From sodium or potassium tetraphenylborons, benzene, phenol, and diphenylboronous acid were obtained. Mixed complexes also reacted.

$$K[B(C_6H_5)_4] \rightarrow C_6H_6 + C_6H_5OH + (C_6H_5)_2BOH$$

$$NH_4[\alpha\text{-}C_{10}H_7B(C_6H_5)_3] \rightarrow C_{10}H_8 + B(C_6H_5)_3 \cdot NH_3$$

$$K[C_6H_5B(\alpha\text{-}C_{10}H_7)_3] \rightarrow 3C_{10}H_8 + C_6H_5B(OH)_2$$

Addition of methanolic bromine to potassium tetraphenylboron and subsequent dilution with water gave bromobenzene, phenylboronic acid, and biphenyl; the two latter compounds were also obtained on heating with ferric chloride (281).

Mixed aralkyl complexes were recently obtained from alkyllithium (methyl, ethyl) compounds and triarylborons (phenyl, α-naphthyl) (281). Lithium methyl–triphenylboron decomposed on exposure to air and fresh aqueous solutions gave no visible evidence of reaction with potassium or ammonium salts; prolonged standing, however, caused precipitation of ammonium tetraphenylboron. Lithium ethyltri(α-naphthyl)boron behaved similarly.

Lithium triphenylborohydride, $Li[HB(C_6H_5)_3]$, was obtained by heating triphenylboron with an excess of lithium hydride (382). It crystallized from dioxane associated with 5 moles of the solvent, three of which were removed by heating to 100°C. It was a powerful reducing agent, converting benzoyl chloride to benzyl alcohol.

Lithium, sodium, and potassium triphenylborohydrides were obtained by the three methods shown below, wherein M denotes the metal (379).

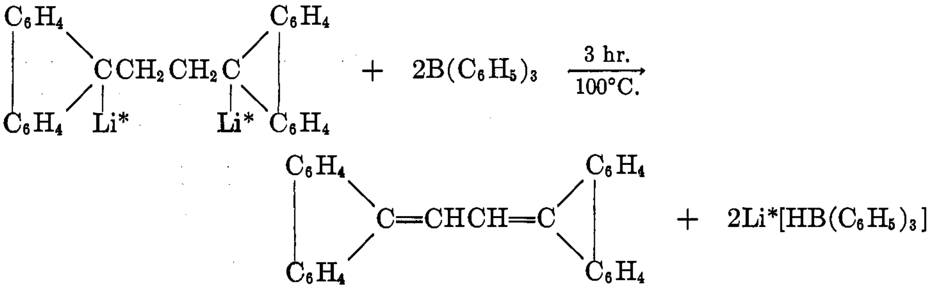
$$2B(C_6H_5)_3 + CH_3ONa + NaH \rightarrow Na[HB(C_6H_5)_3] + Na[CH_3OB(C_6H_5)_3]$$

$$B(C_6H_5)_3 + MH \rightarrow M[HB(C_6H_5)_3]$$

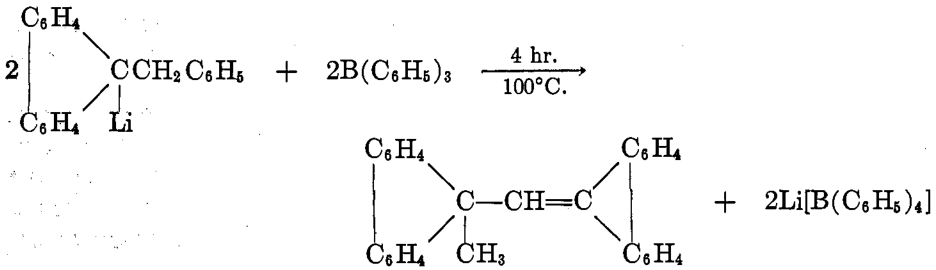
$$2B(C_6H_5)_3M + CH_3OH \rightarrow M[HB(C_6H_5)_3] + M[CH_3OB(C_6H_5)_3]$$

When sodium hydroxide was fused with triphenylboron, sodium triphenylborohydroxide was obtained, which was decomposed by acetic acid (to give sodium acetate) and also by ammonium salts (to give the 1:1 complex between triphenylboron and ammonia), but was unaffected by potassium, rubidium, and cesium salts and reacted with sodium cyanide on heating to give sodium triphenylborocyanide (381). This last compound was also formed by heating sodium cyanide and triphenylboron [the sodium tritolylborocyanides were obtained similarly (377)]; it was unreactive towards acetic acid, but reaction with cesium salts (chloride, perchlorate) produced cationic exchange.

The ease of complex formation shown by triphenylboron has been utilized for the syntheses shown below (379, 382). To this same tendency has also been attributed the observed inhibitor effect of triphenylboron on the tritylsodium-catalyzed polymerization of butadiene (383).



* Or sodium.



Trimethylboron and sodium hydride gave sodium trimethylborohydride (58);

the lithium analog was less stable but was stabilized in the presence of diethyl ether. Uranium borohydride and trimethylboron gave XXXV (m.p. 85°C.; vapor pressure = 8.5 mm. at 50°C.) and XXXVI (m.p. 72–74°C.; vapor pressure = 0.4 mm. at 50°C.) (304). The former was the most volatile uranium compound then known; the structures of both were verified by reactions with water (Section III,C,5) and hydrogen chloride (Section V,H,1).

$$\underset{\text{XXXV}}{U[BH_4]_3[CH_3BH_3]} \qquad \underset{\text{XXXVI}}{U[CH_3BH_3]_4}$$

Lithium aluminum hydride gave lithium methylborotrihydride with trimethylboron (345).

$$B(CH_3)_3 + Li[AlH_4] \rightarrow Li[CH_3BH_3] + (CH_3)_2AlH$$

Propenyllithium and trimethylboron afforded a complex which on hydrolysis gave mixed propenylmethylborons (266).

E. AMINOBORONS AND AMINOBORINES

1. Introduction

The compounds in this section may be divided into three subsections; (*1*) derivatives of triaminoboron, $B(NH_2)_3$; (*2*) derivatives of diaminoborine, $(NH_2)_2BH$; (*3*) derivatives of aminoborine, NH_2BH_2. Only three compounds of type 2 are known; for convenience, these are considered in this introduction,

By heating (dimethylamino)borine with dimethylamine for 10 hr. at 200°C, Wiberg and Bolz (351) obtained bis(dimethylamino)borine (90 per cent), Trimethylamine may also be used (72).

$$(CH_3)_2NBH_2 + (CH_3)_2NH \rightarrow [(CH_3)_2N]_2BH + H_2$$

$$2(CH_3)_2NBH_2 + (CH_3)_3N \rightleftharpoons [(CH_3)_2N]_2BH + BH_3\cdot(CH_3)_3N$$

It has also been prepared by the reversible disproportionation of (dimethylamino)borine (72) and by the reduction by lithium aluminum hydride of bis(dimethylamino)boron chloride (86).

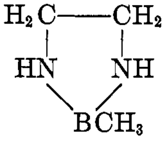
$$3(CH_3)_2NBH_2 \overset{>80°C.}{\rightleftharpoons} [(CH_3)_2N]_2BH + (CH_3)_2NB_2H_5$$

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

Bis(dimethylamino)borine boils at 109°C. (351) and melts at −45°C. (351) or −57.5°C. (72). It is monomeric in the vapor phase (351), and the Trouton constant has been calculated (86, 351). It was hydrolyzed by water (351), affording bis(dimethylamino)boronous acid and hydrogen, but reacted with heavy water to form *N*-deuterodimethylamine (67). Reaction with (dimethylamino)borine gave a copolymer (351). Reactions with diborane (Section V,E,3 and 5) and trimethylamine (Section V,E,2) are discussed later.

Goubeau and Zappel prepared two cyclic compounds (141). By heating (2-aminoethylamino)dimethylboron for 6 hr. at 370°C. the compound XXXVII, m.p. 43.5°C., b.p. (extrapolated) 106°C., was obtained, whereas heating (3-aminopropylamino)dimethylboron at 350°C. gave XXXVIII, b.p. 137°C. (extrapolated), Both the Raman spectra and the action of hydrogen chloride (2 moles of the gas for 1 mole of the compound at room temperature) confirmed their structures.

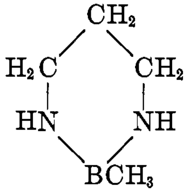
$H_2N(CH_2)_2NHB(CH_3)_2 \rightarrow$



$+ CH_4$

XXXVII

$H_2N(CH_2)_3NHB(CH_3)_2 \rightarrow$



$+ CH_4$

XXXVIII

2. *Triaminoborons*

The first member of this class to have been prepared was tris(dimethylamino)boron, obtained by Wiberg and Schuster (368) by the interaction of excess dimethylamine and boron trichloride in the vapor phase at low temperature. The same reaction has also been carried out using pentane as solvent (86, 316).

$$6(CH_3)_2NH + BCl_3 \rightarrow B[N(CH_3)_2]_3 + 3(CH_3)_2NH\cdot HCl$$

Other methods which have been used for its preparation have been the reaction of bis(dimethylamino)boron chloride and dimethylzinc (86), the pyrolysis of either bis(dimethylamino)borine (72) or (dimethylamino)boron dichloride (44) with trimethylamine, and the reaction of boron tribromide with an excess of dimethylamine (371).

$$[(CH_3)_2N]_2BCl + Zn(CH_3)_2 \rightarrow \underset{\text{(unstable)}}{[(CH_3)_2N]_2BCH_3} \rightarrow \tfrac{1}{2}(CH_3)_2NB(CH_3)_2 + \tfrac{1}{2}B[N(CH_3)_2]_3$$

$$2[(CH_3)_2N]_2BH + (CH_3)_3N \rightarrow B[N(CH_3)_2]_3 + (CH_3)_2NBH_2\cdot(CH_3)_3N$$

$$(CH_3)_2NBCl_2 + (CH_3)_3N \rightarrow 1{:}1\text{ complex} \xrightarrow[\text{24 hr.}]{\text{120°C.}} \tfrac{1}{3}B[N(CH_3)_2]_3 + \tfrac{1}{3}(CH_3)_3N + \tfrac{2}{3}BCl_3\cdot(CH_3)_3N$$

The only other representatives of this class which are known are three tris(arylamino)borons, By the reaction, in equimolecular proportions, of boron trichloride and aniline, a 1:1 addition compound was obtained, which with more aniline (5 moles) gave tris(phenylamino)boron (170). The *p*-tolyl (178) and *p*-anisyl (179) homologs were obtained in like manner.

$$ArNH_2 + BCl_3 \rightarrow 1{:}1 \text{ complex} \xrightarrow{5ArNH_2} B(NArH)_3 + 3ArNH_2 \cdot HCl$$

Absence of association in tris(dimethylamino)boron was indicated by the value of its Trouton constant (368). The heat of hydrolysis in 1 *N* hydrochloric acid was measured; from this data and also the heat of vaporization, the heat of formation and the mean value for the dissociation energy of the boron–nitrogen bonds were calculated (315). This result was compared with a similar calculation for boron–oxygen bonds.

Tris(dimethylamino)boron boils at 147.5°C. and melts at $-16.5°$ to $-16.1°$C. (72) (reference 368 gives a melting point of $-40°$C.). Tris(phenylamino)boron melts at 166–169°C. (170), the *p*-tolyl compound melts at 165–166°C. (178), and the *p*-anisyl analog melts at 124°C. (179).

Tris(dimethylamino)boron readily hydrolyzed in water generating the amine, and hydrogen chloride afforded a trihydrochloride. The reactions with diborane (Section V,E,3 and 5) and boron trichloride (Section V,F,1) are mentioned later.

$$B[N(CH_3)_2]_3 + 3H_2O \rightarrow B(OH)_3 + 3(CH_3)_2NH$$

$$B[N(CH_3)_2]_3 \cdot 3HCl + 3H_2O \rightarrow B(OH)_3 + 3(CH_3)_2NH \cdot HCl$$

Excess dry hydrogen chloride and tris(*p*-tolylamino)boron afforded *N*,*N*′,*N*″-tri-*p*-tolyl-*B*,*B*′,*B*″-trichloroborazole, $(p\text{-}CH_3C_6H_4)_3Cl_3N_3B_3$ (178).

3. Preparation of aminoborines and derivatives

Aminodimethylboron was prepared in quantitative yield by Wiberg, Hertwig, and Bolz (354, 361) by heating trimethylboron and ammonia at 280°C. under a pressure of 20 atm. In a similar way several (dialkylamino)dialkylborons $[(CH_3)_2NB(CH_3)_2, (C_2H_5)_2NB(CH_3)_2, (CH_3)_2NB(C_2H_5)_2,$ and $(C_2H_5)_2NB(C_2H_5)_2]$ have been obtained by heating a trialkylboron with a secondary amine in equimolecular proportions (354).

$$BR_3 + R'_2NH \rightarrow 1{:}1 \text{ complex} \rightarrow R'_2NBR_2 + RH$$

Likewise, heating trimethylboron under pressure with a primary amine [CH_3NH_2 (359); $C_6H_5NH_2$ (360)] afforded alkyl(or aryl)aminodimethylborons, whilst heating under pressure with a primary diamine (141) [$(CH_2NH_2)_2$; $NH_2(CH_2)_3NH_2$] afforded the appropriate (aminoalkylamino)dialkylboron.

$$B(CH_3)_3 + RNH_2 \rightarrow RNHB(CH_3)_2 + CH_4$$

$$B(CH_3)_3 + NH_2(CH_2)_nNH_2 \rightarrow NH_2(CH_2)_nNHB(CH_3)_2 + CH_4$$

Heating diborane under pressure with dimethylamine (71, 353), bis(dimethylamino)borine, or tris(dimethylamino)boron (72) gave (dimethylamino)borine. The deutero analog has been obtained by the first reaction (67).

$$B_2H_6(\text{or } D_6) + 2(CH_3)_2NH(\text{or } D) \rightarrow 2(CH_3)_2NBH_2(\text{or } D_2) + 2H_2(\text{or } D_2)$$

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

$$B_2H_6 + B[N(CH_3)_2]_3 \rightarrow 3(CH_3)_2NBH_2$$

(Dimethylamino)borine has also been obtained by the interaction of an ethereal solution of lithium borohydride and dimethylamine hydrochloride (91 per cent yield) (294), whilst aminodimethylboron has also been prepared from dimethylboron chloride and ammonia (23). The latter method was also used for aminodi-*n*-butylboron, whereas (ethylamino)di-*n*-butylboron was obtained when ethylamine was used (33).

$$LiBH_4 + (CH_3)_2NH\cdot HCl \rightarrow (CH_3)_2NBH_2 + 2H_2 + LiCl$$

$$R_2BCl + 2NH_3 \rightarrow NH_2BR_2 + NH_4Cl$$

$$(C_4H_9)_2BCl + 2C_2H_5NH_2 \rightarrow C_2H_5NHB(C_4H_9)_2 + C_2H_5NH_2\cdot HCl$$

Additional methods for the preparation of (dimethylamino)dimethylboron were by the interaction of dimethylamine with either dimethylboron bromide or tetramethyldiborane (69) and also from bis(dimethylamino)boron chloride (Section V,E,2).

$$(CH_3)_4B_2H_2 + 2(CH_3)_2NH \rightarrow 2(CH_3)_2NB(CH_3)_2 + 2H_2$$

$$(CH_3)_2BBr + (CH_3)_2NH \rightarrow (CH_3)_2NB(CH_3)_2 + HBr$$

Pyrolysis of the 1;1 borine complex with either *N*,*O*-dimethylhydroxylamine, or preferably with methylamine, produced (methylamino)borine (30).

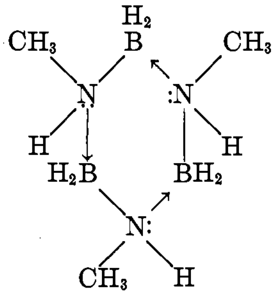
$$BH_3\cdot CH_3NH_2 \xrightarrow{100°C.} CH_3NHBH_2 + H_2$$

Heating the 2;1 complex of borine with *sym*-dimethylhydrazine gave a novel type of boron compound (323).

$$BH_3\cdot CH_3NHNHCH_3\cdot BH_3 \xrightarrow{69°C.} H_2BN(CH_3)N(CH_3)BH_2 + 2H_2$$

4. Physical properties of aminoborines and derivatives

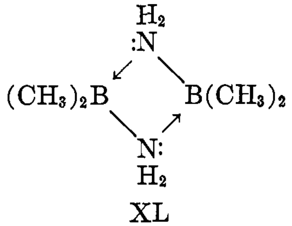
(Methylamino)borine was trimeric (molecular weight in benzene, nitrobenzene, and ammonia) and x-ray diffraction indicated isosterism with 1,3,5-trimethylcyclohexane, presumably indicating the structure shown in formula XXXIX (30).



XXXIX

(Dimethylamino)borine was dimeric at room temperature and atmospheric pressure, but dissociated into the monomer on heating (at 10 mm. 90 per cent was dimeric at 30°C., whilst 90 per cent was monomeric at 105°C.) (353). The infrared spectrum has been described (276) and supported the view (353) that the monomer was isosteric with isobutylene. The entropy of formation of dimeric (dimethylamino)borine has been calculated (313).

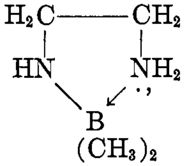
Aminodimethylboron was dimeric (XL) (23, 353) and dissociated into the monomeric form above 30°C. (354). Raman and ultraviolet spectra (23) have been studied and the dipole moment (21) has been measured.



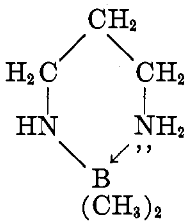
XL

The Raman and ultraviolet spectra of (methylamino)- and (dimethylamino)-dimethylborons (23) have also been studied and force constants were calculated. These indicated boron–nitrogen double-bond character ($\mathrm{B} \Leftarrow \mathrm{N}$) in the monomeric forms. The monomethylamino compound dimerized on cooling (359), while the dimethylamino compound was monomeric in the vapor state (69). The dipole moment (20) and the Trouton constant (69, 86) of the (dimethylamino)dimethylboron have been measured.

The Raman spectra of the (aminoalkylamino)dialkylborons XLI and XLII, as well as the reactions with hydrogen chloride (see next subsection), supported the cyclic structures; the Trouton constants indicated unimolecularity (141).



XLI



XLII

Available physical constants are shown in table 20.

5. Chemical properties of aminoborines and derivatives

Pyrolysis of (methylamino)borine gave *N,N′,N″*-trimethylborazole, but hydrolysis was slow in the cold (30).

$$(CH_3NHBH_2)_3 \xrightarrow{200°\text{C.}} 3H_2 + (CH_3NBH)_3$$

(Dimethylamino)borine disproportionated slowly (72). It appears that the reaction is encouraged by the addition of base, for heating with dimethylamine afforded bis(dimethylamino)borine (351) and heating with trimethylamine gave

TABLE 20

Physical constants of aminoborines and derivatives

Compound	Boiling Point	Melting Point	References
	°C.	°C.	
CH_3NHBH_2		74.5–75	(30, 71)
$(CH_3)_2NBH_2$	76–77	73	(276, 294, 313, 353)
$(CH_3)_2NBD_2$		74.3–74.5	(67)
$(C_2H_5)_2NBH_2$	Sublimes 45–50		(353)
$H_2NB(CH_3)_2$		9 (dimer)	(21, 23, 354, 361)
$CH_3NHB(CH_3)_2$	38.3		(23, 359)
$C_6H_5NHB(CH_3)_2$	184*		(360)
$(CH_3)_2NB(CH_3)_2$	63*		(21, 23, 69, 86, 354)
$(C_2H_5)_2NB(CH_3)_2$	98*		(354)
$(CH_3)_2NB(C_2H_5)_2$	123*		(354)
$(C_2H_5)_2NB(C_2H_5)_2$	161*		(354)
$H_2NB(n\text{-}C_4H_9)_2$	100/0.01 mm.		(33)
$C_2H_5NHB(n\text{-}C_4H_9)_2$	100/0.02 mm.		(33)
XLI	106*	43.5	(141)
XLII	137*		(141)

* These boiling points are the extrapolated values.

this compound and also some tris(dimethylamino)boron (72) (Section V,E,1), The reaction with bis(dimethylamino)borine has been mentioned (Section V,E,1). The dimer reacted neither with hydrogen bromide nor with water, whereas the monomer reacted with both reagents; the ethyl analog behaved similarly (353). Diborane reacted with (dimethylamino)borine to give (dimethylamino)diborane (71); a deutero analog was similarly obtained (67). Sodium hydride at 110°C. afforded sodium borohydride, but lithium hydride did not react (72).

$$\underset{\text{Monomer}}{(CH_3)_2NBH_2} + 2HBr \xrightarrow{100°C.} (CH_3)_2NBBr_2 + 2H_2$$

$$\underset{\text{Monomer}}{(CH_3)_2NBH_2} + 3H_2O \rightarrow B(OH)_3 + (CH_3)_2NH + 2H_2$$

$$2(CH_3)_2NBH_2(\text{or } D_2) + B_2H_6(\text{or } D_6) \rightarrow 2(CH_3)_2NB_2H_5(\text{or } D_5)$$

Hydrogen chloride reacted with aminodimethylboron at 20°C. to give the 1:1 complex of dimethylboron chloride with ammonia, whilst pyrolysis (320–340°C. at 20 atm. pressure) gave *B,B′,B″*-trimethylborazole (361).

$$NH_2B(CH_3)_2 + HCl \rightarrow (CH_3)_2BCl\cdot NH_3$$

$$NH_2B(CH_3)_2 \rightarrow \tfrac{1}{3}(NHBCH_3)_3 + CH_4$$

The pyrolysis and the reaction with hydrogen chloride were similar in the case of (methylamino)dimethylboron (359).

$$CH_3NHB(CH_3)_2 + HCl \rightarrow (CH_3)_2BCl\cdot CH_3NH_2$$

$$CH_3NHB(CH_3)_2 \xrightarrow{450°C.} \tfrac{1}{3}(CH_3NBCH_3)_3 + CH_4$$

(Dimethylamino)dimethylboron gave a 1;1 complex (m.p. 51–52°C.) with methanol (86) (Section IV,D,1). Boron trifluoride at very low temperature gave a 1;1 complex which dissociated at −46°C.; at 0°C. dimethylboron fluoride and (dimethylamino)boron difluoride were obtained (69) (Section V,F,1),

The cyclic compounds XLI and XLII reacted with 1 mole of hydrogen chloride at room temperature (141).

F. AMINOBORON DIHALIDES AND DIAMINOBORON HALIDES

1, *Preparation*

By the interaction of dimethylamine with boron trifluoride diethyl etherate a 1;1 complex was obtained, which on heating gave (dimethylamino)boron difluoride (65). It has also been obtained from boron trifluoride and either (dimethylamino)dimethylboron at low temperatures (−196° to −78°C.), when a 1:1 complex formed initially disproportionated at 0°C. (69), or bis(dimethylamino)boron fluoride.

$$(CH_3)_2NH + BF_3\cdot(C_2H_5)_2O \rightarrow (CH_3)_2NH\cdot BF_3 \rightarrow$$

$$(CH_3)_2NBF_2 + (CH_3)_3N\cdot BF_3 + (CH_3)_4NBF_4$$

$$(CH_3)_2NB(CH_3)_2 + BF_3 \rightarrow 1:1 \text{ complex} \rightarrow (CH_3)_2BF + (CH_3)_2NBF_2$$

$$[(CH_3)_2N]_2BF + BF_3 \rightarrow 2(CH_3)_2NBF_2$$

Bis(dimethylamino)boron fluoride was obtained by heating (dimethylamino)-boron difluoride with trimethylamine (69).

$$2(CH_3)_2NBF_2 + (CH_3)_3N \rightarrow [(CH_3)_2N]_2BF + BF_3\cdot(CH_3)_3N$$

Michaelis and Luxembourg (243), who were the first to obtain members of this class, prepared several (dialkylamino)boron dichlorides (ethyl, *n*-propyl, isobutyl) by the interaction of boron trichloride with the appropriate secondary amine. The same reaction, but using dimethylamine and with both components in the vapor phase, afforded a mixture of products (375). It was noticed that the nature of the products obtained from such a reaction depended upon the relative proportions of the reagents used and it was found that the reaction was a stepwise one, affording (dimethylamino)boron dichloride, bis(dimethylamino)boron chloride, and tris(dimethylamino)boron (368) (Section V,E,2).

$$BCl_3 \xrightarrow{(CH_3)_2NH} (CH_3)_2NBCl_2 \xrightarrow{(CH_3)_2NH}$$

$$[(CH_3)_2N]_2BCl \xrightarrow{(CH_3)_2NH} B[N(CH_3)_2]_3$$

The yields, however, were poor (e.g., 35 per cent for $(CH_3)_2NBCl_2$ (44)), because the hydrogen chloride that was formed reacted both with the amine and with the products (see Section V,E,2 and Section V,F,3). The monochloride has also been prepared in the liquid phase with pentane as solvent (86). A much improved result was obtained if the undesirable hydrogen chloride was removed by carrying out the reaction in the presence of triethylamine. Thus, when the 1:1 complex of dimethylamine and boron trichloride in benzene was added to triethylamine, the dichloride (72 per cent) was obtained (65); similarly, interaction of the dichloride, dimethylamine, and triethylamine in benzene gave the monochloride (316).

$$BCl_3 \cdot (CH_3)_2NH + (C_2H_5)_3N \rightarrow (CH_3)_2NBCl_2 + (C_2H_5)_3N \cdot HCl$$

$$(CH_3)_2NBCl_2 + (C_2H_5)_3N + (CH_3)_2NH \rightarrow [(CH_3)_2N]_2BCl + (C_2H_5)_3N \cdot HCl$$

(Dimethylamino)boron dichloride has also been obtained by the mutual replacement reaction between tris(dimethylamino)boron and boron trichloride (139).

$$B[N(CH_3)_2]_3 + 2BCl_3 \rightarrow 3(CH_3)_2NBCl_2$$

Although an early suggestion was made that the interaction of amines (primary as well as secondary) and boron tribromide was similarly stepwise, no information (except analyses) was given about the products (165). More recently, however, the interaction of 2 moles of a secondary amine (methyl, ethyl) and 1 mole of boron tribromide has been shown to give the appropriate (dialkylamino)boron dibromide (353).

$$BBr_3 + 2R_2NH \rightarrow R_2NBBr_2 + R_2NH \cdot HBr$$

When a larger proportion of the amine was used, the monobromide was obtained (371). The addition of triethylamine to remove formed hydrogen halide has also been employed in the preparation of (dimethylamino)boron dibromide (139),

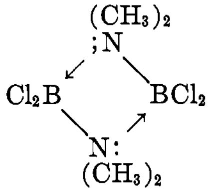
$$BBr_3 + (CH_3)_2NH \rightarrow 1:1\ \text{Complex} \xrightarrow{(C_2H_5)_3N} (CH_3)_2NBBr_2 + (C_2H_5)_3N \cdot HBr$$

The dibromide has also been prepared from hydrogen bromide and (dimethylamino)borine (353) (Section V,E,5).

2. Physical properties

(Dimethylamino)boron difluoride was originally stated to be dimeric (65), but later evidence pointed to a monomer (69).

(Dimethylamino)boron dichloride was shown to be a monomer (vapor density; Trouton constant; parachor) when first formed, but dimerized either after standing for several days or more quickly when heated in a vacuum (cryoscopic in benzene) (44, 65, 368, 369). The monomer was re-formed when the dimer was



XLIII

TABLE 21

Physical constants of aminoboron dihalides and diaminoboron halides

Compound	Boiling Point	Melting Point	References
	°C.	*°C.*	
$[(CH_3)_2N]_2BF$		−44.3	(69)
$(CH_3)_2NBF_2$		167–169	(65, 69).
$[(CH_3)_2N]_2BCl$	146.1	54	(81, 316, 368, 369)
$(CH_3)_2NBCl_2$ (monomer)	51–53/90 mm. ($d_t = 1.1629 - 0.001177t$)	−43 to −46	(44, 65, 139, 316, 368, 369)
$(CH_3)_2NBCl_2$ (dimer)		42.5	
$(C_2H_5)_2NBCl_2$	148 ($d_t = 1.0796 - 0.001161t$)	−23 to −25.5	(139, 243, 262, 354)
$(n\text{-}C_3H_7)_2NBCl_2$	99/45 mm.		(243)
$(i\text{-}C_4H_9)_2NBCl_2$	92–95/17 mm.		(243)
$(CH_3)_2NBBr_2$ (monomer)	163	−21.5	(139, 359)
$(CH_3)_2NBBr_2$ (dimer)		152	
$(C_2H_5)_2NBBr_2$	194	−7.5	(354)

sublimed (65). Structure XLIII was proposed (369) for the dimer and has received confirmation from the observed low dipole moment (44), characteristic of a symmetrical molecule. Raman spectra on monomeric (dimethylamino)boron and (diethylamino)boron dichlorides and on (dimethylamino)boron dibromide indicated nitrogen–boron double-bond character (139).

Bis(dimethylamino)boron chloride was shown to be monomeric (vapor density; Trouton constant) (86, 368). The heats of hydrolysis both of this compound and also of the dichloride, in hydrochloric acid, have been determined (316), and the data have been used to calculate the heats of formation of the two compounds in the liquid state; bond dissociation energies were derived. The results were interpreted (molecular orbital treatment) in terms of "back-coordination" from both nitrogen and chlorine to boron, and the nitrogen atom was considered to be three times more powerful in this effect than the chlorine.

The dibromide, like the dichloride, exists in both monomeric and dimeric forms (353).

Available physical constants are shown in table 21.

3. Chemical properties

Bis(dimethylamino)boron fluoride was unstable; its reaction with boron trifluoride has been mentioned (69) (Section V,F,1).

(Dimethylamino)boron difluoride showed little tendency to disproportionate spontaneously, but this could be induced by the addition of trimethylamine (69) (Section V,F,1). Pyrolysis did not give *N,N′,N″*-trimethyl-*B,B′,B″*-trifluoroborazole, $(CH_3NBF)_3$ (*cf.* 362), but a polymeric material of the same composition.

$$(CH_3)_2NBF_2 \rightarrow BF_3\cdot(CH_3)_3N + \frac{1}{n}(CH_3NBF)_n + (BN)$$

Bis(dimethylamino)boron chloride hydrolyzed readily and formed with hydrogen chloride a 1:2 complex which was itself also readily hydrolyzed (368), The reactions (86) with dimethylzinc (Section V,E,2) and with lithium aluminum hydride (Section V,E,1) have already been described.

$$[(CH_3)_2N]_2BCl + 3H_2O \rightarrow B(OH)_3 + (CH_3)_2NH \cdot HCl + (CH_3)_2NH$$

$$[(CH_3)_2N]_2BCl \cdot 2HCl + 3H_2O \rightarrow B(OH)_3 + 2(CH_3)_2NH \cdot HCl + HCl$$

Monomeric (dimethylamino)boron dichloride was also readily hydrolyzed and formed with hydrogen chloride a 1;1 complex (m.p. 135–139°C. (44)) which was itself also readily hydrolyzed (368). The dimeric form, however, was insoluble in water, acids, and alkalis (369) and did not react with boron trifluoride below 120°C. (44).

$$(CH_3)_2NBCl_2 + 3H_2O \rightarrow B(OH)_3 + (CH_3)_2NH \cdot HCl + HCl$$

$$(CH_3)_2NBCl_2 \cdot HCl + 3H_2O \rightarrow B(OH)_3 + (CH_3)_2NH \cdot HCl + 2HCl$$

The 1:1 hydrogen chloride adduct was considered to be a coordination compound (XLIV) (139), contrary to an earlier suggestion that it was salt-like (XLV) (44), because of its low conductivity in chloroform.

$$\underset{\text{XLIV}}{(CH_3)_2HN;\rightarrow BCl_3} \qquad \underset{\text{XLV}}{[(CH_3)_2NHBCl_2]^+Cl^-}$$

Trimethylamine gave a unimolecular 1:1 complex (m.p. 76–77°C. with decomposition) with monomeric (dimethylamino)boron dichloride, which disproportionated on pyrolysis (Section V,E,2) and from which the (dimethylamino)boron dichloride was displaced, as shown by infrared analysis, by the more powerful Lewis acids boron trifluoride and trimethylboron (44). When the dimer and trimethylamine were heated at 140°C., disproportionation to tris(dimethylamino)boron was also induced.

$$(CH_3)_2NBCl_2 \cdot (CH_3)_3N + BY_3 \rightarrow BY_3 \cdot (CH_3)_3N + (CH_3)_2NBCl_2$$

$Y = F$ or CH_3.

(Diethylamino)boron dichloride reacted similarly with both hydrogen chloride and trimethylamine; the 1;1 complex with the latter melted at 20°C. (262).

G, THE COMPOUNDS R(R′R″N)BX

(Methylamino)methylboron chloride has been obtained by Wiberg and Hertwig (359) by the action of hydrogen chloride on hexamethylborazole at 150°C. On cooling it dimerized.

$$B_3N_3(CH_3)_6 + 3HCl \rightarrow 3CH_3(CH_3NH)BCl$$

Hydrogen chloride at 150°C. converted it to the methylboron dichloride 1;1 complex with methylamine, whereas pyrolysis afforded *N*,*N′*,*N″*-trimethyl-*B*,*B′*,*B″*-trichloroborazole.

$$CH_3(CH_3NH)BCl + HCl \rightarrow CH_3BCl_2 \cdot CH_3NH_2$$

$$CH_3(CH_3NH)BCl \xrightarrow{400\text{–}500^\circ C.} \tfrac{1}{3}(CH_3NBCl)_3 + CH_4$$

By heating methylamine and dimethylboron fluoride a fluorinated borazole was obtained (362). One of the intermediates that was isolated was (methylamino)methylboron fluoride, b.p. 46°C. Similarly, using dimethylamine, an analogous compound, b.p. 58°C., was isolated.

$$(CH_3)_2BF + CH_3NH_2 \rightarrow \underset{\text{(m.p. 68°C.)}}{1:1 \text{ complex}} \xrightarrow{-CH_4}$$

$$CH_3(CH_3NH)BF \xrightarrow{-CH_4} \tfrac{1}{3}(CH_3NBF)_3$$

$$(CH_3)_2BF + (CH_3)_2NH \rightarrow \underset{\text{(m.p. 21°C.)}}{1:1 \text{ complex}} \xrightarrow{-CH_4} CH_3[(CH_3)_2N]BF$$

H. PREPARATION OF ALKYL(AND ARYL)BORON DIHALIDES AND DIALKYL(AND DIARYL)BORON HALIDES

1. Introduction

The most important methods have depended essentially on one of the following three procedures: (*1*) the interaction of organometallic compounds with boron halides or substituted boron halides; (*2*) the reaction of trialkylborons or aminodialkylborons with halogenating agents; and (*3*) the reaction of boronic or boronous acids or derivatives (anhydrides, esters) with boron halides. Other methods are for convenience considered in this introduction.

n-Butylboron difluoride has been obtained by the disproportionation of *n*-butyl *n*-butylfluoroboronite (40) (Section IV,G). Reaction between diborane and tetrafluoroethylene afforded a mixture of diethylboron fluoride, ethylboron difluoride, and boron trifluoride, as well as polymeric fluorocarbons (327). The two first-named compounds were isolated from the mixture by the addition of trimethylamine and subsequent action of boron trifluoride on the separated complexes.

$$(C_2H_5)_nBF_{3-n} + (CH_3)_3N \rightarrow 1:1 \text{ complex} \xrightarrow{BF_3}$$

$$BF_3 \cdot N(CH_3)_3 + (C_2H_5)_nBF_{3-n}$$

$n = 1$ or 2.

A mixture of di-*n*-butylboron chloride and *n*-butylboron dichloride was obtained by the interaction between aluminum chloride (1 mole) and *n*-butylboronic anhydride ($\frac{1}{3}$ mole of trimer) (226); the anhydride did not react with hydrogen chloride, thionyl chloride, phosphorus trichloride, silicon tetrachloride, or silicon tetrabromide.

The reaction of hydrogen chloride with certain uranium borohydrides (Section V,D,4) in producing methylboron dichloride was considered to be evidence for their structures (304).

$$U[BH_4]_3[CH_3BH_3] + 6HCl \rightarrow UCl_4 + 6H_2 + \tfrac{3}{2}B_2H_6 + CH_3BCl_2$$

$$U[CH_3BH_3]_4 + 12HCl \rightarrow UCl_4 + 12H_2 + 4CH_3BCl_2$$

Phenylboron dichloride (70 per cent) was prepared by passing a mixture of benzene and boron trichloride over palladium black at 500–600°C. (264),

$$C_6H_6 + BCl_3 \rightarrow C_6H_5BCl_2 + HCl$$

Di-*n*-propylboron iodide, when reacted with the appropriate antimony trihalide at 100°C., gave the corresponding bromide and chloride, but the method was not successful for the fluoride (101),

$$3(n\text{-}C_3H_7)_2BI + SbX_3 \rightarrow 3(n\text{-}C_3H_7)_2BX + SbI_3$$

2. Organometallic compounds

Phenylboron difluoride, together with some diphenylboron fluoride, has been obtained by the addition of boron trifluoride in diethyl ether to phenylmagnesium bromide and subsequent direct distillation from the reaction mixture (186, 191); the *p*-tolylboron difluoride was similarly obtained (186). This experiment was difficult to reproduce (335), but a 20 per cent yield of phenylboron difluoride has been reported (131). By equimolecular interaction of boron trifluoride and diphenylzinc, phenylboron difluoride (68 per cent) was obtained. A similar method had earlier been used for the preparation of the methyl homolog (354), but in that case complete exchange took place, whereas in the phenyl example only half-exchange was possible (see the equations). By using a greater proportion of dimethylzinc, dimethylboron fluoride was obtained (354), but the use of 1 mole of phenylboron difluoride and 1 mole of *o*-tolylzinc gave phenyldi(*o*-tolyl)-boron and not the monofluoride (335),

$$Zn(C_6H_5)_2 + BF_3 \rightarrow C_6H_5ZnF + C_6H_5BF_2$$

$$qZn(CH_3)_2 + 2BF_3 \rightarrow qZnF_2 + 2(CH_3)_qBF_{3-q}$$

$q = 1$ or 2.

The use of the dimethylzinc method was stated to give quantitative yields of methylboron dichloride and dimethylboron chloride, with boron trichloride (352, 367); this could not be confirmed (22).

Michaelis and Becker (239) obtained the first member of this class with their preparation of phenylboron dichloride from diphenylmercury and boron trichloride. Other aryl [p-$CH_3C_6H_4$— (240); o-$CH_3C_6H_4$—, α- and β-$C_{10}H_7$—, *o*- and p-$CH_3OC_6H_4$—, *o*- and p-$C_2H_5OC_6H_4$— (241); and *o*-, *m*- and *p*-xylyl (238)] homologs were similarly prepared.

$$HgAr_2 + BCl_3 \rightarrow ArHgCl + ArBCl_2$$

The method was not very successful for the monochlorides, but some diphenylboron chloride was obtained from the dichloride and diphenylmercury after 24 hr. at 300–320°C. (238–241).

$$C_6H_5BCl_2 + (C_6H_5)_2Hg \rightarrow C_6H_5HgCl + (C_6H_5)_2BCl$$

In the aliphatic field the method has been successful with the *trans*-2-chlorovinyl compounds (34). Heating 2-chlorovinylmercuric chloride and boron trichloride, in kerosene in a sealed tube, for 2 hr. at 50°C. (or letting the mixture stand for 12 hr. at room temperature) gave the dichloride, whilst bis(2-chlorovinyl)-mercury and boron trichloride, on heating under reflux in benzene, gave the monochloride.

The interaction of a trialkylaluminum and boron trichloride has been recommended (352).

Several arylboron dibromides (phenyl, *p*-tolyl, *m*-xylyl) have been prepared from boron tribromide and the appropriate diarylmercury (244). Diphenylboron bromide has also been obtained by this method.

Trimethylaluminum with boron tribromide gave excellent yields of methylboron dibromide (352).

$$\mathrm{Al(CH_3)_3 + 3BBr_3 \rightarrow 3CH_3BBr_2 + AlBr_3}$$

3, Trialkylborons and aminodialkylborons

By reaction between boron trifluoride and (dimethylamino)dimethylboron, dimethylboron fluoride was obtained (69) (Section V,F,1).

Trimethylboron with boron trichloride gave methylboron dichloride (22, 352), contrary to an earlier statement that there was no reaction (367).

$$\mathrm{B(CH_3)_3 + 2BCl_3 \rightarrow 3CH_3BCl_2}$$

Dialkylboron chlorides have been prepared in high yields by the reaction of hydrogen chloride with trialkylborons. For the methyl and ethyl homologs, reaction at 150–180°C. for 1 hr. was recommended (352), whereas the *n*-butyl compound was prepared by reaction at 110°C. (33). In the last-named reaction, when aluminum chloride was present, *n*-butylboron dichloride was obtained instead and this was also prepared from the monochloride by employing the same reagents,

$$\mathrm{BR_3 + HCl \xrightarrow{-RH} R_2BCl \xrightarrow{HCl,\,AlCl_3} RBCl_2 + RH}$$

By interaction of dimeric (methylamino)dimethylboron with excess hydrogen chloride at 20°C. for 2 hr., dimethylboron chloride was obtained (359),

$$\mathrm{(CH_3)_2BNHCH_3 + HCl \rightarrow (CH_3)_2BCl\cdot NH_2CH_3 \overset{HCl}{\rightleftharpoons} (CH_3)_2BCl + CH_3NH_2\cdot HCl}$$

The first example of the use of the hydrogen halide–trialkylboron method was the preparation of di-*n*-butylboron bromide [$\mathrm{B(}n\text{-}\mathrm{C_4H_9)_3}$ and HBr (166)]; the methyl and ethyl homologs have been obtained similarly (352). By the action of bromine on tri-*n*-butylboron, di-*n*-butylboron bromide was obtained, with *n*-butylboron dibromide as a by-product (166),

$$(n\text{-}\mathrm{C_4H_9})_3\mathrm{B} + \mathrm{Br_2} \rightarrow (n\text{-}\mathrm{C_4H_9})_2\mathrm{BBr} + n\text{-}\mathrm{C_4H_9Br}$$

Hydrogen iodide with trimethylboron afforded dimethylboron iodide when heated at 150–180°C. in a sealed tube (352); the *n*-butyl homolog has been obtained by a similar method, the reaction being complete at room temperature

(318). Despite earlier statements that the trialkylborons and iodine do not react (113, 166), tri-*n*-propylboron and iodine after 3 hr. at 155–165°C. afforded di-*n*-propylboron iodide (69 per cent), the *n*-propyl iodide being removed by distillation as quickly as it formed (220),

4. Boronic and boronous acids and derivatives

By the reaction of boron trifluoride with the anhydrides of either methylboronic or dimethylboronous acids, Burg (66) obtained in 60–80 per cent yields methylboron difluoride and dimethylboron fluoride, respectively. Other alkylboron difluorides have been obtained by the former procedure (226).

$$(CH_3BO)_3 + 2BF_3 \rightarrow 3CH_3BF_2 + B_2O_3$$

$$3[(CH_3)_2B]_2O + 2BF_3 \rightarrow 6(CH_3)_2BF + B_2O_3$$

A corresponding reaction for dichlorides using boron trichloride has been reported but no details are yet available; a similar suggestion has been made with respect to boronic acids and the trichloride (226).

Interaction of boron trifluoride with several alkylboronic acids gave the appropriate alkylboron difluorides (40–50 per cent). No doubt the initial function of the boron trifluoride was to dehydrate the acid (226),

n-Butylboron difluoride was prepared (81 per cent) by saturating di-*n*-butyl *n*-butylboronate with boron trifluoride (39).

$$n\text{-}C_4H_9B(OC_4H_9\text{-}n)_2 + 2BF_3 \rightarrow n\text{-}C_4H_9BF_2 + 2n\text{-}C_4H_9OBF_2$$

Phenylboron dichloride was similarly prepared from several esters (1 mole) of phenylboronic acid and boron trichloride (2 moles), the accompanying dichloroboronite being either unstable (if secondary alkyl), or deliberately decomposed by the addition of a trace of ferric chloride (Section III,G,3) to facilitate separation (39).

I, PROPERTIES OF ALKYL(AND ARYL)BORON DIHALIDES AND DIALKYL(AND DIARYL)BORON HALIDES

1. Physical properties

Methylboron difluoride and dimethylboron fluoride were shown to be unimolecular in the vapor phase and the Trouton constants were obtained (66). Bauer and Hastings (18) have investigated these two compounds by the electron diffraction method and have concluded that the molecules are planar and that in the series $B(CH_3)_3$ (216), $(CH_3)_2BF$, CH_3BF_2, and BF_3 (216) the same configurations and essentially the same interatomic distances are maintained. The relative partial charges on combined hydrogen in the same two compounds have been calculated (292). Ethylboron difluoride was shown to be unimolecular (327).

Dimethyl- (352), diethyl- (352), and di-*n*-propyl- (101) boron chlorides were unimolecular in the vapor phase. The Trouton constant for the *n*-propyl compound has been obtained (101). Methylboron dichloride (vapor density) (352) and phenylboron dichloride (cryoscopic in chloroform) (264) have been shown

TABLE 22

Physical constants of dialkyl(and diaryl)boron halides

R in R_2BX	X in R_2BX	Boiling Point	Melting Point	d_4^{20}	n_D^{20}	References
		°C.	°C.			
CH_3—	F	−42.2 (extrapolated)	−147.3			(18, 66, 69, 352, 362)
CH_3—	Cl	4.9				(22, 352, 359, 367)
CH_3—	Br	31.3	−130			(267, 352, 364)
CH_3—	I	68.8	−107.5			(352)
C_2H_5—	F					(327)
C_2H_5—	Cl	78.5	−84.6			(352)
C_2H_5—	Br	101	−81.0			(352)
$n\text{-}C_3H_7$—	Cl	127	<−125	0.848		(101)
$n\text{-}C_3H_7$—	Br	145	−94	1.095		(101)
$n\text{-}C_3H_7$—	I	172-176	−87	1.521		(101, 220)
$n\text{-}C_4H_9$—	Cl	173				(11, 33, 318)
$n\text{-}C_4H_9$—	Br	44/4 mm.				(166, 318)
$ClCH{=}CH$—	Cl	80-82		1.2759	1.5452	(34)
C_6H_5—	F					(191)
C_6H_5—	Cl	271-272				(241)
C_6H_5—	Br	150-160/8 mm.	24-25			(244)

TABLE 23

Physical constants of alkyl(and aryl)boron dihalides

R in RBX_2	X in RBX_2	Boiling Point	Melting Point	d_4^{25}	References
		°C.	°C.		
CH_3—	F	−62.3 (extrapolated)	−130.4		(18, 66, 352, 362)
CH_3—	Cl	11.1	−127		(304, 352, 367)
CH_3—	Br	60	−110.6		(352, 364)
C_2H_5—	F	−25	−101		(327)
$n\text{-}C_4H_9$—*	F*	36.3-36.5/742 mm.		0.8510	(39, 226)
$n\text{-}C_4H_9$—	Br	107.9			(33)
$n\text{-}C_5H_{11}$—	F	64.5-64.6/743 mm.		0.8550	(226)
$s\text{-}C_5H_{11}$—	F	57.9-58/742 mm.		0.8406	(226)
$t\text{-}C_5H_{11}$—	F	47.7-47.9/748 mm.		0.8448	(226)
$n\text{-}C_6H_{13}$—	F	91.9-92.0/744 mm.		0.8591	(226)
Cyclohexyl	F	95.7-96.0/743 mm.		0.9734	(226)
$ClCH{=}CH$—	Cl	98-100		1.3045†	(34)
C_6H_5—	F	82-85/730 mm.			(131, 186, 191, 335)
C_6H_5—‡	Cl‡	57/8 mm.	7	1.194†	(39, 87, 239, 264)
C_6H_5—	Br	99-101/20 mm.	32-34		(244)
$p\text{-}CH_3C_6H_4$—	F	95-97			(186)
$p\text{-}CH_3C_6H_4$—	Cl		27		(240)
$p\text{-}CH_3C_6H_4$—	Br	145/25 mm.	44-45		(244)
$o\text{-}CH_3C_6H_4$—	Cl	193	6		(241)
$o\text{-}CH_3OC_6H_4$—	Cl				(241)
$p\text{-}CH_3OC_6H_4$—	Cl	182/170 mm.	30		(241)
$o\text{-}C_2H_5OC_6H_4$—	Cl				(241)
$p\text{-}C_2H_5OC_6H_4$—	Cl	220/400 mm.	2		(241)
2,3-$(CH_3)_2C_6H_3$—	Cl	212	0		(238)
3,4-$(CH_3)_2C_6H_3$—	Cl	205			(238)
3,5-$(CH_3)_2C_6H_3$—	Cl	218			(238)
3,5-$(CH_3)_2C_6H_3$—§	Br§	125/15 mm.			(244)
$\alpha\text{-}C_{10}H_7$—	Cl	164/25 mm.			(241)
$\beta\text{-}C_{10}H_7$—	Cl		116		(241)

* $n_D^{20} = 1.3290$. † At 20°C. ‡ $n_D^{20} = 1.5385$. § $d^{15} = 1.57$.

to be unimolecular. By electron diffraction investigation phenylboron dichloride was shown to be planar and the bond lengths and angles were calculated (87). The heats of hydrolysis of di-*n*-butylboron chloride, bromide, and iodide and the heats of reactions of tri-*n*-butylboron with hydrogen bromide [giving $(n\text{-}C_4H_9)_2BBr$] and hydrogen iodide [giving $(n\text{-}C_4H_9)_2BI$] have been measured (318).

Methylboron dibromide, dimethylboron bromide and iodide (364), and di-*n*-propylboron bromide and iodide (101) were all shown to be unimolecular in the vapor phase. The Trouton constants for the *n*-propyl compounds were obtained (101). Available physical constants are shown in tables 22 and 23.

2, *Chemical properties*

The *sec*- and *tert*-amylboron difluorides (226) and di-*n*-propylboron chloride (220) have all been reported as spontaneously flammable,

Halogen in the dialkyl(and diaryl)boron halides and alkyl(and aryl)boron dihalides is extremely easily replaceable. The majority of the reactions which demonstrate halogen replacement have already been discussed [hydrolysis in Section III,C,4, Section IV,B,1, and Section IV,C,1; alcoholysis in Section III,C,4, Section IV,D,4, and Section IV,G; reaction with ammonia and amines in Section V,E,3]. It has been pointed out (40) that these compounds possess general similarity to the boron halides; apart from the above-mentioned reactions, several others also demonstrate this analogy [reactions with organometallic compounds (Section V,B; Section V,H,2); replacement by halogen (Section V,H,1); and a mutual replacement reaction (Section IV,G)].

Other halogen replacement reactions are demonstrated by substitutions by trialkylsilyloxy (364), phosphine (74, 117), and methyl (11) groups.

$$CH_3BBr_2 + 2(C_2H_5)_3SiONa \rightarrow CH_3B[OSi(C_2H_5)_3]_2 + 2NaBr$$

$$(CH_3)_2BBr + [(CH_3)_3Si]_2O \rightarrow (CH_3)_2BOSi(CH_3)_3 + (CH_3)_3SiBr$$

$$(CH_3)_2BBr + PH_3 \xrightarrow{(C_2H_5)_3N} (CH_3)_2BPH_2 + (C_2H_5)_3N\cdot HBr$$

$$(n\text{-}C_4H_9)_2BCl + (C_2H_5)_3N \rightarrow 1;1 \text{ complex} \xrightarrow{PH_3} (n\text{-}C_4H_9)_2BPH_2 + (C_2H_5)_3N\cdot HCl$$

$$n\text{-}C_4H_9BCl_2 + (C_2H_5)_3N \rightarrow 1;1 \text{ complex} \xrightarrow{PH_3} n\text{-}C_4H_9B(PH_2)_2$$

$$(n\text{-}C_4H_9)_2BCl + NaH_2P \xrightarrow{\text{liquid } SO_2} (n\text{-}C_4H_9)_2BPH_2 + NaCl$$

$$n\text{-}C_4H_9BCl_2 + 2NaH_2P \xrightarrow{\text{liquid } SO_2} n\text{-}C_4H_9B(PH_2)_2 + 2NaCl$$

$$(n\text{-}C_4H_9)_2BCl + Na(\text{or } K) \xrightarrow{(C_2H_5)_2O} [(n\text{-}C_4H_9)_2B][Na(\text{or } K)] \xrightarrow{CH_3I} CH_3B(n\text{-}C_4H_9)_2$$

Dimethylboron chloride and methylboron dichloride were said to be unstable, owing to facile disproportionation (367). The former compound reacted with methylamine hydrochloride, when heated (359).

$$3CH_3BCl_2 \rightarrow B(CH_3)_3 + 2BCl_3$$

$$3(CH_3)_2BCl \rightarrow 2B(CH_3)_3 + BCl_3$$

$$(CH_3)_2BCl + CH_3NH_2 \cdot HCl \rightarrow (CH_3)_2BCl \cdot CH_3NH_2 + HCl$$

When di-*n*-butylboron chloride was reacted with sodium or potassium in ether and the solvent evaporated, tri-*n*-butylboron and a solid product of the empirical formula BN were obtained (11). The dichloride with sodium in liquid ammonia gave hydrogen and *B*-*n*-butylborazyne, *n*-$C_4H_9B{=}NH$, b.p. 100°C./0.005 mm. (33).

Phenylboron dichloride reacted with chlorine to give chlorobenzene and boron trichloride (239) and with hydrogen iodide and iodine to give a phenylboron diiodide complex, $C_6H_5BI_2 \cdot 2HI$ (264),

$$C_6H_5BCl_2 + Cl_2 \rightarrow C_6H_5Cl + BCl_3$$

Dimethylboron bromide reacted with trisilylamine at room temperature to give a mixture of products, including silyl bromide, silane, trimethylboron, and $(CH_3)_2BN(SiH_2Br)_2$ (70).

Di-*n*-propylboron iodide did not react with lead fluoride, but with antimony trifluoride it gave tri-*n*-propylboron, probably owing to disproportionation of di-*n*-propylboron fluoride, which formed initially, Silver fluoride gave a mixture of products (220).

Complexes are easily formed with amines; they are listed in table 24. Two properties of such complexes have already been mentioned (Section III,C,6; Section V,G). The mixing of *n*-amylboron difluoride and diethyl ether was

TABLE 24

Physical constants of amine complexes

Compound	Boiling Point	Melting Point	n_D^{20}	d_4^{20}	Reference
	°C.	*°C.*			
$(CH_3)_2BF \cdot NH_3$		51			(362)
$(CH_3)_2BF \cdot CH_3NH_2$		68			(362)
$(CH_3)_2BF \cdot (CH_3)_2NH$		21			(362)
$(CH_3)_2BF \cdot (CH_3)_3N$		33			(362)
$(CH_3)_2BCl \cdot NH_3$					(361)
$(CH_3)_2BCl \cdot CH_3NH_2$					(359)
$CH_3BF_2 \cdot CH_3NH_2$	58				(362)
$CH_3BCl_2 \cdot CH_3NH_2$					(359)
$C_2H_5BF_2 \cdot (CH_6)_3N$		25.3			(327)
$(n\text{-}C_4H_9)_2BCl \cdot (C_2H_5)_3N$					(327)
$n\text{-}C_4H_9BF_2 \cdot C_5H_5N$	78/0.01 mm.		1.4665	1.0755	(40)
$n\text{-}C_4H_9BCl_2 \cdot (C_2H_5)_3N$					(327)
$n\text{-}C_4H_9BCl_2 \cdot C_5H_5N$		77·81			(40)
$C_6H_5BF_2 \cdot CH_3NH_2$		98–101			(335)
$C_6H_5BF_2 \cdot C_6H_5NH_2$		178–179			(335)
$C_6H_5BF_2 \cdot C_5H_5N$		100–102			(40)
$C_6H_5BCl_2 \cdot C_5H_5N$		64			(40)

exothermic, but distillation of this solution led to the recovery of the difluoride (226).

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