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Studies in the Field of Boron-substituted Functional Derivatives of Carbaboranes(12)

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The advances in the synthesis and chemical reactions of boron-substituted functional derivatives of carbaboranes are described. The qualitative and quantitative differences between the reactivities of the functional groups linked to the hexacoordinate boron atom in carbaboranes and the functional groups in the corresponding derivatives of tri-coordinate boron are demonstrated.
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I. INTRODUCTION

One of the most important and interesting fields in the chemistry of carbaborane systems involves the study of the properties of boron-substituted carbaboranes. The increased coordination number of boron atoms in carbaboranes(12), which is 6, alters radically the properties of the functional groups linked to them compared with the compounds of tri-coordinate boron. The presence of an incomplete electron octet in the boron atom in the latter in many respects determines the high reactivity of compounds of this class, since attack by a given reagent is directed primarily to the central atom and this is responsible for the easy cleavage of the boron–element bonds. Boron-substituted carbaboranes exhibit a high chemical stability as regards the rupture of the boron–element bond and resemble chemically the corresponding aliphatic and aromatic derivatives. The lack of convenient methods for the introduction of functional groups at the boron atoms of the carbaborane nuclei retarded for a long time the development of this promising field and only the discovery in 1967 of the reaction involving the introduction of an amino-group into the carbaborane nucleus made it possible to develop extensively the chemistry of boron-substituted carbaboranes and to discover the characteristics and specific features of the behaviour of compounds of this class.

This review reflects the advances in the chemistry of boron-substituted functional derivatives of carbaboranes containing B–N, B–O, B–S, B–C, and B–element (element = metal or non-metal) bonds. The fundamental characteristics of the electrophilic and radical halogenation of carbaboranes will not be considered, since this problem has been described in detail in Grimes's monograph[1] and in dissertations[2–4]. One should only note that the method involving the use of *B*-halogenocarbaboranes for the synthesis of a wide variety of boron-substituted derivatives, which was at first sight seemingly extremely promising, did not justify the hopes associated with it because of the extremely low reactivity of the halogen in *B*-halogenocarbaboranes[5–7].

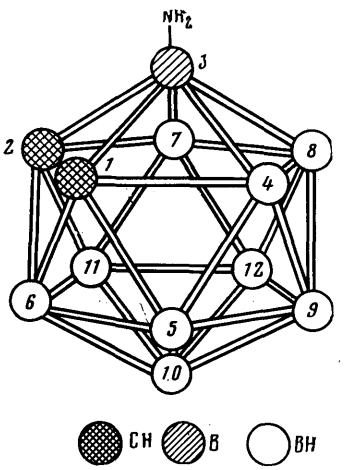
II. THE SYNTHESIS AND PROPERTIES OF BORON-SUBSTITUTED CARBABORANES

1. Carbaboranes with a B–N Bond

In 1967 Zakharkin and Kalinin found[8] that the dicarbadodecaborate(14) dianions, obtained as a result of the addition of two electrons to carbaboranes, react with liquid ammonia at a low temperature with liberation of hydrogen and the formation of *B*-aminated dianions. On oxidation with $KMnO_4$ or $CuCl_2$ in liquid ammonia, the latter are selectively converted into *o*-carbaborane derivatives containing the amino-group in the 3-position (see Figure):

$$RC{-}CR' \xrightarrow[NH_3(liq.)]{2Na} \left(RC{-}CR'\right)^{2-} \xrightarrow[-H_2]{NH_3(liq.)} \left(RC{-}CR'\right)^{2-} \xrightarrow[NH_3(liq.)]{KMnO_4(CuCl_2)} RC{-}CR'$$

$B_{10}H_{10}$ $B_{10}H_{10}$ $B_{10}H_9NH_2$ $B_{10}H_9NH_2$.



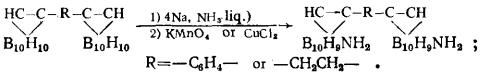
The structure of 3-amino-*o*-carbaborane.

The amination of the dicarbadodecaborate(14) dianion represents nucleophilic substitution at the boron atom linked to the hydrogen atom exhibiting the greatest hydride mobility[8,9]. It has been shown[10] that, in the amination of the dianions, the attacking species is the amide ion. We believe[11] that the possibility of using catalytic amounts of sodium amide in the amination of the dianions apparently arises because the NH_2 group in the amino-derivative of the dianion is less acidic than ammonia. The mechanism of the amination of the dianions remains obscure since final data on the structure of the dicarbadodecaborate(14) dianions have not as yet been obtained.

On the basis of general considerations, one can assume that, when the dicarbadodecaborane(14) dianion is acted upon by ammonia, its *closo*-structure is opened (in the case of a closed structure of the dianion) and the amide ion attacks a specific boron atom, which differs from all others. In the case of an open structure of the dianion the amide ion also attacks only a specific boron atom, linked to the hydrogen atom exhibiting the greatest hydride mobility. On treatment with oxidants, a transition from the *nido*- to the *closo*-structure and the formation of *B*-amino-*o*-carbaborane are observed. This is supported also by the finding that only the monoamino-*o*-carbaborane is formed on amination, while derivatives of *o*-carbaborane with more than one NH_2 group cannot be obtained. Nor was the formation of isomeric *B*-amino-*o*-carbaboranes observed; the reaction product is always only 3-amino-*o*-carbaborane(11).

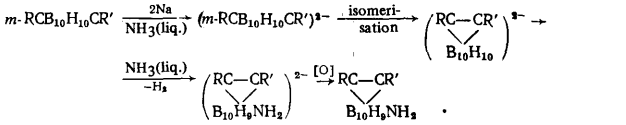
The reaction of dicarbadodecaborate(14) dianions with ammonia is influenced significantly by substituents at the carbon atoms. Whereas the dianion obtained from 1,2-dimethyl-*o*-carbaborane is aminated smoothly with formation of a *B*-amino-derivative, the dianion obtained from 1,2-diphenyl-*o*-carbaborane does not undergo the amination reaction. This is apparently associated with the large bulk of the phenyl groups compared with the methyl groups, which gives rise to steric hindrance to amination. The dianion derived from 1,1′-bis-*o*-carbaborane also does not undergo the amination reaction. *o*-Carbaboranes containing only one substituent at the carbon atom, i.e. 1-substituted *o*-carbaboranes, form dianions which readily undergo the amination reaction.

The application of this reaction to derivatives of *o*-carbaboranes containing two carbaborane nuclei proved to be of interest. It was found that *p*-bis-(*o*-carbaboranyl)benzene and 1,2-bis-(*o*-carbaboranyl)ethane combine with 4 equivalents of sodium to form bisdianions, which interact with ammonia and after oxidation give rise to *p*-bis-(3-amino-*o*-carbaboranyl)benzene and 1,2-bis-(3-amino-*o*-carbaboranyl)-ethane respectively[12,13]:

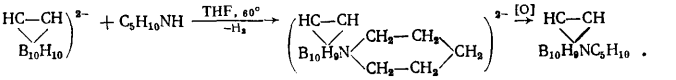


Polyamides[14] and polyureas[15] have been obtained from bis-(aminocarbaboranyl)ethane.

When an attempt is made to obtain *B*-amino-*m*-carbaborane by the reaction of the dianion derived from *m*-carbaborane with ammonia, only 3-amino-*o*-carbaborane is always formed[9]. As shown for the first time by Zakharkin et al.,[16] this is because the dianion obtained from *m*-carbaborane isomerises to the *o*-carbaborane dianion, which subsequently reacts with ammonia:

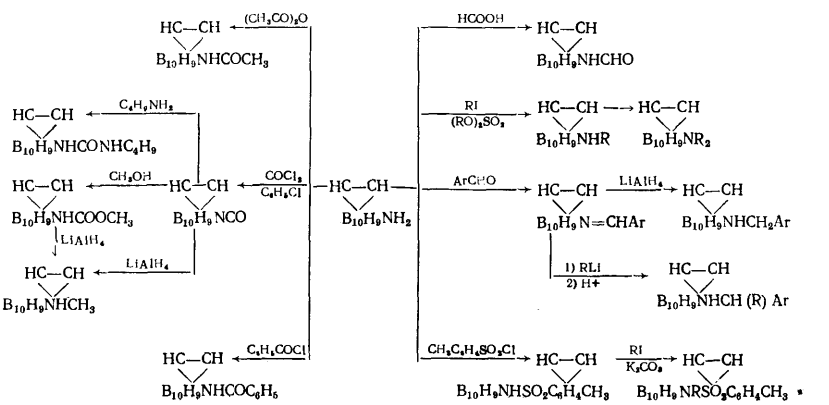


It was found that the dicarbadodecaborate(14) dianion can react with amines to form, after oxidation, derivatives with a B–N bond. Thus, on heating the dicarbadodecaborate(14) dianion in tetrahydrofuran (THF) with piperidine and subsequent oxidation with potassium permanganate in liquid ammonia, *N*-(3-*o*-carbaboranyl)piperidine was obtained[9]:

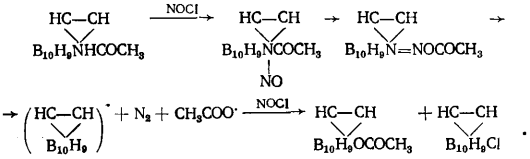


3-Amino-*o*-carbaboranes are colourless readily crystallisable substances resistant to the action of water, aqueous solutions of acids and alkalies, atmospheric oxygen, and heat. They undergo reactions characteristic of aliphatic and aromatic primary amines and are readily acylated by formic acid, acetic anhydride, benzoyl chloride, and *p*-toluenesulphonyl chloride to form the corresponding 3-acylamino-*o*-carbaboranes (Scheme 1).

Scheme 1



3-*o*-Carbaboranylamides of *p*-toluenesulphonic acid have NH groups exhibiting a considerable acidity and are readily alkylated by alkyl halides in acetone solution in the presence of potassium carbonate. When an attempt was made to obtain 3-(*N*-acetamido-*N*-nitroso)-*o*-carbaborane by treating 3-acetamido-*o*-carbaborane with nitrosyl chloride in a mixture of acetic acid and acetic anhydrides in the presence of sodium acetate, the reaction products were 3-acetoxy- and 3-chloro-*o*-carbaboranes[17]. The formation of these two compounds suggests that the decomposition of 3-(*N*-acetamido-*N*-nitroso)-*o*-carbaborane apparently proceeds similarly to the decomposition of *N*-acetyl-*N*-nitrosoarylamines, via a rearrangement to diazoacetate and radical cleavage of the latter. The 3-*o*-carbaboranyl radical formed on decomposition readily reacts with the acetoxy-radical to form 3-acetoxy-*o*-carbaborane, while on interaction with an excess of NOCl it abstracts the chlorine atom and is converted into 3-chloro-*o*-carbaborane:



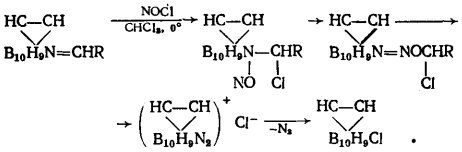
When phosgene is passed into a boiling solution of 3-amino-*o*-carbaborane in chlorobenzene, 3-*o*-carbaboranyl isocyanate is formed readily (Scheme 1). 3-*o*-Carbaboranyl isocyanates exhibit properties characteristic of aliphatic and aromatic isocyanates. For example, they readily react with alcohols and amines to form urethanes and asymmetrically substituted ureas respectively (Scheme 1). However, one should note the high hydrolytic stability of 3-*o*-carbaboranyl isocyanates, which are not hydrolysed on prolonged storage in a moist atmosphere.

The reduction of 3-*o*-carbaboranyl isocyanate with lithium tetrahydroaluminate in ethereal solution yields 3-methylamino-*o*-carbaborane, which is also formed on treatment of methyl 3-*o*-carbaboranyl-carbamate with lithium tetrahydroaluminate.

Like aliphatic and aromatic amines, 3-amino-*o*-carbaboranes condense with aromatic aldehydes to form analogues of Schiff bases containing a B—N bond[17]. *o*-Carbaborane Schiff bases can be readily reduced with lithium tetrahydroaluminate in ethereal solution to the corresponding *N*-arylalkylamines of the 3-*o*-carbaborane series.

o-Carbaborane Schiff bases readily react with organolithium compounds to form products of addition to the C=N double bond; on subsequent hydrolysis, 3-(*N*-alkyl-*N*-arylamino)-*o*-carbaboranes were obtained. *o*-Carbaborane azomethines are readily cleaved to the initial 3-amino-*o*-carbaborane and the aldehyde when they are chromatographed on alumina, which is an effective catalyst of the hydrolysis of azomethines.

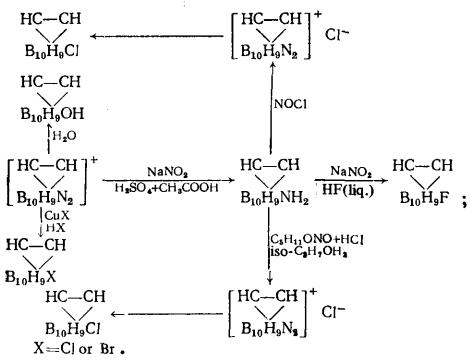
Nitrosyl chloride also cleaves *o*-carbaborane Schiff bases in chloroform, giving rise to *o*-carbaboranyldiazonium chloride, unstable at 0 °C, which decomposes with the liberation of nitrogen and the formation of 3-chloro-*o*-carbaborane[17]:



It is noteworthy that the 3-amino-*o*-carbaboranes themselves readily react with nitrosyl chloride to form 3-chloro-*o*-carbaboranes.

3-Amino-*o*-carbaboranes proved to be capable of being diazotised on treatment with various nitrosating agents with formation of 3-halogeno- and 3-hydroxy-*o*-carbaboranes (Scheme 2).

Scheme 2

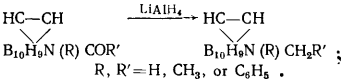


When the diazonium salt obtained by the diazotisation of 3-amino-*o*-carbaborane with nitrosylsulphuric acid in acetic acid is decomposed, the product is 3-hydroxy-*o*-carbaborane[9,18,19]. However, rapid addition of a solution of the diazonium salt to a solution of a copper(I) salt in hydrochloric acid leads readily to the corresponding 3-halogeno-*o*-carbaboranes.

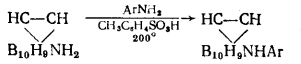
3-Amino-*o*-carbaboranes are also diazotised on treatment with pentyl nitrite in isopropyl alcohol saturated with hydrogen chloride. On subsequent increase of temperature, 3-chloro-*o*-carbaborane is formed[9]. 3-Amino-*o*-carbaboranes readily undergo the Schiemann reaction—the NH_2 groups is substituted by fluorine in liquid HF under the influence of sodium nitrite[9,20].

The decomposition of diazonium salts of the 3-*o*-carbaborane series in polar media apparently proceeds via the intermediate formation of the 3-*o*-carbaboranyl cation, which readily combines with a negative species (OH^-, Cl^-, Br^-, F^-) to form hydroxy- or halogeno-derivatives of the 3-*o*-carbaborane series.

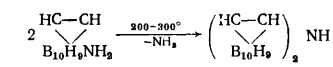
3-Amino-*o*-carbaboranes are alkylated by alkyl sulphates or halides to form secondary and tertiary alkylaminocarbaboranes. The reduction of the corresponding acyl derivatives constitutes a method of synthesis of alkylated aminocarbaboranes which is preparatively more convenient[17]:



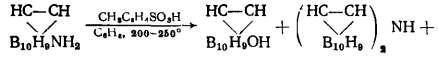
The arylation of 3-amino-*o*-carbaborane, which occurs readily when it is refluxed in an aromatic amine, for example, aniline or *p*-toluidine, in the presence of *p*-toluenesulphonic acid, is an interesting reaction[21,22]:



When 3-amino-*o*-carbaborane is heated to 200–300 °C in benzene under pressure, bis-(*o*-carbaboran-3-yl)amine is formed and NH_3 is evolved:



However, in the presence of an equimolar amount of *p*-toluenesulphonic acid, the unusual reaction involving the substitution of the NH_2 group in the *o*-carbaboranyl nucleus by the OH group takes place; the main product is 3-hydroxy-*o*-carbaborane. At the same time bis(carbaboranyl)amine and bis-(*o*-carbaboranyl) ether were isolated from the reaction products[22]:



The method involving the insertion-synthesis of dicarbollide ions with dialkyldiarylaminoboron dichlorides can be used to synthesise tertiary amines of the carbaborane series[23,24]:

$$7,8\text{-}C_2B_9H_{11}^{2-}2Na^+ + R_2NBCl_2 \rightarrow \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NR_2\end{matrix};$$
$$R=C_2H_5 \text{ or } C_6H_5 .$$

Primary and secondary amines of the 3-*o*-carbaboranes series readily interact with phenyl isocyanate to form asymmetrically substituted ureas[17]:

$$\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NHR\end{matrix} \xrightarrow{C_6H_5NCO} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NRCONHC_6H_5\end{matrix} .$$

Secondary amino-*o*-carbaboranes are readily nitrosated on treatment with sodium nitrite in acetic acid to form stable *N*-nitroso-derivatives. When 3-methylamino-*o*-carbaborane was treated with the nitrating mixture, 3-(*N*-alkylamino-*N*-nitro)-*o*-carbaborane was obtained:

$$\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9N(NO_2)R\end{matrix} \xleftarrow[H_2SO_4]{HNO_3} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NHR\end{matrix} \xrightarrow[CH_3COOH]{NaNO_2} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9N(NO)R\end{matrix} .$$

Treatment of 3-dimethylamino-*o*-carbaborane with methyl iodide in nitromethane leads to the formation of a quaternary salt—3-*o*-carbaboranyltrimethylammonium iodide; thermal decomposition of the salt gives rise to the initial tertiary amine only[17]:

$$\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9N(CH_3)_2\end{matrix} \xrightarrow[CH_3NO_2]{CH_3I} \left[\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9N(CH_3)_3\end{matrix}\right]^+ I^- \xrightarrow{200^\circ} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9N(CH_3)_2\end{matrix} .$$

This mode of thermal cleavage of the quaternary salt indicates a greater stability of the B—N bond compared with the C—N bond in this compound.

When an attempt is made to obtain 3-*o*-carbaboranyltrimethylammonium hydroxide by treating 3-*o*-carbaboranyltrimethylammonium iodide with moist silver oxide, the carbaborane nucleus is cleaved to the dicarbaundecaborate(13) anion with formation of an inner salt[17]:

$$\left[\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9N(CH_3)_3\end{matrix}\right]^+ I^- \xrightarrow{Ag_2O} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_9H_9^-{-}\overset{+}{N}(CH_3)_3\end{matrix} \xleftarrow[K_2CO_3]{CH_3I} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9N(CH_3)_2\end{matrix} .$$

The powerful electron-accepting effect of the trimethylammonium group in the 3-position in the *o*-carbaborane nucleus apparently destabilises the *o*-carbaborane system with respect to the action of bases. When tertiary amines of the o-carbaboranes series are synthesised by the direct alkylation of 3-amino-*o*-carbaborane with alkyl halides or dialkyl sulphates in the presence of potassium carbonate, the yield of the tertiary amine is apparently low and the main product is the inner salt of dicarbadodecahydro-*nido*-undecaborate(13). An interesting property of the inner salt is its ability to sublime *in vacuo* without decomposition.

Like aliphatic and aromatic formamides[25], the formyl derivatives of 3-amino-*o*-carbaboranes react with phosphoryl chloride in pyridine to form 3-*o*-carbaboranylisonitriles, which are capable of rearranging, after brief heating in boiling dodecane, to the corresponding 3-cyano-*o*-carbaboranes[26,27]:

$$\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NHCHO\end{matrix} \xrightarrow[C_5H_5N]{POCl_3} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NC\end{matrix} \xrightarrow{220^\circ} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9CN\end{matrix} .$$

This rearrangement is the first example of the migration of the carbaboranyl group with dissociation of the B—N bond and the formation of a B—C bond. The migration of the C≡N group in the carbaborane nucleus was not observed under these conditions.

m-Carbaboranes containing amino-groups attached to boron atoms are now known. They can be synthesised by several methods. The reaction of *N*-diphenylaminoboron dichloride with the 7,9-dicarbollide ion led to the synthesis of 2-diphenylamino-*m*-carbaborane[24]:

$$7,9\text{-}C_2B_9H_{11}^{2-}2Li^+ + (C_6H_5)_2NBCl_2 \rightarrow m\text{-}HCB_{10}H_9[2\text{-}N(C_6H_5)_2]CH .$$

Treatment of 2-carboxy-*m*-carbaborane (see Section III) with hydrazoic acid in H_2SO_4 (the Schmidt reaction) leads to the migration of the 2-*m*-carbaboranyl group with an excess of electrons towards the nitrogen atom, which has an electron sextet, and after hydrolysis the product is 2-amino-*m*-carbaborane[28,29]:

$$m\text{-}HCB_{10}H_9(2\text{-}COOH)CH \xrightarrow[H_2SO_4]{HN_3} m\text{-}HCB_{10}H_9(2\text{-}CONH{-}\overset{+}{N}{=}N)CH \xrightarrow{-N_2}$$
$$\rightarrow m\text{-}HCB_{10}H_9\left(2\text{-}\begin{matrix}O\\ \|\\ C{-}\overset{+}{N}H\end{matrix}\right)CH \xrightarrow[-H^+]{} m\text{-}HCB_{10}H_9(2\text{-}N{=}C{=}O)CH \xrightarrow{H^+}$$
$$\rightarrow m\text{-}HCB_{10}H_9(2\text{-}NH_2)CH .$$

A novel method of synthesising *B*-amino-*m*-carbaboranes involves the thermal isomerisation of 3-amino-*o*-carbaborane[22]. It was found that, when 3-amino-*o*-carbaborane is passed through a quartz tube at 550—600 °C *in vacuo*, equal amounts of 2- and 4-amino-*m*-carbaboranes are formed in high yields:

$$\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NH_2\text{-}3\end{matrix} \xrightarrow{550\text{-}600^\circ} m\text{-}HCB_{10}H_9(2\text{-}NH_2)CH + m\text{-}HCB_{10}H_9(4\text{-}NH_2)CH .$$

An interesting method for the synthesis of 3-alkyl-2-amino-*m*-carbaboranes consists in the treatment with alkyl iodides in liquid ammonia of the dianion derived from *o*-carbaborane subjected to preliminary amination[30,31]:

$$\left(\begin{matrix}RC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_{10}\end{matrix}\right)^{2-} \xrightarrow[-H_2]{NH_3(liq.)} \left(\begin{matrix}RC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_9NH_2\end{matrix}\right)^{2-} \xrightarrow{Alkl} \begin{matrix}RC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_8(NH_2)(Alk)\end{matrix} .$$
$$R=H, CH_3$$

The structure of the compounds obtained was demonstrated by X-ray diffraction of their reaction products—3-alkyl-2-chloro-9-iodo-*m*-carbaboranes—obtained as a result of the replacement of the amino-group by chlorine with subsequent monoiodination[32].

It has been found[22] that 2- and 4-amino-*m*-carbaboranes exhibit properties typical for organic amines and differ little in their chemical behaviour from 3-amino-*o*-carbaborane.

Thus it has been shown in relation to the reactions of aminocarbaboranes that the behaviour of the NH_2 group in these compounds differs little from that of the behaviour of the same group in aliphatic and aromatic amines. In contrast to the readily hydrolysable and oxidisable classical aminoboranes, aminocarbaboranes are stable organoelemental compounds capable of undergoing a wide variety of reactions via the NH_2 group. This is true also of other carbaborane derivatives containing the B—N bond, which were examined in this section.

2. Carbaboranes with a B—C Bond

A number of *B*-alkyl and *B*-aryl derivatives of carbaboranes have been obtained. A patent[33] reports the alkylation of *o*-carbaborane with methyl iodide in the presence of $AlCl_3$, which results in the formation of a mixture of different polymethylated carbaboranes, none of which have been isolated in a pure form:

$$\begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_{10}\end{matrix} + CH_3I \xrightarrow{AlCl_3} \begin{matrix}HC{-}CH\\ \diagdown\ \diagup\\ B_{10}H_{10-n}(CH_3)_n\end{matrix};$$
$$n=1\text{—}8 .$$

o-Carbaboranes and *m*-carbaboranes are alkylated in exactly the same way under the conditions of the Friedel—Crafts reaction with ethyl bromide and isopropyl bromide[34].

Up to eight ethyl groups can be introduced into the *o*- and *m*-carbaborane molecules, but in the case of isopropyl bromide the main products are mono- and di-substituted derivatives. The rate of electrophilic alkylation of *m*-carbaborane is lower than that of *o*-carbaborane.

The reaction of a mixture of 1- and 2-ethyldecaboranes with acetylene in acetonitrile yields a mixture of 8- and 9-ethyl-*o*-carbaboranes[35]:

$$HC{\equiv}CH + 1\text{- и } 2\text{-}B_{10}H_{13}C_2H_5 \xrightarrow[-H_2]{CH_3CN} \underset{B_{10}H_9C_2H_5\text{-}}{HC{-}CH} \text{ (8 and 9)}.$$

A convenient method for the synthesis of alkyl and aryl derivatives of *o*-carbaboranes is based on insertion synthesis with 7,8-dicarbollide ion to form the icosahedral structure with alkyl- and aryl-boron dihalides, discovered by Hawthorne and Wegner in 1965[36,37]:

$$7,8\text{-}C_2B_9H_{11}^{2-}2Na^+ + RBCl_2 \rightarrow \underset{B_{10}H_9R\text{-}3}{HC{-}CH} .$$

The structure is formed in such a way that the substituent is bound to the boron atom in the 3-position of the *o*-carbaborane nucleus. 3-Methyl-,[29] 3-ethyl-,[37] 3-propyl-,[38] 3-butyl-,[38] 3-vinyl-,[39] and 3-phenyl-*o*-carbaboranes[36,37] as well as various 3-aryl-*o*-carbaboranes substituted in the benzene ring, and *p*- and *m*-tolyl and *p*- and *m*-fluorophenyl-*o*-carbaboranes[40-44] have been synthesised in this way.

It is of interest to note that 3,6-diethyl- and 3,6-diphenyl-*o*-carbaboranes have been synthesised by this method[37]:

$$C_2B_9H_{11}^{2-} + RBCl_2 \rightarrow \underset{B_{10}H_9R}{HC{-}CH} \xrightarrow[2)\ NaH]{1)\ C_2H_5ONa} C_2B_9(R)H_{10}^{2-} \xrightarrow{RBCl_2} \underset{B_{10}H_8R_2}{HC{-}CH} ;$$
$$R{=}C_2H_5 \text{ or } C_6H_5 .$$

The preparation of 1,4-bis-(3-*o*-carbaboranyl)butane containing two 3-*o*-carbaboranyl groups in the molecule has been reported[38]:

$$2C_2B_9H_{11}^{2-} + Cl_2B(CH_2)_4BCl_2 \rightarrow \underset{B_{10}H_9(CH_2)_4B_{10}H_9}{HC{-}CH \quad HC{-}CH} .$$

Insertion synthesis of structures with the aid of alkyl(aryl)-boron dihalides has been extended to the 7,9-dicarbollide ion and 2-vinyl-[28,29] and 2-aryl-*m*-carbaboranes[45] have been obtained by this procedure:

$$7,9\text{-}C_2B_9H_{11}^{2-}2Li^+ + RBCl_2 \rightarrow m\text{-}HCB_{10}H_9(2\text{-}R)CH ;$$
$$R{=}CH_2{=}CH,\ C_6H_5,\ FC_6H_4 \text{ or } CH_3C_6H_4 .$$

A general method of synthesis of substituted *o*-carbaboranes containing a B–C bond consist in the interaction of the dicarbadodecaborate(14) dianions with organolithium and organomagnesium compounds, resulting in the formation of *B*-alkyl(alkenyl, aryl) dianions, which give rise to *B*-alkyl-(alkenyl, aryl)-*o*-carbaboranes after oxidation with $CuCl_2$[46-48]:

$$(HCB_{10}H_{10}CH)^{2-} + RM \xrightarrow[20^\circ]{THF} (HCB_{10}H_9RCH)^{2-} \xrightarrow{CuCl_2} \underset{B_{10}H_9R}{HC{-}CH} ;$$
$$M{=}Li \text{ or } MgX;\ R{=}CH_3,\ C_4H_9,\ CH_2{=}CH,\ C_6H_5CH{=}CH,$$
$$C_6H_5,\ CH_3C_6H_4, \text{ or } FC_6H_4 .$$

The reaction is not selective—a mixture of *B*-substituted carbaboranes containing the substituent in the 3-, 4-, 8-, and 9-positions in the *o*-carbaborane nucleus is always formed. X-Ray diffraction analysis of 1,2-dimethyl-9-phenyl-*o*-carbaborane and 4-(*p*-tolyl)-*o*-carbaborane has been carried out[48].

The reaction of the dianions with organometallic compounds is influenced significantly by the acidity of the hydrocarbon conjugate acid of the carbanion of the organometallic compound. For example, this reaction is not undergone by indenyl-lithium, fluorenyl-lithium, phenylethynyl-lithium, carboranyl-lithium, and cyclopentadienyl-lithium[46].

When the dicarbadodecaborate(14) dianion, obtained from *p*-carbaborane, interacts with arylmagnesium halides and the product is then oxidised, mainly a mixture of *B*-aryl-*m*-carbaboranes is obtained[47,48]:

$$p\text{-}HCB_{10}H_{10}CH \xrightarrow[THF]{2Na} (HCB_{10}H_{10}CH)^{2-} + ArMgX \rightarrow (HCB_{10}H_9ArCH)^{2-} \rightarrow$$
$$\xrightarrow{CuCl_2} m\text{-}HCB_{10}H_9ArCH .$$

Apart from insertion syntheses of the 7,9-dicarbollide ion, high-temperature gas-phase isomerisation of 3-aryl-*o*-carbaboranes *in vacuo*, leading to 2- and 4-aryl-*m*-carbaboranes, has been proposed as a method of synthesis of aryl-*m*-carbaboranes[49,50]:

$$\underset{B_{10}H_9Ar}{HC{-}CH} \xrightarrow{550\text{-}600^\circ} m\text{-}HCB_{10}H_9(2\text{-}Ar)CH + m\text{-}HCB_{10}H_9(4\text{-}Ar)CH .$$

Mironov and coworkers found[51-55] that trichlorovinylsilane alkylates *o*-, *m*-, and *p*-carbaboranes and their derivatives under the conditions of the Friedel–Crafts reaction via the B–H bonds of the carbaborane nuclei:

$$HCB_{10}H_{10}CH + CH_2{=}CHSiCl_3 \xrightarrow{AlCl_3} HCB_{10}H_{10-n}(CH_2CH_2SiCl_3)_nCH ;$$
$$n = 1-3 .$$

Chloromethylvinylsilanes also alkylate carbaboranes under analogous conditions, but, in view of the lower reactivity, the yields of the corresponding products are sharply reduced[55]:

$$HCB_{10}H_{10}CH + CH_2{=}CHSi(CH_3)_xCl_{3-x} \xrightarrow{AlCl_3} HCB_{10}H_{10-n}[CH_2CH_2Si(CH_3)_xCl_{3-x}]_nCH .$$

The mechanism of the silylalkylation of carbaboranes is analogous to the mechanism of the Friedel–Crafts reaction, the sites of the highest electron density in the nuclei being attacked; the trichlorosilylethyl group is therefore located at the boron atoms in the 9(12)-positions in *o*-carbaborane, the 9(10)-positions in *m*-carbaborane, and the 2-position in *p*-carbaborane. The structure of 1,7-bis(trimethylstannyl)-9-[β-(trimethylsilyl)ethyl]-*m*-carbaborane has been confirmed by X-ray diffraction[56].

Studies of the infrared and mass spectra of *B*-substituted carbaboranes have been carried out[57-59].

The formation of aminated *B*-alkyl-*m*-carbaboranes was mentioned above. The special case of the reaction of methyl iodide with the dianion derived from 1,2-di-methyl-*o*-carbaborane in liquid ammonia, resulting in the formation of a mixture of alkylated isomers of *o*- and *m*-carbaboranes[31], is noteworthy:

$$\left(\underset{B_{10}H_{10}}{CH_3C{-}CCH_3}\right)^{2-} \xrightarrow[2)\ CH_3I]{1)\ Na\ (ж)} \underset{(2\text{-isomers})}{CH_3CB_{10}H_9(CH_3)CCH_3} + \underset{(2\text{-isomers})}{CH_3CB_{10}H_8(CH_3)_2CCH_3} .$$

One of the isomers is 1,2,3,6-tetramethyl-*o*-carbaborane[31].

The first functional derivative in the series of carbaboranes, containing a B–C bond, was obtained by Zakharkin and Kalinin in 1968.[39] Oxidation of 3-vinyl-*o*-carbaborane with chromium trioxide in a mixture of acetic and sulphuric acids gives a high yield of 3-carboxy-*o*-carbaborane:

$$\underset{B_{10}H_9CH{=}CH_2}{HC{-}CH} \xrightarrow{CrO_3} \underset{B_{10}H_9COOH}{HC{-}CH} .$$

2-Carboxy-*m*-carbaborane has been obtained by an analogous mechanism from 2-vinyl-*m*-carbaborane[28,29].

o-Carbaborane- and *m*-carbaborane-carboxylic acids have been synthesised by the hydrolysis of 3-cyano-*o*-, 2-cyano-*m*-, and 4-cyano-*m*-carbaboranes[27,60]. Owing to the considerable bulk of the carbaborane nuclei, *B*-cyanocarbaboranes can be hydrolysed only by a two-stage method: in the first stage hydrolysis with sulphuric acid results in the formation of an amide, which is converted into the acid on subsequent treatment with sodium nitrite:

$$HCB_{10}H_9(CN)CH \xrightarrow[CH_3COOH,\ 110^\circ]{H_2SO_4} HCB_{10}H_9(CONH_2)CH \xrightarrow[10^\circ]{NaNO_2} HCB_{10}H_9(COOH)CH .$$

The oxidation of *B*-trimethylsilylethylcarbaboranes with chromium trioxide in a mixture of acetic and sulphuric acids gave 9-carboxy-*o*- and 9-carboxy-*m*-carbaboranes[61,62]:

$$HCB_{10}H_9[9\text{-}CH_2CH_2Si(CH_3)_3]CH \xrightarrow{CrO_3} HCB_{10}H_9(9\text{-}COOH)CH .$$

3-Carboxy-*o*-carbaboranes have the properties of the usual organic acids. They are soluble in aqueous solutions of alkalies and form 3-methoxycarbonyl-*o*-carbaboranes on reaction with diazomethane in ether. In contrast to 1-carboxy-*o*-carbaboranes, 3-carboxy-*o*-carbaboranes are esterified with methanol in the presence of H_2SO_4:

$$\begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9COOH\end{matrix} \xrightarrow[\text{or } CH_3OH,\ H_2SO_4]{CH_2N_2,\ (C_2H_5)_2O} \begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9COOCH_3\end{matrix} .$$

Treatment of 3-carboxy-*o*-carbaboranes with PCl_5 in benzene or with $SOCl_2$ leads to the formation of acid chlorides whose properties are similar to those of the usual carboxylic acid chlorides:

$$\begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9COOH\end{matrix} \xrightarrow[\text{or } SOCl_2]{PCl_5,\ C_6H_6} \begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9COCl\end{matrix} \begin{cases}\xrightarrow{LiAlH_4} \begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9CH_2OH\end{matrix}\\ \xrightarrow[AlCl_3]{C_6H_6} \begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9COC_6H_5\end{matrix}\end{cases} .$$

The reduction of the acid chloride with lithium tetrahydroaluminate in ether leads smoothly to the formation of 3-hydroxymethyl-*o*-carbaborane, while its refluxing in benzene in the presence of $AlCl_3$ gave 3-benzoyl-*o*-carbaborane via the Friedel–Crafts reaction[63].

The reduction of 3-benzoyl-*o*-carbaborane with lithium tetrahydroaluminate in ether led to the formation of a secondary alcohol, while the reaction with CH_3MgI gave a tertiary alcohol[63]:

$$\begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9C(OH)(CH_3)(C_6H_5)\end{matrix} \xleftarrow{CH_3MgI} \begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9COC_6H_5\end{matrix} \xrightarrow{LiAlH_4} \begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9CH(OH)C_6H_5\end{matrix} .$$

The large bulk of the o-carbaboranyl group influences the state of the OH group in primary, secondary, and tertiary alcohols of the type $B_{10}H_9CRR'OH$. Whereas the infrared spectrum of 3-hydroxymethyl-*o*-carbaborane exhibits a broad absorption band at 3200–3500 cm^{-1} due to the OH group of the associated alcohol, the infrared spectrum of (3-*o*-carbaboranyl)phenylmethanol has two absorption bands due to the OH group: a broad band at 3200–3500 cm^{-1}, characteristic of associated alcohols, and a narrow band at 3550–3580 cm^{-1}, characteristic of unassociated alcohols. The infrared spectrum of the tertiary alcohol shows a single narrow band at 3550–3580 cm^{-1}, which indicates the existence of this alcohol solely in the unassociated state. A similar behaviour has been observed for primary, secondary, and tertiary alcohols, where the substituent was the 1-*o*-carbaboranyl group[64].

The hydroxy-group in 3-hydroxymethyl-*o*-carbaborane is readily substituted by chlorine on refluxing with PCl_5 or $SOCl_2$ in benzene:

$$\begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9CH_2OH\end{matrix} \xrightarrow[\text{or } SOCl_2]{PCl_5,\ C_6H_6} \begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9CH_2Cl\end{matrix} .$$

3-Chloromethyl-*o*-carbaborane formed a Grignard reagent in ethereal solution, the carboxylation of which led to the formation of 3-*o*-carbaboranylacetic acid[63]:

$$\begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9CH_2Cl\end{matrix} \xrightarrow[(C_2H_5)_2O]{Mg} \begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9CH_2MgCl\end{matrix} \begin{cases}\xrightarrow[2)\ H^+]{1)\ CO_2} \begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9CH_2COOH\end{matrix}\\ \xrightarrow{H^+} \begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9CH_3\end{matrix} \xleftarrow{7,8\text{-}C_2B_9H_{11}^{2-}+CH_3BCl_2} .\end{cases}$$

The hydrolysis of 3-*o*-carbaboranylmethylmagnesium chloride yielded 3-methyl-*o*-carbaborane, which is also formed when the disodium salt of the 7,8-dicarbollide ion reacts with methylboron dichloride in THF.[29,65]

3-Carboxy-*o*-carbaborane can interact with four equivalents of methyl-lithium in ether and after hydrolysis the product is 3-acetyl-*o*-carbaborane. A ketone can also be obtained when three equivalents of methyl-lithium react with 3-cyano-*o*-carbaborane:

$$\begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9COOH\end{matrix} \xrightarrow{4CH_3Li} \begin{matrix}LiC{-}CLi\\ \diagdown\diagup\\ B_{10}H_9C{-}OLi\\ \diagdown\\ OLi\end{matrix} \xrightarrow{H^+} \begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9COCH_3\end{matrix} \xrightarrow{H^+}$$

$$\xleftarrow{3CH_3Li} \begin{matrix}LiC{-}CLi\\ \diagdown\diagup\\ B_{10}H_9C{-}CH_3\\ \diagdown\\ NLi\end{matrix} \xleftarrow{} \begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9CN\end{matrix} .$$

The chemical properties of 3-carboxy-*o*-carbaborane examined above are also characteristic of other representatives of carbaboranecarboxylic acids—2- and 4-carboxy-*m*-carbaboranes[60] and 9-carboxy-*o*- and 9-carboxy-*m*-carbaboranes[55,61,62].

Silyl and stannyl derivatives of these acids have been obtained from 9-carboxy-*o*-carbaborane and hexamethyldisilazane or hexaethyldistannoxane[62]:

$$\begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9COOSi(CH_3)_3\end{matrix} \xleftarrow[-NH_3]{(CH_3)_3SiNHSi(CH_3)_3} \begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9COOH\end{matrix} \xrightarrow{(C_2H_5)_3SnOSn(C_2H_5)_3} \begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9COOSn(C_2H_5)_3\end{matrix} .$$

A remarkable feature of *B*-carboxycarbaboranes and their derivatives is the possibility of nucleophilic molecular rearrangements accompanied by the dissociation of the B–C bond and the migration of the carbaboranyl group with an electron pair to an electron-deficient reaction centre[63]. The carbaboranyl group migrates to a carbenoid carbon atom (the Wolff rearrangement), a nitrene (the Hofmann, Curtius, and Beckmann rearrangements and the Schmidt reaction), or an oxygen atom with a positive charge (the Baeyer–Villiger reaction) (Scheme 3):

It has been established that these rearrangements proceed intramolecularly, the electron pair does not migrate to other boron atoms in the carbaborane nuclei, and the new B–C, B–N, and B–O bonds are formed with the same boron atom to which the functional group had been linked initially.

Analysis of the literature data for the Curtius rearrangement[66] and the Baeyer–Villiger reaction[67] in the series of polyhedral ions $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ suggests that molecular nucleophilic rearrangements typical for organic chemistry are applicable to the dissociation of the B–C bond when the boron atom forms part of polyhedral borane anions or carbaboranes.

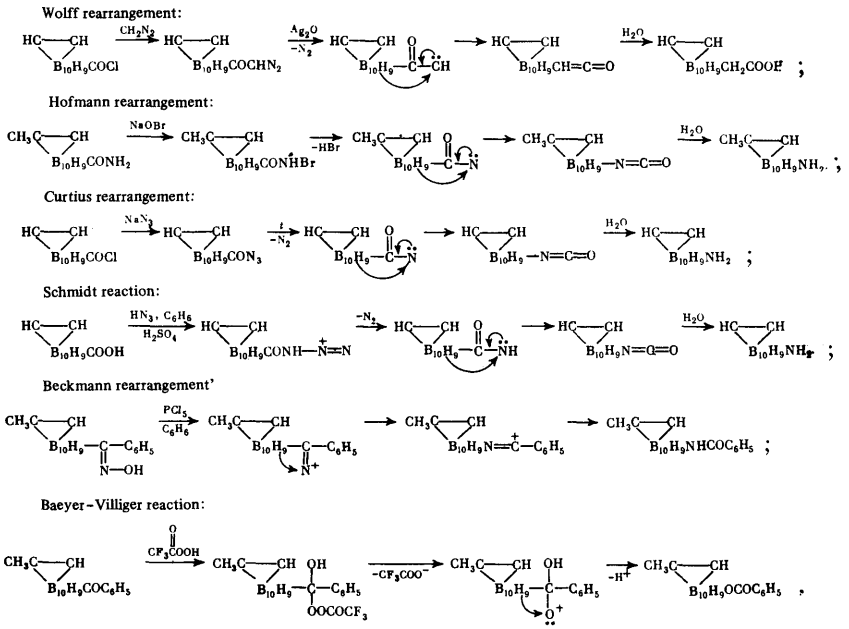
B-Alkenylcarbaboranes undergo the usual reactions characteristic of double bonds. For example, treatment of 3-vinyl-*o*-carbaborane with ozone yields 3-formyl-*o*-carbaborane[39] and hydrostannylation of 2-vinyl-*m*-carbaborane leads to a high yield of 2-triethylstannyl-*m*-carbaborane[68]:

$$\begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9CH{=}CH_2\end{matrix} \xrightarrow{O_3} \begin{matrix}HC{-}CH\\ \diagdown\diagup\\ B_{10}H_9CHO\end{matrix} ;$$

$$m\text{-}HCB_{10}H_9(-CH{=}CH_2)CH \xrightarrow{(C_2H_5)_2SnH} m\text{-}HCB_{10}H_9[-CH_2CH_2Sn(C_2H_5)_3]CH .$$

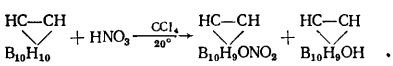
The study of the chemical properties of carbaborane derivatives containing a B–C bond and with functional groups attached to boron atoms, namely carboxy-*o*-carbaboranes and their derivatives, acyl derivatives of carbaboranes, and hydroxy- and chloromethyl-carbaboranes, showed that their chemical properties are similar to those of the corresponding aliphatic and aromatic organic derivatives with *C*-functional groups.

Scheme 3



3. Carbaboranes with a B–O Bond

Historically *B*-hydroxycarbaboranes have been the first known type of compounds containing a functional group attached to a boron atom. In 1965 it was noted[69,70] that prolonged oxidation of *o*-carbaboranes with 100% nitric acid in CCl_4 results in the formation of *B*-hydroxycarbaboranes and the corresponding nitrates:



The sites with the highest electron density in the carbaborane nucleus are the first to be oxidised by nitric acid, i.e. the *B*-hydroxycarbaboranes obtained are largely 9-substituted isomers.

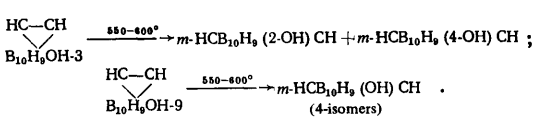
It was found subsequently[71,72] that *o*-, *m*-, and *p*-carbaboranes undergo oxidative hydroxylation on treatment with $KMnO_4$ in acetic acid with formation of all possible isomers: four in the case of *o*- and *m*-carbaboranes and one in the case of *p*-carbaborane:

$$HCB_{10}H_{10}CH + KMnO_4 \rightarrow HCB_{10}H_9OHCH \quad .$$

The oxidation of carbaboranes by treatment with CrO_3 is more selective and in this case the formation of mainly 9-substituted products was observed for *o*- and *m*-carbaboranes[72].

The diazotisation of *B*-amino-*o*-carbaborane with nitrosylsulphuric acid is a convenient method for the synthesis of 3-hydroxy-*o*-carbaboranes[18,19].

Thermal isomerisation of 3-hydroxy-*o*-carbaborane in a flow system at 550–600 °C leads to the formation of 2- and 4-hydroxy-*m*-carbaboranes only, while the isomerisation of 9-hydroxy-*o*-carbaborane gives rise to a mixture of all possible isomeric *B*-hydroxy-*m*-carbaboranes[60]:



3-Hydroxy-*o*- and 2-hydroxy-*m*-carbaboranes readily undergo intramolecular and nucleophilic cleavage in an alkaline medium, forming the corresponding dicarbaundecaborate(13) anions[73]:

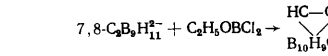
$$HCB_{10}H_9\,(OH)\,CH \xrightarrow{KOH} C_2B_9H_{12}K \quad .$$

B-Hydroxycarbaboranes have the properties of the usual organic hydroxy-derivatives. We shall consider their chemical behaviour in relation to the most thoroughly investigated 3-hydroxy-*o*-carbaboranes. They readily react with acylating agents, such as acetic anhydride, benzoyl chloride and *p*-toluenesulphonyl chloride, forming the corresponding acyloxy-derivatives[19] (Scheme 4):

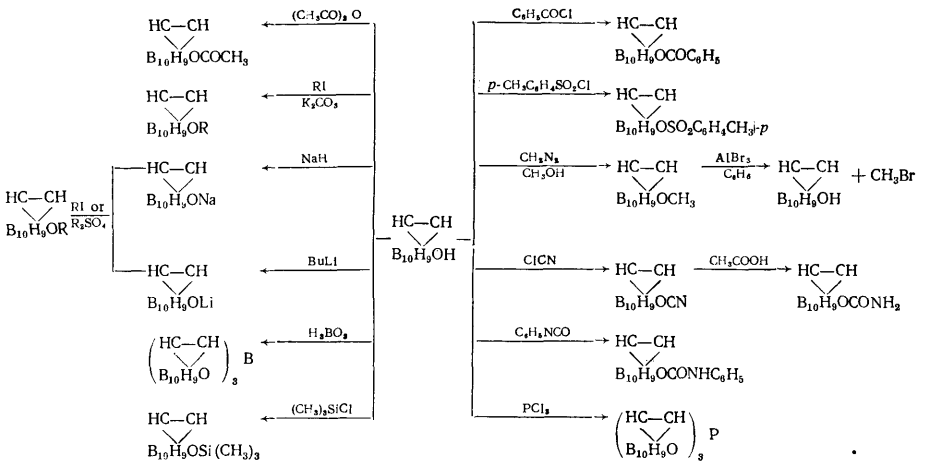
3-*o*-Carbaboranyl tosylates proved to be relatively unreactive in nucleophilic substitution reactions. When 3-*o*-carbaboranyl tosylate was heated with NaI in acetone at 140 °C for 10 h, no substitution products were observed. This result is consistent with the low reactivity of *B*-halogeno-*o*-carbaboranes in nucleophilic substitution reactions[11].

The following procedures can be used to synthesise 3-alkoxycarbaboranes (Scheme 4): (a) treatment of 3-hydroxy-*o*-carbaborane with diazomethane in methanol solution; (b) heating of an acetone solution of 3-hydroxy-*o*-carbaborane with an alkyl iodide in the presence of potassium carbonate; (c) treatment with alkyl iodides or dialkyl sulphates of lithium or sodium 3-*o*-carbaboranoxides prepared by the reaction of butyl-lithium or sodium hydride with 3-hydroxy-*o*-carbaboranes.

3-Ethoxy-*o*-carbaborane has been obtained by the insertion synthesis reaction of the 7,8-dicarbollide ion with ethoxyboron dichloride[23]:



Scheme 4



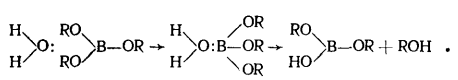
In contrast to boric acid esters, carbaborane ethers are resistant to hydrolysis but, on heating of 3-methoxy-*o*-carbaborane with $AlBr_3$ in benzene, the C–O bond is cleaved with exclusive formation of 3-hydroxy-*o*-carbaborane, while the B–O bond remains unaffected[19].

In this respect 3-methoxy-*o*-carbaboranes behave similarly to mixed aliphatic-aromatic ethers, the 3-*o*-carbaboranyl group playing the role of an aromatic group.

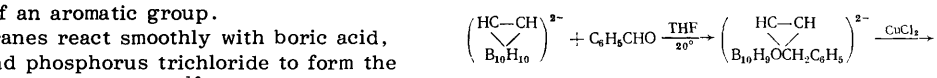
3-Hydroxy-*o*-carbaboranes react smoothly with boric acid, chlorotrimethylsilane, and phosphorus trichloride to form the corresponding ester or ether (Scheme 4).[19]

When 3-hydroxy-*o*-carbaborane reacts with chlorocyanogen in acetone in the presence of triethylamine, 3-*o*-carbaboranyl cyanate is formed smoothly. 3-Carbaboranyl cyanates are solid crystalline substances, which are stable in air. In contrast to aliphatic cyanates, they do not tend to isomerise and trimerise even in the presence of an active catalyst such as $AlCl_3$. 3-*o*-Carbaboranyl cyanates react with acetic acid to form carbamates. The reaction of 3-hydroxy-*o*-carbaborane with phenyl isocyanate leads to the corresponding urethane[11].

In contrast to alkyl(aryl)boronic acids and dialkyl(diaryl)-borinic acids, *B*-hydroxy-*o*-carbaboranes have chemical properties similar to those of aliphatic and aromatic hydroxy-derivatives. The unusually high hydrolytic stability of tris-(3-*o*-carbaboranyl) borate, which is not decomposed by water to boric acid and 3-hydroxy-*o*-carbaborane, in contrast to the readily hydrolysable alkyl and aryl borates[74], proved to be of interest. In the light of the mechanism proposed for the hydrolysis of borate esters[74], the hydrolytic stability can apparently be accounted for by the large bulk of the carbaborane nuclei, which hinders the formation of an intermediate complex with water:



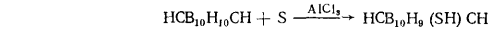
Kalinin and Zakharkin[75,76] discovered an interesting reaction involving the formation of the B–O bond in carbaboranes, which consists in the interaction of the dicarbadodecaborate(14) dianions with aromatic aldehydes and subsequent oxidation of the intermediates to neutral carbaboranes. It was found that the dicarbadodecaborate(14) dianion, obtained from *o*-carbaborane, resembles in terms of some of its properties the tetrahydroborate anion BH_4^-. This is reflected in the ability of the dianion derived from *o*-carbaborane to add to the carbonyl group of benzaldehyde, as a result of the dissociation of the B–H bond with formation of *B*-benzyloxy-dianions, the oxidation of which with copper(II) chloride in THF leads to *B*-benzyloxy-*o*-carbaboranes in high yields:



Although the structure of the dicarbadodecaborate(14) dianions has not been elucidated, there is no doubt that their addition to the carbonyl group of benzaldehyde should proceed via the B–H bonds exhibiting the highest hydride mobility. The main products of the oxidation of benzyloxy-dianions are 3-benzyloxy-*o*-carbaborane (75–80% yield) and 4-benzyloxy-*o*-carbaborane (20–25% yield). 4-Benzyloxy-*o*-carbaborane has been investigated by X-ray diffraction[77].

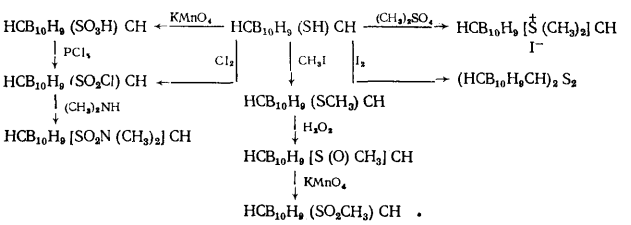
4. Carbaboranes with a B–S Bond

A general method of synthesis of *B*-mercaptocarbaboranes, consisting of the treatment of carbaboranes with elemental sulphur in the presence of $AlCl_3$, has been developed[78,79]:



The sulphur atom in *B*-mercaptocarbaboranes is linked to the boron atom in the 9-position in *o*- and *m*-carbaboranes and in the 2-position in *p*-carbaborane. The chemical properties of 9-mercapto-*o*- and 9-mercapto-*m*-carbaboranes, the main transformation cycle of which is illustrated in Scheme 5, have been investigated in detail[80,81]:

Scheme 5



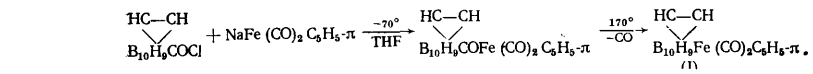
The oxidation of mercaptans with $KMnO_4$ leads to sulphonic acids, which can be readily converted into sulphonyl chlorides and dimethylamides. In an alkaline medium mercaptans are readily *S*-alkylated by virtually any alkylating agents with formation of, for example, methylthiocarbaborane and carbaboranyldimethylsulphonium iodide. The oxidation of methylthiocarbaborane yields either carbaboranyl methyl sulphoxide or the corresponding sulphone, depending on the oxidation potential of the reactant. When mercaptocarbaboranes are treated with iodine, biscarbaboranyl disulphides are formed smoothly and can be reduced in their turn with zinc in acetic acid to mercaptans[78,80,81].

One may conclude that the sulphur derivatives of carbaboranes containing a B–S σ-bond have properties analogous to those of sulphur derivatives with a C–S bond.

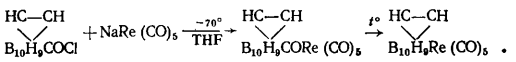
5. Carbaboranes with a B–Metal Bond

A number of carbaborane derivatives containing a bond between boron and a transition or non-transition metal are known. It now appears that there are favourable prospects for the development of the chemistry of this extremely interesting class of compounds.

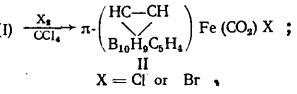
o-Carbaborane derivatives containing a σ-bond between boron and a transition metal were first obtained[82] via acyl derivatives. The reaction of the chloride of 3-*o*-carbaboranecarboxylic acid with $NaFe(CO)_2C_5H_5$-π leads to σ-(*o*-carbaboranyl-3-carbonyl)-π-cyclopentadienyliron dicarbonyl, the decarbonylation of which yields σ-(*o*-carbaboran-3-yl)-π-cyclopentadienyliron dicarbonyl (I):



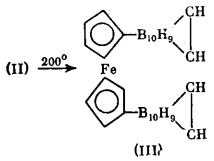
The rhenium derivative has been obtained via a similar mechanism[83]:



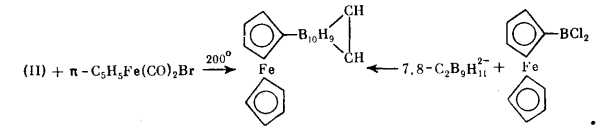
The reaction of halogens with a complex containing a B–Fe bond is of interest. The reaction of compound (I) with chlorine or bromine entails a rearrangement accompanied by the dissociation of the B–Fe bond and the migration of the carbaboranyl group to the cyclopentadienyl ring with formation of π-[(*o*-carbaboran-3-yl)cyclopentadienyl]dicarbonyliron halide (II)[84,85]:



Heating of compound (II, X = Br) at 200 °C in decalin leads to 1,1′-bis-(*o*-carbaboran-3-yl)ferrocene (III)[85,86]:

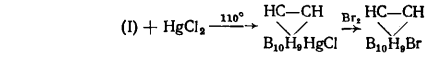


If complex (II) is heated in the presence of $\pi\text{-}C_5H_5Fe(CO)_2.Br$, then (*o*-carbaboran-3-yl)ferrocene is obtained together with ferrocene and compound (III); (*o*-carbaboran-3-yl)-ferrocene has also been obtained by specific synthesis from ferrocenylboron dichloride and the 7,8-dicarbollide ion[85,86]:



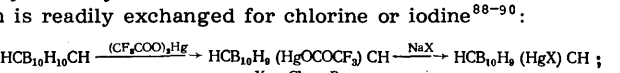
The polarographic reduction of carbaborane complexes with a B–Fe σ-bond proceeds in the same way as for the usual σ-alkyl derivatives and the primary products are the anions $[\pi\text{-}C_5H_5Fe(CO)_2]^-$ and $[RCB_{10}H_9CR]^-$.[87]

In contrast to reactions with the halogens, complex (I) interacts with mercury(II) chloride in the normal manner, yielding the first example of carbaborane derivatives with a B–Hg bond: 3-*o*-carbaboranylmercury chloride[85,86]:

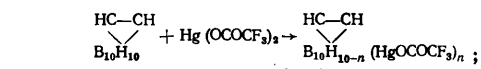


When the latter is treated with bromine, demercuration takes place readily.

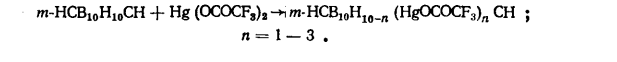
Further development of this branch of the chemistry of carbaborane derivatives with *B*-functional groups was associated with the discovery in 1976 of the reaction involving the mercuration of carbaboranes[88]. It was found that a powerful mercurating agent, such as mercury trifluoroacetate, reacts with o-, *m*-, and p-carbaboranes to form carbaboranylmercury trifluoroacetate, in which the trifluoroacetate anion is readily exchanged for chlorine or iodine[88–90]:



The electrophilic monomercuration of *o*-carbaborane leads to the formation of 15–20% of the 8-substituted derivative and 80–85% of the 9-substituted derivative, while the mercuration of *m*-carbaborane takes place in the 9-position to the extent of 99%. The formation of *B*-polymercurated carbaboranes has also been observed[89,91]. In the reaction of *o*-carbaborane with mercury trifluoroacetate in CF_3COOH mono-, di-, tri-, tetra-, and penta-mercuri-derivatives are formed in succession[89,91]:

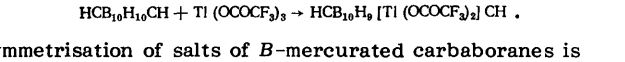


In the case of *m*-carbaborane the reaction proceeds with greater difficulty and after 30 h mainly the trimercuri-derivative is formed[91]:

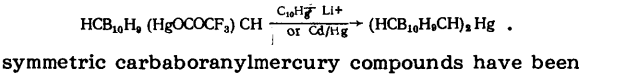


Carbaboranes are also mercurated on treatment with mercury acetate in CH_3COOH in the presence of catalytic amounts of $HClO_4$.[91]

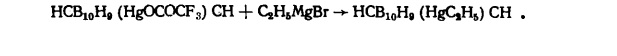
Carbaboranes have been thallated under similar conditions with formation of derivatives having a B–Tl bond[92,93]:



Symmetrisation of salts of *B*-mercurated carbaboranes is achieved by treatment with a solution of the naphthalene radical-anion or (better) with cadmium amalgam[89,90]:



Asymmetric carbaboranylmercury compounds have been obtained by the reaction of carbaboranylmercury trifluoroacetate with a Grignard reagent:



Asymmetric *B*-mercuricarbaboranes are much less stable than their *C*-analogues—they disproportionate even at 100 °C with formation of symmetrical products:

$$HCB_{10}H_9(HgC_2H_5)CH \xrightarrow{100^\circ} (HCB_{10}H_9CH)_2Hg + (C_2H_5)_2Hg .$$

In contrast to *C*-mercuricarbaboranes, symmetrical *B*-substituted compounds readily react with $HgCl_2$, Br_2, and HCl:[89-91]

$$HCB_{10}H_9(HgCl)CH \xleftarrow{HgCl_2} (HCB_{10}H_9CH)_2Hg \begin{cases} \xrightarrow{Br_2} HCB_{10}H_9BrCH \\ \xrightarrow{HCl} HCB_{10}H_9(HgCl)CH \end{cases} .$$

The enhanced electron affinity of the B–Hg bond in *p*-carbaborane under the conditions of polarographic reduction, relative to the corresponding derivatives of *o*- and *m*-carbaboranes, has been noted[94,95].

Bis-carbaboranyl derivatives of mercury can be used in reactions with non-transition metal salts in order to synthesise other derivatives containing a σ-bond between boron and the non-transition element[92,93,96-98]:

$$\left(\begin{matrix}HC-CH\\ \diagdown\ \diagup\\ B_{10}H_9\end{matrix}\right)_2 Hg + EX_3 \xrightarrow{\Delta} \begin{matrix}HC-CH\\ \diagdown\ \diagup\\ B_{10}H_9EX_2\end{matrix} + \begin{matrix}HC-CH\\ \diagdown\ \diagup\\ B_{10}H_9HgX\end{matrix} ;$$

E = As, Sb, or Tl .

When biscarbaboranylmercury is treated with $SnCl_2$, a tin derivative containing a B–Sn bond is formed smoothly[98]:

$$(HCB_{10}H_9CH)_2Hg + SnCl_2 \rightarrow (HCB_{10}H_9CH)_2SnCl_2 .$$

Heating of bis-*m*-carbaboranylmercury with sulphur in a sealed tube at 350 °C leads to the formation of biscarbaboranyl disulphide:

$$(HCB_{10}H_9CH)_2Hg + S \rightarrow (HCB_{10}H_9CH)_2S_2 + Hg .$$

An interesting compound containing a B–S–Hg–B bond has been obtained on adding tetrabutylammonium iodide to a mixture of biscarbaboranylmercury and sulphur[98]:

$$(HCB_{10}H_9CH)_2Hg + S \xrightarrow[DMF]{I^-} \begin{matrix}HCB_{10}H_9CH\\ |\\ S\\ |\\ Hg\\ |\\ HCB_{10}H_9CH\end{matrix} .$$

The formation of derivatives with B–Ge and B–P bonds has been claimed[96].

Biscarbaboranyl derivatives of mercury can be used to synthesise carbaboranes with B–C bonds. For example, when bis-*o* or bis *m*-carbaboranylmercury is acted upon by CH_3COCl in the presence of $AlCl_3$, *B*-acetylcarbaborane is formed[99]:

$$(HCB_{10}H_9CH)_2Hg + CH_3COCl \xrightarrow{AlCl_3} HCB_{10}H_9(COCH_3)CH + HCB_{10}H_9(HgCl)CH .$$

Mercury derivatives have also been used in the synthesis of carbaboranes with a B–Pt σ-bond by the oxidative addition of 9-chloromercuri-derivatives of *o*- and *m*-carbaboranes to $Pt(Ph_3P)_3$:[100]

$$HCB_{10}H_9(HgCl)CH + Pt(Ph_3P)_3 \xrightarrow[20^\circ]{C_6H_6} HCB_{10}H_9[PtCl(Ph_3P)_2]CH .$$

The intramolecular oxidative addition of the B–H bond in 1-dimethylphosphino-o-carbaborane to an iridium atom is of interest.[101,102] It proceeds via the intermediate formation of the complex L_3IrCl, which has not been isolated in a pure state:

$$[Ir(C_8H_{14})_2Cl]_2 + 6\,(CH_3)_2PC-CH \xrightarrow{\Delta} [2\,L_3IrCl] \rightarrow (CH_3)_2PC-CH \quad ;$$

$B_{10}H_{10}$

$L = (CH_3)_2PC-CH$ (L, L, Cl, H around Ir; Ir–$B_{10}H_9$)

$B_{10}H_{10}$.

The iridium atom is coordinated to the boron atom in the 4(5)-positions in the *o*-carbaborane nucleus.

Another version of the synthesis of complexes with B–Ir bonds involves the intermolecular oxidative addition of the B–H bonds in *o*-, *m*-, and *p*-carbaboranes to the corresponding iridium complexes[102,103]:

$$L_2IrCl + HCB_{10}H_{10}CH \rightarrow \underset{(IV)}{HCB_{10}H_9(IrL_2HCl)CH} ;$$

$L = Ph_3P$ or Ph_3As .

When CO is passed through a solution of compound (IV) in benzene or when compound (IV) is heated with triphenylphosphine in toluene, the σ-linked carbaboranyl ligand is readily split off[102]:

$$HCB_{10}H_{10}CH \xleftarrow{CO} (IV) \xrightarrow{Ph_3P} HCB_{10}H_{10}CH .$$

III. THE ELECTRONIC EFFECTS OF *B*-CARBABORANYL GROUPS

As a consequence of the non-uniformity of the distribution of electron density in carbaborane nuclei, the electronic effects of the carbaboranyl groups depend on the site in the nucleus to which the substituent is linked. This postulate was put forward in 1966 by Zakharkin, Kalinin, and Shepilov in connection with the determination of the electronic effects of the 3-*o*-carbaboranyl group[41]. As a result of the advances made in the synthesis of various boron-substituted carbaboranes, the electronic effects of the *B*-carbaboranyl groups have now been investigated in fair detail. The known σ-constants of the *B*-carbaboranyl groups are compiled in the Table.

The σ-constants of the carbaboranyl groups.

Carbaboranyl group	Hammett constants*		References	Inductive and resonance constants**		References
	σ_p	σ_m		σ_I	σ_R^0	
1-*o*-	0.46	0.47	104	0.375	0.003	104
1-*o*-	0.43	0.49	42	0.38	0	43
3-*o*-	0.19	0.19	42	0.11	0.07	43
3-*o*-	—	—	—	0.01	0.06	44
4-*o*-	−0.05	−0.03	48	−0.04	+0.02	47, 48
9-*o*-	—	—	—	−0.23	−0.02	47, 48
1-*m*-	0.33	0.25	42	0.194	−0.089	104
1-*m*-	—	—	—	0.21	−0.05	43
2-*m*-	0.15	0.14	45	0.12	0.05	45
4-*m*	0.02	−0.02	49, 50	−0.04	0.02	49, 50
1-*p*-	—	—	—	0.14	−0.02	105

* Determined from the reaction series for the ionisation of carbaboranylbenzoic acids in 75% ethanol.

** Determined from the ^{19}F chemical shifts in the NMR spectra of fluorophenylcarbaboranes in inert solvents by the Taft method using the equations $\delta_m^F = -7.10\sigma_I + 0.6$ and $\delta_p^F - \delta_m^F = -29.5\sigma_R^0$.

The electronic effects of the *B*-*o*-carbaboranyl groups, for which a change in the nature of the electronic influence from the electron-accepting 3-*o*-carbaboranyl group to the virtually electrically neutral 4-*o*-carbaboranyl group and then the highly electron-donating 9-*o*-carbaboranyl group has been observed, have been studied most fully.

The inductive constants have been calculated for the 3-*o*- and 2-*m*-carbaboranyl groups by Charton's method from the ionisation constants of carbaboranylacetic acids in 80% methylcellosolve. The values of σ_I obtained amount to 0.12 and 0.11 respectively[63].

Evidently the electronic effects of the carbaboranyl groups are to a large extent determined by the charges on the corresponding carbon and boron atoms. Despite the somewhat approximate nature of the quantum-chemical calculations on carbaboranes, which are complex multiatomic systems, the available data (see the relevant reviews[106,107]) for the partial charges on the boron and carbon atoms are consistent with the pK_a of hydroxy-, amino-, and carboxy-carbaboranes[11].

The introduction of substituents at the boron atoms in the carbaborane nuclei is reflected in the nature of the C–H bond. For example, the significant influence of the electronic effects of the substituents at the boron atoms on the integral intensity of the C–H stretching vibration band in the region of 3060 cm^{-1} [108] and on the equilibrium CH acidity of carbaboranes[109] has been demonstrated.

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A series of studies of interest for the problem under consideration have been published recently. The decarboxylation of oxomercury salts of 9-*o*- and 9-*m*-carbaboranecarboxylic acids under the influence of peroxide initiators or ultraviolet radiation leads to salts of 9-*o*- and 9-*m*-carbaboranylmercury[110]. The first examples of peroxides containing the B–C–O–O bond system have been synthesised from the chloride of 9-*m*-carbaboranecarboxylic acid and t-butyl hydroperoxide or hydroxymethyl t-butyl peroxide[111]. 9-Amino-*m*- and 2-amino-*p*-carbaboranes have been obtained and their pK_a determined[112]. The pK_a of 9-carboxy-*o*-, 9-carboxy-*m*-, and 2-carboxy-*p*-carbaboranes have been revised in the same study. Detailed data on the synthesis of 9-acetyl-*o*- and 9-acetyl-*m*-carbaboranes via the corresponding biscarbaboranylmercury derivatives have been published[113]. $LiAlH_4$ has been proposed as a convenient symmetrising agent for 9-chloromercuricarbaboranes[113]. The unusual chemical and thermal stabilities of borothallated carbaboranes compared with their aryl analogues have been noted[114]. A new method for the introduction of substituents at the boron atoms of carbaboranes has been proposed[115].

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