SYNTHESIS OF B-ALKYL DERIVATIVES OF *o*-CARBORANE BY ALKYLATION UNDER ELECTROPHILIC CONDITIONS; SCOPE AND LIMITATION

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The reaction of *o*-carborane with 13 alkylation agents in CS_2 over $AlCl_3$ using different ratios of reactants was investigated. Alkylation succeeded with CH_3X, C_2H_5X and i-C_3H_7X whereas other used agents failed. Only i-C_3H_7Br alkylated in nitromethane. A rich mixture resulted even with *o*-carborane: RX 1 : 1 ratio. In the presence of H_2SO_4 *o*-carborane was isopropylated with i-C_3H_7OH, no other alcohols or olefins reacted. Alkyls enter stepwise B-9(12) > B-8(10) > B-4(5,7,11) positions, facilitating always the introduction of further alkyl into the skeleton. On ethylation, the most ethylated product was 4,5,7,8,9,10,12-$(C_2H_5)_7$-1,2-$C_2B_{10}H_5$. Seven B-alkyl and polyalkyl derivatives were isolated as individua. With C_6H_5Br–$AlCl_3$ no reaction occurred at 27°C, while only a transfer of Br into 9-position was observed at 127°C. Possible mechanisms of B-substitution under electrophilic conditions are discussed.

The alkylation of boranes and heteroboranes with alkyl halogenides in the presence of aluminium chloride is a rather long story. Successful results were recorded first with pentaborane (9) (ref.[1,2]) and decaborane (14) (ref.[2,3]) which became even a ground of the extensive programs HEF and ZIP (ref.[4]), focused on the production of efficient rocket fuels. Since the B-alkylation proceeds under the conditions of an electrophilic substitution, most investigators considered it for a simple analogy of the Friedel–Crafts alkylation of aromatic hydrocarbons, in spite of the fact that the real mechanism was not proved. An application to *closo*-heteroboranes was realized later on. According to the patent literature[5], it is possible to prepare in a similar way from icosahedral *closo*-carborane and alkyl halogenides a mixture of B-alkyl derivatives the separation of which has failed. Recent publication dealing with the alkylation of icosahedral heteroboranes under electrophilic condition has been published by Zakharkin and coworkers[6] who have found that these substrates react with methyl, ethyl and isopropyl halogenides in the presence of $AlCl_3$, yielding a mixture of B-alkyl and polyalkyl derivatives. In some cases, however, the main reaction was exchange of a terminal hydrogen for a halogen from the alkylation agent. This reaction was observed in all cases. The cited authors have presumed that *a*) the alkylation is an electrophilic substitution, *b*) a catalytic amount of $AlCl_3$ is sufficient, *c*) first alkyl facilitates further alkylation, *d*) alkyl conserves its identity also in the product, *e*) up to eight

alkyl groups enter stepwise the molecule of an icosahedral carborane. Alkyls are believed to occupy B-atoms according to the decreasing electron density. Though these presumptions sound very reasonably, the published experimental data do not justify it. The authors[6] worked always with a surplus of halogenide using it as solvent, and practically in all cases they isolated only liquid fractions which were characterized by some physical constants and by the elemental analysis. The number of components was determined by GLC and only exceptionally individual compounds were characterized by mass spectrometry. Possibility of a nucleophilic substitution under electrophilic conditions[7-9] has not be considered though this kind of mechanism cannot be excluded with polyhedral species[10]. It is after all the case of an exchange reaction between icosahedral *closo*-compouds and alkyl halogenides leading to B-halogen derivatives[6].

We have followed the alkylation of *closo*-heteroboranes from the standpoint of the scope, the limitation and a probable mechanism of this reaction. We have limited our experiments to 1,2-dicarba-*closo*-dodecaborane (*o-carborane*; *I*) as the passive component and we have investigated its behaviour towards thirteen alkylation agents without solvent, in CS_2 and partly in nitromethane. Very soon it has been proved that the use of excess halogenide as a solvent[6] is unsuitable for the preparation of individual compounds. Under these conditions an unseparable mixture of B-polyalkyl derivatives was always obtained. With i-C_3H_7Br and t-C_4H_9Cl the reaction proceeds almost explosively, the main products are, however, telomers of appropriate olefines, whereas with the last component, the *o*-carborane can be almost quantitatively recovered.

Much better results have been achieved reacting *I* with RX (molar ratio 1 : 1) in the presence of 0·2 mol of $AlCl_3$ and using carbon disulfide as solvent, *i.e.* under conditions which were successful in alkylations of decaborane[2,3]. Also under these conditions, however, a mixture resulted in which B-monoalkyl and B,B′-dialkyl derivatives prevailed whereas higher polyalkyl derivatives were present only in traces. Nitromethane as a solvent disabled the reaction in all cases with exception of i-C_3H_7Br when it proved to be better solvent than carbon disulfide.

Reaction mixtures were analyzed qualitatively by TLC and in the case of a positive alkylation they were followed quantitatively by HPLC and GLC. With main products, the molecular mass was determined by combined GLC and mass spectrometry. The isolation of crystalline products succeeded when combining sublimation, crystallization from hexane at −75°C and chromatography on a silica gel column. With liquid products, the isolation of individual compounds was successful only by the help of the preparative HPLC. The constitution of pure compounds was proved by mass, ^1H- and ^{11}B-NMR spectrometry. Survey of results is in Table I.

Zakharkin's statement[6] that the first alkyl enables further alkylation has been now confirmed by the fact that even at the 1 : 1 reactants ratio a mixture of several compounds resulted. With methylation, 9-CH_3-1,2-$C_2B_{10}H_{11}$ (*Ia*) and 9,12-$(CH_3)_2$-

-1,2-$C_2B_{10}H_{10}$ (*IIa*) originated. Similar result was obtained with ethylation in which 9-C_2H_5-1,2-$C_2B_{10}H_{11}$ (*Ib*) and 9,12-$(C_2H_5)_2$-1,2-$C_2B_{10}H_{10}$ (*IIb*) resulted. In both cases, the monoalkyl derivative dominated over the dialkyl species. Quantitative results of both of these alkylations are perceptible from Table II, and some properties

TABLE I

Reaction of *o*-carborane with alkylating agents over $AlCl_3$ (molar ratios 1 : 1 : 0·2, in CS_2, 25°C, 48 h)

Alkylating agent	B-Alkyl derivatives, %	*o*-Carborane recovered, %
CH_3Br	48·5	41·3
CH_3I	10·5	77·2
$(CH_3)_2SO_4$	2·0	92·0
C_2H_5Br	64·4	33·3
i-C_3H_7Br[a]	59·5	27·8
n-C_4H_9Br	[c]	95·4
C_6H_5Br	[b]	97·1
t-C_4H_9Cl	[c]	92·1
$(C_6H_5)_3CCl$	[d]	94·7
CH_2=CH—CH_2Cl	[c]	87·3
Cyclohexene	[e]	95·8
1-Heptene	[e]	94·4
C_6H_5—C≡CH	[c]	85·2

[a] Very rich mixture in CS_2 (Table VII); in nitromethane 43% of B-monoisopropyl derivatives and 46% of recovered *I*. No other alkylating agent afforded B-alkyl *o*-carboranes in this solvent. [b] No reaction at 27°C; almost quantitative halogen exchange at 127°C after 2 h. [c] Polymerization of the particular alkene under evolution of alkyl halide was observed, no B-alkyl carborane was detected by TLC. [d] No reaction. [e] Both reactants remained unchanged.

TABLE II

Methylation and ethylation of *o*-carborane in CS_2 under standard conditions (determined by HPLC)

R—X	*o*-Carborane recovered, %[a]	9-R- %	9,12-R_2- %	Polyalkyl %
CH_3Br	41·3	26·0	19·1	3·4
C_2H_5Br	33·3	44·2	18·4	1·8

[a] Based on the peak area ratios.

of compounds *Ia*, *Ib*, and *IIa*, *IIb* together with properties of further described alkyl derivatives are shown in Tables III – V.

Ethylation was also realized in excess ethyl bromide as a solvent, *i.e.* under conditions used by Zakharkin[6]. After 96 h at 20°C a mixture of products was separated on a silica gel column yielding two fractions. Elution with hexane afforded fraction A which contained all defined products of the alkylation. Subsequent elution with benzene yielded fraction B, composed of unidentified polymer-like products. The fraction A contained according to HPLC four compounds which were isolated by the preparative HPLC and their constitution determined by the combination of mass, ^{1}H and ^{11}B-NMR spectroscopy. The data are gathered in Table VI. The fraction B rendered after drying *in vacuo* to a yellow, fragile, in hexane and methanol soluble mass. At TLC with hexane as the eluent it remained on the start, which excluded the presence of a monoskeletal polyalkyl derivative. According to the $CH_{carborane}$: : CH_{alkyl} ratio there are 16 CH_2 fragments on each *o*-carborane molecule. The elemental analysis has documented that product is a mixture with ratio B : C : H : Br = = 10 : 12·4 : 10·7 : 0·26.

The hexaethyl derivative *V* (Table VI) is likely a mixture of all three possible isomers with four substituents in positions 8, 9, 10 and 12, and further two alkyls in positions 4,5 or 4,7 or 4,11. Compound *V* shows only one peak at HPLC and GLC, and also ^{11}B-NMR spectrum (at 32·1 MHz) does not allow to reveal an unhomogeneity. The ^{1}H-NMR spectrum (Table IV) shows, however, presence of isomers, with prevailing 4,5 and 4,7 isomers (*i.e.* those having a symmetry plane) over the 4,11-isomers in a 4 : 1 ratio. This example is a characteristic illustration of difficulties which appear when synthetizing B-alkyl derivatives by the alkylation under electrophilic conditions.

Even more complicated is the action of 2-bromopropane on *o*-carborane. In nitromethane, the alkylation afforded a mixture composed of 46% of unreacted *o*-carborane and 54% of a fraction distilling at 77 – 107°C (bath) and 1·3 Pa. This liquid contained (according to the GLC-mass spectroscopy) B-mono- and B,B′-diisopropyl derivatives in the 9 : 1 ratio. Repeated distillation *in vacuo* at 82 – 87°C (bath) afforded 43%(based on starting compound) of species *Id* (for properties see Table III) which was identified as a mixture of 8- and 9-isopropyl-*o*-carborane in a 1 : 1 ratio. This mixture failed to be separated by HPLC and GLC. An evidence that it is a mixture was given by ^{1}H- (Table IV) and especially ^{11}B-NMR spectroscopy (Table V). Alkylation according to Zakharkin[6], *i.e.* with excess isopropyl bromide as solvent, afforded a mixture, containing at minimum 14 compounds (Table VII) though according to the original paper[6] only a mixture of B-mono- and B,B′-diisopropyl derivatives in a ratio 1 : 1 should originate. It is interesting that in the main fractions (Table VII) no alkylated compound has been found in which the alkyl is a multiple of the starting C_3H_7 group. This shows clearly that the identity of the isopropyl group was not retained in this case. Alkylation in CS_2 with a 1 : 1 component ratio had a similar

TABLE III

Some properties of the B-alkyl *o*-carboranes R_x-1,2-$C_2B_{10}H_{12-x}$

Compound	R_x	Position	M.p., °C	Distil. °C[a]/13 Pa	*M/z*	HPLC[b]	GLC[c]	
							at 132°C	at 180°C
Ia	CH_3	9	163—165	40[d]	160	10·9	7·0	2·0
Ib	C_2H_5	9	14	60	174	9·4	10·6	3·0
IIa	$(CH_3)_2$	9,12	157—158	50[d]	174	8·5	8·5	2·4
IIb	$(C_2H_5)_2$	9,12	liq.	75	202	8·3	—	4·5
III	$(C_2H_5)_4$	8,9,10,12	liq.	115	258	4·9	—	11·3
IV	$(C_2H_5)_5$	4,8,9,10,12	liq.	132	286	4·3	—	19·4
V	$(C_2H_5)_6$	4,y,8,9,10,12	25—27	145	314	3·8	—	32·0
VI	$(C_2H_5)_7$	4,5,7,8,9,10,12	liq.	158	342	3·3	—	52·0
Ic	i-C_3H_7[e]	9	liq.	86	188	10·5	18·5	3·5
Id	i-C_3H_7[f]	8 + 9	liq.	85	188	10·5	18·5	3·5
IIc	i-$(C_3H_7)_2$	n, m[g]	liq.	—	230	8·3	—	7·0

[a] Bath temperature. [b] Retention time in min, *o*-carborane = 14·7, 300 × 3·7 mm column packed with 13 μm silica gel, heptane as eluent 1·5 ml/min, pressure drop 3·1 MPa, refractive index detection. [c] Retention time in minutes; *o*-carborane 6·0 min at 132°C and 1·9 min at 180°C, 2 400 mm column with 3% SE 30 on Chromosorb G-AW, N_2 as carrier gas, FID. [d] Sublimation. [e] From i-C_3H_7OH–H_2SO_4; acording to ^{11}B-NMR *c.* 8% of the isomer 8 was present. [f] From i-C_3H_7Br–$AlCl_3$ in nitromethane, a mixture of isomers 8 and 9 not resolved by HPLC and GLC; about 1 : 1 according to ^{11}B-NMR (Table V). [g] Positions 8(10) and 9(12) are involved, a mixture of isomers is not excluded although they were not resolved by HPLC and GLC.

course. Also under these circumstances, 28% of starting *o*-carborane was recovered but the mutual ratio of components A – O was different from that shown in Table VII, with compounds B – E prevailing. From this mixture, a fraction (25%) composed of three compounds was separated. One of them is compound *Ia*, the remaining two components are – according to GLC-mass spectrometry – *Ib* and a compound which we believe to be B-methyl-B'-ethyl-*o*-carborane. Fig. 1 shows the mass spectra of all three components. As the spectrum of compounds *Ia* and *Ib* demonstrates, at least the first alkyl is split off as a unit. Indisputable presence of compounds *Ia* and *Ib* in the product of "isopropylation" demonstrates that fragmentation of the original alkyl takes place. The course of isopropylation of *o*-carborane is thus distinctly different from the course of the Friedel–Crafts isopropylation of benzene, in which without complication a mixture of mono- and diisopropyl derivatives results.

On the other hand, the isopropylation of *o*-carborane was accomplished with 2-propanol in the presence of sulfuric acid, *i.e.* under conditions similar to those of isopropylation of benzene. In the case of *o*-carborane, practically pure 9-i-C_3H_7--1,2-$C_2B_{10}H_{11}$ (*Ic*) was obtained which according to the ^{11}B-NMR spectrum contained at most 8% of the 8-isomer. Under these conditions, no other alcohols (CH_3OH, C_2H_5OH, $C_5H_{11}OH$, t-C_4H_9OH, $C_6H_{11}OH$) or olefine (cyclohexene, 1-hexene) alkylated *o*-carborane.

TABLE IV

^{1}H-NMR signals of B-alkyl carboranes R_x-1,2-$C_2B_{10}H_{12-x}$ (at 100 MHz in $CDCl_3$)

Compound	R_x	R_x-Positions	C—H Carborane		C—H Alkyl	
			ppm	intensity	ppm	intensity
o-Carborane	H		3·52	2	—	—
Ia	CH_3	9	3·40 + 3·45	1 + 1	0·23	3
Ib	C_2H_5	9	3·38 + 3·43	1 + 1	0·83[a]	5
IIa	$(CH_3)_2$	9, 12	3·32	2	0·21	6
IIb	$(C_2H_5)_2$	9, 12	3·36	2	0·86[a]	10
IV	$(C_2H_5)_5$	4, 8, 9, 10, 12	3·24[a]	2	0·76[a]	25
V	$(C_2H_5)_6$	4, y, 8, 9, 10, 12[b]	3·10 + 3·22	0·4 + 1·6	0·82[a]	30
VI	$(C_2H_5)_7$	4, 5, 7, 8, 9, 10, 12	3·08 + 3·24	1 + 1	0·90[a]	35
Ic	i-C_3H_7	8 + 9 (1 : 9)	3·43[a]	2	0·92[a]	7
Id	i-C_3H_7	8 + 9 (1 : 1)	3·43[a]	2	0·92[a]	4·6
					1·03[a]	2·4

[a] Unresolved signals, centre of the peak is recorded. [b] The 4·7 (or 11), 8, 9, 10, 12 isomer prevails over the 4, 5, 8, 9, 10, 12 isomer by approximately 4 : 1 ratio, see also the footnote in Table VI.

TABLE V

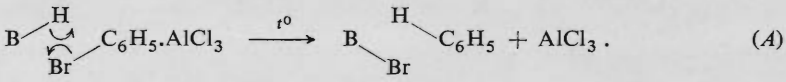
^{11}B-NMR singlets of B-alkyl carboranes R_x-1,2-$C_2B_{10}H_{12-x}$; at 32·1 MHz in $CDCl_3$; related to $BF_3.O(C_2H_5)_2$; the signals in lower magnetic field from the standard are designed as positive

Compound	R_x	R_x-Positions	$B_{9(12)}$		$B_{8(10)}$		$B_{4(5,7,11)}$	
			ppm	intensity	ppm	intensity	ppm	intensity
o-Carborane[a]	H		−3·2	2	−10·0	2	−14·4	4
Ia	CH_3	9	7·4	1	—	—	—	—
Ib	C_2H_5	9	9·5	1	—	—	—	—
IIa	$(CH_3)_2$	9,12	7·4	2	—	—	—	—
IIb	$(C_2H_5)_2$	9,12	9·5	2	—	—	—	—
IV	$(C_2H_5)_5$	4,8,9,10,12	8·7	2	1·7	2	— 4·1	1
V[b]	$(C_2H_5)_6$	4,y,8,9,10,12	8·8	2	1·0	2	— 6·0	2
VI	$(C_2H_5)_7$	4,5,7,8,9,10,12	7·9	2	1·4	2	— 6·0	3
Ic	i-C_3H_7	8 + 9 (1 : 9)	11·2	0·92	5·2	0·08	—	—
Id	i-C_3H_7	8 + 9 (1 : 1)	11·2	0·5	5·2	0·5	—	—

[a] ^{1}H Decoupled, for comparison. [b] A mixture of isomers, not resolved by HPLC and GLC, but revealed by ^{1}H-NMR (Table IV).

From the results of isopropylation it is evident that the mechanism of the alkylation is not so clear as it is in the benzene series. It is probable that with carboranes the electrophilic substitution participate but a tendency to the hydride transfer during the fragmentation of the introduced isopropyl group cannot be excluded.

When studying the probable course of substitution on the *o*-carborane skeleton we have carried out the reaction with bromobenzene in the presence of $AlCl_3$. Whereas no reaction has been observed at room temperature during one week, at 120°C a quantitative bromine transfer proceeded yielding 9-Br-1,2-$C_2B_{10}H_{11}$ as a sole carborane derivative. This reaction cannot be explained as a result of a classical electrophilic substitution but, more likely, it may be considered as a catalyzed exchange of substituents according to the Scheme (*A*)



(*A*)

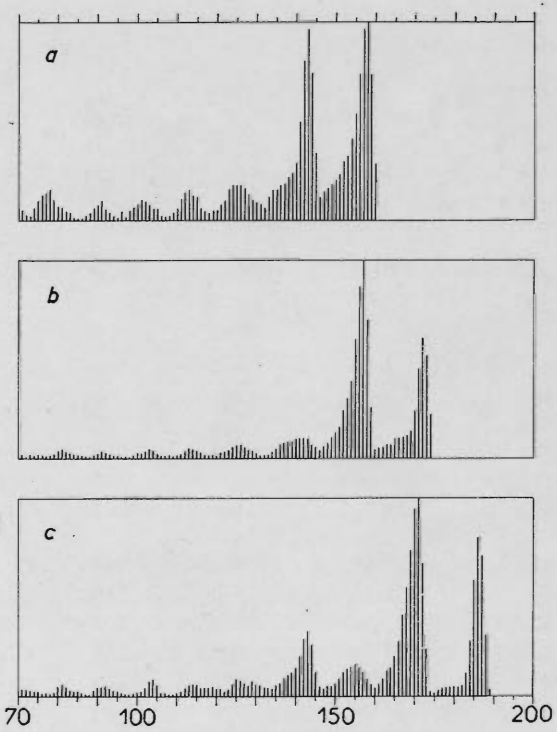


FIG. 1

Mass spectrum of 9-CH_3-1,2-$C_2B_{10}H_{11}$ *a*, 9,12$(CH_3)_2$-1,2-$C_2H_{10}H_{10}$ *b* and CH_3, C_2H_5-1,2-$C_2B_{10}H_{10}$ (*Ib*) *c*

This reaction has therefore rather nucleophilic than electrophilic character. Similar course can be considered in exchange reactions observed by Zakharkin and co-workers in the alkylation with alkyl halides.

TABLE VI

Ethylation of *o*-carborane in excess ethyl bromide (12 mol, 25°C, 96 h)

Product	*m/z*	Yield %
8,9,10,12-$(C_2H_5)_4$-1,2-$C_2B_{10}H_8$ (*III*)	258	2·6[a]
4,8,9,10,12-$(C_2H_5)_5$-1,2-$C_2B_{10}H_7$ (*IV*)	286	13·8
4,y,8,9,10,12-$(C_2H_5)_6$-1,2-$C_2B_{10}H_6$ (*V*)	314	30·2[b]
4,5,7,8,9,10,12-$(C_2H_5)_7$-1,2-$C_2B_{10}H_5$ (*VI*)	342	11·6
Fraction B polymers	—	34·4

[a] Characterized only by *m/z*, the position of the ethyl groups is suggested with great probability. [b] Three isomers are possible with y = 5, 7 or 11. However, the product behaves as a one-peak substance both by HPLC and GLC.

TABLE VII

Products resulting from the alkylation of *o*-carborane by i-C_3H_7Br in CS_2 (components ratio 1 : 1, 25°C, 48 h) determined by GLC-mass spectrometry

Species	Retention time[a], min	Weight, %	*m/z*	C_nH_{2n}[b]
A	4·1	1·2	146	*o*-carborane
B	4·4	0·5	—	—
C	7·1	1·5	—	—
D	8·3	0·6	—	—
E	9·0	9·2	216	C_5H_{10}-
F	10·3	9·6	244	C_7H_{14}-
G	12·3	1·5	—	—
H	15·3	9·0	244	C_7H_{14}-
I	16·9	10·0	258	C_8H_{16}-
K	22·3	21·1	258	C_8H_{16}-
L	25·0	11·1	286	$C_{10}H_{20}$-
M	27·3	11·8	286	$C_{10}H_{20}$-
N	37·0	8·2	—	—
O	45·6	4·9	—	—

[a] 2 400 mm column with QF-1 (10% on Chromosorb G-AW) N_2 as carrier gas, 160°C detection FID. [b] The excess *m/z* over 146 (=$C_2B_{10}H_{12}$) was taken as C_nH_{2n}.

From the results it is possible to conclude: *1*) In the presence of aluminium chloride, the reaction of *o*-carborane with alkylating agents is limited to methyl, ethyl and isopropyl halides, bromides being optimal. Higher halides, olefines and phenylacetylene did not react in this sense. *2*) The composition of products is extremely complex when working without solvent and in case of 2-bromopropane even in solvents and molar ratios of the reactants 1 : 1. *3*) For preparation of individual compounds the reaction is not suitable at least under conditions known up now. Only tedious and most effective isolation methods have led to the successful preparation of seven individual B-mono- and B-polyalkyl derivatives. *4*) The reaction is catalytical, the first alkyl strongly activates the substrate for further substitution and the substituents enter sequentially upon boron atoms according to their decreasing electron density. These statements of Zakharkin[6] were verified and are now based on experimental evidence. *5*) The mechanism of the alkylation remains obscure. The case of "isopropylation" of *o*-carborane shows, that even under mildest conditions a fragmentation and other alterations of the original alkyl occur, in contrast to the common Friedel–Crafts alkylation of benzene derivatives. With bromobenzene and $AlCl_3$, quantitative "halogen exchange" was observed at 127°C whereas no reaction took place at 25°C. *6*) With H_2SO_4 as catalyst, only 2-propanol was capable to alkylate *o*-carborane, yielding almost pure 9-i-C_3H_7-1,2-$C_2B_{10}H_{11}$. Methanol, ethanol, 1-pentanol, tert-butanol, cyclohexanol, as well as cyclohexene and hexene-1 did not alkylate.

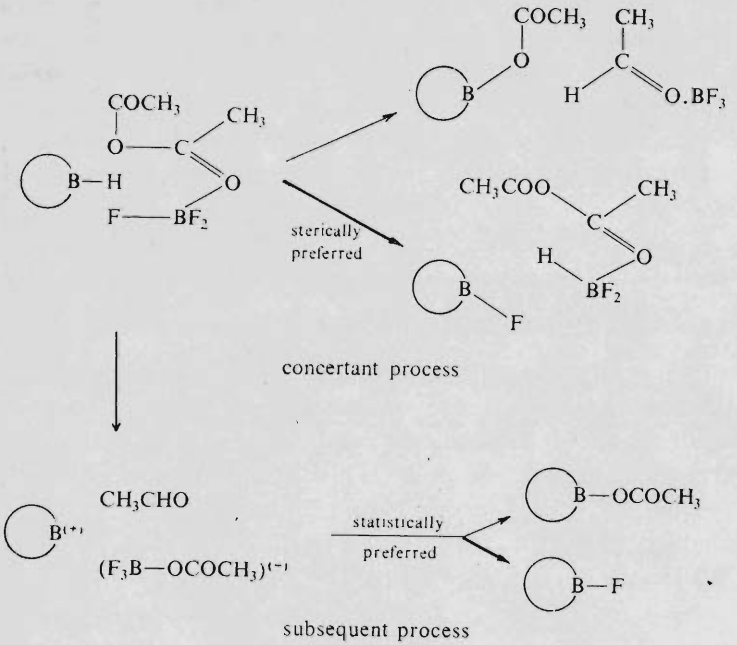
Possible Mechanisms of B-*Substitution in Boranes and Heteroboranes under Electrophilic Conditions*

Some B-substitutions of the parent icosahedral $B_{12}H_{12}^{2-}$ skeleton and of its metallocarborane $C_2B_9H_{11}CoC_5H_5$ derivative[7,10] under electrophilic conditions have shown that the origin of final products cannot be explained as a consequence of an electrophilic substitution but, more likely, as a result of a "nucleophilic substitution under electrophilic conditions"[7–10]. A very probable course of this substitution is a transfer of the hydride-like hydrogen to the attacking particle and a simultaneous or subsequent acceptance of a nucleophilic particle

(*B*)

While in the former reaction (*B*) the course is more likely concertant, in the latter one we cannot prefer any of courses (*C*) and (*D*) due to that fact that in spite of $CH_3COO^{(-)} > F^{(-)}$ decreasing order of nucleophility the A : B ratio is 1 : 3 which

is in accord not only with the statistical frequency of fluorine atoms in the BF_3. $.OCOCH_3^{(-)}$ anion, but also with the sterically preferred approach of BF_3 end. As demonstrated, the above mechanism requires a hydride hydrogen to be substituted, *i.e.* a negative charge on the B – H vertex, which is fullfilled not only with $B_{12}H_{12}^{2-}$ and $C_2B_9H_{11}CoC_5H_5$ but also with some vertices in further borane or heteroborane skeletons. One of them is *o*-carborane where B-9(12) [−0·100 e] and also B-8(10) [−0·071 e] show the negative charge on the B – H vertex in contradistinction to the B-4(5,7,11) positions which bear no charge[11]. In accord with the hydride character of the C-remoted BH-atoms, also *o*-carborane shows a certain disposition to the "nucleophilic substitution under electrophilic conditions". This character has been assigned to the transfer of halogen from bromobenzene to the 9-position in *o*-carborane and can be also considered in the formation of $9\text{-}ONO_2\text{-}1,2\text{-}C_2B_{10}H_{11}$ only when nitrating *o*-carborane by 100% HNO_3 (ref.[12]).

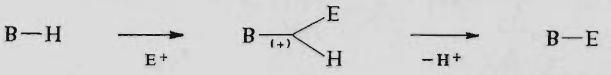


(C)

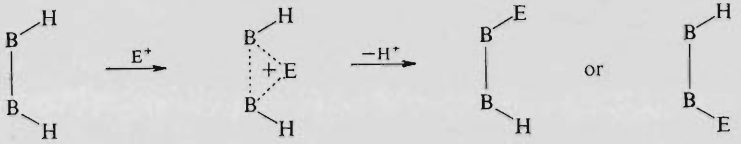
(D)

Some results obtained in this study, *i.e.* the alkylation of *o*-carborane also in 4-position as well as the absence of an alkylation by olefin have indicated, however, that with *o*-carborane the alkylation under Friedel–Crafts conditions has an electrophilic character, and does not proceed through the olefine intermediate. The absence of an accessible π-electron pair in icosahedral skeletons makes the mechanism distinctly different from that in aromatic series.

For the electrophilic substitution of borane skeletons two different mechanisms may be considered: *a*) addition of the electrophilic particle (E^+) to the B – H bond[13] followed by the scission of proton



b) addition of the electrophilic particle to the electron-rich B – B bond (in the sense of localized skeletal bonds), followed by the abstraction of proton and location of E on one of both B-atoms[14,15]



It will depend on the electron density in B–H and B–B bonds, on their steric accessibility to the approaching particle, on character of reacting molecules, and on the associating or ionogenic power of the solvent which of both schemes will realize. This allows to explain the complexity of alkylation results sourcing from slight changes in conditions as have been observed in the present study.

EXPERIMENTAL

The analytical gas liquid chromatography combined with mass spectrometry was performed on the Silicon gummi (Merck) column with temperature gradient of 6°C/min. The mass spectra were recorded with a LKB 9000 instrument at 70 eV. The high-performance liquid chromatography was carried out with a home made equipment[16] on silica gel column, with heptane (preliminary experiments) or pentane (preparative experiments) as eluents. GLC analysis of reaction mixtures was performed on a Chrom-3 instrument (Laboratorní přístroje, Prague, Czechoslovakia) with flame ionization detector. Stainless steel columns were packed with Chromosorb W (DMCS) coated with QF-1 or SE-30 (3%); operating conditions: 160°C, flow-rate 50 ml/min, nitrogen as carrier gas. The ^{1}H-NMR (100 MHz) and the ^{11}B-NMR (32·1 MHz) spectra were obtained in $CDCl_3$ with a Varian XL-100 spectrometer. TLC was carried out on Silufol sheets (silica gel on aluminium foil, starch as a binder; Kavalier, Votice, Czechoslovakia). Melting points were measured on a Kofler block and were not corrected.

Reactions of *I* in the Presence of $AlCl_3$

Preliminary alkylations: *o*-Carborane (0·01 mol) and the alkylating agent (0·01 mol) were dissolved in 20 ml of CS_2, and 0·3 g (0·002 mol) of $AlCl_3$ was added. The flask was fitted with a polyethylene bag in order to exclude moisture and to allow the hydrogen halide to escape. The reaction course was monitored by TLC on Silufol using benzene–hexane 1 : 2 mixture as the eluent. All the B-alkyl-*o*-carboranes had the R_F values exceeding that of *o*-carborane (R_F 0·45). The last probe was taken after 48 h at *c.* 25°C. The mixture was evaporated at ambient temperature and 130 Pa, 20 ml of hexane was added and after cooling to −75°C for one hour,

the solid substance was filtered off. This operation was repeated with two more 10 ml portions of hexane. The remaining solid was sublimed *in vacuo* of 1·3 Pa at 80°C (bath), the sublimate was rinsed with 20 ml of water, dissolved in 20 ml of benzene and after drying *in vacuo* it was resublimed *in vacuo*. The *o*-carborane derivative obtained in this way was pure according to TLC; its quantity is recorded in the last column in Table I.

The same procedure was applied to all of the thirteen alkylating agents in nitromethane instead of CS_2. In this series, only the reaction with i-C_3H_7Br was positive.

Preparative alkylations: A solution of 0·1 mol of an alkylating agent in 20 ml of CS_2 was added during 2 h to the stirred suspension of 14·4 g (0·1 mol) of *o-carborane* and 2·89 (0·022 mol) of $AlCl_3$ in 80 ml of CS_2 under reflux condenser cooled to 0°C. The mixture was maintained at *c.* 25°C for two days (stirring over day and standing over night) and evaporated at *c.* 25°C/130 Pa leaving a residue to which 200 ml of hexane followed by 50 ml of water were added. Only a small quantity of 9-halogenated species (according to TLC) remained undissolved. After filtration, both layers were separated and small sample was taken off for HPLC and GLC investigations. The results are shown in Tables I and II. For isolation of alkyl derivatives, the hexane solution was evaporated to about one half *in vacuo* at ambient temperature, then cooled down to −73°C and kept at that temperature for one hour. The solid was filtered off in the vacuum extractor[15], about 30 ml of the solvent were distilled from the filtrate onto the solid and the mixture was again cooled down to −73°C. This last operation was repeated twice. The solid remaining after the deep freeze operation was essentially pure *o*-carborane which was recovered by sublimation at 1·3 Pa and 80°C (bath). The hexane filtrate was concentrated to about 50 ml *in vacuo*, soaked into 100 g of silica gel, and after drying *in vacuo* at ambient temperature, the resulting powder was added on the top of the column containing 200 g of silica gel. Elution with hexane afforded all partly separated alkyl-*o*-carboranes, followed by the unreacted *o*-carborane. The successive fractions were checked by TLC. The combined eluates of alkyl-*o*-carboranes were evaporated at 130 Pa and at temperature up to 60°C to constant weight. The remainder was taken as "total of B-alkyl derivatives", and it is recorded in Table I. In this way, the reactions with CH_3Br, CH_3I, $(CH_3)_2SO_4$, C_2H_5Br and i-C_3H_7Br were performed. The isolation of individual compounds was carried out specifically in each case.

Methyl derivative Ia *and* IIa: The semisolid remainder (7·2 g) from the alkylation with CH_3Br was dissolved in 20 ml of hexane and chromatographed on 200 g of silica gel with hexane as an eluent. The successive fractions were monitored by TLC and the fractions containing pure compounds *Ia* and *IIa* were analyzed by HPLC. From the particular fractions the solvent was evaporated at *c.* 25°C/130 Pa and the products were isolated by sublimation at 1·3 Pa and at bath temperature of 40°C for *Ia* and of 50°C for *IIa*. In this way, 2·7 g of *Ia* (17·9%) and 1·7 g (9·8%) of *IIa* were obtained together with 2·6 g of a mixture of both compounds. The properties of the compounds *Ia* and *IIa* are recorded in Tables III—V. In comparison with the above results, the methylation with CH_3I yielded 0·7 g of *Ia* and 0·2 g of *IIa*, whereas the alkylation with $(CH_3)_2SO_4$ afforded only 0·1 g of *Ia* and trace amounts of *IIa* evidenced by TLC.

Ethyl derivatives Ib *and* IIb: The liquid residue (12·0 g) after the standard preparative ethylation and rough isolation was distilled at 65—70°C/1·3 Pa yielding 8·0 g of a viscous liquid. A part of this distillate (5·4 g) was separated by the preparative HPLC on the silica gel column (length 500 mm, internal diameter 17 mm, sorbent particle size 29 μm) with pentane–dichloromethane 98 : 2 as an eluent, affording 3·2 g (42·2% total yield) of *Ib* and 1·4 g (15·2%) of *IIb* as the pure compounds. Intermediate fractions contained 0·4 g of a mixture of both isomers. The properties of compounds *Ib* and *IIb* are shown in Tables II—V.

Reaction of o-*carborane with* i-C_3H_7Br *as the solvent*: Aluminium chloride (0·3 g, 2 mmol) was added to a solution of *o*-carborane (1·5 g, 10 mmol) in 2-bromopropane (13·5 g, 120 mmol)

under cooling in an ice-bath). Vigorous reaction accompanied by foaming and evolution of hydrogen bromide was observed. After *c.* 10 min, the reaction ceased and a viscous yellow-brown mass was obtained. After standing for 48 h, the mixture was diluted with 30 ml of hexane and decomposed by the addition of 20 ml of water. The upper layer was washed with 20 ml of water, hexane was evaporated *in vacuo* and the residue was dissolved in 20 ml of hexane. The solution was analyzed by GLC (Table VII). Due to complexity of the mixture no attempts were made to isolate individual compounds.

Isolation of products from the reaction of I *with* i-C_3H_7Br: Liquid residue (8·5 g) from the alkylation of *I* with 2-bromopropane in CS_2 (obtained as a crude product after the standard procedure) contained all species from B to O shown in Table VII with the B—E compounds prevailing. The distillation at 1·3 Pa/60°C (bath) yielded 2·1 g of a semisolid matter which was dissolved in 10 ml of hexane and chromatographed on 100 g of silica gel using hexane as an eluent. Fractions were monitored by TLC. Last fractions contained pure unreacted *o*-carborane (0·9 g, 6·2% of the starting amount) which was isolated by evaporation of hexane and sublimation at 1·3 Pa, and was identified by melting point, mass spectrometry, HPLC and GLC. All preceding fractions were collected and concentrated to a turbid liquid (1·0 g) which was analyzed by the combination of GLC and mass spectroscopy. According to these combined methods, the mixture contained one part of *Ia*, 3 parts of *Ib*, two parts of compounds of the formula B-CH_3-B′-C_2H_5--1,2-$C_2B_{10}H_{10}$ and about one part of other species. The mass spectra of three characterized compounds are shown in Fig. 1.

Reaction of I *with* i-C_3H_7Br *in nitromethane*: The reaction was performed analogously as in CS_2 which was replaced by the same volume of nitromethane. The addition of aluminium chloride into the starting solution of *o*-carborane was carried out under cooling by water. Other reaction conditions and the isolation of the crude product were the same as in the standard procedure; 10·1 g (53·8%) of a mixture of *Ic* with B,B′(C_3H_7)$_2$-1,2-$C_2B_{10}H_{10}$ in the 9 : 1 ratio were obtained. Distillation at 87°C/1·3 Pa afforded 8·0 g (43%) of B(C_3H_7)-1,2-$C_2B_{10}H_{11}$ (*Id*). The properties of this mixture of the 8- and 9-isomers are given in Tables III—V.

Exhaustive ethylation of o-*carborane*: To a stirred solution of 14·4 g (0·1 mol) of *o*-carborane in 130 g (1·2 mol) of ethyl bromide, 2·8 g (0·02 mol) of $AlCl_3$ was added under cooling to 0°C. The mixture was kept at ambient temperature for 96 h (32 h under stirring, 64 h without agitation) and treated similarly as in the procedure in CS_2. According to HPLC, the crude product did not contain the starting compound or *Ib* and *IIb*. The silica gel column chromatography with hexane as the eluent afforded fraction A (20·5 g, 57·2% of total yield) containing all defined products. The subsequent elution with benzene yielded fraction B (12·8 g, 34·4%). The latter solution was evaporated *in vacuo* and dried at 100°C/130 Pa leaving a glassy material, soluble in hexane and methanol. When chromatographed on Silufol, the polymer-like material did not move when eluted with hexane. Unsuccessful separation was also with benzene–hexane 1 : 1 when only a diffuse strip at R_F 0·0—0·3 was observed. According to the ^{1}H-NMR in $CDCl_3$, the material contained about 16 methylene groups per one carborane unit. The elemental analysis showed that the material was not an individuum, exhibiting the element ratio $C_{12·4}B_{10}H_{30·7}$·.$Br_{0·26}$ (34·80% B, 47·99% C, 9·91% H, 6·04% Br). The composition of the fraction A was revealed by the combination of GLC and mass spectrometry (Table VI). Distillation at 1·3 Pa up to 175°C (bath) afforded 12·1 g of a distillate which was separated by the preparative HPLC under similar conditions as with compounds *Ib* and *IIb*, except that two columns in series were used. After evaporating the particular fractions, and after distillation of the residue *in vacuo*, 1·4 g of *IV*, 3·2 g of *V* and 1·1 g of *VI* were obtained. Their properties are shown in Tables III—V. The compound *III* was also separated but its quantity was too small for isolation and *III* was characterized by its mass spectrum only.

Reaction of *I* in the Presence of H_2SO_4

Preliminary experiments: The mixture of *o*-carborane (0·01 mol), alcohol or olefine (0·02 mol), concentrated H_2SO_4 (0·02 mol), and 50 ml of hexane was stirred at ambient temperature for 24 h. The mixture was checked by TLC for the presence of B-alkyl derivatives (slightly faster than *o*-carborane). The test was positive only in the case of 2-propanol. All other investigated compounds did not react with *o*-carborane. The alkylating agents were: CH_3OH, C_2H_5OH, t-C_4H_9OH, $C_5H_{11}OH$, $C_6H_{11}OH$, 1-hexene and cyclohexene.

Preparative isopropylation to Ic: 2-Propanol (12·0 g, 0·2 mol) was added to a stirred two-layer mixture of *o*-carborane (14·4 g, 0·1 mol), sulfuric acid (98 g, 1·0 mol) and 100 ml of hexane within two hours. The mixture was agitated for additional 48 h at ambient temperature. All solid substances disappeared. The black sulfuric acid layer was separated and the supernatant pink hexane solution was stirred for 30 min with additional 50 ml of fresh sulfuric acid. The hexane layer was washed with 100 ml of water and 100 ml of 5% KOH solution. The main part of *o*-carborane was separated by the "freezing out" technique described above, and the last remainder was isolated as the first fraction during the vacuum distillation of the crude product. In total, 3·4 g (23·6%) of *o*-carborane were recovered. Continuing the distillation, 8·7 g (46·8%) of a liquid was obtained at 13 Pa and 80—90°C (bath). This liquid was almost pure 9-i-C_3H_7-1,2-$C_2B_{10}H_{11}$, the individuality of which followed from HPLC (r.t. 10·5 min; *o*-carborane 14·4 min). The structure was proposed on the ground of $m/z = 188$, corresponding to $^{12}C_5{}^{11}B_{10}{}^{1}H_{18}$, of the ^{1}H-NMR spectrum showing signals at δ 3·43 (singlet, 2 CH_{carb}), 0·94 (doublet, $^3J = 11$ Hz, 2 CH_3) and 0·94 ppm ($CH_{i\text{-}C_3H_7}$), and of the ^{11}B-NMR spectrum which has shown signals of relative intensities 1 : 1 : 2 : 2 : 2 : 2 at 11·4 (1, singlet), −2·3 (1, 154 Hz), −9·4 (2, 158 Hz) and −14·3 ppm (6) (ppm values are related to $BF_3.O(C_2H_5)_2$ and ordered according to the increasing shielding). The ^{11}B-NMR spectrum indicated also the presence of a small amount (<10%) of another *o*-carborane derivative (singlet at 4·9 ppm).

Exchange halogenation of I *by bromobenzene*: The mixture of 2·9 g (0·02 mol) of *o*-carborane, 10·0 g (0·064 mol) of bromobenzene and 2·0 g (0·015 mol) of aluminium chloride was heated to 125°C for 2 h. With TLC, only a small spot of the starting compound and a strong one of 9-Br-1,2-$C_2B_{10}H_{11}$ were observed. After the addition of 10 ml water and 50 ml of benzene, the layers were separated and the undissolved matter was filtered. The benzene solution was concentrated to the volume of 30 ml, soaked into a 100 g silica gel column and chromatographed using successively hexane and benzene–hexane 1 : 2 as eluents. After the elution of bromobenzene and of fluorescent organic compounds, small quantity (0·05 g, 1·7%) of the starting compound was obtained. The main fraction contained 4·1 g (94·0%) of 9-Br-1,2-$C_2B_{10}H_{11}$ which was identified by TLC, mass and ^{11}B-NMR spectroscopy. The same mixture as above did not show any change after standing for one week at 25°C (according to TLC).

The ^{11}B-NMR spectra were measured by Mr P. Pech, the mass spectra by Drs V. Kubelka and J. Mitera, Prague Institute of Chemical Technology, Prague. The ^{1}H-NMR spectra were recorded by Dr F. Mareš, Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Řež. All these colleagues are thanked for their assistance.

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