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Sulphur-containing Organic Compounds of Boron

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This article gives the present state of the chemistry of the organic compounds of boron which include sulphur in their composition. Methods of preparation and the chemical properties of the ortho- and meta-thioborates, esters of halogenothioboric acids, esters of organothioboric acids, alkylthio-1,3,2-dioxaborolanes, 1,2-thiaborolanes, *B*-alkylthio-derivatives of borazole, alkylthioboranes, and dialkylamino(alkylthio)boranes are examined. The sulphur-containing boron compounds exhibit high reactivity and many types of compounds with B–S bonds which are now readily available are used successfully for the synthesis of the most diverse classes of organoboron compounds, including various boron–nitrogen heterocyclic systems and boron-containing polymers. The esters of thioboric and organothioboric acids also find application for the synthesis of organosulphur compounds. There is a bibliography of 124 references.

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I. INTRODUCTION

The first mention of sulphur-containing organic compounds of boron dates from 1878, when Councler[1] obtained from tri-isobutyl borate and phosphorus(V) sulphide a compound which was taken to be tri-isobutyl thioborate. From 1908 [2] for half a century the investigations in this field were carried out sporadically and only became systematic in 1959. This division of boron chemistry can now be regarded as comparatively well studied. There are simple and preparatively convenient methods for the synthesis of the main types of compound with B–S bonds, such as thioborates, esters of organothioboric acids, alkylthioboranes, compounds with mixed functions, and sulphur-containing heterocyclic boron compounds of various types. The chemical properties of sulphur-containing organoboron compounds have been rather widely studied.

The problems of the chemistry of sulphur-containing boron compounds has been partly covered in a review article[3] and in Gerrard's book[4]. Compounds with B–S bonds but not containing B–C bonds were examined in Steinberg's book[5] published in 1964.

II. ORTHO- AND META-THIOBORATES

As a result of the reaction of tri-isobutyl borate with phosphorus(V) sulphide a yellow substance was obtained, which was assumed to be slightly impure tri-isobutyl thioborate[1]. It is very doubtful, however, whether this substance was a thioborate, since it decomposed in a vacuum, whereas alkyl thioborates distil without decomposition. The first representative of the esters of thioboric acid—trimethyl thioborate—was made in 1952 by the action of silver or lead hydrogen sulphide on boron tribromide[6].

A. METHODS OF PREPARATION

1. Synthesis of Thioborates from Boron Trihalides

The most convenient and economic method for obtaining thioborates consists in the action of thiols on boron trichloride:

$$BCl_3 + 3\,RSH \rightarrow B(SR)_3 + 3\,HCl\,.$$

Despite the apparent simplicity of this reaction, the first attempts to use it for the synthesis of thioborates were unsuccessful. Thus as a result of the reaction of boron trichloride and methanethiol, methylthioboron dichloride was obtained as the dimer $(CH_3SBCl_2)_2$, which does not react further with the thiol[6]. The reaction with thiophenol also does not go to completion[7]. As was shown later, all the chlorine atoms can be replaced by alkylthio-groups under more severe conditions. On mixing boron trichloride and thiols in the cold, crystalline complexes

$$Cl_3B \cdot S\begin{matrix}R\\H\end{matrix},$$

are formed, which lose a molecule of hydrogen chloride at 0–40°C. On carrying out the reaction with higher thiols, which have a rather high boiling point, subsequent heating of the reaction mass at 80–150°C gave alkylthioborates[8]. Propyl thioborate (30%) and butyl thioborate (67%) were obtained by this method. Pentyl thioborate was obtained in 57% yield by boiling a decane solution of boron trichloride and pentanethiol[9].

The reaction of boron trichloride with thiols in the presence of tertiary amines or pyridine proceeds more smoothly. When the reaction is carried out without heating, the yields of thioborates under these conditions are moderate. Thus, in the care of boron trichloride and methanethiol in pentane at 0°C in the presence of trimethylamine the yield of trimethyl thioborate was only 34%.[9] However, on boiling an ethereal solution of a mixture of methanethiol, boron trichloride, and triethylamine for 2 h trimethyl thioborate could be obtained in 80% yield. The reaction with other thiols also proceeds smoothly (yields of 70–90%)[8]:

$$BCl_3 + 3\,RSH + 3\,R'_3N \rightarrow B(SR)_3 + 3R'_3NHCl\,.$$

The reactions of boron tribromide with thiols were also investigated. With methanethiol BBr_3 forms a monosubstituted compound—the dimer of methylthioboron dibromide[6,10]; reaction with pentane-1-thiol in the presence of pyridine leads to pentyl thioborate in 27% yield[9]; with thiophenol, triphenyl thioborate is obtained[7,11].

Thioborates can be obtained by the action of metal mercaptides on boron trihalides. Trimethyl thioborate is synthesised by boiling a benzene solution of boron trichloride and silver or lead hydrogen sulphide (but not potassium hydrogen sulphide)[6] or by heating BBr_3 with sodium hydrogen sulphide without a solvent[12].

By starting from boron tribromide with silver thiocyanate, boron thiocyanate was synthesised[2], which was subsequently assigned the isothiocyanate structure[13].

2. Synthesis of Thioborates on the Basis of Diborane

The trimers of the alkylthioboranes (1,3,5-cyclotriborathianes) obtained by the action of thiols on diborane react at 100–120°C with thiols to form alkyl thioborates[14]:

$$(RSBH_2)_3 + 6\,RSH \xrightarrow{100-120^\circ} 3\,B(SR)_3 + 6\,H_2\,.$$

Alkyl thioborates can also be obtained by heating di(alkylthio)boranes[15,16] or trialkylamine–boranes[17,18] with thiols:

$$(RS)_2BH + RSH \xrightarrow{60-150^\circ} B(SR)_3 + H_2$$

$$H_3B \leftarrow NR_3 + 3\,RSH \xrightarrow{60-100^\circ} B(SR)_3 + NR_3 + 3\,H_2\,.$$

3. Various Reactions in Which Orthiothioborates, Their Derivatives, and Metathioborates Are Formed

A series of reactions are known, mostly not of preparative value, as a result of which thioborates are formed.

The reaction of methanethiol, hexanethiol, or phenylmethanethiol and hydrogen chloride with tris(dialkylamino)-boron gave the corresponding thioborates[9,19].

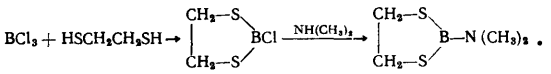
Ethyl thioborate was obtained by the action of hydrogen sulphide on ethylthioboron dibromide[20]:

$$3\,C_2H_5SBBr_2 + 3\,H_2S \rightarrow B(SC_2H_5)_3 + B_2S_3 + 6\,HBr\,.$$

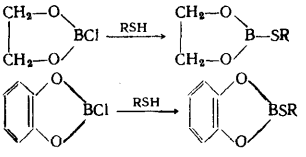
The polymer of methylthioborane undergoes disproportionation into methyl thioborate and diborane at 140°C;[12] trimethylamine–methylthioborane[12] and the methyl esters of methyl- and dimethyl-thioboric acids[21] also disproportionate (145°C) to methyl thioborate. Triphenyl thioborate was obtained by the reaction of potassium tetrafluoroborate and tris(phenylthio)aluminium[22]:

$$KBF_4 + Al(SC_6H_5)_3 \xrightarrow{260^\circ} B(SC_6H_5)_3 + AlF_3 + KF\,.$$

The action of ethane-1,2-dithiol on boron trichloride gave 2-chloro-1,3,2-dithiaborolane, which was converted into the dimethylamino-derivative[23]:

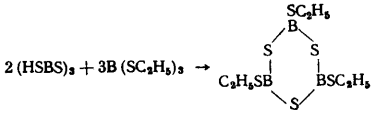


2-Alkylthio-1,3,2-dioxaborolanes are obtained from the corresponding chloro-derivatives and thiols[24–26]:



where R = n-C_4H_9 or n-C_8H_{17}.

Prolonged boiling of a carbon disulphide solution of metaboric acid[27,28] and triethyl borate gives a trimer of an ester of metaboric acid[29]:



which is converted on distillation into the dimer $(C_2H_5SBS)_2$.

B. PROPERTIES

Trialkyl thioborates are liquids with a very unpleasant odour; triphenyl thioborate is a solid melting over a wide range.

The ^{11}B chemical shift in tributyl thioborate is –47.9 p.p.m. in relation to trimethyl borate[17]. Thioborate exhibits an intense absorption band in the 10–11 μm range and a weaker one in the 13.25–13.50 μm range.

1. Hydrolysis and Alcoholysis

Thioborates are readily hydrolysed by water with the formation of boric acid and thiols[12,17]; with alcohols they give alkyl borates and thiols[6]:

$$B(SR)_3 + 3\,ROH \rightarrow B(OR)_3 + 3\,RSH\,.$$

2. Reactions with Amines

Trimethyl thioborate and pyridine form a 1 : 1 adduct[8]; triethyl thioborate gives an unstable complex with pyridine, which decomposes on heating into the initial components[30].

As the example of triethyl thioborate showed, the reaction of thioborates with primary or secondary amines proceeds by successive replacement of alkylthio-groups by the corresponding alkylamino-groups and as a result, depending on the ratio of the reagents, the products[30] are *N*-substituted bis(alkylthio)aminoborane, an alkylthiodiaminoborane, or triaminoborane, unchanged on distillation:

$$B(SC_2H_5)_3 + RR'NH \rightarrow RR'NB(SC_2H_5)_2 + C_2H_5SH\,,$$
$$B(SC_2H_5)_3 + 2\,RR'NH \rightarrow (RR'N)_2BSC_2H_5 + 2\,C_2H_5CH\,,$$
$$B(SC_2H_5)_3 + 3\,RR'NH \rightarrow (RR'N)_3B + 3\,C_2H_5SH\,,$$

where R = H or Alk.

Bis(ethylthio)phenylaminoborane, obtained by the action of 1 mole aniline on triethyl thioborate, is symmetrised at room temperature into tris(phenylamino)boron and triethyl thioborate.

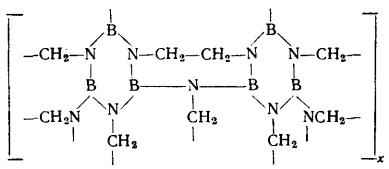
The compound $[(CH_3)_2NBS]_3$ which is a trimer of the anhydride of dimethylaminothioboric acid, is synthesised by the action of tris(dimethylamino)boron on metathioboric acid[31,32] or the anhydride of bromothioboric acid[32] and also from metathioboric acid and $Al[N(CH_3)_2]_3$:[33]

$$(HSBS)_3 + B[N(CH_3)_2]_3 \rightarrow [(CH_3)_2NBS]_3 + B(SH)_3\,,$$
$$(BrBS)_3 + B[N(CH_3)_2]_3 \rightarrow [(CH_3)_2NBS]_3 + BBr_3\,.$$

$(CH_3NHBS)_3$ was also obtained by the action of methylamine on $(BrBS)_3$:[20]

$$(BrBS)_3 + 3NH_2CH_3 \rightarrow (CH_3NHBS)_3 + 3HBr\,.$$

The action of ethylenediamine on triethyl thioborate (1 : 1) gives a polymer which does not contain ethylthio-groups and to which is ascribed the structure[30]:



3. Exchange Reactions with Boron Compounds

Trialkyl thioborates undergo exchange reactions with esters of organoboron acids[34-36] or boron trialkyls[21,34,37], as a result of which esters of organothioboron acids are formed. These conversions are a method for the synthesis of the last class of compound, considered in Section III, A, 3.

4. Reactions with Carbonyl Compounds and Vinyl Esters

The high reactivity of thioborates appears in their reactions with various organic compounds, such as aldehydes, ketones, amides of acids, and vinyl esters.

Trialkyl thioborates react with aldehydes and ketones to form thioacetals or thioketals and boron sesquioxide[38]. The reaction between triethyl thioborate and benzaldehyde in benzene solution is exothermic and yields boron sesquioxide and the bis(ethylthio) acetal of benzaldehyde in 91% yield:

$$3C_6H_5CHO + 2B(SC_2H_5)_3 \rightarrow 3C_6H_5CH(SC_2H_5)_2 + B_2O_3\,.$$

On heating a benzene solution of acetone and tributyl thioborate, the bis-(n-butylthio) ketal of acetone is formed in 90% yield:

$$3CH_3COCH_3 + 2B(SC_4H_9)_3 \rightarrow 3(CH_3)_2C(SC_4H_9)_2 + B_2O_3\,.$$

Under similar conditions triethyl thioborate and acetophonone give acetophenone diethylthio ketal smoothly.

The process evidently proceeds by the addition of thioborate at the carbonyl group:

$$R_2CO + B(SR)_3 \rightarrow R_2C\begin{matrix}OB(SR)_2\\SR\end{matrix}$$

and further conversion of the addition product by the scheme:

$$R_2C\begin{matrix}OB(SR)_2\\SR\end{matrix} + B(SR)_3 \rightarrow R_2C(SR)_2 + (RS)_2BOB(SR)_2\,.$$
$$\downarrow B(SR)_3 + B_2O_3$$

Dimethylformamide reacts like aldehydes and ketones with thioborates[39]:

$$3(CH_3)_2NCHO + 2B(SC_4H_9)_3 \rightarrow (CH_3)_2NCH(SC_4H_9)_2 + B_2O_3\,.$$

The comparatively high yield (66%) of bis(butylthio)-dimethylaminomethane shows the possibility of using this reaction for the preparation of amidomercaptals.

On heating thioborates with vinyl esters, alkyl vinyl sulphides and alkyl borates are obtained[39]:

$$3CH_2{=}CHOR + B(SR)_3 \xrightarrow{100-150^\circ} CH_2{=}CHSR + B(OR)_3$$

Butyl vinyl sulphide was obtained in 71% yield from tributyl thioborate and butyl vinyl ether by this method. Tripropyl thioborate and butyl vinyl ether react similarly, as do tributyl thioborate and ethyl vinyl ether.

It must be assumed that the thioborate adds at the double bond of the vinyl ether and the addition product then undergoes β-decomposition with the elimination of an alkyl vinyl sulphide:

$$CH_2{=}CHOR + B(SR)_3 \rightarrow (RS)_2BCH_2CH\begin{matrix}OR\\SR\end{matrix} \rightarrow$$
$$\rightarrow (RS)_2B\overset{RO-CH-SR}{\overset{|}{\underset{|}{CH_2}}} \rightarrow (RS)_2BOR + CH_2{=}CHSR\,.$$
$$\downarrow B(OR)_3 + B(SR)_3$$

This mechanism for the reaction agrees well with the tendency of β-alkoxy-derivatives of alkylboron acids to eliminate ethylene[40].

III. ESTERS OF ORGANOTHIOBORIC ACIDS

Like thioborates, esters of organothioboric acids have attracted attention only in recent years. The first representatives of this class of compounds—the dodecyl and

octyl esters of 2-chlorovinylthioboric acid—were obtained[41] in 1946. Several other representatives of this class of compound were described subsequently but systematic study of the esters of organothioboric acids only began in 1959. Preparative methods for their synthesis are based on the use of organoboron halides, boron trialkyls, and esters of organoboron acids. The esters of organothioboric acids are, like the thioborates, very reactive substances, and are used successfully for the synthesis of various classes of boron compounds.

A. METHODS OF PREPARATION

1. Synthesis of Esters of Organothioboric acids from Organoboron Halides

One of the general methods of synthesis of esters of organothioboric acids consists in the action of thiols or metal mercaptides on organoboron halides. This method allows esters of organothioboric acids of the aliphatic and aromatic series to be obtained.

Octyl (2-chlorovinyl)chlorothioborate was first obtained by this method from octanethiol and 2-chlorovinylboron dichloride[41]. It was found subsequently that the replacement of one or both halogen atoms in alkylboron dihalides by an alkylthio-group depends on the ratio of the reagents, the temperature, and the duration of heating.

On boiling a mixture of an alkylboron dichloride or alkylboron dibromide with an excess of butane-1-thiol for 10–15 h, n-butyl alkylthioborates are formed smoothly[42]:

$$RBX_2 + 2n\text{-}C_4H_9SH \rightarrow RB(SC_4H_9\text{-}n)_2 + 2HX.$$

n-Butyl phenylthioborate is obtained similarly from phenylboron dichloride[42].

On heating mixtures of alkylboron dichlorides with an excess of ethanethiol, in addition to the diethyl esters of the alkylthioboric acids, products of the incomplete replacement of chlorine atoms are also formed—ethyl esters of (alkylthio)chloroboric acids[43].

$$RBCl_2 \xrightarrow{C_2H_5SH} RB(SC_2H_5)_2 + RBCl(SC_2H_5).$$

Esters of (alkythio)chlorothioboric acids undergo partial symmetrisation into esters of alkylthioboric acids and alkylboron dichlorides when distilled in a vacuum so that esters of alkylchlorothioboric acids cannot be obtained in high yields even in experiments with an equimolecular ratio of the reagents.

Ethyl esters of alkylbromothioboric acids are obtained in 65–75% yields by the reaction of alkylboron dibromides with ethanethiol in 1 : 1 ratio[43]:

$$RBBr_2 + C_2H_5SH \rightarrow RBBr(SC_2H_5) + HBr.$$

Bromothio-esters have a much greater thermal stability than chlorothio-esters and can be distilled in a vacuum without decomposition. Phenylboron dibromide undergoes a similar reaction with ethanethiol[43].

The preparation of esters of alkylchlorothioboric acids can also be effected by an exchange reaction between alkylboron dichlorides and the esters of alkylthioboric acids[43]. Thus, when an equimolecular mixture of n-propylboron dichloride and diethyl n-propylthioborate is left at room temperature for 20 h then by distilling the reaction mixture the ethyl chloro(propyl)thioborate can be isolated in 50% yield.

$$n\text{-}C_3H_7BCl_2 + n\text{-}C_3H_7B(SC_2H_5)_2 \rightarrow 2n\text{-}C_3H_7B(SC_2H_5)Cl.$$

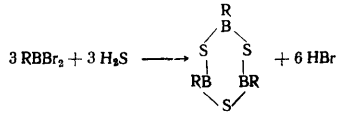
The difference in stability of the esters of the organo-(halogeno)thioboric acids and their oxygen analogues merits attention. Among the compounds of the latter class the tendency to disproportionation is observed only in the esters of organofluoroboric acids[44], whereas the esters of chloro- and bromo-organic acids distil unchanged[45,46].

Yet another method for obtaining esters of alkyl(halogeno)organothioboric acids must be mentioned, consisting in the action of boron halides on the esters of alkylthioboric acids at room temperature[43]. Thus n-butyl isopentylthioborate and boron tribromide gave n-butyl isopentylbromothioborate [bromo(butylthio)isopentylborane]:

$$3iso\text{-}C_5H_{11}B(SC_4H_9\text{-}n)_2 + BBr_3 \xrightarrow[80\%]{} 3iso\text{-}C_5H_9B(SC_4H_9\text{-}n)Br + B(SC_4H_9\text{-}n)_3.$$

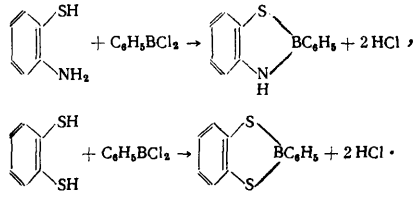
Dialkylboron halides[21,47] and diarylboron halides[42] are converted into the esters of dialkyl- and diaryl-thioboric acids respectively on heating with thiols. In this method various metal mercaptides can be used instead of thiols. Thus the di-n-pentyl ester of phenylthioboric acid [phenyldi(pentylthio)borane] was synthesised by the reaction of phenylboron dichloride with methylthiosodium[48].

When heated with hydrogen sulphide in an inert solvent (benzene, carbon disulphide), phenylboron dibromide[49] and alkylboron dibromides[20] are converted respectively into the anhydrides of phenyl- or alkyl-thioboric acids, which exist as cyclic trimers:



where R = n-C_4H_9, iso-C_4H_9, or C_6H_5.

Cyclic esters of organothioboric acids are formed in the reaction of organoboron dihalides with *ortho*-thio-derivatives of benzene. Thus phenylboron dichloride and 2-aminothiophenol or dithiocatechol gave 2-phenylbenzo-1,3,2-thiazaborolane and 2-phenylbenzo-1,3,2-dithiaborolane respectively[50]:



2. Synthesis of Esters of Organothioboric Acids from Boron Trialkyls

a. Use of thiols. A simple method of obtaining esters of dialkylthioboric acids is the reaction between boron trialkyls and thiols[51,53]. The reaction starts at room temperature and is accompanied by evolution of heat; additional heating of the reaction mass at 110–160°C is necessary to complete the process:

$$BR_3 + R'SH \rightarrow R_2BSR' + RH.$$

A detailed study of this reaction disclosed that it is initiated by peroxide compounds in ultraviolet light[54]. Only freshly distilled boron trialkyls, which almost always contain traces of peroxy-compounds >BOOR, start to react with thiols at room temperature. Furthermore, boron trialkyls freed from peroxides (by heating at 100°C for a few

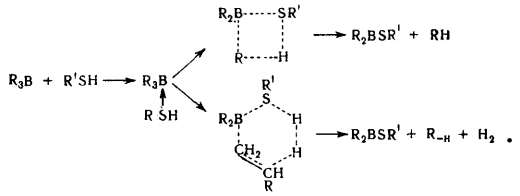
hours or by keeping at room temperature for a few months) do not react with thiols below 150°C. When a little (2–10 ml) air or pieces of porcelain or diatomaceous brick is introduced into a mixture of such "deactivated" boron trialkyls and a thiol a reaction starts, accompanied by the formation of a thioester R_2BSR and an alkane. Reaction takes place at a still greater rate on adding drops of hydrogen peroxide or an alkyl hydroperoxide to the mixture.

The peculiarities of the behaviour of thiols in relation to boron trialkyls, sharply distinguishing them from other nucleophilic reagents, such as water, alcohols, and amines, with which boron trialkyls react at 150–200°C,[51] are explained evidently by the ability of thiols to participate in radical processes brought about by organoboron peroxides.

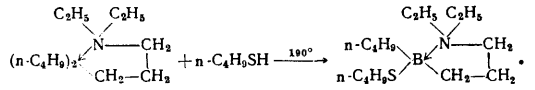
Unlike thiols, thiophenol[51,52] reacts with boron trialkyls on heating and in addition to saturated hydrocarbons the products include alkenes and hydrogen, as when other nucleophilic reagents are used[52]:

$$BR_3 \xrightarrow[150-170^\circ]{C_6H_5SH} R_2BSC_6H_5 + RH + R_{-H} + H_2 .$$

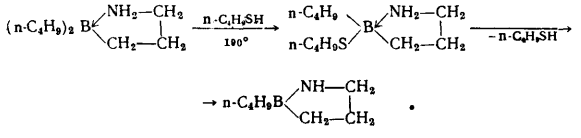
Evidently the formation of saturated hydrocarbons in this reaction occurs through a four-centre transition state, whereas the alkene and hydrogen are obtained by a six-centre mechanism:



It is interesting that mercaptans are capable of reacting with inner complexes of boron trialkyls, but only at a high temperature (190°C). Thus in the action of butane-1-thiol on 3-(diethylamino)propyldibutylboron butyl butyl-3-(diethylamino)propylborate is obtain in 55% yield:



3-Aminopropyldibutylboron also reacts with thiols at high temperature, but the ester of 3-aminopropylbutylthioboric acid formed as an intermediate is immediately converted with loss of a thiol into 2-n-butyl-1,2-azaborolidine[55]:



An increased ability to exchange a radical by an alkylthio-group is exhibited by triallylboron[56,57], which reacts with ethanethiol at temperatures between −10° and −15°C; at an equimolecular ratio of the reagents ethyl diallylthioborate and propene are formed. In the action of 2 moles ethanethiol on 1 mole triallylboron the main reaction product is diethyl allylthioborate but in addition ethyl diallylthioborate and ethyl 3-ethylthiopropylthioborate are obtained:

$$B(CH_2CH=CH_2)_3 + 2\,C_2H_5SH \rightarrow CH_2=CHCH_2B(SC_2H_5)_2 + 2\,C_3H_6$$
$$\downarrow C_2H_5SH$$
$$C_2H_5-S-CH_2-CH_2CH_2B(SC_2H_5)_2 .$$

Diethyl 3-ethylthiopropylthioborate can be obtained by the direct action of ethanethiol on diethyl allylthioborate.

The high reactivity of triallylboron in relation to thiols and also to other nucleophilic reagents[58–61] is evidently connected with an allyl rearrangement in these compounds. As investigation by proton magnetic resonance showed[62], the allyl rearrangement in triallylboron:

$$(C_3H_5)_2\overset{*}{B}CH_2CH=CH_2 \rightleftarrows \overset{\text{transition state}}{\rightleftarrows} (C_3H_5)_2BCH_2CH=\overset{*}{C}H_2$$

proceeds with a velocity from 4.7 Hz at −25°C to 3.3 kHz at 88°C, that is, the average life time of each state varies in this temperature range from 2×10^{-1} to 3×10^{-4} s.

b. Use of Sulphur. One of the features of boron trialkyls is their ability to react with oxygen to form esters of dialkyl- or alkyl-boric acids, depending on the condition. It seemed that sulphur is also capable of reacting with boron trialkyls on heating with formation of esters of dialkylthioboric acids[63,64]:

$$BR_3 + S \xrightarrow{140^\circ} R_2BSR .$$

c. Use of thioborates. At elevated temperatures boron trialkyls enter into an exchange reaction with thioborates to form esters of organothioboric acids. Methyl dimethylthioborate was obtained by this method on prolonged heating of methyl thioborate with trimethylboron in the presence of traces of diborane[21]:

$$2\,B(CH_3)_3 + B(SCH_3)_3 \rightleftarrows 3\,(CH_3)_2BSCH_3 .$$

By heating a 1 : 2 mixture of boron trialkyls and ethyl thioborate for 30–35 h at 250°C ethyl alkylthioborates were obtained in 65–75% yields[37]:

$$BR_3 + 2\,B(SC_2H_5)_3 \xrightarrow{250^\circ} 3\,RB(SC_2H_5)_2 .$$

The reaction of boron trialkyls with butyl thioborate under similar conditions proceeds less smoothly.

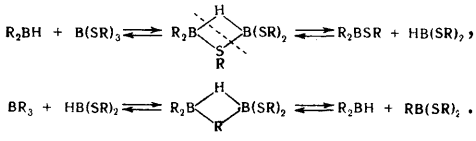
In the reaction products there is a certain amount (10–15%) of an ester of a dialkylthioboric acid and also the initial compounds, which is explained by the reversibility of the reactions:

$$BR_3 + B(SR')_3 \rightleftarrows R_2BSR' + RB(SR')_2 ,$$
$$R_2BSR' + B(SR)_3 \rightleftarrows 2\,RB(SR')_2 .$$

In the reaction with triethyl borate the equilibrium is shifted to the right to a greater extent than in that with tributyl thioborate.

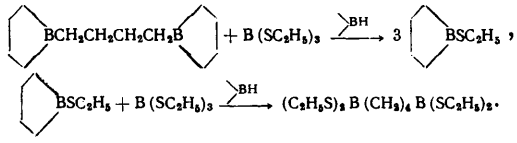
The use of tetra-alkyldiborane as a catalyst allows a much lower temperature and a shorter reaction time to be used in the reaction of tributylboron with tributyl thioborate. The yield of dibutyl butylthioborate was 73%.[34]

The catalytic action of tetra-alkylboranes and also other compounds with B–H bonds, just as in exchange reactions between boron trialkyls and orthoborates[34,65–67], explains their ability to form dimeric intermediate compounds with three-centre B–H–B bonds, for example:



In the presence of compounds with B–H bonds 1,4-di-(1-boracyclopentyl)butane is smoothly converted by ethyl

thioborate into 1-ethylthioboracyclopentane, and the latter into an ester of butane-1,4-dithioboric acid[68]:



3. Synthesis of Esters of Organothioboric Acids from Esters of Organoboric Acids

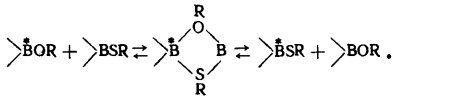
A universal and preparatively very simple method for the synthesis of esters of organothioboric acids is an exchange reaction between esters of organoboric acids and thioborates or esters of organothioboric acids.

Whereas in organoboron compounds the exchange of an alkyl radical for an alkoxy- or alkylthio-radical is effected smoothly only in the presence of compounds with B–H bonds the exchange of alkoxy- and alkylthio-groups in organic compounds of boron can be effected without a catalyst[35,36]:

$$3RB(OR')_2 + 2B(SR'')_3 \rightleftarrows 3RB(SR'')_2 + 2B(OR')_3,$$
$$3R_2BOR' + B(SR'')_3 \rightleftarrows 3R_2BSR'' + B(OR')_3,$$
$$RB(OR')_2 + R''B(SR''')_2 \rightleftarrows RB(SR''')_2 + R''B(OR')_2,$$
$$RB(OR')_2 + 2R''_2B(SR''') \rightleftarrows RB(SR''')_2 + R''_2BOR',$$
$$R_2BOR' + R''_2BSR''' \rightleftarrows R_2BSR''' + R''_2BOR'.$$

These reactions are reversible and the equilibrium can be displaced by the removal of the most volatile component in a vacuum with the reaction mass at 80–150°C. Under these conditions even after 2–3 h the equilibrium is almost completely displaced in favour of a low-boiling compound and the yields of the compounds sought is usually $\lhd$ 90%. On using esters with radicals of different molecular weight exchange reactions of the types mentioned could be effected in any direction. This is an extremely valuable procedure for the production of esters of low molecular weight from esters of higher molecular weight. For example, with ethyl thioborate butyl propylthioborate or dibutylthioborate gave the corresponding ethyl esters in 87–97% yields.

The reaction mechanism leads to the formation of intermediate dimeric compounds and their subsequent decomposition in an energetically favourable direction:



This method of synthesis of esters of organothioboric acids was used with success for a series of alkanediboric and triboric compounds. Thus tetramethyl propane-1,3-diborate is converted into tetramethyl propane-1,3-dithioborate on heating with methyl thioborate[68]:

$$3(CH_3O)_2B(CH_2)_3B(OCH_3)_2 + 4B(SCH_3)_3 \rightarrow (CH_3S)_2B(CH_2)_3B(SCH_3)_2 + 4B(OCH_3)_3.$$

Tetraethyl butane-1,4-dithioborate was obtained from tetramethyl butane-1,4-diborate and triethylthioborate[70]:

$$3(CH_3O)_2B(CH_2)_4B(OCH_3)_2 + 4B(SC_2H_5)_3 \rightarrow$$
$$\rightarrow (C_2H_5S)_2B(CH_2)_4B(SC_2H_5)_2 + 4B(OCH_3)_3.$$

The corresponding 1,1,5,9,9-penta-alkylthio-1,5,9-triboranononanes were synthesised from 1,1,5,9,9-pentamethoxy-1,5,9-triboranononane and trimethyl thioborate or triethyl thioborate[71]:

$$3(CH_3O)_2B(CH_2)_3\underset{\displaystyle OCH_3}{B}(CH_2)_3B(OCH_3)_2 + 5B(SR)_3 \rightarrow$$
$$\rightarrow 3(RS)_2B(CH_2)_3\underset{\displaystyle SR}{B}(CH_2)_3B(SR)_2 + 5B(OCH_3)_3$$

where R = CH_3 or C_2H_5.

When the polymers which are formed in the hydroboronation of dimethyl allylthioborate are heated with methyl thioborate in the presence of tetrapropyl diborane they give tetramethyl propane-1,3-dithioborate[72].

4. Synthesis of Esters of Organothioboric Acids from Alkylthioboranes and Unsaturated Hydrocarbons

Di(butylthio)borane reacts with hex-1-ene or oct-1-ene to form the esters of the corresponding organothioboric acids[73]:

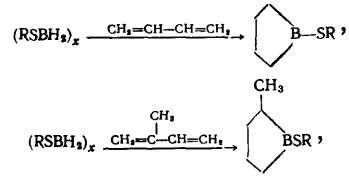
$$(n\text{-}C_4H_9S)_2BH + CH_2{=}CHR \rightarrow RCH_2CH_2B(SC_4H_{9}\text{-}n)_2.$$

The reaction with propene or 2-methylpropene is complex, leading to mixtures of butyl alkylthioborates, dialkylthioborates, and tributyl thioborate. The reaction of polymeric butylthioborane with ethylene or propene is also complex but with hex-1-ene an ester of dihexylthioboric acid is obtained in 60% yield[74]:

$$(n\text{-}C_4H_9SBH_2)_x + 2x\,CH_2{=}CHC_4H_9 \rightarrow x(C_6H_{13})_2BSC_4H_{9}\text{-}n.$$

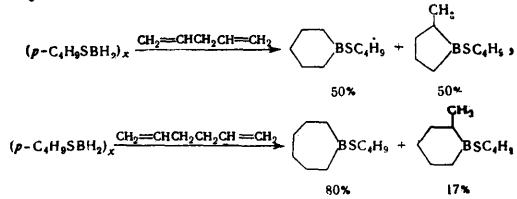
Methyl esters of diethylthioboric, dihexylthioboric, and dicyclohexylthioboric acids were obtained from methylthioborane polymer and ethylene, hex-1-ene, and cyclohexene[74].

1-Alkylthioboracycloalkanes can be synthesised from polymers of alkylthioboranes and diene hydrocarbons. Thus the reaction of polymers of methylthioborane or butylthioborane with dienes (buta-1,3-diene or isoprene) in ethereal medium gave 1-methylthioboracyclopentane[74], 1-butylthioboracyclopentane[75,76], 3-methyl-1-methylthioboracyclopentane[74], and 3-methyl-1-butylthioboracyclopentane[76]:



where R = CH_3 or n-C_4H_9.

The reaction of the polymer of butylthioborane with penta-1,4-diene or hexa-1,5-diene gives a mixture of alkylthioboracyclanes[76]:



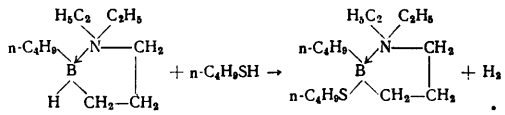
5. Synthesis of Esters of Organothioboric Acids from Alkyldiboranes or Aminoalkyl(aryl)boranes

Esters of organodialkylthioboric acids are formed by the action of thiols on tetra-alkyldiboranes[12,77]:

$$R_4B_2H_2 + 2RSH \rightarrow 2R_2BSR + 2H_2 .$$

The reactions are complicated by the formation of small amounts of side-products, owing to the symmetrisation of the initial compounds.

Butyl-(3-diethylaminopropyl)borane reacts with a thiol at 190°C to form an ester of butyl-(3-diethylaminopropyl)-thioboric acid[55]:



Esters of alkylthioboric acids are formed on heating trimethylamine–alkylboranes with thiols[17,78]:

$$RBH_2 \cdot N(CH_3)_3 + 2RSH \xrightarrow{60-100^\circ} BB(SR')_2 + 2H_2 + N(CH_3)_3 .$$

Esters of dialkylaminoarylboric acids are obtained by the action of thiols on dialkylaminoarylboranes[79].

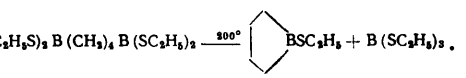
B. PROPERTIES

1. Thermal Conversions

Esters of organothioboric acids are compounds of rather high thermal stability. Thus propyl dipropylthioborate is unchanged after heating for 4 h at 160°C.[64] However, long heating at a high temperature leads to disproportionation of thioesters. After 34 days at 84°C dimethyl methylthioborate is 10% symmetrised into methylthioborate and methyl dimethylthioborate[21], and dibutyl isobutylthioborate after 10 h at 240–250°C was 30% converted into butyl thioborate and butyl di-isobutylthioborate[37]:

$$\text{iso-}C_4H_9B(SC_4H_9\text{-}n)_2 \rightleftarrows (\text{iso-}C_4H_9)_2BSC_4H_9\text{-}n + B(SC_4H_9\text{-}n)_3 .$$

On heating, esters of butane-1,4-dithioboric acid are converted into thioborate and 1-alkylthioboracyclopentane[70]:



2. Hydrolysis and Alcoholysis

Esters of organothioboric acids are readily hydrolysed by water with the formation of organoboric acids and thiols:

$$R_2BSR + H_2O \rightarrow R_2BOH + RSH .$$

Under the action of alcohols esters of organothioboric acids are also readily converted into esters of organoboric acids[64]. With alcohols, alkylthio-derivatives of boracycloalkanes give 1-alkoxyboracycloalkanes[75].

Smooth and rapid reaction of thioesters with alcohols allows esters of dialkylboric acids to be synthesised from boron trialkyls under mild conditions including the difficultly accessible methyl esters by using a catalytic quantity of thiol in the reaction[80]:

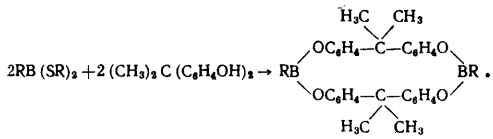
$$BR_3 + CH_3OH \xrightarrow[65-70^\circ]{RSH} R_2BOCH_3 + RH .$$

The thiol and the boron trialkyl form esters of dialkylthioboric acids and thiol, which again reacts with the boron trialkyl. In this way tris-(3-dimethoxyborylpropyl)boron is smoothly converted into 1,1,5,9,9-pentamethoxy-1,5,9-triboranonane and dimethyl propylborate[81]:

$$B[CH_2CH_2CH_2B(OCH_3)_2]_3 + CH_3OH \xrightarrow{C_2H_5SH,\ 100^\circ} \rightarrow (CH_3O)_2B(CH_2)_3B(CH_2)_3B(OCH_3)_2 + n\text{-}C_3H_7B(OCH_3)_2 .$$

Under the action of alcohols, esters of alkylthioboric acids give dialkyl alkylborates.

Dialkyl esters of organoalkylthioboric acids and organoarylthioboric acids form heterocyclic compounds with 2,2-bis-(4-hydroxyphenyl)propane[82] [Bisphenol A]:



3. Reactions with Ammonia and Amines

Esters of dialkylthioboric acids give dialkylboramines with ammonia[63,80,83]. On introducing ammonia into a cooled ester of organothioboric acid an adduct is formed, which decomposes at ~20°C with loss of thiol into dialkylboramines with almost quantitative yield:

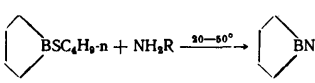
$$R_2BSR' + NH_3 \rightarrow R_2BSR' \cdot NH_3 \rightarrow R_2BNH_2 + R'SH .$$

Dialkylboramines can be obtained starting directly from boron trialkyls and ammonia by using a little thiol, which plays the part of a catalyst of the reaction[80,83]. The thioester formed in the first stage of the reaction between the boron trialkyl and the thiol reacts with the ammonia to regenerate the thiol, which again reacts with the boron trialkyls, and the process is repeated until the boron trialkyl is completely consumed. Esters of diarylthioboric acids also react smoothly in the cold with ammonia to form diarylboramines[42].

With amines the esters of dialkylthioboric acids form *N*-substituted dialkylboramines[63,64,83]:

$$R_2BSR' + NH_2R'' \rightarrow R_2BNHR'' + R'SH .$$

Just as in the synthesis of dialkylboramines, the production of their *N*-substituted derivatives is possible directly from boron trialkyls and amines in the presence of trace amounts of thiols[80,83]. Esters of diarylthioboric acids and 1-alkylthioboracyclopentane[76,85] react similarly with aliphatic[42] and aromatic amines[84]:



With hexamethylenediamine the esters of dialkylthioboric acids form *NN'*-di(dialkylboryl)-1,6-diaminohexanes:

$$2R_2BSR' + H_2N(CH_2)_6NH_2 \xrightarrow[85\%]{160-180^\circ} R_2BNH(CH_2)_6NHBR_2 + 2R'SH;$$

with hydrazine they give 1,2-bis(dialkylboryl)hydrazines

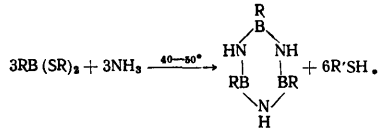
$$2R_2BSR' + NH_2-NH_2 \xrightarrow[80\%]{150-180^\circ} R_2BNH-NHBR_2 + 2R'SH;$$

and with phenylhydrazine they are converted into 2-(dialkylboryl)-1-phenylhydrazines[63]:

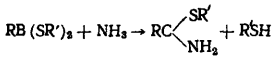
$$R_2BSR' + NH_2NHC_6H_5 \xrightarrow[70\%]{160-200^\circ} R_2BNH-NHC_6H_5 + R'SH .$$

The reactions of esters of alkylthioboric and arylthioboric acids with ammonia and amines leads to a different nitrogen-containing compound of boron.

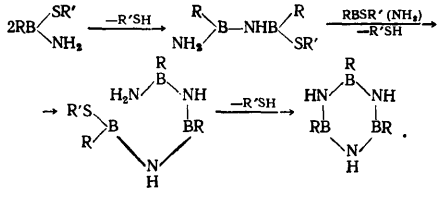
Ammonia with dialkyl esters of organothioboric acids gives *B*-trialkylborazoles smoothly[42,86]



The mechanism of the reaction leads to the formation of an amino-ester in the first stage:



which then is apparently condensed by the following scheme:



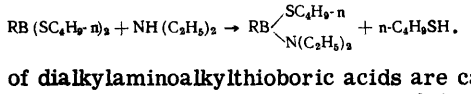
This is an effective method for the synthesis of *B*-trisubstituted borazoles, which is also applicable for the production of *B*-triallylborazole[57].

Unlike the reactions with ammonia, with 2 moles of primary aliphatic amines both alkylthio-groups in esters of alkylthioboric acids are replaced by alkylamino-groups to form *N*-alkyl-substituted alkylborondiamines[87]:

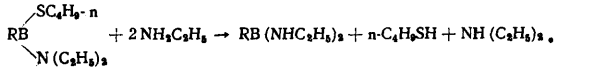
The reaction of equimolecular amounts of reagents gives a mixture of an *N*-alkyl-substituted alkylboron diamine, an aminothioester, and the initial thioester.

Diethyl allylthioborate and butylamine form allyldibutylaminoboron[57].

Esters of alkylthioboric acids behave quite differently with secondary aliphatic amines (for example, diethylamine). Here only one alkylthio-group is replaced by an alkylamino-residue with formation of esters of dialkylamino-acids[87]:



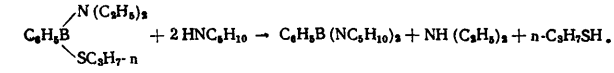
Esters of dialkylaminoalkylthioboric acids are capable of reacting with ethylamine; when an excess of the amine is used both the alkylthio- and the diethylamino-groups are replaced by the ethylamino-group and *N*-ethyl derivatives of alkylborondiamine are obtained[87]:



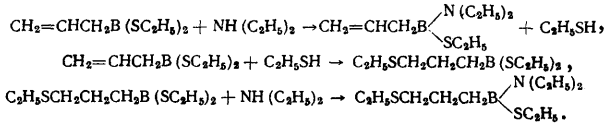
The difference in the behaviour of the esters of diethylaminoalkylthioboric acids towards ethylamine and diethylamine is evidently due to the latter's lower ability to form complexes.

Esters of dialkylaminoaryl thioboric acids behave in relation to primary amines similarly to compounds of the alkyl series, with both alkylthio- and dialkylamino-groups being replace by alkylamino-groups to form *N*-alkyl-substituted arylborondiamines[79].

The esters of dialkylaminoarylthioboric acids are more stable towards secondary amines. When a secondary amine with a high boiling point is used and the thiol and low-boiling secondary amine produced are distilled off from the reaction mass, bis(dialkylamino)arylboron can be obtained[48]:



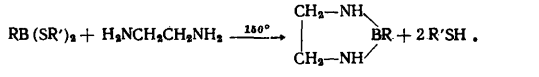
The reaction of diethyl allylthioborate with diethylamine is unique[57]. Approximately equal amounts of ethyl diethylaminoallylthioborate and ethyl diethylamino-3-ethylthiopropylthioborate are obtained. In the first stage of the reaction the ethylthio-group is replaced by diethylamino-, then the ethylthiol thus obtained adds to the initial ester and the ester of 3-ethylthiopropylthioboric acid formed exchanges an alkylthio-group for a diethylamino-group:



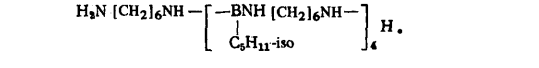
The replacement of an ethylthio-group by diethylamino- in mixed esters does not take place, as for the esters of alkylthioboric acids[87].

Dibutyl phenylthioborate and diethylamine react to form butyl diethylamino(phenyl)borate[79].

The reactions of esters of alkylthioboric acids with diamines proceed differently, depending on the nature of the latter. With ethylenediamine, 2-alkyl-1,3,2-diazoborolidines are obtained[42]:

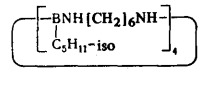


Gentle heating of dibutyl isopentylthioborate with two moles of hexamethylenediamine followed by removal of butylthiol and the unreacted diamine in a vacuum yields a benzene-soluble resinous linear polymer (I) of molecular weight 900, which includes in its structure four $RBNH[CH_2]_6NH-$ chains and an $NH_2[CH_2]_6NH$ terminal group[82]:



(I)

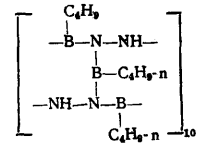
The reaction with equimolecular amounts of the reagents gives the cyclic polymer (II): structure:



(II)

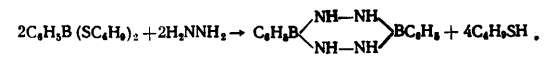
A similar polymer is obtained in the reaction of hexamethylenediamine and dibutyl butylthioborate.

With hydrazine, the esters of alkylthioboric acids give polymers[82] probably having a reticular cyclic structure (III) in which each link contains three $RB\diagdown$ groups and two $\diagup N-NH-$ groups, and the number of links is shown by molecular weight determinations to be 10.

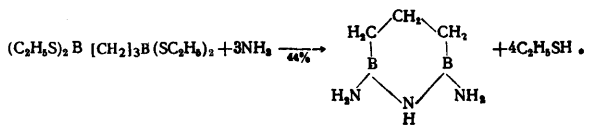


(III)

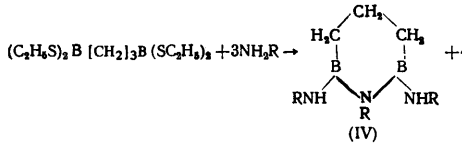
The reaction of hydrazine with an ester of phenylthioboric acid proceeds differently, leading to the formation of 3,6-diphenyl-3,6-dibora-1,2,4,5-tetrazine[82]:



The action of ammonia on tetraethyl propane-1,3-dithioborate yields 2,5-diamino-1-aza-2,5-diboracyclohexane[88]:

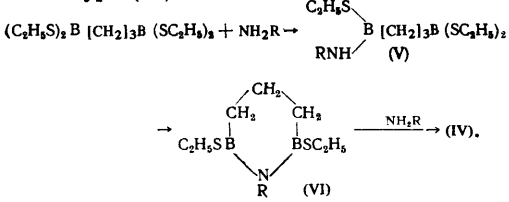


With primary amines (methylamine or ethylamine), cyclic compounds (IV) are also obtained—1-alkyl-2,5-di-(alkylamino)-1-aza-2,5-diboracyclohexanes:



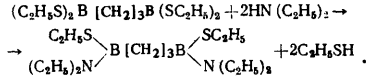
(IV)

In the first stage of the reaction one of the alkylthio-groups in the thio-ester is replaced by an alkylamino-group and the compound (V) which results is cyclised with loss of a thiol into compound (VI), which subsequently exchanges an alkylthio-group, being converted into a compound of type (IV):

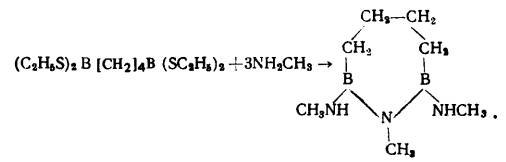


The reaction of tetraethyl propane-1,3-dithioborate with dimethylamine leads to 1,3-bis-[di(dimethylamino)bora]-propane[88].

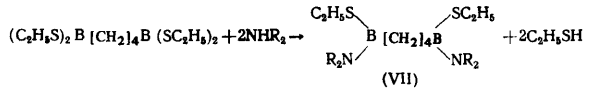
With diethylamine, esters of propane-1,3-dithioboric acid give, like esters of alkylthioboric acids, mixed (alkylamino)alkylthio-derivatives[88]:



The esters of butane-1,4-dithioboric acid react with amines similarly to the esters of propane-1,3-dithioboric acid[70]. The action of an excess of methylamine gives smoothly a seven-membered heterocyclic compound—1-methyl-2,7-bis(methylamino)-1-aza-2,7-diboracycloheptane:

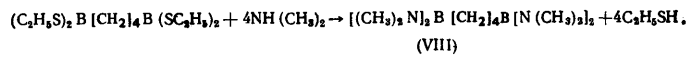


In the reaction with secondary amines the replacement of two alkylthio-groups takes place very readily with the formation of 1,4-bis(dialkylaminoethylthiobora)butane (VII)[70]:



(VII)

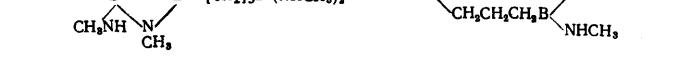
The further replacement of alkylthio-groups is effected by the use of a large excess of the dialkylamine, heating (80–100°C), and periodically distilling off in a vacuum the thiol formed in the reaction:



(VIII)

The reverse reaction—the replacement of the dimethylamino-group in compound (VIII) by ethylthio-groups—also proceeds with difficulty, only two of them being replaced, with formation of the compound (VII; R = CH_3).

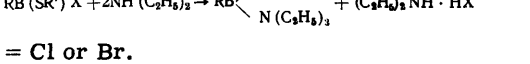
1,1,5,9,9-Penta-alkylthio-1,5,9-triboranonanes react vigorously with dimethylamine[71], exchanging all the alkylthio-groups for dialkylamino-groups:



With methylamine a substance with structure (IX) or (X) is formed:

(IX) (X)

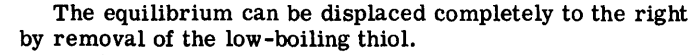
The action of diethylamine on esters of halogenoalkylthioboric acids causes halogen atom replacement by an alkylamino-group, with formation of esters of (diethylamino)alkylthioboric acids[43] resistant to further action by diethylamine:



where X = Cl or Br.

4. Reactions with Thiols, Hydrogen Sulphide, and Hydrogen Cyanide

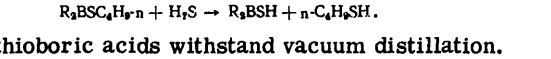
Esters of dialkylthioboric acids are readily re-esterified by higher thiols on heating[52]:



The equilibrium can be displaced completely to the right by removal of the low-boiling thiol.

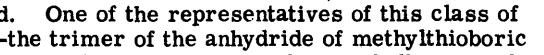
Diethyl allylthioborate adds ethanethiol to form an ester of 3-ethylthiopropylthioborate[56,57].

When treated with hydrogen sulphide and heated to 140–180°C esters of organodialkylthioboric acids form dialkylthioboric acids and a thiol[89]:



Organothioboric acids withstand vacuum distillation. Prolonged heating of dibutylthioboric acid at 180–250°C decomposes it into hydrogen sulphide, hydrogen, butene, butane, and uninvestigated sulphur-containing organoboron compounds.

The reaction of esters of organoalkylthioboric acids with hydrogen sulphide, as a result of which anhydrides of alkylthioboric acids could be obtained, has not been investigated. One of the representatives of this class of compound—the trimer of the anhydride of methylthioboric acid—was obtained by the reaction of trimethylboron and metathioboric acid[90]:



The trimer is stable only in the solid state; in solutions a greater association of the anhydride is observed.

In solution the polymeric anhydride of metathioboric acid is oxidised by oxygen into $(CH_3OBS)_3$,[90] which can also be obtained by the action of trimethyl borate on metathioboric acid[31] or $(BrBS)_3$:[91]

$$(HSBS)_3 \xrightarrow[-B(SH)_3]{B(OCH_3)_3} (CH_3OBS)_3 \xleftarrow[-BBr_3]{B(OCH_3)_3} (BrBS)_3 .$$

Butyl dialkylthioborates react with hydrogen cyanide in the cold or on gentle heating to form dialkylcyanoborons[89]:

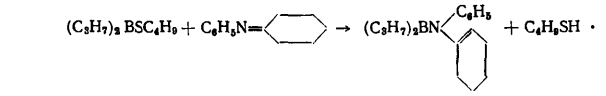
$$R_2BSC_4H_9\text{-}n + HCN \rightarrow [R_2BSC_4H_9\text{-}n \cdot HCN] \rightarrow R_2BCN + n\text{-}C_4H_9SH .$$

5. Reactions with Vinyl Esters, Cyclohexylideneaniline, and Nitriles

Esters of dialkylthioboric acids are capable of reacting with various classes of unsaturated organic compounds. Like thioborates they react with alkyl vinyl ethers, as a result of which alkyl vinyl sulphides and esters of dialkylboric acids are formed[39]. Evidently, as for thioborates the process proceeds by addition of the thioester at the multiple bond followed by β decomposition:

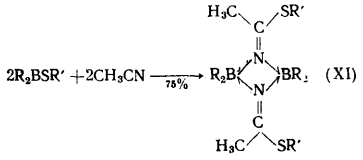
$$R_2BSC_4H_9 + CH_2=CHOC_4H_9 \rightarrow \left[R_2BCH_2CH\begin{matrix}OR\\SC_4H_9\end{matrix}\right] \rightarrow CH_2=CHSC_4H_9 + R_2BOR.$$

On heating an ester of dipropylthioboric acid with cyclohexanone anil, (cyclohexenylyl)phenylaminodipropylboron and a thiol are formed[39]:



Evidently the anil reacts in the tautomeric form as an enamine.

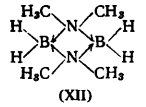
Esters of dialkyl and diaryl-thioboric acids are capable of adding at room temperature to acetonitrile with formation of 1,3-di-(1-alkylthioethylidene)-2,2,4,4-tetra-alkylcyclodiborazones (XI):[92]



where R′ = C_2H_5, or n-C_4H_9.

Infrared spectroscopy showed that in the first stage of the reaction the addition product $R_2BN{=}CCH_3(SR)$ is formed, which then dimerises into compound (XI). This is unchanged in air and is not decomposed at room temperature by alcohol, water, or even hydrochloric acid.

Concerning the nature of the chemical bond in derivatives of cyclodiborazane (XI), in these compounds, as in the dimers of aminoboranes (cyclodiborazanes), the trimers of aminoboranes (cyclotriborazanes), and other such compounds (trimers of phosphinoboranes, alkylthioboranes), all the bonds of the boron atom with a heteroatom (N, P, S) are equivalent. The equivalence of the chemical bonds in this type of compound, for example, in 1,1,3,3-tetramethylcyclodiborazane (XII)



(XII)

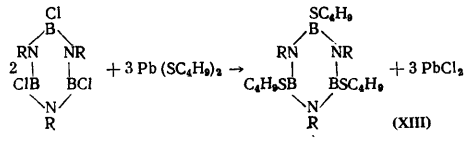
is attained by the formation of a special type of coordinate bond between the boron atom and the heteroatom. In this coordination interaction, each boron atom allows one tetrahedral orbital (sp^3) and one electron for covalent bonds with hydrogen atoms and one sp^3-orbital and $\frac{1}{2}$ electron for bonds with each neighbouring nitrogen atom. On the other hand, each nitrogen atom supplies an sp^3-orbital and one electron for its bonds with each carbon atom and one sp^3-orbital and 1.5 electrons for bonds with each neighbouring boron atom. It is desirable to call this type of bond semicoordinate and to represent it with a half-arrow.

In cyclodiborazanes of type (XI) the bond between the boron and nitrogen atoms also has a semicoordinate nature, the only difference being that each nitrogen atom in a $tr^2trtr\pi$ valence state provides for the double bond with the carbon atom one trigonal orbital (sp^2, or in another notation tr) and one π orbital whereas for the bond with each neighbouring boron atom one trigonal orbital (tr). The semicoordinate bonds formed by the trigonal orbitals of the nitrogen atom are stronger than those with tetrahedral orbitals.

IV. *B*-ALKYLTHIOBORAZOLES

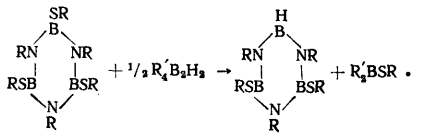
A. METHODS OF PRODUCTION

B-Trialkylthioborazoles (XIII) were synthesised by heating *B*-trichloroborazoles with lead mercaptides in benzene, the yields being 70–90%:[93]



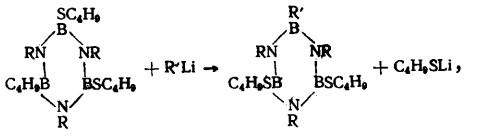
where R = H, CH_3, C_2H_5.

B-Trialkylthioborazoles served as starting materials for the synthesis of unsymmetrical *B*-dialkylthioborazoles. The latter were obtained by heating *B*-trialkylthioborazoles with tetrapropyldiborane[94]:



B-Dialkylthio-derivatives of borazole can also be obtained by the action of tetra-alkyldiborane on *B*-trichloroborazoles with subsequent treatment of the reaction products with lead mercaptide.

In the reaction of organomagnesium compounds with *B*-trialkylthioborazoles small yields of *B*-alkyl-*B*-dialkylthioborazoles are obtained[95]. With organolithium compounds the stepwise replacement of alkylthio-groups by alkyl radicals proceeds more smoothly and from *B*-trialkylthio-*N*-trialkylborazoles it was possible to obtain by this method *B*-alkyl-*B*-dialkylthio-*N*-trialkylborazoles in 62–65% yields:



where R = CH_3, C_2H_5, R′ = C_2H_5, n-C_4H_9.

B. PROPERTIES

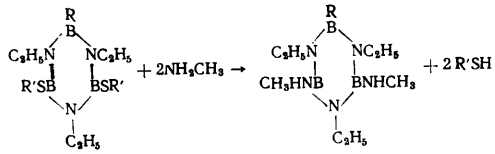
B-Trialkylthioborazoles are, like esters of organothioboric acids, highly reactive. With alcohols they exchange alkylthio-groups for alkoxyl groups in the cold to give *B*-trialkoxyborazoles.[95]

B-Tributylthioborazoles react in the cold with primary or secondary amines, forming the corresponding *B*-alkylamino-derivatives[93]. Thus *B*-tributylthioborazole and dimethylamine gave *B*-tri(dimethylamino)borazole (yield 97%) and the action of aniline on *B*-tributylthioborazole or *B*-tributylthio-*N*-triethylborazole gave respectively *B*-triphenylaminoborazole and *B*-triphenylamino-*N*-triethylborazole.

On introducing ammonia into a benzene solution of *B*-trialkylthioborazoles, *B*-triamino-substituted borazoles are obtained[93]. Like the esters of organothioboric acids, *B*-trialkylthioborazoles are capable of re-esterification on heating with higher thiols[96].

The synthesis of various unsymmetric derivatives of borazole has been effected from *B*-alkyl-*B*-dialkylthio-*N*-trialkylborazoles[95]. *B*-Butyl-*B*-dimethoxy-*N*-triethylborazole was obtained by treatment of *B*-butyl-*B*-dibutylthio-*N*-triethylborazole with methanol.

The reactions with primary or secondary amines take place with high yields:

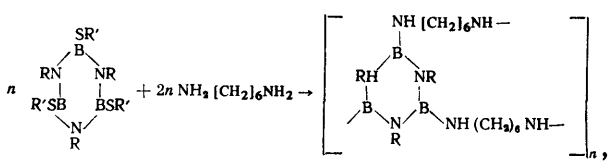


where R = C_2H_5, n-C_4H_9, R′ = n-C_4H_9.

B-Dialkylthio-*N*-trialkylborazoles undergo analogous exchange reactions with amines[96].

Starting from *B*-alkylthio-derivatives of borazole, three-dimensional and linear polymers can be obtained[97]. Polycondensation with participation of *B*-alkylthio-derivatives of borazole takes place under mild conditions ensuring retention of the borazole ring and the regularity of the repeating units.

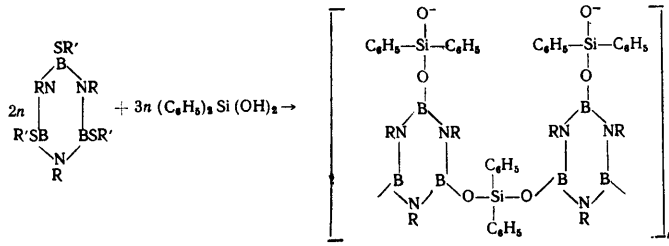
The condensation of the *B*-tributylthio-*N*-trialkylborazoles with hexamethylenediamine in *o*-xylene at 125°C gave polymers (XIV) which were thermostable powders, insoluble in ordinary organic solvents, hydrolysing in air:



(XIV)

where R = CH_3, C_2H_5.

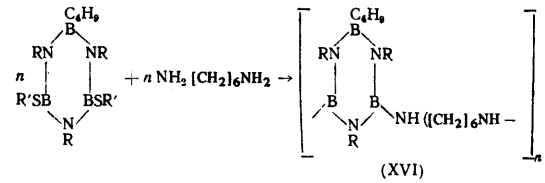
B-Tributylthio-*N*-trimethylborazole with diphenylsilandiol (1 : 1.5) in ethereal medium gives a powdered thermostable polymer (XV) not hydrolysed in air, soluble in tetrahydrofuran or dioxan:



(XV)

where R = CH_3.

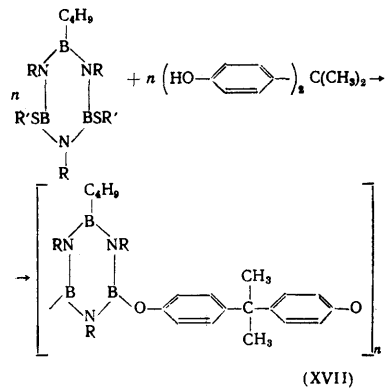
The condensation of *B*-butyl-*B*-dibutylthio-*N*-trialkylborazoles with hexamethylenediamine (1 : 1) in benzene gave linear polymers (XVI) which are brittle substances, less hydrolysed in air than three-dimensional polymers and more stable thermally (decomposition temperature > 400°C)[97]:



(XVI)

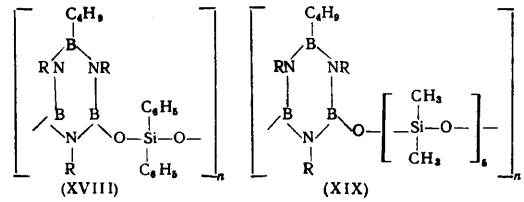
where R = CH_3, C_2H_5.

Linear polymers from *B*-butyl-*B*-dibutylthio-*N*-trialkylborazoles and 2,2-bis-(4-hydroxyphenyl)propane (XVII) are comparatively low-melting but more resistant to hydrolysis than polymers from hexamethylenediamine:



(XVII)

The reaction of *B*-butyl-*B*-dibutylthio-*N*-trimethylborazole and diphenylsilandiol[97] in boiling ethereal solution gives a viscous liquid of molecular weight ~ 1200, which corresponds with a cyclic trimer (XVIII; *n* = 3). Heating in a vacuum at 200°C converts the trimer into a brittle solid polymer (XVIII):



(XVIII) (XIX)

The condensation of *B*-butyl-*B*-dibutylthio-*N*-trimethylborazole with decamethyl-1,9-dihydroxypentasiloxane[97] in ethereal solution leads to a liquid with molecular weight ~ 1100, evidently possessing a cyclic structure (XIX; $n = 2$). On heating in a vacuum the dimer is converted into an elastic polymer (XIX) m.p. 146–149°C, which is not hydrolysed in air.

V. 1,2-THIABOROLANES

A. METHODS OF PREPARATION

1,2-Thiaborolanes are obtained by the addition of 1,2-dialkyl or 1,2-diaryl diboranes to allylthiol[98,99]:

$$^1/_2(RBH_2)_2 + CH_2{=}CHCH_2SH \rightarrow RB\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix} + H_2 ,$$

where R = n-C_4H_9, iso-C_4H_9, or C_6H_5.

2-Alkyl-1,2-thiaborolanes can be synthesised by heating mixtures of a boron trialkyl, trialkylamine–borane, and allenethiol[98]:

$$R_3B + 2\,H_3B\cdot N(C_2H_5)_3 + 3\,CH_2{=}CHCH_2SH \xrightarrow{110^\circ} 3\,RB\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix}.$$

B. PROPERTIES

Unlike the 2-alkyl-1,2-azaborolidines, which tend to dimerise[100], 1,2-thiaborolanes exist in a monomeric form. A feature of the cyclic structure of the 1,2-thiaborolanes appears in the definite ability to form complexes with amines which sharply distinguishes them from the related esters of dialkylthioboric acids R_2BSR.

An increase in the complex-forming ability of 1,2-thiaborolanes (and other such compounds: 1,2-azaborolidines, 1,2-oxaborolanes) is explained by the smaller reorganisation energy of the molecule compared with the acyclic compounds, when the boron atom changes from a trigonal to a tetrahedral valence state. The losses in reorganisation energy add up to the difference between the promotion energies of the boron atom from the ground state into tetrahedral and trigonal, 2.1 eV [101] and the decrease in the boron–element (C, S, N, O) bonds with decrease in the *s*-character of the boron orbitals.

In cyclic boron compounds, in which the angle of the C–B–X bonds in the ring (X = C, S, N, O) approaches the tetrahedral angle, during complex formation there is a weakening of only one (acyclic) boron–element bond, and not three, as occurs in compounds of the type BX_3, which is due to a decrease in the reorganisation energy. Strictly speaking, the energy of the outer B–X bond in the cyclic compound decreases to a larger extent in complex formation than in the compounds of the type BX_3, so that the *s*-character of the boron orbitals in this bond is greater than 0.33, but evidently the energetic losses occurring during this are less than in the change of two B_{tr}–X bonds into B_{te}–X bonds. The gain in reorganisation energy during complex formation in cyclic boron compounds in comparison with the acyclic analogues is adequate equal to more than adequate to compensate for the strain energy in the ring.

2-Butyl-1,2-thiaborolane forms a stable liquid complex with pyridine capable vacuum distillation without decomposition. Like other coordination compounds of boron this complex has a high dipole moment (5.2 D), whereas the dipole moment of the original thiaborolane is only 1.5 D.

Alkylthiaborolanes also form stable complexes with secondary and primary amines or ammonia (XX) which distil in vacuum without decomposition:

$$RB\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix} + L \rightarrow \begin{matrix}R\\ L\end{matrix}\!\!>\!B\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix} \quad (XX)$$

where R = n-C_4H_9, iso-C_4H_9; L = NH_3, $NH_2C_2H_5$, $NH(C_2H_5)_2$, NHn-C_4H_9, $NH(n\text{-}C_4H_9)_2$, HNC_5H_{10}.

In the infrared spectra of the compounds (XX; L = NHR_2) there are absorption bands in the region 3050–3300 cm^{-1} corresponding to the stretching vibrations of the N–H bonds and the absence of S–H bands. In the infrared spectrum of the compound (XX; L = NH_2R) there is an intense band with a maximum at 1582 cm^{-1} due to the deformation vibrations of the NH_2 groups.

Less stable complexes are given by alkylthiaborolanes with sterically hindered amines. Thus 2-butyl-1,5-thiaborolane forms a complex, with evolution of heat, with t-butylamine; however, on heating, the complex decomposes into the initial substances.

Unlike the primary and secondary amines, when alcohols act on 2-alkyl-1,2-thiaborolanes there is breaking of the B–S bond with formation of esters of (3-mercaptopropyl)alkylboric acids (XXI):

$$RB\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix} + R'OH \rightarrow \begin{matrix}R\\ R'O\end{matrix}\!\!>\!B{-}CH_2CH_2CH_2SH . \quad (XXI)$$

2-Butylthiaborolane reacts with 2-aminoethanol similarly to give crystalline 2-aminoethyl (3-mercaptopropyl)-butylborate:

$$n\text{-}C_4H_9B\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix} + HOCH_2CH_2NH_2 \rightarrow \begin{matrix}n\text{-}C_4H_9\\ HSCH_2CH_2CH_2\end{matrix}\!\!>\!B\begin{matrix}NH_2{-}CH_2\\ |\\ O{-}CH_2\end{matrix}.$$

The infrared spectra of compounds (XXI) have an absorption band in the 2580 cm^{-1} range (S–H); there is also strong absorption in the range for the B–O bond but OH absorption is absent. The fact that this reaction does not stop at the complex formation stage and nucleophilic substitution occurs at the boron atom can be explained by the weaker complex-forming ability of alcohols in comparison with amines and the higher energy of the B–O bond in comparison with the B–N bond.

In the reaction of butanol with the pyridine complex of 2-butyl-1,2-thiaborolane breaking of the B–S bond also occurs and pyridine and butyl (3-mercaptopropyl)butylborate are formed:

$$\begin{matrix}n\text{-}C_4H_9\\ C_5H_5N\end{matrix}\!\!>\!B\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix} + n\text{-}C_4H_9OH \rightarrow \begin{matrix}n\text{-}C_4H_9\\ n\text{-}C_4H_9O\end{matrix}\!\!>\!B{-}CH_2CH_2CH_2SH + C_5H_5N.$$

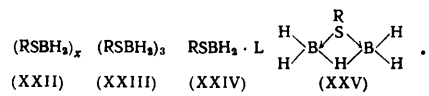
With piperidine the latter loses a molecule of alcohol, forming a piperidine complex of alkylthiaborolane:

$$\begin{matrix}n\text{-}C_4H_9\\ n\text{-}C_4H_9O\end{matrix}\!\!>\!BCH_2CH_2CH_2SH + C_5H_{11}N \rightarrow \begin{matrix}n\text{-}C_4H_9\\ C_5H_{11}N\end{matrix}\!\!>\!B\begin{matrix}S{-}CH_2\\ |\\ CH_2{-}CH_2\end{matrix} + n\text{-}C_4H_9OH.$$

VI. ALKYLTHIOBORANES

Various types of compound with alkylthio-groups and hydrogen atoms at the boron atom are known. These compounds, which differ in structure and properties, are classified together under the common name of "alkylthioboranes", since they contain the groupings $RSBH_2$ and

$(RS)_2BH$, with different modes of mutual coordination. Alkylthioboranes $RSBH_2$ are unknown in the monomeric form. They exist in the form of polymers (XXII), trimers (XXIII), and complexes with secondary or tertiary amines (XXIV):

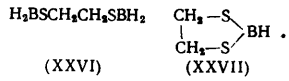


(XXII) (XXIII) (XXIV) (XXV)

A single representative of a fourth type of compound with an $RSBH_2$ grouping has been described, formed by coordination of methylthioborane with borane (XXV).

Of the $(RS)_2BH$ type of compounds di-t-butylthioborane, which exists in monomeric form, is stable. Other known dialkylthioboranes are associated to a certain extent and show a significant tendency to disproportionation.

1,2-Di(borylthio)ethane (XXVI) and 1,3,2-dithiaborolane (XXVII) have been obtained in associated form:



(XXVI) (XXVII)

1. Methods of Preparation

The reaction between diborane and thiols was first investigated by Burg and Wagner[12] for the example of methanethiol. On mixing the reagents at −78°C and holding the reaction mixture at that temperature for a few days a solid polymer of methylthioborane was obtained:

$$x/2\ B_2H_6 + x\ CH_3SH \rightarrow (CH_3S\ B\ H_2)_x + x\ H_2\ .$$

Treatment of the partly depolymerised reaction product with trimethylamine led to trimethylamine–methyl thioborane, $CH_3SBH_2.N(CH_3)_3$.

The action of diborane on a polymer of methylthioborane or trimethylamine–methylthioborane gave the thermally unstable methylthiodiborane, which rapidly decomposes at room temperature into diborane and the polymer $(CH_3SBH_2)_x$:

$$(CH_3SBH_2)_x + x/2\ B_2H_6 \rightarrow x\ CH_3SB_2H_5\ ,$$
$$CH_3SBH_2 \cdot N(CH_3)_3 + B_2H_6 \rightarrow CH_3SB_2H_5 + H_3B \cdot N(CH_3)_3\ .$$

Subsequently the reactions between diborane and thiols were carried out in ethereal medium using the ordinary laboratory techniques, which allowed experiments to be performed on a large scale and the properties of the compounds thus formed to be widely investigated.

On introducing 1 mole diborane into an ethereal solution of 2 moles thiol a steady evolution of hydrogen was observed. After the reaction had ceased and the solvent had been removed in a vacuum the residue contained a solid polymer (when methanethiol or 2-methylpropane-2-thiol were used) or a syrupy product (for ethanethiol, propane-1-thiol, or butane-1-thiol)[14,102]:

$$x/2\ B_2H_6 + x\ RSH \rightarrow (RSBH_2)_x + x\ H_2\ .$$

The polymers of ethyl-, propyl-, and butyl-thioborane are converted on standing into trimers of alkylthioboranes (1,3,5-trialkylcyclotriborathianes); the polymers of methyl- and t-butyl-thioboranes are converted into trimers in tetrahydrofuran solution[14,102]:

$$(RSBH_2)_x \rightarrow x/3\ (RSBH_2)_3\ .$$

The trimers of alkylthioboranes, with the exception of the trimer of t-butyl thioborane (m.p. 105–107°C) are liquids which distil without decomposition in a vacuum.

When pentane-1-thiol, phenylmethanethiol, or thiophenol react with diborane (2 : 1) in tetrahydrofuran or Diglyme 2 moles hydrogen are rapidly liberated. The RS-substituted boranes thus formed are not isolated from the solutions and are identified solely by their infrared and NMR spectra[103,104].

Polymeric 1,2-di(borylthio)ethane is obtained from diborane and 1,2-dithioethyleneglycol[105]:

$$B_2H_6 + HSCH_2CH_2SH \rightarrow H_2BSCH_2CH_2SBH_2 + 2\ H_2\ .$$

Dipropylthioborane and dibutylthioborane are obtained by passing diborane into ethereal solutions of the corresponding thiols (1 : 4) and subsequent distillation of the reaction products[15,16]:

$$B_2H_6 + 4\ RSH \rightarrow 2\ (RSH)_2BH + 2\ H_2\ .$$

The general method for obtaining dialkylthioboranes is the reduction of alkylthioborates with lithium tetrahydroaluminate in ethereal medium[106]:

$$4\ B\ (SR)_3 + LiAlH_4 \rightarrow 4\ (RS)_2BH + LiSR + 2\ Al(SR)_3\ .$$

Dialkylthioboranes can be obtained from the trimers of alkylthioboranes and thioborates in the distillation of mixtures of these substances in the ratio 1 : 3.

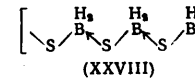
$$(RSBH_2)_3 + 3\ (RS)_3B \rightarrow 6\ (RS)_2BH\ .$$

The synthesis of di-t-dodecylthioborane from aminoborane and t-dodecanethiol[49] has also been described[49]. Associated 1,3,2-dithiaborolane is obtained by the reaction of diborane and dithioethylene glycol[105]:

In the reaction of diborane and triphenylthioborate (1 : 4) in tetrahydrofuran, diphenylthioborane is formed[104], which was not isolated in a pure state and was identified solely by its NMR spectrum (doublet at −24 p.p.m., J = 140 Hz).

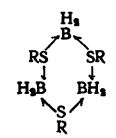
2. Physical Properties

The polymers of the alkylthioboranes are solids or syrupy substances and most of them swell in ether, are insoluble in benzene, but soluble in tetrahydrofuran. The association of the molecules of alkylthioboranes is effected by donor–acceptor bonds between the boron and sulphur atoms (XXVIII):



(XXVIII)

The trimers of alkylthioboranes are liquids with a cyclic structure (XXIX) with semicoordinate bonds between the boron and sulphur atoms, similar to the semicoordinate B–N bonds (see p. 944).



(XXIX)

The dipole moment of 1,3,5-triethylcyclotriborathiane is 2.90 D, and that of 1,3,5-tributylcyclotriborathiane, 3.16 D.

The infrared spectra of 1,3,5-trialkylcyclotriborathianes have two intense absorption bands in the range 2412–2420 cm^{-1} and 2465–2470 cm^{-1}, corresponding to the stretching vibrations of the B–H bonds.

In the ^{11}B NMR spectra of 1,3,5-triethylcyclotriborathiane at 25°C there is a broad peak (chemical shift +31 p.p.m. relative to trimethyl borate). At 90°C the broad peak is converted into a triplet with a 1 : 2 : 1 ratio of intensities[107].

In the proton magnetic resonance spectrum of 1,3,5-trimethyl cyclotriborathiane (internal standard tetramethylsilane, $\delta = 0$) there is a singlet from the protons of the methyl groups at $\delta = 2.14 \pm 0.03$ p.p.m. and a quadruplet from the protons connected with the boron, centred at $\delta = 2.35 \pm 0.02$ p.p.m., $J_{BH} = 115 \pm 5$ Hz.

The properties of the dialkylthioboranes are determined by the nature of the alkyl groups. The infrared spectrum of monomeric di-t-butylthioborane has an absorption band at 2545 cm^{-1} corresponding to the B–H stretching vibrations. The ^{11}B NMR spectrum at room temperature is a weakly resolved doublet with chemical shift −40.7 p.p.m. relative to $B(OCH_3)_3$. Other dialkylthioboranes tend to disproportionate and even in freshly distilled specimens the presence of ~ 20% thioborate and alkylthioboranes of a different degree of association is observed spectroscopically. During the disproportionation of the methyl and ethyl derivatives equilibrium is reached when the mixture contains ~ 20% dialkylthioborane:

$$2(RS)_2BH \rightleftarrows (RS)_3B + RSBH_2 .$$

On standing, di-isopropylthio- and dibutylthio-boranes are completely symmetrised[108]. 1,3,2-Dithiaborolane exists in the gas phase as a monomer[105]. The frequency of the B–H vibrations drops from 2595 cm^{-1} in the vapour to 2435 cm^{-1} in the solid state.

3. Chemical Properties

a. Thermal Changes. Most of the known polymers of the alkylthioboranes are slowly and spontaneously converted into trimers at room temperature[14,102]. The solid polymers of methylthioborane and t-butylthioborane are exceptions; they are converted into trimers on dissolution in tetrahydrofuran.

The trimers of alkylthioboranes (1,3,5-trialkylcyclotroborathianes) are more stable thermally and can be distilled in a vacuum, with the exception of the trimer of n-butylthioborane, which undergoes partial decomposition on distillation. Other trimers also decompose above 100°C. Thus the trimer of ethylthioborane distils from a small fractionating column without decomposition but in distillation with an efficient column the trimer decomposes, the products obtained being readily volatile substances and a very viscous distillate which ultimate analysis shows to have the composition $[(C_2H_5S)_3B_2H_3]_x$.

The results[107] suggesting that the polymeric product of composition $[(C_2H_5S)_3B_2H_3]_x$ is formed in the reaction of diborane with ethanethiol in the ratio 1 : 3 is erroneous. In reality at this ratio the reagents replace two of the hydrogen atoms in BH_3 by ethylthio-groups to only a slight extent and on distillation of the reaction products the trimer of ethylthioborane $(C_2H_5SBH)_3$ is obtained in high yield (up to 80%)[108].

b. Oxidation and Protonolysis. The trimers of the alkylthioboranes (1,3,5-trialkylcyclotriborathianes) are stable in relation to oxidants. They are almost unchanged in air and are completely unoxidised even on boiling with hydrogen peroxide in alkaline solution[14].

The polymers and trimers of the alkylthioboranes exhibit different stability towards hydrolysis. The polymers are readily hydrolysed at room temperature, whereas the trimers are only slowly hydrolysed on heating in water.

With alcohols the polymers of the alkylthioboranes readily react in the cold; alcoholysis of the trimers at room temperature proceeds very slowly, but on boiling with the alcohols they are completely decomposed, being converted into the corresponding borates, with liberation of hydrogen[14]:

$$(RSBH_2)_3 + 9\,R'OH \rightarrow 3\,B(OR')_3 + 6\,H_2 + 3\,RSH .$$

With thiols the trimers react at 100–120°C to form alkyl thioborates[14]:

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

Dialkylthioboranes are quantitatively hydrolysed by water in the cold to boric acid; with alcohols they give alkyl borates. The replacement of hydrogen by the alkylthio-group in dialkylthioboranes starts only at 50–60°C and proceeds rather vigorously at ~ 100°C.[15,16]

c. Reactions with amines. The trimers of the alkylthioboranes react at room temperature with secondary and tertiary amines. The reactions take place with breaking of the ring and lead to the formation of amine complexes of alkylthioboranes[109,110]:

$$(RSBH_2)_3 + 3\,R'_2R''N \rightarrow 3\,RSBH_2 \cdot NR'_2R'' ,$$

where R″ = H or alkyl.

The polymers of alkylthioboranes also give aminoalkylthioboranes with amines.

Amine complexes of the alkylthioboranes are formed by the reaction of diborane with aliphatic sulphenylamines[111]:

$$^1/_2\,B_2H_6 + CH_3SNR_2 \rightarrow CH_3SNR_2 \cdot BH_3 \rightarrow CH_3SBH_2 \cdot NHR_2 .$$

The complexes of the alkylthioboranes with tertiary amines are non-associated liquids, stable at room temperature but partly decomposing on heating[110].

The complexes of the alkylthioboranes with secondary amines undergo further changes on heating with formation both of products of the replacement of the alkylthio-groups (dialkylaminoboranes) and products with replacement of hydrogen—dialkylamino(alkylthio)boranes[110,111]:

$$RSBH_2 \cdot NHR'_2 \rightarrow \begin{cases} \rightarrow R'_2NBH_2 + RSH \\ \rightarrow \begin{matrix} RS \\ R'_2N \end{matrix}\!\!>\!BH + H_2 \end{cases} .$$

The reactions of amine complexes of alkylthioboranes with hydrogen chloride and with halogen derivatives of hydrocarbons have been studied[109,112]. The complexes of alkylthioboranes with dimethylamine are converted into the corresponding boronium salts with these reagents:

$$2\,RSBH_2 \cdot NH(CH_3)_2 + HCl \rightarrow \{H_2B[NH(CH_3)_2]_3\}Cl + 1/3\,(RSBH_2)_3 + RSH$$
$$2\,RSBH_2 \cdot NH(CH_3)_2 + R'X \rightarrow \{H_2B[NH(CH_3)_2]_2X + 1/3(RSBH_2)_3 + RSR .$$

Trialkylamine–alkylthioboranes are split by hydrogen chloride, regenerating the orginal trimer. They undergo exchange reactions with the halogen derivatives of hydrocarbons, as a result of which amine complexes of halogenoboranes and dialkyl sulphides are obtained:

$$RSBH_2 \cdot NR'_3 + R''X \rightarrow XBH_2 \cdot NR'_3 + RSR'' .$$

The complexes of alkylthioboranes with pyridine behave uniquely in relation to the halogen derivatives of hydrocarbons. With carbon tetrachloride they are converted into bis(pyridine)boronium chloride:

$$RSBH_2 \cdot NC_5H_5 + CCl_4 \rightarrow [H_2B(NC_5H_5)_2]Cl$$

and with alkyl halides they exchange an alkylthio-group for halogen:

$$RSBH_2 \cdot NC_5H_5 + R'X \rightarrow XBH_2 \cdot NC_5H_5 + RSR' .$$

There is a very interesting reaction between dimethylamine–ethylthioborane and dimethylammonium chloride, leading to the formation of bis(dimethylamino)boronium chloride:

$$RSBH_2 \cdot NH(CH_3)_2 + (CH_3)_2NH_2Cl \rightarrow \{H_2B[NH(CH_3)_2]_2\}Cl + RSH .$$

1,3,5-trialkylcyclotriborathiane also reacts readily with primary amines but the reaction is different from that with secondary and tertiary amines[113]. When methylamine or ethylamine react with the trimers of the alkylthioboranes, irrespective of the ratio of the reagents, boronium salts are obtained–mercaptides of bis(methylamino)boronium or bis(ethylamino)boronium, respectively:

$$(RSBH_2)_3 + 6\,R'NH_2 \rightarrow 3\,[H_2B(NH_2R')_2]SR .$$

The mercaptide ion of bis(alkylamino)boronium mercaptides is replaced by the chloride ion when they are treated with an ethereal solution of hydrogen chloride:

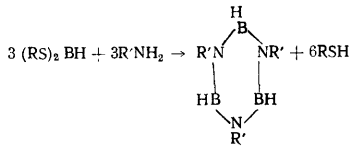
$$[H_2B(NH_2R')_2SR + HCl \rightarrow [H_2B(NH_2R')_2]Cl + RSH .$$

A similar exchange takes place on reaction with benzyl chloride.

Bis(alkylamino)boronium chlorides can be obtained directly from the trimers of alkylthioboranes with primary amines in the presence of benzyl chloride:

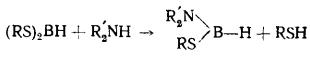
$$(RSBH_2)_3 + 6\,NH_2R' + 3\,C_6H_5CH_2Cl \rightarrow 3\,[H_2B(NH_2R')_2]Cl + 3\,C_6H_5CH_2SR .$$

Dialkylthioboranes react with amines at room temperature. With primary amines, dialkylthioboranes give *N*-trialkylborazoles[16]:



where $R' = C_2H_5$, n-C_4H_9.

With secondary amines, depending on the nature of the reagents dialkylamino(alkylthio)boranes $RS(R_2N)BH$ or bis(dialkylamino)boranes are obtained[114]:



$$(RS)_2BH + 2R'_2NH \rightarrow (R'_2N)_2BH + 2RSH .$$

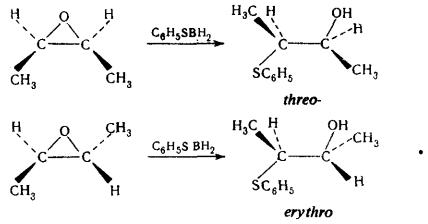
The reactions of dialkylthioboranes with tertiary amines lead to the formation of $(RS)_2BH$.amine complexes. 1,3,2-Dithiaborolane forms complexes with trimethylamine and trimethylphosphine[105].

d. Reactions with Ethers, Oxides, and Carbonyl Compounds. Phenylthioborane, pentylthioborane, and benzylthioborane are split into ethers at room temperature[103,104]:

$$RSBH_2 + R'—O—R' \rightarrow RSR + H_2BOR'' .$$

For example, in 1,2-dimethoxyethane at 25°C phenylthioborane is 79% converted after 20 h into thioanisole, and in tetrahydrofuran it gives 4-(phenylthio)butan-1-ol in 45% yield after 3 h.

Oxides of unsaturated hydrocarbons react with phenylthioborane and alkylthioboranes (pentylthio- and benzylthio-derivatives) with breaking of the oxide ring[104,115] The stereochemical direction of these reactions depends on the nature of the oxides[115]. In the reaction of phenylthioborane with *cis*- and *trans*-2,3-epoxybutane trans-opening of the epoxide ring occurs, since as a result only the *threo*- and only the *erythro*-3-phenylthiobutan-2-ols respectively are formed:



The reaction of phenylthioborane with cyclohexene is just as selective, leading to the trans-2-phenylthiocyclohexanol. The stereochemical course of these reactions is inconsistent both with a four-centre mechanism[103] and a mechanism with participation of carbonium ion intermediates. The mechanism of the trans-opening of the oxide ring in this reaction remains uncertain.

The reaction of phenylthiol with *trans*-$\alpha\alpha'$-epoxybibenzyl is complicated, and with diglyme as a solvent only 6% *threo*- and 6%-*erythro*-1,2-diphenyl-2-phenylthioethanol are obtained, the main product (45%) being 1,2-diphenylethanol.

Phenylthioboranes obtained from thiophenol and diborane in tetrahydrofuran, react with optically active L-(−)-styrene oxide with the formation of only L-(−)-2-phenyl-2-phenylthioethanol.

Phenylthioborane reduces carbonyl compounds and acids (benzaldehyde, acetophenone, benzoic acid, ethyl benzoate) in alcohols but does not react with benzyl chloride[104].

d. Reactions with alkenes. The polymers of alkylthioboranes react with alkenes in ethereal medium, and the course of the process depends on the nature of the reagents[74]. A polymer of methylthioborane in the form of a gelatinous mass containing only a little solid polymer adds to ethylene, hex-1-ene, or cyclohexene with gentle heating (1.5 h at 50°C) with the formation of the corresponding esters of dialkylthioboric acids:

$$(CH_3SBH_2)_x + \text{olefin} \rightarrow R_2BSCH_3 .$$

The hydroboronation of ethylene or propene by the polymer of butylthioborane is accompanied by symmetrisation in which, as well as the butyl dialkylborate, appreciable amounts of borontrialkyl and dibutylthioborane are obtained. The reaction with hex-1-ene is smoother, leading to a satisfactory yield of an ester of dihexylthioboric acid.

In the hydroboronation of hex-1-ene by phenylthioborane in tetrahydrofuran solution (25°C, 1–1.5 h) and subsequent methanolysis of the reaction products methyl dihexylborate (45%) and dimethyl hexylborate (21%) are formed. The reaction of phenylthioborane with styrene is similar. Oxidation of the hydroboronation products gives 2-phenylethanol and 1-phenylethanol in 91 : 9 ratio[104].

The reaction of polymers of alkylthioboranes with diene hydrocarbons leads to the boron-containing heterocyclic compounds (see Section III. A. 4.).

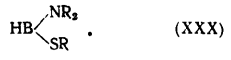
The trimers of alkylthioboranes do not react with unsaturated compounds at room temperature. When the reaction is carried out in boiling ether a complex mixture of substances is obtained. Thus in the reaction of the trimer of ethylthioborane (erroneously taken to be triethylthiodiborane) and oct-1-ene triethyl borate (10%), diethyl octylthioborate (20%), and ethyl dioctylthioborate (15%) are formed[116].

Dialkylthioboranes are less active hydroboronation agents than the polymers of alkylthioboranes. The reaction of dibutylthioborane with hex-1-ene, oct-1-ene, or cyclohexene takes place at room temperature and more rapidly on heating, and butyl esters of the corresponding alkylthioboric acids are obtained[73].

In the reaction of diphenylthioborane with styrene in tetrahydrofuran and the subsequent oxidation of the reaction products, 2-phenylethanol and 1-phenylethanol were isolated in 95 : 5 ratio with a yield of 77%.[104]

VI. DIALKYLAMINO(ALKYLTHIO)BORANES

An unusual class of mixed sulphur-containing compounds of boron is the dialkylamino(alkylthio)boranes (XXX):

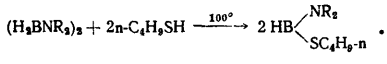


(XXX)

A. METHODS OF PREPARATION

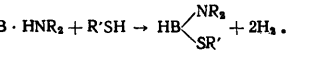
1. Synthesis of Dialkylamino(alkylthio)boranes from Dimers of Dialkylaminoboranes

Dialkylamino(alkylthio)boranes are obtained on heating dimers of dialkylaminoboranes with thiols[117,118]:

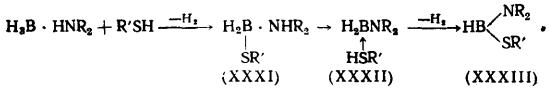


2. Synthesis of Dialkylamino(alkylthio)boranes from Dialkylamine–Boranes

It is preparatively more convenient to obtain dialkyl amino(alkylthio)boranes by heating dialkylamine-boranes with thiols[117,119]. Reaction with liberation of hydrogen starts 70–80°C, proceeds vigorously at 100°C, and ends on briefly raising the temperature to 120–130°C

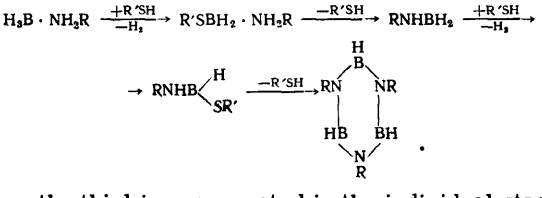


In the first stage of the reaction a complex of dialkylamine with alkylthio boranes (XXXI) is formed with liberation of hydrogen and is then converted into a complex of a dialkylaminoborane with a thiol (XXXII). The latter loses hydrogen to give the final product (XXXIII):



(XXXI) (XXXII) (XXXIII)

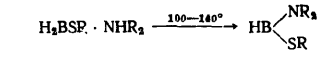
It should be noted that when heated with a thiol the complexes of borane with primary amines are converted into *N*-trialkylborazoles in high yield[120]



Since the thiol is regenerated in the individual stages of the reaction the synthesis of *N*-trialkylborazoles can be carried out using a catalytic amount of the thiol.

3. Synthesis of Dialkylamino(alkylthio)boranes from Dialkylamine–Alkylthioboranes

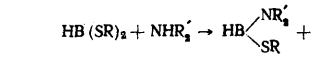
Complexes of the alkylthioboranes give, on heating with secondary amines, dialkylamino(alkylthio)boranes in 60–88% yield[110]:



The processes are complicated by side-reactions, as a result of which a thiol and a bis(dialkylamino)borane are formed.

4. Synthesis of Dialkylamino(alkylthio)boranes from Dialkylthioboranes and Amines

Dialkylamino(alkylthio)boranes are obtained by the reaction of dialkylthioboranes and secondary amines[114]:



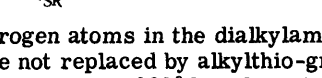
The reaction starts at room temperature and requires brief heating to complete it.

B. PROPERTIES

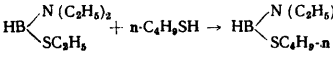
Dialkylamino(alkylthio)boranes are colourless mobile liquids with an extremely unpleasant odour, rather rapidly hydrolysed and oxidised in air. They are miscible with organic solvents in any proportions; they are not decomposed nor symmetrised at ~200°C. In the infrared spectra there are absorption bands in the range 2485–2500 cm^{-1}, corresponding to the B–H vibrations.

1. Reactions with Alcohols and Thiols

Dialkylamino(alkylthio)boranes react vigorously with alcohols at room temperature with liberation of hydrogen; initially the R_2N–and RS groups are replaced and then the dialkoxyboranes already formed are converted into borates[121]:

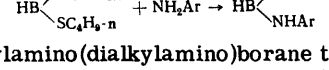


The hydrogen atoms in the dialkylamino(alkylthio)-boranes are not replaced by alkylthio-groups on heating with thiols, even up to 200°C. On using higher thiols re-esterification[12] occurs, like that which takes place in the esters of dialkylthioboric acids[52]:



2. Reactions with Amines

Dialkylamino(alkylthio)boranes with aromatic amines under mild conditions exchange an alkylthio-group for an arylamino-group[121]:



The arylamino(dialkylamino)borane thus formed reacts in its turn with an aromatic amine at 60–80°C, with the

arylamino-group replacing not hydrogen but the dialkylamino-group, as a result of which a bis(arylamino)borane is obtained:

$$HB\begin{matrix}N(C_2H_5)_2\\ NHAr\end{matrix} + NH_2Ar \rightarrow HB(NHAr)_2 + NH(C_2H_5)_2 .$$

Similarly, under the action of primary aliphatic amines, bis(arylamino)boranes are obtained[118]:

$$HB\begin{matrix}N(CH_3)_2\\ SR'\end{matrix} + 2NH_2R \rightarrow HB(NHR)_2 + NH(CH_3)_2 + R'SH .$$

The reaction of dialkylamino(alkylthio)boranes with secondary amines is peculiar[121,122]. When diethylamino-(butylthio)borane is heated with diethylamine the equilibrium:

$$HB\begin{matrix}N(C_2H_5)_2\\ SC_4H_9\text{-}n\end{matrix} + NH(C_2H_5)_2 \rightleftarrows HB[N(C_2H_5)_2]_2 + n\text{-}C_4H_9SH$$

is established.

Heating bis(dimethylamino)borane with butylthiol leads to the same equilibrium mixture. In this last instance a dialkylamino-group at the boron atom is replaced by an alkylthio-group, whereas the reverse process—the replacement of the RS group by the R_2N group—usually occurs, as in the action of amines on esters of organothioboric acids[63,87]. The above equilibrium can be displaced completely to the right if the amine used boils at a higher temperature than the thiol product, which can then be distilled from the reaction mixture:

$$HB\begin{matrix}N(C_5H_{11}\text{-iso})_2\\ SC_3H_7\text{-}n\end{matrix} + NH(C_5H_{11}\text{-iso})_2 \rightarrow HBN(C_5H_{11}\text{-iso})_2 + n\text{-}C_3H_7SH .$$

Under the action of an equimolecular amount of methylaniline on diethylamino(butylthio)borane both the RS–and R_2N–groups are replaced, and half the original organoboron compound remains. At a reagent ratio of 1 : 2, bis-(*N*-methyl-*N*-phenylamino)borane is obtained in 83% yield[122].

The low mobility of the hydrogen atom in dialkylamino-(alkylthio)boranes also appears in their inability to add to alkenes even under comparatively severe conditions in which the dimer of diethylaminoborane hydroborates but-1-ene and oct-1-ene[117]. Hence the ease of nucleophilic replacement of various groups at the boron atom in dialkylamino(alkylthio)boranes decreases in the following series: RS > NR_2 > H.

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As the above shows, sulphur-containing organic compounds of boron exhibit increased reactivity in comparison with their oxygen analogues, expressed in their tendency to form complexes and exchange RS groups for other groupings. This is explained, on the one hand, by the lower ionisation potential[123] of the unshared pair at the sulphur atom (13.64 eV) in comparison with oxygen (18.70 eV), and on the other by the relatively low value of the energy of the B–S bond ($\sim$ 70 kcal mole^{-1})[5] compared with that of the B–O bond (110–115 kcal mole^{-1}) and at the same time there is the similarity in the energies of the N–H (85 kcal mole^{-1}), B–N (80 kcal mole^{-1}), and S–H (87 kcal mole^{-1}) bonds[124]. Because of this, reactions with breaking of B–S bonds, leading to the formation of bonds between the boron and other elements (N, O), seem energetically favourable.

Readily accessible alkylthioborates which are smoothly obtained from boron trichloride and thiols in the presence of tertiary amines seemed suitable for the synthesis of various classes of sulphur-containing esters of organothioboric acids. In turn these esters can be used with success in the synthesis of various other types of organoboron compounds.

A feature of the methods of synthesis developed is that Grignard reagents are not used. The starting compounds are boron trialkyls, obtainable from diborane and alkenes, which by a combination of new synthetic procedures are readily converted into reactive sulphur-containing organoboron compounds, which can then be used for further syntheses. A second source of organoboron compounds is the "alkylthioboranes" obtainable from diborane and thiols, which are of independent theoretical interest in the chemistry of boron.

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