

**OXIDATION OF 7,8-DICARBA-*nido*-UNDECABORATE
TO 5,6,-DICARBA-*nido*-DECABORANE(12) AND ITS DEHYDROGENATION
TO 1,2-DICARBA-*closo*-DECABORANE(10)***

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The anion $7,8\text{-C}_2\text{B}_9\text{H}_{12}^-$ is oxidized by aqueous ferric chloride in a 47% yield to a weakly acidic *nido*-carborane, $5,6\text{-C}_2\text{B}_8\text{H}_{12}$, which undergoes pyrolytic dehydrogenation at 240°C in a high yield to a new *closo*-carborane, $1,2\text{-C}_2\text{B}_8\text{H}_{10}$. The temperature of dehydrogenation can substantially be reduced by the addition of *N*-ethylpiperidine-borane(3).

The oxidation of isomeric anions $\text{C}_2\text{B}_9\text{H}_{12}^-$ under various conditions has been studied by Hawthorne and coworkers^{1,2}. Whereas oxidation of the anion $7,9\text{-C}_2\text{B}_9\text{H}_{12}^-$ (*I*) by chromic acid brought about a selective splitting-off of two boron atoms and gave rise to the carborane $\text{C}_2\text{B}_7\text{H}_{13}$ (ref.¹), an analogous oxidation of the isomer $7,8\text{-C}_2\text{B}_9\text{H}_{12}^-$ (*II*) by the action of aqueous ferric chloride resulted in a complete degradation to boric acid as a sole product². The oxidative degradation of *C*-monosubstituted anions *I* and *II* by chromic acid at 100°C has also been studied by Zacharkin and coworkers^{3,4}. These authors state that either isomer gives the same organic oxidation products, but the fate of the borane residue is not described.

The present paper deals with oxidation of 7,8-dicarba-*nido*-undecaborate (*II*) by aqueous ferric chloride. With the aid of gas-liquid chromatography and thin layer chromatography it has been found that there were formed at least five volatile compounds, the total of which constituted about a half of the original content of boron. The main part of this mixture (c. 90%) was 5,6-dicarba-*nido*-decaborane(12) (*III*); some of its physico-chemical properties were described in a preliminary report⁵. The *C,C*-dimethyl derivative of 5,6-dicarba-*nido*-decaborane(12) has recently been described by Rietz and Schaeffer⁶, who synthesized it from octaborane(12) and 2-butene. In this communication⁶ they also mention an analogous synthesis of the parent carborane *III*, whose complete characterization appeared later⁷ and revealed its identity with the compound *III* described herein. This compound is isoelectronic with the dianion $\text{B}_{10}\text{H}_{12}^{2-}$ (not with decaborane(14), as was erroneously supposed⁶) and represents a second known dicarba-*nido*-decaborane, out of the 16 possible

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ones. The first isomer, 5,7-dicarba-*nido*-decaborane(12), has been described by Hawthorne and coworkers⁸.

The structural formulae allow us to infer that 5,6-dicarba-*nido*-decaborane(12) arises from an oxidative displacement of the atom B₍₉₎ from the anion 7,8-C₂B₉H₁₂⁻. The formed skeleton has no feature of symmetry, in agreement with the ¹¹B NMR spectrum of compound *III*, exhibiting 8 distinctive doublets (Fig. 1a), and with the ¹H NMR spectrum, containing 2 different CH signals. It is surprising that the infrared spectrum lacks the typical absorbances of the carborane CH bond beyond 2600 cm⁻¹. A *nido*-structure of the carborane *III* is evident from the character of the mass spectrum (Fig. 2a), as well as from the marked absorption of ultraviolet light at 251 and 278 nm. The existence of hydrogen bonds has been confirmed by the stretching vibrations B—H—B in the regions 1400–1600 and 1800–2000 cm⁻¹, by the acidity of compound *III* (pK_a 6.18) and by exchange of the B—D—B bridges for B—H—B in a system D₂O–acetonitrile. Since the carborane C₂B₈H₁₂

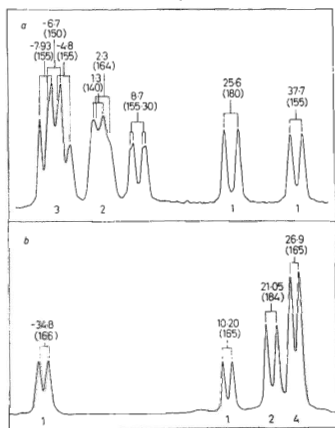


FIG. 1

¹¹B NMR Spectra at 70.6 MHz (related to BF₃·O(C₂H₅)₂)

a 5,6-C₂B₈H₁₂; b 1,2-C₂B₈H₁₀.

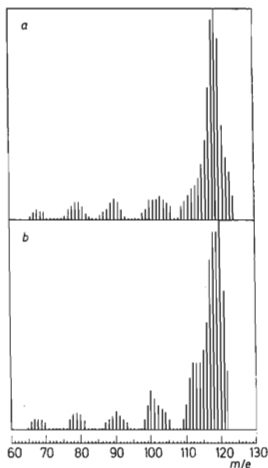
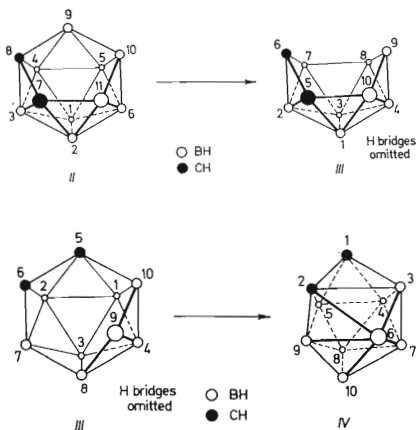


FIG. 2

Mass Spectrum (70 eV)

a 5,6-C₂B₈H₁₂; b 1,2-C₂B₈H₁₀.

and decaborane have strikingly similar IR spectra, both in the absorbance region of hydrogen bonds and in the region of the skeletal vibrations, we prefer the alternative of two adjacent hydrogen bridges, among atoms $B_{(8)}-B_{(9)}-B_{(10)}$, to the alternative of two isolated hydrogen bonds at positions $B_{(7)}-B_{(8)}$ and $B_{(9)}-B_{(10)}$.



Another convincing item of evidence for the postulated structure of carborane III was its reaction with N-ethylpiperidine-borane(3), by which about 10% of the starting anion II was recovered. The chief product of this reaction was the new *closo*-carborane $C_2B_8H_{10}$ (IV), m.p. 181°C, partially characterized in a preliminary report⁵. The mass spectrum of compound IV is characteristic of *closo*-compounds (Fig. 2b) and its protonic NMR spectrum contains two non-equivalent C—H signals, τ 4.40 and 6.59. Out of the possible 7 *closo*-carborane isomers $C_2B_8H_{10}$ only the 1,2 and 1,6-isomers can have non-equivalent C—H bonds. The isomer 1,6- $C_2B_8H_{10}$ (V), m.p. 145–146°C, was described previously⁹ and is known to exhibit chemical shifts τ 4.8 and 8.1; these values are considerably different from those found with the carborane IV, which, consequently, is the 1,2-dicarba-*closo*-decaborane(10). This structure is in agreement with the ^{11}B NMR spectrum (Fig. 1b), exhibiting four doublets of relative intensities 1 : 1 : 2 : 4, centred at -34.8 , $+10.20$, 21.05 and 26.91 p.p.m., respectively. The doublet at -34.8 p.p.m. is associated with the apical B-10 atom, and its relative intensity 1 suggests that the other apex is a C-atom. The doublet

at 26.91 p.p.m. is composed of 2 doublets, each having a relative intensity 2. Pyrolytic dehydrogenation without catalysis by N-ethylpiperidine-borane(3) requires higher temperatures (c. 240°C) and leads to the 1,2-isomer, *IV*, contaminated with 1,6- $C_2B_8H_{10}$.

Compound *IV* is the third known isomer of the dicarba-*closo*-decaborane series. The first two, *viz.* 1,6- and 1,10- $C_2B_8H_{10}$, were obtained by Hawthorne and co-workers⁹ by pyrolytic dehydrogenative disproportionation of carborane $C_2B_7H_{13}$.

Compounds *III* and *IV* are the most accessible ones of their series of isomers and facilitate development of chemistry in this field.

EXPERIMENTAL

¹H NMR spectra were measured on a spectrometer Varian XL 100; the values τ relate to tetramethylsilane. ¹¹B NMR spectra were measured with an apparatus Varian HR-220; the δ values relate to $BF_3 \cdot O(C_2H_5)_2$. The infrared spectra were obtained with a spectrophotometer UR 10, the ultraviolet spectra with a spectrophotometer Beckman DK 1. Gas-liquid chromatography was carried out on a gas-chromatograph Chrom-3. Mass spectra were measured at 70 eV and an emitter temperature of 150°C with a mass spectrometer LKB 9000. Thin-layer chromatography was performed on Silufol plates with starch as binder (Kavalič, Votice, Czechoslovakia) in chambers 20 × 20 × 7 cm. All melting points were determined in sealed capillaries and are not corrected.

5,6-Dicarba-*nido*-decaborane(12) (*III*)

To 100 ml of a 1M aqueous solution of 7,8-dicarbaundecaborate anion under a layer of hexane (100 ml) were added rapidly under stirring 400 ml of 1M aqueous $FeCl_3$. The mixture spontaneously warmed up to about 50°C and 800–1000 ml of hydrogen evolved. After 2 hours' stirring the hexane layer was separated and the aqueous layer was shaken with 60 ml of hexane. GLC and TLC of the combined hexane portions revealed a mixture of compounds (Table I). The hexane solution was shaken with 100 ml of 2M aqueous K_2CO_3 , the hexane was then distilled off over

TABLE I
Chromatographic Separation and Composition of the Mixture after Oxidation of Anion *II*

Compound	<i>III</i>	A ^a	B ^b	C	D ^b
Yield, %	90	4.5	4.5	0.5	0.5
GLC ^c retention time, s	120	159	204	294	327
(related to 1,2- $C_2B_{10}H_{12}$ 100)	43	63	69	100	111
TLC ^d R_F hexane	0.25	0.08	—	0.0	—
(related to 1,2- $C_2B_{10}H_{12}$ (100))	313	100	—	0	—

^a Different from compound *IV*, in spite of the same chromatographic behaviour; ^b unstable; ^c 240 cm column packed with Chromosorb W coated with 20% fluorosilicon polymer QF 1, N_2 as carrier gas, temperature 174°C, detector, FID; ^d silufol sheet, detection: I_2 vapour or $AgNO_3$.

a Vigreux column, the remaining solvent was removed at 10 Torr and room temperature, and the solid residue was sublimed at 100°C and 10^{-2} Torr, the temperature of the cool finger being -20°C . Resublimation at $70^{\circ}\text{C}/10^{-2}$ Torr and a cool finger temperature of 15°C gave 5.65 g (46%) of carborane III, m.p. $98-99^{\circ}\text{C}$. An increase in the concentration of the reactants drastically reduced the yield. At a concentration of 5M the yield was a few % only.

The compound III was soluble in organic solvents, including aliphatic hydrocarbons. Its ^1H NMR spectrum had a few intense and very wide B—H signals and two wide and intense CH signals of relative intensities 1 : 1 and τ values 3.62 and 5.02 p.p.m. The ^{11}B NMR spectrum and the mass spectrum are shown in Fig. 1a and Fig. 2a, respectively. The infrared spectrum (in CCl_4) has been found to contain bands at (cm^{-1}): 688 m, 712 m, 858 m, 868 sh m, 897 s, 915 w, 938 m, 943 s, 969 m, 998 s, 1013 s, 1050 m, 1062 w, 1094 s, 1112 w, 1232 w, 1305 m, 1470 sh m, 1483 s, 1505 sh m, 1555 m, 1875 w, 1948 w, 2585 vs, 3040 vw, 3060 vw. The ultraviolet spectrum had overlapped bands at 251 nm, sh (ϵ 2280) and a peak at 278 nm (ϵ 2775). The titration equivalent was determined by potentiometric titration of 24.8 mg of carborane III in 10 ml of 50% ethanol with 0.05M-NaOH. The titration equivalent was close to the theoretical value if the overall time of dissolution and titration did not exceed 3 minutes. Prolongation of this time markedly raised the value of the titration equivalent.

Recovery of carborane III from its alkaline solution in water: A solution of compound III (1.24 g, 0.01 mol) in 10 ml of ether was shaken 5 min with 50 ml of 4M-KOH and the ether was evaporated under a vacuum of 5 Torr at room temperature. Bubbles of a gas slowly evolved from the remaining solution. After 30 min the solution was acidified with 60 ml of 4M-HCl and shaken with two 20-ml portions of hexane. The hexane extracts were combined, the solvent removed at room temperature and 10 Torr and the residue was sublimed at $70^{\circ}\text{C}/10^{-2}$ Torr. There was recovered 0.78 g (63%) of compound III, m.p. $98-99^{\circ}\text{C}$, chromatographically pure (TLC).

Reaction with sodium hydride: A solution of compound III (1.24 g, 0.01 mol) in 50 ml of diethyl ether was added dropwise in the course of 10 min to a stirred suspension of NaH (2.4 g, 0.1 mol) in 50 ml of diethyl ether. The mixture immediately started liberating hydrogen and turned yellow. The evolution of hydrogen stopped almost immediately after addition of the last drop of the solution of III, during the following 2 h of stirring no further hydrogen was released. The total of hydrogen was 220 ml (corr.), i.e. 0.0098 mol. The solution was filtered *in vacuo* and ether was removed *in vacuo*. Hexane (50 ml) was added to the yellow solid residue and after cooling the mixture to 0°C 20 ml of 6M-HCl was added. Carborane III was isolated from the separated hexane layer as in the foregoing case, recovery 1.15 g (93%) of the starting compound, m.p. $98-99^{\circ}\text{C}$, chromatographically pure (TLC).

Dehydrogenation of Carborane III

a) *In the presence of N-ethylpiperidine-borane(3):* A mixture of 5,6- $\text{C}_2\text{B}_8\text{H}_{12}$ (5.0 g, 0.04 mol) and N-ethylpiperidine-borane(3) (3.0 g) was heated under a reflux condenser to 120°C for 4 h. The volume of the released gas was 920 ml (uncorr.). The volatile portions were removed by sublimation at $100^{\circ}\text{C}/10^{-2}$ Torr. The non-subliming residue was crystallized from 200 ml of boiling water acidified with 10 ml of conc. hydrochloric acid (dissolving was accompanied by hydrolysis of the excessive N-ethylpiperidine-borane). After cooling down 0.98 g (10%) of N-ethylpiperidinium 7,8-dicarba-*nido*-undecaborate separated in the form of leaf-like crystals, identified by comparison of the infrared spectrum with that of an authentic sample, obtained in a different way. The compound was purified by sublimation, dissolved in 20 ml of hexane and chromatographed on a column of 200 g of silica gel. The fractions were analysed by TLC on silica gel. Those containing only the new carborane were pooled, the hexane was distilled off over

a 30 cm Vigreux column, the remaining solvent was removed at 10 Torr and room temperature and the carborane was resublimed at $70^{\circ}\text{C}/10^{-2}$ Torr; yield 3.7 g (74%) of carborane $\text{C}_2\text{B}_8\text{H}_{10}$ (IV), m.p. 181°C . The compound proved soluble in hydrocarbons and other organic solvents. In addition to wide and non-significant BH bands, the PMR spectrum exhibited two intense and wide CH signals of τ 4.4 and 6.59 p.p.m. The ^{11}B NMR spectrum is given in Fig. 1b and the mass spectrum in Fig. 2b. The infrared spectrum (in CCl_4) had bands at (cm^{-1}): 910 w, 940 m, 968 s, 1005 m, 1030 w, 1043 m, 1108 s, 1133 w, 1222 w, 1805 vw, 1862 vw, 2575 vs, 2610 vs, 3070 m, 3115 s. The ultraviolet spectrum (CCl_4) had no maximum up to 200 nm.

b) *Pyrolytic dehydrogenation*: A solution of 5,6- $\text{C}_2\text{B}_8\text{H}_{12}$ (1.24 g, 0.01 mol) in 5 ml of hexadecane and 0.05 ml of heptane (to wash back the sublimed carboranes into the hot solution) was boiled (245°C in the boiling liquid) under a reflux condenser for 6 h; 250 ml of H_2 (uncorr.) had liberated. Thin-layer chromatography on silica gel revealed only 1,2- $\text{C}_2\text{B}_8\text{H}_{10}$ and traces of the 1,6-isomer. All the volatile portions were sublimed at $100^{\circ}\text{C}/10^{-2}$ Torr, dissolved in 5 ml of hexane and chromatographed on a column of 100 g silica gel. Isolation of the pure compound IV was the same as in the preceding cases, yield 1.02 g (83%) of carborane IV, m.p. 181°C .

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REFERENCES

1. Garrett P. M., George T. A., Hawthorne M. F.: *Inorg. Chem.* 8, 2008 (1969).
2. Young D. C., Howe D. V., Hawthorne M. F.: *J. Am. Chem. Soc.* 91, 859 (1969).
3. Zacharkin L. I., Kalinin V. N., Podvisockaja L. S.: *Izv. Akad. Nauk SSSR, Ser. Chim.* 1966, 1867.
4. Zacharkin L. I., Kalinin V. N.: *Izv. Akad. Nauk SSSR, Ser. Chim.* 1967, 462.
5. Plešek J., Heřmánek S.: *Chem. Ind. (London)* 1971, 1267.
6. Rietz R. R., Schaeffer R.: *J. Am. Chem. Soc.* 93, 1263 (1971).
7. Rietz R. R.: *Thesis*. Indiana University, Bloomington, USA 1971; private communication.
8. Garrett P. M., Ditta D. S., Hawthorne M. F.: *J. Am. Chem. Soc.* 93, 1265 (1971).
9. Garrett P. M., Smart J. C., Ditta G. S., Hawthorne M. F.: *Inorg. Chem.* 8, 1907 (1969).

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