Journal of Organometallic Chemistry, 216 (1981) 295—320
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

SYNTHESIS OF ORGANOSILICON COMPOUNDS WITH A CARBORANYLMETHYL RADICAL

V.N. KALININ *, B.A. IZMAILOV, A.A. KAZANTSEV, V.D. MYAKUSHEV, A.A. ZHDANOV and L.I. ZAKHARKIN

Institute of Organo-element Compounds, Academy of Sciences, Vavilova St. 28, Moscow (U.S.S.R.)

(Received March 17th, 1981)

Summary

The methods of synthesizing *C*-mono and *C,C'*-bis[alkoxy(organo)silylmethyl]-*o*(*m*)-carboranes by the reaction between the corresponding lithium carboranes and chloromethyl(organo)alkoxysilanes have been developed. Various *C*-mono- and *C,C'*-bis[chloro- and hydroxy(organo)silylmethyl]-*o*(*m*)-carboranes have been obtained from these compounds and their properties have been studied.

Introduction

At present a vast number of silicon derivatives of carboranes are known, and they are used in the synthesis of polymers and contain the Si—C_{cb}^{*} bond or the system of bonds $\text{Si—(CH}_2)_{3-4}\text{—C}_{cb}$ [1,2]. A major disadvantage of compounds of this type resides in the fact that the Si—C_{cb} bond is highly labile towards the action of nucleophilic and electrophilic reagents and, therefore, easily ruptured; in addition, the thermal stability of the system of $\text{Si—(CH}_2)_{3-4}\text{—C}_{cb}$ bonds is low and the system is readily destroyed by thermal oxidation [1]. Hence, the development of methods of synthesizing reactive silicon derivatives of carboranes of a new type is of a particular importance for this class of compounds.

This paper deals with a study of the reaction between chloromethyl(organo)alkoxysilanes and lithium carboranes, which gives rise to compounds having a methylene group between the silicon atom and the carborane ring. Such compounds are characterized by a high stability of the system of $\text{Si—CH}_2\text{—C}_{cb}$ bonds towards both nucleophilic and electrophilic reagents and towards thermal

---

* C_{cb} denotes the carbon atom of the carborane ring.

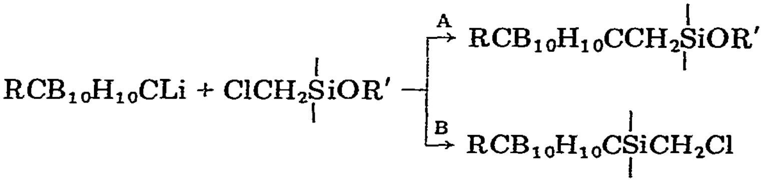
0022-328X/81/0000—0000/$02.50

oxidation. Their functional alkoxy groups at the silicon atom react readily with the formation of different derivatives: *C*- and *C,C'*-[chloro, -acetoxy], and hydroxy-(organo)silylmethyl-substituted compounds, and oligomeric and polymeric products.

Results and discussion

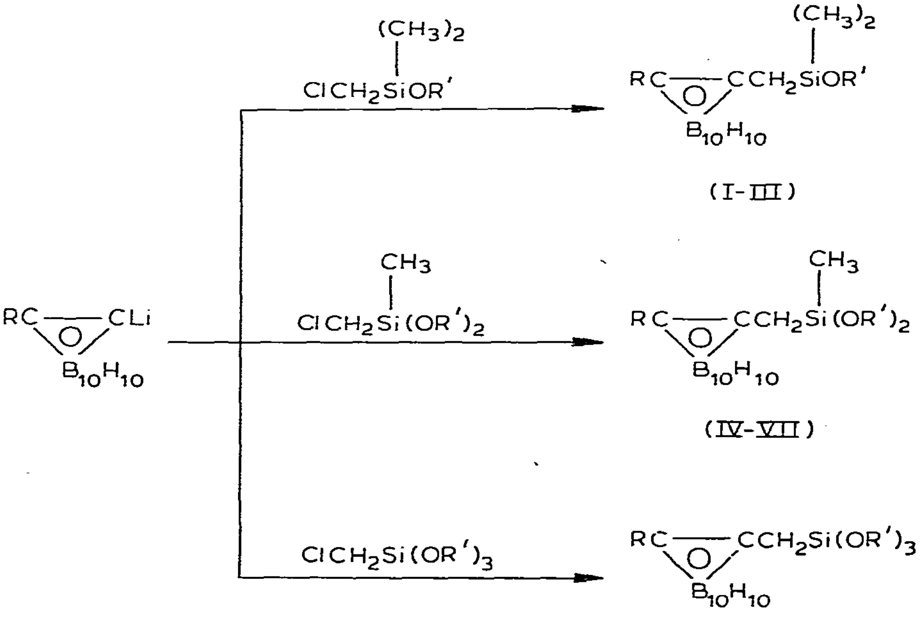
Reaction of lithium carboranes with chlroromethyl(organo)alkoxysylanes

C- and *C,C'*-alkoxy(organo)silylmethyl-substituted *o*- and *m*-carboranes are an interesting class of compounds since they can be used for preparing new monomers, oligomers, and polymers. To synthesize them, we studied the reactions of lithium carboranes with chloromethyl(organo)alkoxysilanes of different functionality [3]. Two main routes are possible for the reaction: the replacement of the chlorine atom in a chloromethyl group at the silicon atom with a carboranyl residue and formation of carboranylmethyl(organo)alkoxysilanes



$$RCB_{10}H_{10}CLi + ClCH_2\overset{|}{\underset{|}{Si}}OR' \longrightarrow \begin{cases} \xrightarrow{A} RCB_{10}H_{10}CCH_2\overset{|}{\underset{|}{Si}}OR' \\ \xrightarrow{B} RCB_{10}H_{10}C\overset{|}{\underset{|}{Si}}CH_2Cl \end{cases}$$

(A) or, the replacement of the alkoxy group at the silicon atom and formation of compounds with the $Si{-}C_{cb}$ bond (B):

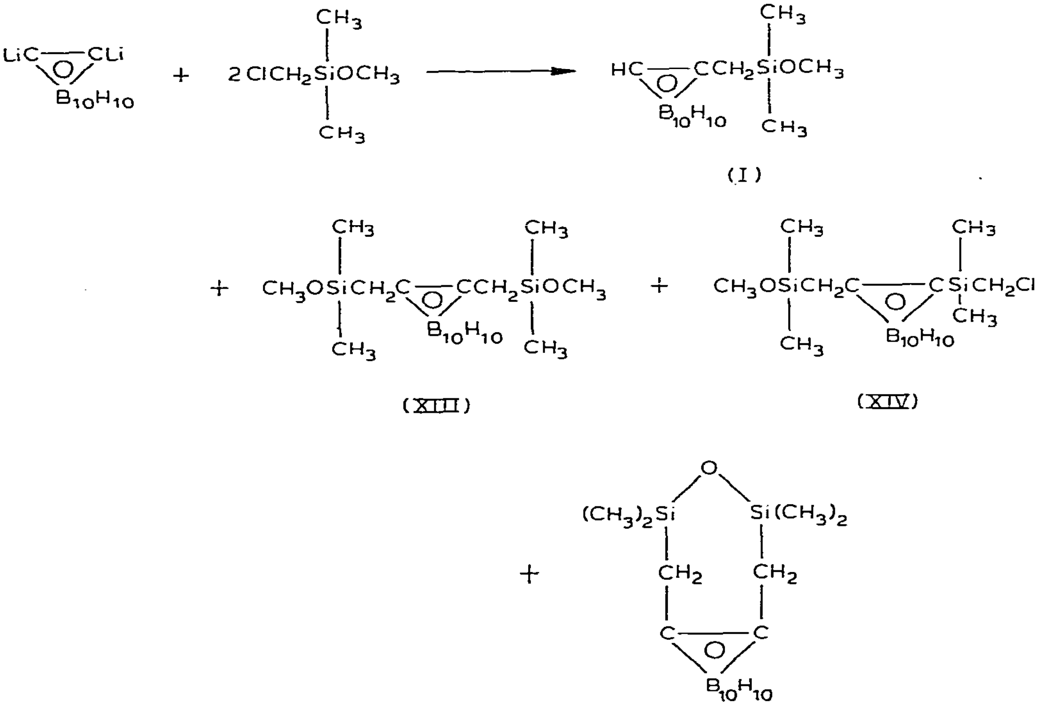


R = H, R' = CH_3(I), R' = C_2H_5 (II); R = CH_3, R' = CH_3 (III); R = H, R' = CH_3 (IV); R = H, R' = C_2H_5 (V); R = CH_3, R' = C_2H_5 (VI); R = C_6H_5, R' = C_2H_5 (VII); R = H, R' = CH_3 (VIII), R' = C_2H_5 (IX); R = CH_3, R' = C_2H_5 (X); R = $CH_2{-}C(CH_3)$, R' = C_2H_5 (XI); R = C_6H_5, R' = C_2H_5 (XII).

The formation of bis- and tris(carboranyl) derivatives of (organo)silanes by the replacement of the chlorine atom and alkoxy group in the initial chloromethylmono-, di- and trialkoxysilanes is also possible.

It is evident that the predominant route for the reaction depends on many factors; the most important of which are the relative reactivity of the chlorine atom in the chloromethyl group and that of the alkoxy groups in the initial (organo)silane as well as the polarity of the Li—C_{cb} bond. The reaction conditions (medium, temperature) can also affect the direction of the process. We have found that interaction of monolithium-*o*-carboranes with chloromethyl(dimethyl)alkoxysilane, chloromethyl(methyl)dialkoxysilane, and chloromethyltrialkoxysilane in a solution of ether and benzene, or in the same solution but with tetrahydrofuran, or in a heterogeneous medium (heptane), is accompanied only by a selective substitution of a carboranyl residue for the chlorine atom in the chloromethyl group. As a result, the corresponding carboranylmethyl(organo)alkoxysilanes are formed in 60—95% yield:

The reaction between dilithium-*o*-carborane and chloromethyl(dimethyl)methoxysilane in ether or heptane is complicated by the simultaneous parallel reactions yielding a mixture of the following products: 1,2-bis[methoxy(dimethyl)silylmethyl-*o*-carborane (XIII) (27%), 1-methoxy(dimethyl)silylmethyl-2-chloromethyl(dimethyl)silyl-*o*-carborane (XIV) (29%), and 1,2-(*o*-carboranyleno)-4,6-bis(dimethylsilyl)-5-oxacyloheptane (XV) (8%). The mixture also contains 1-methoxy(dimethyl)silylmethyl-*o*-carborane (I) (36%):



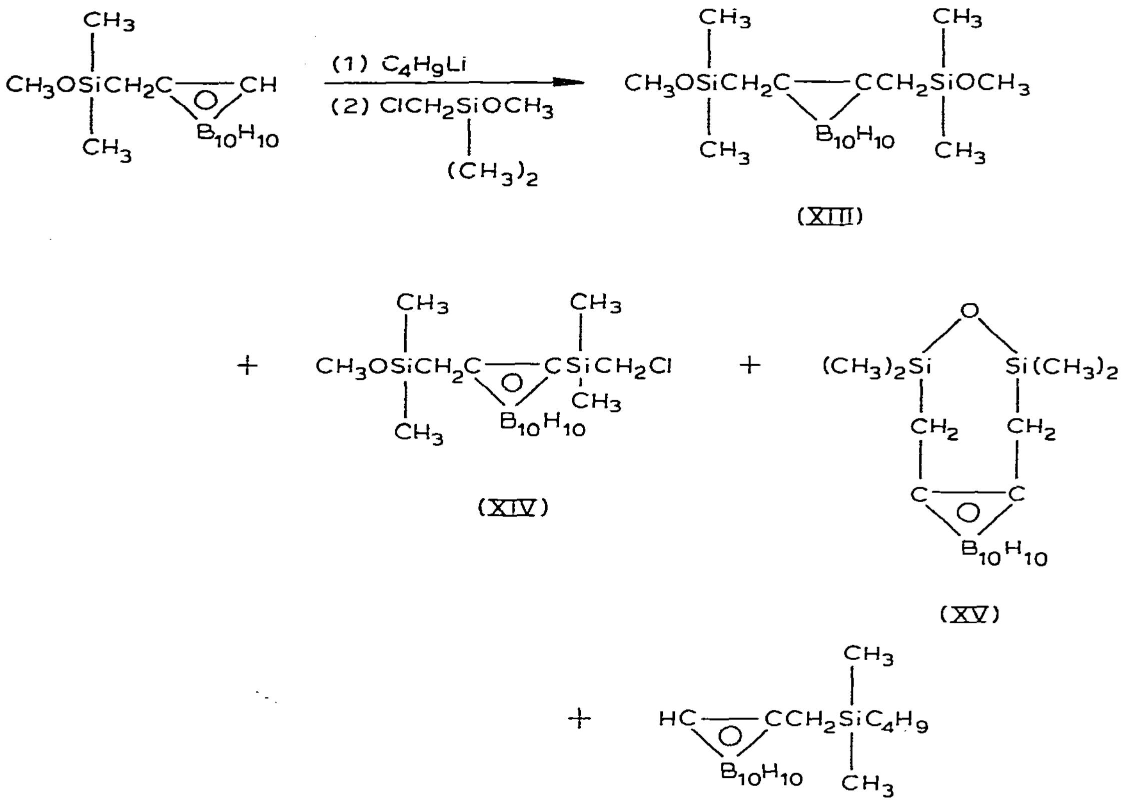
(I)

(XIII)

(XIV)

(XV)

We have assumed that the introduction of a methoxy(dimethyl)silylmethyl group onto the carbon atom of the carborane ring favours the reaction of lithium derivatives of 1-methoxy(dimethyl)silylmethyl-*o*-carborane via two possible routes (A and B). To support this assumption, we have studied the reaction of 1-lithium-2-methoxy(dimethyl)silylmethyl-*o*-carborane with chloromethyl(dimethyl)methoxysilane. It was shown that in this case the mixture of the products formed is similar to that obtained during the reaction of dilithium-*o*-carborane with chloromethyl(dimethyl)methoxysilane:



(XIII)

(XIV)

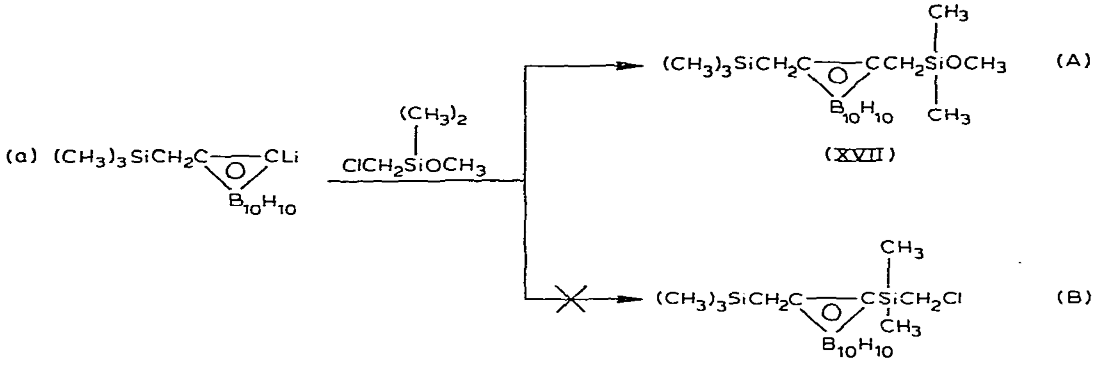
(XV)

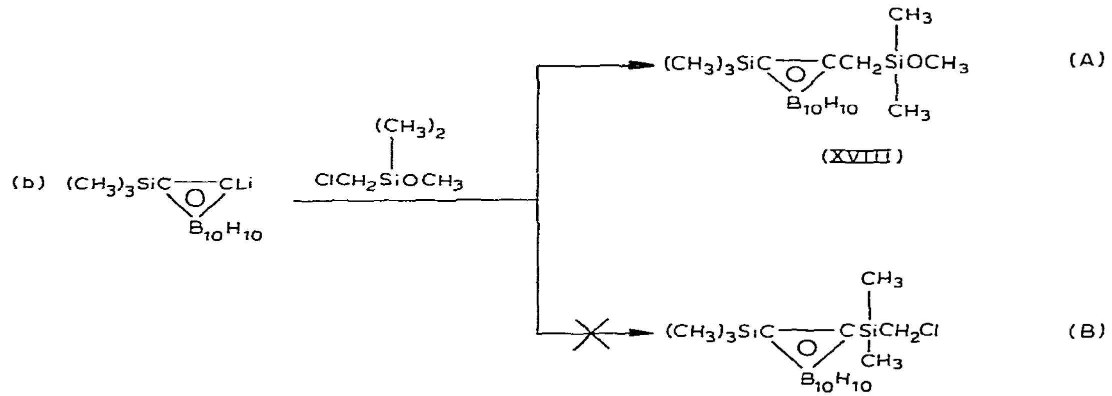
(XVI)

However, in this case 1-butyl(dimethyl)silylmethyl-*o*-carborane (XVI) is also formed in small amounts; which points to a possible partial replacement of an alkoxy group at the silicon atom of carboranylmethyl(dimethyl)methoxysilane (I) by a butyl radical.

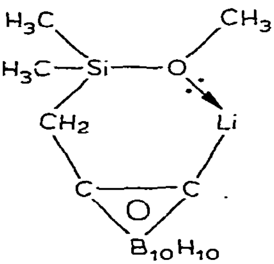
We thought that such a direction of the reaction must be due to the considerable electron-releasing effect of the methoxy(dimethyl)silyl group, which enhances the nucleophilic character of the carborane residue and favours both routes A and B of the reaction.

In this connection we studied the reaction of chloromethyl-(dimethyl)-methoxysilane with 1-lithium-2-trimethylsilylmethyl-*o*-carborane (a) and 1-lithium-2-trimethylsilyl-*o*-carborane (b). In these cases one would expect the reaction to follow both routes A and B. But we observed only the formation of 1-trimethylsilylmethyl-2-methoxy(dimethyl)silylmethyl-*o*-carborane (XVII) and 1-trimethylsilyl-2-methoxy(dimethyl)-silylmethyl-*o*-carborane (XVIII).



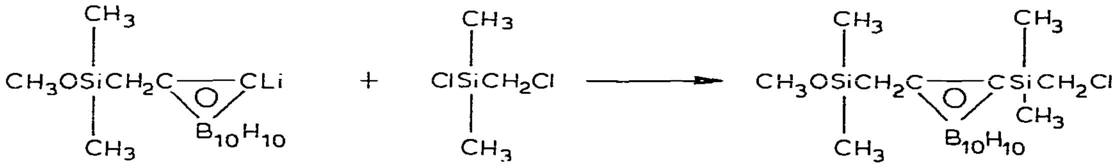


No products were present which could have been formed as a result of the replacement of the alkoxy group at the silicon atom in chloromethyl(dimethyl)-methoxysilane. Hence, the electron-releasing effect of a trimethylsilylmethyl, trimethylsilyl, or alkoxy(dimethyl)silylmethyl group is not a determining factor in reactions (a) and (b) of *o*-carborane-lithium derivatives with chloromethyl(organo)alkoxysilanes. It seems most probable to us that intramolecular coordination of the oxygen atom of the alkoxy group in carboranylmethyl(dimethyl)methoxysilane with the lithium atom near the neighbouring carbon atom is responsible for the reaction of 1-lithium-2-methoxy(dimethyl)silylmethyl-*o*-carborane with chloromethyl(dimethyl)methoxysilane via two routes (A and B).



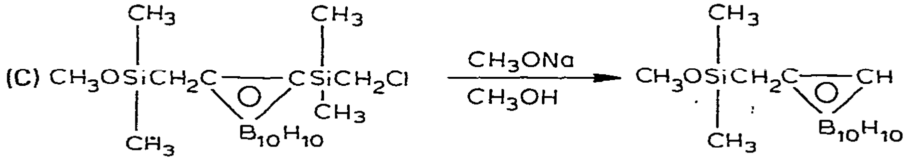
Such coordination must increase the polarity of the Li—C_{cb} bond and, as a result, favour the reaction of carboranylmethyl(dimethyl)methoxysilane with chloromethyl(dimethyl)methoxysilane via both routes A and B. The possibility of intramolecular coordination of the metal atom in *o*-carborane with the heteroatom of the substituent near the neighbouring carbon atom has been reliably established [4,5].

In XIII, the silicon and carbon atoms in a carborane ring are separated by a methylene group. Such compounds are characterized by a high stability of the system of Si—CH$_2$—C$_{cb}$ bonds [3], in contrast to compound XIV where, along with the Si—CH$_2$—C$_{cb}$ bond, the Si—C$_{cb}$ bond is also present. We obtained compound XIV by independent synthesis as well, namely, by the reaction of 1-lithium-2-methoxy(dimethyl)silylmethyl-*o*-carborane with chloromethyl(dimethyl)chlorosilane. Due to the considerably higher reactivity of the Si—Cl bond as compared with the C—Cl bond of the chloromethyl group in chloromethyl(dimethyl)chlorosilane, only 1-methoxy(dimethyl)silylmethyl-2-chloromethyl(dimethyl)silyl-*o*-carborane XIV is formed in this case.



(XIV)

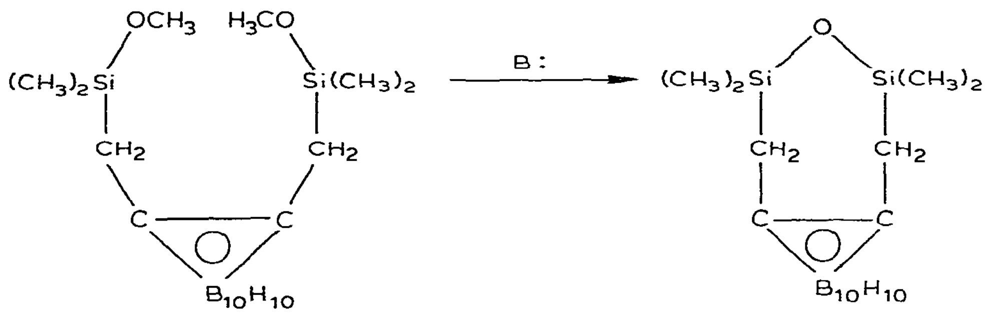
The Si—C$_{cb}$ bonds are readily split under the action of nucleophilic and electrophilic reagents [1]; therefore, additional treatment with sodium methoxide in methanol of XIV obtained by independent synthesis, and of the reaction mixture from the reaction between dilithium-*o*-carborane and chloromethyl(dimethyl)methoxysilane (i.e. XIII + XIV + XV) leads to a splitting of the Si—C$_{cb}$ bonds in XIV and to formation of methoxy(dimethyl)silylmethyl-*o*-carborane (I).



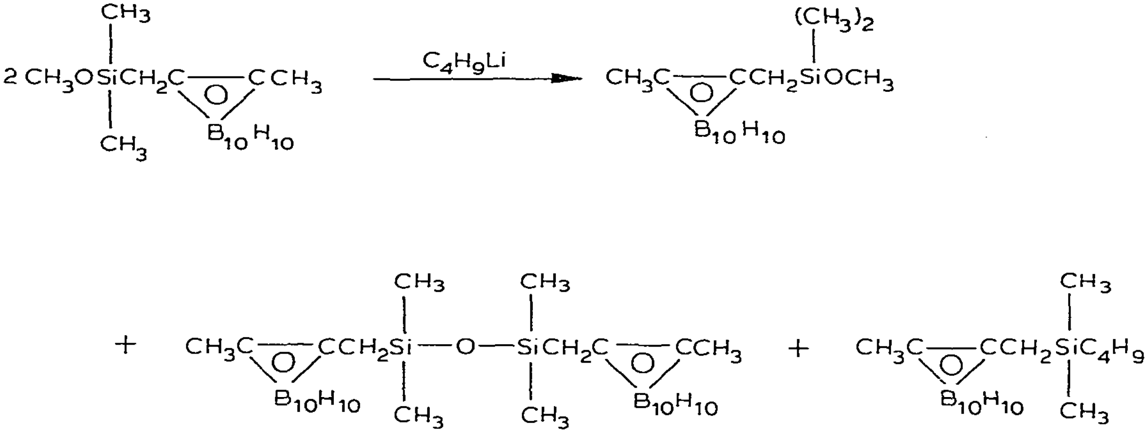
(XIV)

(I)

Compound XV is a seven-membered exocyclic product. Its formation is related to the condensation of alkoxy groups at the silicon atom in XIII under the action of alkaline agents present in the reaction mixture, including lithium carboranes. Lithium derivatives of I can act as a condensing agent in the cyclization of XIII into XV. Consumption of lithium derivative in this reaction may explain the presence of I in the mixture formed in the reaction of dilithium *o*-carborane with chloromethyl(dimethyl)methoxysilane. The possiblility of the formation of exocyclic products is due to the fact that the substitutents at the carbon atoms of the *o*-carborane ring are in *cis* positions with respect to one another. Such an arrangement favours the formation of exocycles with a siloxane bond:



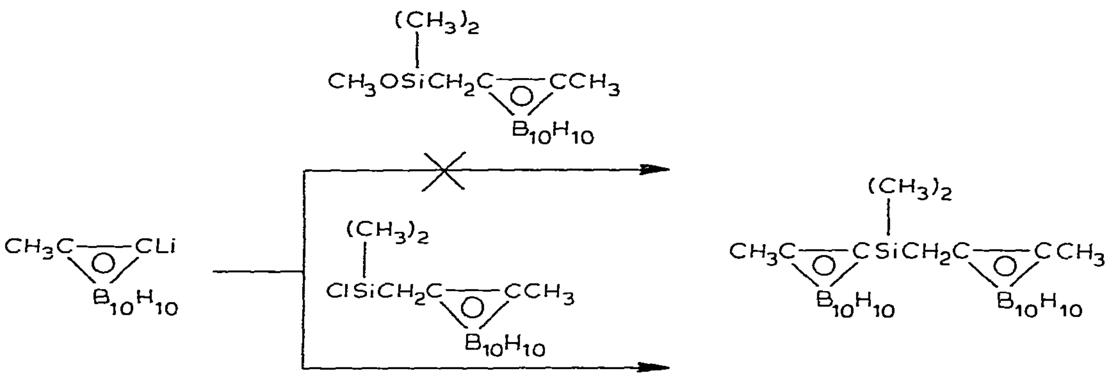
The formation of a siloxane bond under such conditions was demonstrated by us for the reaction of 1-methoxy(dimethyl)silylmethyl-2-methyl-*o*-carborane with butyllithium:



(XIX) (XX)

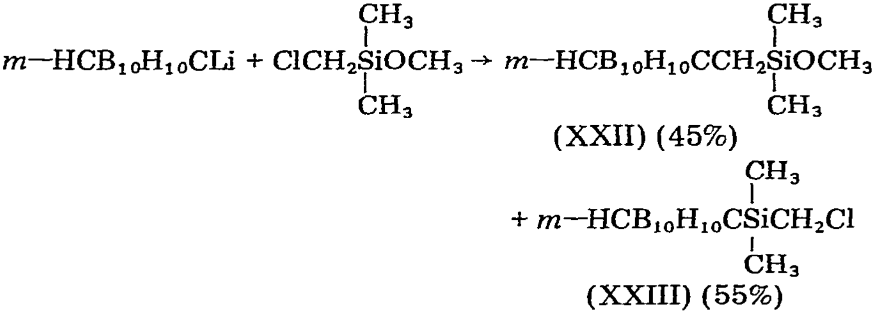
It should be noted that, along with the formation of 1,3-bis(methylcarbonylmethyl)-1,1,3,3-tetramethyldisiloxane (XIX), the substitution of a butyl radical for methoxyl groups also takes place, which is accompanied by formation of 1-methyl-2-butyl(dimethyl)silylmethyl-*o*-carborane (XX). Earlier, when studying the interaction of butyllithium with carboranylmethyl(dimethyl)methoxysilane (I), we had already established the possibility of such a substitution of a butyl radical for methoxy groups at a silicon atom. However, the reaction of 1-lithium-2-methyl-*o*-carborane with 1-methoxy(dimethyl)silylmethyl-2-methyl-*o*-carborane is not accompanied by the substitution of a methylcarboranyl radical for methoxy groups at silicon atoms since no (methyl-*o*-carboranyl)(methyl-*o*-carboranylmethyl)dimethylsilane (XXI) is formed. The latter was obtained only upon interaction of 1-lithium-2-methyl-*o*-carborane with 1-chloro(dimethyl)-silylmethyl-2-methyl-*o*-carborane.

This indicates that the replacement of a methoxy group at a silicon atom in carbonylmethyl(dimethyl)methoxysilane is possible only when this group is subjected to the action of carbanions more nucleophilic than carboranyl anions. The decisive role of the nature of the carboranyl anion in the reactions of chloromethyl(organo)alkoxysilanes with lithium carboranes is clearly pro-



(XXI)

nounced when they interact with monolithium-*m*-carboranes. We have found that chloromethyl(dimethyl)methoxysilane reacts with monolithium-*m*-carborane via the two possible routes A and B with the formation of the products of substitution of both the chlorine atom in the chloromethyl group and the alkoxy group at the silicon atom:



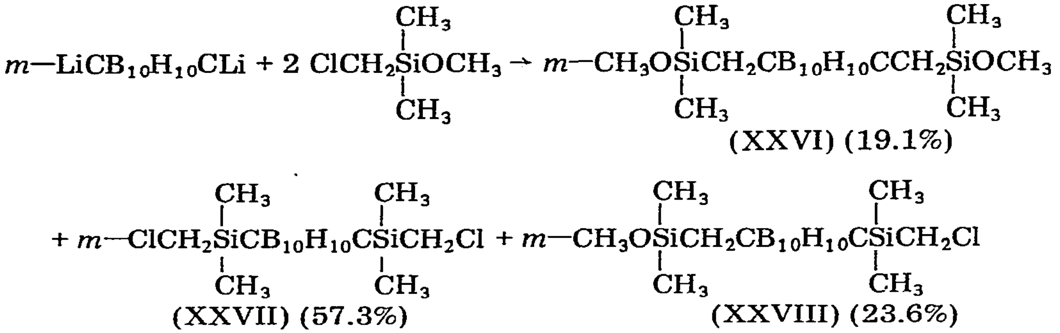
$$m\text{—}HCB_{10}H_{10}CLi + ClCH_2\overset{CH_3}{\underset{CH_3}{Si}}OCH_3 \rightarrow m\text{—}HCB_{10}H_{10}CCH_2\overset{CH_3}{\underset{CH_3}{Si}}OCH_3 \quad \text{(XXII) (45\%)}$$

$$+\ m\text{—}HCB_{10}H_{10}C\overset{CH_3}{\underset{CH_3}{Si}}CH_2Cl \quad \text{(XXIII) (55\%)}$$

In a similar way, *m*-carboranylmethyl(methyl)dimethoxysilane (XXIV) and *m*-carboranylmethyltrimethoxysilane (XXV) were obtained.

Such a strong difference in the reactivity of lithium-*o*- and lithium-*m*-carboranes with respect to chloromethyl(organo)alkoxysilanes may be due to different polarities of the Li—C_{cb} bonds in these compounds. The carbon atoms in *o*-carborane have larger partial positive charges, namely, C (+0.25) [6] and C′(+0.25) [7], than in *m*-carborane, C (+0.15) [6] and C′ (+0.06) [7]. Lithium carboranes are characterized by a localization of the negative charge on the carbon atoms of the carboranyl anion, whereas in carbanions of fatty aromatic hydrocarbons the negative charge is delocalized over the whole hydrocarbon skeleton [8]. As a result, the transfer of electron density from the metal (lithium) atom to the carbon atom of the carborane ring will result in a higher dipole moment of the Si—C_{cb} bond in *m*-carborane than than in *o*-carborane. The higher polarity of the Si—C_{cb} (*m*-) bond ensures, apparently, the possibility of the reaction between lithium-*m*-carborane and chloromethyl(organo)alkoxysilanes following both routes A and B.

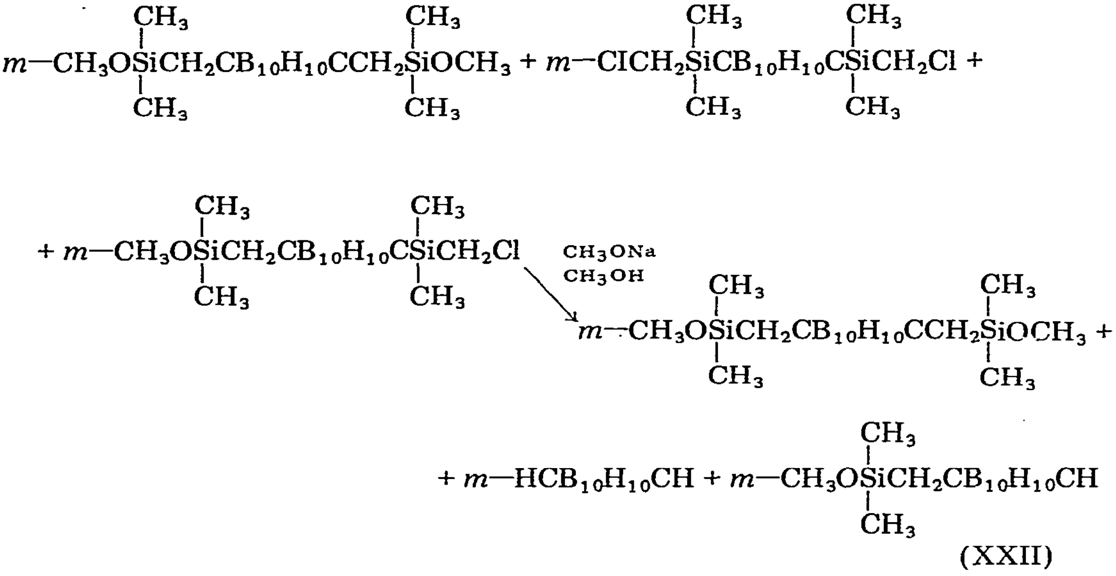
Interaction of dilithium-*m*-carboranes with chloromethyl(organo)alkoxysilanes yields three products: 1,7-bis[methoxy(dimethyl)silylmethyl]-*m*-carborane (XXVI), 1,7-bis[chloromethyl(dimethyl)silyl]-*m*-carborane (XXVII), and 1-methoxy(dimethyl)silylmethyl-7-chloromethyl(dimethyl)silyl-*m*-carborane (XXVIII).



$$m\text{—}LiCB_{10}H_{10}CLi + 2\,ClCH_2\underset{CH_3}{\overset{CH_3}{Si}}OCH_3 \rightarrow m\text{—}CH_3O\underset{CH_3}{\overset{CH_3}{Si}}CH_2CB_{10}H_{10}CCH_2\underset{CH_3}{\overset{CH_3}{Si}}OCH_3 \;\text{(XXVI) (19.1\%)}$$

$$+\, m\text{—}ClCH_2\underset{CH_3}{\overset{CH_3}{Si}}CB_{10}H_{10}C\underset{CH_3}{\overset{CH_3}{Si}}CH_2Cl \;\text{(XXVII) (57.3\%)} + m\text{—}CH_3O\underset{CH_3}{\overset{CH_3}{Si}}CH_2CB_{10}H_{10}C\underset{CH_3}{\overset{CH_3}{Si}}CH_2Cl \;\text{(XXVIII) (23.6\%)}$$

The tendency of the Si—C_{cb} bond to split under the action of nucleophilic reagents was used by us in this case as well for isolating XXVI by treating the reaction mixture at 20°C with an alcohol solution of sodium methoxide:



$$m\text{—}CH_3O\underset{CH_3}{\overset{CH_3}{Si}}CH_2CB_{10}H_{10}CCH_2\underset{CH_3}{\overset{CH_3}{Si}}OCH_3 + m\text{—}ClCH_2\underset{CH_3}{\overset{CH_3}{Si}}CB_{10}H_{10}C\underset{CH_3}{\overset{CH_3}{Si}}CH_2Cl +$$

$$+\, m\text{—}CH_3O\underset{CH_3}{\overset{CH_3}{Si}}CH_2CB_{10}H_{10}C\underset{CH_3}{\overset{CH_3}{Si}}CH_2Cl \xrightarrow[CH_3OH]{CH_3ONa} m\text{—}CH_3O\underset{CH_3}{\overset{CH_3}{Si}}CH_2CB_{10}H_{10}CCH_2\underset{CH_3}{\overset{CH_3}{Si}}OCH_3 +$$

$$+\, m\text{—}HCB_{10}H_{10}CH + m\text{—}CH_3O\underset{CH_3}{\overset{CH_3}{Si}}CH_2CB_{10}H_{10}CH \;\text{(XXII)}$$

The products obtained can be separated by distillation. The properties and analysis are given in Table 1.

The chemical reactivity of alkoxyl groups in compounds I—XXVIII makes their use for various reactions with organic and organoelement compounds possible. The reactions of these compounds with chlorine-containing compounds and with water are of a special interest. Thus, under the action of acetyl chloride or phosphorus trichloride on compounds I—XXVIII, the substitution of chlorine atoms for alkoxyl groups takes place, as a result of which the corresponding *C*- and *C,C'*-[chloro(organo)silylmethyl]-*o*- and -*m*-carboranes are formed. The reaction with water leads to hydrolysis of the compounds with the formation of the corresponding *C*- and *C,C'*-[hydroxy(organo)silylmethyl]-*o*- and -*m*-carboranes.

TABLE 1

ANALYTICAL DATA FOR COMPOUNDS I—XV, XVII—XIX, XXII AND XXIV—XXVI

No.	Compound	Boiling point (°C) (1 mmHg)	n_D^{20}	Analysis. Found (calcd.) (%)		
				C	H	Si
1	I	132—134 M.p. 40—41		29.14 (29.24)	8.98 (8.99)	11.32 (11.40)
2	II	154—156	1.5055	32.97 (32.27)	9.18 (9.28)	10.70 (10.78)
3	III	135—137	1.5290	32.15 (32.27)	9.17 (9.28)	11.01 (10.78)
4	IV	135—137	1.5170	30.01 (29.24)	9.11 (8.99)	11.74 (11.39)
5	V	150—152	1.5320	33.40 (33.07)	9.05 (9.02)	9.19 (9.66)
6	VI	140—143	1.5350	35.91 (35.49)	9.35 (9.26)	9.50 (9.22)
7	VII	183—185	1.5450	48.50 (45.86)	8.51 (8.24)	6.70 (7.66)
8	VIII	146—148	1.5069	26.57 (25.88)	8.00 (7.96)	9.20 (10.09)
9	IX	154—156	1.5530	34.20 (33.72)	8.77 (8.80)	8.69 (8.76)
10	X	142—144	1.5388	36.29 (35.90)	8.96 (9.03)	8.17 (8.39)
11	XI	143—145	1.5065	40.26 (39.97)	9.01 (8.94)	7.63 (7.79)
12	XII	183—186	1.5470	45.80 (45.42)	8.28 (8.13)	7.00 (7.08)
13	XIII	177—180	1.5229	35.21 (34.45)	9.27 (9.25)	15.78 (16.11)
14	XIV	173—175	1.5380	31.11 (30.61)	8.90 (8.27)	15.37 (15.90)
15	XV	— M.p. 167		31.20 (31.76)	8.62 (8.65)	18.07 (18.56)
16	XVII	160—162 M.p. 62		35.57 (36.10)	9.21 (9.69)	17.15 (16.88)
17	XVIII	135—136 M.p. 113—115		34.20 (33.92)	9.31 (9.49)	17.93 (17.62)
18	XIX	— M.p. 120—121		30.91 (30.36)	8.71 (8.91)	12.09 (11.83)
19	XXII	115—117	1.5160	29.70 (29.24)	9.11 (8.99)	11.8 (11.40)
20	XXIV	125—127	1.5100	29.03 (29.24)	9.12 (8.99)	11.83 (11.39)
21	XXV	130—133	1.5008	26.12 (25.88)	8.11 (7.96)	11.00 (10.09)
22	XXVI	168—170	1.5105	35.00 (34.45)	9.18 (9.25)	16.31 (16.11)

---

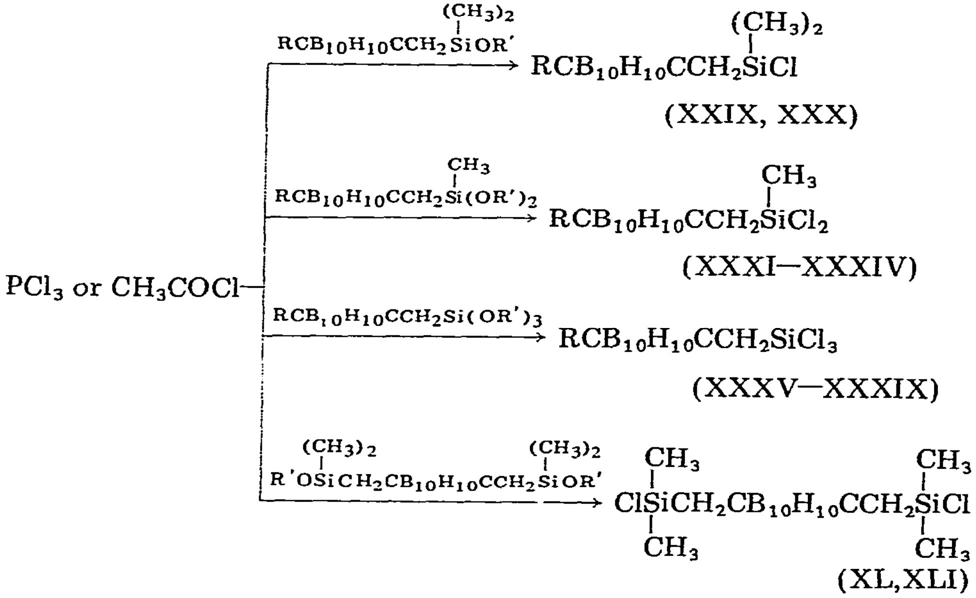
[a] With respect to external HMDS.

Synthesis and properties of C- and C,C'-[chloro(organo)silylmethyl]-o- and -m-carboranes

C- and *C,C'*-[chloro(organo)silylmethyl]-*o*- and -*m*-carboranes represent the most interesting class of monomeric carborane-organosilicon compounds. They

	Empirical formula	PMR spectra (ppm, in CCl_4 with respect to external TMS)
B		
44.03 (43.86)	$C_6H_{22}SiB_{10}O$	$CH_3 = 0.47$; $CH_2 = 2.14$; $OCH_3 = 3.72$; $CH_{cb} = 4.15$
41.20 (41.50)	$C_7H_{24}SiB_{10}O$	CH_{3} = 0.30; $CH_{3\ ethoxy} = 1.40$; $CH_2 = 2.00$; $OCH_{2\ ethoxy} = 3.90$; $CH_{cb} = 4.07$
42.00 (41.50)	$C_7H_{24}SiB_{10}O$	$CH_3 = 0.25$; $CH_2 = 1.62$; $CH_{3\ cb} = 2.07$; $OCH_3 = 3.42$ [a]
44.12 (43.86)	$C_6H_{22}SiB_{10}O_2$	$CH_3 = 0.22$; $CH_2 = 1.80$; $OCH_3 = 3.44$; $CH_{cb} = 3.89$
37.75 (37.21)	$C_8H_{26}SiB_{10}O_2$	$CH_3 = 0.42$; $CH_{3\ ethoxy} = 1.41$; $CH_2 = 2.05$; $OCH_{2\ ethoxy} = 3.98$; $CH_{cb} = 4.34$ [a]
35.15 (35.49)	$C_9H_{28}SiB_{10}O_2$	$CH_3 = 0.28$; $CH_{3\ ethoxy} = 1.60$; $CH_2 = 2.03$; $CH_{3\ cb} = 2.43$; $OCH_{2\ ethoxy} = 4.25$
29.20 (29.49)	$C_{14}H_{30}SiB_{10}O_2$	$CH_3 = 0.31$; $CH_{3\ ethoxy} = 1.07$; $CH_2 = 1.55$; $OCH_{2\ ethoxy} = 3.31$; $C_6H_{5cb} = 6.66$
37.80 (38.82)	$C_6H_{22}SiB_{10}O_3$	$CH_2 = 1.89$; $OCH_3 = 3.64$; $CH_{cb} = 4.07$
33.90 (33.72)	$C_9H_{28}SiB_{10}O_3$	$CH_{3\ ethoxy} = 1.28$; $CH_2 = 1.88$; $OCH_{2ethoxy} = 3.90$; $CH_{cb} = 4.07$
31.52 (31.31)	$C_{10}H_{30}SiB_{10}O_3$	$CH_{3ethoxy} = 1.60$; $CH_2 = 2.03$; $CH_{3cb} = 2.43$; $OCH_{2ethoxy} = 4.25$
29.87 (29.97)	$C_{12}H_{32}SiB_{10}O_3$	$CH_{3ethoxy} = 1.55$; $CH_2 = 1.81$; $(-\underset{\substack{\mid \\ CH_3}}{C}=) = 2.32$; $OCH_{2ethoxy} = 4.17$; $CH_{2isopropyl} = 5.88$, 5.98
27.80 (27.28)	$C_{15}H_{32}SiB_{10}O_3$	$CH_{3ethoxy} = 1.55$; $CH_2 = 2.00$; $OCH_{2ethoxy} = 4.13$; $C_6H_{5cb} = 7.9$ [a]
29.69 (31.00)	$C_{10}H_{32}Si_2B_{10}O_2$	$CH_3 = 0.33$; $CH_2 = 1.73$; $OCH_3 = 3.42$
29.63 (30.61)	$C_9H_{29}Si_2B_{10}OCl$	$CH_3 = 0.48$; $CH_2 = 1.69$; $OCH_3 = 3.30$ [a]
35.90 (35.73)	$C_8H_{26}Si_2B_{10}O$	$CH_3 = 0.32$; $CH_2 = 2.01$ [a]
32.68 (32.49)	$C_{10}H_{32}Si_2B_{10}O$	$(CH_3)_3 = 0.183$; $(CH_3)_2 = 0.23$; $CH_2 = 1.46$, 1.52; $OCH_3 = 3.36$
33.54 (33.92)	$C_9H_{30}Si_2B_{10}O$	$(CH_3)_2 = 0.23$; $(CH_3)_3 = 0.33$ [a]; $CH_2 = 1.73$; $OCH_3 = 3.36$
44.98 (45.52)	$C_{12}H_{42}Si_2B_{20}O$	$CH_3 = 0.31$; $CH_2 = 1.62$; $CH_{3cb} = 2.04$ [a]
44.00 (43.86)	$C_6H_{22}SiB_{10}O$	$CH_3 = 0.27$; $CH_2 = 1.70$; $CH_{cb} = 3.00$; $OCH_3 = 3.55$
44.10 (43.86)	$C_6H_{22}SiB_{10}O_2$	$CH_3 = 0.33$; $CH_2 = 1.36$; $CH_{cb} = 2.80$; $OCH_3 = 3.30$
39.4 (38.82)	$C_6H_{22}SiB_{10}O_3$	$CH_2 = 1.51$; $CH_{cb} = 2.88$; $OCH_3 = 3.55$
31.90 (31.00)	$C_{10}H_{32}Si_2B_{10}O_2$	$CH_3 = 0.325$; $CH_2 = 1.70$; $OCH_3 = 3.59$

are some of the most important starting material for preparing carboranylmethyl(organo)siloxane oligomers and polymers and can be readily synthesised. We have found that the alkoxy groups at the silicon atoms in *C*- and *C,C'*-[alkoxy(organo)silylmethyl]-*o*- and -*m*-carboranes posses a reactivity with organic radicals typical for organoalkoxysilanes [9], and can be easily replaced with chlorine atoms under the action of acetyl chloride or phosphorus trichloride to form the corresponding *C*- and *C,C'*-[chloro(organo)silylmethyl-*o*- and -*m*-carboranes:



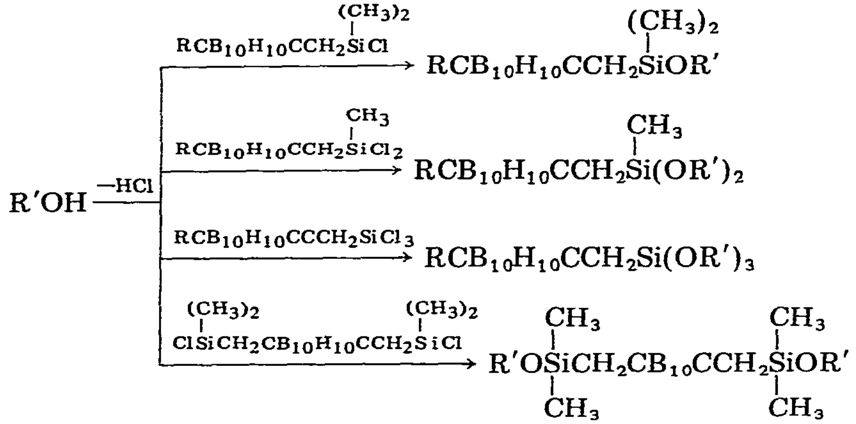
$$PCl_3 \text{ or } CH_3COCl \left\{ \begin{array}{l} RCB_{10}H_{10}CCH_2\overset{(CH_3)_2}{Si}OR' \longrightarrow RCB_{10}H_{10}CCH_2\overset{(CH_3)_2}{Si}Cl \quad \text{(XXIX, XXX)} \\ RCB_{10}H_{10}CCH_2\overset{CH_3}{Si}(OR')_2 \longrightarrow RCB_{10}H_{10}CCH_2\overset{CH_3}{Si}Cl_2 \quad \text{(XXXI—XXXIV)} \\ RCB_{10}H_{10}CCH_2Si(OR')_3 \longrightarrow RCB_{10}H_{10}CCH_2SiCl_3 \quad \text{(XXXV—XXXIX)} \\ R'O\overset{(CH_3)_2}{Si}CH_2CB_{10}H_{10}CCH_2\overset{(CH_3)_2}{Si}OR' \longrightarrow Cl\underset{CH_3}{\overset{CH_3}{Si}}CH_2CB_{10}H_{10}CCH_2\underset{CH_3}{\overset{CH_3}{Si}}Cl \quad \text{(XL,XLI)} \end{array} \right.$$

R = H (XXIX-*o*-), (XXX-*m*-); R = H (XXXI-*o*-), (XXXII-*m*-); R = CH_3 (XXXIII-*o*-); R = C_6H_5 (XXXIV-*o*-); R = H (XXXV-*o*-), (XXXVI-*m*-); R = CH_3 (XXXVII-*o*-); R = $CH_2{=}C(CH_3)$- (XXXVIII-*o*-); R = C_6H_5 (XXXIX-*o*-); (XL-*o*-), (XLI-*m*-).

It was found that with an increase in the number of the alkoxy groups at silicon atoms which can be replaced with chlorine, the duration of the reaction increased considerably. Substitution of alkoxy groups in monoalkoxysilanes takes place more readily than in dialkoxysilanes and in dialkoxysilanes more readily than in trialkoxysilanes. Methoxy groups are more easily substituted than ethoxy groups. A large excess of a chlorinating agent is required for the substitution reaction. The high chemical activity of the chlorines in compounds XXIX—XLI makes their use for various reactions with organic compounds possible. Their reactions with water and with hydroxyl-containing compounds are of a particular interest. Under the action of water the chlorine atoms are readily substituted by hydroxyl groups, as a result of which the corresponding *C*- and *C,C'*-[hydroxy(organo)silylmethyl]-*o*- and -*m*-carboranes are formed. Hydrolysis of compounds XXIX—XLI, the condensation processes which accompany the hydrolysis, and the structures and properties of the reaction products are discussed in detail below.

The chloro-substituted compounds described above react with alcohols and organic acids to yield the corresponding *C*- and *C,C'*-[alkoxy] or [carboxy-(organo)silylmethyl]-*o*- and *m*-carboranes. The bulky carboanylmethyl radicals in *C*-[chloro(organo)silylmethyl]-*o*(*m*)-carboranes and a carboranylenodimethylene fragment in *C,C'*-chloro(organo)silylmethyl]-*o*(*m*)carboranes shield the chlorine silicon bonds, which reduces the activity of the chlorine atoms in these reactions.

The reaction of carboranylmethyl(organo)-mono-, -di-, and -trichlorosilanes (XXIX—XXXIX) and 1,7-bis[chloro(dimethyl)silylmethyl]-*m*-carborane (XLI) with alcohols proceeds with the formation of the corresponding alkoxy-substituted compounds.

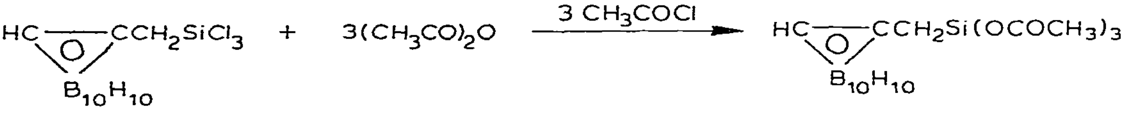


$$R'OH \xrightarrow{-HCl} \begin{cases} \xrightarrow{RCB_{10}H_{10}CCH_2\overset{(CH_3)_2}{Si}Cl} RCB_{10}H_{10}CCH_2\overset{(CH_3)_2}{Si}OR' \\ \xrightarrow{RCB_{10}H_{10}CCH_2\overset{CH_3}{Si}Cl_2} RCB_{10}H_{10}CCH_2\overset{CH_3}{Si}(OR')_2 \\ \xrightarrow{RCB_{10}H_{10}CCCH_2SiCl_3} RCB_{10}H_{10}CCH_2Si(OR')_3 \\ \xrightarrow{Cl\overset{(CH_3)_2}{Si}CH_2CB_{10}H_{10}CCH_2\overset{(CH_3)_2}{Si}Cl} R'O\underset{CH_3}{\overset{CH_3}{Si}}CH_2CB_{10}CCH_2\underset{CH_3}{\overset{CH_3}{Si}}OR' \end{cases}$$

The properties and analytical data of these compounds are listed in Table 2.

The bulk of the organic radical in the alcohol component and the number of methyl radicals bonded to the silicon atom in the carboranylmethyl(organo)-chlorosilanes are the main factors determining the interaction of compounds XXIX—XXXIX and XLI with alcohols. Esterification of these compounds with methyl or ethyl alcohol always proceeds with the formation of small amounts of condensation products. Thus, interaction of carboranylmethyl(dimethyl)-chlorosilane with ethyl alcohol yields, along with carboranylmethyl(dimethyl)-ethoxysilane, 1,3-bis(carboranylmethyl)-1,1,3,3,-tetramethyldisiloxane (XLVII) in small amounts. However, if this reaction is carred out in the presence of urea which binds the liberated hydrogen chloride, one can block the side reactions which favour the formation of the condensation products and enhance the yield of the main product to up to 90—95%.

The substitution of an acid residue for the chlorine atoms in compounds XXIX—XXXIX and XLI can be achieved by reaction with, for instance, acetic acid or acetic anhydride. Thus, the reaction of *o*-carboranylmethyltrichlorosilane with acetic anhydride proceeds vigorously, with the formation of *o*-carboranylmethyltriacetoxysilane (XLII):



(XLII)

The properties and the data of elemental analysis of compounds (XXIX—XLII) are given in Table 2.

TABLE 2

ANALYTICAL DATA FOR COMPOUNDS XXIX—XLII

Compounds	Boiling point (°C) (1 mmHg)	n_D^{20}	Analysis found (calcd.) (%)				Empirical formula	PMR spectra (ppm, in CCl_4, internal reference $CHCl_3$)
			C	H	Si	B		
XXIX	115—117	1.5665	24.52 (23.94)	7.97 (7.64)	10.87 (11.19)	41.92 (43.09)	$C_5H_{19}SiB_{10}Cl$	$CH_3 = 0.71$; $CH_2 = 2.18$; $CH_{cb} = 3.73$ [a]
XXX	114—116 M.p. 34		24.22 (23.94)	7.94 (7.64)	10.91 (11.19)	42.12 (43.09)	$C_5H_{19}SiB_{10}Cl$	$CH_3 = 0.51$; $CH_2 = 1.81$; $CH_{cb} = 2.93$ [a]
XXXI	120—123	1.5320	17.90 (17.70)	5.90 (5.94)	10.00 (10.35)	40.00 (39.83)	$C_5H_{16}SiB_{10}Cl$	$CH_3 = 0.90$; $CH_2 = 2.27$; $CH_{cb} = 3.70$
XXXII	119—122	1.5319	17.60 (17.70)	5.87 (5.95)	9.98 (10.35)	40.6 (39.83)	$C_4H_{16}SiB_{10}Cl_2$	$CH_3 = 0.90$; $CH_2 = 2.03$; $CH_{cb} = 2.90$
XXXIII	139—140	1.5550	22.2 (21.05)	6.85 (6.36)	9.20 (9.85)	35.70 (37.87)	$C_5H_{18}SiB_{10}Cl_2$	—
XXXIV	180—182	1.5832	35.00 (34.56)	5.70 (5.81)	8.00 (8.08)	31.00 (31.11)	$C_{10}H_{20}SiB_{10}Cl_2$	$CH_3 = 0.97$; $CH_2 = 1.73$ $C_6H_{5cb} = 7.31$ [a]
XXXV	125—127	1.5540	12.87 (12.34)	5.25 (4.49)	9.26 (9.62)	35.70 (37.06)	$C_3H_{13}SiB_{10}Cl_3$	$CH_2 = 2.64$; $CH_{cb} = 3.75$
XXXVI	118—120	1.5550	12.72 (12.34)	5.20 (4.49)	9.12 (9.62)	35.80 (37.06)	$C_9H_{13}SiB_{10}Cl_3$	$CH_2 = 2.40$; $CH_{cb} = 3.33$ [a]
XXXVII	136—139	1.5562	16.35 (15.71)	5.12 (4.95)	8.70 (9.18)	33.80 (35.34)	$C_4H_{15}SiB_{10}Cl_3$	$CH_2 = 2.26$; $CH_{3cb} = 2.17$ [a]
XXXVIII	136—138	1.5675	22.50 (21.71)	5.50 (5.16)	8.10 (8.47)	31.50 (32.57)	$C_6H_{17}SiB_{10}Cl_3$	$CH_2 = 1.28$; $(=\underset{\underset{CH_3}{\vert}}{C}-) = 1.95$; $CH_{2isoprop} = 5.48$
XXXIX	178—181	1.5924	40.10 (29.40)	4.85 (3.64)	6.64 (7.64)	28.20 (29.38)	$C_9H_{17}SiB_{10}Cl_3$	—
XL	173—175 M.p. 156—157		27.60 (26.87)	7.43 (6.33)	14.78 (15.72)	28.95 (30.23)	$C_8H_{26}Si_2B_{10}Cl_2$	$CH_3 = 0.66$; $CH_2 = 1.97$ [a]
XLI	152—154	1.5340	27.20 (26.87)	7.28 (7.33)	15.20 (15.72)	29.20 (30.23)	$C_8H_{26}Si_2B_{10}Cl_2$	$CH_3 = 0.48$; $CH_2 = 1.30$
XLII	— M.p. 77—78		29.69 (29.82)	6.03 (6.12)	7.51 (7.75)	27.92 (29.83)	$C_9H_{22}SiB_{10}O_6$	$CH_2 = 2.02$; $OCOCH_3 = 2.17$; $CH_{cb} = 3.53$ [a]

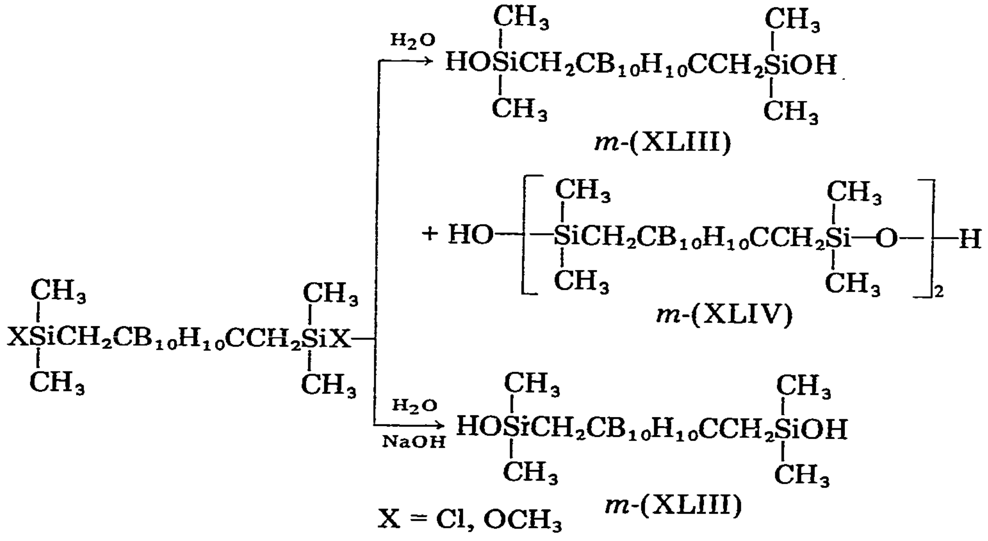
---

[a] With respect to external HMDS.

Hydrolysis of C- and C,C′-[alkoxy- and chloro(organo)silylmethyl]-o(m)-carboranes

We have studied the hydrolysis of *C*-[chloro(organo)silylmethyl]-*o*-carboranes [10]. The methylene bridge between the carborane ring and the silicon atom decreases the electron accepting effect of the carborane ring on silicon, causing the $Si—CH_2—C_{cb}$ bond system to become less polar and more stable. One would expect the hydrolysis of these compounds to be strongly affected by the large volume of the carborane ring (d = 4 Å [11]).

We have established that hydrolysis of both *C*-mono- and *C,C′*-bis[chloro-(dimethyl)silylmethyl]-*m*-carboranes yields mixtures of organosilanols and organosiloxanols. Thus, hydrolysis of 1,7-bis[chloro(dimethyl)silylmethyl]-*m*-carborane furnishes a mixture of 1,7-bis[hydroxy(dimethyl)silylmethyl]-*m*-carborane (XLIII) and the product of its dimerization (XLIV) *.



$$XSi(CH_3)_2CH_2CB_{10}H_{10}CCH_2Si(CH_3)_2X \xrightarrow{H_2O} HOSi(CH_3)_2CH_2CB_{10}H_{10}CCH_2Si(CH_3)_2OH + HO\left[-Si(CH_3)_2CH_2CB_{10}H_{10}CCH_2Si(CH_3)_2-O-\right]_2H$$

m-(XLIII) m-(XLIV)

$$XSi(CH_3)_2CH_2CB_{10}H_{10}CCH_2Si(CH_3)_2X \xrightarrow[NaOH]{H_2O} HOSi(CH_3)_2CH_2CB_{10}H_{10}CCH_2Si(CH_3)_2OH$$

m-(XLIII)

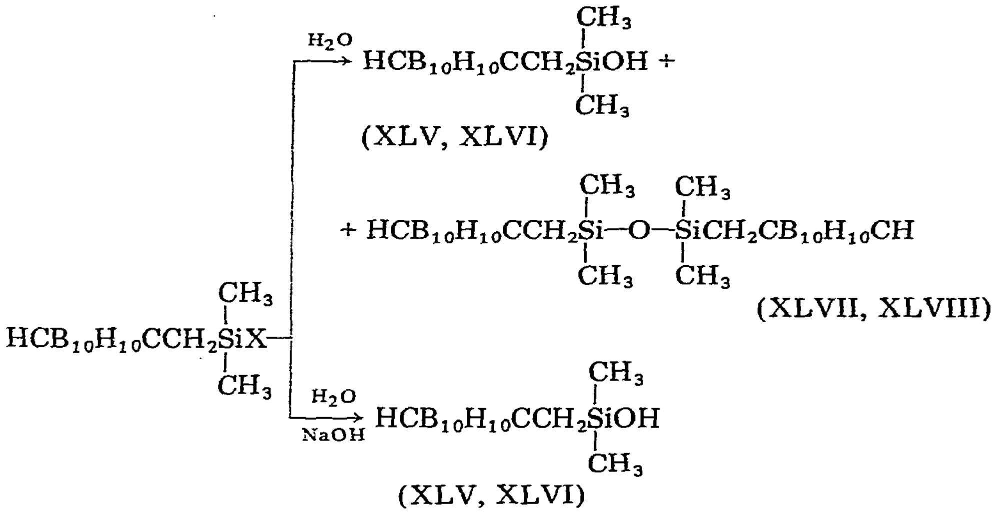
$X = Cl, OCH_3$

In a similar way, hydrolysis of *o*- and *m*-carboranylmethyl(dimethyl)chlorosilanes is accompanied by formation of mixtures of the corresponding carboranylmethyl(dimethyl)hydroxysilanes (XLV, XLVI) and 1,3-bis(carboranylmethyl)-1,1,3,3-tetramethyldisiloxanes (XLVII, XLVIII).

A high content (op to 30%) of organosilanols XLIII—XLVI in the products of hydrolysis formed in an acid medium may be due to a stabilizing effect on the hydroxyl groups at a silicon atom of both the carboranylenedimethylene fragment and the carboranylmethyl radicals. The composition of the products of hydrolysis indicates that the rate of hydrolysis of the corresponding organochlorosilanes into organosilanols and the rate of condensation of unhydrolyzed organochlorosilanes with the corresponding organosilanols in an acid medium are higher than the rate of homocondensation of these organosilanols. If

---

* Hydrolysis of 1,2-bis[chloro(dimethyl)silylmethyl]-o-carborane gives only XV.



(*o*-(XLV, XLVII); *m*-(XLVI, XLVIII))

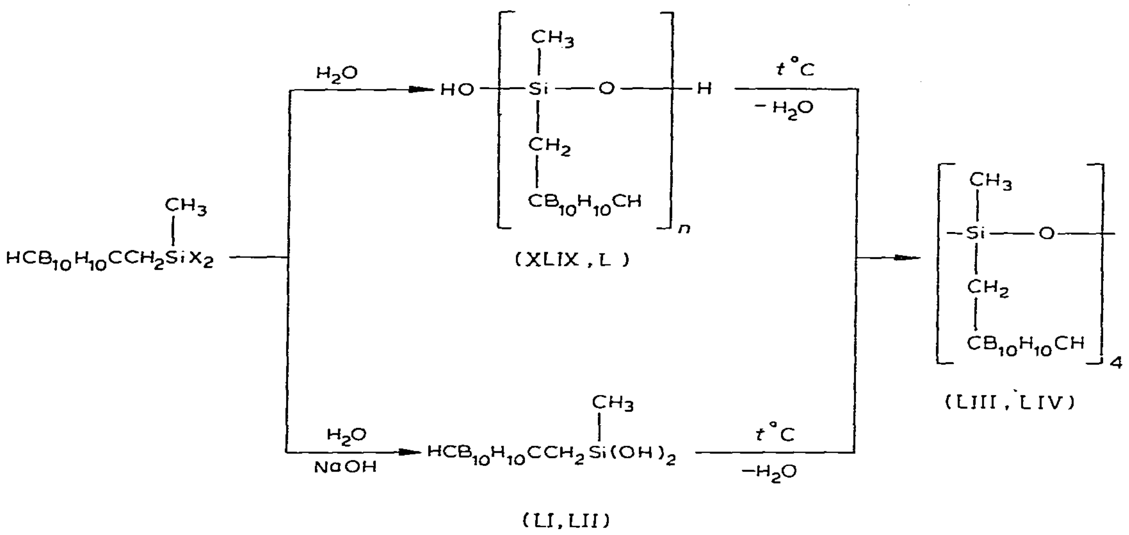
organochlorosilanes are hydrolyzed in the presence of base (for eg. sodium hydroxide) then, due to an increased rate of hydrolysis, it becomes possible to eliminate condensation with the organosilanols formed and to enhance the yield of the latter. Hydrolysis of these organochlorosilanes in the presence of base gives the corresponding organosilanols XLIII—XLVI in 90—95% yield.

It should be noted that 1,7-bis[methoxy(dimethyl)silylmethyl]-*m*-carborane and *o*- and *m*-carboranylmethyl(dimethyl)methoxysilanes are less readily hydrolyzed than the corresponding organochlorosilanes. Thus, no noticeable hydrolysis is observed, even when they are stirred in water for 10 hours at 60°C. If hydrolysis is performed in 15% hydrochloric acid, in all cases mixtures are formed of the corresponding organosilanols (XLIII—XLVI) with the products of their condensation (XLIV, XLVII, XLVIII), just as in the case of hydrolysis of the corresponding organochlorosilanes.

Hydrolysis of *o*- and *m*-carboranylmethyl(methyl)dichlorosilanes must follow the more complicated route since the presence of two chlorine atoms makes possible the formation of not only linear but cyclic compounds as well. However, in contrast to the hydrolysis of ordinary diorganodichlorosilanes [9], hydrolysis of *o*- and *m*-carboanylmethyl(methyl)dichlorosilanes yields no cyclic products in significant amounts. As the main products only organosiloxanes where observed.

The composition of the products is to a great extent determined by the conditions of hydrolysis. Thus, hydrolysis at room temperature gives as the main product, 1,3-dihydroxy-1,3-bis(carboranylmethyl)-1,3-dimethyldisiloxane (XLIX). If hydrolysis is carried out at 60°C, 1,7-dihydroxy-1,3,5,7-tetra-bis-(*o*-carboranylmethyl)-1,3,5,7-tetramethyltetrasiloxane (L) is the main product. Hydrolysis in the presence of bases furnishes the corresponding *o*- and *m*-carboranylmethyl(methyl)dihydroxysilanes (LI, LII).

Carboranylmethyl(methyl)dimethoxysilanes are less susceptible hydrolysis than the corresponding diorganodichlorosilanes [9]. Thus, *o*-carboranylmethyl(methyl)dimethoxysilane is not appreciably hydrolyzed upon stirring with water for 6 hours at 60°C. If its hydrolysis is conducted in 15% hydrochloric



$n = 2$ (XLIX-o-) : $n = 4$ (L-o-) ; o-(LI, LIII) ; m-(LII, LIV)

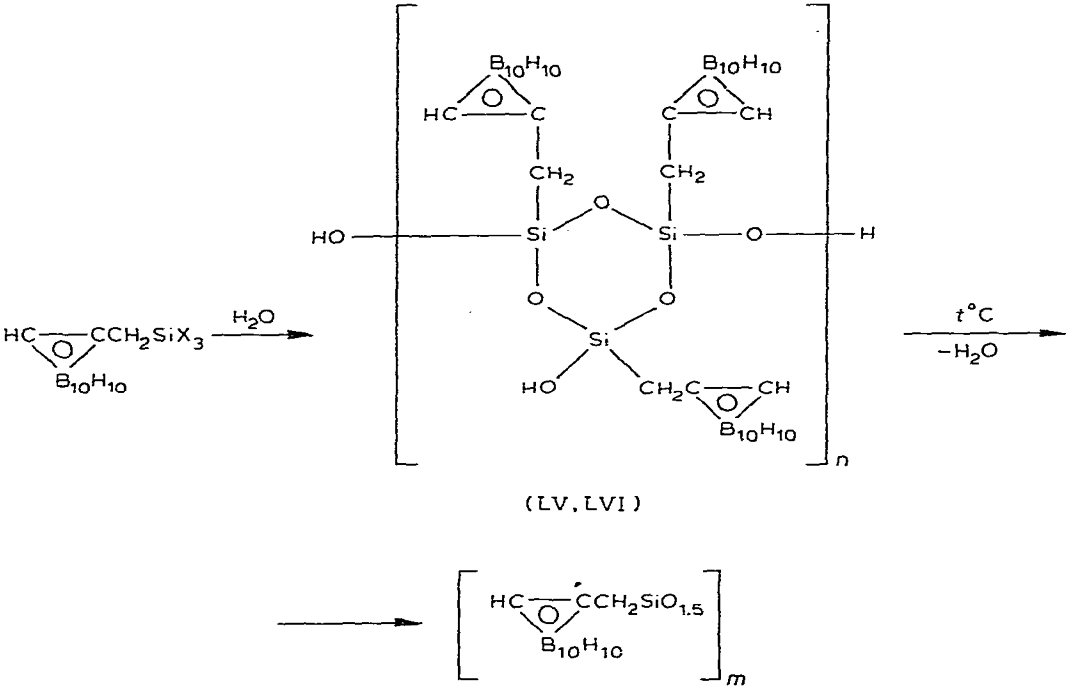
acid, even at room temperature a mixture of organosiloxanols XLIX (80%) and L (15% is formed. Hydrolysis at 60°C proceeds with the formation of organosiloxanols L (95%).

It is of interest that the products XLIX—LI, when heated to 250°C, transform quantitatively into 1,3,5,7-tetrakis(*o*-carboranylmethyl)-1,3,5,7-tetramethylcyclotetrasiloxane (LIII) elimination of with water; the product LII transforms into 1,3,5,7-tetrakis(*m*-carboranylmethyl)-1,3,5,7,-tetramethylcyclotetrasiloxane (LIV).

That carboranylmethyl radicals hinder the formation of high molecular weight compounds, is supported by the study of hydrolysis of *o*-carboranylmethyltrichlorosilane. A complex mixture is formed in this case, containing low molecular weight oligomers of a silsesquioxanic structure with a high content of silanol groups; the general formula of the mixture can be presented as LV or LVI.

The composition of the products is also to a great extent determined by the conditions of hydrolysis. If it is conducted at room temperature, a mixture of products of general formula LV which contain up to six carboranylmethylsilsesquioxanic units is formed. Hydrolysis at 40—45°C gives a mixture of products of general formula LVI, which contain up to nine carboranylmethylsilsesquioxanic units. In a neutral medium *o*-carboranylmethyltrimethoxysilane is hydrolytically stable and remains unchanged upon stirring in water for 6 hours at 40—45°C. Hydrolysis of this compound in 15% hydrochloride acid at room temperature gives a mixture of carboranylmethylsilsesquioxanes of general formular LV, and at 40—45°C a mixture of carboranylmethylsilsequioxanes of general formula LVI.

Condensation of oligomers LV—LVI, even at 250°C does not yield the cross-linked and insoluble products typical of the products of hydrolysis of ordinary organotrichlorosilanes [12]. In this case the soluble products of general for-



(LV, LVI)

(LVII, LVIII)

$n = 2$ (LV), 3 (LVI); $m = 18$ (LVII), 24 (LVIII)

mulae LVII or LVIII, which contain up to eighteen or twenty four carboranylmethylsilsesquioxanic units, are always formed.

The properties and the analytical data of compounds and oligomers XLIII—LVIII are given in Table 3.

Experimental

All compounds synthesized (I—LVIII) are colorless liquid, glass-like or white crystalline or amorphous products readily soluble in ether, acetone, benzene, toluene, and other organic solvents.

Gas liquid chromatography was used to identify the compounds with LKIM-LKIM-8 chromatograph at 230—270°C. The columns (2 m high and 4 mm in diameter) were filled with 5% SE-30 on chromatone (0.205 mm) or 15% "SKTFT-50" on chromatone. Helium was used as carrier gas. The PMR spectra were recorded on Hitachi-Perkin-Elmer R-20 (60 MHz) and Varian T-60A (60 MHz) spectrometers. The IR spectra were recorded on an UR-10 instrument in KBr, NaCl, and LiF plates within the 400—4000 cm^{-1} region.

I. Preparation of C- and C,C'-[alkoxy(organo)silylmethyl]-o(m)-carboranes

Methoxy(dimethyl)silylmethyl-o-carborane (I). A benzene (heptane) solution of butyllithium (0.1 mol, 1.27 *N*) in 79 ml of solvent was added to 14.4 g

TABLE 3

ANALYTICAL DATA FOR COMPOUNDS XLIII—LVIII

Compound	Melting point (°C)	Analysis found (calcd.) (%)						Empirical formula	PMR spectra (ppm, in CCl_4, intern. ref. $CHCl_3$)
		C	H	Si	B	OH	Molecular weight		
XLIII	128.5—129	29.80 (29.97)	8.65 (8.80)	17.39 (17.52)	33.88 (33.72)	10.35 (10.61)	316 (320.59)	$C_8H_{28}Si_2B_{10}O_2$	CH_3 = 0.133; CH_2 = 1.67; OH = 2.16
XLIV [a]		30.15 (30.84)	8.57 (8.73)	18.30 (18.03)	34.92 (34.70)	5.17 (5.46)	632 (623.17)	$C_{16}H_{54}Si_4B_{20}O_3$	—
XLV	52—52.5	25.80 (25.84)	8.50 (8.67)	12.51 (12.08)	46.91 (46.52)	6.60 (7.32)	230 (232.41)	$C_5H_{20}SiB_{10}O$	CH_3 = 0.133; CH_2 = 1.70; OH = 1.90; CH_{cb} = 3.70
XLVI	76—76.5	26.61 (25.84)	8.70 (8.67)	12.24 (12.08)	46.70 (46.52)	7.10 (7.32)	238 (232.41)	$C_5B_{20}SiB_{10}O$	CH_3 = 0.10; CH_2 = 1.46; CH = 2.11; CH_{cb} = 2.80
XLVII	125	26.40 (26.88)	8.44 (8.57)	11.85 (12.57)	48.27 (48.39)	—	415 (446.80)	$C_{10}H_{38}Si_2B_{20}O$	CH_3 = 0.22; CH_2 = 1.66; CH_{cb} = 3.46
XLVIII	93.5—94	26.53 (26.88)	8.20 (8.57)	12.04 (12.57)	48.45 (48.39)	—	430 (446.80)	$C_{10}H_{38}Si_2B_{20}O$	CH_3 = 0.20; CH_2 = 1.53; CH_{cb} = 2.90
XLIX	57—58	22.57 (21.32)	7.77 (7.60)	12.67 (12.46)	47.65 (47.97)	7.50 (7.54)	456 (450.75)	$C_8H_{34}Si_2B_{20}O$	CH_3 = 0.178; CH_2 = 1.80; CH_{cb} = 3.85; OH = 4.11
L	107—108	21.81 (21.75)	7.62 (7.53)	13.15 (12.72)	50.20 (48.95)	4.40 (3.85)	855 (883.48)	$C_{16}H_{66}Si_4B_{40}O_5$	CH_3 = 0.30; CH_2 = 1.80 CH_3 = 0.30; CH_2 = 1.80
LI [b]	—	21.20 (20.50)	7.60 (7.74)	11.33 (11.98)	46.45 (46.13)	14.03 (14.51)	240 (234.38)	$C_4H_{18}SiB_{10}O_2$	CH_3 = 0.25; CH_2 = 1.76; CH_{cb} = 3.83; OH = 4.06
LII [c]	—	20.91 (20.50)	7.51 (7.74)	11.73 (11.98)	46.72 (46.13)	13.70 (14.51)	251 (234.38)	$C_4H_{18}SiB_{10}O_2$	—
LIII	133	22.06 (22.20)	7.30 (7.45)	13.59 (12.98)	48.45 (49.97)	—	930 (865.47)	$C_{16}H_{64}Si_4B_{40}O_4$	CH_3 = 0.38; CH_2 = 1.83; CH_{cb} = 3.75
LIV	77—78	22.15 (22.20)	7.21 (7.45)	31.64 (12.98)	49.02 (49.97)	—	897 (865.47)	$C_{16}H_{64}Si_4B_{40}O_4$	CH_3 = 0.33; CH_2 = 1.60; CH_{cb} = 2.93
LV	—	15.20 (16.73)	6.07 (6.40)	13.92 (13.04)	49.10 (50.20)	5.58 (5.26)	1200 (1292.02)	$C_{18}H_{82}Si_6B_{60}O_{11}$	—
LVI	—	15.95 (16.81)	6.20 (6.40)	13.91 (13.10)	50.02 (50.44)	5.38 (4.41)	2060 (1929.02)	$C_{27}H_{122}Si_9B_{90}O_{16}$	—
LVII	—	16.32 (17.21)	6.18 (6.26)	14.03 (13.42)	50.51 (51.64)	—	3800 (3767.97)	$C_{54}H_{234}Si_{18}B_{180}O_{27}$	—
LVIII	—	16.10 (17.21)	6.21 (6.26)	13.87 (13.42)	50.63 (51.64)	—	4950 (5023.96)	$C_{72}H_{312}Si_{24}B_{240}O_{36}$	—

[a] n_D^{20} = 1.5560. [b] n_D^{20} = 1.5294. [c] n_D^{20} = 1.5401.

(0.1 mol) of *o*-carborane in 100 ml of abs. ether in an argon atmosphere while stirring at room temperature. The reaction mixture was refluxed for 2—3 hours and cooled down to 0°C; 14 g (0.1 mol) of chloromethyl(dimethyl)methoxysilane in 20 ml of abs. ether were added and the mixture was refluxed for 3—5 hours, cooled to room temperature and the residue of lithium chloride was filtered off. The solvents were distilled off in a rotary evaporator and the residue distilled in vacuum. Compound I was obtained (23 g, 93%). Compounds II—XXVIII were prepared by similar procedures.

Ethoxy(dimethyl)silylmethyl-o-carborane (II). Compound II was obtained (23 g, 88%) from 14.4 g (0.1 mol) of *o*-carborane, 79 ml (0.1 mol) of a benzene solution of butyllithium (1.27 *N*), and 15.3 g (0.1 mol) of chloromethyl(dimethyl)ethoxysilane.

1-Methyl-2-methoxy(dimethyl)silylmethyl-o-carborane (III). Compound III (22 g, 84%) was obtained from 16 g (0.1 mol) of methyl-*o*-carborane, 79 ml (0.1 mol) of a benzene solution of butyllithium (1.27 *N*), and 14 g (0.1 mol) of chloromethyl(dimethyl)methoxysilane.

Dimethoxy(methyl)silylmethyl-o-carborane (IV). Compound IV (21 g, 80%) was obtained from 14.4 g (0.1 mol) of *o*-carborane, 60 ml (0.1 mol) of a benzene solution of butyllithium (1.66 *N*), and 15.5 g (0.1 mol) of chloromethyl(methyl)dimethoxysilane.

Diethoxy(methyl)silylmethyl-o-carborane (V). Compound V (24.3 g, 83%) was obtained from 14.4 g (0.1 mol) of *o*-carborane, 60 ml (0.1 mol(of a benzene solution of butyllithium (1.66 *N*), and 18.5 g (0.11 mol) of chloromethyl(methyl)diethoxysilane.

1-Methyl-2-diethoxy(methyl)silylmethyl-o-carborane (VI). Compound VI (23.4 g, 77%) was obtained from 16 g (0.1 mol) of methyl-*o*-carborane, 79 ml (0.1 mol) of a benzene solution of buthyllithium (1.27 *N*), and 18.3 g (0.1 mol) of chloromethyl(methyl)diethoxysilane.

1-Phenyl-2-diethoxy(methyl)silylmethyl-o-carborane (VII). Compound VII (15.6 g, 65%) was obtained from 15 g (0.068 mol) of phenyl-*o*-carborane, 50 ml (0.068 mol) of a benzene solution of butyllithium (1.51 *N*) and 13 g (0.08 mol) of chloromethyl(methyl)diethoxysilane.

Trimethoxysilylmethyl-o-carborane (VIII). Compound VIII (21 g, 78%) was obtained from 14.4 g (0.1 mol) of *o*-carborane, 89 ml (0.1 mol(of a benzene solution of butyllithium (1.12 *N*), and 17 g (0.1 mol) of chloromethyltrimethoxysilane.

Triethoxysilylmethyl-o-carborane (IX). Compound IX (22.4 g, 70%) was obtained from 14.4 g (0.1 mol) of *o*-carborane, 88 ml (0.1 mol (of butyllithium in benzene (1.14 *N*), and 21.3 g (0.1 mol) of chloromethyltriethoxysilane.

1-Methyl-2-triethoxysilylmethyl-o-carborane (X). Compound X (18.4 g, 87%) was obtained from 10 g (0.06 mol) of methyl-*o*-carborane, 46 ml (0.06 mol) of a benzene solution of butyllithium (1.51 *N*) and 16 g (0.08 mol) of chloromethyltriethoxysilane.

1-Isopropenyl-2-triethoxysilylmethyl-o-carborane (XI). Compound XI (21.4 g, 85%) was obtained from 13 g (0.07 mol) of isopropenyl-*o*-carborane, 50 ml (0.07 mol) of a benzene solution of butyllithium (1.4 *N*), and 15 g (0.07 mol) of chloromethyltriethoxysilane.

1-Phenyl-2-triethoxysilylmethyl-o-carborane (XII). Compound XII was obtained from 22 g (0.1 mol) of phenyl-*o*-carborane, 100 ml (0.1 mol) of a benzene solution of butyllithium (1.04 *N*) and 21.3 g (0.1 mol (of chloromethyltriethoxysilane.

Reaction between dilithium-o-carborane and chloromethyl(dimethyl)-methoxysilane. A mixture (40 g) containing 36% of compound I, 27% of compound XIII, and 8% of compound XV was obtained from 14.4 g (0.1 mol) of *o*-carborane, 160 ml (0.2 mol) of a benzene solution of butyllithium (1.27 *N*), and 28 g (0.2 mol) of chloromethyl(dimethyl)methoxysilane, after filtration and distillation of the solvents.

Treatment of 1-methoxy(dimethyl)silylmethyl-2-chloromethyl(dimethyl)-silyl-o-carborane (XIV) with sodium methoxide. A solution of sodium methoxide (0.2 g Na in 50 ml of absolute methanol) was added at room temperature to 40 g of the mixture obtained as described in the previous experiment; the reaction mixture was allowed to stand for 1 h and then poured into water; 50 ml of ether were added and the ether extract, washed with distilled water to a neutral reaction, was dried over magnesium sulphate. The solvent was removed and 35 g of a mixture was obtained; consisting of 55% of compound I, 32% of XIII and 13% of XV (according to GLC). Distillation in vacuum yielded 17 g of I, 4.3 g of XIII, and 1.5 g of XV.

Reaction between 1-methoxy(dimethyl)silylmethyl-2-lithium-o-carborane and chloromethyl(dimethyl)methoxysilane. A mixture (34 g) containing 39.5% of XIII, 40.5% of XIV, 14% of XV, and 6% of XVI (according to GLC) was obtained from 25 g (0.1 mol) of methoxy(dimethyl)silylmethyl-*o*-carborane, 80 ml (0.1 mol) of a benzene (or heptane) solution of butyllithium (1.27 *N*) and 14 g (0.1 mol) of chloromethyl(dimethyl)methoxysilane after filtration and removal of the solvent.

A solution of sodium methoxide (0.2 g Na in 50 ml of absolute methanol) was added to the mixture and kept for 1 h at room temperature. Then the reaction mixture was poured into water and 50 ml of ether were added. The ether extract was washed with distilled water to neutral reaction and dried over magnesium sulphate; after removal of the solvent, 28 g of a mixture was obtained containing (according to GLC) 33.4% of I, 44% of XIII, 16.8% of XV, and 6.8% of XVI. Compounds I (4 g) and XIII (6 g) were separated by vacuum distillation.

1-Methoxy(dimethyl)silylmethyl-2-chloromethyl(dimethyl)silyl-o-carborane (XIV). Compound XIV (30 g, 84.9%) was obtained from 24.6 g (0.1 mol) of methoxy(dimethyl)silylmethyl-*o*-carborane, 79 ml (0.1 mol) of a benzene solution of butyllithium (1.27 *N*), and 14.3 (0.1 mol) of chloromethyl(dimethyl)-chlorosilane.

Butyl(dimethyl)silylmethyl-o-carborane (XVI). A mixture containing 98% of the initial compound (I) and 2% of XVI (as identified by GLC) was obtained from 2.5 g (0.01 mol) of methoxy(dimethyl)silylmethyl-*o*-carborane (I) and 8 ml (0.01 mol) of a benzene solution of butyllithium (1.20 *N*) after the reaction mixture had been allowed to stand for 1 h.

1-Trimethylsilylmethyl-2-methoxy(dimethyl)silylmethyl-o-carborane (XVII). Compound XVIII (3.26 g, 98%) was obtained from 2.3 g (0.01 mol) of trimethylsilylmethyl-*o*-carborane, 8 ml (0.01 mol) of a benzene solution of butyllithium (1.2 *N*) and 1.4 g (0.01 mol) of chloromethyl(dimethyl)methoxysilane.

1-Trimethylsilyl-2-methoxy(dimethyl)silylmethyl-o-carborane (XVIII). Compound XVIII (3.12 g, 98%) was obtained from 2.2 g (0.01 mol) of trimethylsilyl-*o*-carborane, 8 ml (0.01 mol) of a heptane solution of butyllithium (1.2 *N*), and 1.4 g (0.01 mol) of chloromethyl(dimethyl)methoxysilane.

1,3-Di(methyl-o-carboranylmethyl)-1,1,3,3-tetramethyldisiloxane (XIX). (a) A mixture containing 85% of III, 8% of XIX, and 7% of XX (as identified by GLC) was obtained from 2.6 g (0.01 mol) of III and 8 ml (0.01 mol) of a benzene solution of butyllithium (1.2 *N*).

(b) A mixture (2 g) containing 60% of III and 40% of XIX (as identified by GLC) was obtained from 5.2 g (0.02 mol) of III after standing for 1 h in 20 ml of 15% HCl, dissolution in water, extraction with 50 ml of ether, washing of the ether extract with distilled water to a neutral reaction, drying over $MgSO_4$, and evacuation of the solvent. Compound III was distilled off from the mixture and the residue, containing only XIX, was recrystallized from heptane; 0.5 g of XIX was obtained.

1-Methyl-2-butyl(dimethyl)silylmethyl-o-carborane (XX). Compound III (2.6 g or 0.01 mol) and 8 ml (0.01 mol) of a benzene solution of butyllithium (1.2 *N*) were kept at 60°C for 1 h. Compound XX was identified by GLC.

(Methyl-o-carboranylmethyl)(methyl-o-carboranyl)dimethylsilane (XXI). A mixture consisting of (as identified by GLC) 93% of XXI and 7% of the inital methyl-*o*-carborane was obtained from 1.6 g (0.01 mol) of methyl-*o*-carborane, 10 ml (0.01 mol) of a benzene solution of butyllithium (1.2 *N*) and 2.6 g (0.01 mol) of 1-methyl-2-chloro(dimethyl)silylmethyl-*o*-carborane.

Methoxy(dimethyl)silylmethyl-m-carborane (XXII). A reaction mixture containing (as identified by GLC) 45% of XXII and 55% of XXIII was preapred from 14.4 g (0.1 mol) *m*-carborane, 100 ml (0.1 mol) of a benzene solution of butyllithium (1.4 *N*) and 14 g (0.1 mol) of chloromethyl(dimethyl)methoxysilane.

A solution of sodium methoxide (0.2 g Na in 50 ml of absolute methanol) was added to the mixture and kept at room temperature for 1 h; then the mixture was poured into water and 50 ml of ether was added; the ether extract was washed with distilled water to neutral reaction and dried over magnesium sulphate. After removal of the solvent the mixture obtained contained (by GLC data) 70% of XXII and 30% of *m*-carborane. Compound XXII was separated from the mixture by vacuum distillation.

Chloromethyl(dimethyl)silyl-m-carborane (XXIII). A reaction mixture containing only XXIII (according to GLC) was prepared from 1.4 g (0.01 mol) of *m*-carborane, 10 ml (0.01 mol) of a benzene solution of butyllithium (1.04 *N*), and 1.4 g (0.01 mol) of chloromethyl(dimethyl)chlorosilane.

Dimethoxy(methyl)silylmethyl-m-carborane (XXIV). Compound XXIV (7 g) was obtained from 14.4 g (0.1 mol) of *m*-carborane, 100 ml (0.1 mol) of a benzene solution of butyllithium (1.04 *N*), and 14 g (0.1 mol) of chloromethyl(methyl)dimethoxysilane.

Trimethoxysilylmethyl-m-carborane (XXV). Compound XXV (6.3 g) was prepared from 14.4 g (0.1 mol) of *m*-carborane, 100 ml (0.1 mol) of a benzene solution of butyllithium (1.04 *N*), and 14 g (0.1 mol) of chloromethyltrimethoxysilane.

Reaction between dilithium-m-carborane and chloromethyl(dimethyl)-methoxysilane. A mixture (40 g) consisting of 19.1% of XXVI, 57.3% of XXVII and 23.6% of XXVIII (according to GLC) was prepared from 14.4 g (0.1 mol) of *m*-carborane, 160 ml (0.1 mol) of a benzene solution of butyllithium (1.27 *N*), and 28 g (0.2 mol) of chloromethyl(dimethyl)methoxysilane after filtration and removal of the solvents.

Treatment of 1,7-bis[chloromethyl(dimethyl)silyl]-m-carborane and 1-methoxy(dimethyl)silylmethyl-7-chloromethyl(dimethyl)silyl-m-carborane with sodium methylate. A solution of sodium methylate (0.2 g Na in 100 ml of absolute methanol) was added to the mixture obtained as described in the previous experiment and kept at room temperature for 1 h; then the reaction mixture was poured into water and 50 ml of ether was added. The ether extract was washed with distilled water to neutral reaction and dried over magnesium sulphate; the solvents were distilled off and the mixture (36 g) was obtained consisting of (as identified by GLC) 39% of XXVI, 38% of XXII, and 23% *m*-carborane. Compounds XXII (13 g) and XXVII (5 g) were isolated from the mixture by vacuum distillation.

1,2-Bis[chloromethyl(dimethyl)silyl]-m-carborane XXVII. A mixture containing 8% of XXV and 92% of XXVII (as identified by GLC) was obtained from 1.4 g (0.01 mol) of *m*-carborane, 16 ml (0.02 mol) of a benzene solution of butyllithium (1.27 *N*) and 2.8 g of chloromethyl(dimethyl)chlorosilane.

1-Methoxy(dimethyl)silylmethyl-2-chloromethyl(dimethyl)silyl-m-carborane. A mixture consisting of 3% of XXVI and 97% of XXVII (as identified by GLC) was prepared from 2.5 g (0.01 mol) of methoxy(dimethyl)silylmethyl-*m*-carborane (XXII), 8 ml (0.01 mol) of a benzene solution of butyllithium (1.27 *N*) and 1.4 g (0.01 mol) of chloromethyl(dimethyl)chlorosilane.

II. Preparation of C- and C,C′-[chloro(organo)silylmethyl]-o-(m)-carboranes

Chloro(dimethyl)silylmethyl-o-carborane (XXIX). A mixture of compound I (25 g, 0.1 mol) and phosphorus trichloride (28 g, 0.2 mol) or acetyl chloride (16 g, 0.2 mol) or a mixture of compound (II) (26 g, 0.1 mol) and phosphorus trichloride (28 g, 0.2 mol) or acetyl chloride (16 g, 0.2 mol) was kept in a sealed glass ampoule for 10—12 h at 170—175°C. Low-boiling products were distilled off from the mixtures and the residues were subjected to vacuum distillation. Compound XXIX was obtained in 97% yield (24.3 g) and 93% (23.3 g), respectively.

Compounds XXX—XLI were prepared by following the similar procedure.

Chloro(dimethyl)silylmethyl-m-carborane (XXX). Compound XXX (24.3 g, 97%) was obtained from 25 g (0.1 mol) of XXII and phosphorus trichloride (28 g, 0.2 mol).

Dichloro(methyl)silylmethyl-o- (XXXI) and -m-(XXXII)-carboranes. Compounds XXXI (15.6 g, 97%) and XXXII (15.3 of 95%) were prepared from compound V (17 g, 0.06 mol) and phosphorus trichloride (36 g, 0.26 mol) and from XXIV (17 g, 0.06 mol) and phosphorus trichloride (36 g, 0.26 mol), respectively.

1-Methyl-2-dichloro(methyl)silyl-o-carborane (XXXIII). (Compound

XXXIII (27 g, 95%) was obtained from VI (31 g, 0.1 mol) and phosphorus trichloride (25 g, 0.2 mol).

1-Phenyl-2-dichloro(methyl)silylmethyl-o-carborane (XXXIV). Compound XXXIV (14 g, 95%) was obtained from VII (16 g, 0.04 mol) and phosphorus trichloride (25 g, 0.2 mol).

Trichlorosilylmethyl-o- (XXXV) and -m-(XXXVI)-carboranes. Compounds XXXV (19 g, 94%) and XXXVI (20 g, 95%) were prepared from IX (23 g, 0.07 mol) and phosphorus trichloride (48 g, 0.6 mol) and from XXV (23 g, 0.07 mol) and phosphorus trichloride (48 g, 0.6 mol), respectively.

1-Methyl-2-trichlorosilylmethyl-o-carborane (XXXVII). Compound XXXVII (28 g, 93%) was obtained from X (34 g, 0.1 mol) and phosphorus trichloride (48 g, 0.6 mol).

1-Isopropenyl-2-trichlorosilylmethyl-o-carborane (XXXVIII). Compound XXXVIII (31 g, 94%) was obtained from XI (36 g, 0.1 mol) and phosphorus trichloride (48 g, 0.6 mol).

1-Phenyl-2-trichlorosilylmethyl-o-carborane (XXXIX). Compound XXXIX was prepared in 96% yield (35 g) from XII (40 g, 0.1 mol) and phosphorus trichloride (48 g, 0.6 mol).

1,2-Bis[chloro(dimethyl)silylmethyl]-o-carborane (XL). Compound XL (34 g, 95%) was obtained from XIII (35 g, 0.1 mol) and phosphorus trichloride (48 g, 0.6 mol).

1,7-Bis[chloro(dimethyl)silylmethyl]-m-carborane (XLI). Compound XLI (34 g, 95%) was obtained from 35 g (0.1 mol) of XXVI and 48 g (0.6 mol) of phosphorus trichloride.

III. Hydrolysis of C- and C,C'-[alkoxy- and chloro(organo)silylmethyl]-o(m)-carboranes

a) A solution (25%) of 1,7-bis[chloro(dimethyl)silylmethyl]-m-carborane in abs. ether (toluene) was added upon stirring into distilled water of equal volume at a given temperature (20° C). The reaction mixture was stirred for another 3 h, the ether layer was separated, washed to neutral reaction and dried over sodium sulphate. The solvent was removed on a rotary evaporator and the product of hydrolysis was obtained containing, as identified by GLC, 30% of 1,7-bis[hydroxy(dimethyl)silylmethyl]-*m*-carborane (XLIII) and 60% of the product of its dimerization (XLIV).

b) A solution (25%) of 1,7-bis[methoxy(dimethyl)silylmethyl]-*m*-carborane in ether (toluene) was added with stirring to the same volume of 15% hydrochloric acid at 20° C. After performing this operations, we obtained the product of hydrolysis which consisted, according to the GLC data, of 30% of 1,7-bis[hydroxy(dimethyl)silylmethyl]-*m*-carborane (XLIII) and 60% of the product of its dimerization (XLIV).

c) 1,7-Bis[chloro(dimethyl)silylmethyl]-*m*-carborane (2 g or 5.6×10^{-3} mol) as a 25% ether solution was added with intensive stirring to 0.45 g (1.1×10^{-2} mol) of 5% aqueous sodium hydroxide at 0 to —4° C; the ether layer was separated and dried over sodium sulphate; the solvent was removed on a rotary evaporator and the residue was recrystallized from heptane; 1,7-bis[hydroxy(dimethyl)silylmethyl]-*m*-carborane (XLIII) was obtained in 95% yield (1.7 g).

o-Carboranylmethyl(dimethyl)hydroxysilane (XLV) and 1,3-bis(o-car-

boranylmethyl)-1,1,3,3-tetramethyldisiloxane (XLVII). A hydrolysis product (8.76 g, 95%) was obtained from 10 g (3.98×10^{-2} mol) of *o*-carboranylmethyl(dimethyl)chlorosilane by following procedure (a) above; compounds XLV and XLVII were separated from the hydrolysis in product 29.9% (2.77 g) and 59.6% (5.25 g yields), respectively.

8.64 g (93.3%) of the hydrolysis product was prepared from 10 g (4.06×10^{-2} mol) of *o*-carboranylmethyl(dimethyl)methoxysilane by following the procedure (b); 2.8 g (30.2%) of XLV and 5.41 g (60.7%) of XLVII were isolated from the hydrolysis product.

Compound XLV (13 g) was obtained in 90% yield from 15.6 g (6.2×10^{-2} mol) of *o*-carboranylmethyl(dimethyl)chlorosilane in the presence of 2.49 g (6.2×10^{-2} mol) by following procedure (c).

m-Carboranylmethyl(dimethyl)hydroxysilane (XLVI) and 1,3-bis(m-carboranylmethyl)-1,1,3,3,-tetramethyldisiloxane (XLVIII). The hydrolysis product (8.52 g, 92%) was prepared from 10 g (3.98×10^{-2} mol) of *m*-carboranylmethyl(dimethyl)chlorosilane as described in (a) above; compounds XLVI and XLVIII were isolated from the product of hydrolysis in 26% (2.41 g) and 63.8% (5.68 g) yields, respectively.

The hydrolysis product (8.72 g, 94%) was obtained from 10 g (4.06×10^{-2} mol) of carboranylmethyl(dimethyl)methoxysilane as described in (a); compounds XLVI and XVLIII were isolated in 29.7% (2.75 g) and 64.5% (5.75 g) yields, respectively.

Compound XLVI was obtained in 95% (8.62 g) yield from 9.8 g (3.9×10^{-2} mol) of *m*-carboranylmethyl(dimethyl)chlorosilane in the presence of 1.56 g (3.9×10^{-2} mol) of sodium hydroxide.

1,3-Dihydroxy-1,3-bis(o-carboranylmethyl)-1,3-dimethyldisiloxane (XLIX) and 1,7-dihydroxy-1,3,5,7-tetrakis(o-carboranylmethyl)-1,3,5,7-tetramethyltetrasiloxane (L). The hydrolysis product was obtained in 93.6% yield (7.78 g) from 10 g (3.68×10^{-2} mol) of *o*-carboranylmethyl(methyl)dichlorosilane by following the procedure described in (a); compound (XLIX) was isolated from the hydrolysis product in 87.9% yield (7.3 g).

The hydrolysis product (7.80 g, 95.8%) was prepared from 10 g (3.68×10^{-2} mol) of *o*-carboranylmethyl(methyl)dichlorosilane as described in (a) at 60°C; compound L was isolated in 91.6% (7.46 g) yield.

The hydrolysis product (91.4%, 7.85 g) was obtained from 10 g (3.81×10^{-2} mol) of carboranylmethyl(methyl)dimethoxysilane by following the procedure described in (b) at 20°C; compounds XLIX and L were isolated from the product of hydrolysis in (6.28) and 15% (1.17 g) yields, respectively.

The hydrolysis product (85%, 8.24 g) was prepared from 10 g (3.81×10^{-2} mol) of *o*-carboranylmethyl(methyl)dimethoxysilane at 60°C as described in (b); compound L was isolated in 95% yield (8 g).

o-Carboranylmethyl(methyl)dihydroxysilane (LI). Compound LI was obtained in 93.8% yield (4.6 g) from 5.7 g (2.1×10^{-2} mole) of carboranylmethyl(methyl)dichlorosilane in the presence of 1.68 g (4.2×10^{-2} mol) of sodium hydroxide by following the procedure described in (c).

m-Carboranylmethyl(methyl)dihydroxysilane (LII). Compound LII was obtained in 94.7% yield (8.6 g) from 9.8 g (3.9×10^{-2} mol) of *m*-carboranylmethyl)dichlorosilane in the presence of 3.12 g (7.8×10^{-2} mol) of sodium hydroxide as described in (c).

Oligo(o-carboranylmethyl)silsesquioxanes (LV and LVI). The hydrolysis product (7 g, 94.8%) consisting of a mixture of oligomers of the general formula LV was prepared from 10 g (3.43×10^{-2} mol) of *o*-carboranylmethyltrichlorosilane by following the procedure described in (a) at 20°C.

The hydrolysis product (7.2 g, 93.1%) consisting of a mixture of oligomers of the general formula LV was obtained from 10 g (5.59×10^{-2} mol) of *o*-carboranylmethyltrimethoxysilane as described in (b) at 20°C.

The hydrolysis product (6.98 g, 95%) consisting of a mixture of oligomers of the general formula LVI was obtained from 10 g (3.43×10^{-2} mol) of *o*-carboranylmethyltrichlorosilane as described in (a) at 40—45°C.

The hydrolysis product (7.24 g, 94%) consisting of a mixture of oligomers of the general formula LVI was obtained from 10 g (3.59×10^{-2} mol) of *o*-carboranylmethyltrimethoxy silane as described in (b).

IV. Thermal condensation of the hydrolysis products.

The hydrolysis products were heated at 250°C in a flow of dry argon or nitrogen for 45 hours. The condensate thus obtained was recrystallized from heptane.

1,3,5,7-tetra(o-carboranylmethyl)-1,3,5,7-tetramethylcyclotetrasiloxane (LIII). Compound LIII was obtained in 88.1% yield (8.64 g) from 10 g (2.2×10^{-2} mol) of XLIX, in 89.8% yield (8.8 g) from 10 g (1.1×10^{-2} mole) of L, and in 86% yield (6.35) from 8 g (3.4×10^{-2} mol) of LI.

1,3,5,7-tetra(m-carboranylmethyl)-1,3,5,7-tetramethylcyclotetrasiloxane (LIV). Compound LIV was obtained in 87.3% yield (6.85 g) from 8.5 g (3.6×10^{-2} mol) of LII.

Oligo(o-carboranylmethyl)silsesquioxanes (LVII and LVIII). A condensation product was obtained in 90% yield (8.75 g) from 10 g of a mixture of oligomers of the general formula LI; the product consisted of a mixture of oligomers of the general formula LVII. A condensation product consisting of a mixture of the general formula LVIII was prepared in 89% yield (8.1 g) from 10 g of a mixture of oligomers of the general formula LVI.

REFERENCES

1 R. Grimes, Carboranes (Russian translation), Mir, Moscow, 1974.
2 V.V. Korshak, V.A. Zamyatina and N.I. Bekasova, Organoboron Polymers, Nauka, Moscow, 1975.
3 V.N. Kalinin, B.A. Izmailov, A.A. Kazantsev, L.I. Zakharkin and K.A. Andrianov, Dokl. Akad. Nauk SSSR, 426 (1970) 616.
4 N.G. Nokii, Yu.T. Struchkov, V.N. Kalinin and L.I. Zakharkin, Zh. Strukt. Khim., 19 (1978) 380.
5 N.G. Furmanova, Yu.T. Struchkov, V.N. Kalinin, B.Ya. Finkel'shtein and L.I. Zakharkin, Zh. Strukt. Khim., in press.
6 R. Hoffman and W.N. Lipscomb, J. Chem. Phys., 36 (1962) 3489.
7 T.F. Koetzle and W.N. Lipscomb, Inorg. Chem. 9 (1970) 2743.
8 V.N. Kalinin, Doc. Thesis, Moscow, 1977.
9 K.A. Andrianov, Methods of Organoelement Chemistry, Silicon, Nauka, Moscow, 1968.
10 B.A. Izmailov, V.N. Kalinin, V.D. Myakushev, A.A. Zhdanov and L.I. Zakharkin, Zh. Obsch. Khim., 50 (1980) 1558.
11 H. Schroeder, Inorg. Macrom. Rev., 1 (1970) 45.
12 K.A. Andrianov, Polymers with Inorganic Main Chains of Molecules, Nauka, Moscow, 1962.