Arachno-6,9-$C_2B_8H_{14}$ DICARBABORANE AND ITS 1- AND 5--MONOHALOGENATED DERIVATIVES

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Reduction of *nido*-5,6-$C_2B_8H_{12}$ with sodium tetrahydroborate in ethanolic sodium hydroxide as a new method for preparing *arachno*-6,9-$C_2B_8H_{14}$ is reported. Electrophilic halogenation of 6,9-$C_2B_8H_{14}$ occurs at the $B_{(1)}$ site to give a series of 1-X-6,9-$C_2B_8H_{13}$ (X = Cl, Br, and I) derivatives. Stereoselective addition of hydrogen halides to the $B_{(5)}$—$C_{(6)}$ bond in the [6,9--$C_2B_8H_{10}]^{2-}$ anion results in the formation of 5-X-6,9-$C_2B_8H_{13}$ (X = F, Cl, Br, I and 5'-0--6,9-$C_2B_8H_{13}$) compounds. Constitution of all compounds isolated is suggested on the basis of their ^{1}H and ^{11}B NMR data and the effects of halogen substituents on the ^{11}B NMR shielding of individual cage boron atoms are discussed in terms of $\Delta\delta$ and k_2 values.

Arachno-6,9-$C_2B_8H_{14}$ (*I*), as the first representative of the ten-vertex *arachno*-family of dicarbaboranes, was first isolated in our laboratory[1] in the reaction of *nido*-5,6-$C_2B_8H_{12}$ with sodium amalgam in ethanol at 50°C. A new, more convenient way for obtaining carborane *I* and the reactions leading to its 1- and 5-substituted halo derivatives were reported in two preliminary communications[2,3]. We wish to report herein experimental details of the syntheses and to discuss the effects of halogen substituents on the ^{11}B NMR shielding of individual boron atoms in the series of 1- and 5-halogenated derivatives of *I*.

Treatment of the 5,6-$C_2B_8H_{12}$ species[4] with sodium tetrahydroborate in a re-fluxing alkaline ethanolic solution, followed by the acidification of the reaction mixture, resulted in the formation of carborane *I* in moderate yields. The product thus obtained is slightly contaminated with 5-C_2H_5O-6,9-$C_2B_8H_{13}$, which can be easily removed either by crystallization or by column chromatography. The above described procedure is more convenient than the sometimes irreproducible original method[1].

Formation of carborane *I* is consistent with the earlier proposed[1] reductive cleavage of the $C_{(5)}$—$C_{(6)}$ bond in the framework of 5,6-$C_2B_8H_{12}$, followed by moving the $C_{(6)}$ vertex into a new position. This mode of rearrangement of the 10-vertex *nido*-borane cage strongly parallels the mechanism proposed for the $6 \rightarrow 5$ rearrangement in the iridadecaborane series[5]. The reduction of 5,6-$C_2B_8H_{12}$ to 6,9-$C_2B_8H_{14}$ represents another example of a typical *nido-arachno* transformation

and, in this respect, it is an analogue of the well-known reduction of $B_{10}H_{14}$ to $[B_{10}H_{14}]^{2-}$ with the tetrahydroborate ion[6].

The $AlCl_3$-catalyzed halogenation of carborane I with CCl_4, Br_2 and I_2 produces a series of 1-halogenated derivatives, $1\text{-}X\text{-}6,9\text{-}C_2B_8H_{13}$ (II) (X = .Cl, IIa; Br, IIb, and I, IIc), the structure of which is in agreement with the ^1H and ^{11}B NMR data (Table I and II). The explicit preference for electrophilic substitution at the $B_{(1)}$ site

TABLE I

Properties and ^1H NMR spectra of monosubstituted $X\text{-}6,9\text{-}C_2B_8H_{13}$ compounds

X	M.p., °C	m/z	R_F	$\delta(^1H\ NMR)^a$		
				$CH_{(eq)}$	$CH_{(ax)}$	μH
H^b	$146-147^1$	126	0·32	0·86(2)	−0·66(2)	−2·84(2)
1-Cl	155−158	162	0·11	1·11(2)	−0·35(2)	−2·10(2)
1-Br	184−186	206	0·10	1·10(2)	−0·38(2)	−2·22(2)
1-I	146−147	252	0·18	1·12(2)	−0·38(2)	−2·23(2)
5-F	142−144	144	0·20	0·94(2)	−0·50(2)	−2·91(2)
5-Cl	64−66	122	0·21	1·05(2)	−0·09	−0·02
					−0·41	−2·65
5-Br	47−48	122	0·20	1·17	0·03	−1·01
				1·02	−0·47	−2·54
5-I	38−40	122	0·18	1·23	0·09	−1·22
				1·03	−0·55	−2·52
$5\text{-}C_2H_5O$	48−50	166	0·05	0·74(2)	−0·61(2)	$−2·94(2)^c$
5,5′-O	$200−220^d$	266	0·10	0·89(2)	−0·48(2)	−2·92(2)

^{a} All the signals are singlets, intensity other than 1 in parentheses; ^{b} relevant data of parent $6,9\text{-}C_2B_8H_{14}$ for comparison; ^{c} two additional signals of the C_2H_5O group at δ 3·69 (2 H, q, $J = 7$ Hz, CH_2), 1·16 (3 H, t, $J = 7$ Hz, CH_3); ^{d} decomposition.
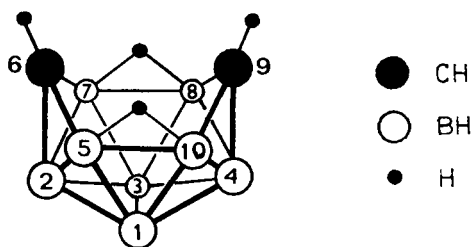

CH

BH

H

FIG. 1

Simplified structure and numbering system of $arachno\text{-}6,9\text{-}C_2B_8H_{14}$

TABLE II
^{11}B NMR signal assignments of monosubstituted X-6,9-C$_2$B$_8$H$_{13}$ compounds

| X	B(2)	B(4)	B(5)	B(10)	B(7)	B(8)	B(1)	B(3)
1-Cl	4·35(2)[a] / 166[c]		−16·50(2) / 150			−16·80(2) / 150	−18·10[b] / —	−35·90 / 160
1-Br	4·50(2) / 170		−15·90(2) / 160/50			−16·65(2) / 158/50	−25·45[b] / —	−35·20 / 158
1-I	4·95(2) / 166		−15·10(2) / 160/150			−16·20(2) / 160/50	−43·00[b] / —	−34·25 / 157
5-F	3·26 / 145	0·71 / 156	4·55[b] / —	−21·45 / 145/51	−19·44 / 135/51	−23·56 / 140/49	−39·26 / 154	−39·26 / 154
5-Cl	5·90 / 164	1·90 / 162	−5·50[b] / 57	−18·20 / 161/54	−17·15 / 158/55	−20·55 / 152/49	−37·50 / 150	−37·90 / 151
5-Br	6·55 / 166	2·50 / 164	−13·02[b] / 61	−17·25 / 157/51	−16·34 / 157/54	−19·55 / 150/50	−35·00 / 154	−37·35 / 153
5-I	7·20 / 175	3·40 / 173	−30·00[b] / 50	−15·75 / 160/34	−15·75 / 160/50	−18·05 / 140/50	−34·25 / 157	−36·70 / 157
5-C$_2$H$_5$O	2·10 / 160	0·65 / 166	5·45[b] / —	−22·70 / 144	−20·60 / 150/52	−24·10 / 144	−38·75 / 147	−40·85 / 142
5,5'-O	1·97 / 179	0·75 / 173	3·25 / —	−21·15 / 157/59	−20·35 / 154/43	−23·85 / 173/35	−38·79 / 155	−39·08 / 144

[a] δ_B in ppm relative to BF$_3$.O(C$_2$H$_5$)$_2$, intensity higher than 1 in parentheses, all the signals are doublets; [b] singlets of the substituted boron atom; [c] $J(^{11}B—^1H)$ coupling constants (in Hz).

is consistent with the previously reported results[1] of deuteration of carborane I in the ^{2}HCl–AlCl$_3$–CS$_2$ system.

A series of *arachno*-5-X-6,9-C$_2$B$_8$H$_{13}$ compounds (III) $(X = F, IIIa;$ Cl, $IIIb;$ Br, $IIIc,$ and I, $IIId)$ is obtained in a courious high-yield reaction of the *nido*-[6,9--C$_2$B$_8$H$_{10}$]$^{2-}$ dianion[7,8] with hydrogen halides in benzene, as in the following equation:

$$[6,9\text{-}C_2B_8H_{10}]^{2-} + 3\,HX \rightarrow 5\text{-}X\text{-}6,9\text{-}C_2B_8H_{13} + 2\,X^- . \qquad (A)$$
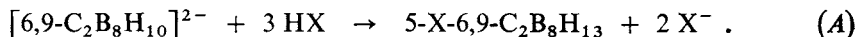
When c. 97% hydrogen fluoride is used, 5,5'-O-(6,9-C$_2$B$_8$H$_{13}$)$_2$ $(IIIe)$ is generated as a main product besides the expected 5-fluoro derivative $IIIa$. Deuterium chloride yields trideuterio derivative 5-Cl-^{2}H$_3$-6,9-C$_2$B$_8$H$_{10}$ $(IIIf)$ the ^{1}H NMR spectrum of which indicates almost quantitative deuteration at the C$_{(6)}$ axial CH site, c. 50% deuteration at the bridging positions, and a progressive deuteration at the C$_{(9)}$ axial position.

0660 [6,9–C$_2$B$_8$H$_{10}$]$^{2-}$ [5–Cl–^{2}H$_{(ax)}$–6,9–C$_2$B$_8$H$_{10}$]$^{2-}$ $III\,f$
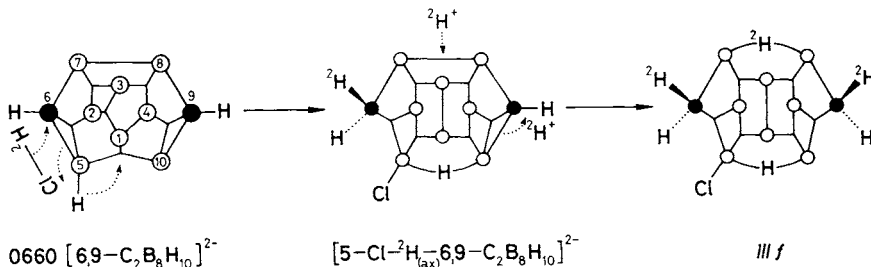
SCHEME 1

Formation of 5-chlorodervative $IIIf$ *via* stereoselective addition of ^{2}HCl to the B$_{(5)}$–C$_{(6)}$ bond

Taking into account the above facts, reaction (A) seems to be likely a consequence of an unsaturated character of the [6,9-C$_2$B$_8$H$_{10}$]$^{2-}$ dianion whose electronic structure can be expressed in terms of the only possible 0660 topological formula indicating a partial double bond character of the B$_{(5)}$–C$_{(6)}$ bond. A reasonable mechanism, demonstrated in Scheme 1 for the reaction with ^{2}HCl, should consist in a highly stereoselective addition of ^{2}HCl to this bond to give an intermediate [5-Cl-^{2}H$_{(ax)}$-6,9-C$_2$B$_8$H$_{10}$]$^{2-}$ anion. Subsequent addition of two more deuterons, one at the bridging site and the other at the C$_{(9)}$ atom, then generates species $IIIf$ with two axial C—^{2}H bonds and one B—^{2}H—B bridge. Of course, the same mechanism of this typical *nido-arachno* transformation can be applied to the reactions of other hydrogen halides and water in the case of compound $IIIe$. In the latter case the formed 5-HO-6,9-C$_2$B$_8$H$_{13}$ intermediate is dehydrated by excess hydrogen fluoride to produce a system in which two 6,9-C$_2$B$_8$H$_{13}$ moieties are joined by the oxygen atom. When more diluted acid is used, the discussed 5-HO derivative undergoes

further $B_{(5)}$ degradation to give a high yield of 4,6-$C_2B_7H_{13}$, as demonstrated earlier in the reaction with diluted hydrochloric acid[7].

^{1}H NMR spectra of 1-substituted derivatives *IIa−IIc* consist of three signals of equal intensity, attributable to $CH_{(eq)}$, $CH_{(ax)}$ and μH protons, reading upfield. Consistent with the asymmetrical 5-substitution are the corresponding spectra of species *IIIa−IIIe*, displaying six singlets of noneqivalent $CH_{(eq)}$, $CH_{(ax)}$, and B— —H—B groups, some signals being superimposed in a few cases. Table I shows a general trend for the decrease in shielding of these groups due to the presence of halogens in both 1- and 5-substituted series with minor and mostly irregular differences for individual halogens.

^{11}B NMR spectra of 1-halogenated derivatives consist of one singlet of the substituted $B_{(1)}$ atom and 2 : 2 : 2 : 1 patterns of doublets, while the spectra of 5-substituted compounds display one $B_{(5)}$ singlet and seven doublets of the remaining boron atoms (Table II). An unambiguous assignment of signals in both series has been made on the basis of recent 2D $\{^{11}B—^{11}B\}$ NMR study[9] which confirmed the preliminary reported results in the 1-halogenated series[1]. Nevertheless, the original assignment of the $B_{(7,8,10)}$ atoms in the 5-substituted series[2], based on the analogy with that for 5-halogenated derivatives of decaborane(14)[10], has been corrected to show that the trends in $\Delta\delta$ observed in the *nido*-series cannot be simply applied in the *arachno*-series of compounds.

Table III reflects the effect of 1- and 5-substituents on the shielding of individual boron atoms in the *arachno*-6,9-$C_2B_8H_{14}$ system in terms of $\Delta\delta$ and k_2 values, *i.e.* in a similar manner as in the series of halogenated derivatives of decaborane(14)[10]. Inspection of Table III immediately reveals a trend of decreasing shielding of halogen substituted atoms in the order $\sigma(I) > \sigma(Br) > \sigma(Cl) > \sigma(F)$. There is a good linear correlation between relevant $\Delta\delta$ values and the electronegativity of the halogen in both series, the low-field shift being more pronounced in the 1-halogenated series due to higher charge density at the B(1) site.

Taking into account the effect of halogens on the shielding of the unsubstituted atoms, a general shielding decreasing in the order $\sigma(F) > \bar{\sigma}(Cl) > \sigma(Br) > \sigma(I)$ is expected[10]. Such a trend is seen in the mean shift values $(\Delta\delta)$ for the substitution at the 1- and 5-sites, as shown in Table III. The found shifts also show a variation in the sensitivity to the site of substitution as indicated by the variance (k_2) of the shift from the mean value. The relatively high k_2 values for 5-substituted compounds indicate increased sensitivity toward substitution at $B_{(5)}$ and thus reflect the electron deficient nature of that part of the molecule. The regular descrease in k_2 on going through the 5-F, 5-Cl, 5-Br, and 5-I series seems to be caused by the descreasing overlap between the substituent *n* orbitals and the cage. However, in contrast to $B_{10}H_{14}$ (ref. 10), for the 1-halogenated compounds, a reverse trend of increase in k_2 is clearly seen in Table III and we have not any reasonable explanation of this observation. The very low k_2 values for the 1-X-6,9-$C_2B_8H_{13}$ series indicate a rela-

TABLE III

^{11}B NMR Chenical shift changes ($\Delta\bar{\delta}_B$) and mean shift values ($\bar{\delta}(k_2)$) of individual boron atoms for monosubstituted X-6,9-$C_2B_8H_{13}$ compounds (superscripts V, T, M, A, and S stand for vicinal, trans, meta, antipodal, and substituent effects, respectively)

X	$B_{(2)}$	$B_{(4)}$	$B_{(5)}$	$B_{(10)}$	$B_{(7)}$	$B_{(8)}$	$B_{(1)}$	$B_{(3)}$	$\Delta\bar{\delta}(k_2)$
1-Cl	0·63^V		0·99^V		0·69^M		19·55^S	1·75^V	0·91(0·18)
1-Br	0·70^V		1·59^V		0·84^M		12·20^S	2·45^V	1·24(0·44)
1-I	0·78^V		2·39^V		1·29^M		−5·35^S	3·40^V	1·76(0·97)
5-F	−0·46^V	−3·01^M	22·04^S	−3·96^V	−1·95^{M,T}	−6·17^A	−1·61^V	−1·61^M	−2·68(3·61)
5-Cl	2·18^V	−1·82^M	11·99^S	−0·71^V	0·34^{M,T}	−3·06^A	1·95^V	−0·25^M	−0·20(3·60)
5-Br	2·83^V	−1·22^M	4·47^S	0·24^V	1·55^{M,T}	−2·06^A	2·65^V	0·35^M	0·56(3·35)
5-I	3·48^V	−0·32^M	−12·51^S	1·74^V	1·74^{M,T}	−0·56^A	3·40^V	0·95^M	1·49(2·58)
5-C_2H_5O	−1·62^V	−3·07^M	22·94^S	−5·21^V	−3·11^{M,T}	−6·61^A	−1·10^V	−3·20^M	−3·41(3·71)
5,5'-O	−1·75^V	−2·97^M	14·24^S	−3·66^V	−2·86^{M,T}	−6·36^A	−1·14^V	−2·33^M	−3·01(2·87)

tive insensitivity toward substitution as a consequence of a relatively high negative $B_{(1)}$ charge.

Mass spectra of all 1-substituted derivatives and those of 5-F and 5,5'-O compounds exhibit the expected cut-offs, while the spectra of 5-X-6,9-$C_2B_8H_{13}$ (X = Cl, Br, and I) derivatives show a cut-off at m/z 122, corresponding to a *closo*-$[C_2B_8H_{10})^+$ molecular ion, which is consistent with a loss of H_2 and HX under the conditions of the mass spectral experiment. The spectrum of 5-C_2H_5O-6,9-$C_2B_8H_{13}$ (m/z 166) is compatible with double dehydrogenation to a *closo*-C_2H_5O—$C_2B_8H_9$ species under comparable conditions.

EXPERIMENTAL

[1]H (200 MHz) and ^{11}B (64·18 MHz) NMR spectra were obtained on a Varian XL-200 equipment and the ^{19}F NMR spectrum (94·1 MHz) on a Varian XL-100 device in deuteriochloroform at 25°C. Chemical shifts are given in δ (ppm, relative to tetramethylsilane, $BF_3.O(C_2H_5)_2$ and $CFCl_3$, positive values downfield). [11]B chemical shift changes are defined as $\Delta\delta_i = \delta_i^s - \delta_i^p$, the superscripts s and p relate to the ith atom of the substituted and parent 6,9-$C_2B_8H_{14}$ compound. Positive values of $\Delta\delta$ denote a low-field shift change. Mean shift values ($\overline{\Delta\delta}$) and the values of variance of the shift from the mean value (k_2) relate to unsubstituted atoms, being defined as $\Delta\delta = 1/7 \sum_{i=1}^{i=7} \Delta\delta_i$ and $k_2 = 1/6 \sum_{i=1}^{i=7} (\Delta\delta_i - \overline{\Delta\delta})^2$. Low resolution mass spectra were measured at 70 eV using a GC/MS HP-5989 spectrometer. Melting points were determined in sealed capillaries under nitrogen and are uncorrected. Purity of individual compounds was monitored by TLC on Silufol (silica gel on aluminium foil, producer Kavalier, Czechoslovakia) in benzene––hexane (1 : 2). Unless otherwise stated, all reactions were carried out under dry nitrogen and standard operations, such — as filtration and evaporation of solvents, were performed in *vacuo*. Benzene was distilled with $NaAlH_2(OC_2H_4OCH_3)_2$, tetrachloromethane and carbon disulphide with P_4O_{10} prior to use. Deuterium chloride was prepared by the reaction of benzoyl chloride with deuterium oxide (Merck, 99·9%). Hydrogen bromide was generated in the reaction of bromine with boiling tetraline and then liquified at $-78°C$. Hydrogen iodide was evolved by adding dropwise concentrated hydroiodic acid to excess P_4O_{10} and was solidified at $-78°C$. Gaseous HBr and HI were evolved by slow evaporation of the condensed products. 5,6-$C_2B_8H_{12}$ and $[6,9-C_2B_8H_{10}]Na_2$ were prepared according to previously reported procedures[6,7]. Properties of all compounds isolated are summarized in Tables I—III.

6,9-Dicarba-*arachno*-decaborane(14), 6,9-$C_2B_8H_{14}$ (*I*)

Under stirring, a solution of 5,6-$C_2B_8H_{12}$ (12·3 g; 0·1 mol) in ethanol (150 ml) was added over 15 min at 0°C to a solution of $NaBH_4$ (3·8 g; 0·1 mol) and NaOH (4·0 g; 0·1 mol) in ethanol (150 ml). The mixture turned yellow and hydrogen was evolved during this period. The mixture was then heated to reflux and the reflux was continued for 4 h. The mixture was cooled down to ambient temperature, the precipitate was filtered off and the filtrate was evaporated. The residue was shaken with water (100 ml) and benzene (20 ml) and the organic portion was evaporated to give the first crop (3·4 g) of pure carborane *I*. The aqueous layer was neutralized with diluted HCl and the filter cake from the first filtration was added to the suspension thus formed. The mixture was shaken with three 20 ml-portions of benzene and the filtered benzene

fractions were evaporated leaving a product which was combined with the first portion of *I* and crystallized from hexane to obtain 3 g of pure carborane *I*. The mother liquors were evaporated with silica gel (5 g) and the solids were placed onto a silica gel column (2·5 × 30 cm). Elution with benzene–hexane (1 : 2) developed two major bands of compound *I* (R_F 0·32) and *IIIe* (R_F 0·05). Both compounds were isolated on evaporating pure fractions to obtain additional 1·2 g of 6,9-$C_2B_8H_{14}$ (total yield 37%) along with 0·2 g (1·2%) of 5-C_2H_5O-6,9-$C_2B_8H_{13}$.

1-Chloro-6,9-dicarba-*arachno*-decaborane(14), 1-Cl-6,9-$C_2B_8H_{13}$ (*IIa*)

A solution of carborane *I* (0·5 g; 4 mmol) in tetrachloromethane (30 ml) was treated with anhydrous aluminium chloride (0·1 g; 0·75 mmol) under reflux for 30 min. Water (20 ml) was added dropwise after cooling to room temperature and under intensive stirring for 30 min. The organic layer was separated, dried with $MgSO_4$, filtered and evaporated. The solid residue was dissolved in benzene (10 ml) and placed onto a column (2·5 × 25 cm) of silica gel. Elution with benzene developed two main fractions of R_F 0·32 and 0·11 (checked by TLC) from which recovered compound *I* (0·1 g; 20%) and 1-Cl-6,9-$C_2B_8H_{13}$ (0·3 g; 47%) were isolated after evaporating the collected fractions and recrystallization of *IIa* from cyclohexane–benzene (2 : 1).

1-Bromo-6,9-dicarba-*arachno*-decaborane(14), 1-Br-6,9-$C_2B_8H_{13}$ (*IIb*)

To a solution of compound *I* (1 g; 8 mmol) in carbon disulphide (20 ml), aluminium chloride (0·1 g; 0·75 mmol) was added together with a solution of bromine (0·5 ml; 11 mmol) in carbon disulphide (10 ml). The mixture was stirred at room temperature for 8 h and the volatiles were then stripped off *in vacuo*. After adding water (10 ml) and benzene (30 ml) under shaking, the benzene layer was dried with $MgSO_4$, filtered and concentrated to a volume of c. 10 ml. The solution was placed onto a column of silica gel and eluted with benzene to isolate 0·6 g (37%) of 1-Br-6,9-$C_2B_8H_{13}$ after evaporating the main fraction of R_F 0·10 (checked by TLC) and crystallizing the product from cyclohexane–benzene (1 : 2).

1-Iodo-6,9-dicarba-*arachno*-decaborane(14), 1-I-6,9-$C_2B_8H_{13}$ (*IIc*)

Aluminium chloride (0·1 g; 0·75 mmol) was added to a solution of carborane *I* (0·5 g; 4 mmol) and iodine (1·5 g; 5 mmol) in benzene (50 ml) and the resulting mixture was refluxed for 5 h. After cooling down to ambient temperature, shaking with 5% Na_2SO_3 and two 25 ml-portions of water, the benzene layer was dried with $MgSO_4$ and the benzene was removed. The pink residue was recrystallized from cyclohexane–benzene (2 : 1) to isolate 0·8 g (80%) of 1-I-6,9-$C_2B_8H_{13}$.

5-Fluoro-6,9-dicarba-*arachno*-decaborane(14), 5-F-6,9-$C_2B_8H_{13}$ (*IIIa*),
and 5,5′-Oxido-bis[6,9-dicarba-*arachno*-decaborane(14)], 5,5′-O-(6,9-$C_2B_8H_{13}$)$_2$ (*IIIe*)

To a suspension of [6,9-$C_2B_8H_{10}$]Na_2 (2·4 g; 0·014 mol) in benzene (50 ml) c. 97% hydrogen fluoride (2 ml) was added in a polyethylene reaction vessel and the mixture was stirred for 2 h at 10°C. Excess hydrogen fluoride was neutralized with solid Na_2CO_3, the mixture was filtered and the solids were washed with benzene (20 ml). The benzene filtrate was evaporated and the residue was recrystallized from benzene–hexane (1 : 1) (20 ml) to obtain 0·6 g of crude compound *IIIe*. The mother liquors were evaporated with silica gel (5 g) and placed atop a silica gel column (2·5 × 30 cm). Elution with benzene–hexane (1 : 2) developed two major fractions of R_F 0·20 and 0·10. The former fraction was evaporated and the residue was sublimed at 100 to 120°C (bath) 1·3 Pa^{-1} to give 0·2 g (10%) of 5-F-6,9-$C_2B_8H_{13}$, which can be recrystallized from

hexane to form needles. The ^{19}F NMR spectrum of *IIIa* shows a quartet ($J_{F-B} = 5\,4Hz$) at δ_F –133·2 ppm. The second fraction of R_F 0·1 was evaporated, combined with the first crop of *IIIe* and the combined products were recrystallized from benzene–hexane (1 : 1) to give 0·65 g (35%) of pure 5,5'-O-6,9-$(C_2B_8H_{13})_2$.

5-Chloro-6,9-dicarba-*arachno*-decaborane(14), 5-Cl-6,9-$C_2B_8H_{13}$ *(IIIb)*

Anhydrous hydrogen chloride was introduced slowly at 25°C to a suspension of $[6,9\text{-}C_2B_8H_{10}]$. .Na$_2$ (1·5 g; 9 mmol) in benzene (50 ml) for 1 h and the resulting mixture was filtered. Excess HCl was removed *in vacuo*, the clear filtrate was evaporated and the residual oily crude product was chromatographed on a column (2·5 × 30 cm) of silica gel in benzene–hexane (2 : 1). The combined fractions of R_F 0·21 (checked by TLC) were stripped off, the residue was dried at 25°C 1·3 Pa^{-1} and distilled at 80°C (bath) 1·3 Pa^{-1} to give 1·0 g (70%) of crystalline 5-Cl-6,9-$C_2B_8H_{13}$ after spontaneous cooling to room temperature.

5-Chloro-trideuterio-6,9-dicarba-*arachno*-decaborane(14), 5-Cl-$^2H_3$-6,9-$C_2B_8H_{10}$, *(IIIf)*

Anhydrous deuterium chloride was introduced for 1 h at 25°C to a stirred suspension of $[6,9\text{-}C_2B_8H_{10}]Na_2$ (0·6 g; 3·6 mmol) in benzene (50 ml). Excess deuterium chloride was removed in vacuo, the mixture was filtered and the filtrate was evaporated and dried at 25°C 1·3 Pa^{-1}. The residue was sublimed at 50°C 1·3 Pa^{-1} onto a finger cooled to 0°C to collect 0·05 g of material which was discarded. Crystalline *IIIf* was obtained by distilling the residue at 80°C (bath) 1·3 Pa^{-1} (0·5 g; 85%), m.p. 65—68°C; $^1H\{^{11}B\}$ NMR spectrum (100 MHz, $C_6^2H_6$): δ 0·40 (2 H, $CH_{(eq)}$), –1·20 (c. 0·1 H, $C_{(6)}$—$H_{(ax)}$), –1·50 (c. 1 H, $C_{(9)}$—$H_{(ax)}$, μH), –3·30 (c. 0·5 H, μH), the ^{11}B NMR spectrum of *IIIf* being almost identical with that of *IIIb*.

5-Bromo-6,9-dicarba-*arachno*-decaborane(14), 5-Br-6,9-$C_2B_8H_{13}$ *(IIIc)*

In an apparatus equipped with a reflux condenser cooled to –78°C, gaseous hydrogen bromide was slowly passed through a stirred suspension of $[6,9\text{-}C_2B_8H_{10}]Na_2$ (1·05 g; 6·3 mmol) in benzene (50 ml) for 1 h at 25°C. Excess hydrogen bromide was removed *in vacuo*, the mixture was filtered and the filtrate was then evaporated. Further work up of the product as in the case of compound *IIIb* resulted in the isolation of 1·1 g (86%) of 5-Br-6,9-$C_2B_8H_{13}$.

5-Iodo-6,9-dicarba-*arachno*-decaborane(14), 5-I-6,9-$C_2B_8H_{13}$ *(IIId)*

Anhydrous hydrogen iodide was slowly introduced to a stirred suspension of $[6,9\text{-}C_2B_8H_{10}]Na_2$ (0·6 g; 3·6 mmol) in benzene (50 ml) for 1 h at room temperature. Excess hydrogen iodide was removed *in vacuo*, the mixture was filtered and the filtrate was washed with 2% Na$_2$SO$_3$ (50 ml) and water (50 ml). The benzene layer was dried over MgSO$_4$ and filtered. Similar work up of the filtrate as in the preceding experiment yielded 0·6 g (67%) of 5-I-6,9-$C_2B_8H_{13}$.

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