Synthesis of mono-, di-, tri-, and tetraethyl-*o*-carboranes by electrophilic alkylation of *o*-carborane with ethyl bromide in the presence of $AlCl_3$ and their transformations

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Optimal conditions for the preparation of 9-ethyl-, 9,12-diethyl, 8,9,12-triethyl-, and 8,9,10,12-tetraethyl-*o*-carboranes under the action of EtBr on *o*-carborane in the presence of $AlCl_3$ were determined. The behavior of these *o*-carborane derivatives towards electrophilic and nucleophilic reagents was studied. The presence of four ethyl groups in positions 8, 9, 10, and 12 of the carborane polyhedron increases the electron density on the boron atoms in positions 4, 5, 7, and 11 to the point where they are able to enter into reactions of electrophilic substitution, and in positions 3 and 6 to the point that they become resistant to the action of nucleophilic reagents. Reactions of 1,2-dilithium-8,9,10,12-tetraethyl-*o*-carborane with various electrophilic reagents were studied.

Key words: *o*-carborane, alkylation, Friedel—Crafts reactions, *B*-ethyl-*o*-carboranes, metallation, electrophilic and nucleophilic reactions.

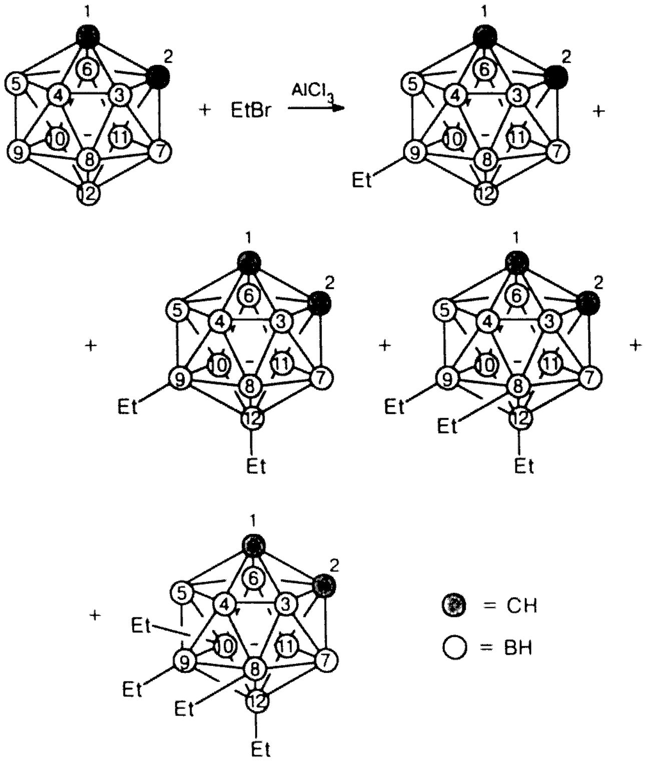
The effect of electron-withdrawing substituents bonded to a boron atom of the polyhedron on the properties of the *o*-carborane system has been studied in detail.[1] At the same time, the effect of electron-releasing substituents at boron atoms on the properties of the *o*-carborane system has not been investigated at all.

In this work, the ethyl group, with the induction constant $\sigma^* = -0.115$,[2] was chosen as the electron-releasing substituent.

Previously, we have shown[3] that *B*-ethyl-(*o* and *m*)-carboranes are readily obtained in the electrophilic alkylation of *o*- and *m*-carboranes by ethyl bromide in the presence of aluminum chloride. Our data were confirmed later by Czech authors.[4]

The reaction of ethyl bromide with *o*-carborane in the presence of $AlCl_3$ results in a mixture of *B*-ethyl-*o*-carboranes of different degrees of alkylation since the electron-releasing effect of the first ethyl group attached to the boron atom facilitates the introduction of the second and subsequent ethyl groups.

A detailed investigation of the alkylation of *o*-carborane by ethyl bromide in the presence of $AlCl_3$ showed that the formation of each of *B*-mono-, -di-, -tri-, and -tetraethylsubstituted *o*-carboranes in the course of the reaction appears to pass through its maximum at a point where the reaction can be brought to a halt, and the desired *B*-ethyl-*o*-carborane can be isolated individually from the mixture of *B*-ethyl-*o*-carboranes obtained by vacuum distillation on a rectification column.



Since up to eight ethyl groups can be introduced[3] in the alkylation of *o*-carborane by ethyl bromide (*i.e.*, not only the boron atoms in positions 8, 9, 10, and 12, as in the electrophilic halogenation of *o*-carborane,[5] but also those in positions 4, 5, 7, and 11 enter the reaction), the question of the order of the replacement of hydrogen

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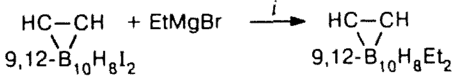
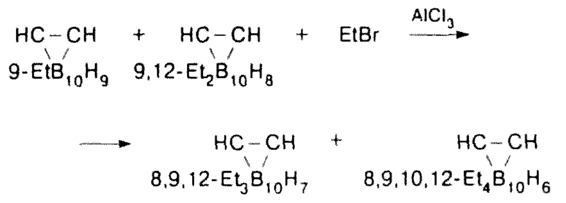
atoms bonded to the boron atoms by ethyl groups inevitably arises. It was shown (using GLC techniques and ^1H and ^{11}B NMR spectroscopy) that *B*-ethyl-, *B*-diethyl-, *B*-triethyl- and *B*-tetraethyl-*o*-carboranes are individual compounds. This is only possible if the first three ethyl groups replace hydrogen atoms in positions 8, 9, and 12, while the first four ethyl groups replace hydrogen atoms in positions 8, 9, 10, and 12 of the *o*-carborane polyhedron. It follows that the order of the introduction of four ethyl groups into *o*-carborane in electrophilic alkylation by ethyl bromide corresponds to the order of the substitution in electrophilic halogenation, and alkylation proceeds first at the boron atoms in positions 8, 9, 10, and 12 of the *o*-carborane polyhedron; in this case no other boron atoms are involved, and only thereafter does the fifth ethyl group enter position 4 (5, 7, 11). This points to the fact that though the introduction of ethyl groups to the boron atoms of *o*-carborane increases the electron density on the boron atoms in positions 4, 5, 7, and 11, this increase is less than on the boron atoms in positions 8 and 10.

The structure of 9-ethyl-*o*-carborane was confirmed by its identity with the product obtained previously from 9-iodo-*o*-carborane.[6] The structure of 9,12-diethyl-*o*-carborane was confirmed by its synthesis from 9,12-diiodo-*o*-carborane and EtMgBr in the presence of Pd-catalyst in a THF solution, analogously to the synthesis of 9,12-dimethyl-*o*-carborane by a procedure we proposed previously:[7]



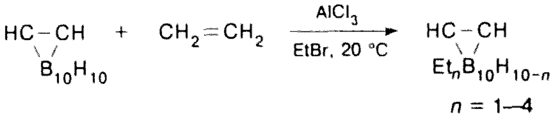
i. THF, Pd-catalyst.

We assumed that the most interesting compound for studying the effect of electron-releasing substituents on the properties of the *o*-carborane system is 8,9,10,12-tetraethyl-*o*-carborane (**1**) because of the pronounced effect of its four ethyl groups on the properties of the *o*-carborane polyhedron. To obtain **1** in a maximum yield, the alkylation reaction is brought to a halt when traces of *B*-pentaethyl-*o*-carborane appear in the reaction mass. The mixture of 9-ethyl- and 9,12-diethyl-*o*-carboranes formed can be further alkylated to 8,9,12-triethyl-*o*-carborane and carborane **1**:



1

Ethylene can be used to obtain $o\text{-}C_2B_{10}H_{10-n}Et_n$ when the reaction proceeds in a solution of ethyl bromide at 20 °C. In this case, the HBr liberated in alkylation is added to ethylene in the presence of $AlCl_3$ to form ethyl bromide, which immediately enters the reaction:



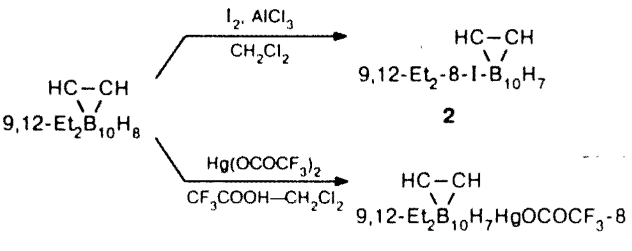
This procedure is of particular convenience for obtaining large amounts of **1**, since in this case much hydrogen bromide is liberated without using ethylene.

The elemental analysis data and several physicochemical properties of $C_2H_2B_{10}H_{10-n}Et_n$ (n = 1—4) are presented in Table 1.

It was found that 9,12-diethyl-*o*-carborane is readily iodinated by iodine in CH_2Cl_2 in the presence of $AlCl_3$ and mercurated by mercury trifluoroacetate in a $CF_3COOH-CH_2Cl_2$ mixture to form 9,12-diethyl-8-iodo-*o*-carborane (**2**) and 9,12-diethyl-8-(trifluoroacetoxy)mercury-*o*-carborane (**3**), respectively:

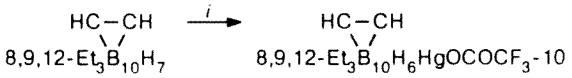
Table 1. Physicochemical properties and the elemental analysis data of *B*-ethylcarboranes *o*-, $m\text{-}C_2H_2B_{10}H_{10-n}Et_n$ (n = 1—4)

Compound	B.p. /°C (1 Torr)	n_D^{20}	d_4^{20}	Found / Calculated (%) C	H	B	Molecular formula
9,12-Diethyl-*o*-carborane	90	1.5342	0.9147	36.81 36.00	9.94 10.00	54.13 54.00	$C_6H_{20}B_{10}$
9,10,12-Triethyl-*o*-carborane	100	1.5350	0.9183	42.35 42.10	10.41 10.53	47.13 47.37	$C_8H_{24}B_{10}$
1	117—118	1.5313	0.9198	46.71 46.80	10.89 10.95	42.04 42.18	$C_{10}H_{28}B_{10}$
9,10-Diethyl-*m*-carborane	87—88	1.5200	0.9072	35.81 36.00	9.79 10.00	54.41 54.00	$C_6H_{20}B_{10}$



3

8,9,12-Triethyl-*o*-carborane is also readily mercurated by mercury trifluoroacetate in a $CF_3COOH-CH_2Cl_2$ mixture to form 8,9,12-triethyl-10-(trifluoroacetoxy)mercury-*o*-carborane (**4**):



4

i. $Hg(OCOCF_3)_2$, $CF_3COOH—CH_2Cl_2$

It is interesting to note that 9,10-diethyl-*m*-carborane is mercurated under these conditions to form 9,10-diethyl-5-(trifluoroacetoxy)mercury-*m*-carborane (**5**):

$$9,10\text{-Et}_2\text{-}m\text{-HCB}_{10}\text{H}_8\text{CH} \xrightarrow[\text{CF}_3\text{COOH—CH}_2\text{Cl}_2]{\text{Hg(OCOCF}_3)_2}$$

$$\longrightarrow 9,10\text{-Et}_2\text{-5-HgOCOCF}_3\text{-}m\text{-HCB}_{10}\text{H}_7\text{CH}$$

5

9,10-Diethyl-*m*-carborane was synthesized from 9,10-diiodo-*m*-carborane and EtMgBr according to a previously described procedure:[7]

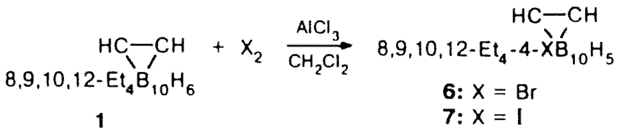
$$9,10\text{-I}_2\text{-}m\text{-HCB}_{10}\text{H}_8\text{CH} + \text{EtMgBr} \xrightarrow{i}$$

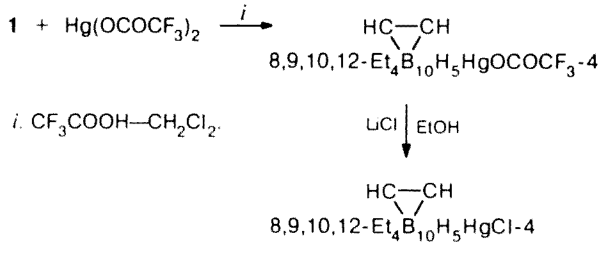
$$\longrightarrow 9,10\text{-Et}_2\text{-}m\text{-HCB}_{10}\text{H}_8\text{CH}$$

i. THF, Pd-catalyst.

It is known[5] that in electrophilic halogenation of *o*-carborane by halogens (Cl_2, Br_2, I_2) in the presence of $AlCl_3$, the hydrogen atoms at the boron atoms in positions 8, 9, 10, and 12 are subjected to substitution to form 8,9,10,12-tetrahalogen-*o*-carboranes, and no further substitution in positions 4, 5, 7, and 11 occurs.

As it has turned out, an increase in the electron density on the boron atoms in position 4 (5, 7, 11) of compound **1** makes the boron atom in this position capable of electrophilic bromination, iodination, and mercuration.





i. $CF_3COOH—CH_2Cl_2$.

8

The reactions presented above are the first examples of electrophilic replacement of the hydrogen atoms in position 4 (5, 7, 11) of the *o*-carborane polyhedron by bromine and iodine atoms. The introduction of a substituent to position B(4) of *o*-carborane converts it into a chiral molecule that can exist as two enantiomers or a racemate.

The structures of *B*-ethyl-*o*-carboranes and of some of their derivatives were confirmed by their ^{11}B and ^1H NMR spectra, whose parameters are listed in Table 2

Table 2. Parameters of ^{11}B NMR spectra of *B*-ethyl-*o*-carboranes $o\text{-}C_2H_2B_{10-n}Et_n$ (n = 2—4) and compounds **7**, **8**, **23** (acetone as solvent)

Compound	δ	$J_{^{11}B-^1H}$ /Hz	Intensity	B (*i*)
9,12-Diethyl-*o*-carborane	8.67 s	—	2	9, 12
	−8.93 d	150	2	8, 10
	−14.42 d	112	4	4, 5, 7, 11
	−16.20 d	124	2	3, 6
8,9,12-Triethyl-*o*-carborane	8.35 s	—	2	9, 12
	1.96 s	—	1	8
	−9.44 d	144	1	10
	−14.16 d	154	2	5, 11
	−15.72	156	3	4, 7, 6
	−18.99 d	166	1	3
1	7.75 s	—	2	9, 12
	1.55 s	—	2	8, 10
	−15.62 d	157	4	4, 5, 7, 11
	−19.64 d	173	2	3, 6
7	8.86 s	—	1	9 (12)
	7.83 s	—	1	12 (9)
	1.69 s	—	2	8, 10
	−12.6÷ −19.1	—	5	3, 5, 6, 7, 11
	−25.1 s	—	1	4
8	8.75 s	—	2	9, 12
	3.09 s	—	2	8, 10
	−6.90* s	—	1	4
	−14.25	172	3	5, 7, 11
	−18.26 d	172	2	3, 6
23	9.01 s	—	2	8, 9
	2.37 s	—	2	10, 12
	−12.32	161	4	4, 5, 7, 11
	−14.49	151	2	3, 6

* $J_{^{199}Hg-^{11}B_4}$ = 2825 Hz.

Table 3. Parameters of ^1H NMR spectra *B*-ethyl-*o*-carboranes (in $(CD_3)_2CO$)

Compound	δ (*J*/Hz)				
	B(9, 12)—CH_2	B(8, 10)—CH_2	B(9, 12)—CH_3	B(8, 10)—CH_3	Other signals
9,12-Diethyl-*o*-carborane	0.65 (q, 4 H, *J* = 7.6)	—	0.84 (t, 6 H, *J* = 7.6)	—	4.25 (br.s, 2 H, carborane CH)
8,9,12-Triethyl-*o*-carborane	0.54 (q, 4 H, *J* = 7.5)	0.66 (q, 2 H, *J* = 7.5)	0.84 (t, 6 H, *J* = 7.5)	1.01 (t, 3 H, *J* = 7.5)	4.17 (br.s, 2 H, carborane CH)
1	0.43 (q, 4 H, *J* = 7.4)	0.65 (q, 4 H, *J* = 7.4)	0.84 (t, 6 H, *J* = 7.4)	1.03 (t, 6 H, *J* = 7.4)	4.09 (br.s, 2 H, carborane CH)
8	0.48 (quintet, 2 H, *J* = 7.8) 0.52 (quintet, 2 H, *J* = 7.8)	0.69 (quintet, 2 H, *J* = 7.8) 0.72 (quintet, 2 H, *J* = 7.8)	0.85 (dt, 3 H, *J* = 7.8) 0.90 (dt, 6 H, *J* = 7.8)	1.03 (dt, 3 H, *J* = 7.8) 1.08 (dt, 3 H, *J* = 7.8)	4.33 (br.s, 1 H, carborane CH) 4.43 (br.s, 1 H, carborane CH)
18	0.43 (q, 4 H, *J* = 7.6)	0.67 (q, 4 H, *J* = 7.6)	0.84 (t, 6 H, *J* = 7.6)	1.02 (t, 6 H, *J* = 7.6)	5.18 (s, 2 H, SCH_2S)
19	0.41 (q, 4 H, *J* = 7.7)	0.69 (q, 4 H, *J* = 7.7)	0.83 (t, 6 H, *J* = 7.7)	1.03 (t, 6 H, *J* = 7.7)	3.27 (s, 4 H, SCH_2CH_2S)
22	0.47 (q, 4 H, *J* = 7.8)	0.65 (q, 4 H, *J* = 7.8)	0.83 (t, 6 H, *J* = 7.8)	1.01 (t, 6 H, *J* = 7.8)	1.50 (s, 12 H, C—CH_3)
23	0.50 (q, 2 H, *J* = 7.7)	0.70 (q, 2 H, *J* = 7.7)	0.86 (t, 3 H, *J* = 7.7)	1.05 (t, 3 H, *J* = 7.7)	2.83 (br.s, 2 H, OH); 4.47 (br.s, 2 H, carborane CH)

and Table 3, respectively. The assignment of the ^{11}B and ^1H NMR signals for these compounds was made by comparing them to the spectra obtained in the absence of the $^{11}B—^1H$ spin-spin decoupling, taking into account the multiplicity and relative intensities of the spectral lines, as well as by using two-dimensional homonuclear $^{11}B—^{11}B$ correlation NMR spectroscopy based on the analysis of the number and positions of the off-diagonal cross-peaks.

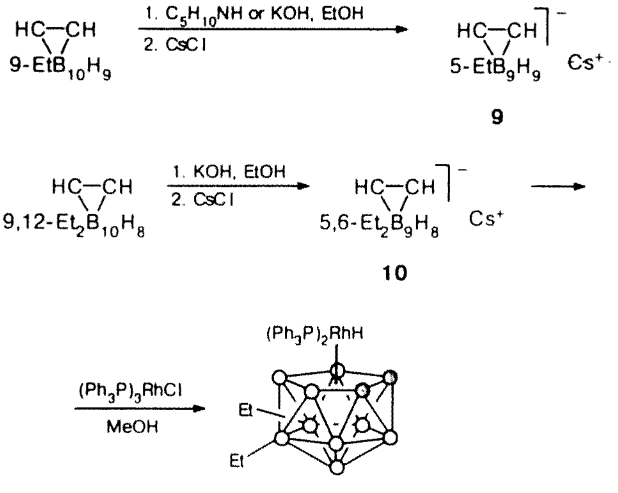
As can be seen from Table 2, the replacement of the hydrogen atoms at the boron atoms of *o*-carborane in positions 9 and 12 by ethyl groups results in appreciable deshielding of the corresponding boron nuclei (Δδ = 11.8). The nuclei of the boron atoms in positions 8 and 10 (Δδ = 0.7) undergo appreciably less deshielding. Introduction of the third ethyl group to position 8 of the *o*-carborane polyhedron results in a downfield shift of the B(8) atom (Δδ = 11.6), whereas the B(10) atom is hardly affected by the shielding effect. The introduction of four ethyl groups in positions 8, 9, 10, and 12 of the *o*-carborane polyhedron also causes a pronounced downfield shift of the signals of the nuclei of these boron atoms, in this case the signals of the nuclei of other boron atoms are shifted upfield. The introduction of a HgCl group in position 4 of compound **1** (compound **8**) causes the strongest deactivation of the nuclei of the atoms in positions 4, 8 and 10, while the introduction of an iodine atom (compound 7) has nearly the same deactivation effect on the boron atoms in positions 8 and 10 (but causes a pronounced upfield shift of the signal of the boron atom in position 4).

The structures of *B*-ethyl-*o*-carboranes *o*-$C_2H_2B_{10}H_{10-n}Et_n$ (*n* = 2—4) were also confirmed by the ^1H NMR spectra (Table 3), in which two groups of signals, corresponding to methylene protons and methyl protons, are clearly seen. It should be noted that the signals of the methylene protons belonging to the ethyl groups are upfield of the signals of the methyl protons, and in all compounds investigated (see Table 3), except for compound **8**, they appear as quadruplets. The signals of the methyl protons are downfield and appear as triplets. A comparison of the ^1H NMR spectra of *B*-ethyl-*o*-carboranes containing different numbers of ethyl groups showed that the values of the chemical shifts of the methyl and methylene protons depend on their position in the polyhedron.

The cleavage of the *closo*-carborane cage under the action of amines[8] or alcoholic alkali[9] to form a *nido*-7,8-dicarbaundecaborate (*nido*-7,8-$C_2B_9H_{12}$)$^-$ anion and remove the boron atom in position 3 or 6 (which have the lowest electron density of all ten boron atoms) from the *o*-carborane polyhedron, is an important reaction in the *o*-carborane series. The presence of electron-withdrawing substituents in *o*-carborane facilitates this reaction.[10]

Under the action of piperidine or alcoholic alkali on *B*-ethyl-*o*-carboranes, 9-ethyl- and 9,12-diethyl-*o*-carboranes appeared to be easily cleaved to form

5-ethyl- and 5,6-diethyl-*nido*-7,8-dicarbaundecaborate anions, respectively:



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11

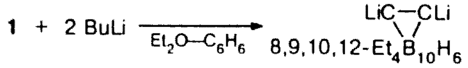
These anions exhibit properties characteristic of *nido*-7,8-dicarbaundecaborate anions. Thus, cesium 5,6-diethyl-*nido*-7,8-dicarbaundecaborate (**10**) readily forms 9,12-Et_2-3,3-$(Ph_3P)_2$-3-H-3,1,2-$RhC_2B_9H_9$ (**11**) with $(Ph_3P)_3RhCl$. Complex **11** is the first representative of rhodacarboranes containing two organic substituents at the boron atoms of the polyhedron.

It has turned out that 8,9,12-triethyl-*o*-carborane and carborane **1** differ significantly from *o*-carborane in their reactions with piperidine and alcoholic alkali: they are stable when boiled in an alcohol solution of potassium hydroxide or with piperidine. This behavior of triethyl- and tetraethyl-*o*-carboranes shows that the introduction of three and four ethyl groups in positions 8, 9, and 12 and 8, 9, 10, and 12, respectively, results in an increase in the electron density on the boron atoms in positions 3 and 6 to the point where they become incapable of undergoing nucleophilic attack by amines and alcoholic alkali.

The acidity of the CH-groups constituting the polyhedral cage is the most important characteristic of *o*-carborane. The value of pK_a of *o*-carborane is 23.3.[11] It was found (using competing metallation by BuLi in an ether-benzene solution of *m*-carborane and tetraethyl-*o*-carborane **1** according to the procedure described in Ref. 12) that the acidity of the CH-groups in compound **1** is 25.4, which is 2.1 pK_a units lower than the acidity of the *o*-carborane and 2.5 pK_a units higher than the acidity of *m*-carborane.

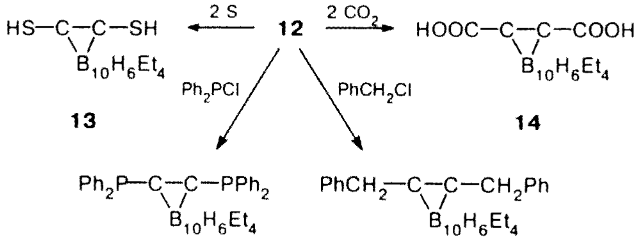
The introduction of four ethyl groups into the *o*-carborane molecule results in the following changes: an increase in its resistance to bases and a decrease in the acidity of the CH-groups and in the electron-withdrawing effect of the 1-*o*-carboranyl group.

Compound **1** with such acidity of its CH-groups, is readily metallated by BuLi in an ether-benzene solution at both CH-groups to form 1,2-dilithium-8,9,10,12-tetraethyl-*o*-carborane (**12**):



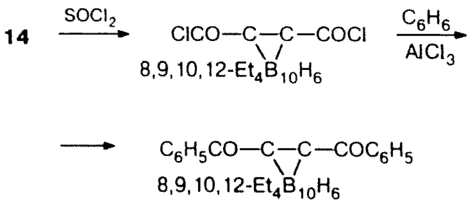
12

Like 1,2-dilithium-*o*-carborane and 1,7-dilithium-*m*-carborane, the dilithium derivative **12** smoothly enters reactions with CO_2, S, Ph_2PCl, and $PhCH_2Cl$, yielding the corresponding disubstituted derivatives:



15 **16**

The properties of compounds **13**, **14**, and **16** and those of the corresponding derivatives of the *o*-carborane differ in a way. Thus, treatment of 1,2-dicarboxylic acid **14** with $SOCl_2$ yields 8,9,10,12-tetraethyl-*o*-carborane-1,2-dicarbonyl dichloride, whereas the use of PCl_5 is needed to obtain of *o*-carborane-1,2-dicarbonyl dichloride.[13] In addition, this dichloride enters conventional Friedel—Crafts reactions with benzene in the presence of $AlCl_3$ to form 1,2-bis(benzoyl)-8,9,10,12-tetraethyl-*o*-carborane (**17**) following the scheme:



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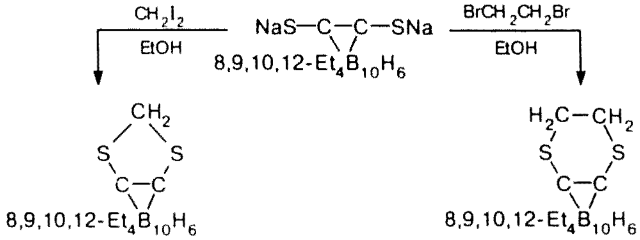
o-Carborane-1,2-dicarbonyl dichloride yields no 1,2-bis(benzoyl)-*o*-carborane in the analogous reaction, since the latter decomposes in the course of the reaction and the *o*-carborane polyhedron is destroyed.[14]

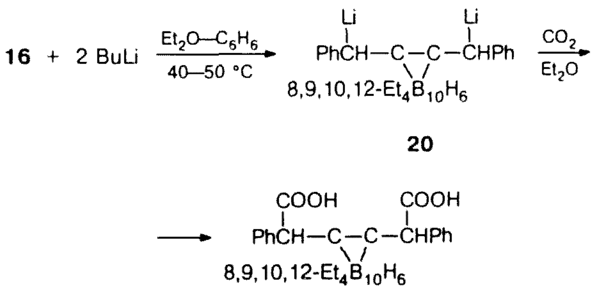
With an alcoholic solution of NaOH the bismercapto derivative **13** forms a disodium derivative, whose reaction with CH_2I_2 and $BrCH_2CH_2Br$ yields compounds **18** and **19** containing five- and six-membered annelated cycles:



18 **19**

The structures of compounds **18** and **19** were confirmed by their mass-spectra and ^1H NMR spectra (Table 3). Note that in contrast to the disodium salt of compound **13** the disodium derivative of 1,2-bismercapto-*o*-carborane forms with 1,2-dibromoethane a dimeric compound, 2,2′-di-μ-(1,2-dithioethane)-bis-*o*-carborane,[15] and its reaction with CH_2I_2 results in a product of cleavage of the *o*-carborane cage, a dimeric anion of 7,7′-8,8′-di-μ-(dithiomethane)-bis-(7,8-dicarbaundecaborate).

In contrast to 1,2-dibenzyl-*o*-carborane,[11] 1,2-dibenzyl-8,9,10,12-tetraethyl-*o*-carborane (**16**) is metallated at methylene groups with BuLi in $Et_2O-C_6H_6$ solution only after prolonged heating and forms a dark-red dilithium derivative **20**, which is insoluble in the $Et_2O-C_6H_6$ mixture. Under the action of CO_2 on compound **20**, the dicarboxylic acid **21** is formed:



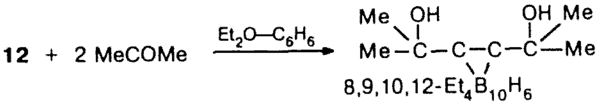
$$\mathbf{16} + 2\,\mathrm{BuLi} \xrightarrow[40-50\ ^\circ C]{Et_2O-C_6H_6} \underset{8,9,10,12\text{-}Et_4B_{10}H_6}{Ph\overset{Li}{C}H-C-C-\overset{Li}{C}HPh} \xrightarrow[Et_2O]{CO_2}$$

20

$$\longrightarrow \underset{8,9,10,12\text{-}Et_4B_{10}H_6}{Ph\overset{COOH}{C}H-C-C-\overset{COOH}{C}HPh}$$

21

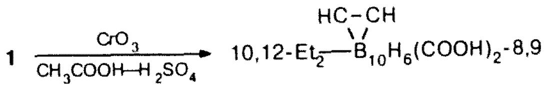
A decrease in the electron-withdrawing effect of the *C*-carboranyl group in compound **1** leads (contrary to *o*-carborane[16]) to a reaction of the dilithium derivative **12** with acetone that yields a di-*tertiary* glycol **22**, which is resistant to bases.



$$\mathbf{12} + 2\,\mathrm{MeCOMe} \xrightarrow{Et_2O-C_6H_6} \underset{8,9,10,12\text{-}Et_4B_{10}H_6}{Me-\overset{Me\ \ OH}{C}-C-C-\overset{OH\ \ Me}{C}-Me}$$

22

Oxidation of **1** with CrO_3 in CH_3COOH under the conditions of the oxidation of 9-alkyl-*o*-carboranes[7] results in oxidation of two ethyl groups and the formation of dicarboxylic acid (**23**):



$$\mathbf{1} \xrightarrow[CH_3COOH-H_2SO_4]{CrO_3} 10,12\text{-}Et_2-\overset{HC-CH}{B_{10}}H_6(COOH)_2\text{-}8,9$$

23

It follows from the ^1H NMR spectrum of acid **23** that the ethyl groups at the nonequivalent boron atoms (B-8 and B-9) are oxidized. This is likely associated with the redistribution of the electron density on the boron atoms in positions 8, 9, 10, and 12 due to the electron-withdrawing effect of the carboxylic group formed. It should be noted that only one methyl group is oxidized to form 9-methyl-12-carboxy-*o*-carborane when 9,12-dimethyl-*o*-carborane undergoes oxidation under these conditions.[7]

It was shown if Ref. 17 that 1-hexyl-*o*-carborane, which is highly lipophilic, has a strong affinity for low-density lipoproteins and may be of interest for boron neutron capture therapy of cancer. In connection with this, the ability of readily available 8,9,12-triethyl- and 8,9,10,12-tetraethyl-*o*-carboranes, having high lipophilicity and low density (d_4^{20} 0.9082 and d_4^{20} 0.9054, respectively), to be accumulated in low-density lipoproteins will be studied.

Experimental

^1H NMR spectra were recorded on a Bruker WP-200SY spectrometer in $(CD_3)_2CO$. ^{11}B NMR spectra were obtained on an AMX-400 spectrometer, and chemical shifts were measured relative to $BF_3 \cdot OEt_2$. Starting substances and reaction products were TLC- and GLC-analyzed on a LKhM-8MD chromatograph (a column (2000×3 mm) with 5% SE-30 on Chromaton N-AW at 120—240 °C; helium was used as the carrier gas at a rate of 80 mL min^{-1}).

General procedure of alkylation of *o*-carborane by ethyl bromide. *o*-Carborane (30 g) and dry EtBr (180 g) were placed into a flask equipped with a stirrer and a reflux condenser connected to a delivery tube for the evolved HBr. After dissolution of *o*-carborane, $AlCl_3$ (3 g) was added, and the mixture was stirred for 2—3 h at 20 °C. Intense HBr liberation occurred. The reaction was GLC-monitored, and samples were taken at fixed intervals. The reaction was completed when the whole amount of *o*-carborane had entered the reaction, the amount of 9-ethyl-*o*-carborane had reached a minimum, and pentaethyl-*o*-carborane had not yet formed. The reaction mass was then poured into water, and two transparent layers were formed. The lower layer was separated, washed with water, and dried over $CaCl_2$. The excess EtBr was removed *in vacuo*, the residue was distilled *in vacuo*, b.p. 78—125 °C (1 Torr), and a mixture of *B*-ethyl-*o*-carboranes (42 g) was obtained. To isolate 9,12-diethyl-, 8,9,12-triethyl-, and 8,9,10,12-tetraethyl-*o*-carboranes, the mixture obtained was fractionally distilled on a rectification column. Several physicochemical properties and the elemental analysis data of *B*-ethyl-*o*-carboranes obtained are listed in Table 1.

9,12-Diethyl-*o*-carborane. A mixture of 9,12-diiodo-*o*-carborane (3.96 g, 10 mmol), ethylmagnesium bromide (40 mmol), and $(Ph_3P)_4Pd$ (0.2 mmol) in abs. THF (60 mL) was boiled for 8 h under an argon atmosphere until disappearance of the starting 9,12-diiodo-*o*-carborane (GLC-monitoring). Then the reaction mass was poured into a 5% solution of HCl (100 mL) and extracted with ether (2×20 mL). The ethereal extracts were washed with water and dried with Na_2SO_4. The solvents were removed, and the residue was distilled *in vacuo*. The yield was 1.9 g (95%), b.p. 90—91 °C (1 Torr).

Alkylation of *o*-carborane by ethyl bromide in the presence of ethylene. *o*-Carborane (30 g) and dry EtBr (100 g) were placed into a flask equipped with a stirrer, a reflux condenser, and an inlet tube for ethylene. After dissolution of *o*-carborane, $AlCl_3$ (3 g) was added, and ethylene was passed into the reaction mass with stirring at 20 °C. The reaction was GLC-monitored. The 9,12-diethyl-, 8,9,12-triethyl-, and

8,9,10,12-tetraethyl-*o*-carboranes obtained were isolated as described above.

9,12-Diethyl-8-iodo-*o*-carborane (2). A mixture of 9,12-diethyl-*o*-carborane (2.0 g, 10 mmol), I_2 (2.54 g, 10 mmol), and $AlCl_3$ (0.13 g, 1 mmol) in methylene dichloride (20 mL) was boiled for 30 min. The reaction mass was poured into water, and the organic layer was separated, washed with a 5% solution of $Na_2S_2O_3$ (20 mL), water, and dried with Na_2SO_4. CH_2Cl_2 was removed *in vacuo*, and the residue was chromatographed on a column with SiO_2 (1.5×10 cm), with heptane as the eluent. Compound **2** (2.6 g, 79%) was obtained after distillation *in vacuo* (b.p. 151 °C, 1 Torr). Found (%): C, 22.34; H, 5.85; I, 39.12. $C_6H_{19}B_{10}I$. Calculated (%): C, 22.08; H, 5.83; I, 38.96.

9,12-Diethyl-8-(trifluoroacetoxy)mercuro-*o*-carborane (3). A mixture of 9,12-diethyl-*o*-carborane (1.8 g, 9 mmol), and $Hg(OCOCF_3)_2$ (3.8 g, 9 mmol) in 10 mL of CH_2Cl_2 was stirred for 1.5 h at 20 °C and then boiled for 1 h (until disappearance of 9,12-diethyl-*o*-carborane from the reaction mixture, TLC-monitoring). The solvent was removed *in vacuo*. Water (20 mL) was added to the residue and the crystals that precipitated were filtered off and recrystallized from a benzene—heptane mixture. White crystals **3** (4.2 g, 91%) were obtained, m.p. 102—103 °C (benzene—heptane). Found (%): C, 18.70; H, 3.58; B, 20.58. $C_8H_{19}B_{10}F_3HgO_2$. Calculated (%): C, 18.72; H, 3.70; B, 21.06.

8,9,12-Triethyl-10-(trifluoroacetoxy)mercuro-*o*-carborane (4). Compound **4** (1.2 g, 85 %) was obtained under the conditions of the synthesis of compound **3** from 8,9,12-triethyl-*o*-carborane (1.2 g, 5.2 mmol) and $Hg(OCOCF_3)_2$ (2.2 g, 5.2 mmol), m.p. 113 °C (benzene—heptane). Found (%): C, 22.17; H, 4.51; B, 19.73. $C_{10}H_{23}B_{10}F_3HgO_2$. Calculated (%): C, 22.19; H, 4.25; B, 19.97.

5-Chloromercuro-9,10-diethyl-*m*-carborane (5) was obtained analogously under the conditions of the synthesis of compound **3** from 9,10-diethyl-*m*-carborane (2 g, 10 mmol) and $Hg(OCOCF_3)_2$ (4.26 g, 10 mmol). The product was isolated as a chloride by treatment of the residue with LiCl in ethanol (2 g in 20 mL). The ethanol was removed, water (30 mL) was added to the residue, and the precipitate was filtered off. Compound **5** (4 g, 92%) was obtained, m.p. 94—95 °C (heptane). Found (%): C, 16.79; H, 4.30; B, 24.76. $C_6H_{19}B_{10}ClHg$. Calculated (%): C, 16.53; H, 4.36; B, 24.83.

9,10-Diethyl-*m*-carborane. A mixture of 9,10-diiodo-*m*-carborane (3.96 g, 10 mmol), ethylmagnesium bromide (40 mmol), and $(Ph_3P)_4Pd$ (0.2 mmol) in abs. THF (60 mL) was boiled for 8 h in an argon atmosphere until disappearance of the starting 9,10-diiodo-*m*-carborane (GLC-monitoring). Then the reaction mass was poured into a 5% solution of HCl (100 mL) and extracted with ether (2×20 mL), and the ethereal extracts were washed with water and dried with Na_2SO_4. The solvents were removed, and the residue was distilled *in vacuo*, b.p. 87—88 °C (1 Torr), n_D^{20} = 1.5200, d_4^{20} = 0.9072.

4-Bromo-8,9,10,12-tetraethyl-*o*-carborane (6). A mixture of **1** (1.8 g, 7 mmol), Br_2 (1.12 g, 7 mmol), and $AlCl_3$ (0.1 g, 0.7 mmol) in CH_2Cl_2 (20 mL) was boiled for 15 min. The reaction mass was poured into water, and the organic layer was separated, washed with water, and dried with Na_2SO_4. CH_2Cl_2 was removed *in vacuo*, the residue was chromatographed on a column with SiO_2 (1.5×10 cm), with heptane as the eluent. Compound **6** (1.9 g, 81%) was obtained after distillation *in vacuo* (b.p. 161 °C, 1 Torr). Found (%): C, 35.88; H, 7.99; Br, 23.96. $C_{10}H_{27}B_{10}Br$. Calculated (%): C, 35.80; H, 8.06; Br, 23.87.

8,9,10,12-Tetraethyl-4-iodo-*o*-carborane (7). A mixture of **1** (1.8 g, 7 mmol), I_2 (1.8 g, 7 mmol), and $AlCl_3$ (0.1 g, 0.7 mmol) in CH_2Cl_2 (20 mL) was boiled for 30 min. The reaction mass was poured into water, and the organic layer was separated, washed with a 5% solution of $Na_2S_2O_3$ (20 mL), water, and dried with Na_2SO_4. CH_2Cl_2 was removed *in vacuo*, the residue was chromatographed on a column (1.5×12 cm) with SiO_2; hexane was used as eluent. Compound **7** (2.3 g, 87%) was obtained, m.p. 42—43 °C (pentane). Found (%): C, 31.74; H, 7.15; I, 33.26. $C_{10}H_{27}B_{10}I$. Calculated (%): C, 31.41; H, 7.06; I, 33.25.

4-Chloromercuro-8,9,10,12-tetraethyl-*o*-carborane (8). A mixture of **1** (1.8 g, 7 mmol) and $Hg(OCOCF_3)_2$ (2.98 g, 7 mmol) was boiled for 2 h in a CH_2Cl_2—CF_3COOH mixture. The solvent was removed *in vacuo*, and the residue was washed with water (30 mL). The water was decanted, and the residue was dissolved in EtOH and filtered. A solution of LiCl in ethanol (2 g in 20 mL) was added to the filtrate. The EtOH was distilled off *in vacuo*, and the residue was washed with water and recrystallized from a benzene—heptane mixture. Compound **8** (3.23 g, 89%) was obtained, m.p. 162—163 °C. Found (%): C, 24.73; H, 6.21; Hg, 39.01. $C_{10}H_{27}B_{10}ClHg$. Calculated (%): C, 24.46; H, 6.15; Hg, 38.55.

Action of ethanolic alkali on 9-ethyl- and 9,12-diethyl-*o*-carboranes. A solution of a corresponding ethylcarborane (10 mmol) and KOH (2 g) was boiled for 5 h in 20 mL of ethanol. The ethanol was distilled off *in vacuo*, and the residue was dissolved in water (15 mL) and extracted with ethyl acetate (2×10 mL). The ethyl acetate was distilled off *in vacuo*, and the residue was dissolved in water (5 mL) and treated with aqueous solution of CsCl; the residue was filtered off and dried. Cesium salts **9** and **10** were obtained. Cesium salt of 5-ethyl-*nido*-7,8-dicarbaundecaborate (**9**): the yield was 2.5 g (86%). Found (%): C, 16.50; H, 5.74; B, 36.44. $C_4H_{16}B_9Cs$. Calculated (%): C, 16.37; H, 5.45; B, 36.83. Cesium salt of 5,6-diethyl-*nido*-7,8-dicarbaundecaborate (**10**): the yield was 2.6 g (82%). Found (%): C, 22.64; H, 6.31; B, 29.95. $C_6H_{20}B_9Cs$. Calculated (%): C, 22.42; H, 6.23; B, 30.26.

Action of piperidine on 9-ethyl- and 9,12-diethyl-*o*-carboranes. Piperidine (40 mmol) was added to 10 mmol of 9-ethyl- or 9,12-diethyl-*o*-carborane in C_6H_6 (10 mL). The reaction mass was kept for 1 h at 20 °C. The solvent was removed *in vacuo*, the residue was suspended in a 10% solution of HCl (20 mL), and ether (20 mL) was added and the mixture was shaken until the salt disappeared. The ethereal solution was separated and washed with water. After removal of ether, the residue was dissolved in water and treated with an aqueous solution of CsCl. Salts **9** and **10** were crystallized from aqueous ethanol in 82—84 % yield.

***Closo*-9,12-diethyl-3,3-bis(triphenylphosphino)-3-hydrido-3,2,1-rhodacarborane (11).** $(Ph_3P)_3RhCl$ (0.92 g, 1 mmol) was added to a solution of salt **10** (0.32 g, 1 mmol) in methanol (20 mL). A light-orange product was formed after stirring and boiling. After the $(Ph_3P)_3RhCl$ disappeared, the methanol was distilled off *in vacuo*; the residue was dissolved in 10 mL of CH_2Cl_2 and filtered, and pentane was added to the filtrate. The yellow crystals that precipitated were filtered off. Complex **11** (0.72 g, 90%) was obtained. Found (%): B, 11.96; Rh, 12.44. $C_{42}H_{50}B_9P_2Rh$. Calculated (%): B, 11.90; Rh, 12.62.

Action of ethanolic alkali on 9,10,12-triethyl-*o*-carborane. A mixture of 9,10,12-triethyl-*o*-carborane (2.3 g, 10 mmol) and KOH (2 g) was boiled in ethanol (20 mL) for 24 h. The ethanol was distilled off *in vacuo*, and the residue was dissolved in water (20 mL) and extracted with hexane, in order to separate unreacted starting 9,10,12-triethyl-*o*-carborane. To isolate 1,5,6-triethyl-*nido*-7,8-dicarbaundecaborate, the aqueous layer was extracted with ethyl acetate (2×10 mL). After distillation of ethyl acetate *in vacuo*, the 1,5,6-triethyl-*nido*-7,8-dicarbaundecaborate anion was not observed. 9,10,12-Triethyl-*o*-carborane (2.0 g) was obtained from the hexane extract.

Action of KOH in ethanol on compound 1. A mixture of **1** (2.5 g, 10 mmol) and KOH (2.5 g) was boiled in ethanol for 24 h. The reaction mass was treated as described above. No 1,5,6,10-tetraethyl-*nido*-7,8-dicarbaundecaborate was observed; compound **1** (2.2 g) was obtained.

1,2-Dilithium-8,9,10,12-tetraethyl-*o*-carborane (12). BuLi (20 mmol) in benzene was added to a solution of **1** (2.56 g, 10 mmol) in abs. ether (20 mL), with stirring under an argon atmosphere at 20 °C. The mixture was stirred for 0.5 h at 20 °C and then for 15 min at boiling. The solution of the dilithium derivative **12** obtained was used in further reactions to synthesize compounds **13**, **14**, **15**, **16**, and **22**.

8,9,10,12-Tetraethyl-1,2-bis(mercapto)-*o*-carborane (13). BuLi (16.9 mmol, 12 mL, 1.45 M^{-1}) in benzene was added to a solution of **1** (2 g, 7.8 mmol) in ether (15 mL) at 10—15 °C. The solution was heated for 30 min at 40 °C and cooled to 20 °C. Powdered sulfur (0.6 g, 18.2 mmol) was added, and the solution was boiled for 3 h. Then the reaction mass was cooled, and water (30 mL) was added. The organic layer was separated, washed with a solution of KOH, and dried with $CaCl_2$. Compound **13** (2.4 g, 93%) was obtained after removal of the solvent, m.p. 63—64 °C (pentane). Found (%): C, 37.78; H, 8.60; S, 20.13. $C_{10}H_{28}B_{10}S_2$. Calculated (%): C, 37.50; H, 8.75; S, 20.00.

1,2-Dicarboxy-8,9,10,12-tetraethyl-*o*-carborane (14). A benzene solution of BuLi (6 mL, 1.42 *M*) was added to a solution of **1** (1 g, 3.9 mmol) in ether (10 mL) at 10—15 °C. The solution was heated for 30 min at 40 °C, cooled, and poured into a mixture of solid carbon dioxide with abs. ether. Water (20 mL) was added to the reaction mass after evaporation of CO_2, and the aqueous solution was acidified with hydrochloric acid. The acid that formed was extracted with ether. Acid **14** (1.15 g, 85%) was obtained after drying over Na_2SO_4 and removal of ether, m.p. 236—237 °C (with decomp.) from a benzene—heptane mixture. Found (%): C, 42.36; H, 8.28; B, 31.19. $C_{12}H_{28}B_{10}O_4$. Calculated (%): C, 41.86; H, 8.14; B, 31.40.

8,9,10,12-Tetraethyl-1,2-bis(diphenylphosphino)-*o*-carborane (15). Ph_2PCl (1.6 g, 8.1 mmol) in abs. ether (5 mL) was added to dilithium derivative **12**, obtained analogously as described above from 1 g of compound **1** and 6 mL of benzene solution of BuLi (1.45 *M*) in 10 mL of abs. ether. The mixture was heated for 1 h, cooled, water (20 mL) was added, and the mixture was extracted with benzene (2×10 mL). Phosphine **15** (2.3 g, 93%) was obtained after drying over Na_2SO_4 and removal of benzene, m.p. 223—224 °C (benzene—hexane). Found (%): C, 65.88; H, 7.33; B, 17.68. $C_{34}H_{46}B_{10}P_2$. Calculated (%): C, 65.38; H, 7.37; B, 17.30.

1,2-Dibenzyl-8,9,10,12-tetraethyl-*o*-carborane (16). $PhCH_2Cl$ (4 g, 11.7 mmol) in 20 mL of abs. ether was added to dilithium derivative **12** obtained analogously as described above from 3 g of compound **1** and 18 mL of benzene solution of BuLi (1.42 *M*). The mixture was boiled for 3 h. LiCl precipitated. The mixture was cooled, poured into water (40 mL), extracted with ether, and dried with $CaCl_2$. Compound **16** (4.7 g, 90%) was obtained after removal of ether *in vacuo*, m.p. 67 °C (pentane). Found (%): C, 66.16; H, 9.33; B, 24.18. $C_{24}H_{40}B_{10}$. Calculated (%): C, 66.05; H, 9.16; B, 24.80.

1,2-Bis(benzoyl)-8,9,10,12-tetraethyl-*o*-carborane (17). A mixture acid **14** (0.4 g, 1.2 mmol) in $SOCl_2$ (4 mL) was boiled for 3 h, and the excess $SOCl_2$ was distilled off *in vacuo*. Dry benzene (5 mL) and $AlCl_3$ (0.2 g, 1.5 mmol) were added to the residue, and it was boiled for 1 h until HCl evolution ceased. The reaction mass was cooled, washed with a 5% solution of HCl, water, and dried with Na_2SO_4. Compound **17** (0.5 g, 90%) was obtained after removal of the solvent and crystallization from pentane, m.p. 69—70 °C. Found (%): C, 62.17; H, 7.79; B, 22.98. $C_{24}H_{36}B_{10}O_2$. Calculated (%): C, 62.06; H, 7.75; B, 23.29. IR (KBr), ν/cm^{-1}: 1674 (CO), 2600 (BH).

8′,9′,10′,12′-Tetraethylcarborano[1,2-*d*]-1,3-dithiolane (18). CH_2I_2 (1.2 g, 4.4 mmol) was added to the disodium derivative obtained from bismercapto derivative **13** (1.2 g, 3.8 mmol) and Na (0.2 g) in EtOH (10 mL). The mixture was heated for 30 min, cooled, poured into water, and extracted with hexane (2×10 mL). The hexane extracts were washed with a 2% solution of KOH (2×5 mL) and dried over $CaCl_2$. Compound **18** (1.18 g, 91%) was obtained after removal of hexane, m.p. 54—55 °C (pentane). MS, *m/z*: 332 [M$^+$]. Found (%): C, 40.02; H, 8.38; S, 18.93. $C_{11}H_{28}B_{10}S_2$. Calculated (%): C, 39.76; H, 8.43; S, 19.30.

8′,9′,10′,12′-Tetraethylcarborano[1,2-*b*]-1,4-dithiane (19) was obtained analogously to the preceding compound from bismercapto derivative **13** (1.2 g), Na (0.2 g) in EtOH (10 mL), and dibromoethane (0.8 g). Compound **19** (1.17 g, 90%) was obtained after the usual workup, m.p. 62—63 °C (pentane). MS, *m/z*: 346 [M$^+$]. Found (%): C, 41.43; H, 8.77; S, 18.32. $C_{12}H_{30}B_{10}S_2$. Calculated (%): 41.56; H, 8.67; S, 18.49.

1,2-Di(α-carboxybenzyl)-8,9,10,12-tetraethyl-*o*-carborane (21). A benzene solution of BuLi (15 mL, 1.4 *M*) was added to a solution of compound **16** (2.18 g, 10 mmol) in abs. ether (15 mL) at 10—15 °C. The solution turned pale yellow. The mixture turned dark-red in the course of boiling for 3 h, and two layers were formed. The reaction mass was cooled and poured into a mixture of solid carbon dioxide in abs. ether. After evaporation of CO_2, the mixture was acidified with a 10% solution of HCl, and the ether-benzene layer was separated and dried over $CaCl_2$. Acid **21** (4.82 g, 92%) was obtained after removal of the solvents *in vacuo*, m.p. 163 °C (heptane). Found (%): C, 60.03; H, 7.87; B, 21.01. $C_{26}H_{40}B_{10}O_4$. Calculated (%): C, 59.54; H, 7.63; B, 20.64. IR (KBr), ν/cm^{-1}: 1730 (CO), 2600 (BH), 3000 (OH).

8,9,10,12-Tetraethyl-1,2-di(2′-hydroxyisopropyl)-*o*-carborane (22) was synthesized from dilithium derivative **12** (obtained from compound **1** (2.56 g, 10 mmol) in abs. ether (20 mL) and 16.7 mL of BuLi, 1.32 *M*) and acetone (1.5 g, 25 mmol). The reaction mass was stirred for 3 h at 20 °C, boiled for 30 min, cooled to 15 °C, and acidified with a 10% solution of HCl. The organic layer was separated, washed with water, and dried over Na_2SO_4. Glycol **22** (3.1 g, 90%) was obtained as a viscous oil after removal of the solvents. The identity of the product was established by TLC. Found (%): C, 52.00; H, 10.93; B, 29.54. $C_{16}H_{40}B_{10}O_2$. Calculated (%): C, 51.61; H, 10.75; B, 29.03. IR (KBr), ν/cm^{-1}: 2600 (BH); 2850—3000 (CH_2, CH_3); 3464 (OH assoc.); 3595 (OH nonassoc.).

8,9-Dicarboxy-10,12-diethyl-*o*-carborane (23). CrO_3 (7 g, 70 mmol) was added portionwise with stirring to a solution of **1** (2.4 g, 9.3 mmol) in a mixture of CH_3COOH (25 mL) and H_2SO_4 (2.5 mL) at 15 °C. The mixture was stirred for 2 h at 20 °C until **1** disappeared (TLC-monitoring). The reaction mass was poured into water (100 mL) and extracted with ether. The ethereal solution was extracted with a 7% solution of KOH (50 mL). The alkaline extract was acidified with HCl, the acid that precipitated was extracted with ether and dried with Na_2SO_4. Acid **23** (2.3 g, 85%) was obtained after removal of ether *in vacuo*, m.p. 240 °C (benzene—heptane). Found (%): C, 33.30; H, 7.03; B, 37.88. $C_8H_{20}B_{10}O_4$. Calculated (%): C, 33.33; H, 6.94; B, 37.50.

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