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SOME REACTIONS OF 5,6-DICARBA-*nido*-DECABORANE(12)

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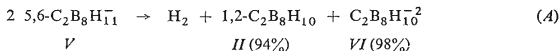
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Thermal decomposition of 5,6-dicarba-*nido*-decaborane(12) (*I*) to 1,6-dicarba-*closo*-decaborane(10) and 1,10-dicarba-*closo*-decaborane(10) (*IV*) is described. On heating at 200°C the sodium salt of compound *I* disproportionates to 1,2-dicarba-*closo*-decaborane(10) (*II*) and the anion $C_2B_8H_{10}^{-2}$, isomeric with the anion prepared by addition of sodium to compound *II*. The preparation of anions of the $C_2B_8H_{10}^{-2}$ and $C_2B_8H_{12}^{-2}$ type is also described.

In our previous papers^{1,2} we described the preparation of 5,6-dicarba-*nido*-decaborane(12) (*I*) and its dehydrogenation to 1,2-dicarba-*closo*-decaborane(10) (*II*). The existence of compound *I* was mentioned recently in the literature^{3,4}, while compound *II* has not yet been described. In the present paper we discuss some other reactions of compounds *I* and *II*.

Compound *I* easily undergoes thermal dehydroisomerization when passed through an evacuated tube (10^{-2} Torr) at 500°C. Under such conditions a mixture is formed containing 1,6-dicarba-*closo*-decaborane(10) (*III*) and 1,10-dicarba-*closo*-decaborane(10) (*IV*). On repeating the operation, substance *IV* is obtained exclusively. Compound *IV* was described for the first time by Hawthorne and coworkers⁵ who obtained it on rearrangement of compound *III* in a sealed ampoule at 350°C. We found that under the same conditions compound *IV* is also formed quantitatively from the isomer *II*. Isomerization dehydrogenation of compound *I* or thermal isomerization of compound *II* are presently the most accessible preparative procedures for carborane *IV*.

The thermolysis of the sodium salt^{1,2} of *nido*-carborane *I* (*V*) at 120–200°C/ 10^{-2} Torr took place according to the following equation:

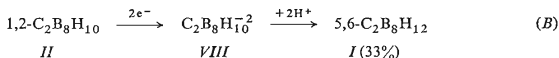


Compound *II* is obtained absolutely pure in contrast to the procedures described

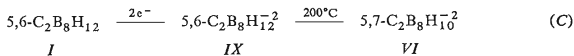
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earlier^{1,2}. On hydrolysis in acid medium the anion *VI* afforded 90% of 1,3-dicarbano-*nido*-nonaborane(13) (*VII*)* which was prepared earlier⁶ by another route. The anion *VI* is evidently a product of intramolecular rearrangement and both carbon atoms are no longer in the original vicinal positions, but probably in positions 5 and 7. By this, the unambiguous and smooth course of its hydrolysis to *nido*-carborane *VII* may be explained easily, which takes place without the reorganisation of the skeletal atoms. It is probable that the anion 5,7-C₂B₈H₁₀⁻² (*VI*) is identical with the product of the addition of two atoms of sodium to *closo*-carborane⁷ *III*.

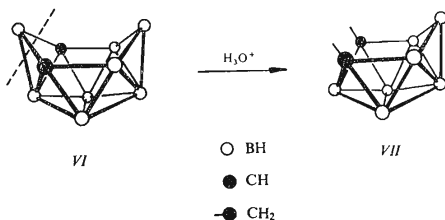
The addition of sodium to *closo*-compound *II* gives rise to anion C₂B₈H₁₀⁻² (*VIII*) which is undoubtedly isomeric with anion *VI*, as on acidification in aqueous medium it gives compound *I* as the main product. Hence, it is evident that during the addition of sodium no shift of the skeletal carbon atoms took place from the original vicinal positions:



Nido-carborane *I* is also capable of adding sodium under formation of anion 5,6-C₂B₈H₁₂⁻² (*IX*), which undergoes thermal dehydroisomerization at 200°C and is transformed to anion *VI*:



The identity of anions obtained by both procedures was proved by ¹¹B NMR spectra.



EXPERIMENTAL

All operations connected with the isolation of substances were carried out in a standard vacuum apparatus⁸ unless stated otherwise. The IR spectra were measured on a Beckmann IR 20 A, ¹¹B NMR spectra on an apparatus developed in Czechoslovakia, at 25 MHz. Gas chromatography was carried out on a Chrom III apparatus. The melting points were measured in sealed capillaries and they are not corrected.

* The numbering according to Hawthorne⁶ was used.

Dehydroisomerization of 5,6-Dicarba-*nido*-decaborane(12) (*I*)

Through a quartz tube (11 mm diameter, 500 mm length) 3.7 g (0.03 mol) of compound *I* were sublimated at 550°C and 10^{-2} Torr for 3.5 hours; the sublimate was collected at -78°C . After the first passage through the tube 3.05 g (82.4%) of the mixture were collected, which after gas chromatography contained compounds *III* and *IV* in a 1 : 1 ratio. The occurrence of two C—H bands of unequal intensity in the IR spectrum also indicated the presence of the 1,6-isomer. After repeated pyrolysis 3.00 g (81%) of sublimate, m.p. 156–157°C, were collected. According to gas chromatography the substance was pure and identical with 1,10-isomer *IV*; a single C—H absorption band was observed in the IR spectrum. Literature⁴ gives m.p. 161–162°C.

Isomerization of 1,2-Dicarba-*closo*-decaborane(10) (*II*)

A glass ampoule with 0.2 g (1.63 mmol) of compound *II* was evacuated at $-78^{\circ}\text{C}/10^{-2}$ Torr, sealed, and heated at $350 \pm 10^{\circ}\text{C}$ for 4 hours. After cooling to room temperature the ampoule was opened and the content sublimated at $20^{\circ}\text{C}/10^{-2}$ Torr affording 0.19 g (97%) of isomer *IV*, which was identified on the basis of its ^{11}B NMR spectrum in hexane (doublet $\delta = 12.5$ p.p.m., referred to $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$, $J = 165$ Hz).

Thermal Decomposition of Sodium 5,6-Dicarba-*nido*-undecahydrodecaborate (*V*)

A solution of 2.1 g (0.017 mol) of compound *I* in 40 ml of diethyl ether was added dropwise to a suspension of 0.95 g (0.04 mol) of sodium hydride in 70 ml of diethyl ether. When the evolution of hydrogen ceased (0.015 mol) the reaction mixture was filtered and the unreacted sodium hydride washed with distilled ether. The clear filtrate was evaporated to dryness, the residue dried at $40^{\circ}\text{C}/10^{-2}$ Torr for 2 hours, and then slowly heated at 10^{-2} Torr in a flask provided with a tube and cooling finger. The tube wall was cooled in one place at -30°C , while the cooling finger was cooled at -78°C . The decomposition started at 120°C and at 160°C it was practically terminated; at 200°C the reaction was interrupted. During the reaction 0.95 g (94%) of 1,2-dicarba-*closo*-decaborane(10) (*II*), m.p. 183°C , sublimated on the tube walls. The product was identified by its IR spectrum and thin-layer chromatography on silica gel (Silufol, *n*-hexane, R_F 0.1), by comparison with an authentic sample. When the decomposition was finished, the residue in the flask was 1.4 g (98%) of compound *VI*. For $\text{C}_2\text{B}_8\text{H}_{10}\text{Na}_2$ (166.8) calculated: 27.59% Na, 14.41% C, 51.94% B, 6.05% H; found: 26.13% Na, 15.32% C, 50.13% B, 6.22% H. The ^{11}B NMR spectrum in tetrahydrofuran is composed of three broad unresolved signals of relative intensities 1 : 5 : 2, centered about -20 , 7, and 34 p.p.m. (referred to $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$). In the IR spectrum (KBr pellet) the vibrations of $\nu(\text{B}-\text{H})_{\text{term}}$ at 2430 cm^{-1} and $\nu(\text{C}-\text{H})$ at 2970 , 2990 (sh) cm^{-1} were found; no B—H bridge vibration was present.

Solvolysis of Disodium 5,7-Dicarba-*nido*-decahydrodecaborate (*VI*)

A solution of 1 g (6 mmol) of compound *VI* in 20 ml of water was overlaid with 25 ml of *n*-hexane and acidified dropwise under shaking with dilute HCl (1 : 1) to pH 1. When the evolution of hydrogen ceased the aqueous layer was extracted several times with hexane and the combined hexane extracts were separated and evaporated at $20^{\circ}/15$ Torr. The residue was sublimated at 20 – $40^{\circ}\text{C}/10^{-2}$ Torr into a tube cooled at -30°C . Yield 0.6 g (89%) of compound *VII*, m.p. 59 – 60°C (lit.⁶ 60.5 – 61°C), which had identical IR spectrum with 1,3-dicarba-*nido*-nonaborane(13) prepared according to literature⁶. For $\text{C}_2\text{B}_7\text{H}_{13}$ (112.9) calculated: 21.30% C, 66.95% B, 11.60% H; found: 21.76% C, 66.81% B, 11.7% H. In the mass spectrum the molecular peak was $m/e = 114$, corresponding to the ion $^{11}\text{B}_7^{12}\text{C}_2^+\text{H}_{13}^+$.

Disodium Dicarba-*nido*-decahydrodecarborate (VIII)

To a stirred suspension of 0.5 g (0.022 mol) of sodium in 30 ml of tetrahydrofuran 0.2 g (1.6 mmol) of naphthalene were added. When the dark green coloration appeared a solution of 0.6 g (5 mmol) of compound *II* in 25 ml of tetrahydrofuran was added dropwise. The mixture changed colour immediately to orange-yellow. After 4 hours stirring the mixture was filtered, the filtrate evaporated *in vacuo* and the residual oil extracted repeatedly with *n*-hexane. The insoluble residue was added with 25 ml of *n*-hexane, and after addition of 25 ml of water the mixture was acidified under vigorous shaking with dilute HCl to pH 1. When the evolution of hydrogen ceased (due to partial hydrolysis) the hexane layer was separated, concentrated to approx. 10 ml and separated chromatographically on 40 g of silica gel (Silpearl, Kavalier) with hexane (dry column method^{9,10}). From the layer containing compound *I* 0.2 g (33%) of carborane *I* were obtained by extraction with dichloromethane and sublimation, which was identified by thin-layer chromatography on Silufol, R_F 0.2.

Disodium 5,6-Dicarba-*nido*-dodecahydrodecarborate (IX) and its Thermal Decomposition

A mixture of 1.0 g (0.044 mol) of sodium and 0.2 g (1.6 mmol) of naphthalene in 25 ml of tetrahydrofuran was stirred until a dark green solution was formed. A solution of 1.3 g (0.01 mol) of compound *I* in 25 ml of tetrahydrofuran was then added dropwise to the above mixture. During the addition the green colour disappeared and a yellow solution of compound *IX* was formed. No hydrogen evolved. After 5 hours stirring the mixture was filtered, the volatile components evaporated *in vacuo*, and the residue heated gradually to 200°C/10⁻² Torr. During the heating 0.2 g (100%) of naphthalene sublimated out. The residue was washed several times with *n*-hexane and dried at 20°C/10⁻² Torr. Yield 1.7 g of a product, the identity of which with compound *VI* was demonstrated by ¹¹B NMR spectra in tetrahydrofuran. The ¹¹B NMR spectrum of the anion *IX* in tetrahydrofuran displayed 4 to 5 broad, unresolved signals centered around -33, -12.5, +2.3, 11.5 and 27.3 p.p.m. (referred to BF₃·O(C₂H₅)₂).

Acidification of Disodium 5,6-Dicarba-*nido*-dodecahydrodecarborate (IX)

From 1 g (8.2 mmol) of compound *I* and 0.4 g (0.017 mol) of sodium a solution of compound *IX* in 40 ml of tetrahydrofuran was prepared in the presence of naphthalene by the preceding procedure. After filtration the volatile substances were evaporated to dryness, the residue was dried at 20°C/10⁻² Torr and extracted with *n*-hexane until all naphthalene had passed into the extract. The undissolved residue was mixed with 30 ml of *n*-hexane and 20 ml of water and acidified with dilute hydrochloric acid to pH 1. When the evolution of hydrogen ceased the hexane layer was separated and, after concentration, chromatographed with hexane on a dry column of 40 g silica gel (Silpearl with a UV indicator). The layer containing substance *I* was extracted with dichloromethane and the residue after evaporation was sublimated (40°C/10⁻² Torr), yielding 0.45 g (45%) of *nido*-carborane *I* which was identified by thin-layer chromatography on silica gel (Silufol, *n*-hexane, R_F 0.2).

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