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Selective fluorination of *o*- and *m*-carboranes. Synthesis of 9-monofluoro-, 9,12-difluoro-1, 8,9,12-trifluoro-, and 8,9,10,12-tetrafluoro-*o*-carboranes and 9-monofluoro-, and 9,10-difluoro-*m*-carboranes. Molecular structure of 8,9,10,12-tetrafluoro-*o*-carborane

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Abstract

Reaction of *o*- and *m*-carboranes * with antimony pentafluoride results in replacement of hydrogen by fluorine at the boron atoms, to give in succession 9-fluoro-; 9,12-difluoro-; 8,9,12-trifluoro-; 8,9,10,12-tetrafluoro-*o*-carboranes and 9-fluoro-; 9,10-difluoro-*m*-carboranes. An X-ray structural study of the 8,9,10,12-tetrafluoro-*o*-carborane has been carried out. The compounds synthesized have been characterized by elemental analysis and ^1H, $^{11}B\{^1H\}$, ^{19}F NMR spectroscopy.

Introduction

Electrophilic halogenation of *o*-carborane (I) and *m*-carborane (II) gives *B*-polyhalogeno-*o*- and -*m*-carboranes. The reaction is selective, with substitution occurring at the sites of maximum electron density in the carborane cage viz., at the 8,9,10 and 12 and the 9 and 10 positions in the *o*- and *m*-carboranes, respectively [1,2]. In contrast, photochemical chlorination is not as selective and occurs at all positions of the carborane cage [3].

Up to now no data on electrophilic fluorination of I and II were available. The reaction of I and II with elemental fluorine yielded the *B*-decafluoro-*o*- and -*m*-carboranes [4]. The latter, in contrast to *B*-decachloro-*o*,*m*-carboranes [5], undergo a surprisingly rapid hydrolysis by moisture in the air to give boric acid. 3- and

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* *o*-Carborane, 1,2-dicarbaclosododecaborane (12) = *o*-$C_2H_2B_{10}H_{10}$; *m*-carborane, 1,7-dicarbacloso-dodecaborane (12) = *m*-$C_2H_2B_{10}H_{10}$

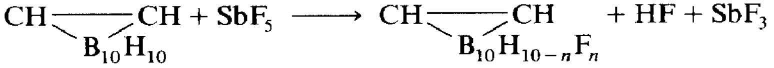
0022-328X/90/$03.50

9-fluoro-*o*-carboranes and 2- or 9-fluoro-*m*-carboranes have also been reported [6–8]. Here we suggest a highly regioselective method of fluorination of (I) and (II), which is unprecedented in carborane chemistry.

Results and discussion

We have found that hydrogen atoms of the BH groups in I can be replaced by fluorine under the action of SbF_5 (III) *. In the absence of solvent the reaction begins at 40–60 ° C and becomes uncontrolled because it is very exothermic. The use of perfluorinated hydrocarbons as solvents avoids this difficulty; therefore, we used perfluorochlorobenzene, perfluorodecalin and perfluorotripropylamine.

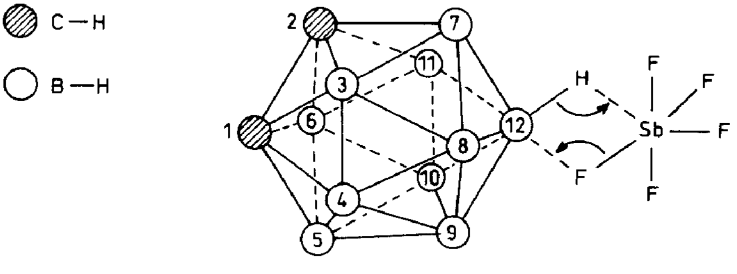
1-Fluoro-, 9,12-difluoro-, 8,9,12-trifluoro- and 8,9,10,12-tetrafluoro-*o*-carboranes are formed in succession in high yields by the reaction of (I) with (III):



$$\underset{B_{10}H_{10}}{CH{-}CH} + SbF_5 \longrightarrow \underset{B_{10}H_{10-n}F_n}{CH{-}CH} + HF + SbF_3$$

(IV, $n = 1$; V, $n = 2$;
VI, $n = 3$; VII, $n = 4$)

We isolated the individual compounds in high yields by varying the reaction conditions (temperature, solvent, ratio of reactants). The reaction is regioselective and starts at those boron atoms (9,12) which are farthest from the carbon atoms and proceeds to the adjacent boron atoms (8 and 10) with the highest electron density. The carbon atoms, as well as the boron atoms directly bonded to them (positions 3,4,5,6,7,11), are inert towards fluorination under these conditions. That the fluorination of I and II with SbF_5 proceeds in the same order as the electrophilic halogenation [1], and the chlorination of I and (II) with CCl_4 and $CHCl_4$ in the presence of $AlCl_3$ [9] also points to an ionic mechanism for the fluorination of I or II with SbF_5. We believe that the fluorination occurs via the four-membered intermediate complex (X) in which the transfer of the fluorine atom occurs synchronously with the shift of the hydrogen atom on the most electronegative boron towards the antimony atom.



(X)

Decomposition of this complex (X) gives the neutral *B*-fluoro-*o*-carborane (IV), HF, and SbF_3. Formally the process is the reduction of Sb^{5+} to Sb^{3+} by action of I.

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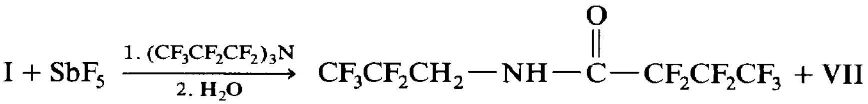
* See V.N. Lebedev, L.I. Zakharkin, Izv. Akad. Nauk SSSR, Ser. Khim., 1986, p. 253 for preliminary report.

The reaction of I with SbF_5 in perfluorotripropylamine solution gives the 3,3,3-trifluoro-2,2-difluoropropylamide of perfluorobutanoic acid which was isolated along with VII from the reaction mixture:



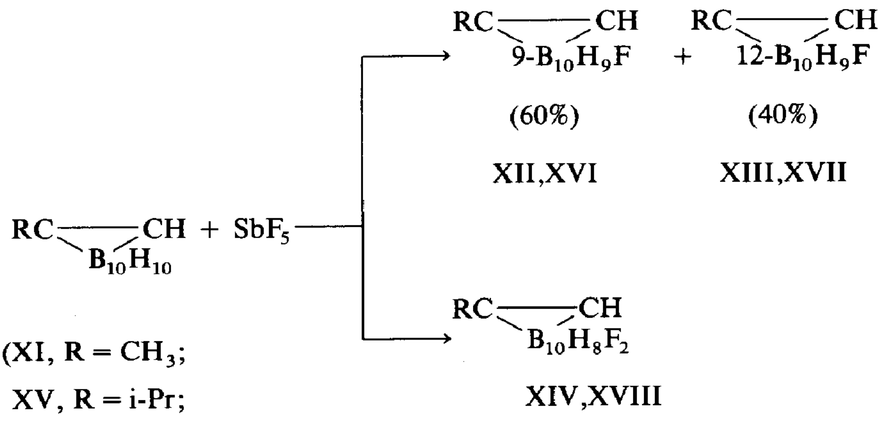
$$\mathrm{I} + SbF_5 \xrightarrow[2.\ H_2O]{1.\ (CF_3CF_2CF_2)_3N} CF_3CF_2CH_2{-}NH{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CF_2CF_2CF_3 + \mathrm{VII}$$

We believe that this amide results from the reaction of the carbocation, formed from the amine and III [10] and hydride ion from which it originates (I).

Reaction of *m*-carborane (II) with III is also regioselective, but in this case replacement of hydrogen by fluorine occurs at the boron atoms in the positions 9 and 10.

$$\underset{\mathrm{II}}{m\text{-}HCB_{10}H_{10}CH} + SbF_5 \longrightarrow \underset{\substack{(\mathrm{VIII},\ n=1;\\ \mathrm{IX},\ n=2)}}{m\text{-}HCB_{10}H_{10-n}F_nCH} + HF + SbF_3$$

Fluorination of 1-organyl-o-carborane is of special interest. Thus, methyl and isopropyl groups are not liable to fluorination. Previously it was reported [11] that electrophilic chlorination of1-methyl-*o*-carborane (XI) yields equal amounts of 1-methyl-9-chloro- and 1-methyl-12-chloro-*o*-carboranes. The influence of the alkyl substituent at the carbon atom on the regioselectivity of the fluorination was first illustrated in the fluorination of 1-alkyl-*o*-carboranes (XI, XV).



(XI, R = CH_3;
XV, R = i-Pr;
XII,XIII,XIV, R = CH_3;
XVI,XVII,XVIII, R = i-Pr)

It was shown previously that the alkyl substituent at the carbon atom of the *o*-carborane cage enhances the electron density at the 9 and 12 positions [12]. 1-Alkyl-9-fluoro-*o*-carboranes (XI, XVI) are the major products of the fluorination of VII and XV; in these compounds the fluorine atom is bonded to the boron atom nearest to the carbon atom bearing the alkyl substituent (*meta* position). Thus, the electron-donating effect of the alkyl group bonded to the carbon atom the in 1 position enhances the electron density of the boron atom in the 9 position (*meta* position). This fact is consistent with published data [13] which show that the

Table 1

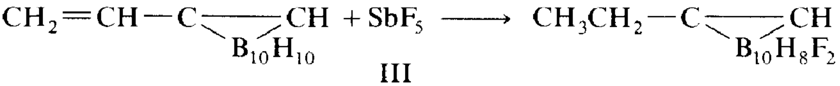
Properties and NMR spectra of polyfluoro-*o*- and -*m*-carboranes

Compound	B.p./M.p. (°C)	Anal. (Found (calc) (%))			Yield (%)	^{11}B NMR (ppm (J(BH) Hz))	^{19}F (ppm (J(BF) Hz))
		C	H	F			
IV	285 ref. 7	23.28 (23.06)	5.82 (6.17)	18.43 (19.10)	42	16.2(0); −4.2(−); −10.7(−); −15.7(−); −17.7(−)	107.9(55.2) F(9)
V	321–322	13.32 (13.43)	5.55 (5.49)	21.09 (21.01)	80	13.1(0); −13.2(152); −18.7(145); −21.4(150)	109.6(55.0 F(9.12)
VI	313	12.10 (12.03)	4.54 (4.35)	28.75 (28.55)	65	10.5(0); 5.6(0); −16.5(145); −20.5(155); −22.2(155); −29.7(150)	112.3(50.0) (9.12) 130.1(57.0) F(8)
VII	332	11.10 (11.06)	3.70 (3.60)	35.15 (34.95)	65	7.4(0); 2.8(0); −23.6(145); −32.1(152)	116.3(57.0) F(9.12) 136.2(57.0) F(8.10)
VIII	251 ref. 7	23.28 (23.01)	5.82 5.79)	18.43 18.25)	75	11.1(0); −7.9(160); −14.5(128); −16.3 (115.0); −19.9(179); −28.2(179)	126.3 (51.0)
IX	293–294	13.32 (13.15)	5.55 (5.40)	21.09 (21.10)	65	7.4(0); −6.9(155); −14.3(137); −18.7(187); −27.1(183)	128.7(50.0)

XII,XIII	195–199	20.43 (20.40)	7.38 (7.04)	10.78 (10.70)	50	XII: 14.2(0); −3.5(168); −10.8(188), −14.3(183) XIII 16.1(0); −8.6(164); −10.8(188); −16.0(180)	XII, 115.0 (55.0) F(9) XIII, 103.2 (57.1) F(12)
XIV	209–210	18.54 (18.40)	6.18 (6.17)	19.57 (20.08)	67	12.8(0); 10.8(0); −13.49143); −15.6(165); −18.2(160)	121.3(55.0), F(9) 109.5(55.0), F(12)
XVI–XVII	99–110 1 mmHg	29.41 (29.87)	8.41 (8.41)	9.31 (9.18)	70	XVI: 15.3(0); −7.3(144); −15.2(189); −16.8(171). XVII: 15.3(0); −4.9(125); −11.3(146); −13.7(173)	XVI: 112.6(55.0) F(9) XVII: 104.6(50.0) F(12)
XVIII	35	26.69 (27.00)	7.10 (7.20)	17.10 (17.15)	80	11.9(0); −13.6(169); −17.0(171); −19.0(122); −20.6(122)	118.4(50.00 F(9) 110.3(50.0) F(12)
XX	100–110 1 mmHg	22.91 923.06)	6.69 (6.72)	18.10 (18.26)	15		120.1(50.0) F(9) 110.3(50.0) F(12)
XXII	80–83	35.50 (35.49)	4.75 (4.66)	20.80 (21.50)	9	15.9(0); −3.9(141); −10.5(151); −14 2(165)	110.1(54.0) F(9) 102.8(54.0) F(12) 33.5

chlorine atom in the 9 position of the *o*-carborane cage causes a more significant increase in the acidity of the SH group at the carbon atom in the 1 position than at the carbon atom in the 2 position of the *o*-carborane cage.

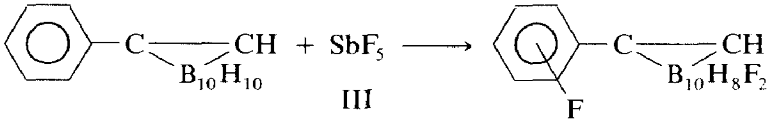
1-Ethyl-9,12-difluoro-*o*-carborane (XX) was obtained from the fluorination of 1-vinyl-*o*-carborane (XIX) in an unexpectedly low yield. In this case ionic hydrogenation of vinyl group probably occurs along with B–F bond formation. Addition of the proton to the vinyl group with the formation of carbocation is the first step of the reaction, then the carbocation abstracts hydride ion from XIX with synchronous fluorination of the boron atoms:



$$CH_2{=}CH{-}C\underset{B_{10}H_{10}}{\frown}CH + SbF_5 \longrightarrow CH_3CH_2{-}C\underset{B_{10}H_8F_2}{\frown}CH$$

XIX III XX

The reaction of 1-phenyl-*o*-carborane with (III) fluorinates both the phenyl group and the carborane cage:



XXI III XXII

Polyfluoro-*o*- and- *m*-carboranes (IV–IX) are white crystalline hydrophobic compounds, soluble in benzene, alcohol, ether. The B–F bond proved to be extremely stable. For instance the carboranyl derivative (VII) does not take part in the Friedel–Krafts reaction and undergoes no changes on refluxing in benzene with $AlCl_3$ or on treatment with $LiAlH_4$, $NaBH_4$ or BuLi.

The chemical shift of a fluorine nucleus in ^{19}F NMR spectra of polyfluoro-*o*-carboranes depends greatly on the position of the boron atom to which the fluorine is bonded. Thus the signals of the fluorine atoms bonded to the 9,12-boron atoms are shifted downfield relative to those of the fluorine atoms bonded to the 8,10-boron atoms (Table 1). It is noteworthy that in general the chemical shifts of fluorine nuclei of polyfluoro-*o*- and -*m*-carboranes lie upfield of the chemical shifts for other compounds having B–F bonds (BF_3, RBF_2, BF_4^-). Shielding of the fluorine nuclei in this case is probably attributable to the polarization of B–F bond in (IV–IX). The signals of the substituted boron nuclei in the ^{11}B NMR spectra are shifted downfield.

The mass spectra of the polyfluoro-*o*- and -*m*-carboranes show peaks corresponding to the molecular ions (M^+). The primary fragmentation pathways involve dehydrogenation, elimination of a fluorine atom, and the degradation of the carborane cage. Reactions of the latter type yield the ions $(M - H_nB)^+$ and $(M - H_nBF)^+$, The $(M - H_nBF_2)^+$ ion peaks are characteristic of the di- or polyfluoro-substituted compounds.

An X-ray diffraction study has confirmed the structure of compound VII to be 8,9,10,12-tetrafluoro-*o*-carborane. Its structure is shown in Fig. 1. Molecule VII occupies a special position on the crystallographic two-fold axis, which passes through the mid-points of the C(1)–C(2) and B(9)–B(12) bonds. However, within experimental error, molecule (VII) and the unsubstituted *o*-carborane have a non-

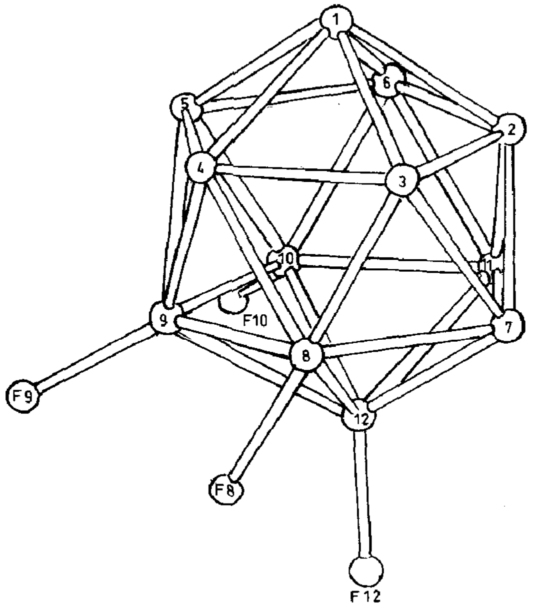


Fig. 1. The structure of VII

crystallographic *mm*2 symmetry (one mirror plane contains the C(1)–C(2) and B(9)–B(12) bonds and the other is normal to the first plane and contains the atoms B(3), B(6), B(8), B(10), F(8), F(10)). Bond lengths and bond angles are listed in Tables 2 and 3 respectively.

Molecule VII represents a distorted icosahedron showing geometric parameters usual for *o*-carborane derivatives. The C–C and C–B bond lengths are 1.633(3) and 1.681(2)–1.709(2) Å, respectively. The B–B distances span the range 1.769(2)–1.809(2) Å, the longest B–B edges involving those B atoms which are the farthest removed from the C atom of the carborane cage: B(9)–B(10) 1.809(2), B(8)–B(9) 1.796(2) and B(9)–B(12) 1.805(3) Å. Similar elongation of the B–B bonds on moving

Table 2

Atomic coordinates ($\times 10^4$, for F$\times 10^5$, for H$\times 10^3$) and their equivalent isotropic (for H atoms—isotropic) temperature factors

Atom	*x*	*y*	*z*	$B_{\text{iso}}^{\text{eq}}$ (Å^2)
F(8)	65580(10)	28493(9)	65940(10)	4.19(2)
F(9)	90090(20)	36739(8)	87317(9)	3.97(2)
C(I)	9504(2)	398(1)	8122(1)	3.07(3)
B(3)	8088(3)	734(1)	6993(2)	3.21(3)
B(4)	7955(3)	1480(2)	8288(2)	3.05(3)
B(5)	10314(3)	1478(2)	8902(2)	3.06(3)
B(8)	8070(2)	2232(1)	6992(2)	2.73(3)
B(9)	9445(2)	26949(1)	8186(2)	2.60(3)
H(I)	916(3)	−31(2)	844(2)	4.7(4)
H(3)	712(3)	17(2)	676(1)	3.5(4)
H(4)	659(3)	134(2)	882(2)	5.1(5)
H(5)	1053(3)	135(2)	977(2)	4.8(5)

Table 3

Bond lengths d(Å) [a]

⎰ F(8)–B(8)	1.358(2)	B(3)–B(8)	1.780(2)
⎱ F(9)–B(9)	1.367(2)	B(4)–B(5)	1.781(2)
C(1)–C(2)	1.633(3)	⎰ B(4)–B(8)	1.786(2)
⎰ C(1)–B(3)	1.708(2)	⎱ B(7)–B(8)	1.782(2)
⎱ C(1)–B(6)	1.709(2)	⎰ B(4)–B(9)	1.775(2)
⎰ C(1)–B(4)	1.681(2)	⎱ B(7)–B(12)	1.783(2)
⎱ C(1)–B(5)	1.679(2)	⎰ B(8)–B(12)	1.809(2)
⎰ B(3)–B(4)	1.782(2)	⎱ B(8)–B(9)	1.796(2)
⎱ B(5)–B(6)	1.769(2)	B(9)–B(12)	1.805(3)

[a] The values for the bonds related by non-crystallographic mirror planes are joined by braces.

farther from the C atoms in the *o*-carborane icosahedron has been found in 9,12-dibromocarborane [14]. It is noteworthy that the opposite trend viz., elongation of the B–B edges nearest to the carbon vertices has also been described in a review [15]. Indeed, in accordance with the inductivity rule [16] the B atoms adjacent to the electronegative C atoms are likely to be electron-deficient and therefore would form weaker and longer B–B bonds compared with those which involve B atoms remote from the carbon vertices. Obviously the introduction of strong electron-accepting substituents (such as F in VII) in the 8, 9, 10 and 12 positions causes redistribution of electron density in the carborane cage which would make the B atoms bonded to these substituents relatively electropositive and the bonds between these atoms would be elongated. Just this situation was observed in molecules having electron-accepting substituents such as F and Br. The carborane cage has remarkable rigidity so that even the introduction of four substituents with the pronounced electron-accepting properties results in barely discernable geometric changes of the icosahedron.

Compound VII is the first fluorinated carborane to be structurally characterized, and therefore no data on the B_{carb}–F distances were previously available. The B_{carb}–F bond lengths in VII 1.358(2) and 1.367(2) Å greatly exceed the B–F distances in BF_3 (the mean B–F bond length is 1.289 Å [17]; the boron atom has planar trigonal coordination). At the same time the B_{carb}–F bonds in VII are considerably shorter than the corresponding bonds in the $H_3N \cdot BF_3$ complex (1.389 Å) which has a tetrahedral boron atom [18]. The bond angles BBF 121.0(1)–123.1(1)° are close to the ideal value of 121.7° for an icosahedron exopolyhedral angle (Table 4).

Table 4

Exopolyhedral bond angles (°) [a]

F(8)B(8)B(3)	123.1(1)	⎰ F(9)B(9)B(4)	122.3(1)
⎰ F(8)B(8)B(4)	122.6(1)	⎱ F(9)B(9)B(5)	122.5(1)
⎱ F(8)B(8)B(7)	122.7(1)	⎰ F(9)B(9)B(10)	121.5(1)
⎰ F(8)B(8)B(12)	121.2(1)	⎱ F(9)B(9)B(8)	121.5(1)
⎱ F(8)B(8)B(9)	121.0(1)	F(9)B(9)B(12)	121.60(7)

[a] The values for the bonds related by non-crystallographic mirror planes are joined by braces.

Experimental

The ^{11}B, ^{19}F, ^{1}H NMR spectra were recorded with a WP-200SY Bruker spectrometer with $BF_3 \cdot OEt_2$, CF_3COOH, HMDS as standards respectively. IR spectra were recorded with an UR-20 spectrometer. Mass spectra were recorded with an MS-30 spectrometer at at an ionization energy of 70 eV and an ionization chamber temperature of 250 ° C. Evaporation of the substances was carried out by means of a direct introduction system at 40–80 ° C.

*X-Ray diffraction study of 8,9,10,12-tetrafluoro-*o*-carborane (VII)*

Crystals of VII are orthorhombic at +20 ° C, $a = 6.873(3)$, $b = 11.886(5)$, $c = 11.922(4)$ Å, $d_{calc} = 1.470$ g/cm^3, $Z = 4$, space group *Pbcn*, the molecule is in a special position on the two-fold axis. The unit cell parameters and intensities of 845 independent reflections with $F^2 \geq 3\sigma$ were measured with a four-circle automated diffractometer CAD-4 (+20 ° C, $\lambda(MoK_\alpha)$, graphite monochromator, the scan rate ratio $\omega/\theta = 1.2:1$, $\theta \leqslant 28°$). The structure was solved by direct methods and refined by the full-matrix least-squares technique first isotropically and then anisotropically. All hydrogen atoms were located in the difference Fourier synthesis and included in the isotropic refinement. The final R-factor was 0.038 ($R_w = 0.049$). All calculations were by the SDP-PLUS program package [19] on a PDP-11/23 PLUS computer. The atomic coordinates and the temperature factors are listed in Table 2.

*9-Fluoro-*o*-carborane (IV)*

To a solution of 6.9 g (0.03 mol) of III in 10 ml of $C_{10}F_{18}$ cooled to 5 ° C * was added 1.73g (0.012 mol) of (I) on stirring in small portions with stirring. When the addition of the reagent was complete, the reaction mixture was maintained successively at 30, 40, 50, 80 and 110–125 ° C for 1, 1, 1, 5 and 4 hours, respectively, and a dark oil settled at the bottom of the flask. On decantation of $C_{10}F_{18}$ (8 ml) the residue was mixed with 20 ml of water. The precipitate that formed was filtered, dissolved in 30 ml of Et_2O, and dried over $CaCl_2$. The ether was then evaporated to give 2.2 g of a solid mixture of initial I and product IV. The mixture was separated by column chromatography (benzene : hexane = 1 : 3) to give 0.81 g of IV. ^{1}H NMR (δ, ppm): 4.30. IR spectrum (ν, cm^{-1}): 1145, 1160, 1210, 1230, 1260, 2620, 3048.

*9,12-Difluoro-*o*-carborane (V)*

With the addition of 14.4 (g (0.1 mol) of I in small portions to a homogeneous mixture of 87.7 g (0.4 mol) of III and 80 ml of $C_{10}H_{18}$ the temperature of the reaction mixture rose to 50 ° C. The mixture was then stirred at 120 ° C for 6 hours. The dark oil that settled was separated, mixed with 400 ml of water, the precipitate was filtered, dissolved in 200 ml of ether and dried over $CaCl_2$. The ether was evaporated off, and the residue was sublimed to give 14.4 g of V. ^{1}H NMR (δ, ppm): 4.27. IR spectrum (ν, cm^{-1}): 1140, 1160, 1210, 1230, 1260, 2620, 3048.

*8,9,12-Trifluoro-*o*-carborane (VI)*

To a mixture of 19.5 g (0.09 mol) of (III) in 15 ml of $C_{10}F_{18}$ was added 1.3 g (0.009 mol) of (I). Once the addition was complete the reaction mixture was kept at

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* The temperature of the reaction mixture must not exceed 100 ° C.

120 °C for 7 hours. Then, the upper clear layer was separated off the residue was mixed with 100 ml of water, and the precipitate that formed was filtered, dissolved in 50 ml of ether and dried over $CaCl_2$. Evaporation of the ether followed by sublimation gave 1.16 g of VI. ^{1}H NMR (δ, ppm): 4.02. IR spectrum (ν, cm^{-1}): 1090, 1140, 1220, 1280, 1295, 2630, 3105.

*8,9,10,12-Tetrafluoro-*o*-carborane (VII)*

To a solution of 91 g (0.42 mol) of (III) in 78 g (0.36 mol) of perfluorotripropylamine was added 8.64 g (0.06 mol) of (I) with vigorous stirring; the temperature of the reaction mixture was kept below 60 °C during the addition. The reaction mixture was then kept at 70 °C for 10 hours. The upper light layer was separated off and the dark oil that was left was mixed with 200 ml of water. The aqueous layer was separated off, and the residual dark oil was filtered to give 10 g of dark solid and 20 g of filtrate, which separated spontaneously into two layers; the dark upper layer was isolated and dried over $MgSO_4$, to give 8.4 g of VII on sublimation of the solid. ^{1}H NMR spectrum (δ, ppm): 4.01. IR spectrum (ν, cm^{-1}): 1140, 1210, 1230, 1279, 1780, 2640, 2655, 2680. Vacuum distillation of the filtrate gave 2.0 g of the 3,3,3-trifluoro-2,2-difluoropropylamide of perfluorobutanoic acid. ^{19}F NMR (δ, ppm): 6.2(s); 44.2(t); 45.9(s); 7.4(s); $J(CH_2CF_2) = 15.2$ Hz. ^{1}H NMR ($(CH_3)_2CO$-d_6, δ, ppm): 4.2(t, CH_2); 9.3(NH), $J(NHCH_2) = 6.6$ Hz.

*9-Fluoro-*m*-carborane (VIII)*

A mixture of 38.8 g (0.174 mol) of III, 30 ml of $C_{10}H_{18}$, and 8.1 g (0.056 mol) of II was heated at 70 °C during one hour. The residue left after the separation of The upper clear layer was removed and the residue was mixed with 200 ml of water, to give a precipitate which was filtered, dissolved in 100 ml of ether and dried over $CaCl_2$. The ether was evaporated off and column chromatography (silica gel, petroleum ether) of the residue gave 6.8 g of VIII was isolated.

*9,10-Difluoro-*m*-carborane (IX)*

To a solution of 21.7 g (0.1 mol) of III in 30 ml of $C_{10}F_{18}$ was added 4.32g (0.03 mol) of II, and the mixture was kept at 120 °C for 7 hours. The dark oil that formed was separated and mixed with 50 ml of water, to give a precipitate which was filtered, dissolved in ether and dried over $CaCl_2$. The ether was evaporated off and the residue was sublimed to give 3.15 g of IX.

*1-Methyl-9-fluoro- (XII), 1-methyl-12-fluoro-*o*-carborane (XIII)*

To a mixture of 8.3 g (0.037 mol) of III in 10 ml of C_6F_5Cl was added 2.8 g (0.018 mol) (XI) in portions, and was kept at 100 °C for 1.5 hours. The reaction mixture was then poured into 50 ml of water. The lower dark organic layer was separated off, and the aqueous layer was extracted with ether. The combined ether extract was and separated organic layer was dried over $CaCl_2$. After evaporation of the solvent in vacuo the residue was sublimed twice to give 1.6 g of a mixture of XII 60% and XIII 40%.

*1-Methyl-9,12-difluoro-*o*-carborane (XIV)*

A mixture of 18.4 g (0.085 mol) of III, and 3.16 g (0.02 mol) of (XI) in 10 ml of $C_{10}F_{18}$ was kept at 120 °C for 9 hours. The dark lower layer was separated off and mixed with 100 ml of water; the precipitate that formed was filtered and dried over P_2O_5. The solid residue (4.5 g) was sublimed in vacuo to give 2.6 g of XIV.

*1-Isopropyl-9-fluoro-(XVI), l-isopropyl-12-fluoro-*o*-carborane (XVII)*

A procedure similar to that previously described was used to obtain 2.0 g of a mixture of XVI and XVII in a ratio of 64 and 36% respectively from a mixture of 2.6 g (0.014 mol) of XV and 6.4 g (0.029 mol) of III in 15 ml of C_6F_5Cl, kept at 90 °C for 2 hours.

*1-Isopropyl-9,12-difluoro-*o*-carborane (XVIII)*

To a 39.4 g (0.182 mol) fo III in 30 ml of $C_{10}F_{18}$ was added 8.4 g (0.043 mol) of XV in portions, and the mixture was kept at 120 °C for 10 hours. The precipitate that formed was separated by filtration, washed with 100 ml of water, dissolved in 200 ml of ether, and dried over $CaCl_2$. The ether was evaporated off and the residue was distilled in vacuo to give 7.6 g of XVIII.

*1-Ethyl-9,12-difluoro-*o*-carborane (XX)*

To 21.6 g (0.1 mol) of III in 20 ml of $C_{10}F_{18}$ was added 3.4 g (0.02 mol) of XIX in portions. The mixture was kept at 120 °C for 16 hours. The oil, that separated was isolated and treated with 100 ml of water. The aqueous suspension was extracted with benzene (2 × 50 ml) and the benzene solution was dried over CaCl. The benzene was evaporated off in vacuo and the residue distilled to give 0.4 g of XX. ^{1}H NMR ($HCCl_3$-*d*, δ, ppm): 1.12(t, 3H); 2.33(q); 3.22 (s, 1H).

*1-(*m*-Fluorophenyl)-9,12-difluoro-*o*-carborane (XXII)*

A mixture of 30.35 g (0.14 mol) of III in 30 ml of $C_{10}F_{18}$ and 4.4 g (0.022 mol) of XXI was kept at 120 °C for 18 hours. The solid was separated off by filtration, washed with 100 ml of water, dissolved in ether, and dried over $CaCl_2$. The ether was evaporated off and the residue was sublimed to give 1.0 g of XXII.

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