Destruction of *B*-polyfluorosubstituted *o*-carboranes into anions of *B*-fluorosubstituted *nido*-7,8-dicarbaundecaborates by the action of ethanolic alkali and amines

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The destruction of *B*-polyfluorosubstituted *o*-carboranes by the action of ethanolic alkali and amines was studied. The destruction of trifluoro-*o*-carborane was found to occur regioselectively. The nature of the amine was shown to affect the stereochemistry of the destruction of trifluoro-*o*-carborane. The intermediate of the reaction of tetrafluoro-*o*-carborane with diethylamine was detected.

Key words: *B*-polyfluorosubstituted *o*-carboranes, *B*-fluorosubstituted *nido*-7,8-dicarbaundecaborates.

It is known that the destruction of *o*-carboranes by the action of sodium ethoxide in ethanol[1] and amines[2] occurs through elimination of one boron atom from the 3(6) position to afford *nido*-7,8-dicarbaundecaborate(−1) anions.

Previously,[3] the kinetics of the destruction of *o*-carboranes by the action of sodium ethoxide in dry ethanol and amines was studied. The destruction is generally a second-order reaction, *i.e.*, first-order with respect to a base and first-order with respect to an *o*-carborane. The authors proposed a multistep mechanism of this reaction involving consecutive formation of intermediates, which, however, were not observed experimentally.

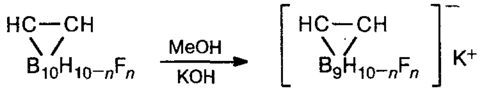
In the present work we studied the destruction of 9-fluoro-, 9,12-difluoro-, 8,9,12-trifluoro-, and 8,9,10,12-tetrafluoro-*o*-carboranes by the action of ethanolic alkali and a series of amines.

It was of interest to reveal the effect of electronegative fluorine atoms on the direction of the attack of the *o*-carboranes by bases and on the stereochemistry of decomposition. The presence of fluorine atoms in the molecules allowed us to hope that ^{19}F NMR spectroscopy will help to detect the intermediates of this reaction.

Results and Discussion

The destruction of the *o*-carborane ring by the action of an ethanolic solution of potassium hydroxide occurs faster in *B*-fluoro-*o*-carboranes than in a nonsubstituted *o*-carborane, 8,9,10,12-tetrafluoro-*o*-carborane, which is readily decomposed. The attack by the base is directed to the boron atoms at the 3(6) positions, which is explained by a decrease in the electron density on the boron atoms at the 3(6) positions due to the strong electronegative effect of fluorine atoms. These data are in good agreement with the values of the dipole moments of polyfluoro-*o*-carboranes.[4] The introduction of fluorine atoms into the molecule of *o*-carborane does not change the direction of the attack by the nucleophilic reagent at the *o*-carborane ring. The action of alkaline potassium hydroxide on 9-fluoro- and 9,12-difluoro-*o*-carboranes readily results in formation of anions of 5-fluoro- and 5,6-difluoro-*nido*-7,8-dicarbaundecaborates[8] isolated as potassium, caesium, and trimethylammonium salts.

Scheme 1



1 (n = 1)
2 (n = 2)

3 (n = 1)
4 (n = 2)

The ^{19}F NMR spectra of anions **3** and **4** contain signals of fluorine atoms as quadruplets with coupling constants of 50—55 Hz, which are shifted upfield as compared with the starting *B*-fluorosubstituted

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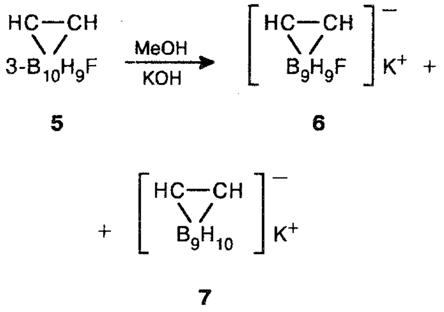
o-carboranes **1** and **2**. In the ^{11}B NMR spectra of anions **3** and **4**, the signal of the boron atom linked to the fluorine atom is shifted upfield and is recorded as a broadened singlet.

It is interesting that the action of KOH on 3-fluoro-*o*-carborane unexpectedly results in two anions (in a ratio of 1:1), the nonsubstituted 7,8-dicarbaundecaborate(−1) ion[1] and the 3-fluoro-7,8-dicarbaundecaborate(−1) ion (Scheme 2).

Scheme 2



However, it has been shown for 3-phenyl-*o*-carborane[9] and 3-amino-*o*-carborane[10] as examples that the destruction occurs at the boron atom in non-substituted position 6. In our case, the reaction is not regioselective.

In the destruction of 8,9,12-trifluoro-*o*-carborane (**8**) with ethanolic alkali, the boron atom can be removed both from position 3 and from position 6 to afford the anion of 5,6,10-trifluoro-*nido*-7,8-dicarbaundecaborate (**9**) and the anion of 1,5,6-trifluoro-*nido*-7,8-dicarbaundecaborate (**10**), respectively (Scheme 3).

Scheme 3

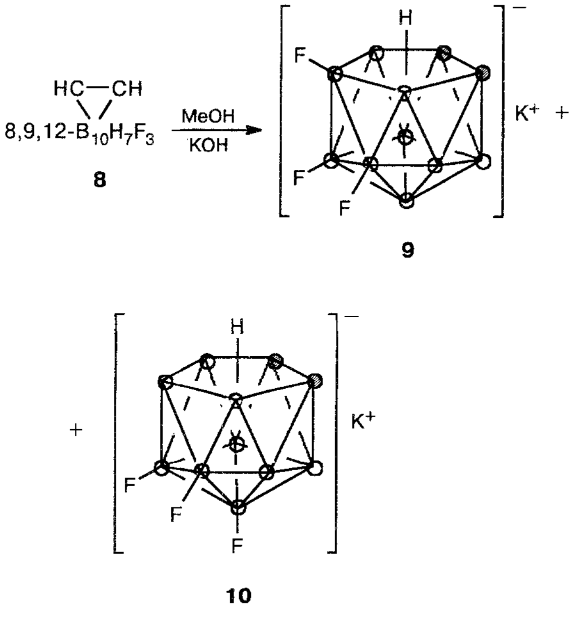


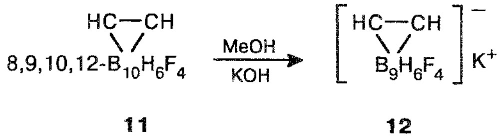
Table 1. ^{19}F NMR and ^{11}B NMR spectra of polyfluoro-7,8-dicarbaundecaborates

Anion	^{19}F, δ (J_{B-F}/Hz)	^{11}B, δ (J_{B-H}/Hz)
3	116.3 (55.0)	11.6; −12.5 (147.0); −15.2 (154.0); −19.6 (147.0); −21.6 (140.0); −23.9 (135.0); −25.6 (130.0); −31.9 (133.0; 49.0); −38.9 (140.0)
4	135.7 (55.0)	7.2; −14.3 (142.0); −22.5 (130.0); −24.0 (128.0); −31.7 (126.0; 51.2); −38.8 (141.0)
6*	129.7 (55.0)	−1.6; −13.8 (134.0); −20.2 (128.0); −24.4 (120.0); −40.9 (130.0); −42.8 (134.0)
9	139.7 (55.0) 152.0 (64.0)	4.4; −11.7 (64.0); −15.4 (141.0); −26.6 (154.0); −41.3 (140.0)
10	137.5 (55.0) 194.0 (55.0)	4.4; −18.1; −28.0 (130.0); −33.7 (128.0)
12	143.0 (55.0) 156.0 (49.0; 25.0) 199.0 (47.0)	0.5; −10.5; −13.8; −20.5 (160.0); −19.1 (148.0)

* The formation of anion 7 was confirmed by ^{11}B NMR.

The structure and isomer ratio were established using ^{19}F NMR and ^{11}B NMR spectroscopy. According to the ^{19}F NMR spectra (Table 1), isomer **9**, which contains a fluorine atom at position 10 of the pentagonal plane, is formed in an amount twice as high as isomer **10**. Hence, we were the first to establish that the destruction of the carborane ring can occur regioselectively due to the effect of substituents at the boron atom in position 8. In compound **8**, the boron atom at position 3, which is linked with the B(8) atom carrying a fluorine atom, is removed more readily than the boron atom at position 6. The regioselective attack of a nucleophilic reagent at position 3 is related to the fact that the fluorine atom at the B(8) atom connected with the B(3) atom decreases the electron density of the boron atom at position 3 as compared with that of the boron atom at position 6 due to the electronegative effect. This results in preferential attack of the nucleophilic reagent at the boron atom in position 3.

The destruction of 8,9,10,12-tetrafluoro-*o*-carborane (**11**) with ethanolic alkali gives 1,5,6,10-tetrafluoro-*nido*-7,8-dicarbaundecaborate anion (**12**) isolated as potassium, caesium, and trimethylammonium salts.



The structure of anion **12** was confirmed by ^{19}F NMR and ^{11}B NMR spectra. Three signals split into a quartet (J_{BF} = 55 Hz) with integral intensities of 2:1:1

are observed in the ^{19}F NMR spectrum. The fluorine nuclei in anion **12** are strongly shielded as compared with those in the starting tetrafluoro-*o*-carborane **11**. This means that on going from *closo*- to *nido*- structure, electrons are more strongly withdrawn from substituted boron atoms. One of the reasons for this may be the existence of a negative charge in the anion.

The fluorine atom located on an opened face near B(10) appears as a doublet of quartets. In this case we were the first to observe the coupling constant of the fluorine atom with the *endo*-hydrogen atom (*endo*-H, $^2J_{\mathrm{F-H\text{-}endo}}$ = 25 Hz) of the pentagonal face.

Anions **9** and **12** are of interest because they contain one of the fluorine atoms at the B(10) atom located at the pentagonal plane of the *nido*-carborane. The position of this boron atom is symmetrical with respect to carbon atoms and, according to the previously published data,[6] this atom is connected with a hydrogen atom in an axial position to the pentagonal plane formed by *nido*-7,8-dicarbaundecaborate anions (*endo*-H). It has been proposed in a series of other works that this hydrogen atom is a bridging atom and is connected either with two boron atoms, B(10) and B(9) (or B(10) and B(11)), or with three boron atoms, B(9), B(10), and B(11).[1] The ^{19}F NMR data for compounds **9** and **12** obtained by us indicate that the *endo*-hydrogen is located primarily at the B(10) atom (Table 1).

Having established the regioselectivity of the destruction of compound **8** on treatment with ethanolic potassium hydroxide, we then studied the effect of various amines on this regioselectivity. The results obtained are given in Table 2. The ratios of isomers **9** and **10** were determined using ^{19}F NMR spectroscopy (Table 2).

As can be seen from the data in Table 2, the destruction of compound **8** in the presence of primary and secondary amines occurs very quickly at 25 °C without any steric hindrance. The destruction occurs slowly even at 70 °C in the case of sterically hindered diisopropylamine, very quickly at 70 °C in the case of aniline, which has weak basic properties, rather readily at 25 °C in the presence of ammonia, and only at 70 °C in the presence of trimethylamine. All of the amines studied exhibit regioselectivity in the destruction of compound **8**, the nature of amine influencing significantly the ratio of the isomeric anions **9** and **10** formed. All these amines give predominantly isomer **9**, which contains the fluorine atom at the B(10) atom involved in the pentagonal plane of the polyhedron. The regioselectivity is the greatest in the case of piperidine, dimethylamine, and ammonia, which give isomers **9** and **10** in the ratio of 6 and more. Hence, as in the case of the destruction with ethanolic potassium hydroxide, the amines indicated attack mainly the B(3) atom in compound **8**, this regioselectivity being significantly lower for some amines. Diethylamine, which attacks primarily the B(6) atom to give the anions in the ratio of 1 : 2, is an exception. Now we are unable to explain this difference of behavior of diethylamine in the reaction with **8** as compared with other amines.

Table 2. Stereochemistry of destruction of 8,9,12-trifluoro-*o*-carborane (**8**) with amines

Amine	Experimental conditions		Ratio of isomers	
	t/min	*T*/°C	**9**	**10**
Piperidine	5	25	6.5	1.0
Morpholine	5	25	3.5	1.0
Aniline	10	70	2.5	1.0
Diisopropylamine	60	70	2.0	1.0
Diethylamine	5	25	1.0	2.0
Benzylamine	5	25	2.0	1.0
Dimethylamine	5	25	6.0	1.0
Trimethylamine	10	70	1.2	1.0
Ammonia	10	25	6.0	1.0

The destruction of *o*-carborane by the action of ethanolic alkali does not allow us to find out whether dicarbollide anion 7,8-$C_2B_9H_{11}^{2-}$ is one of the intermediates, since this anion undergoes protonation in alkali to give the 7,8-$C_2B_9H_{12}^{-}$ anion. At the same time, as we have shown previously,[7] dicarbollide anion 7,8-$C_2B_9H_{11}^{2-}$ is stable in anhydrous ammonia, suggesting that it would be stable in aliphatic amines.

We found that the reaction of diethylamine with **11** affords the 1,5,6,10-tetrafluorodicarbollide anion (**13**).

$$\mathbf{11} + 4\mathrm{Et_2NH} \xrightarrow{25\ ^{\circ}\mathrm{C}}$$

$$\longrightarrow 7{,}8\text{-}\mathrm{C_2B_9H_7F_4^{-2}\cdot(Et_2N^{+}H)} + \mathrm{HB(NEt)_2}$$

13

The structure of compound **13** was confirmed by its ^{19}F NMR spectrum, in which the $^2J_{\mathrm{F-H}}$ spin-spin splitting constant was absent. The formation of the dicarbollide anion on the destruction of *o*-carborane and its derivatives has not been observed earlier. It has only been suggested that this anion is formed on the destruction of *o*-carboranes with bases.

If the reaction of compound **11** with diethylamine is carried out at −20 °C, the ^{19}F NMR and ^{11}B NMR spectra indicate the formation of intermediate **14** along with anion **13**. Ten boron atoms are observed in the ^{11}B NMR spectrum. The signals of four of them are shifted upfield, and three substituted boron atoms have the same chemical shifts.

$$\mathbf{11} + 4\mathrm{Et_2NH} \longrightarrow \mathrm{C_2B_{10}H_8F_4\cdot Et_2NH} \longrightarrow$$

$$\longrightarrow \mathrm{C_2B_9H_7F_4^{-2}\cdot(NH_2Et_2)_2^{+}} + \mathrm{HB(NHEt_2)_2}$$

14

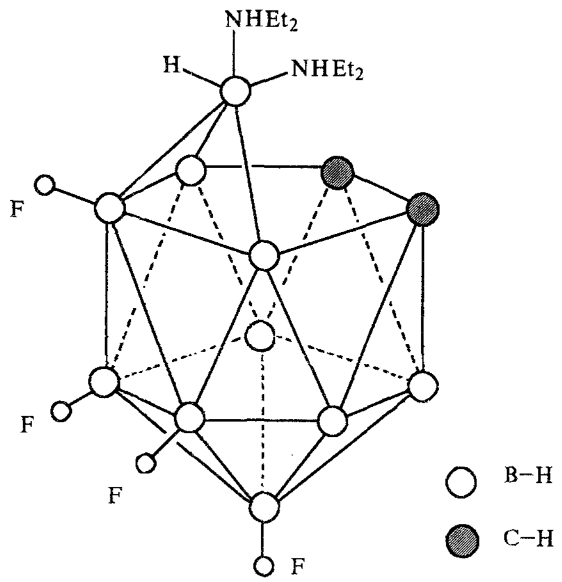


Fig. 1. Intermediate **14**.

Intermediate **14** has the following NMR spectral parameters: ^{19}F, δ: 131 (3 F); 179 (1 F); ^{11}B, δ: −30.2 (J = 155 Hz, 1 B); −22.5 (J = 145 Hz, 2 B); −20.3 (J = 150 Hz, 2 B); −16.3 (J = 160 Hz, 1 B); 5.6 (J = 0 Hz, 3 B); 10.1 (J = 0 Hz, 3 B).

Two broadened signals of fluorine nuclei with integral intensities of 3:1 are observed in the ^{19}F NMR spectrum at −20°C. The structure of compound **14** may be assigned as a partially opened *closo*-structure (Fig. 1), in which the B(3) atom is coordinated with two amine molecules, the bond with two carbon atoms being significantly weakened or absent.

When a mixture of an amine and compound **11** is heated to room temperature, only the spectral parameters of anion **13** are recorded.

Experimental

^{19}F NMR and ^{11}B NMR spectra were recorded on a Bruker WP-200SY spectrometer. The starting *B*-polyfluorosubstituted *o*-carboranes were obtained by the previously described procedure.[5] Before use, amines were distilled over KOH. The reaction was monitored by TLC on Silufol UV-254 plates (Czechoslovakia).

General procedure for the preparation of salts of polyfluoro-7,8-dicarbaundecaborates. Preparation of potassium salts. A corresponding polyfluoro-*o*-carborane (0.01 mol) was added in portions to a solution of KOH (0.04 mol) in 15 mL of MeOH. The mixture was heated until the starting polyfluoro-*o*-carborane disappeared (Table 3). The reaction was monitored by TLC (benzene—hexane). The reaction mixture was filtered, the filtrate was evaporated, and the residue was dissolved in distilled water and extracted with ethyl acetate. The solution in ethyl acetate was dried with $MgSO_4$. The solvent was evaporated to give a wet potassium salt. The salt was dissolved in dry

Table 3. Conditions of preparation and characteristics of the salts of polyfluoro-7,8-dicarbaundecaborates

Anion	Cation	Conditions of preparation of potassium salts		Yield (%)	M.p. /°C	Found/Calculated (%)		
		T/°C	t/h			C	H	F
3	K^+	64	4	80	—	12.74 12.62	6.93 5.78	9.72 9.99
	Me_3NH^+	—		75	299	28.27 28.41	9.68 9.94	
	Cs^+	—		70	320	8.24 8.45	3.79 3.87	6.67 6.69
4	K^+	64	2	82	—	11.76 11.53	5.32 4.80	
	Me_3NH^+	—		70	278	27.02 26.20	9.46 8.73	11.74 10.28
	Cs^+	—		75	315	8.02 7.94	3.36 3.31	13.20 12.53
Mixture of isomeric anions **9** and **10**	K^+	50	5	85	256	12.64 10.62	4.21 3.98	22.28 25.22
	Me_3NH^+	—		75	260	23.51 24.29	7.24 7.69	22.81 23.08
	Cs^+	—		77	298	7.43 7.50	2.99 2.81	17.73 17.81
12	K^+	25	4	83	258	10.39 9.84	3.67 3.28	30.21 31.15
	Me_3NH^+	—		75	265	22.35 22.64	7.35 6.79	29.74 28.68
	Cs^+	—		78	310	6.91 7.10	2.18 2.37	21.81 22.48

Et_2O and filtered, and the solvent was evaporated to give a dry potassium salt.

Preparation of trimethylammonium salts. A solution of trimethylamine hydrochloride (0.011 mol) in a minimal amount of H_2O was added to the potassium salt of the corresponding polyfluoro-7,8-dicarbaundecaborate (0.01 mol) dissolved in a minimal amount of H_2O. The precipitate that formed was filtered, dried with P_2O_5, and crystallized from CH_2Cl_2.

Preparation of cesium salts. A solution of CsCl (0.011 mol) was added to a solution of the potassium salt of the corresponding polyfluoro-7,8-dicarbaundecaborate (0.01 mol) in a minimal amount of H_2O. The precipitate was filtered, crystallized from H_2O, and dried with P_2O_5 (Table 3).

Destruction of *B*-fluoro-*o*-carboranes with amines. A benzene solution of *B*-fluoro-*o*-carborane (**8** or **11**) was added dropwise to an amine, and the mixture was kept for 0.1—1.0 h at room temperature. The excess amine was removed *in vacuo*. The anions were identified with ^{19}F NMR and ^{11}B NMR spectra in ethanolic solutions.

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