A CONVENIENT PREPARATION OF 1-$CB_{11}H_{12}^-$ AND ITS C-AMINO DERIVATIVES

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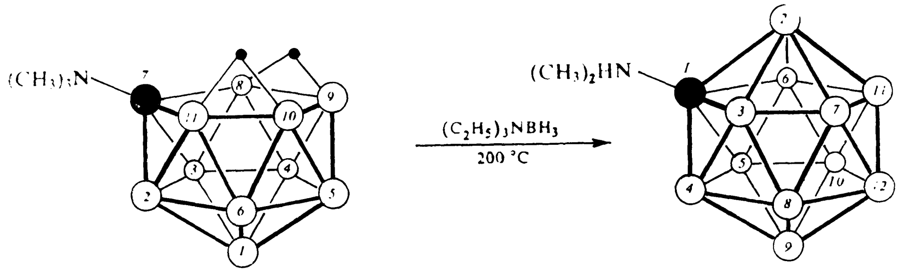
Treatment of 7-$(CH_3)_3N$-7-$CB_{10}H_{12}$ with triethylamineborane(3) at 180—200°C proceeds under splitting off one methyl group and inserting one boron vertex to obtain 1-$(CH_3)_2NH$-1-$CB_{11}H_{11}$. Methylation of the latter compound produces 1-$(CH_3)_3N$-1-$CB_{11}H_{11}$ which can be reduced to the parent 1-$CB_{11}H_{12}^-$ anion with sodium in liquid ammonia. The constitution of all compounds was established by NMR and mass spectroscopy.

The 1-$CB_{11}H_{12}^-$ anion, a monocarba analogue of $B_{12}H_{12}^{2-}$, was first obtained by Knoth[1,2] as a single representative of the 1-carba-*closo*-dodecaborate(1) series in the reaction of triethylamineborane(3) with the *nido*-7-$CB_{10}H_{13}^-$ anion. We report herein an efficient synthesis of further representatives of the $CB_{11}H_{12}^-$ family including the parent compound.

We have recently[3] found an interesting reaction taking place on heating the 7-$(CH_3)_3N$-7-$CB_{10}H_{12}$ (*I*) carbaborane with triethylamineborane(3) at 180—200°C. The reaction resulted in inserting one more boron atom into the open pentagonal face of compound *I* (Scheme 1) to complete the 12-vertex icosahedral framework



I

II

SCHEME 1

● CH
○ BH
• H

and in splitting off one methyl group under the formation of $1\text{-}(CH_3)_2NH\text{-}1\text{-}CB_{11}H_{11}$ (*II*) on hydrolysis of an amorphous reaction intermediate by hydrochloric acid. The zwitterionic compound *II*, as a weak N-acid, can be alkylated with dimethyl sulphate to form $1\text{-}(CH_3)_3N\text{-}1\text{-}CB_{11}H_{11}$ (*III*). Two-electron reduction of compound *III* with sodium in liquid ammonia afforded pure parent anion $1\text{-}CB_{11}H_{12}^-$ (*IV*) (60%) along with the recovered compound *II* (35%) as a result of an unusual abstraction of one methyl group from compound *III*.

In connection with this work, we have modified[4] the synthesis of the starting $6\text{-}NCB_{10}H_{13}^{2-}$ anion by substituting one equivalent of the cyanide anion for sodium hydroxide and using concentrated hydrochloric acid in place of an ion exchanger according to scheme:

$$B_{10}H_{14} \xrightarrow{OH^-} B_{10}H_{13}^- \xrightarrow{CN^-} B_{10}H_{13}CN^{2-} \xrightarrow[0\,°C]{\text{conc. HCl}}$$

$$\longrightarrow 7\text{-}H_3N\text{-}7\text{-}CB_{10}H_{12} \xrightarrow[\text{dimethyl sulphate}]{OH^-} \underset{I,\ 97\%}{7\text{-}(CH_3)_3\text{-}7\text{-}CB_{10}H_{12}} \qquad (1)$$

to develop a safer and more convenient procedure for obtaining compound *I* upon careful acidification of $6\text{-}NCB_{10}H_{13}^{2-}$. The above described array of multistep reactions, giving a total 64% yield of anion *IV* (based on the recovered compound *II*) from decaborane, represents now a convenient process suitable for obtaining larger amounts of various so far unexplored derivatives of $1\text{-}CB_{11}H_{12}^-$.

The ^1H NMR spectrum of compound *II*, displaying one singlet of the two $(CH_3)_2N$ groups (δ 3·14), and its ^{11}B NMR spectrum, showing the 1 : 5 : 5 patterns of doublets, are in agreement with the proposed $1\text{-}(CH_3)_2NH\text{-}1\text{-}CB_{11}H_{11}$ gross geometry. The derivative behaves as a weak acid (pK_a 5·7) to form the $1\text{-}(CH_3)_2N\text{-}1\text{-}CB_{11}H_{11}^-$ anion characterized as the tetramethylammonium salt the ^1H NMR spectrum of which exhibits the $(CH_3)_2N$ signal (δ 2·25) shifted upfield in comparison to compound *II*. Its ^{11}B NMR spectrum shows two overlapping signals of intensity 5 and one doublet of intensity 1 due to the $B_{(12)}$ atom. In agreement with the proposed $1\text{-}(CH_3)_3N\text{-}1\text{-}CB_{11}H_{11}$ arrangement for compound *III* are also its ^1H and ^{11}B spectra displaying one signal of the $(CH_3)_3N$ group and three 1 : 5 : 5 ^{11}B signals. The NMR characteristics of the parent $1\text{-}CB_{11}H_{12}^-$ anion, isolated as the tetramethylammonium salt, correspond well to the earlier reported data[1,2,5].

EXPERIMENTAL

^1H (200 MHz) and ^{11}B (64·18 MHz) NMR spectra were recorded on a Varian XL-200 equipment in hexadeuterioacetone; chemical shifts are given in δ (ppm relatively to tetramethylsilane and $BF_3O(C_2H_5)_2$, positive values downfield). Mass spectra were obtained on a GC/MS HP-5985 spectrometer. The purity of individual compounds was checked by TLC on Silufol (silica gel on aluminium foil, starch as binder, producer Kavalier, Votice, Czechoslovakia). Melting points were determined in sealed capillaries and are uncorrected. Decaborane(14) was sublimed at 90°C/ /1·3 Pa and ammonia was dried by passing through a column packed with potassium hydroxide pellets prior to use.

7-Trimethylamine-7-carba-*nido*-undecaborane(12) (*I*)

A slurry of decaborane(14) (24·4 g; 0·2 mol) in hexane (50 ml) and an aqueous solution (200 ml) containing sodium cyanide (10·8 g; 0·22 mol) and sodium hydroxide (8·8 g; 0·22 mol) was vigorously stirred under cooling to 20°C until all decaborane dissolved (*c.* 2 h). The two layer mixture was chilled to 0°C and concentrated hydrochloric acid (50 ml) was added under stirring during 20 min to evolve some gas. The residual hydrogen cyanide and all hexane were evaporated *in vacuo*, the clear solution was cooled down to 0°C and a solution of sodium hydroxide (40 g; 1·0 mol) in water (160 ml) was added. Addition fo dimethyl sulphate (88·4 g; 0·7 mol) under stirring for 20 min and agitation of the mixture for an additional 1 h at ambient temperature caused precipitation of a white product which was sucked off, washed with water (300 ml), 50% ethanol (100 ml) and dried overnight to obtain 37 g (96·6%, based on decaborane used) of crude compound *I* slightly contaminated by 6-$(CH_3)_3N$-6-CB_9H_{11} (2—5%). This contamination had no adverse effect on the following preparation.

1-Dimethylamine-1-carba-*closo*-dodecaborane(11) (*II*)

A suspension of the crude *I* (28·6 g; 0·15 mol) in 53 ml (41·0 g; 0·35 mol) triethylamineborane(3) was heated under nitrogen to 200°C for 8 h to evolve gaseous products. The suspension gradually disappeared and triethylamine was distilled off. After standing overnight, methanol (150 ml) was added (hydrogen evolution). During 1 h, concentrated hydrochloric acid (45 ml) was added at such a rate as to control the vigorous hydrogen evolution and spontaneous warming up of the mixture which was then refluxed for 6 h. Water (150 ml) was added, the volatiles were stripped off *in vacuo* and the amorphous product was decanted. The residue was washed with hot water (50 ml) and digested with three 100 ml portions of 10% sodium hydroxide. The alkaline extract was filtered and acidified with hydrochloric acid to precipitate a voluminous white product which was sucked off, washed three times with water (50 ml) and dried at 20°C to yield 21·2 g (75·8%) of compound *II* as a white species not melting up to 280°C, readily soluble in alcohols, acetone and ethyl acetate; *m*/*z* 189 (corresponding to $^{11}B_{11}{}^{12}C_3{}^{1}H_{18}{}^{14}N^+$); ^1H NMR spectrum: δ 3·14 (6 H, $(CH_3)_2N$); ^{11}B NMR spectrum: δ_B −8·37 (1 B, d, 142, $B_{(12)}$), −13·65 (5 B, d, 136), −15·69 (5 B, d, 148); pK_a (50% ethanol) 5·7.

Tetramethylammonium salt: To a solution of compound *II* (1 g; 5·34 mmol) in 2% sodium hydroxide (20 ml), 1M tetramethylammonium chloride (10 ml) was added. The suspension was heated and enough ethanol was added to obtain a clear solution. After standing overnight, thin needles of 1-$(CH_3)_2N$-1-$CB_{11}H_{11}^-N(CH_3)_4^+$, 1·2 g (85%) separated. The salt is practically insoluble in water but soluble in acetone. ^1H NMR spectrum: δ 3·46 (12 H, s, $(CH_3)_4N^+$), 2·25 (6 H, s, $(CH_3)_2N$); ^{11}B NMR spectrum: δ_B −11·68) (1 B, d, 140, $B_{(12)}$), −14·86 (10 B, d, $B_{(2-11)}$).

1-Trimethylamine-1-carba-*closo*-dodecaborane(11) (*III*)

To a solution of compound *II* (17·8 g; 0·1 mol) in 50% methanol (200 ml) containing sodium hydroxide (8·0 g; 0·2 mol), dimethyl sulphate (14·0 g; 0·11 mol) was added during 20 min and the mixture was stirred for 3 h at ambient temperature. The separated product was sucked off' washed with water (200 ml) followed by methanol (30 ml) and dried at ambient temperature to obtain 18·4 g (95·4%) of 1-$(CH_3)_3N$-1-$CB_{11}H_{11}$ as a white powder, not melting up to 280°C and moderately soluble in acetone; *m/z* 203 (corresponding to ${}^{11}B_{11}{}^{12}C_4{}^{1}H_{20}{}^{14}N^+$); ${}^1H$ NMR spectrum: δ 3·47 (9 H, s, $(CH_3)_3N$); ${}^{11}B$ NMR spectrum: δ_B −7·40 (1 B, d, 141, $B_{(12)}$), −13·65 (5 B, d, 140), −15·07 (5 B, d, 140).

Dodecahydro-1-carba-*closo*-dodecaborate (1-) (*IV*)

To a stirred suspension of compound *III* (8·05 g; 0·04 mol) in liquid ammonia (100 ml), sodium (2·0 g; 0·088 gat) was added during 1 h in several portions. The blue colour quickly disappeared, only after adding the last portion it persisted for *c.* 10 min. Methanol (10 ml) was added during 5 min and the ammonia was left to evaporate overnight. The residue was shortly evacuated, water (50 ml) was added, the solution was acidified with hydrochloric acid to precipitate 2·6 g (35%) of compound *II* which was identified by its ${}^{11}B$ NMR spectrum. The filtrate was treated with an aqueous solution of trimethylamine hydrochloride and the voluminous salt was dissolved by warming after an addition of sufficient amount of ethanol. On standing overnight, the product was sucked off, washed with water and dried at ambient temperature to give 4·9 g (60%) of pure trimethylammonium salt as white needles.

Tetramethylammonium salt: To a suspension of the trimethylammonium salt (1 g; 4·92 mmol) in water (20 ml), sodium hydroxide (0·5 g) was added, trimethylamine and some water removed *in vacuo* from the formed clear solution and tetramethylammonium chloride (0·5 g) in water (10 ml) was added. The resulting slurry was dissolved by adding acetone (*c.* 30 ml), the acetone was then slowly distilled off to separate gradually thin needles which were filtered, washed with water (10 ml) and dried at ambient temperature to obtain 1 g (93%) of 1-$CB_{11}H_{12}^-N(CH_3)_4^+$; ${}^1H$ NMR spectrum: δ 3·43 (12 H, s, $(CH_3)_4N$), 2·24 (1 H, s, CH skel.); ${}^{11}B$ NMR spectrum: δ_B −6·90 (1 B, d, 135, $B_{(12)}$), −13·30 (5 B, d, *c.* 130), −16·31 (5 B, d, *c.* 160).

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REFERENCES

1. Knoth W. H.: J. Amer. Chem. Soc. *89*, 1274 (1967).
2. Knoth W. H.: Inorg. Chem. *10*, 598 (1971).
3. Plešek J., Štíbr B., Drdáková E.: Czech. Appl. PV 3769—83.
4. Plešek J., Štíbr B.: Czech. 214 587.
5. Aftandilian V. D., Miller H. C., Muetterties E. L.: J. Amer. Chem. Soc. *83*, 2471 (1961).

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