Synthesis of 9-benzyl-*o*- and 9-benzyl-*m*-carboranes containing functional substituents in the benzene ring by electrophilic alkylation of *o*- and *m*-carboranes by the corresponding *R*-benzyl halides

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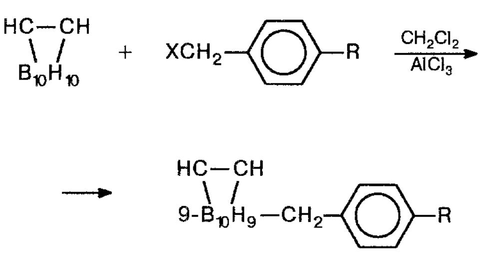
9-Benzyl-*o*- and *m*-carboranes containing NO_2, COOH, COOMe, and COPh groups in the *para*-position of the benzene ring were synthesized by the Friedel—Crafts reaction.

Key words: *o*- and *m*-carboranes, benzyl halides, electrophilic alkylation.

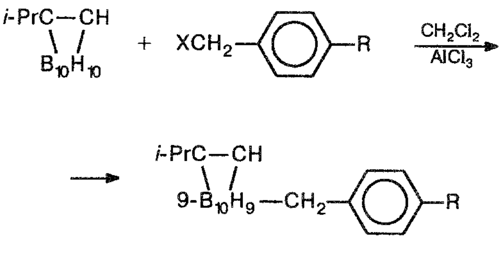
It has been shown previously that the reaction of electrophilic alkylation of *o*- and *m*-carboranes by alkyl halides[1,2] or by ω-halocarboxylic acids[3] under the action of aluminum chloride can be used as a method for synthesizing organocarboranes, in which the organic group is connected to the boron atom of the carborane ring. In the case of alkyl halides, this method is, however, restricted to only the lowest alkyl halides from C_1 to C_3, while C_4 and higher alkyl halides are not capable of alkylating carboranes because of their destruction by aluminum chloride.[2,4]

In the present work we found that benzyl halides that contain such electron withdrawing substituents as NO_2, COOH, COOMe, and COPh readily alkylate *o*- and *m*-carboranes in CH_2Cl_2 in the presence of equimolar amounts of aluminum chloride according to Scheme 1:

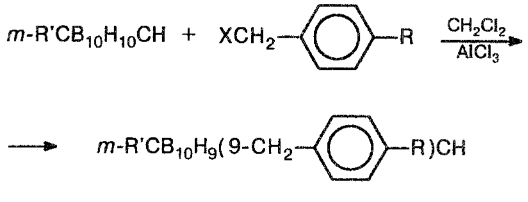
Scheme 1



X = Cl, Br
1: R = NO_2
2: R = COOMe
3: R = COOH
4: R = COPh



X = Cl, Br
5: R = NO_2
6: R = COOMe
7: R = COOH



8: R' = Pr^i, R = NO_2
9: R' = H, R = COPh

In order to obtain monosubstituted derivatives, the reaction was carried out with a small excess of *o*- and *m*-carboranes. The structure of the R-benzyl derivatives of carboranes obtained was confirmed by ^{11}B NMR spectra. The ^{11}B NMR spectra of all 9-benzyl-*o*-

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Table 1. Physicochemical properties of the 9-R-benzyl-substituted *o*- and *m*-carboranes obtained

Compound		Yield (%)	M.p. /°C	Molecular formula	Found / Calculated (%) C	H	B
9-(4′-Nitrobenzyl)-*o*-carborane	(**1**)	90	222	$C_9H_{15}B_{10}O_2$	38.85 38.97	5.34 5.41	38.85 39.01
9-(4′-Carbomethoxybenzyl)-*o*-carborane	(**2**)	88	92—93	$C_{11}H_{20}B_{10}O_2$	42.03 42.20	7.04 6.84	37.32 36.98
9-(4′-Carboxybenzyl)-*o*-carborane	(**3**)	85	221	$C_{10}H_{18}B_{10}O_2$	43.65 43.16	5.98 6.47	38.79 38.84
9-(4′-Benzoylbenzyl)-*o*-carborane	(**4**)	89	120—121	$C_{16}H_{22}B_{10}O$	57.02 56.80	6.60 6.50	31.71 31.95
1-Isopropyl-9-(4′-nitrobenzyl)-*o*-carborane	(**5**)	79	75	$C_{12}H_{23}B_{10}O_2$	45.01 44.84	7.19 7.16	33.49 33.66
1-Isopropyl-9-(4′-carbomethoxybenzyl)-*o*-carborane	(**6**)	90	86—87	$C_{14}H_{26}B_{10}O_2$	50.13 50.29	7.68 7.78	32.55 32.33
1-Isopropyl-9-(4′-carboxybenzyl)-*o*-carborane	(**7**)	78	230	$C_{13}H_{24}B_{10}O_2$	49.01 48.75	7.61 7.50	33.51 33.75
1-Isopropyl-9-(4′-nitrobenzyl)-*m*-carborane	(**8**)	87	210—211*	$C_{12}H_{23}B_{10}O_2$	45.19 44.84	7.17 7.16	33.37 33.66
9-(4′-Benzoylbenzyl)-*m*-carborane	(**9**)	89	102—103	$C_{16}H_{22}B_{10}O$	56.68 56.80	6.48 6.50	32.07 31.95

Note. Compounds **2**, **4**, **5**, **6**, **9** were crystallized from hexane; compounds **1**, **3**, **7** — from a mixture of benzene—heptane (1 : 1).
*B.p. 210—211 °C (1 Torr).

carboranes obtained have similar symmetry and indicate the substitution at the B-9 atom of the *o*- or *m*-carborane polyhedron.

The method that we propose for the synthesis of benzyl derivatives of *o*- and *m*-carboranes containing different electron-withdrawing functional substituents into the benzene ring makes this class of compounds accessible and opens a possibility for introducing other substituents in the benzene ring, including electron-donating substituents, by transformations of the functional groups mentioned above.

Earlier[5] it was shown that the interaction of perfluorotoluene with *o*- and *m*-carboranes in the presence of SbF_5 affords 9-fluoro-*o*- and *m*-carboranes,

Table 2. Parameters of ^{11}B NMR spectra in acetone

Compound	δ	$J_{^{11}B-^{1}H}$ /Hz	*I* (%)	Assignment
1	6.99	0	1	B-9
	−2.33	147	1	B-12
	−8.91	168	2	B-8, 10
	−13.69	158	6	B-4, 5, 7, 11, 3, 6
5	4.99	0	1	B-9
	−2.71	148	1	B-12
	−8.94	168	2	B-8, 10
	−11.98	182	2	B-3, 6
	−13.11	169	4	B-4, 5, 7, 11
2	5.01	0	1	B-9
	−3.61	152	1	B-12
	−7.91	163	2	B-8, 10
	−13.25	171	6	B-4, 5, 7, 11, 3, 6
3	6.79	0	1	B-9
	−2.51	148	1	B-12
	−8.63	169	2	B-8, 10
	−13.24	160	6	B-4, 5, 7, 11, 3, 6
4	7.13	0	1	B-9
	−7.71	158	1	B-12
	−10.02	184	2	B-8, 10
	−15.18	170	6	B-4, 5, 7, 11, 3, 6
7	0.87	0	1	B-9
	−3.14	165	2	B-5, 12
	−7.91	172	1	B-10
	−11.71	169	2	B-4, 8
	−13.30	168	2	B-6, 11
	−16.34	181	1	B-3
	−19.57	172	1	B-2
9	0.72	0	1	B-9
	−6.12	168	2	B-5, 12
	−9.71	179	1	B-10
	−12.62	169	2	B-4, 8
	−13.40	167	2	B-6, 11
	−16.80	182	1	B-3
	−19.47	171	1	B-2

9-fluoro-10-(α,α-dihydro-2,3,4,5,6-pentafluorobenzyl)-*o*- and *m*-carboranes, *i.e.*, the formation of fluorobenzylcarboranes in this case is accompanied by reduction of the CF_3 group to CH_2F due to hydrogen atoms of the carborane ring, which results in the introduction of fluorine atoms at the boron atoms of the carborane. In our case, the benzylation reaction is not accompanied by side processes.

Experimental

^{11}B NMR spectra were obtained on a Bruker WP-200SY spectrometer in Me_2CO. The chemical shifts of ^{11}B nuclei (64.2 MHz) were measured relative to $BF_3 \cdot OEt_2$.

General procedure for the synthesis of 9-(*p*-benzyl-substituted) *o*- and *m*-carboranes. A solution of the corresponding carborane (0.0024 mol) in 20 % excess, *p*-R—$C_6H_4CH_2X$ refluxed (0.02 mol), and $AlCl_3$ (0.02 mol) in 25 mL of CH_2Cl_2 was boiled until the benzyl halide disappeared (0.5—2 h). The reaction mixture was poured into water, washed with diluted (1 : 1) HCl and water, and dried with Na_2SO_4. The CH_2Cl_2 was distilled off *in vacuo*, and the product was purified by crystallization or chromatography on a SiO_2 column. The physicochemical characteristics of the compounds obtained are given in Table 1. The ^{11}B NMR spectra are given in Table 2.

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