Russian Journal of General Chemistry, Vol. 72, No. 5, 2002, pp. 741–743. Translated from Zhurnal Obshchei Khimii, Vol. 72, No. 5, 2002, pp. 794–796.
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Alkylation of *nido*-7,8-Dicarbollide Anion with Propargyl Bromide in Liquid Ammonia with Formation of 8-Propargyl-*nido*-7,9-dicarbaundecaborate and 9-Propargyl-*nido*-7,8-dicarbaundecaborate Anions

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Received May 31, 2000

Abstract—Alkylation of *nido*-7,8-dicarbollide anion with propargyl bromide in liquid ammonia is accompanied by skeleton rearrangements and yields, depending on the reaction conditions, 8-propargyl-nido-7,9-dicarbaundecaborate or 9-propargyl-*nido*-7,8-dicarbaundecaborate anion.

Transformations of carboranes are often accompanied by skeleton rearrangements [1, 2]. Owing to structural features of the open face of the *nido*-7,8-dicarbollide anion, its alkylation with electrophilic agents occurs at the boron atoms of the open pentagonal plane and is accompanied by structural rearrangements of the molecular skeleton.

Previously we studied alkylation of 7,8-dimethyl-*nido*-7,8-dicarbollide anion with benzyl chloride in liquid ammonia and found that, depending on conditions, the reaction yielded 7,9-dimethyl-8-benzyl-*nido*-7,9-dicarbaundecaborate or 7,8-dimethyl-9-benzyl-*nido*-7,8-dicarbaundecaborate anion [2]. It was interesting to study alkylation of *nido*-7,8-dicarbollide anion in liquid ammonia with propargyl bromide containing an acidic acetylenic hydrogen atom. We expected that this acidic hydrogen would protonate the dicarbollide dianion to give *nido*-7,8-dicarbaundecaborate anion, according to the following scheme:

$$\textit{nido}\text{-7,8-}C_2B_9H_{11}^{2-}Na^+ + BrCH_2C{\equiv}CH$$

$$\xrightarrow{NH_3(l.)} \textit{nido}\text{-7,8-}C_2B_9H_{12}^{-}Na^+ + BrCH_2C{\equiv}CNa.$$

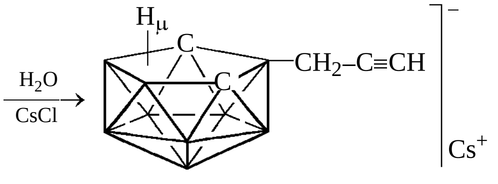
However, actually instead of proton interchange the *nido*-7,8-$C_2B_9H_{11}^{2-}$ anion underwent alkylation at the boron atom of the pentagonal plane. As demonstrated in [2] by the example of the reaction of 7,8-Me_2-*nido*-7,8-$C_2B_9H_9^{2-}$ with benzyl chloride, alkylation of *nido*-7,8-$C_2B_9H_{11}^{2-}$ with alkyl halides is a complex process and is accompanied by a rearrangement of the polyhderon to form, in the case of the 7,8-dimethyl derivative, the intermediate 2,7-Me_2-11-$PhCH_2$-2,7-$C_2B_9H_9^{2-}$ anion which, depending on the reaction conditions, transforms into 7,9-dimethyl-8-benzyl-*nido*-7,9-dicarbaundecaborate or 7,8-dimethyl-9-benzyl-*nido*-7,8-dicarbaundecaborate anion.

We found that the reaction of *nido*-7,8-$C_2B_9H_{11}^{2-}$ with propargyl bromide in liquid ammonia also yields two compounds depending on the reaction conditions. Undoubtedly, this reaction also involves a skeleton rearrangement of the polyhedron with the formation of the intermediate 11-$HC{\equiv}CCH_2$-*nido*-2,7-$C_2B_9H_{11}^-$ anion.

$$\underset{\mathbf{I}}{\textit{nido}\text{-7,8-}C_2B_9H_{11}^{2-}} + \underset{\mathbf{II}}{HC{\equiv}C{-}CH_2Br}$$

$$\xrightarrow{NH_3(l.)} \underset{\mathbf{III}}{\text{11-}HC{\equiv}C{-}CH_2\text{-2,7-}C_2B_9H_{11}^-}$$

$$\xrightarrow{NH_3\text{ evaporation}} \underset{\mathbf{IV}}{\text{8-}HC{\equiv}C{-}CH_2\text{-}\textit{nido}\text{-7,9-}C_2B_9H_{10}^-}$$



V

In this reaction, substitution of a hydrogen atom at the boron atom of the pentagonal plane by the $HC{\equiv}CCH_2$ group is accompanied by a polyhedral rearrangement with migration of one of the carbon atoms from the open pentagonal plane to the core of the polyhedron, with the C–C bond being preserved (compound **III**). Then, after ammonia evaporation, the residue was heated at 40°C, which was accompanied

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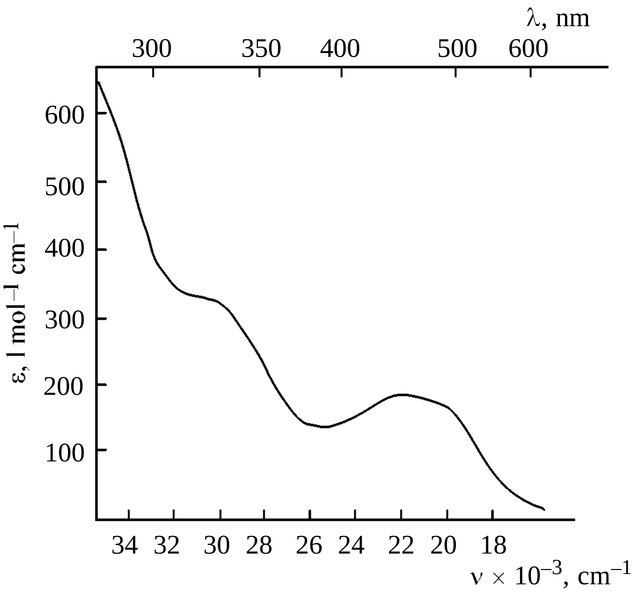
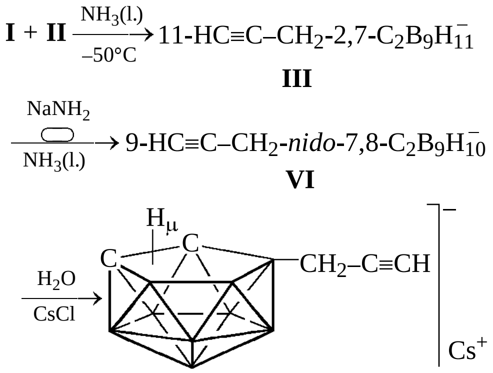


Electronic absorption spectrum of **VII** (15×10^{-3} M) in methanol in the presence of H_2SO_4.

by a new rearrangement with cleavage of the C–C bonds and formation of two new C–B bonds. The resulting anion **IV**, when treated with aqueous CsCl, gave cesium salt **V**.

When the reaction of **I** and **II** is performed in liquid ammonia in the presence of a small amount of a strong base such as $NaNH_2$, the resulting major rearrangement product, 11-HC≡CH_2-2,7-$C_2B_9H_{11}^-$, further rearranges into the 9-HC≡CCH_2-*nido*-7,8-dicarbaundecaborate anion **VI**, which after ammonia vaporization and treatment with aqueous CsCl yields 9-HC≡CCH_2-*nido*-7,8-$C_2B_9H_{11}^-Cs^+$ (**VII**).



$$\text{I} + \text{II} \xrightarrow[-50°\text{C}]{NH_3(\text{l.})} \text{11-HC≡C–}CH_2\text{-2,7-}C_2B_9H_{11}^-$$

III

$$\xrightarrow[NH_3(\text{l.})]{NaNH_2} \text{9-HC≡C–}CH_2\text{-}nido\text{-7,8-}C_2B_9H_{10}^-$$

VI

VII

The structure of anions **V** and **VII** was confirmed by the IR and ^{11}B NMR spectra. The number of signals in the ^{11}B NMR spectrum of **V** is the same as in the spectrum of the unsubstituted *nido*-7,9-$C_2B_9H_{12}^-$ anion **VIII** and suggests symmetrical substitution. The substituted B^8 atom located between the two carbon atoms in the open pentagonal plane gives a narrow singlet with δ_B 1.2 ppm, shifted by 6.5 ppm downfield relative to the B^8 signal in the spectrum of **VIII**. The presence of a doublet of doublets (relative intensity 2B) with δ_B –22.2 ppm ($J_{^{11}B-^{1}H}$ 130, $J_{^{11}B-H_\mu}$ 45 Hz) also confirms the symmetrical structure of the anion. This signal belongs to the equivalent B^{10} and B^{11} atoms in the open pentagonal plane. The ^{11}B NMR spectrum of **VII** consists of nine signals, which shows that the structure is unsymmetrical. The signal of the substituted B^9 atom (δ_B –1.31 ppm) is shifted downfield by 4.9 ppm relative to the unsubstituted *nido*-7,8-$C_2B_9H_{12}^-$ anion. The spectrum also contains a doublet of doublets from B^{10}, δ_B –33.33 ppm ($J_{^{11}B-^{1}H}$ 140, $J_{^{11}B-H_\mu}$ 36 Hz). The chemical shifts of the other boron signals of **V** and **VII** differ insignificantly.

Compounds **V** and **VII** exhibit a peculiar property untypical of carborane derivatives. A solution of **VII** in methanol or ethanol under the action of dilute acids such as HCl, H_2SO_4, or $BF_3 \cdot OEt_2$ turns red, whereas solutions of **V** under the action of the same acids turn light yellow. The spectrum of **VII** in the presence of sulfuric acid (see figure) contains an absorption band in the visible range. We have not elucidated why solutions of **VII** become strongly colored in the presence of acids and solutions of **V** do not.

EXPERIMENTAL

The IR spectra were recorded on a UR-20 spectrometer in KBr pellets. The UV spectra were taken with a Specord M-40 spectrophotometer. The ^{11}B NMR spectra were measured on a Bruker AMX-400 spectrometer (128.28 MHz, acetone-d_6); the signals (δ_B, ppm) are given relative to $BF_3 \cdot OEt_2$.

Cesium 8-propargyl-*nido*-7,9-dicarbaundecaborate V. A 1.2-g portion of sodium was gradually added with stirring to a solution of 8.6 g of *nido*-7,8-$C_2B_9H_{12}^-K^+$ in 100 ml of liquid ammonia at –50°C. The solution initially turned blue, and then the color gradually disappeared with evolution of hydrogen. After dissolution of sodium, a colorless solution of dicarbollide anion **I** formed, to which 5.9 g of propargyl bromide was added at –50°C. The mixture was stirred to completely evaporate ammonia, and the residue was heated at 40°C for 30 min. Then 20 ml of ice-cold water was carefully added, and the mixture was fitered. To the filtrate, excess aqueous CsCl was added, and the precipitate was filtered off and recrystallized from aqueous ethanol. Compound **V** was obtained; yield 13.7 g (90%). IR spectrum, ν,

cm^{-1}: 2099 (C≡C), 2547 (BH), 3025 (CH of polyhedron), 3287 (≡CH). ^{11}B NMR spectrum, δ_B, ppm ($J_{^{11}B-^{1}H}$, Hz): 1.2 s (1B, B^8), –5.4 d (2B, $B^{2,5}$, 148), –19.7 d (2B, $B^{3,4}$, 145), –22.2 d.d (2B, $B^{10,11}$, 130, 45), –32.7 d (1B, B^6, 141), –36.3 d (1B, B^1, 141). Found, %: C 19.81; H 4.90; B 31.85. $C_5H_{14}B_9Cs$. Calculated, %: C 19.72; H 4.63; B 31.98.

Cesium 9-propargyl-*nido*-7,8-dicarbaundecaborate VII. A 1.1-g portion of sodium was gradually added with stirring to a solutiuon of 8.0 g of *nido*-7,8-$C_2B_9H_{12}^-K^+$ in 100 ml of liquid ammonia at –50°C. The solution initially turned blue, and then the color gradually disappeared with evolution of hydrogen. After dissolution of sodium, a colorless solution of dicarbollide anion **I** formed, to which 5.6 g of propargyl bromide was slowly added with stirring. After several minutes, 0.4 g of NaH was added, and the mixture was stirred to completely evaporate ammonia. To the residue, 20 ml of ice-cold water was added, and the mixture was filtered. Excess aqueous CsCl was added to the filtrate, and the precipitate was filtered off and recrystallized from aqueous ethanol. Compound **VII** was obtained; yield 12.6 g (92%). IR spectrum, ν, cm^{-1}: 2105 (C≡C); 2550 (BH), 3037 (CH of polyhedron), 3291 (≡CH). ^{11}B NMR spectrum, δ_B, ppm ($J_{^{11}B-^{1}H}$ Hz): –1.31 s (1B, B^9), –10.91 d (1B, B^{11}, 138), –14.7 d (1B, B^3, 155), –17.44 d (1B, B^5, 161), –18.85 d (1B, B^6, 154), –21.6 d (1B, B^4, 152), –24.10 d (1B, B^2, 154), –33.33 d.d (1B, B^{10}, 140, 36), –37.59 d (1B, B^1, 133). Found, %: C 20.01; H 4.75; B 32.15. $C_5H_{14}B_9Cs$. Calculated, %: C 19.72; H 4.63; B 31.98. Protonated form of **VII**, methanolic solution (obtained under the action of concentrated H_2SO_4), UV spectrum, λ, nm (ε, l mol^{-1} cm^{-1}): 325 sh (320), 455 (180).

REFERENCES

1. Knyazev, S.P., Brattsev, V.A., and Stanko, V.I., *Dokl. Akad. Nauk SSSR*, 1977, vol. 234, no. 5, pp. 1093–1096.
2. Zakharkin, L.I., Zhigareva, G.G., Antonovich, V.A., Yanovskii, A.I., and Struchkov, Yu.T., *Zh. Obshch. Khim.*, 1986, vol. 56, no. 9, pp. 2066–2076.