yield. $B_7C_2H_{11}$ has never been fully purified owing to its thermal and hydrolytic instability; however, $B_8C_2H_{12}$ has been characterized. Infrared and pmr spectra are consistent with a decaborane(14)-like structure. The ^{11}B nmr spectra are nearly superimposable on those of $B_8C_2H_{10}(CH_3)_2$, and an exact mass match gave 124.16818 (calcd for $^{11}B_8{}^{12}C_2{}^{1}H_{12}{}^{+}$: 124.16835). To our knowledge, this species and a new $B_8C_2H_{12}$ containing nonadjacent carbon atoms[11] represent the first cases of skeletal isomers in *nido*-carboranes.

Pyrolysis products of $B_7C_2H_9(CH_3)_2$ include 15 volatile carboranes, of which 4,5-$B_5C_2H_5(CH_3)_2$, 1,6-$B_6C_2H_6(CH_3)_2$, *nido*-5,6-$B_8C_2H_{10}(CH_3)_2$, 1,2-$B_8C_2H_8(CH_3)_2$, 1,8-$B_9C_2H_9(CH_3)_2$, and 1,7-$B_{10}C_2H_{10}(CH_3)_2$ have been identified.[2] Evidence supporting other new *closo*-carborane isomers is being pursued.

Acknowledgments. We gratefully acknowledge the support of the National Science Foundation through Grants No. GP4944X and GU2003 and the Indiana University Foundation for a graduate fellowship to R. R. R. We are also indebted to Mr. A. O. Clouse for invaluable assistance in obtaining the ^{11}B nmr spectra.

(11) P. M. Garrett, G. S. Ditta, and M. F. Hawthorne, *J. Amer. Chem. Soc.*, 93, 1265 (1971).

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Received October 31, 1970

Preparation and Reactions of a Dicarba-*nido*-decaborane(12)

Sir:

The carboranes $B_4C_2H_8$,[1] $B_9C_2H_{13}$,[2] and $B_8C_2H_{12}$[3] have been reported as representative members of the $B_nC_2H_{n+4}$ *nido*-carborane family. We wish to report the preparation of yet another *nido*-$B_8C_2H_{12}$ carborane system and at the same time propose the possible existence of a new bonding feature present in this *nido*-$B_8C_2H_{12}$. The $B_8C_2H_{12}$ isomer reported here is markedly different from that of the $B_8C_2H_{12}$ species reported by Rietz[3,4] and appears as a moderately stable intermediate in the hydroboration route[5] leading from 1,3-$B_7C_2H_{13}$ to 1,6-$B_8C_2H_{10}$.

Treatment of 1,3-$B_7C_2H_{13}$ (I) with NaH in a 1:1 molar ratio in diethyl ether solvent followed by the slow addition of B_2H_6 produced 1,3-$B_7C_2H_{13}$, $NaBH_4$, 1,6-$B_8C_2H_{10}$, and the air- and moisture-sensitive product $B_8C_2H_{12}$ (II, mp 139–140°). Thermal decomposition of II *in vacuo* at 150° produced 1,6-$B_8C_2H_{10}$ and H_2 in quantitative yield. Attempts to further characterize II by mass spectroscopy and elemental analyses were complicated by the instability of II.

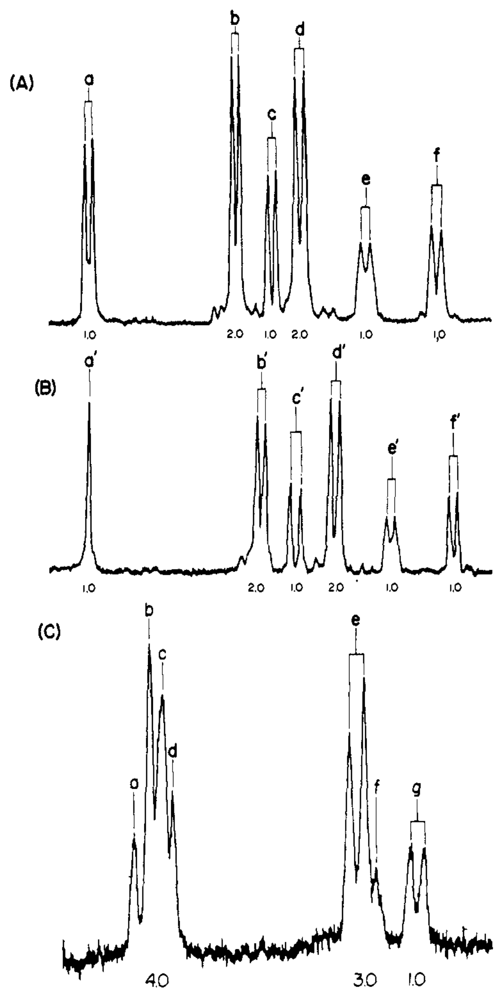

Figure 1. The 80.52-MHz ^{11}B nmr spectra of (A) $B_8C_2H_{12}$ and (B) $ClB_8C_2H_{11}$ in carbon disulfide solvent and (C) $B_8C_2H_{12}N(CH_3)_3$ in toluene. Chemical shifts (ppm, with reference to $BF_3O(C_2H_5)_2$) and coupling constants (Hz) are for (A): (a) −36.3, 175; (b) −1.0, 155; (c) +7.9, 157; (d) +13.7, 154; (e) +27.8, 150; and (f) +44.7, 155. (B): (a′) −37.2; (b′) +1.4, 158; (c′) +9.1, 155; (d′) +17.8, 156; (e′) +30.6, 151; and (f′) +44.5, 161. (C): (a) +2.9; (b) +4.9; (c) +6.7; (d) +8.1; (e) +32.5; (f) +35.0; and (g) 40.2, 151.

The 80-MHz ^{11}B nmr spectrum of II (Figure 1) consisted of six doublets of relative intensities 1:2:1:2:1:1, while the ^1H nmr spectrum (60 MHz) exhibited a broad singlet at τ 7.04. These spectra, when considered along with the presence of a B–H–B bridge band at 2050 cm^{-1} in the infrared, lead us to propose the structure of this $B_8C_2H_{12}$ isomer to be that shown in Figure 2. Reaction of crude II with trimethylamine led to the formation of a ligand adduct derivative, $B_8C_2H_{12}N(CH_3)_3$ (III, mp 142–144°). *Anal.* Calcd for $B_8C_5H_{21}N$: B, 47.59; C, 33.05; H, 11.65; N, 7.71. Found: B, 45.93; C, 33.01; H, 12.42; N, 7.44. Thermal decomposition of III at 150° *in vacuo* afforded quantitative yields of 1,6-$B_8C_2H_{10}$, $N(CH_3)_3$, and H_2. The 60-MHz ^1H nmr spectrum of III consisted of a broad singlet identified as a carborane CH resonance of relative intensity 2 at τ 9.61 and an amine CH_3 resonance of relative intensity 9 at τ 8.25. The 80-MHz ^{11}B nmr spectrum of III is shown in Figure 1. The presence of B–H–B bridge bands in the infrared spectrum of III (2075 cm^{-1}) is in accord with its proposed structure (Figure 3).

Reaction of III with anhydrous HCl in a 3:1 ratio in CH_2Cl_2 solvent at −80° gave pure II in moderate

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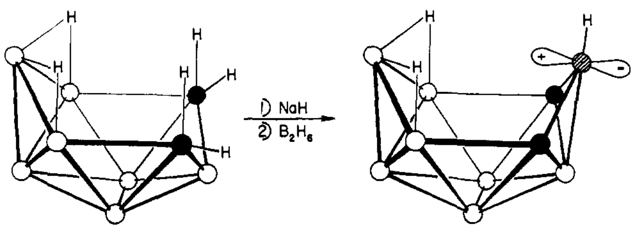
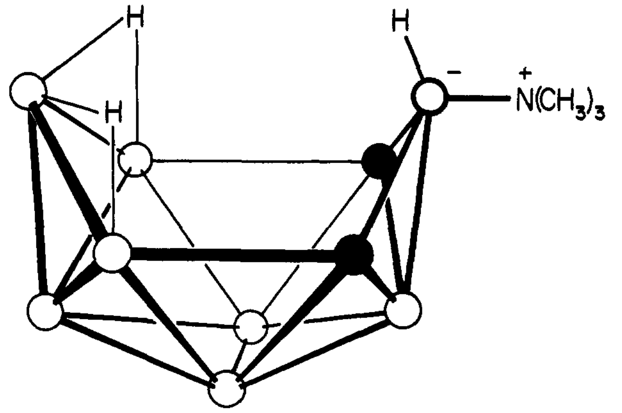


I II

Figure 2. The reaction of $B_7C_2H_{13}$ (I) with (1) sodium hydride and (2) diborane, which produces $B_8C_2H_{12}$ (II), and the proposed structure of II. For I, ○ = BH, ● = carbon; for II, ○ = BH, ● = CH, ◉ = sp-hybridized boron atom with empty p orbital.



III

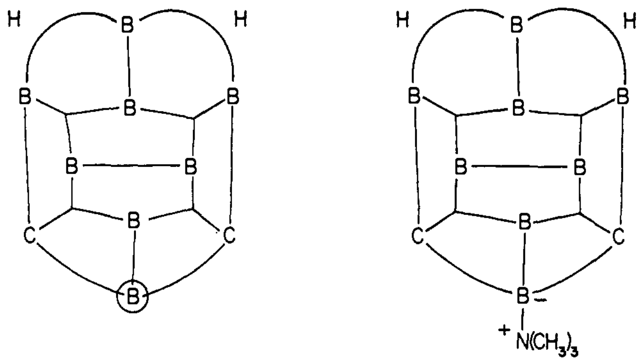
Figure 3. Proposed structure of $N(CH_3)_3B_8C_2H_{12}$ (III): ○ = BH, ◯ = boron, ● = CH.

yield, unreacted III, and trimethylammonium chloride. The reaction of II, prepared by this route, with $N(CH_3)_3$ regenerated III in quantitative yield.

The reaction of III with anhydrous HCl in CH_2Cl_2 at −80° in a 1:2 ratio afforded trimethylammonium chloride, hydrogen, and a 65% yield of a $B_8C_2H_{11}Cl$ (IV, mp 73–75°). The 80-MHz ^{11}B nmr spectrum of IV is presented in Figure 1 and proves that IV is a substitution product having a chlorine and no hydrogen atom attached to the unique low-field boron atom. The 60-MHz ^1H nmr spectrum consisted of a broad carborane CH singlet at τ 7.78. The structure proposed for this compound is identical with that of II except that Cl replaces H on the unique boron atom (Figure 2).

Thermal decomposition of IV *in vacuo* produced hydrogen and a monochlorinated carborane characterized as one of the 1,6-$B_8C_2H_9Cl$ isomers (mp 75–77°). The mass spectrum of this new species exhibited a sharp cutoff at *m/e* 158 which corresponds to the $^{11}B_8{}^{12}C_2{}^1H_9{}^{37}Cl$ parent ion. The ^1H nmr spectrum consisted of two broad singlet carborane CH resonances of equal area at τ 7.96 and 5.00. The 80-MHz ^{11}B nmr spectrum exhibited a singlet at +6.5 ppm (relative to $BF_3 \cdot O(C_2H_5)_2$). The chlorine atom is therefore most likely bonded to either the 2 or 3 boron atoms which have chemically equivalent environments in the 1,6-$B_8C_2H_{10}$ structure.

The reaction of IV with deuterium oxide in a 3:1 molar ratio gave quantitative yields of $B(OD)_3$, DCl,



II III

Figure 4. One topological representation of the proposed 2550 $B_8C_2H_{12}$ (II) and 2551 $B_8C_2H_{12}N(CH_3)_3$ (III) structures where B = BH, C = CH, and Ⓑ = sp-hybridized B atom with empty p orbital and contained in an open three-center C–B–C bond.

and $B_7C_2H_{11}D_2$,[6] which were identified by their characteristic nmr and infrared spectra. The $B_7C_2H_{11}D_2$ bears deuterium on the polar positions of the methylene carbon atoms. The fact that these products were obtained from the hydrolysis of IV is excellent chemical evidence in favor of the proposed structure of II and the supposition that the chlorine atom in IV is bonded to the unique boron atom added by hydroboration.

Proposed topological representations[7] of II and its amine adduct III are presented in Figure 4. In the case of II and IV, a situation unique to carborane chemistry may exist. That is the possible presence of an unfilled p orbital (Figure 2) associated with the unique sp-hybridized boron atom which is assumed to be bonded to the two carbon atoms. This situation would account for the low-field ^{11}B nmr resonance (Figure 1) observed in II and IV and the upfield shift of this resonance in the amine adduct. In the case of III, the p orbital would be filled by the nitrogen lone pair and a normal ligand bond would be established. The chloro derivative IV could be considered equivalent to II with the open p orbital partially filled by back-bonding from chlorine. The formation of IV from III most likely involves the generation of II by amine dissociation and acid capture followed by Cl^- addition to the sp boron atom. The resulting chloride ion adduct could then be protolyzed by additional HCl with the production of hydrogen and the chloro derivative.

Further work is in progress and will be reported elsewhere.

Acknowledgment. This research was supported in part by the Office of Naval Research. We wish to thank Professor F. A. L. Anet and Dr. Richard J. Wiersema for the 80-MHz ^{11}B nmr spectra.

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Received November 9, 1970