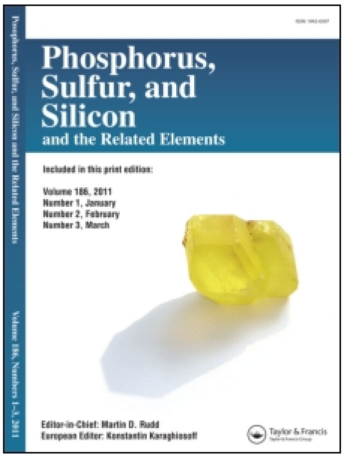

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A NEW SIMPLE METHOD FOR THE PRODUCTION AND SOME CONVERSIONS OF B-S BONDCONTAINING *o*- AND *m*-CARBORANYL

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A NEW SIMPLE METHOD FOR THE PRODUCTION AND SOME CONVERSIONS OF B—S BOND-CONTAINING *o*- AND *m*-CARBORANYL[a]

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A new method of synthesis of *o*- and *m*-carboranyl-B-thiols and *o*- and *m*-carboranyl-B,B′-dithiols via the electrophilic sulfuration of *o*-, *m*-carboranes with S_2Cl_2 in the presence of $AlCl_3$ is described. The reaction of *o*-carborane with excess S_2Cl_2 in the presence of $AlCl_3$ gives B,B′,B″,B‴-tetrathiol-*o*-carborane. Various chemical conversions of carborane sulfur derivatives are studied. A description is made of carboranyl derivatives of di-, tetra- and hexavalent sulfur, such as sulfenyl chlorides, thiocyanates, disulfides, alkyl- and aryl sulfides, aryl sulfones and aryl sulfoxides. 9-*m*-Carboranylsulfinic acid was found to readily disproportionate to thiosulfonate and sulfonic acid. The chemical behaviour of *o*- and *m*-carboranyl sulfur derivatives in which the sulfur atom is σ-bound to the six-coordinated boron atom was also found to be similar to that of organic sulfur derivatives.

INTRODUCTION

Earlier the B—S bond-containing *o*- and *m*-carboranylthiols and *o*- and *m*-carboranyldithiols have been obtained via the interaction of *o*- and *m*-carboranes with sulfur in the presence of $AlCl_3$.[1,2] This reaction is similar to that of benzene and sulfur under the effect of $AlCl_3$ to give thiophenol.[3] 9-*o*-Carboranylthiol[4] and 9-*m*-carboranylthiol[4,5] give a number of di-, tetra- and hexavalent sulfur derivatives, however only limited studies have been made of the properties of carboranylthiols in which the sulfur atom is bound to the six-coordinated boron atom. One reason for this fact consists in a fairly complicated technique usually employed to obtain carboranylthiols. This paper describes a novel and a simpler method for the production of *o*- and *m*-carboranylthiols and *o*- and *m*-carboranyldithiols.

DISCUSSION

It is known that the reaction of S_2Cl_2 with benzene in the presence of $AlCl_3$ constitutes a preparative method for the production of diphenyl sulfide[6] and belongs to the reactions of electrophilic substitution in the benzene ring. Sometimes *o*- and *m*-carboranes also enter into such reactions at the icosahedron boron atoms where the electronic density is the highest.[7,8] For *o*-carborane these will the 9, 12, 8 and 10

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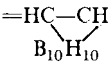
[a] *o*-Carborane = 1,2-dicarba-closo-dodecaborane (12), *o*-$H_2C_2B_{10}H_{10}$=

$HC—CH$ over $B_{10}H_{10}$

m-Carborane = 1,7-dicarba-closo-dodecaborane (12), *m*-$H_2C_2B_{10}H_{10}$=$HCB_{10}H_{10}CH$.

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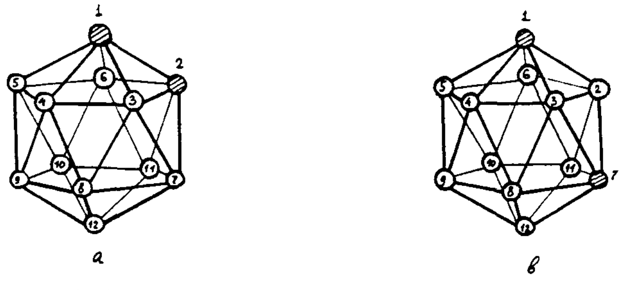
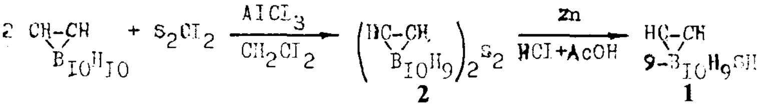


FIGURE 1 Positions of the boron atoms in the *o*- and *m*-carboranes: a—*o*-carborane = $\underset{B_{10}H_{10}}{HC\!-\!CH}$ = *o*-$H_2C_2B_{10}H_{10}$; b—*m*-carborane = $HCB_{10}H_{10}CH$ = *m*-$H_2C_2B_{10}H_{10}$. ▨—CH; ○—BH.

positions, and for *m*-carborane the 9 and 10 positions (Figure 1). Our studies of the interaction of S_2Cl_2 with *o*- and *m*-carboranes in the presence of $AlCl_3$ indicate occurrence of a ready electrophilic sulfuration to give bis(*o*- and *m*-carboranyl)disulfides, respectively. These compounds can be readily isolated or practically quantitatively reduced (without isolation) to *o*- and *m*-carboranylthiols with zinc dust in a mixture of hydrochloric and acetic acids or in a mixture of hydrochloric acid and ethanol:



$$2\,\underset{B_{10}H_{10}}{CH\!-\!CH} + S_2Cl_2 \xrightarrow[CH_2Cl_2]{AlCl_3} \underset{\mathbf{2}}{\Big(\underset{B_{10}H_9}{HC\!-\!CH}\Big)_2S_2} \xrightarrow[HCl+AcOH]{Zn} \underset{\mathbf{1}}{\underset{9\text{-}B_{10}H_9SH}{HC\!-\!CH}} \qquad (1)$$

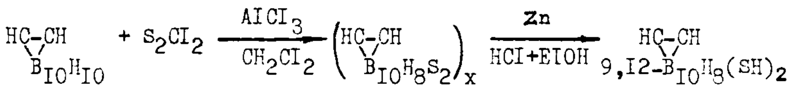
$$2\ m\text{-}H_2C_2B_{10}H_{10} + S_2Cl_2 \xrightarrow[CH_2Cl_2]{AlCl_3} \underset{\mathbf{4}}{(m\text{-}H_2C_2B_{10}H_9)_2S_2} \xrightarrow[HCl+AcOH]{Zn} \underset{\mathbf{3}}{m\text{-}H_2C_2B_{10}H_9(9\text{-}SH)} \qquad (2)$$

interaction of *o*- and *m*-carboranes with S_2Cl_2 in the presence of $AlCl_3$ belongs to the reactions of electrophilic substitution in a carborane cage and, like other electrophilic reactions in this series, occurs at the sites where the electron density is the highest, i.e., in the 9-*o*- and *m*-carborane positions. In the case of *o*-carborane, along with the 9-*o*-carboranylthiol, one can observe the formation of ca. 8% of the 8-*o*-carboranylthiol. Thus the reaction of S_2Cl_2 with *o*- and *m*-carboranes in the presence of $AlCl_3$ differs from that with benzene.

The interaction of *o*- and *m*-carboranes with SCl_2 in the presence of $AlCl_3$ in CH_2Cl_2 solution turned out to give also bis(*o*- and *m*-carboranyl)disulfides similar to those obtained in their reaction with S_2Cl_2. In this case, along with the disulfides, there will be formed the boron-chlorinated *o*- and *m*-carboranes. This seems to be due to the disproportionation of the intermediate carboranylsulfenyl chloride to the bis(carboranyl)disulfide and Cl_2 which, under the action of $AlCl_3$, partially chlorinates the carborane:

$$2\ o,m\text{-}H_2C_2B_{10}H_{10} + S\,Cl_2 \xrightarrow[CH_2Cl_2]{AlCl_3} (o,m\text{-}H_2C_2B_{10}H_9)_2S_2 + o,m\text{-}H_2C_2B_{10}H_9Cl \qquad (3)$$

As has been shown by us, such a reaction route is favoured by a ready disproportionation of the 9-*o*- and *m*-carboranylsulfenyl chlorides to the corresponding bis(carboranyl)disulfides and Cl_2. In the interaction of the *o*- and *m*-carboranes with S_2Cl_2 in the molar ratio 1 : 2 in the presence of $AlCl_3$ in CH_2Cl_2 solution two sulfur atoms are inserted into the carborane cage. After the reaction products had been reduced with sodium borohydride in alcohol or with zinc dust in a mixture of hydrochloric acid and alcohol, the 9,12-*o*- and 9,10-*m*-carboranyldithiols, respectively, were obtained:



(4)

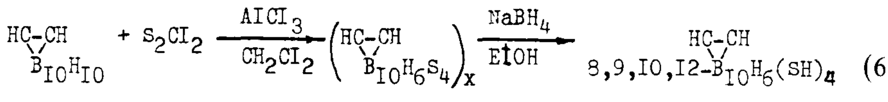
5

$$m\text{-}H_2C_2B_{10}H_{10} + S_2Cl_2 \xrightarrow[CH_2Cl_2]{AlCl_3} (m\text{-}H_2C_2B_{10}H_8S_2)_x \xrightarrow[EtOH]{NaBH_4} m\text{-}H_2C_2B_{10}H_8(9,10\text{-}SH)_2 \qquad (5)$$

6

In the case of the *m*-carborane, the reaction proceeds regiospecifically to give the 9,10-*m*-carboranyldithiol only whereas in the case of the *o*-carborane, along with the 9,12-*o*-carboranyldithiol, there appears a negligible amount (ca. 3%) of, seemingly, the 8,9-*o*-carboranyldithiol.

We have found out that as few as four thiol groups can be inserted into the *o*-carborane cage when using excess S_2Cl_2 in CH_2Cl_2:



(6)

7

The structure of the resulting *o*-carboranyltetrathiol, viz., its 8,9,10,12-variety, has been assumed by analogy with that of the products of the other electrophilic reactions of the *o*-carborane. In these reactions the first four substituents, as a rule, enter into the 8, 9, 10 and 12 positions of the carborane cage.[9] As distinct from the *o*-carborane, it has been impossible to insert more than two thiol groups into the *m*-carborane cage, which is in accord with the data on a significantly lower reactivity of the other positions of the *m*-carborane cage in reactions of electrophilic substitution as compared with the 9 and 10 positions.[9]

The structures of the resulting mono- and dithiols have been confirmed by their ^1H- and ^{11}B NMR spectra (Table I). The ^1H NMR spectra of the monothiols **1** and **3** and dithiols **5** and **6** exhibit a splitting of the SH signal to a quartet with $^2J_{B-H}$ ca. 4 Hz due to the interaction of the protons with the boron atoms of the carborane cage. With a larger number of the thiol groups inserted into the carborane cage, the signals of the substituent-bound boron atoms will be found in the downfield region both for the *o*- and *m*-carborane.

The action of CH_3I on an alcohol solution of $9,12\text{-}(SH)_2\text{-}1,2\text{-}C_2H_{10}B_{10}$ or $9,10\text{-}(SH)_2\text{-}1,7\text{-}C_2H_{10}B_{10}$ and sodium hydroxide gave the $9,12\text{-}(CH_3S)_2\text{-}1,2\text{-}$

TABLE I

^{1}H and ^{11}B NMR spectra for some compounds

Compound	^{1}H NMR, δ, ppm[a]				^{11}B NMR[b]	
	Solvent	S—H	C—H, carborane	C—H, remaining	Solvent	$\frac{\delta\text{, ppm}(J_{B-H}\text{, Hz})}{\text{position}}$
1	CCl_4	0.064	3.43 3.26	—	CCl_4	$\frac{-4.3(0)}{9}$; $\frac{-1.9(151)}{12}$; $-\frac{-8.8(151)}{8,10}$; $\frac{-13.5(151), -14.6(166)}{4,5,7,11}$; $\frac{-15.7(161)}{3,6}$
3	CH_2Cl_2	0.086	2.81	—	CCl_4	$\frac{-2.7(0)}{9}$; $\frac{-6.3(176)}{5,12}$; $\frac{-9.4(180)}{10}$; $\frac{-12.9(166), -14.2(166)}{4,6,8,11}$; $\frac{-17.8(186)}{3}$; $\frac{-21.1(186)}{2}$
5	CD_3COCD_3	0.58	3.56	—	CH_2Cl_2	$\frac{4.8(0)}{9,12}$; $\frac{-7(155)}{8,10}$; $\frac{-14.2(161)}{4,5,7,11}$; $\frac{-16.7(170)}{3,6}$
6	CD_3COCD_3	0.66	3.08	—	CH_2Cl_2	$\frac{-1.5(0)}{9,10}$; $\frac{-5.1(161)}{5,12}$; $\frac{-13.5(168)}{4,6,8,11}$; $\frac{-21.5(183)}{2,3}$
7	—	—	—		CCl_4	$\frac{6.8(0)}{9,12}$; $\frac{-0.6(0)}{8,10}$
8	CCl_4	—	3.49		CH_2Cl_2	$\frac{7.5(0)}{9,12}$; $\frac{-9.4(152)}{8,10}$; $\frac{-14.9(164)}{4,5,7,11}$; $\frac{-17.1(155)}{3,6}$
9	CCl_4	—	2.69		CCl_4	$\frac{0.97(0)}{9,10}$; $\frac{-7.8(161)}{5.12}$; $\frac{-14.0(170)}{4.6,8,11}$; $\frac{-21.4(182)}{2,3}$
10	CD_3COCD_3	—	4.78	$\left.\begin{array}{l}7.71\\7.41\end{array}\right\}C_6H_5$ 6.23 H	CD_3COCD_3	$\frac{10.4(0)}{9,12}$; $\frac{-0.08(156)}{8}$; $\frac{-6.9(156)}{10}$; $\frac{-13.95(156), -16.2(154)}{3,6;\ 4,5,7,11}$
11	CD_3COCD_3	—	4.19 4.24	$\left.\begin{array}{l}7.75\\7.45\end{array}\right\}C_6H_5$ 6.47 H	CD_3COCD_3	$\frac{5.2(0)}{9,10}$; $\frac{0.8(178)}{5}$; $\frac{-4.8(166)}{12}$; $\frac{-13.7(154), -15.7(149)}{4,6,8,11}$; $\frac{-19.8(185)}{2,3}$

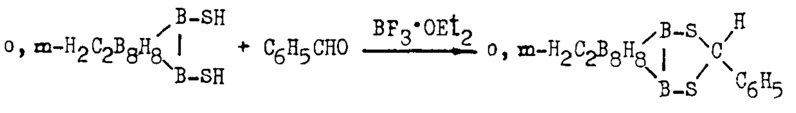
[a] Relative to tetramethylsilane.
[b] Relative to $BF_3.OEt_2$.

$C_2H_{10}B_{10}$ **8** and 9,10-$(CH_3S)_2$-1,7-$C_2H_{10}B_{10}$ **9**:

$$o,m\text{-}H_2C_2B_{10}H_8(SH)_2 \xrightarrow[2.\,CH_3I]{1.\,NaOH} o,m\text{-}H_2C_2B_{10}H_8(SCH_3) \qquad (7)$$

8,9

The ^1H NMR spectrum of 9 shows a splitting of the methyl group signal to a quartet with $^3J_{B-H}$ ca. 2 Hz. The adjacent position of two SH groups in the 9,12-*o*- and 9,10-*m*-carboranyldithiols is suggested by the fact that they give the corresponding 9,12-*o*- and 9,10-*m*-carboranylmercaptal, **10** and **11**, respectively, from benzaldehyde in the presence of $BF_3.\ OEt_2$:



(8)

10,11

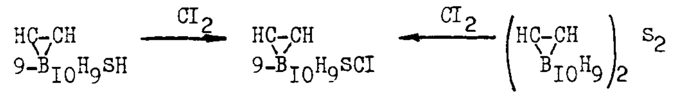
We have also studied the ^{11}B and ^1H NMR spectra of **10** and **11**. Analysis of the ^{11}B NMR spectrum indicates that in the formation of **11** the boron atoms in the 9 and 10 positions remain equivalent although their signals are shifted downfield by ca. 6.7 ppm. As compared with the unsubstituted dithiol **6**, the boron atoms show a significant nonequivalence for B5 and B12 and a somewhat lower one for B4, B6, B8 and B12. We attribute this to the fact that in the presence of various substituents at the five-membered cycle carbon two parts of the carborane icosahedron become magnetically nonequivalent with respect to one another, i.e., relative to the plane of symmetry through this carbon atom and the centre of the B9–B10 bond normal to the latter. In the ^1H NMR spectrum of **11** one can also observe two signals from the CH group of the carborane cage, which suggests proton nonequivalence at the carbon atom.

Similarly, when compound **10** is formed, its ^{11}B NMR spectrum indicates that the magnetic equivalence of B9 and B12, i.e., those atoms that contain substituents, remains intact, although their signal is shifted downfield by 5.6 ppm. Due to the differing magnetic environments, B8 and B10 will show the largest nonequivalence whereas the one for the more remoted B4, B5, B7 and B11 will be much lower. The ^1H NMR spectrum of 10 exhibits a signal from the CH group of the carborane cage. It follows from this fact that in the *o*-carboranylmercaptal the protons at the icosahedron carbons are completely equivalent.

Our method for the production of *o*- and *m*-carboranylthiols and -dithiols has a number of advantages over the known technique[1,2] in that the reaction can be carried out under milder conditions and proceed smoothly.

In this work conversions of the 9-*m*-carboranylthiol **3** were primarily studied since it is formed without any isomer impurities thereby eliminating a need for a laborious separation of the isomers as in the case of the 9- and 8-*o*-carboranylthiols. In addition, the 9-*o*- and 9-*m*-carboranylthiols are expected to have similar properties as the 9-*o*- and *m*-carboranyl groups possess identical electron-donor effects ($\sigma_i = -0.16$ and -0.12, respectively).[10]

The action of Cl_2 on the 9-*o*- and *m*-carboranylthiols **1** and **3** or disulfides **2** and **4** produces the 9-*o*- and *m*-carboranylsulfenyl chlorides, respectively:

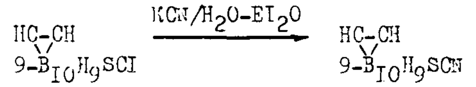


1 **12** **2** (9)

$$m\text{-}H_2C_2B_{10}H_9(9\text{-}SH) \xrightarrow{Cl_2} m\text{-}H_2C_2B_{10}H_9(9\text{-}SCl) \xleftarrow{Cl_2} (m\text{-}H_2C_2B_{10}H_9)_2S_2 \qquad (10)$$

3 **13** **4**

When stored at 20°C or chromatographed on a silica gel column, both the *o*- and *m*-carboranylsulfenyl chlorides undergo ready disproportionation to give the corresponding disulfides with chlorine evolution. Like organic sulfenyl chlorides, **12** and **13** are very reactive compounds. The chlorine atom in these compounds can be readily substituted by the CN group when treated with $(CH_3)_3SiCN$ in CH_2Cl_2 solution or with KCN in aqueous ether solution to give the 9-*o*- and *m*-carboranylthiocyanates:



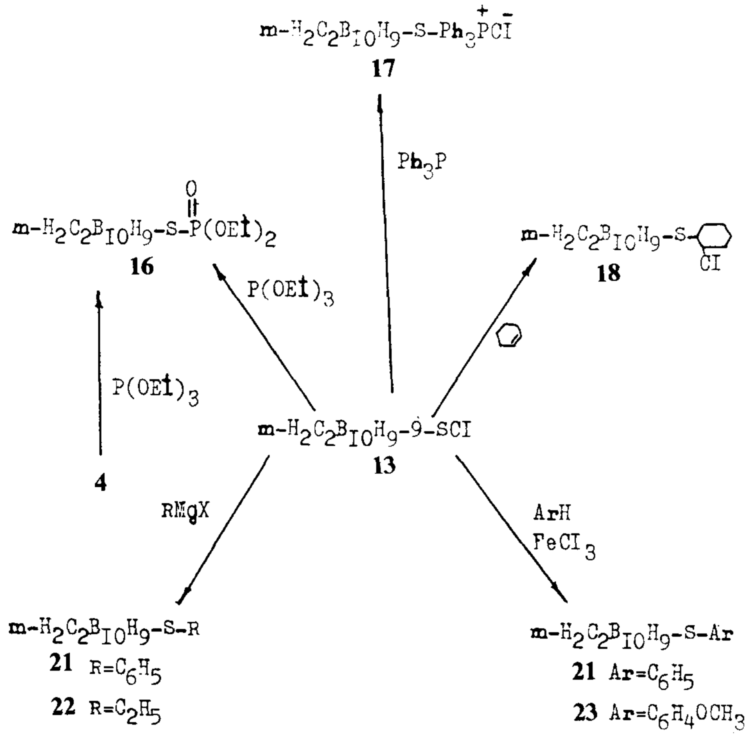
12 **14** (11)

$$m\text{-}H_2C_2B_{10}H_9(9\text{-}SCl) \xrightarrow[\text{or } (CH_3)_3SiCN/CH_2Cl_2]{KCN/H_2O\text{-}Et_2O} m\text{-}H_2C_2B_{10}H_9(9\text{-}SCN) \qquad (12)$$

13 **15**

Compounds **14** and **15** are thermally stable. As opposed to the alkylthiocyanates, they do not isomerize into carboranylisothiocyanates when heated at 190°C or in the presence of $ZnCl_2$ and are isolated in unaltered form. Various conversions of the 9-*m*-carboranylsulfenyl chlorides are illustrated in Scheme 1. Compound **13** interacts with triethyl phosphite with a normal Arbuzov rearrangement to give the (9-*m*-carboranyl)thiodiethyl phosphate **16** which also results from the reaction of **4** with triethyl phosphite. As opposed to the known alkyl- and arylthiophosphonium salts, the S—B bond of the carboranylthiophosphonium salt **17** formed by the action of Ph_3P on **13** does not suffer cleavage when heated in vacuo at 190°C. Instead of the 9-chloro-*m*-carborane which is expected to result from the cleavage of the S—B bond one can observe the formation of the 9-*m*-carboranylthiol in 92% yield. This suggests cleavage of the bond in the thermolysis of **17**. The formation mechansim of thiol in this reaction is not yet understood.

Addition of **13** to unsubstituted compounds, as exemplified by cyclohexene, occurs in the usual manner to give the 1-chlorocyclohexyl(9-*m*-carboranyl)sulfide **18**. It is known that alkyl- and arylsulfides are readily obtained by the Friedel–Krafts reaction or in the interaction of a Grignard with sulfenyl chlorides. The behaviour of

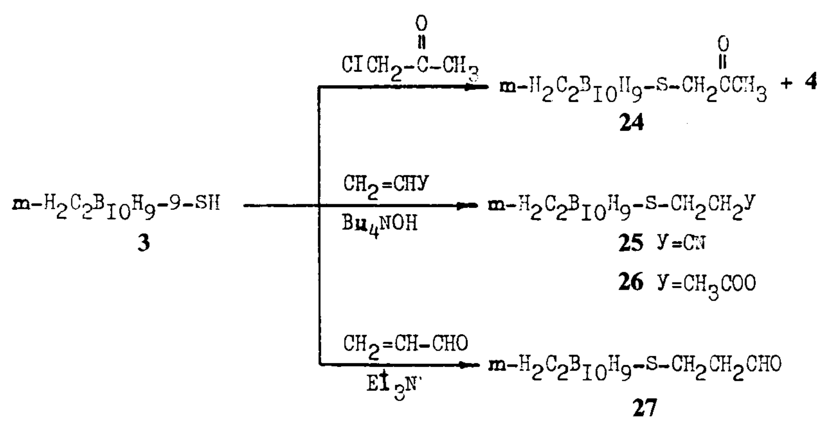


SCHEME 1 Chemical conversions of the 9-*m*-carboranyl sulfenyl chloride.

13 in such a reaction is similar to that of aromatic RSCl to give aryl carboranyl sulfides. The interaction of **13** with a Grignard reagent occurs somewhat differently as compared with that in the case of aromatic sulfenyl chlorides. Along with the normal occurrence of the reaction and formation of the alkyl- or aryl carboranyl sulfide, there is a substitution of MgX by a chlorine atom and formation of as much as 30% of the magnesium mercaptide **19** whose hydrolysis gives **3**. To reveal the presence of **19** in the reaction mixture, the latter was treated with CH_3I. In this case the methyl(9-*m*-carboranyl)sulfide **20** was formed as follows:

$$\underset{\mathbf{19}}{m\text{-}H_2C_2B_{10}H_9\text{-}9\text{-}SMgX} + CH_3I \longrightarrow \underset{\mathbf{20}}{m\text{-}H_2C_2B_{10}H_9\text{-}9\text{-}SCH_3} + MgXI \qquad (13)$$

Compound **3** in CH_3COOH solution in the presence of HCl reacts with chloroacetone to give a mixture of the 1-(*m*-carboranyl)propanone-2 **24** and disulfide **4**. However, the reaction is much more retarded than in the case of $C_2H_5\text{-}SH$[11] (Scheme 2). Like organic thiols, compound **3** can be readily attached to the activated double olefinic bond in the presence of basic catalysts. The interaction of **3** with acrylonitrile and methyl acrylate was performed in the presence of Bu_4NOH to give the (9-*m*-carboranyl)thiopropionitrile **25** and (9-carboranyl)thiomethyl propionate **26**, respectively.

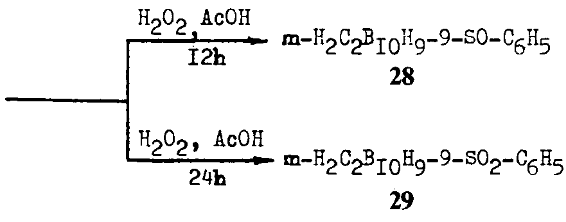


SCHEME 2 Chemical conversions of the 9-*m*-carboranylthiol.

To obtain the 9-*m*-carboranylthiopropanal **27**, we have made a study of how **3** is attached to acrolein in the presence of such catalysts as Bu_4NOH, Et_3N and $Cu(OAc)_2.2H_2O$. The best results have been obtained by use of Et_3N.

It has been shown earlier[4,5] that alkyl carboranyl sulfides are readily oxidized to sulfoxides or sulfones. The present authors have oxidized the phenyl(9-*m*-carboranyl)sulfide **21** with H_2O_2 in CH_3COOH to find that after 12 h this process gives the phenyl(9-*m*-carboranyl)sulfoxide **28** and after 24 h phenyl(9-*m*-carboranyl)sulfone **29** as follows:

21

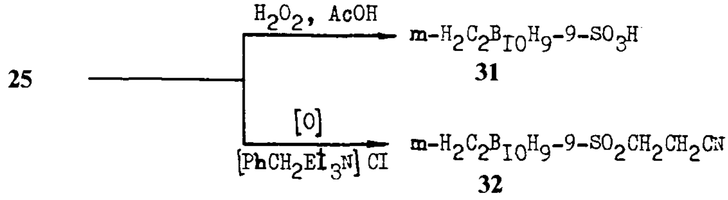


(14)

However, compound **29** has been found to be obtained more conveniently by reaction of the 9-*m*-carboranyl sulfonyl chloride **30** with benzene in the presence of $AlCl_3$ as follows:

$$\underset{\mathbf{30}}{m\text{-}H_2C_2B_{10}H_9\text{-}9\text{-}SO_2Cl} + C_6H_6 \xrightarrow{AlCl_3} \underset{\mathbf{29}}{m\text{-}H_2C_2B_{10}H_9\text{-}SO_2\text{-}C_6H_5} \qquad (15)$$

As distinct from the alkyl carboranyl sulfides and **21**, oxidation of **25** with H_2O_2 in CH_3COOH solution is accompanied by cleavage of the C—S bond and formation of the 9-*m*-carboranylsulfonic acid **31**. It has been possible to obtain the (9-*m*-carboranylsulfonyl)propionitrile **32** by oxidation of $KMnO_4$ or $K_2Cr_2O_7$ in the case of interphase catalysis in the presence of $PhCH_2Et_3N^+Cl^-$ as follows:



$$25 \xrightarrow{H_2O_2,\ AcOH} \underset{31}{m\text{-}H_2C_2B_{10}H_9\text{-}9\text{-}SO_3H}$$
$$25 \xrightarrow[\text{[PhCH}_2\text{Et}_3\text{N] Cl}]{[O]} \underset{32}{m\text{-}H_2C_2B_{10}H_9\text{-}9\text{-}SO_2CH_2CH_2CN} \qquad (16)$$

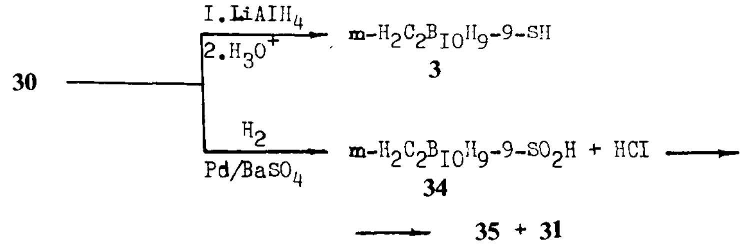
Compound **32** was used as the starting species[12] to obtain a Na salt of the 9-*m*-carboranylsulfinic acid **33**:

$$32 + m\text{-}H_2C_2B_{10}H_9\text{-}9\text{-}SNa \xrightarrow{EtOH} \underset{33}{m\text{-}H_2C_2B_{10}H_9\text{-}SO_2Na} + 25 \qquad (17)$$

Careful acidification of an aqueous solution of **33** gave the 9-*m*-carboranylsulfinic acid **34** whose isolation in the individual state turned out to be impossible due to the fact that it quickly disproportionated to the 9-*m*-carboranylthiosulfonate **35** and 9-*m*-carboranylsulfonic acid **31**:

$$33 \xrightarrow{H_3O^+} \underset{34}{m\text{-}H_2C_2B_{10}H_9\text{-}9\text{-}SO_2H} \longrightarrow$$
$$\longrightarrow \underset{35}{m\text{-}H_2C_2B_{10}H_9\text{-}9\text{-}SO_2S\text{-}H_9B_{10}C_2H_2} + \underset{31}{m\text{-}H_2C_2B_{10}H_9\text{-}9\text{-}SO_3H} \qquad (18)$$

We have also attempted to obtain **34** by some other methods. It has been impossible to stop the reduction of **30** with $LiAlH_4$ at the stage of sulfinic acid by the method described elsewhere[13] as this process readily occurs to **3**. In the catalytic hydrogenation of **30** on $Pd/BaSO_4$ in acetone solution the resulting sulfinic acid readily disproportionated to **35** and **31**:



$$30 \xrightarrow[2.\,H_3O^+]{1.\,LiAlH_4} \underset{3}{m\text{-}H_2C_2B_{10}H_9\text{-}9\text{-}SH}$$
$$30 \xrightarrow[Pd/BaSO_4]{H_2} \underset{34}{m\text{-}H_2C_2B_{10}H_9\text{-}9\text{-}SO_2H} + HCl \longrightarrow 35 + 31 \qquad (19)$$

Chlorination of **4** in the presence of acetic anhydride by the method described elsewhere[14] gave again, instead of **34**, a mixture of **35** and **31**. The ease with which **34** disproportionates to **35** and **31** makes it strongly different from the 1-*m*-carboranylsulfinic acid that is stable in the crystalline state and in solutions at 20°C whereas at 50°C in solution it decomposes to *m*-carborane and SO_2.[15] In other words, **34** behaves more like the aliphatic sulfinic acids than the 1-*m*-carboranylsulfinic acid.

Our data indicate that the chemical behaviour of the carboranyl sulfur derivatives in which the sulfur atom is attached to the six-coordinated boron atom by the σ-bond is very much the same as that of the ordinary sulfur derivatives. However, the B—S bond appears to be stronger than the C—S bond.

EXPERIMENTAL

Prior to use all the solvents and reagents were dried and distilled. Experiments with **12** and **13** were made under an inert atmosphere. Compound **20** was obtained by the method described elsewhere.[4] The reaction was monitored by TLC on Silufol plates and by GLC (a Tsvet chromatograph, a column 2 m × 3 mm, 5% SKTFT on celite 545, carrier gas—helium, temperature 180–220°C). IR spectra were measured on a UR spectrometer in pellets with KBr.^1H and ^{11}B NMR spectra were obtained on a Bruker WP-200 SY spectrometer. Mass spectra were taken on an MS-30 AEI spectrometer. Column chromatography was carried out by use of silica gel L 100/160.

General method for the production of bis-carboranyl disulfides from o- and m-carboranes and S_2Cl_2. To 0.01 mole of carborane and 0.01 mole of anhydrous $AlCl_3$ in 30 ml of CH_2Cl_2 was added dropwise with stirring and cooling to −10°C a solution of 0.005 mole of S_2Cl_2 in 5 ml of CH_2Cl_2. The reaction mixture was refluxed for 3–4 h until disappearance of the starting carborane (GLC and TLC monitoring), cooled and poured into water. The organic layer was separated, washed with water and dried over $MgSO_4$. After removal of the solvent, the residue was chromatographed on a silica gel column (eluent—hexane–$CHCl_3$, 1 : 1) and recrystallized. The following products were obtained: bis(9-*o*-carboranyl)disulfide **2**, yield 83%, m.p. 332–333°C (heptane–toluene) and bis(9-*m*-carboranyl)disulfide **4**, yield 74%, m.p. 312–314°C (heptane–toluene).

General method of reacting o- and m-carboranes with SCl_2. To 0.01 mole of carborane and 0.01 mole of anhydrous $AlCl_3$ in 30 ml of CH_2Cl_2 was added dropwise with stirring and cooling to −10°C 0.01 mole of SCl_2 in CH_2Cl_2. The reaction mixture was refluxed for 4 h. After cooling it was poured into water. The organic layer was separated, washed with water and dried over $CaCl_2$. After the solvent had been distilled off, the residue was treated with hexane. The precipitate obtained was crystallized from a heptane–toluene mixture. In the hexane layer GLC showed the presence of 9-chloro-*o*- or *m*-carborane. Yield of **2**: 64%, yield of **4**: 51%.

Reduction of bis-carboranyl disulfides to carboranylthiols with Zn and HCl. To 0.01 mole of the disulfide in a mixture of CH_3COOH and HCl (1 : 1) was carefully added excess Zn powder. The mixture was refluxed for 0.5–2 h. The reaction mixture was poured into water and extracted with ether. The ether layer was washed with water and the thiol was extracted with 10% KOH. The alkaline solution was acidified with HCl and treated with ether. After removal of the solvent the product was crystallized from hexane. The following products were obtained: 9-*o*-carboranylthiol **1**, yield 80%, m.p. 201–202°C and 9-*m*-carboranylthiol **3**, yield 74%, m.p. 253–254°C.

9,12-Bis(Mercapto)-o-carborane **5**. To a solution of 2.8 g (19.4 mmole) of *o*-carborane in 25 ml of CH_2Cl_2 at −50°C was added 7.8 g (58.6 mmole) of $AlCl_3$. To the suspension obtained was added with stirring 5.3 g (38.9 mmole) of S_2Cl_2 in 5 ml of CH_2Cl_2 at −15°C. Then the reaction mixture was heated on boiling for 6 h. After cooling, the mixture in the form of a viscous liquid was poured into water. The resulting precipitate was filtered off, washed with water and dried over P_2O_5. This gave 4.4 g of the dry product (A), and another 0.7 g of the same product was isolated from the mother solution.

(a) To a suspension of 5.1 g of (A) in 150 ml of 2% NaOH alcohol solution was gradually added 4 g of $NaBH_4$. The reaction mixture was stirred at 20°C for 7 h until disappearance of (A), as monitored by TLC, and poured into water. The filtered solution was saturated with CO_2. The precipitate was extracted with ether. The organic layer was separated, washed with water and dried over $MgSO_4$. Removal of the solvent and crystallization of the residue gave the title compound. Yield: 3.0 g (74%), m.p. 235–236°C (cyclohexane). As shown by TLC, the resulting product contained ca. 3% of bis(mercapto)-*o*-carborane. Anal. Calcd for $C_2H_{12}B_{10}S_2$: C, 11.52; H, 5.80; B, 51.85; S, 30.77. Found: C, 11. 96; H, 5.81; B, 51.39; S, 30.88.

(b) To a suspension of 2.6 g of (A) in 100 ml of an EtOH-HCl mixture (10 : 1) was carefully added excess Zn dust. The reaction mixture was refluxed for 6 h and poured into water. The product obtained was extracted with ether. The organic layer was separated and washed with water. The resulting dithiol was purified with a potassium salt in the usual manner. Removal of the solvent and crystallization of the residue gave the title compound. Yield: 1.3 g, m.p. 235–236°C. As shown by TLC, it contained ca. 3% of 8,9-bis(mercapto)-*o*-carborane.

9,10-Bis(mercapto)-m-carborane **6**. To a solution of 2.2 g (15.3 mmole) of *m*-carborane in 25 ml of CH_2Cl_2 at -50°C was added 7.4 g (57.9 nmmole) of $AlCl_3$. To the mixture obtained was added dropwise at -15°C 4.12 g (30.5 mmole) of S_2Cl_2 in 5 ml of CH_2Cl_2. After completion of the dropwise addition the temperature of the reaction mixture was gradually raised and it was refluxed for 10 h until disappearance of the starting *m*-carborane, as monitored by TLC. Then the mixture was poured into water. The product was extracted with ether. The organic layer was separated, washed with water and dried over $MgSO_4$. To a suspension of the product obtained after removal of the solvent, in 100 ml of 2% NaOH alcohol solution, was gradually added with stirring 2.5 g of $NaBH_4$. The suspension was stirred at room temperature for 4 h and then poured into water. The aqueous solution was saturated with CO_2. The precipitate was extracted with ether. After evaporation in vacuo the organic layer showed the presence of 2.9 g of a product composed (as indicated by TLC) of a mixture of 22% of **3** and 78% of **6**. The mixture was chromatographed on a silica gel column (eluent—hexane–methylene chloride, 4 : 1) to give the title compound. Yield: 1.8 g (56%), m.p. 193–194°C. Anal. Calcd for $C_2H_{12}B_{10}S_2$: S, 30.77. Found: S, 30.88.

8,9,10,12-Tetra(mercapto)-o-carborane **7**. To a solution of 2.8 g (19.4 mmole) of *o*-carborane in 30 ml of CH_2Cl_2 at -50°C was added 7.8 g (58.6 mmole) of $AlCl_3$ and then at -15°C was added dropwise 7.8 g (77.8 mmole) of S_2Cl_2 in 10 ml of CH_2Cl_2. The reaction mixture was refluxed for 6 h and poured into water. The resulting precipitate was filtered off, washed with water and dried over P_2O_5. The yield of the precipitate was 7.7 g. Then 4 g of the precipitate was reduced in 100 ml of 2% alcohol NaOH with 2 g of $NaBH_4$. After the usual treatment the mercaptane obtained was purified by sublimation (220°C, 1 mm Hg) and then chromatographed on a silica gel column (eluent—benzene).Yield: 0.7 g, m.p. 349–350°C; m/e 272 (M). Anal. Calcd for $C_2H_{12}B_{10}S_4$: S, 47.05. Found: S, 46.34.

9,12-Bis(methylthio)-o-carborane **8**. To 0.4 g of **5** in 10 ml of abs. alcohol was added 0.088 g of Na and 0.54 g of CH_3I. After the reaction mixture had been refluxed for 4 h, it was evaporated to dryness and added with benzene. The precipitated NaI was filtered off. The benzene mother solution was washed with 10% KOH and water and dried over $MgSO_4$. Yield: 0.4 g (89%), m.p. 110–111°C (hexane–toluene). Anal. Calcd for $C_4H_{16}B_{10}S_2$: C, 20.31; H, 6.82; S, 27.11. Found: C, 20.67; H, 6.74; S, 26.80.

9,10-Bis(methylthio)-m-carborane **9**. The title compound was obtained from 0.3 g of **6** and 0.07 g of Na in 10 ml of abs. alcohol and 0.41 g of CH_3I after crystallization from hexane by the method described above for **8**. Yield: 0.3 g (90%), m.p. 121–122°C. Anal. Calcd for $C_4H_{16}B_{10}S_2$: C, 20.31; H, 6.82; S, 27.11. Found: C, 20.76; H, 6.73; S, 26.98.

4-Phenyl-1,2-(o-9′,12′-carboranyl)-3,5-dithiapentane **10**. To a solution of 0.3 g of 5 in 10 ml of dry ether was added at 5°C with stirring 0.2 ml of $BF_3.OEt_2$ and 0.15 ml of C_6H_5CHO. Precipitation was observed to take place immediately. After 4 h of stirring at room temperature the precipitate was filtered off, washed with water and dried in vacuo over P_2O_5. Yield: 0.3 g (75%), m.p. 275–276°C (benzene-THF, decomp.). Anal. Calcd. for $C_9H_{16}B_{10}S_2$: C, 36.64; H, 5.52; S, 21.55. Found: C, 37.04; H, 5.40; S, 21.08.

4-Phenyl-1,2-(m-9′,10′-carboranyl)-3,5-dithiapentane **11**. A method similar to that described above for **10** was used to obtain the title compound from 0.2 g of **6** in 10 ml of dry ether, 0.1 g of $BF_3.OEt_2$ and 0.1 ml of C_6H_5CHO. Yield: 0.2 g (69%), m.p. 272–273°C (benzene). Anal. Calcd for $C_9H_{16}B_{10}S_2$: C, 36.64; H, 5.42; S, 21.56. Found: C, 36.32; H, 5.36; S, 21.70.

9-m-Carboranyl sulfenylchloride **13**. Through a solution of 0.5 g of **3** or **4** in 30 ml of dry CH_2Cl_2 was passed an equimolar amount of Cl_2 at -35°C. The reaction mixture was stirred at -15°C for 2 h. The solvent was evaporated in vacuo. The title compound was obtained in the form of an orange oil and was observed to solidify on cooling. Yield: 0.6 g. Anal. Calcd for $C_2H_{11}B_{10}ClS$: C, 11.41; H, 5.27; S, 15.24. Found: C, 11.94; H, 5.14; S, 15.75.

9-m-Carboranylthiocyanate **15**

(a) To a solution of 1.9 g of **13** in 20 ml of ether was added dropwise a solution of 0.59 g of KCN in 3 ml of water. After 0.5 h the organic layer was separated, washed with water and dried over $MgSO_4$. After removal of the solvent the title compound was purified chromatographically on a silica gel column (eluent —benzene-hexane, 3 : 2). Yield: 1.7 g (86%), m.p. 59–59.5°C (heptane). IR spectrum: 2155 cm^{-1} (SCN).

Anal. Calcd for $C_3H_{11}B_{10}NS$: C, 17.89; H, 5.51; B, 53.72; N, 6.96; S, 15.92. Found: C, 18.04; H, 5.80; B, 53.69; N, 6.51; S, 15.94.

(b) To a solution of 1.6 g of **13** in 20 ml of CH_2Cl_2 was added dropwise 1.4 g of $(CH_3)_3SiCN$[16] in 5 ml of CH_2Cl_2 at 20°C. After 4 h of stirring the reaction mixture, the solvent was removed and the title compound was obtained from the residue as described above under (a). Yield: 1.3 g (85%), m.p. 59–59.5°C.

9-o-Carboranylthiocyanate **14**. Through a solution of 1.0 g of **1** or **2** in 15 ml of dry CH_2Cl_2 was passed an equimolar amount of Cl_2 at -35°C. The reaction mixture was stirred at -15°C for 1 h and the solvent was removed in vacuo. The resulting crystalline **12** of the yellow colour was dissolved in 10 ml of abs. ether and to the solution was added dropwise at 20°C 0.38 g of KCN in 2 ml of water. After 30 min of stirring, the organic layer was separated, washed with water and dried over $MgSO_4$. After removal of the solvent the residue was crystallized from hexane and chromatographed on a silica gel column (eluent—benzene). Yield: 0.74 g (65%), m.p. 81–81.5°C. IR spectrum: ν 2145 cm^{-1} (SCN). Anal. Calcd for $C_3H_{11}B_{10}SN$: C, 17.89; H, 5.51; S, 15.92. Found: C, 17.96; H, 5.67; S, 15.84.

(9-m-Carboranylthio)diethyl phosphate **16**

(a) To a solution of 2.0 g of **13** in 20 ml of toluene was added dropwise 3.0 g of $P(OEt)_3)$ in 5 ml of toluene. The mixture was observed to be significantly heated up. After 10 h of stirring at 20°C the solvent and the excess $P(OEt)_3$ were distilled off in vacuo. The residue was ground in hexane and purified chromatographically on a silica gel column (eluent—chloroform). Yield: 2.3 g (80%), m.p. 69–70°C (hexane–toluene). Anal. Calcd for $C_6H_{21}B_{10}O_3PS$: C, 23.06; H, 6.77; P, 9.91. Found: C, 23.06; H, 6.80; P, 9.91.

(b) A solution of 2.0 g of **4** and 2.4 g of $P(OEt)_3$ in 20 ml of toluene was stirred on boiling for 18 h. The excess $P(OEt)_3$ and the solvent were removed in vacuo. Crystallization of the mixture from hexane gave compounds **22** and **16**. Yields: 1.2 g and 1.2 g (71%), respectively, m.p. 61–62°C and 69–70°C, respectively.

Interaction of **13** *with* Ph_3P. To a solution of 1.2 g of **13** in toluene at 20°C was added dropwise 1.49 g of Ph_3P in 10 ml of toluene. Precipitation began immediately and the solution turned decolourized. The precipitate was filtered off under an argon atmosphere and washed several times on the filter with abs. ether. The residue was dried in vacuo to give **17**. Yield: 3.1 g (94%), m.p. 208–210°C (decomp.). Anal. Calcd for $C_{20}H_{26}B_{10}ClPS$: Cl, 7.49; P, 6.55; S, 6.78. Found: Cl, 7.05; P, 6.33; S, 6.94.

Then 1.0 g of **17** was heated at 190°C (1 mm Hg) with sublimation of the reaction products. After 4 h compound **3** was obtained. Yield: 0.34 g (92%).

1-Chlorocyclohexyl(9-m-carboranyl)sulfide **18**. To a solution of 0.3 g of cyclohexene in 10 ml of CH_2Cl_2 at -35°C was added a solution of 0.6 g of **13** in 5 ml of CH_2Cl_2. The reaction mixture was stored at -35°C for 0.5 h and at 25°C for another 2 h. After removal of the solvent the residue was crystallized from hexane. Yield: 0.6 g (75%), m.p. 77–78°C. Anal. Calcd for $C_8H_{15}B_{10}ClS$: C, 33.50; H, 5.23; B, 37.73; Cl, 12.38; S, 11.16. Found: C, 33.53; H, 7.17; B, 37.26; Cl, 12.41; S, 11.08.

Phenyl(9-m-carboranyl)sulfide **21**

(a) To 10 ml of benzene and 0.3 g of $FeCl_3$ was added 2.5 g of **13**. The reaction mixture was refluxed for 10 h. After cooling the mixture, to it were added water and ether. The organic layer was separated, washed with water and dired over $MgSO_4$. After removal of the solvent the residue was chromatographed on a silica gel column (eluent—hexane). Yield: 1.0 g (48%), m.p. 82°C (hexane). Anal. Calcd for $C_2H_{16}B_{10}S$: C, 38.05; H, 6.39; S, 12.70. Found: C, 38.09; H, 6.44; S, 12.69.

(b) To an ether solution of PhMgBr (4.95 g of PhBr and 0.9 g of Mg) at 15°C was added an ether solution of 4.4 g of **13**. The reaction mixture was exothermic. The mixture was refluxed for 2 h and decomposed with diluted HCl. The ether layer was separated and washed with alkaline solution to remove **3** and then washed with water and dried over $MgSO_4$. The solvent was distilled off and the residue was chromatographed on a silica gel column (eluent—hexane). Yield: 3.5 g (66%). Then 0.5 g of **3** was isolated from the alkaline solution.

Ethyl(9-m-carboranyl)sulfide **22**

(a) The title compound was obtained from 1.0 g of **3** and 0.17 g of Na in 10 ml of abs. alcohol.[4] Yield: 0.93 g (80%), m.p. 61.5–62°C (hexane). Anal. Calcd for $C_4H_{16}B_{10}S$: C, 23.50; H, 7.88; S, 15.69. Found: C, 23.54; H, 7.87; S, 15.74.

(b) To EtMgI solution (1.5 g of EtI and 0.3 g of Mg) was added with stirring an ether solution of 1.5 g of **13** at 10°C. The reaction mixture was refluxed for 1.5 h. GLC showed the ratio **3** : **22** = 45 : 55%. The mixture was treated with CO_2 to remove the excess EtMgI, to it was added 0.57 g of CH_3I and then it was refluxed, the sampling being done every 0.5 h. After 1 h the mixture contained 27.6% of **3**, 55% of **22** and 17.4% of **20**.

n-Anisyl(9-m-carboranyl)sulfide **23**. The title compound was obtained from 2.4 g of **13** in 15 ml of anisole and 0.3 g of $FeCl_3$ by the method similar to that described above for **21** under (a) by chromatography of a silica gel column (eluent—hexane). Yield: 2.0 g (65.6%), m.p. 71–72°C (hexane). Anal. Calcd for $C_9H_{18}B_{10}OS$: C, 38.26; H, 6.42; S, 11.35. Found: C, 38.61; H, 6.48; S, 11.18.

1-(9-m-Carboranylthio)propanone-2 **24**. To a mixture of 1.2 g of acetone chloride, 10 ml of CH_3COOH and a drop of HCl at 20°C was added 1.76 g of **3**. The solution was stirred at 90–100°C for 14 h, then poured into water and extracted with ether. The organic layer was separated and then washed with water to attain a neutral reaction and dried over $MgSO_4$. After removal of the solvent the mixture was chromatographed on a silica gel column (eluent—benzene–hexane, 2 : 1). Yields: 0.3 g of **4** and 1.3 g (56%) of **24**, m.p. 47–48°C (pentane). IR spectrum: ν 1710 cm^{-1} (C=O). Anal. Calcd for $C_5H_{16}B_{10}OS$: C, 25.85; H, 6.94; S, 13.18. Found: C, 25.69; H, 6.95; S, 14.19.

(9-m-Carboranylthio)propionitrile **25**. To a solution of 1.0 g of **3** and 0.36 g of acrylonitrile in 15 ml of THF were added 2–3 drops of 10% aqueous Bu_4NOH at 20°C. After 0.5 h of stirring the reaction mixture was poured into water and extracted with ether. The organic layer was separated, washed with water and dired over $MgSO_4$. Yield: 1.25 g (96%), m.p. 37–37.5°C (heptane). IR spectrum: ν 2250 cm^{-1} (C≡N). Anal. Calcd for $C_5H_{15}B_{10}NS$: C, 26.17; H, 6.59; N, 6.10. Found: C, 26.19; H, 6.30; N, 6.11.

(9-m-Carboranylthio)methyl propionate **26**. To a solution of 0.5 g of **3** and 0.29 g of methyl acrylate in 10 ml of THF were added 2–3 drops of aqueous Bu_4NOH at 20°C. After 1 h of stirring the reaction mixture was poured into water. Then it was treated in the usual manner. Yield: 0.6 g (82%), light-yellow oil solidifying on intensive cooling. Anal. Calcd for $C_6H_{18}B_{10}O_2S$: C, 27.45; H, 6.91; S, 12.21. Found: C, 27.96; H, 7.32; S, 12.31.

(9-m-Carboranylthio)propanal **27**. To a solution of 0.3 g of acrolein in 5 ml of THF were added several drops of Et_3N. Then to the mixture obtained was added a solution of 0.63 g of **3** in 5 ml of THF at 0°C. The reaction mixture was stirred at 0°C for 1 h and at 20°C for another 4 h. Then it was poured into water. The usual treatment of the mixture gave the title compound in the form of a clear viscous liquid solidifying on cooling. Yield: 0.6 g (72%), m.p. 29°C (hexane), 2,4-DNPH **27**, m.p. 217–218°C (ethyl-acetate). Anal. Calcd for $C_{11}H_{20}B_{10}N_4O_4S$: N, 13.57. Found: N, 13.40.

Phenyl(9-m-carboranyl)sulfoxide **28**. To 0.2 g of **21** in 5 ml of CH_3COOH was added 1 ml of 30% H_2O_2. The solution was stored at 20°C for 12 h and then to it was added 15 ml of water. The precipitate was extracted with ether. The organic layer was separated, washed with $NaHCO_3$ and dried over $MgSO_4$. Removal of the solvent and crystallization of the residue gave **28**. Yield: 0.2 g (96%), m.p. 147–148°C (toluene–hexane). Anal. Calcd for $C_8H_{16}B_{10}OS$: C, 35.79; H, 6.00; S, 11.95. Found: C, 35.71; H, 6.02; S, 12.12.

Phenyl(9-m-carboranyl)sulfone **29**

(a) To 1.2 g of **30** in 10 ml of benzene at 10°C was added with stirring 0.9 g of $AlCl_3$. The reaction mixture was refluxed for 3h and then poured into water. The organic layer was separated, washed with water and dried over $MgSO_4$. Removal of the solvent and crystallization of the residue gave the title compound. Yield: 1.1 g (79%), m.p. 162–163°C (toluene). Anal. Calcd for $C_8H_{16}B_{10}O_2S$: C, 33.77; H, 5.67; S, 11.27. Found: C, 34.43; H, 5.72; S, 11.07.

(b) To 0.1 g of **21** in 5 ml of CH_3COOH was added 1 ml of 30% H_2O_2. After being stored at 20°C for 24 h, the solution was poured into water. The title compound was obtained as described above for **28**. Yield: 0.1 g (83%), m.p. 163°C.

(9-m-Carboranylsulfonyl)propionitrile **32**

(a) To 0.5 g of **25** in 5 ml of CH_3COOH was added 0.37 ml of 21% H_2O_2. The reaction mixture was stirred at 20°C for 8 h and at 60°C for another 3 h, then it was poured into water and filtered. The hydrogen peroxide was decomposed in the filtrate with Pt-black and the solution was evaporated to dryness. Crystallization from toluene gave **31**. Yield: 0.7 g (85%), m.p. 114°C.[14]

(b) To a solution of 0.5 g of **25** in 10 ml of benzene at 8°C was added a solution of 0.96 g of $K_2Cr_2O_7$ in 20 ml of 50% H_2SO_4 and 0.2 g of $PhCH_2Et_3N^+Cl^-$. The reaction mixture was stirred at 20°C for 1 h. The organic layer was separated, washed with water and dried over $MgSO_4$. After removal of the solvent the residue was treated with hexane. Yield: 0.45 g (79%), m.p. 93–94°C (hexane–toluene). Anal. Calcd for $C_5H_{15}B_{10}NO_2S$: C, 22.97; H, 5.74; S, 12.27. Found: C, 23.78; H, 5.85; S, 12.50.

(c) To a solution of 0.64 g of $KMnO_4$ in 15 ml of water and 1 ml of CH_3COOH at 5°C was added 0.5 of **25** in 10 ml of benzene and 0.2 g of $PhCH_2Et_3N^+Cl^-$. The reaction mixture was stirred at 20°C for 6 h and the precipitated MnO_2 was removed. The organic layer was separated, washed with $Na_2S_2O_3$ solution, then with water and dried over $MgSO_4$. The solvent was removed. Yield: 0.3 g (52%), m.p. 93–94°C.

9-m-Carboranyl sodium sulfinate **33**. To a suspension of 0.15 g of **32** in 10 ml of abs. alcohol was added a solution of 0.12 g of $m\text{-}C_2H_2B_{10}H_9\text{-}9\text{-}SNa$ in 3 ml of abs. alcohol. The reaction mixture was stirred for 2 h and the solvent was distilled off in vacuo. The residue was dissolved in water and extracted with ether. The usual treatment of the organic layer gave compound **25**. Yield: 0.1 g (77%), m.p. 36°C (heptane). The aqueous solution of **33** was carefully acidified with diluted HCl and extracted with ether. After removal of the solvent the organic layer gave **35**. Yield: 0.07 g, m.p. 295°C (decomp.). After evaporation to dryness the aqueous solution gave **31**. Yield: 0.04 g.

Attempted production of the 9-m-carboranylsulfinic acid **34**

(a) *Reduction of the 9-m-carboranyl sulfochloride* **30**. To a stirred solution of 0.7 g of **30** in 10 ml of abs. ether was added 0.12 g of $LiAlH_4$ in abs. ether at −20°C. Then the reaction mixture was stirred at 20°C for 3 h. After decomposition of the excess $LiAlH_4$ the mixture was treated with diluted HCl. The ether layer was separated and extracted with 5% KOH. After acidification the alkaline solution gave **3**. Yield: 0.5 g (96%).

(b) *Catalytic hydration of the 9-m-carboranyl sulfochloride* **30**. Initially 0.6 g of **30** was hydrated in 5 ml of acetone over $Pd/BaSO_4$ to the complete absorption of hydrogen. After removal of the catalysts from the reaction mixture the latter was evaporated to dryness and the residue was crystallized from a toluene-hexane mixture to give **35**. Yield: 0.27 g (80%), m.p. 295°C (decomp.). Anal. Calcd for $C_4H_{22}B_{10}O_2S_2$: C, 12.57; H, 5.76; B, 56.65; S, 16.75. Found: C, 12.92; H, 5.78; B, 56.56; S, 16.81; m/e 382 (M).

Also compound **30** was obtained. Yield: 0.14 g (82%). Anilinium salt, m.p. 255–256°C (decomp.). Anal. Calcd for $C_8H_{11}B_{10}NO_3S$: C, 30.26; H, 6.03; N, 4.41. Found: C. 30.02; H, 5.71; N, 4.59.

(c) *Chlorination of* **4** *in the presence of acetic anhydride*. To a solution of 1.0 g of **4** in 15 ml of CH_2Cl_2 was added 0.58 g of acetic anhydride. Then Cl_2 was passed through the mixture at −30°C for 40 min (to the complete disappearance of **13** as shown by TLC). The volatile products were evaporated in vacuo. The residue was dissolved in abs. ether and hydrolyzed with 0.1 ml of water in 5 ml of abs. ether. After evaporation of the ether the residue was found to be a mixture of **4** and **35**. Compound **31** was isolated from the aqueous solution.

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