

**SYNTHESIS OF 6,9-DICARBA-*nido*-DECABORANE(14) FROM
5,6-DICARBA-*nido*-DECABORANE(12)***

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Received June 25th, 1973

The reduction of 5,6-C₂B₈H₁₂ by a sodium amalgam in ethanol was accompanied by dislocation of a carbon atom with the formation of a new carborane, 6,9-C₂B₈H₁₄, isostructural with the anion B₁₀H₁₄²⁻. Reaction with D₂O replaced hydrogen by deuterium in the two hydrogen bonds and in the axial C—H bonds. The action of DCl in the presence of AlCl₃ brought about substitution of deuterium for the terminal hydrogen atoms at positions 1 and 3.

Since the first discovery¹ of a carborane, C₂B₁₀H₁₂, nearly a score of other carboranes with closed polyhedral skeletons, *closo*-carboranes C₂B_nH_{n+2}, have been described². In addition to these *closo* compounds there have been discovered a few carboranes with the so-called *nido* structure, C₂B_nH_{n+4}, *viz.* C₂B₃H₇ (ref.³) C₂B₄H₈ (ref.⁴) C₂B₇H₁₁ (refs^{5,6}), 5,6-C₂B₈H₁₂ (refs^{6,7}), 5,7-C₂B₈H₁₂ (ref.⁸), 7,8-C₂B₉H₁₃ (ref.⁹) and 2,9-C₂B₉H₁₃ (ref.¹⁰). Existence of the so-called *arachno*-carboranes, C₂B_nH_{n+6}, has also been reported on^{11,12}, but only two members of this series have as yet been described, C₂B₇H₁₃¹³ and C₂B₈H₁₄¹⁴. The synthesis and deuteration of the latter, C₂B₈H₁₄ (*I*), previously described in a preliminary communication¹⁴, is the subject of the present paper.

Reduction of 5,6-dicarba-*nido*-decaborane(12) (*II*) by a sodium amalgam in 96% ethanol at 40–60°C gave the carborane C₂B₈H₁₄ in about a 26% yield. The ¹¹B NMR spectrum of this carborane contained 3 doublets of an intensity ratio 2 : 4 : 2 (Fig. 1). The character of the spectrum fits the isomer 6,9-C₂B₈H₁₄ (Fig. 2), which is isostructural and isoelectronic with the anion B₁₀H₁₄²⁻. The split doublet of the relative intensity 4 indicates hydrogen bridges between atoms 5 and 10, and 7 and 8. The ¹H NMR spectrum had two signals of equal intensities at 0.81 and –0.70 p.p.m. (based on tetramethylsilane), which can be assigned to the axial and equatorial hydrogen atoms of the CH₂ groups, like in the carborane C₂B₇H₁₃ (ref.¹³). The infrared spectrum had weak CH absorption bands at 2980 sh, 3000 and 3050 cm⁻¹, a strong terminal B—H stretching vibration at 2580 cm⁻¹, weak B—H—B vibration

* Part XXXV in the series Chemistry of Boranes; Part XXXIV: This Journal 39, 821 (1974).

in the region $1750 - 1920 \text{ cm}^{-1}$ and strong deformation vibrations B—H—B at 1420 and 1625 cm^{-1} . The rather simple IR spectrum accords with the symmetrical structure of the carborane *I*. Unlike the known *nido*-carboranes, the carborane *I* showed no absorption in the UV region.

The carborane *I* proved rather heat-stable and up to 350°C no dehydrogenation or rearrangement of C atoms occurred. In the medium of a 50% aqueous ethanol it behaved as a weak monohydric acid, $\text{p}K_a$ 9.2, in water at room temperature it was stable for tens of hours.

6,9-Dicarba-*nido*-decaborane(14) exposed to the action of deuterium oxide in diethyl ether replaced 4 atoms of hydrogen by deuterium, the compound $\text{D}_4\text{C}_2\text{B}_8\text{H}_{10}$, being formed. Its IR spectrum lacked the bands at 1625 and 1420 cm^{-1} , which shifted to 1216 and 1062 cm^{-1} (deformation vibrations B—D—B). There appeared new bands at 2222 and 2225 (sh) cm^{-1} , associated with $\nu(\text{C—D})$, instead of the $\nu(\text{C—H})$ bands at 2580 and 3000 (sh) cm^{-1} in the original spectrum. We also detected a weak $\nu(\text{B—D})$ band at 1804 cm^{-1} . The region of the $\nu(\text{C—H})$ vibrations contained weak bands at 2920 , 2975 , 3015 and 3045 cm^{-1} . The ^{11}B NMR spectrum of $\text{D}_4\text{C}_2\text{B}_8\text{H}_{10}$ was essentially similar to that of $\text{C}_2\text{B}_8\text{H}_{14}$. The only difference was the sharpening of the doublet of intensity 4 and reduction of its half-width from 106 Hz to 64 Hz . This can be accounted for by disappearance of the interaction constant $J_{\text{B—}\mu\text{H}}$, which is not operative in the deuterated product. From these facts it can be inferred that the deuteration occurred on the hydrogen bridges and probably even on the axial C—H groups, to a small extent even at the terminal B—H bonds. The reaction with D_2O suggests that each of the two C atoms, uncharged in $6,9\text{-C}_2\text{B}_8\text{H}_{14}$, bears a fractional positive charge δ^+ . The substitution of deuterium for the two

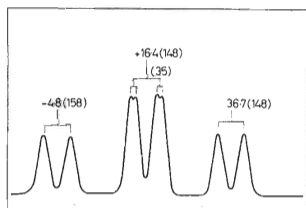


FIG. 1
 ^{11}B NMR Spectrum (25 MHz) of 6,9- $\text{C}_2\text{B}_8\text{H}_{14}$ (p.p.m. relative to $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$)

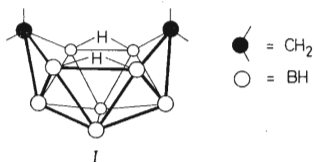
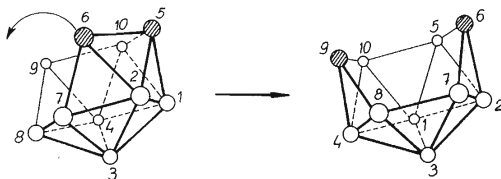


FIG. 2
Proposed Structure of 6,9- $\text{C}_2\text{B}_8\text{H}_{14}$

μH indicates an acidic nature of these hydrogen bridges, which was not observed¹³ with the isoelectronic borane derivatives $\text{L}_2\text{B}_{10}\text{H}_{12}$.

Deuteration by deuterium chloride in the presence of aluminium chloride in carbon disulphide gave rise to the deuterio derivative $\text{D}_2\text{C}_2\text{B}_8\text{H}_{12}$. Consequently, under the conditions of a Friedel-Crafts reaction, the replacement of hydrogen atoms by deuterium occurs at positions 1 and 3. Since these positions are the most remote from $\delta^+\text{C}$ atoms they bear a fractional negative charge (δ^-) of the molecule. The ^{11}B NMR spectrum of $\text{D}_2\text{C}_2\text{B}_8\text{H}_{12}$ at 32 MHz, compared to that of the starting compound *I*, shows transformation of the doublet in the highest field into a singlet centred at 36.5 p.p.m., which, according to the recent empirical rules¹⁵, can be assigned to the boron atoms at positions 1 and 3. The IR spectrum contained a band of $\nu(\text{B}-\text{H}_i)$ at 2575 cm^{-1} and a band of $\nu(\text{B}-\text{D}_i)$ at 1929 cm^{-1} . The bands of the hydrogen bridge vibrations at 1613 and 1418 cm^{-1} were fully preserved.

The conversion of 5,6- $\text{C}_2\text{B}_8\text{H}_{12}$ (*II*) into 6,9- $\text{C}_2\text{B}_8\text{H}_{14}$ (*I*) under relatively very mild conditions is rather strange. It probably consists in disruption of the bonds $\text{C}_{(5)}-\text{C}_{(6)}$ and $\text{C}_{(6)}-\text{B}_{(2)}$ in the molecule *II*, followed by turning over of the atom $\text{C}_{(6)}$ to a vicinity of the atoms $\text{B}_{(8)}$ and $\text{B}_{(9)}$.



EXPERIMENTAL

Gas chromatography was carried out in an apparatus Chrom 3 (a column 240 cm long, packed with Chromosorb W coated with 20% w/w of fluorosilicone polymer QF 1, nitrogen as carrier, temperature 123°C). The NMR spectra were measured using a prototype apparatus constructed at the Institute of Scientific Instruments, Brno; ^{11}B spectra were measured at 25 and 32 MHz, for ^1H at 100 MHz. Mass spectra were recorded using an apparatus LKB 9000 at 70 eV and an inlet temperature of 20°C . Thin-layer chromatography was carried out on Silufol plates (Kavalier, Votice, Czechoslovakia), starch as binder; the eluant was *n*-hexane, the spots were detected by exposure to I_2 vapour followed by spraying the plate with a solution of AgNO_3 . A high resolution mass spectrum was obtained with an apparatus AEJ — 902. The melting points were determined in sealed capillaries and were not corrected. The infrared spectra were measured on an apparatus Beckman IR 20 A.

6,9-Dicarba-*nido*-decaborane(14) (*I*)

A solution of 1.5 g (0.012 mol) of 5,6-dicarba-*nido*-decaborane (12) (*II*) in 100 ml of 96% ethanol was treated with 144 g of 1.5% sodium amalgam at 40 to 60°C for 5 h under stirring. After

cooling to 15°C the mixture was diluted with 200 ml of water and shaken with 100 ml of n-hexane. The aqueous layer was acidified to pH 1 and shaken with 50 ml of dichloromethane. The combined organic extracts were evaporated to dryness and the residue was sublimed at 10^{-2} Torr. Up to 50°C there sublimed the unreacted 5,6-C₂B₈H₁₂, the crude product sublimed at 70–100°C. After resublimation at 100°C/ 10^{-2} Torr onto a "finger" cooled to 10°C there was obtained 0.4 g (26.3%) of carborane 6,9-C₂B₈H₁₄, m.p. 143–144°C. An analytical grade product, melting at 146–147°C, was obtained by another resublimation in a tube heated to 350°C. For C₂B₈H₁₄ (124.8) calculated: 69.42% B, 19.26% C, 11.32% H; found: 68.45% B, 20.00% C, 11.26% H. From the sublimation forerun 0.2 g (13.5%) of the carborane *II* was recovered by chromatography with hexane on a dry column of silica gel. The R_F values of compound *I* on Silufol: 0.05 (hexane), exhibited a molecular cut-off $m/e = 126$; at the high resolution m/e was 126.184009. For ¹²C₂¹¹B₈¹H₁₄⁺ calculated $m/e = 126.184037$.

Deuteration of 6,9-Dicarba-*nido*-decaborane(14) (*I*)

A) To a solution of 0.1 g (8 mmol) of compound *I* in 5 ml of ether was added 3 ml of 99.9% D₂O. After a brief shaking the mixture was left standing for 40 h. The ethereal layer was separated and taken to dryness. The residue was sublimed at 70–100°C/ 10^{-2} Torr; yield 0.1 g of a product whose mass spectrum had a molecular cut off $m/e = 130$, corresponding to C₂B₈H₁₀D₄. The ¹¹B NMR at 32 MHz was composed of 3 doublets at -4.2 (168) (2), +16.9 (155) (4) and +37.1 (152) (2) p.p.m.

B) Through a solution of 0.1 g (8 mmol) of *I* in 50 ml of CS₂ + 0.05 g of AlCl₃ was bubbled DCl (0.3 mol, generated by reaction of D₂O with C₆H₅COCl). After standing for 24 h the mixture was filtered and the substance collected on the filter was washed with carbon sulphide. The filtrate and the washing were combined and distilled to remove the solvent. The residue was sublimed at 100°C/ 10^{-2} Torr; yield 0.1 g of a product with a molecular cut off $m/e = 128$, corresponding to C₂B₈H₁₂D₂. The ¹¹B NMR spectrum (32 MHz) accorded with the expected substitution at positions 1 and 3; it had 2 doublets, at -4.1 (145) (2) and +16.1 (162) (4), and 1 singlet at +36.5 p.p.m.

The infrared and ultraviolet spectra were measured by Dr F. Hanousek and Mr F. Haruda, gas chromatography was performed by Mr J. Stuchlík, all of the Institute of Inorganic Chemistry, Czechoslovak Academy of Sciences, Prague. The ¹¹B NMR spectra were measured by Dr K. Švéda, Institute of Instrumental Technique, Brno. The mass spectra were determined by Dr V. Kubelka and Dr J. Mitera, Institute of Chemical Technology, Prague, and by Dr L. Dolejš, Institute of Organic Chemistry and Biochemistry, Czechoslovak Academy of Sciences, Prague. The help of all these colleagues is gratefully acknowledged.

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Translated by J. Salák.