Journal of Organometallic Chemistry, 73 (1974) 277—296
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Review

METALLOBOROXANES AND RELATED COMPOUNDS

S.K. MEHROTRA, G. SRIVASTAVA and R.C. MEHROTRA
The Chemical Laboratories, University of Rajasthan Jaipur 302004 (India)

(Received December 20th, 1973)

Contents

Introduction

Compounds containing one or more B—O—M (M = metal) linkages may be termed metalloboroxanes. These derivatives constitute a part of a much bigger and wider group of compounds called heterometalloxanes containing the M—O—M′ linkage.

The break-through in polymer chemistry with the discovery of silicones $(R_2SiO)_n$ about three decades ago, prompted detailed study of other polymeric systems which could withstand higher temperatures than conventional organic polymers. The systems which have received maximum attention in this direction are polymetallosiloxanes [1—3] with the Si—O—M backbone and trialkylsilyl oxides of a variety of main group [4] and transition metals [5] have been synthesised and investigated as test models. Work has also been extended to similar Sn—O—M [6] and P—O—M [7—9] systems.

In view of the high B—O bond energy and the marked similarities between silicon and boron, studies of metalloboroxanes with the B—O—M linkage could be expected to yield fruitful results, but very little information appears to be available on this class of compounds in comparison with the metallosiloxanes. This might be due to the following two practical reasons:

(i) The search for boroxy polymers, which attracted a great deal of attention in the late fifties and early sixties, did not yield any products of much practical value because they were readily hydrolysed.

(ii) Although simple metalloboroxane units are of considerable interest, the easily oxidisable boron—carbon bond complicates their syntheses, and derivatives having alkyl or aryl groups bonded to boron have to be handled by vacuum techniques or under an inert atmosphere.

Except for some poorly characterised alkali metal salts of substituted boric acids and alkylene hydrogen borates, the study of metalloboroxanes was limited to the syntheses of siloxy derivatives [10] and it is only in recent years that germanoxy and stannoxy derivatives have been described. A few phosphinoxy derivatives are also known.

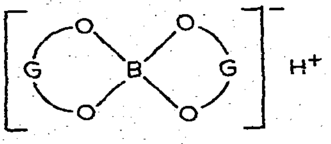
Alkali metal derivatives

In view of the strongly ionic nature of the bond between oxygen and strongly electropositive alkali metals, salts of boric and substituted boric acids with these elements do not involve a direct B—O—M linkage. Such derivatives are, therefore, described only briefly here.

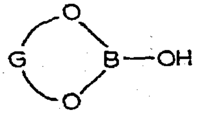
The very weak monobasic acid character exhibited by boric acid may be represented as:

$$B(OH)_3 + H_2O \rightarrow [B(OH)_4]^- + H^+ \tag{1}$$

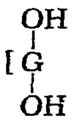
The increase in its acid strength in presence of certain diols and polyols has been explained on the basis of the formation of a complex (I), and a number of such tetrahedral species (I) and their salts have been characterised.



(I)

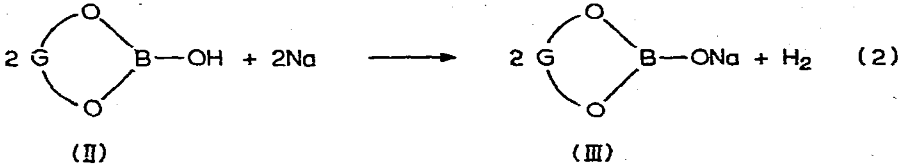


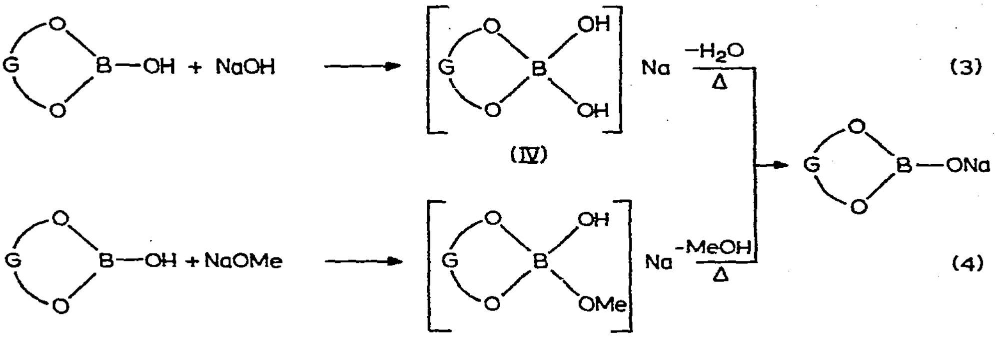
(II)



$[\,\overset{\displaystyle OH}{\underset{\displaystyle OH}{G}}$ represents glycol]

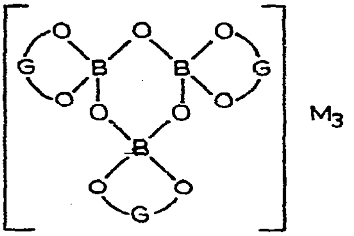
Alkylene hydrogen borates (II) have also been synthesized by several methods [10], and again these trigonal species are very weak acids. A few (such as the derivatives of hexylene glycol and butane-2,3-diol) have been converted into their alkali metal salts (III) either by treating them with the metal directly (eqn. 2) or by heating them alternatively with the metal hydroxide or methoxide:



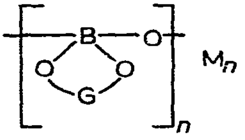


The salts (III) are readily converted into the tetrahedral species (IV) on exposure to atmospheric moisture and can be titrated with strong acid in aqueous solution to methyl orange end point.

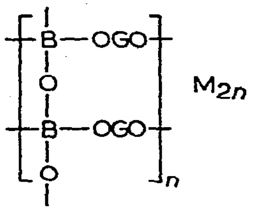
The structural aspects of these salts (III) have not been much investigated [10]. The solubility of the salts of hexylene hydrogen borate in various solvents was determined and appeared to be maximum in benzene. Cryoscopic molecular weight measurements of these derivatives in benzene showed them to have a degree of association ranging from 3.5 to 30 and a trimeric structure (V), a linear polymeric structure (VI), and a cross-linked polymeric structure (VII) have been suggested [10]:



(V)

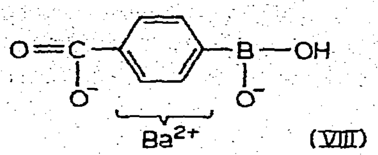


(VI)



(VII)

There is negligible information on salts of boronic and borinic acids. Isolation of a sodium salt of n-butylboronic acid and a barium salt of *p*-carboxyphenylboronic acid have been claimed [11]. The latter has been assigned the following structure (VIII):



(VIII)

Silicon, germanium and tin derivatives

Methods of synthesis

Organosiloxy, -germanoxy and -stannoxy derivatives of boron have been prepared from the following types of boron sources.

A. From boron halides

Boron halides react with trialkylsilanols in the presence of pyridine [12] or directly with sodium trialkylsilanolates [13]:

$$BX_3 + 3R_3SiOH + 3C_5H_5N \rightarrow (R_3SiO)_3B + 3C_5H_5NHX \qquad (5)$$

$$BX_3 + 3R_3SiONa \rightarrow (R_3SiO)_3B + 3NaX \qquad (6)$$

The latter type of reaction, which gives better yields, has been utilized to prepare *B,B′,B″*-tris(triphenylsiloxy)-*N,N′,N″*-trialkylborazines [14]:

$$(ClBNR)_3 + 3Ph_3SiONa \rightarrow (Ph_3SiOBNR)_3 + 3NaCl$$

$$R = H, Me \text{ and } Ph \qquad (7)$$

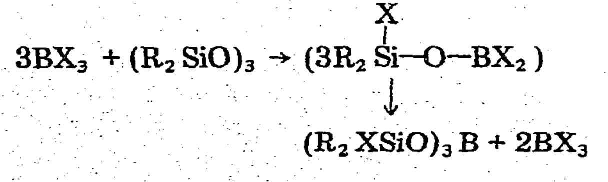
Alkoxysilanes have been used in place of silanols in reaction (5) and the course of the reaction has been found to be governed by the nature of the alkoxy and alkyl groups present on silicon [15] e.g.,

$$BCl_3 + Si(OBu)_4 \rightarrow (BuO)_3SiCl + BuOBCl_2 \qquad (8)$$

$$BCl_3 + 3Cl_3SiOBu\text{-}s \rightarrow (Cl_3SiO)_3B + 3s\text{-}BuCl \qquad (9)$$

The cleavage of the Si—O—Si linkage in $(Me_3Si)_2O$ [16] and $(R_2SiO)_3$ [17, 18] has also been studied. The resulting siloxydihaloborane undergoes decomposition in the former but disproportionates in the latter case to give silyl borate. However, Wiberg and Krüerke [16] were able to isolate $(Et_3SiO)_2BBr$ by the reaction of $(Et_3Si)_2O$ and BBr_3:

$$\begin{array}{l} BX_3 + (Me_3Si)_2O \rightarrow (Me_3SiOBX_2 + Me_3SiX) \\ \qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad 2Me_3SiX + (OBX) \end{array} \qquad (10)$$



$$\begin{array}{l} 3BX_3 + (R_2SiO)_3 \rightarrow (3R_2\overset{X}{\overset{|}{Si}}—O—BX_2) \\ \qquad\qquad\qquad\qquad\quad \downarrow \\ \qquad\qquad\qquad\quad (R_2XSiO)_3B + 2BX_3 \end{array}$$

(11)

$$2(Et_3Si)_2O + BBr_3 \rightarrow (Et_3SiO)_2BBr + 2Et_3SiBr \qquad (12)$$

Disiloxane, $(H_3Si)_2O$, is also cleaved by boron halides [19].

B. From boric acid (and oxide)

Boric acid reacts with a variety of compounds containing the M—X bond ($X = H$, Cl, OH and OR). Monofunctional starting materials, R_3MX, yield simple tris(trialkylmetal) borates whereas di- and tri-functional compounds (e.g., R_2MX_2 and RMX_3) give polymers.

(a) Reactions with organometal hydrides. Trialkylsilanes have been reported to react with boric acid at 100—130° in the presence of a catalyst (e.g., colloidal nickel or nickel, platinum or palladium halide) [20—24]:

$$H_3BO_3 + 3R_3SiH \rightarrow (R_3SiO)_3B + 3H_2 \tag{13}$$

An initial attack at the silicon atom by boroxy oxygen followed by elimination of hydrogen has been suggested as a plausible mechanism [10].

Tris(triethylgermyl) borate was similarly prepared from triethylgermane using copper powder as catalyst [25]:

$$H_3BO_3 + 3Et_3GeH \rightarrow (Et_3GeO)_3B + 3H_2 \tag{14}$$

(b) Reactions with organometal halides. Trialkylchlorosilanes react with boric acid with elimination of hydrogen chloride and formation of siloxyboranes. Yields are poor [26] but can be increased by a longer reflux time [27]:

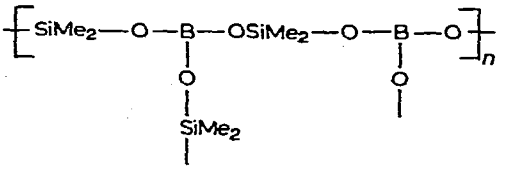
$$H_3BO_3 + 3R_3SiCl \rightarrow (R_3SiO)_3B + 3HCl \tag{15}$$

Bis(triethylsiloxy)phenylborane was similarly prepared from phenylboronic acid and triethylbromosilane [28]:

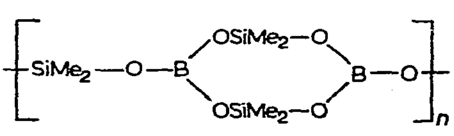
$$PhB(OH)_2 + 2Et_3SiBr \rightarrow PhB(OSiEt_3)_2 + 2HBr \tag{16}$$

Dialkyldichlorosilanes [26, 29] on the other hand, yield polymeric materials (eqn. 17) which have been formulated as (IX) [24, 30] and (X) [29]:

$$2H_3BO_3 + 3R_2SiCl_2 \rightarrow [B_2(OSiR_2)_3] + 6HCl \tag{17}$$



(IX)



(X)

Reaction of hexylene hydrogen borate with tributylchlorogermane has been shown to occur in the presence of triethylamine as hydrogen chloride acceptor [31]:

(18)

(c) Reactions with organometal hydroxides and oxides. Azeotropic removal of water from a mixture of boric acid or boric oxide and trialkylsilanol or trialkyltin hydroxide yields the corresponding tris(trialkylmetal) borate:

$$H_3BO_3 + 3R_3MOH \rightarrow (R_3MO)_3B + 3H_2O \qquad (19)$$

M = Si [12, 22, 23] and Sn [32, 33]

The method has been extended to the synthesis of bis(trimethylsiloxy)alkylboranes [34]:

$$RB(OH)_2 + 2Me_3SiOH \rightarrow RB(OSiMe_3)_2 + 2H_2O \qquad (20)$$

Bis(trialkylmetal) oxides have been used in place of the corresponding hydroxides:

$$2H_3BO_3 + 3(R_3M)_2O \rightarrow 2(R_3MO)_3B + 3H_2O \qquad (21)$$

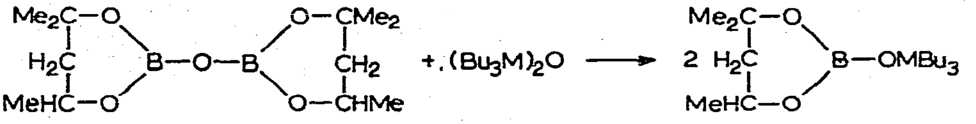
M = Ge [31] and Sn [32, 33, 35—37]

Claims in a Patent [36] to have prepared mono- and bis-(trialkylstannyl) borates, $R_3SnOB(OH)_2$ and $(R_3SnO)_2BOH$, could not be substantiated [37].

Boric oxide has also been frequently used [20, 23, 26, 38] in place of boric acid in reactions of type (19) and (21) and organometal metaborates could be synthesized by taking boric oxide and organometal oxide in the appropriate molar ratio:

$$3B_2O_3 + 3(R_3M)_2O \rightarrow 2(OBOMR_3)_3 \quad M = Sn\ [33],\ Ge\ [39] \qquad (22)$$

The method has been extended to the reactions of hexylene glycol pyroborate with bis(trialkylmetal) oxides:

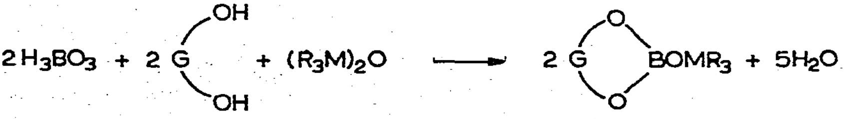


(23)

(XI)

M = Ge [31] and Sn [37]

More simply an equimolar mixture of glycol and boric acid can be used in place of the pyroborate and a large variety of derivatives of type (XI) have been prepared by this method:

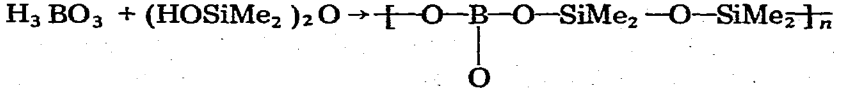


(24)

M = Ge [31] and Sn [37]

Qualitatively, it has been observed that reactions of type (19) to (24) occur more readily when M = Sn than when M = Ge or Si. Thus, bis(trialkyltin) oxide and trialkyltin hydroxide react with boric acid easily in refluxing benzene [39] (Me_3SnOH, a stable sublimable dimer, is an exception and reacts at a rather slow rate), whereas bis(trimethylsilyl) oxide reacts with boric oxide in an autoclave at 350° to give tris(trimethylsilyl) borate in only 20% yield [26]. The pyroborate of hexylene glycol could be recovered unchanged after refluxing it with an excess of bis(trimethylsilyl) oxide for 12 h [62].

An interesting polymeric borosiloxane (XII) has been prepared from an equimolar mixture of boric acid and tetramethyldisiloxane-1,3-diol [40]:



$$H_3BO_3 + (HOSiMe_2)_2O \rightarrow \left[O-\underset{\underset{|}{O}}{\overset{}{B}}-O-SiMe_2-O-SiMe_2 \right]_n \qquad (25)$$

(XII)

Low molecular weight dimethylpolysiloxanes were heated with boric acid at 150—200° [41]. The resulting products were highly polymerised and showed the properties of a "bouncing putty". Similarly, borosiloxane polymers with interesting water-proofing properties have been prepared from boric acid and the dichlorodisiloxane (XIII) [42].

$$Cl-(SiR_2O)_2-SiR_2Cl$$

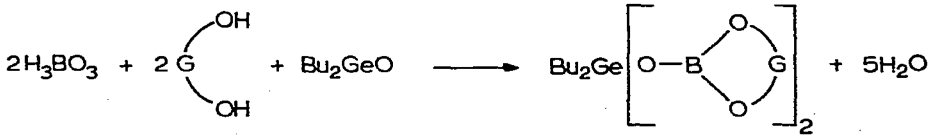
(XIII)

The product obtained by azeotropic removal of water from a mixture of dibutyltin oxide and boric acid was claimed to be dibutyltin borate [43, 44], but a recent reinvestigation [45] indicated that the product does not contain any B—O—Sn linkage, and in all probability it is a mixture of dibutyltin oxide and boric oxide.

Azeotropic dehydration of a mixture of boric acid, dibutylgermanium oxide and a glycol (e.g., hexylene glycol or pinacol) gave germanoxyboranes (XIV) and (XV) as shown below [46]:

(26)

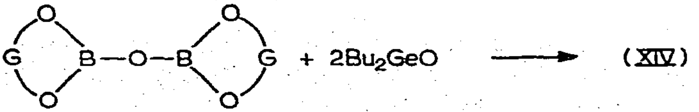
(XIV)



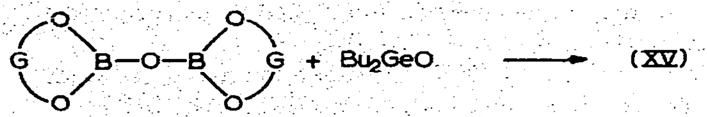
(27)

(XV)

The products (XIV) and (XV) are monomeric liquids which disproportionate into dibutylgermanium oxide and alkylene pyroborate during attempted distillation. On the other hand, a mixture of dibutylgermanium oxide and alkylene pyroborate, on being kept at 120—140° for 3—4 h, rearranges to give (XIV) and (XV):

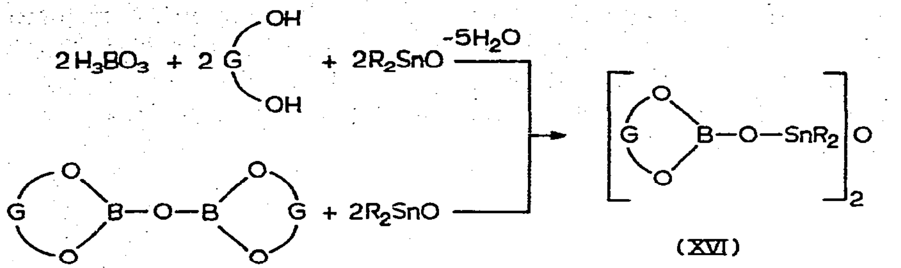


(28)

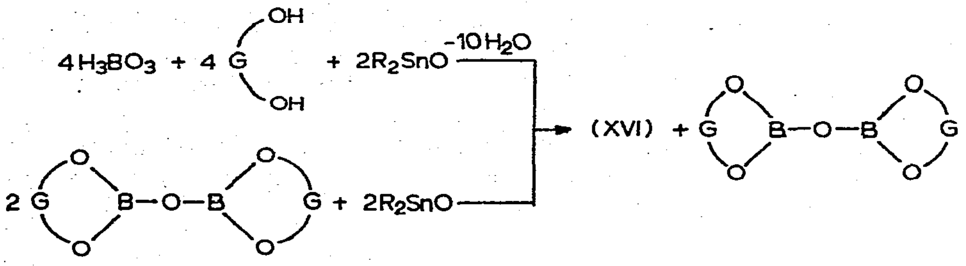


(29)

Reactions (26) and (27) with dialkyltin oxide in place of dibutylgermanium oxide have been also reported and interestingly the diboroxy tetraalkyldistannoxane (XVI), a dialkyltin analogue of (XIV), was obtained as the final product in each case:



(30)



(31)

Evidence for the dimeric nature of the products (XVI) was obtained from molecular weight determinations and PMR spectra and a ladder like structure has been suggested [45].

(d) Reactions with organometal alkoxides. The reaction between boric acid and tetraalkyl silicate occurs via transfer of alkoxy groups from silicon to boron [48]:

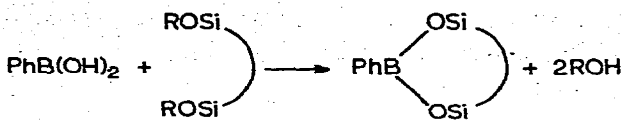
$$4H_3BO_3 + 3Si(OR)_4 \rightarrow 4B(OR)_3 + 3SiO_2 + 6H_2O \qquad (32)$$

Ethoxytrimethylsilane, in a similar reaction, gave mainly the ethyl borate [26]. However, other alkoxytrialkylsilanes have been shown to yield silyl borates [26, 49, 50]. *p*-Toluenesulphonic acid has been used as a catalyst [49]:

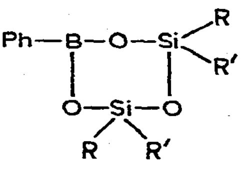
$$H_3BO_3 + 3R_3SiOR' \rightarrow (R_3SiO)_3B + 3R'OH \qquad (33)$$

Polymeric borosiloxanes have been obtained by the condensation of boric acid with dialkyldialkoxysilanes in 1/2 and 2/3 molar ratios [51] and with alkyltrialkoxysilanes in equimolar ratio [26, 50]. Similar reactions with 1,1-dimethoxysilacyclopentane and 1,1-dimethoxy-3,4-benzosilacyclopentane also gave polymeric products [52].

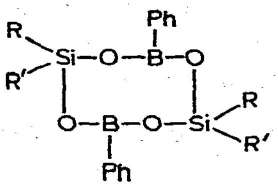
Adrianov and coworkers [53, 54] have extended the above type of reactions to phenylboronic acid and have synthesised a variety of cyclic borosiloxanes (e.g., XVII—XX) by its condensation with dialkoxysilanes and siloxanes:



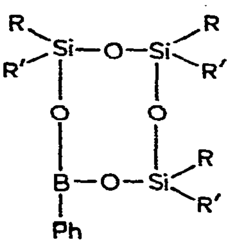
(34)



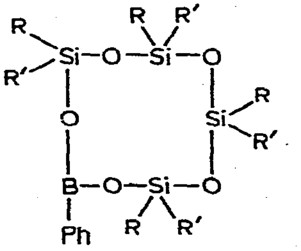
(XVII)



(XVIII)



(XIX)



(XX)

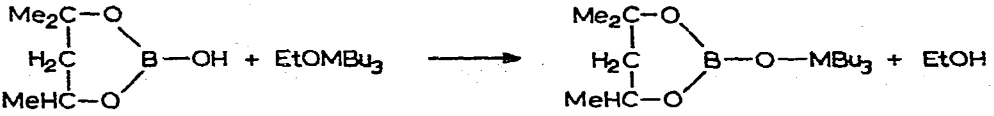
Abel and Singh [12] have reported the cleavage of trimethylethoxysilane with boric oxide:

$$B_2O_3 + 3Me_3SiOEt \rightarrow (Me_3SiO)_3B + B(OEt)_3 \qquad (35)$$

In the reactions of boric acid or oxide with alkylalkoxysilanes, an initial nucleophilic attack on silicon has been postulated. It appears from reaction 36 that the reactivity of the Si—OR group towards boric acid is less than that of the Si—Cl group [27]:

$$H_3BO_3 + 3Me_2Si(OEt)Cl \rightarrow [Me_2(EtO)Si]_3B + 3HCl \qquad (36)$$

Condensations of hexylene hydrogen borate with tributylgermanium ethoxide and tributyltin ethoxide have been reported recently:



(37)

M = Ge [31] and Sn [37]

(e) Reactions with organometal acetates. The reactions of acetoxysilanes with boric acid have been shown to yield tris(trialkylsilyl) borates by Voronkov et al. [64]:

$$H_3BO_3 + 3R_3SiOAc \rightarrow B(OSiR_3)_3 + 3AcOH \qquad (38)$$

C. From orthoboric esters

Like boric acid, orthoborates also react with organometal halides, hydroxides and carboxylates with the formation of the B—O—M linkage.

Tributoxyborane and triethylchlorosilane reacted together in the presence of ferric chloride giving tris(triethylsilyl) borate in 10% yield [26]:

$$(BuO)_3B + 3Et_3SiCl \rightarrow (Et_3SiO)_3B + 3BuCl \qquad (39)$$

The corresponding reactions with trialkylsilanol gave better yields of silylborate [12, 26, 55]:

$$(BuO)_3B + 3R_3SiOH \rightarrow (R_3SiO)_3B + 3BuOH \qquad (40)$$

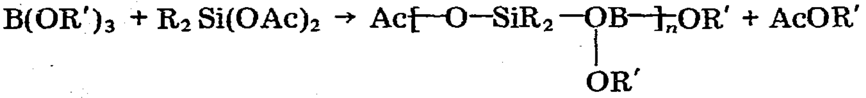
The mixed borate (XXI) has been similarly prepared by taking the reagents in the appropriate ratio [55]:

$$(EtO)_3B + 2Et_3SiOH \rightarrow \underset{\text{(XXI)}}{(Et_3SiO)_2BOEt} + 2EtOH \qquad (41)$$

The derivative (XXI) reacted further with dialkyldiacetoxy silane to yield a product formulated as (XXII) [55]:

$$2(\text{XXI}) + R_2Si(OAc)_2 \rightarrow \underset{\text{(XXII)}}{R_2Si[OB(OSiEt_3)_2]_2} + 2EtOAc \qquad (42)$$

Dialkyldiacetoxysilanes have been treated directly with trialkylborates giving low molecular weight borosiloxane polymers [56, 57]:



$$B(OR')_3 + R_2Si(OAc)_2 \rightarrow Ac\left[-O-SiR_2-O\underset{\displaystyle OR'}{\underset{|}{B}}-\right]_n OR' + AcOR' \qquad (43)$$

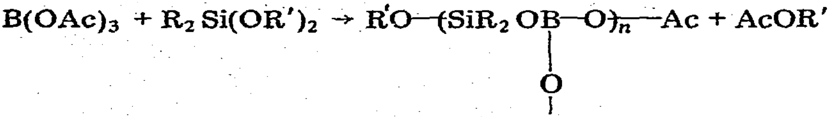
A similar method has been claimed in the patent literature for the synthesis of mixed stannylalkylborates [58]:

$$B(OR)_3 + nBu_3SnOAc \rightarrow (Bu_3SnO)_nB(OR)_{3-n} + AcOR \qquad (44)$$
$$n = 1 \text{ and } 2$$

A recent investigation, however, shows that the reactivity of tributyltin acetate towards alkyl borates is of a very low order and the reactions are incomplete even in refluxing toluene.

D. From boron triacetate

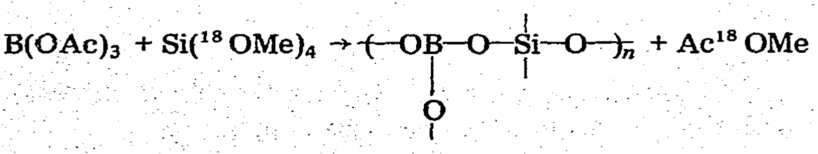
The interaction between boron triacetate and alkoxysilanes constitutes another direct method for the synthesis of low molecular weight borosiloxane polymers [40] e.g.,



$$B(OAc)_3 + R_2Si(OR')_2 \rightarrow R'O-\left(SiR_2O\underset{\underset{|}{O}}{\underset{|}{B}}-O\right)_n-Ac + AcOR' \qquad (45)$$

Andrianov et al. [59] showed that ^{18}O labelled alkoxides always gave labelled alkyl acetate. The reactions may be represented as below:

$$B(^{18}OMe)_3 + Et_2Si(OAc)_2 \rightarrow (-OSiEt_2OBO-)_n + Ac^{18}OMe \qquad (46)$$



$$B(OAc)_3 + Si(^{18}OMe)_4 \rightarrow \left(-O\underset{\underset{|}{O}}{\underset{|}{B}}-O-\overset{|}{\underset{|}{Si}}-O-\right)_n + Ac^{18}OMe \qquad (47)$$

E. Miscellaneous methods

The following further reactions have also been shown to produce the B—O—M linkage, but these reactions have been applied as yet only to a limited extent.

$$(Et_2N)_3B + 3Et_3SiOH \rightarrow (Et_3SiO)_3B + 3Et_2NH \qquad \text{(ref. 12)} \quad (48)$$

$$H_3BO_3 + 3Et_3SiNHPh \rightarrow (Et_3SiO)_3B + 3PhNH_2 \qquad \text{(ref. 60)} \quad (49)$$

$$(Me_3SiO)_3B + 3Et_3SiOH \rightarrow (Et_3SiO)_3B + Me_3SiOH \qquad \text{(ref. 12)} \quad (50)$$

(51)

M = Ge[31] and Sn[37]

Properties

As pointed out earlier, the study of the B—O—M linkage has been confirmed mainly to the synthetic aspects. The reactivity of this linkage towards various reagents is now beginning to be investigated and a number of such reactions are already known. However, the structural aspects as well as the effect of various types of groups present on boron and metal on the reactivity of B—O—M linkage are some of the main problems which have yet to be explored.

A. Thermal stability

Simple trialkyl-silyl and -germyl borates are thermally stable and can be distilled unchanged. The corresponding stannyl derivatives show slight decomposition during vacuum distillation whereas silyl borates are completely decomposed into boric oxide and hexaalkyl disiloxane in the presence of ferric chloride:

$$2(R_3SiO)_3B \rightarrow B_2O_3 + R_3SiOSiR_3 \qquad (52)$$

Dialkylhalosiloxydihaloboranes disproportionate rapidly during attempted vacuum distillation [17, 18]:

$$3R_2XSi{-}O{-}BX_2 \rightarrow (R_2XSiO)_3B + 2BX_3 \qquad (53)$$

The resulting tris(dialkylhalosilyl) borates are again less stable than tris(trialkylsilyl) borates and during distillation under atmospheric pressure disproportionate into boric oxide and *sym*-tetraalkyldihalodisiloxane:

$$2(R_2XSiO)_3B \rightarrow B_2O_3 + R_2XSi{-}O{-}SiR_2X \qquad (54)$$

The ease of disproportionation in reactions (53) and (54) appeared to decrease in the series $X = F > Cl > Br$. This was correlated with the ability of the halogen atom to form a $(p \rightarrow d)\pi$ bond with silicon.

B. Hydrolytic stability

Like metal alkoxides, metalloboroxanes are also hydrolysed in the presence of moisture. The hydrolytic stability of tris(trimethylsilyl) borate [12] in water appears to be roughly of the same order as that of tri-t-butylborate [61]. It, therefore, appears that in the former, the effect of decreased $(p \rightarrow p)\pi$ bonding between oxygen and boron is offset by the steric effect of bigger trimethylsilyl groups.

Silyl borates are hydrolysed more rapidly in hot water [57]. The hydrolysis is also catalysed by acids and bases [13, 26, 56]. Halosiloxyboranes are, understandably, hydrolysed much more quickly than other silyl borates [16].

Germyl as well as stannyl borates are also easily hydrolysed with the exception of 1,3-diboroxytetraalkyldi-stannoxane and -germoxane derivatives which require a higher temperature for hydrolysis. Germyl borates, however, appear to have in general, more hydrolytic stability than the corresponding stannyl borates.

Reactions with protic reagents. Reactions of tris(tributylstannyl) borate with thiols, phenol and acetic acid have been studied in benzene. Boric acid is precipitated in each case:

$$(Bu_3SnO)_3B + 3HA \rightarrow 3Bu_3SnA + H_3BO_3 \qquad (55)$$

A = SBu, SPh, OPh and OAc

However, no reaction was observed between tris(tributylstannyl) borate and isopropyl acetate.

Reactions with hydrogen halides. The M—O—B linkage is readily cleaved by hydrogen halides, e.g.:

$$(R_3MO)_3B + 3HX \rightarrow 3R_3MX + H_3BO_3 \qquad M = Si\ [12]\ and\ Sn\ [33] \qquad (56)$$

Reactions with acyl halides. The ready reactivity of the Sn—O—B linkage with acetyl chloride has also been demonstrated:

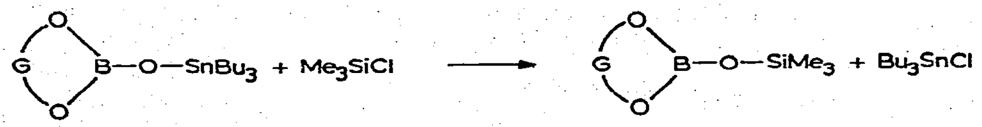
$$(Bu_3SnO)_3B + 3AcCl \rightarrow 3Bu_3SnCl + B(OAc)_3 \qquad (57)$$

In all the above types of reactions, the more electronegative portion of the attacking reagent becomes attached to the organotin moiety.

Reactions with organometal halides. Stannyl borates are readily cleaved by trialkylhalosilanes and -germanes:

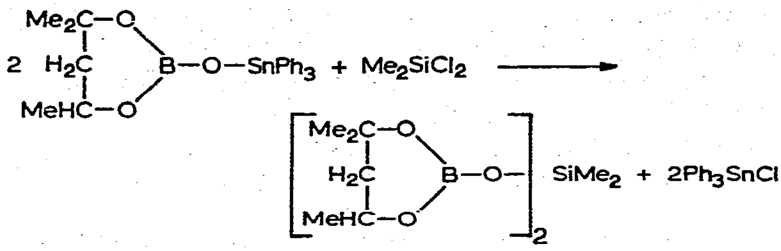
$$(Bu_3SnO)_3B + 3R_3MCl \rightarrow 3Bu_3SnCl + (R_3MO)_3B \qquad M = Si\ and\ Ge \qquad (58)$$

The method has been utilized in the synthesis of a variety of 2-trimethylsiloxy-1,3,2-dioxa-borolanes and -borinanes [62]:



(59)

A bis-boroxy derivative (XXIII) was also obtained as a distillable liquid from reaction (60), whereas the dibutylgermanium analogue of (XXIII) disproportionates during distillation. Corresponding dialkyltin derivatives could not be isolated.



(60)

(XXIII)

The cleavage of the Ge—O—B linkage by trimethylchlorosilane has also been demonstrated [46]:

$$(Bu_3GeO)_3B + 3Me_3SiCl \rightarrow (Me_3SiO)_3B + 3Bu_3GeCl \quad (61)$$

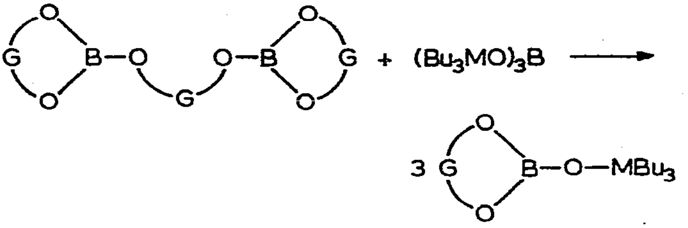
Reactions with orthoborate esters. Exothermic reactions were observed between tris(tributylstannyl) borate and isopropyl borate:

$$(Bu_3SnO)_3B + 2(i\text{-}PrO)_3B \rightarrow 3Bu_3SnOB(OPr\text{-}i)_2 \quad (62)$$

$$2(Bu_3SnO)_3B + (i\text{-}PrO)_3B \rightarrow 3(Bu_3SnO)_2BOPr\text{-}i \quad (63)$$

The unsymmetrical borates, however, are thermally unstable and disproportionate during distillation.

Reactions of stannyl and germyl borates with diborontriglycollate have also been studied:



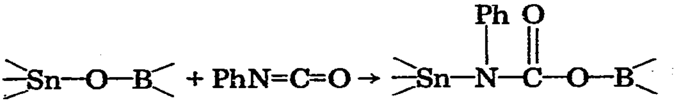
(64)

M = Ge[31] and Sn[37]

Reaction with boric oxide. Stannyl, germyl, and silyl orthoborates react with boric oxide on heating and are converted into the corresponding metaborates:

$$B_2O_3 + (R_3MO)_3B \rightarrow (R_3MOBO)_3 \quad M = Si\ [12],\ Ge\ [39]\ \text{and}\ Sn\ [33] \quad (65)$$

Insertion reactions. Insertion of phenyl isocyanate into Sn—O—B linkages has been demonstrated. The exothermic reactions have been assumed to occur via cleavage of the Sn—O bond because it is more polar than the B—O bond:



$$\rangle Sn{-}O{-}B\langle + PhN{=}C{=}O \rightarrow \rangle Sn{-}\overset{Ph}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}B\langle \quad (66)$$

C. Spectral properties

The vibrational spectra of a large number of metalloboroxanes have been studied. The ν_{as}(B—O—M) absorption is the most important diagnostic peak in such derivatives and appears in the following range: ν(B—O—Si), 1333 ± 8; B—O—Ge, 1285 ± 15; B—O—Sn, 1285 ± 15 cm^{-1}, the ν_{as}(B—O—C) vibration appears in the range 1330 ± 20 cm^{-1} and a clear shift to lower frequency occurs as carbon is replaced successively by higher atomic weight elements.

The Raman spectra of a few silyl borates have been reported by Voronkov et al. [64].

The PMR spectra of a variety of silyl [65], germyl [46] and stannyl [33, 45] borates have been recorded, and have been found useful in characterising the products.

Phosphorus derivatives

Trialkyl phosphates form complexes with boron trichloride [66]. These addition complexes slowly evolve alkyl chloride in the temperature range 0—300°, giving a polymeric product with the P—O—B—O linkage and finally boron phosphate:

$$(RO)_3P{=}O{,}BCl_3 \xrightarrow{\text{heat}} 3RCl + (PBO_4)_n \tag{67}$$

The complexes with triaryl phosphates, on the other hand, are very stable and do not give aryl halide on heating [67]. This work was extended to derivatives of diethyl ethylphosphonate. The complex, $(EtO)_2(Et)P{=}OBCl_3$, in this case, decomposed slowly to give an insoluble polymeric solid, the composition of which corresponds to $(EtPO_3BCl)_n$.

The reaction between boron trichloride and trialkyl phosphites appears to proceed via chloride—alkoxide interchange [68] even at —70°:

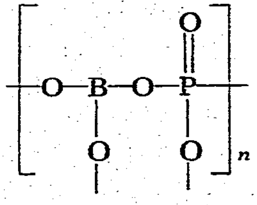
$$(RO)_3P + BCl_3 \rightarrow (RO)_2PCl + ROBCl_2 \tag{68}$$

The above type of reaction with triphenyl phosphite occurs at room temperature [69].

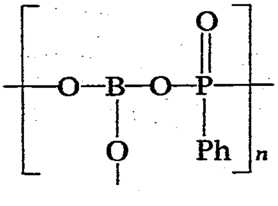
Orthoboric esters react with phosphoric acid and boron phosphate is obtained as the final product [70]:

$$(RO)_3B + H_3PO_4 \rightarrow (BPO_4)_n + 3ROH \tag{69}$$

Reactions of boron triacetate with ethyl phosphate and diethyl phenylphosphonate have also been studied and polymeric products (XXIV) and (XXV) have been obtained [71, 72]:



(XXIV)

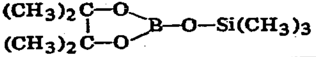


(XXV)

A list of the compounds studied is given in Table 1.

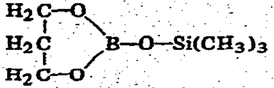
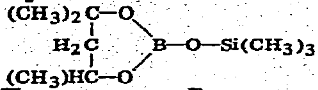
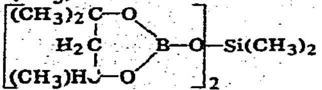
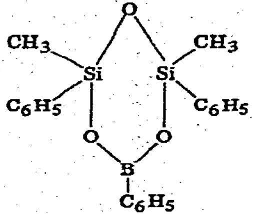
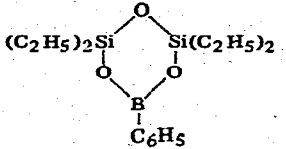
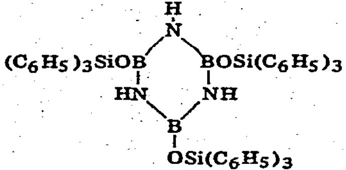
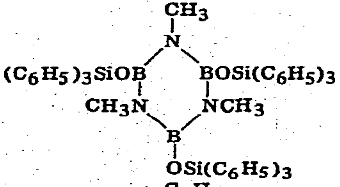
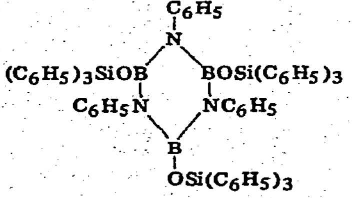
TABLE 1

LIST OF METALLOBOROXANES

Compound	Boiling point (°C/mm)	Melting point	Method of preparation indicated by equation number	References
Derivatives having the B—O—Si linkage				
$[(CH_3)_3SiO]_3B$	184.5		23, 38	26, 64
	186		5	12
	47/5		15	27
	48/5		14	26
	90		33	49
	62-64/6		57	62
$[C_2H_5Si(CH_3)_2O]_3B$	93-94/6		13	23
$[(C_2H_5)_2Si(CH_3)O]_3B$	131-133/6		33, 38	26, 64
	138-140/6		13	23
$[(C_2H_5)_3SiO]_3B$	120-130/1		15, 33, 38, 39, 40	26, 64
	185/20		5, 6, 19, 40, 48, 50	12
	183/17		6	13
	145-146/2		40	55
	152-154/3		23	38
	154-155/4		13	23
	172-174/6		13	22
	195/9.5		13	20
$[(n\text{-}C_3H_7)_2Si(CH_3)O]_3B$	157-160/1		33	26
	185/3		13	20
$[(n\text{-}C_3H_7)_2Si(C_2H_5)O]_3B$	214/3		13	20
$[(n\text{-}C_3H_7)_3SiO]_3B$	215-217/1		13	20
$[(n\text{-}C_4H_9)_2Si(C_2H_5)O]_3B$	235/3		13	20
$[(n\text{-}C_5H_{11})_2Si(CH_3)O]_3B$	273-274/9		13	20
$[(n\text{-}C_4H_9)_3SiO]_3B$	273-274/3		13	20
$[(i\text{-}C_5H_{11})_2Si(C_2H_5)O]_3B$	297-298/11		13	20
$[(C_6H_5)Si(C_2H_5)_2O]_3B$	250-255/6		19	23
$[(C_6H_5)_2Si(CH_3)O]_3B$	320-325/3		13, 19, 38	22, 23, 64
$[(C_6H_5)_2Si(C_2H_5)O]_3B$	354-358/8		13	21
$[(CH_3)_2Si(Cl)O]_3B$	81.5-82/2		11	17
	60/0.1		11	15
	98-98.5/11		8	15
$[(CH_3)_2Si(Br)O]_3B$			11	18
$[(CH_3)_2Si(F)O]_3B$			11	18
$[(C_2H_5)_2Si(Cl)O]_3B$	137.5-138/2		11	17
$[(C_2H_5)_2Si(Br)O]_3B$			11	17
$[(C_2H_5)_2Si(F)O]_3B$			11	18
$(Cl_3SiO)_3B$	98-102/12		9	15
$[(CH_3)_2Si(OC_2H_5)O]_3B$			14	27
$[(C_6H_5)_3SiO]_3B$		150°	13, 38	22, 23, 64
$[(C_2H_5)_3SiO]_2B(OCH_3)$			11	16
$[(C_2H_5)_3SiO]_2B(CH_3)$			6	13
$[(C_2H_5)_3SiO]_2B(CH_3)$			5	13
$[(CH_3)_3SiO]_2B(C_3H_7)$	60/15		20	34
$[(CH_3)_3SiO]_2B(C_6H_5)$	114/13		20	34
$[(CH_3)_3SiO]_2B(CF_3C_2H_4)$	172		20	34
$[(CH_3)_3SiO]_2B(m\text{-}CF_3C_6H_4)$	118/13		20	34
$[(C_2H_5)_3SiO]_2B(Br)$			13	16
$[(C_6H_5)B(OC_2H_5)OSi(CH_3)]_2O$	123-125/1		34	54
$(C_2H_5O)[(CH_3)_2SiO]_3B(C_6H_5)(OC_2H_5)$	116-118/3		34	54
$[(C_2H_5O)(C_6H_5)BOSi(CH_3)_2]_2O$	123-125/1-2		34	53
$[(C_2H_5O)_2BOSi(CH_3)_2]_2O$	116-118/3		34	53
	51-53/6		59	62
	64/5		59	62

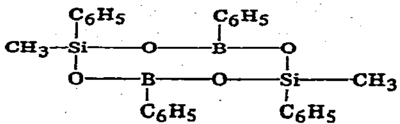
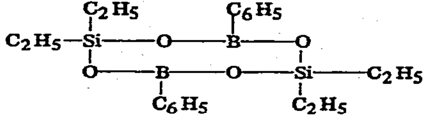
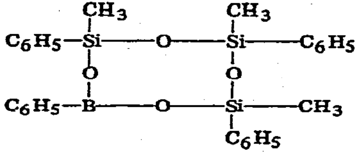
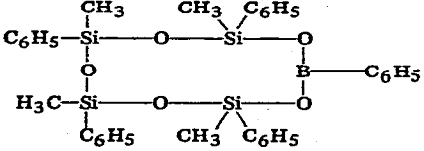
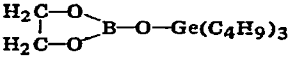
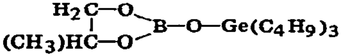
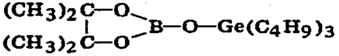
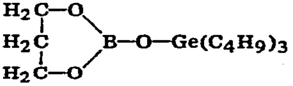
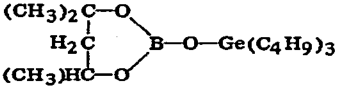
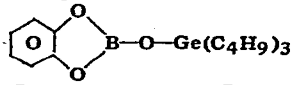
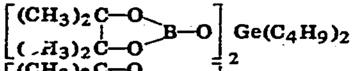
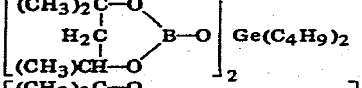
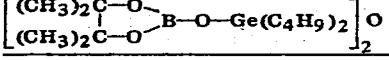
(continued)

Table 1 *(continued)*

Compound	Boiling point (°C/mm)	Melting point	Method of preparation indicated by equation number	References
	60/7		59	62
	70/6		59	62
	100/0.3		60	62
$[(CH_3)_3SiOBO]_3$			65	12
$[(C_2H_5)_3SiOBO]_3$			65	12
	222-224/3		34	53, 54
	171/3		34	53, 54
		164-167	7	14
		206	7	14
		234-235	7	14

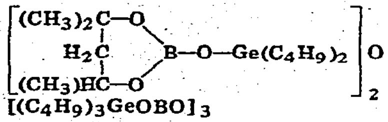
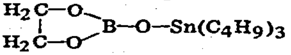
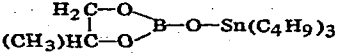
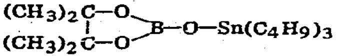
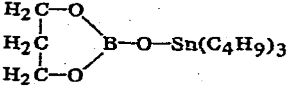
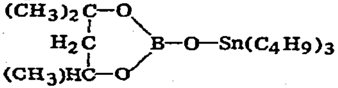
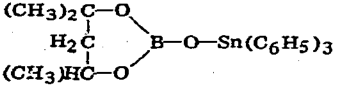
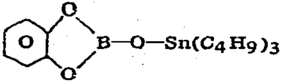
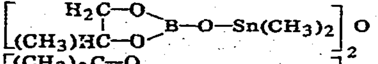
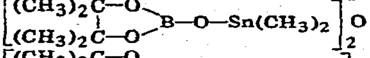
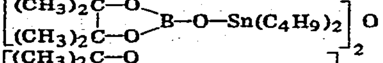
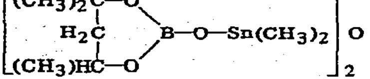
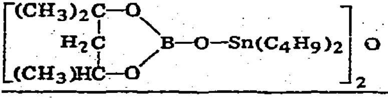
(continued)

Table 1 *(continued)*

Compound	Boiling point (°C/mm)	Melting point	Method of preparation indicated by equation number	References
	245-246/1-2		34	53, 54
	148-149/2-3 123-125/1-2		34 34	54 53
	274-276/2-3		34	53, 54
	279-281/1		34	53, 54
Derivatives having the B—O—Ge linkage				
$[(CH_3)_3GeO]_3B$	75/6		58	39
$[(C_4H_9)_3GeO]_3B$	193/0.6		21	31
$[(C_2H_5)_3GeO]_3B$			14	25
	119/0.9		24	31
	109/0.7		24	31
	115/0.6		24	31
	124/0.7		24	31
	122/0.6		18, 23, 24, 37, 51	31
	142/0.7		24	31
			27, 29	46
			27, 29	46
			26, 28	46

(continued)

Table 1 *(continued)*

Compound	Boiling point (°C/mm)	Melting point	Method of preparation indicated by equation number	References
			26, 28	46
$[(C_4H_9)_3GeOBO]_3$			22	39
Derivatives having the B—O—Sn linkage				
$[(CH_3)_3SnO]_3B$	130-132/14		19	33
$[(C_2H_5)_3SnO]_3B$	140-145/0.5		19	33
$[(C_3H_7)_3SnO]_3B$	152-153/0.1		21	32, 33, 35, 36
$[(C_4H_9)_3SnO]_3B$	195-200/0.1		21	32, 33, 35, 36, 37
$[(i\text{-}C_4H_9)_3SnO]_3B$	180-185/0.05		21	33
$[(C_6H_5)_3SnO]_3B$		128-130	19	32, 33
	125-135/0.2		24	37
	120-121/0.2		24	37
	161/0.8		24	37
	132/0.5		24	37
	155/0.5		23, 24, 37, 51	37
			23, 24	62
	143-148/0.1		23	37
$[(C_2H_5)_3SnOBO]_3$			64	33
$[(C_3H_7)_3SnOBO]_3$			64	33
$[(C_4H_9)_3SnOBO]_3$			22, 64	33
$[(i\text{-}C_4H_9)_3OBO]_3$			64	33
		188-190	31	45
		287-288	30, 31	45
		84-86	30, 31	45
		166-168	30, 31	45
		56-57	30, 31	45

References

1 K.A. Andrianov, Metalorganic Polymers, Interscience Publishers, 1965.

2 J.I. Jones in M.F. Lappert and G.J. Leigh, (Eds.), Developments in Inorganic Polymer Chemistry, Chapters 7 and 8, Elsevier Publishing Co., Inc., New York, 1962.

3 F.G.A. Stone and W.A.G. Graham (Eds.), Inorganic Polymers, Academic Press, New York, 1962.

4 H. Schmidbaur, Angew. Chem. Int. Ed. Engl., 4 (1965) 201.

5 F. Schindler and H. Schmidbaur, Angew. Chem. Int. Ed. Engl., 6 (1967) 683.

6 P.G. Harrison, Organometal. Chem. Rev., 4 (1969) 379.

7 K. Issleib and B. Walther, Angew. Chem. Int. Ed. Engl., 6 (1967) 88.

8 G.H. Dahl and B.P. Block, Inorg. Chem., 6 (1967) 1439.

9 S. Freireich, D. Gertner and A. Zilkha, J. Organometal. Chem., 25 (1970) 111.

10 H. Steinberg, Organoboron Chemistry, Vol. 1, Wiley, New York, 1964.

11 W. Gerrard, The Organic Chemistry of Boron, Academic Press, London, 1961, p. 67.

12 E.W. Abel and A. Singh, J. Chem. Soc., (1959) 690.

13 E. Wiberg and U. Kruerke, Z. Naturforsch. B, 8 (1953) 609; Chem. Abstr., 48 (1954) 4346.

14 A. Meller, Monatsh., 94 (1963) 183; Chem. Abstr., 59 (1963) 7553.

15 M.J. Frazer, W. Gerrard and J.A. Strickson, J. Chem. Soc., (1960) 4701.

16 E. Wiberg and U. Kruerke, Z. Naturforsch. B, 8 (1953) 610; Chem. Abstr., 48 (1954) 4346.

17 P.A. McCusker and T. Ostdick, J. Amer. Chem. Soc., 80 (1958) 1103.

18 P.A. McCusker and T. Ostdick, J. Amer. Chem. Soc., 81 (1959) 5550.

19 M. Onyzchuk, Can. J. Chem., 39 (1961) 808.

20 B.N. Dolgov, Yu.I. Khudobin and N.P. Kharitonov, Doklady Akad. Nauk. SSSR, 122 (1958) 607; Chem. Abstr., 53 (1959) 4110.

21 B.N. Dolgov, Yu.I. Khudobin and N.P. Kharitonov, U.S.S.R. Pat. 116,880 (1959); Chem. Abstr., 53 (1959) 19975.

22 N.F. Orlov and B.N. Dolgov, U.S.S.R. Pat. 115,167 (1958); Chem. Abstr., 53 (1959) 13107.

23 N.F. Orlov, B.N. Dolgov and M.G. Voronkov, Izv. Akad. Nauk. S.S.S.R. Otdel. Khim. Nauk, (1960) 1607; Chem. Abstr., 55 (1961) 9316; ibid, Khim. i Prakt. Primenenie Kremneorg. Soed. Trudy Konf. Leningrad, 1 (1958) 161; Chem. Abstr., 54 (1960) 4360.

24 M. Wick, Kunststoffe, 50 (1960) 433; Chem. Abstr., 54 (1960) 23395.

25 M. Lesbre and J. Satge, C.R. Acad. Sci. Paris, 254 (1962) 4051.

26 M.G. Voronkov and V.N. Zgonnik, Zh. Obshch. Khim., 27 (1957) 1476; Chem. Abstr., 52 (1958) 3673.

27 A.J. Barry, U.S. Pat., 2,611,775 (1952); Chem. Abstr., 47 (1953) 8092.

28 H.G. Schafer and A. Linser, Chem. Tech. (Berlin), 2 (1950) 181.

29 R.L. Vale, J. Chem. Soc., (1960) 2252.

30 J.G.E. Wright, U.S. Pat. 2,541,851 (1951); Chem. Abstr., 45 (1951) 4485.

31 S.K. Mehrotra, G. Srivastava and R.C. Mehrotra, J. Organometal. Chem., 54 (1973) 139.

32 G. Weissenberger, U.S. Pat. 3,312,725 (1967); Chem. Abstr., 67 (1967) 10686.

33 S.K. Mehrotra, G. Srivastava and R.C. Mehrotra, J. Organometal. Chem., in press.

34 V.F. Gridina, A.L. Klepanslsii, B.A. Bartashev, L.P. Dorofeenko, N.V. Kozlova and L.E. Krupnova, Zh. Obshch. Khim., 36 (1966) 1283; Chem. Abstr., 65 (1966) 15415.

35 S.A. Agripat, Ger. Pat. 1,246,731 (1967); Chem. Abstr., 67 (1967) 90938.

36 M.E. Lombardo, Fr. Pat. 1,482,847 (1967); Chem. Abstr., 68 (1968) 49780.

37 S.K. Mehrotra, G. Srivastava and R.C. Mehrotra, J. Organometal. Chem., 47 (1973) 39.

38 B.I. Yakovlev and N.V. Vinogradova, Zh. Obshch. Khim., 29 (1959) 695; Chem. Abstr., 54 (1960) 260.

39 S.K. Mehrotra, Ph.D. Thesis, Rajasthan University, India, 1973.

40 R.W. Martin, U.S. Pat. 2,644,805 (1953); Chem. Abstr., 48 (1954) 310.

41 H. Jedlicka, Ger. Pat. 1,045,092 (1958); Chem. Abstr., 54 (1960) 23424.

42 W.I. Patnode, U.S. Pat. 2,434,953 (1948).

43 Metal and Thermit Corpn., Brit. Pat. 772,646 (1957); Chem. Abstr., 51 (1957) 15551.

44 H.E. Ramsden, U.S. Pat. 2,876,641 (1959); Chem. Abstr., 53 (1959) 6082.

45 S.K. Mehrotra, G. Srivastava and R.C. Mehrotra, J. Organometal. Chem., in press.

46 S.K. Mehrotra, G. Srivastava and R.C. Mehrotra, unpublished results.

47 A.G. Davies, L. Smith, P.J. Smith and W. McFarlane, J. Organometal. Chem., 29 (1971) 245.

48 A.P. Kreshkov, J. Appl. Chem., U.S.S.R., 23 (1960) 545.

49 R.H. Krieble, U.S. Pat., 2,440,101 (1948); Chem. Abstr., 42 (1948) 6376.

50 British Thomson-Houston Co. Ltd., Brit. Pat. 643,298 (1950); Chem. Abstr., 45 (1951) 7819.

51 A.P. Kreshkov, D.A. Karateev and V. Fyurst, Zh. Obshch. Khim., 31 (1961) 2139; Chem. Abstr., 56 (1962) 494.

52 K.A. Andrianov and M.N. Ermakova, Izv. Akad. Nauk S.S.S.R., Ser. Khim., 4 (1968) 896; Chem. Abstr., 69 (1968) 67458.

53 K.A. Andrianov, T.V. Vail'eva and R.A. Romanova, Doklady Akad. Nauk S.S.S.R., 168 (1966) 1057; Chem. Abstr., 65 (1966) 12227.

54 K.A. Andrianov and T.V. Vassil'eva (U.S.S.R.) Kremniiorg. Soedin, Tr. Soveshch., 3 (1967) 51; Chem. Abstr., 69 (1968) 87069.

55 K.A. Andrianov and M.N. Ermakova, Zh. Obshch. Khim., 31 (1961) 1310.

56 K.A. Andrianov and L.M. Volkova, Izv. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk, (1957) 303; Chem. Abstr., 51 (1957) 14544; ibid, Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci., (1957) 317; Chem. Abstr., 52 (1958) 14525.

57 F.A. Henglein, R. Lang and K. Scheinost, Makromol. Chem., 15 (1955) 177.
58 Y. Murayama and H. Shinno, Jap. Pat. 29,370 (1968); Chem. Abstr., 70 (1969) 87951.
59 R.V. Kudryavtsev, D.N. Kursanov and K.A. Andrianov, Zh. Obshch. Khim., 29 (1959) 1497; Chem. Abstr., 54 (1960) 8595.
60 K.A. Andrianov, V.V. Astalshin and I.V. Sukhanova, Izvest. Akad. Nauk S.S.S.R. Otdel. Khim. Nauk (1962) 1478; Chem. Abstr., 58 (1963) 3455.
61 H. Steinberg and D.L. Hunter, Ind. Eng. Chem., 49 (1957) 174.
62 S.K. Mehrotra, G. Srivastava and R.C. Mehrotra, Syn. Inorg. Metalorg. Chem., in press.
63 P. Pulay and F. Torok, Acta Chim. Acad. Sci. Hung., 45 (1965) 123.
64 M.G. Voronkov and N.F. Orlov, Latvijas PSR Zinatu. Akad. Vestis. Kim. Ser. No. 1 (1961) 93; Chem. Abstr., 58 (1963) 2466.
65 H. Schmidbaur and M. Schmidt, Angew. Chem., 74 (1962) 328.
66 W. Gerrard and P.F. Griffey, J. Chem. Soc., (1960) 3170.
67 M.J. Frazer, W. Gerrard and J.K. Patel, J. Chem. Soc., (1960) 726.
68 W. Gerrard and Lindsay, Chem. Ind., (1960) 152.
69 M.J. Frazer, W. Gerrard and J.K. Patel, Chem. Ind., (1959) 728.
70 E. Cherbuliez, J.P. Leber and A.M. Ulrich, Helv. Chim. Acta, 36 (1953) 910.
71 A. Burg and R. Wagner, J. Amer. Chem. Soc., 76 (1954) 3307.
72 K.H. Krause, KunststRundsch., 10 (1959) 10.