

# TETRACARBA-*dinido*-DOCOSABORANE (C<sub>4</sub>B<sub>18</sub>H<sub>22</sub>), A NEW TYPE OF CARBORANE, ITS CHEMISTRY AND STRUCTURE

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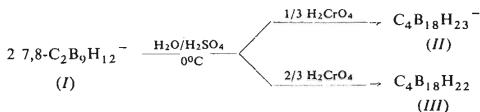
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Oxidation of the anion 7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub><sup>-</sup> by chromic acid gave either *dinido*-carborane C<sub>4</sub>B<sub>18</sub>H<sub>22</sub> or the anion C<sub>4</sub>B<sub>18</sub>H<sub>23</sub><sup>-</sup>, depending on the quantity of the acid. On the basis of their <sup>11</sup>B NMR spectra and some chemical reactions structures for the two compounds are propounded.

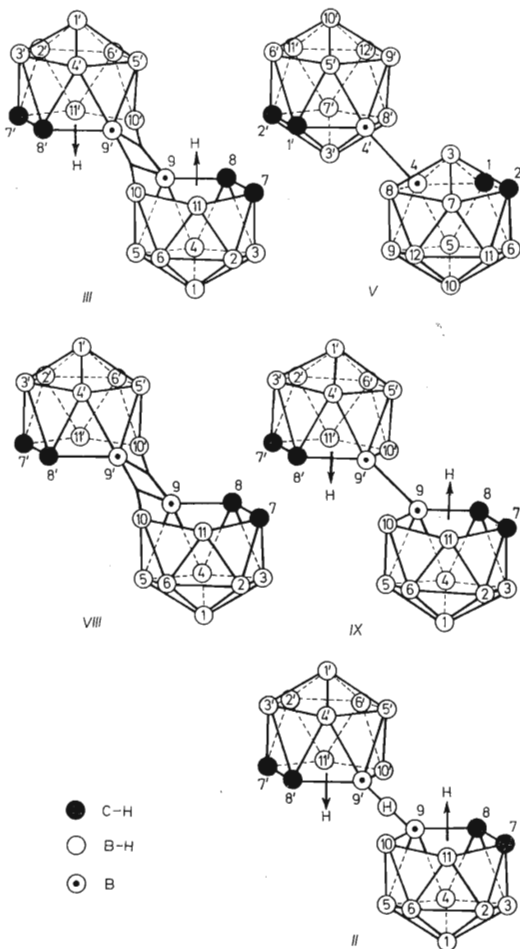
Since the discovery<sup>1</sup> of the first *nido*-carborane 7,8-C<sub>2</sub>B<sub>9</sub>H<sub>13</sub> in 1964, the number of compounds of this series has been continuously growing. At present the known *nido*-carboranes with two atoms of carbon are: C<sub>2</sub>B<sub>3</sub>H<sub>7</sub> (ref.<sup>2</sup>), C<sub>2</sub>B<sub>4</sub>H<sub>7</sub> (ref.<sup>3</sup>), C<sub>2</sub>B<sub>7</sub>H<sub>11</sub> (ref.<sup>4</sup>), 5,7-C<sub>2</sub>B<sub>8</sub>H<sub>12</sub> (ref.<sup>5</sup>), 5,6-C<sub>2</sub>B<sub>8</sub>H<sub>12</sub> (refs.<sup>6,7</sup>), 7,8-C<sub>2</sub>B<sub>9</sub>H<sub>13</sub> (ref.<sup>1</sup>), 2,9-C<sub>2</sub>B<sub>9</sub>H<sub>13</sub> (ref.<sup>8</sup>), C<sub>2</sub>B<sub>7</sub>H<sub>13</sub> (ref.<sup>9</sup>) and 6,9-C<sub>2</sub>B<sub>8</sub>H<sub>14</sub> (ref.<sup>10</sup>).

This paper deals with the synthesis and properties of the first *dinido*-carborane, the formation of which in the oxidation of the 7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub><sup>-</sup> anion has been reported in a preliminary communication<sup>11</sup>. The oxidation of isomeric C-monosubstituted anions C<sub>2</sub>B<sub>9</sub>H<sub>12</sub><sup>-</sup> by chromic acid has also been investigated by Zakharkin and co-workers<sup>12,13</sup>. Whereas these authors paid attention only to the organic products of the reaction, our experiments on the oxidation of the anion 7,8-C<sub>2</sub>B<sub>9</sub>H<sub>12</sub><sup>-</sup> (I) by chromic acid revealed two new *nido*-compounds of the carborane series<sup>11</sup>. One was the anion C<sub>4</sub>B<sub>18</sub>H<sub>23</sub><sup>-</sup> (II), isolated in the form of its caesium and tetramethylammonium salts, the other was a uncharged carborane, C<sub>4</sub>B<sub>18</sub>H<sub>22</sub> (III):



This reaction resembles the well-known<sup>14,15</sup> oxidative dimerization of anion B<sub>10</sub>H<sub>10</sub><sup>2-</sup> to anions B<sub>20</sub>H<sub>19</sub><sup>3-</sup> and B<sub>20</sub>H<sub>18</sub><sup>2-</sup>, but has no parallel in the carborane series. In our preliminary communication<sup>11</sup>, based on the <sup>11</sup>B NMR spectra, we proposed

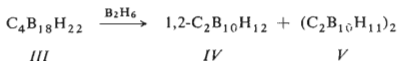
\* Part XXXVI in the series Chemistry of Boranes; Part XXXV: This Journal 39, 1805 (1974).



for the carborane *III* a structure representing an unusual connexion, hitherto undescribed with *nido*-compounds, of two *nido*-skeletons by a pair of three-centre *exo* bonds. This structure was advanced on the basis of analogy to the anion  $B_{20}H_{18}^{2-}$  (ref.<sup>15</sup>), but the point of connexion was assigned intuitively and the positions of the carbon atoms in the open-face pentagon remained to be determined. On the basis of new chemical and physical data, compiled in the present paper, we now ascribe this carborane structure *III*.

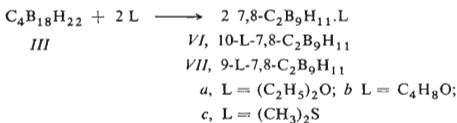
The carborane *III* in aqueous ethanol behaves as a dibasic acid of  $pK_a^I = pK_a^{II} = 2.4$ . Its  $^{11}B$  NMR spectrum (Fig. 1) has 7 doublets of relative intensities 1:1:1:1:1:2:1, and one singlet of relative intensity 1 at  $\delta -4.15$  p.p.m. The presence of only nine boron signals in the molecule  $C_4B_{18}H_{22}$  (*III*) and the fact that the IR spectrum exhibits absorptions at 1830 and 1890  $cm^{-1}$ , characteristic of B—H—B bonds, accord with the view that the molecule  $C_4B_{18}H_{22}$  (*III*) is a combination of two identical  $C_2B_9H_{11}$  *nido*-skeletons. From the singlet ( $-4.15$  p.p.m.) in the  $^{11}B$  NMR spectrum it can further be inferred that the two skeletons are connected by two three-centre bonds through B atoms not carrying the terminal hydrogen atoms ( $B_{(9)}-B_{(9)}$ ). The absence of carbon atoms in these positions also follows from the fact that every atom of carbon in the molecule  $C_4B_{18}H_{22}$  (*III*) carries one atom of hydrogen as shown by the  $^1H$  NMR spectrum exhibiting a sole, unusually wide C—H band at  $\delta 3.3$  p.p.m. (relative to tetramethylsilane), composed of two adjacent C—H signals; the ratio of their area to that of all the proton signals together is 4:22.

The persisting neighbourhood of carbon atoms from the parent anion *I* has been demonstrated by reaction of the carborane *III* with diborane under a higher pressure, which gave *ortho*-carborane *IV* and the hitherto unknown dicarboranyl *V*.



The dicarboranyl *V* melts at 230°C and, consequently, is not identical with the dicarboranyl I(1'-1',2'- $C_2B_{10}H_{11}$ )-1,2- $C_2B_{10}H_{11}$ , m.p. 309–310°C, synthesized by Dupont and Hawthorne<sup>16</sup>. The  $^{11}B$  NMR spectrum of the dicarboranyl *V* (Fig. 2) is analogous to that of the *ortho* carborane<sup>17</sup>. The distinct doublet in the lowest field (1.27 p.p.m.) is associated with the atoms 9,12 in the *ortho*-carborane, and, consequently, rules out substitution at these positions. The ratio of the area of the doublet in the lowest field to the integrated area of the other signals is 1:4. The  $^{11}B$  NMR spectra and  $^1H$  decoupled  $^{11}B$  NMR spectra at 32.1 MHz showed that the band at 6.86 p.p.m. is not a singlet, but is part of a doublet, probably associated with the atoms 8,8' and 10,10'. Judging from the character of the  $^{11}B$  NMR spectrum and from the assumed genesis of the compound *V* it seems to us most likely that the connexion is realized through the atoms 4-4'.

The carborane *III* is readily split by Lewis bases to neutral ligand derivatives of the type 7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>-L, some of which were described previously by Hawthorne and coworkers<sup>18</sup>.



Reaction with diethyl ether gave rise to the symmetrically substituted derivative *VIa*. With tetrahydrofuran the predominant product was the symmetrically substituted derivative *VIb*, besides which there was isolated a small amount of the asymmetrically substituted derivative *VIIIb*. Reaction with dimethyl sulphide produced the symmetrically substituted derivative *VIc* and the asymmetrically substituted derivative *VIIc* in a ratio of 3 : 2. By thin-layer chromatography of the reaction mixture there were detected traces of further two compounds. Their mass spectra proved them to be isomers of the compounds *VIc* and *VIIc*, with the ligand located elsewhere than in the open-face pentagon of the skeleton C<sub>2</sub>H<sub>9</sub>B<sub>11</sub>. The <sup>11</sup>B NMR spectra of compounds of type *VI* and *VII* are shown in Figs 3 and 4. Reaction of the carborane *III* with pyridine or liquid ammonia led to unidentified products. The formation of 9-L and 10-L-7,8-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub> derivatives, in reactions of the carborane *III* with Lewis bases accords with the proposed structure.

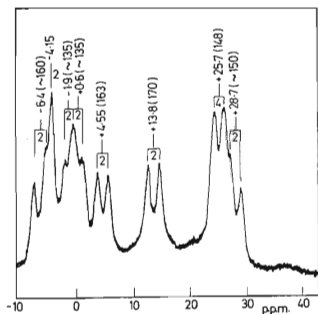


FIG. 1

80.5 MHz <sup>11</sup>B NMR Spectrum of Carborane C<sub>4</sub>B<sub>18</sub>H<sub>22</sub> (*III*) in Chloroform

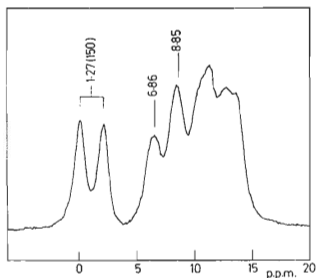


FIG. 2

70.6 MHz <sup>11</sup>B NMR Spectrum of Dicarboranyl *V* in Dichloromethane

Hawthorne has shown<sup>19</sup> that the anion  $B_{20}H_{18}^{2-}$  is reduced by sodium in liquid ammonia with the formation of a tetravalent anion  $(B_{10}H_9-B_{10}H_9)^{4-}$ , where the two polyhedral  $B_{10}$  skeletons are connected by a B—B linkage at the position from which the two three-centred bonds originally projected. Similarly, the dicaesium salt of the carborane III,  $Cs_2C_4B_{18}H_{20}$  (VIII), is reduced by sodium in liquid am-

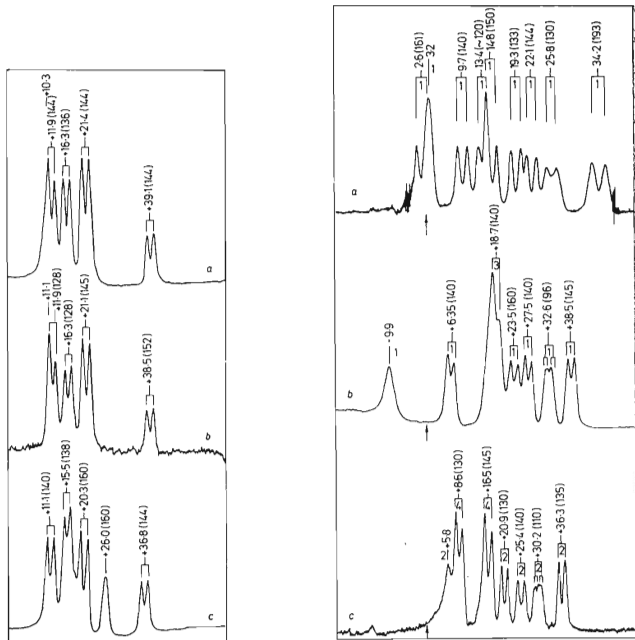


FIG. 3

80.5 MHz  $^{11}B$  NMR Spectra in Benzene

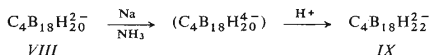
a)  $10-(C_2H_5)_2O-7,8-C_2B_9H_{11}$  (VIa), b)  $10-(C_4H_8O)-7,8-C_2B_9H_{11}$  (VIb), c)  $10-(CH_3)_2S-7,8-C_2B_9H_{11}$  (VIc).

FIG. 4

80.5 MHz  $^{11}B$  NMR Spectra

a)  $9-(CH_3)_2S-7,8-C_2B_9H_{11}$  (VIIc) in acetone, b)  $9-(C_4H_8O)-7,8-C_2B_9H_{11}$  (VIIb) in benzene, c)  $C_4B_{18}H_{22}^{2-}$  (IX) in aqueous acetone.

monia to the dianion  $C_4B_{10}H_{22}^{2-}$  (*IX*). The carborane *III* itself cannot be reduced in this way because of its high reactivity with Lewis bases.



The anion *IX* was isolated in good yield in the form of its dicaesium salt, whose  $^{11}B$  NMR spectrum (Fig. 4) corresponds to the spectrum of a substituted anion *I* (cf. Hawthorne's<sup>20</sup> and Todd's<sup>21</sup> assignments). Comparison of the spectrum of anion *IX* with the spectra of 9-L-7,8- $C_2B_9H_{11}$  (Fig. 4) reveals that the substitution occurred at position 9. The formation of the anion *IX* allows us to assign the carborane  $C_4B_{18}H_{22}$  (*III*) the structure of a dinido derivative where carbon atoms are in positions 7,8 and 7',8' and two three-centred bonds project from the atoms 9,10 and 9',10'.

The similarity of the oxidative coupling of *nido*-anions 7,8- $C_2B_9H_{12}^-$  (*I*) and of polyhedral anions  $B_{10}H_{10}^{2-}$  justifies us to assume that the anion  $C_4B_{18}H_{23}^-$  (*II*) is an analogue of the anion  $B_{20}H_{19}^{2-}$  (ref.<sup>15</sup>), i.e. a pair of  $C_2B_9H_{11}$  frameworks connected by a hydrogen bond. If there is a hydrogen bond between boron atoms in the open-face pentagons of two skeletons  $C_2B_9H_{11}$  there are three ways of combining the two skeletons into the anion *II*. The  $^{11}B$  NMR spectrum of the anion *II* (Fig.5)

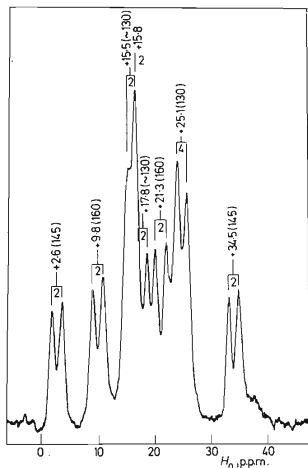
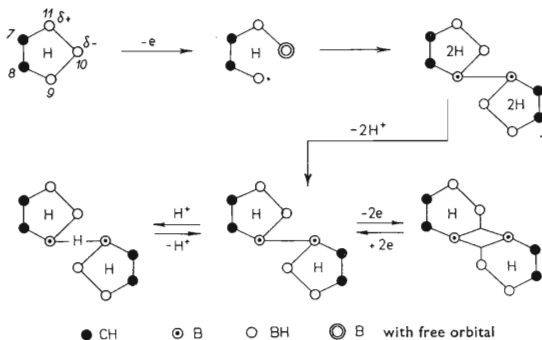


FIG. 5  
80.5 MHz  $^{11}B$  NMR Spectrum of  $C_4B_{18}H_{23}^-$  (*II*) in Acetone



Scheme 1

Assumed Course of Oxidation of the Anion  $7,8\text{-C}_2\text{B}_9\text{H}_{12}^-$  (I) by Chromic Acid

The scheme illustrates only the atoms of the open-face pentagon. To make the scheme easier to survey the other atoms of the icosahedral skeleton are left out.

contains eight signals, *i.e.* seven doublets of relative intensities 1 : 1 : 1 : 1 : 1 : 2 : 1 and one singlet of intensity 1. The presence of only one singlet rules out a hydrogen bond between atoms 9 and  $10'$ . A symmetrical connexion by a hydrogen bond between atoms 10 and  $10'$  is not possible either because there are altogether eight signals in the spectrum (with a hydrogen bond between atoms 10 and  $10'$  the spectrum should contain only six signals, five doublets and one singlet). The only possibility consistent with the spectrum is a hydrogen bond between atoms 9 and  $9'$  (IIa).

In view of all the facts described above the oxidation of the anion I to the carborane III seems to proceed by Scheme 1. The reaction probably starts by detachment of an electron from the place of the greatest electron density; this place in the anion I is the atom  $B_{(10)}$ . The radical A thus formed dimerizes to the reactive intermediate B, which readily loses two protons and forms the dianion IX. This can combine with a proton and produce the anion II, or undergo further oxidation to the neutral carborane III.

In addition to the anion II and the carborane III, oxidation of the anion I gave a small amount of the isomeric carborane  $\text{C}_4\text{B}_{18}\text{H}_{22}$  (X), behaving in aqueous ethanol as a monobasic acid of  $\text{p}K_a$  6.8.

## EXPERIMENTAL

$^{11}\text{B}$  NMR spectra at 80.5 MHz were measured on an apparatus developed by Professor F. A. L. Anet, University of California, Los Angeles; at 70.6 MHz on an apparatus Varian HR-220,

Indiana University, Bloomington; at 32.1 MHz on Varian XL-100, Institute of Chemical Technology, Prague. The spectra are related to  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ . The infrared spectra were measured in the region 4000 to  $250 \text{ cm}^{-1}$  with spectrophotometers UR-10, Zeiss-Jena, and IR 20A Beckman. The ultraviolet spectra were measured with a spectrophotometer Beckman DK-1 in paired suprasil cells, 1 cm thick, in the region 210–360 nm. The mass spectra were obtained with an apparatus LKB 9000 at 70 eV and an inlet temperature of  $20^\circ\text{C}$ . The X-ray powder patterns were taken with an apparatus Mikrometa II in Guinier-de Wolf's focussing chamber. Its diameter corresponded to Debye-Scherrer cell (229.2 nm). The radiation employed was  $\text{Cu}_{K\alpha_1} = 1.54051 \text{ \AA}$ . Thin-layer chromatography was carried out on Silufol sheets with starch as binder (Kavalier, Votice, Czechoslovakia). The chromatographs were exposed to iodine vapour and developed with an aqueous solution of silver nitrate. The melting points were determined in sealed capillaries and were not corrected. Anion  $7,8\text{-C}_2\text{B}_9\text{H}_{12}^- (I)$  was prepared according to Hawthorne<sup>22</sup> by degradation of *ortho*-carborane.

#### Synthesis of Tetracarba-*dinido*-docosaborane(22) (III)

To a solution of 5 ml of concd. sulphuric acid in 100 ml of water was added 100 ml of a 1M aqueous solution of potassium salt of the anion *I*; the temperature was not allowed to exceed  $0^\circ\text{C}$ . To this mixture was added 100 ml of chloroform and, dropwise, 80 ml of an oxidation solution composed of 10 g (0.033 mol) of potassium dichromate and 10 ml of concentrated sulphuric acid. The oxidation solution was added slowly so that the reaction mixture never contained an appreciable excess of the oxidant. After 20 min the orange-coloured chloroform layer was separated from the blue aqueous layer. The latter was mixed with another 100 ml portion of chloroform and the oxidation was repeated with the same amount of the oxidation solution. After removing the chloroform layer the procedure was repeated once more. The combined chloroform extracts were washed with water and filtered. After distilling off the chloroform there was obtained 11 g of a substance, which was crystallized from a chloroform-hexane mixture (1 : 1); yield 2.5 g. The mother liquor was shaken with an aqueous solution of sodium carbonate (10 g in 100 ml of water). The aqueous layer was separated and acidified with hydrochloric acid. The separated solid was extracted into chloroform. After concentration by evaporation there was obtained another 3 g of crystals. The total yield was 5.5 g (42%) of a compound whose mass spectrum exhibited a molecular cut-off at  $m/e = 268$ , which corresponds to the formula  $^{12}\text{C}_4^{11}\text{B}_{18}^1\text{H}_{22}$ . Crystallization from the chloroform-hexane mixture (1 : 1) gave 2 g of compound *III*; m.p.  $174^\circ\text{C}$ , which could be sublimated at  $100^\circ\text{C}/10^{-5}$  Torr. The IR spectrum had the following characteristic absorptions:  $\nu(\text{CH})$  3050 ms,  $\nu(\text{BH}_a)$  2580 vs,  $\nu(\text{BH}_b)$  1880 w, 1825 w  $\text{cm}^{-1}$ . The UV spectrum exhibited an absorption at  $\lambda_{\text{max}} 226 \text{ nm}$  ( $\epsilon = 12700$ ) and at  $\lambda_{\text{cristal}} 291 \text{ nm}$  ( $\lambda 2840$ ).

The mother liquor after the first crystallization and extraction of the carborane *III* into the solution of sodium carbonate was distilled to remove the solvents and the residue was chromatographed on a column with hexane as eluant; yield 0.05 g of compound *X*,  $R_F$  0.68 (benzene). Its mass spectrum had a molecular cut off at  $m/e = 268$ , corresponding to the formula  $^{12}\text{C}_4^{11}\text{B}_{18}^1\text{H}_{22}$ . After recrystallization from hexane the new carborane, *X*, melted at  $148\text{--}149^\circ\text{C}$ . The IR spectrum exhibited the following characteristic absorptions:  $\nu(\text{CH})$  3065 s,  $\nu(\text{BH}_a)$  2580 vs,  $\nu(\text{BH}_b)$  1805, 1552  $\text{ms cm}^{-1}$ .

#### Synthesis of the Anion $\text{C}_4\text{B}_{18}\text{H}_{23}^- (II)$

To 100 ml of an aqueous solution containing 10 ml of concd. sulphuric acid there was added 100 ml of a 1M aqueous solution of potassium salt of the anion *I*. The mixture was cooled until it froze to a slush, then 5 g (0.017 mol) of potassium dichromate in 100 ml of water and 10 ml of concd.



sulphuric acid were added dropwise under constant stirring and cooling. The colour of the solution went from tawny to light blue. The mixture was shaken with ether, the ethereal layer was separated and mixed with 100 ml of water. The ether was removed by evaporation *in vacuo*. Caesium chloride was added to the remaining aqueous solution, whereby the yellow caesium salt of *II* precipitated (3.5 g, 7.5%). After crystallization from water the yield was 1 g. For  $\text{CsC}_4\text{B}_{13}\text{H}_{23}$  (398.9) calculated: 33.30% Cs, 48.8% B; found: 32.93% Cs, 48.08% B. The IR spectrum had the following characteristic bands:  $\nu(\text{CH})$  3030 vw, 3060 vw;  $\nu(\text{BH}_1)$  2540 vs  $\text{cm}^{-1}$ .

#### Reaction of Carborane *III* with Diborane

A 100-ml pressure vessel was charged with a suspension of 1 g (0.0037 mol) of the carborane *III* in 30 ml of hexane and 1 mol of diborane was added under pressure. After 24 hours' heating to 90–95°C the vessel was cooled and the unreacted diborane was stripped off. The hexane solution was filtered to remove yellow polymeric substances, which were washed with several portions of hexane. The filtrate, combined with the washings, was distilled to remove the solvent. The residue was 1.5 g of a solid, which was dissolved in benzene and shaken with aqueous potassium hydroxide. The aqueous layer was acidified with hydrochloric acid and 0.2 g of the carborane *III* was recovered. The benzene solution was taken to dryness and the residue was sublimated at 80°C/10<sup>12</sup> Torr, yield 0.35 g of the *o*-carborane *IV* (40%, based on the reacted *III*). The residue after the sublimation was crystallized from hexane. There was obtained 0.2 g (23%, based on the reacted *III*) of a compound melting at 230°C. Its mass spectrum had a molecular cut-off at  $m/e = 290$ , corresponding to the formula  $^{12}\text{C}_4\text{B}_{20}^{11}\text{H}_{22}$ . According to the  $^{11}\text{B}$  NMR spectra (Fig. 2) it was the dicarboranyl *V*. The IR spectrum had absorptions  $\nu(\text{CH})$ , at 3065 vs, and  $\nu(\text{BH}_1)$ , at 2580 vs  $\text{cm}^{-1}$ .

#### Reaction of Carborane *III* with Lewis Bases

a) *Reaction with diethyl ether*: The behaviour of a solution of 2 g (0.0074 mol) of the carborane *III* in 50 ml of diethyl ether was followed by thin-layer chromatography. Immediately on dissolving the carborane *III* the developed chromatogram showed the presence of a reducing compound (the carborane *III*) on the start. This practically disappeared in 6 days, whereas the quantity of another reducing compound,  $R_f$  0.39 (chloroform), kept increasing. After 6 days of standing at room temperature the diethyl ether was distilled off and the residue was extracted with pentane. Evaporation of pentane from the combined extracts left 1.5 g (48%) of the product, which was heated 2 h at 80°C/15 Torr. Chromatography on a column of silica gel gave 1 g of the compound *Vla*, m.p. 54–55°C. Its mass spectrum had a molecular cut off at  $m/e = 208$ , corresponding to the formula  $^{12}\text{C}_6\text{B}_9\text{H}_{21}^{16}\text{O}$ . The  $^{11}\text{B}$  NMR spectrum (Fig. 3) corroborates that it was 10-( $\text{C}_2\text{H}_5$ )<sub>2</sub>O-7.8- $\text{C}_2\text{B}_9\text{H}_{11}$  (*Vla*). The infrared spectrum exhibited bands  $\nu(\text{CH})$  3020 ms and  $\nu(\text{BH}_1)$  2540 vs  $\text{cm}^{-1}$ .

b) *Reaction with tetrahydrofuran*. In 20 ml of tetrahydrofuran 2.6 g (0.0086 mol) of the carborane *III* was dissolved. The temperature of the reaction mixture moderately rose. The decrease in the content of the carborane *III* was followed by thin-layer chromatography. After two days tetrahydrofuran was distilled off and the residue (4 g) was shown by thin-layer chromatography to be a mixture of two compounds. These were separated by column chromatography on dry silica gel (with chloroform as eluant). There was obtained 3 g (74%) of a yellowish substance, m.p. 143–144°C, whose mass spectrum had a molecular cut off at  $m/e = 206$ . According to the  $^{11}\text{B}$  NMR spectrum it was 10- $\text{C}_4\text{H}_8\text{O}$ -7.8- $\text{C}_2\text{B}_9\text{H}_{11}$  (*Vlb*); the spectrum was identical with that of this compound prepared by Hawthorne<sup>18</sup>. The IR spectrum had bands  $\nu(\text{CH})$  3020 ms,

$\nu(\text{BH}_2)$  2550 vs  $\text{cm}^{-1}$ .  $R_F$  0.44 (chloroform). From the chromatographic column there was also isolated a small quantity of a compound, m.p. 151°C (with decomposition),  $R_F$  0.22 (chloroform), having the same molecular edge as the compound *Vib*. According to the  $^{11}\text{B}$  NMR spectrum (Fig. 4) it was 9- $\text{C}_4\text{H}_8\text{O}$ -7,8- $\text{C}_2\text{B}_9\text{H}_{11}$  (*VIIb*). The IR spectrum had bands  $\nu(\text{CH})$  3050 ms, 3015 ms;  $\nu(\text{BH}_2)$  2540  $\text{cm}^{-1}$ .

c) *Reaction with dimethyl sulphide*. One g (0.0037 mol) of the carborane *III* was dissolved in 20 ml of dimethyl sulphide. Immediately on dissolution four reducing compounds could be detected by thin-layer chromatography;  $R_F$  0.32, 0.15, 0.12 and 0.08 (benzene). After five days of standing at room temperature the chromatographic pattern was unchanged. Dimethyl sulphide was then distilled off and the residue was chromatographed on a column of silica gel (benzene as eluant), but the four compounds were not separated. Crystallization from a hexane-chloroform mixture (1 : 2) gave a crop with *VIIc* as the predominant constituent,  $R_F$  0.15 (benzene), whereas the parent liquor was enriched in compound *VIc*,  $R_F$  0.32. The crystalline portion was extracted with diethyl ether. The insoluble residue was a practically pure compound of  $R_F$  0.12 (benzene). Its mass spectrum had a molecular cut-off at  $m/e = 196$ , corresponding to one of the possible isomers 7,8- $\text{C}_2\text{B}_9\text{H}_{11}\cdot\text{S}(\text{CH}_3)_2$ . The ethereal extracts were combined, the solvent removed by distillation and the residue was crystallized from the hexane-chloroform mixture (1 : 2). After 3 days the yield was 0.2 g of the compound 9-( $\text{CH}_3$ ) $_2\text{S}$ -7,8- $\text{C}_2\text{B}_9\text{H}_{11}$  (*VIIc*), which after drying *in vacuo* had a m.p. of 147–148°C. The IR spectrum had bands  $\nu(\text{CH})$  3020 ms,  $\nu(\text{BH}_2)$  2530 vs  $\text{cm}^{-1}$ . The mother liquor gave a small amount of the compound with  $R_F$  0.08 (benzene). The molecular cut-off was again at  $m/e = 196$ . The addition compound 10-( $\text{CH}_3$ ) $_2\text{S}$ -7,8- $\text{C}_2\text{B}_9\text{H}_{11}$  (*VIc*) was isolated from the parent liquor after the first crystallization of the whole mixture. Recrystallization from hexane gave 0.3 g of compound *VIc*, m.p. 92–93°C, with a molecular cut-off at  $m/e = 196$ . The IR spectrum had bands  $\nu(\text{CH})$  3010 ms,  $\nu(\text{BH}_2)$  2550 vs  $\text{cm}^{-1}$ .

#### Preparation of Dicaesium Salt of Tetracarba-*dinido*-docosaborane (*VIII*)

Potassium salt of the anion *I* (0.1 mol) in an aqueous solution was oxidized in the same way as in the preparation of the neutral carborane *III*. The chloroform extracts after the oxidation were combined and shaken with aqueous sodium carbonate (10 g of  $\text{Na}_2\text{CO}_3$  in 100 ml of water). Caesium chloride was added to the aqueous layer and the precipitated caesium salt was collected on a filter and dried at 100°C/ $10^{-2}$  Torr. The crude product, 8.4 g (32%), crystallized from water in the form of colourless prisms, yield 4 g. For  $\text{Cs}_2\text{C}_4\text{B}_{18}\text{H}_{20}$  (528.8) calculated: 9.09% C, 3.81% H, 36.83% B, 50.27% Cs; found: 9.05% C, 3.88% H, 36.56% B, 49.90% Cs. The IR spectrum had absorption bands  $\nu(\text{CH})$  3040 w, 3020 ms,  $\nu(\text{BH}_2)$  2580 vs  $\text{cm}^{-1}$ .

#### Reduction of the Dicaesium Salt *VIII*

To 6.4 g (0.012 mol) of the salt *VIII* under nitrogen at  $-76^\circ\text{C}$  was added 100 ml of condensed ammonia. The solution was treated with a gradually increasing amount of sodium until it remained blue (a total of 0.8 g of Na, 0.035 gramatom). After 1 h the ammonia was removed by evaporation. The residue was suspended in hexane and decomposed in water under cooling. The insoluble portion was filtered off and crystallized from water; yield 4 g (62%) of  $\text{Cs}_2\text{C}_4\text{B}_{18}\text{H}_{22}$  (*IX*). For  $\text{Cs}_2\text{C}_4\text{B}_{18}\text{H}_{22}$  (530.8) calculated: 50.08% Cs, 36.69% B; found: 49.77% Cs, 36.71% B. The IR spectrum had the following characteristic absorption bands:  $\nu(\text{CH})$  3060 w, 3010 w;  $\nu(\text{BH}_2)$  2500 vs,  $\nu(\text{BH}_2)$  1440 ms. The X ray powder patterns showed the following interplane distances  $d(\text{\AA})$ : 10.16 ms, 5.70 s, 5.44 w, 4.921 s, 4.749 vs, 4.590 s, 4.453 s, 4.273 s, 4.042 vw, 3.962 m, 3.811 vw, 3.732 m, 3.709 m, 3.584 vw, 3.535 vw, 3.346 m, 3.267 m, 3.233 m, 3.143 m,

3-090 m, 3-038 vw, 2-984 vw, 2-936 vw, 2-853 m, 2-814 m, 2-727 m, 2-697 vw, 2-646 m, 2-511 vw, 2-398 mw, 2-365 vw, 2-219 w, 2-153 vw, 2-137 vw, 2-023 vw, 1-935 vw, 1-859 vw, 1-851 vw (calibrated with Ag).

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