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Electrophilic Substitution Reactions of 1,6-Dicarba-*closo*-nonaborane(9)

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Electrophilic substitution reactions of 1,6-dicarba-*closo*-nonaborane(9) have been studied and found to occur preferentially at the boron atom in the 8 position. Methyl, ethyl, bromo, and tetrabromo derivatives have been prepared and structurally characterized by ^1H and ^{11}B nmr spectroscopy.

Several reactions of boron hydrides and carboranes are known in which electrophilic substitution occurs at the boron atoms which carry a relative negative charge in the ground state. Substitution by electrophiles preferentially occurs at the boron atoms in the 2,4 positions in decaborane, $B_{10}H_{14}$,[2] which are the most negative and electron-rich atoms in the ground-state molecule.[3] Similarly, pentaborane undergoes substitution reactions at the boron atom in the 1 position[4] which is the most negative[3] and in the carboranes 1,2-$C_2B_{10}H_{12}$[5] and $C_2B_4H_8$[6] substitution occurs at the boron atoms bearing the highest ground-state electron densities. Calculations show that in the ground state 1,6-dicarba-*closo*-nonaborane(9), 1,6-$C_2B_7H_9$,[7] (Figure 1) the boron atom in the 8 (apex) position, is the most negative[8] and by analogy this suggests that electrophilic substitution reactions should occur most readily at this position. The work reported here confirms this assumption although the correspondence of calculated ground-state negative charge density and substrate reactivity may be fortuitous since no knowledge of the transition-state configuration is available.

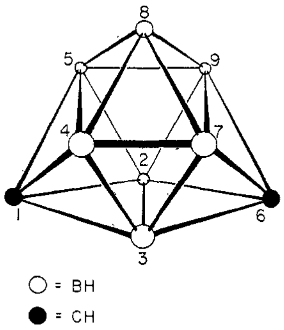

Figure 1.—The molecular structure of 1,6-$C_2B_7H_9$.

Experimental Section

Apparatus and Procedures.—All operations involving carboranes were carried out using standard high-vacuum techniques. An Aerograph Model A-350 gas chromatograph containing a $^3/_8$ in. × 10 ft aluminum column packed with 30% Apiezon L on Chromosorb P was employed. Helium was used as carrier gas at 60-cm^3/min flow rate. Samples were collected in traps cooled in Dry Ice–2-propanol. Infrared spectra of gases were obtained using a 10-cm Pyrex cell with sodium chloride windows with a Perkin-Elmer 137 sodium chloride spectrophotometer. Nuclear magnetic resonance measurements were obtained with a Varian Model A-60 for proton spectra and a Varian Model HA-100 operating at 32.1 MHz for boron-11 spectra. Mass spectra were obtained using a a Hitachi Perkin-Elmer RMU-6D mass spectrometer.

Methyl chloride and ethylene were obtained from Matheson Co. and were passed through traps cooled in Dry Ice–2-propanol. Bromine was obtained from Mallinckrodt Chemical Works and collected in a trap cooled in methanol slush (−98°) after passing through a trap cooled in Dry Ice–2-propanol. Carbon disulfide was obtained from Mallinckrodt and distilled *in vacuo* directly from molecular sieves into the reaction vessel. Anhydrous aluminum chloride was obtained from Mallinckrodt and sublimed *in vacuo* directly into the reaction vessel from a side arm which was subsequently sealed off. Hexamethylenetetramine, $(CH_2)_6N_4$, was obtained from Matheson Coleman and Bell and sublimed before use. The 1,6-$C_2B_7H_9$ and its C-methyl and C,C′-dimethyl derivatives were prepared and purified according to literature methods.[9]

1. **8-CH_3-1,6-$C_2B_7H_8$.**—Anhydrous aluminum chloride, 3–5 mg, was sublimed from the side arm described above into a 50-ml Pyrex bulb fitted with a breakoff. The side arm was sealed off and 0.1681 g (1.54 mmol) of 1,6-$C_2B_7H_9$ and 3.1 mmol of methyl chloride were condensed into the bulb and the bulb was sealed. The bulb was allowed to warm to room temperature and remain for 36 hr during which time a red liquid formed. The mixture was passed through traps maintained at −80° (Dry Ice–2-propanol), −145° (petroleum ether slush), and −196° (liquid N_2). The −145° trap contained 1.95 mmol of unreacted methyl chloride. The −196° trap contained 0.89 mmol of hydrogen chloride contaminated with a small amount of methyl chloride. The contents of both traps were identified by their infrared spectra. The reaction vessel contained a small amount of a dark, viscous, oily material which was not characterized. The contents of the −80° trap were passed through the vpc column operating a 155° and two major fractions were collected. The first fraction collected was unreacted 1,6-$C_2B_7H_9$. The second fraction collected was identified as 8-CH_3-1,6-$C_2B_7H_8$ (Table I).

2. **1,8-$(CH_3)_2$-1,6-$C_2B_7H_7$.**—In a reaction conducted as in section 1 above (Table II), the −145° trap contained 1.5 mmol of CH_3Cl contaminated with BCl_3. The −196° trap contained 1.3 mmol of HCl contaminated with traces of CH_3Cl and BCl_3. The contents of the −80° trap were passed through the vpc column operating at 155° and two fractions were collected.

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TABLE I

YIELD AND MASS SPECTRAL DATA

Compound	Yield, %	*m/e* cutoff
8-$CH_3C_2B_7H_8$	35.7	124
1,8-$(CH_3)_2C_2B_7H_7$	29.6	138
1,6,8-$(CH_3)_3C_2B_7H_6$	76.0	152
8-$C_2H_5C_2B_7H_8$	40.5[a]	138
1-CH_3-8-$C_2H_5C_2B_7H_7$	49.0[a]	152
1,6-$(CH_3)_2$-8-$C_2H_5C_2B_7H_6$	50.0[a]	166
8-$BrC_2B_7H_8$	61.0	190
1-CH_3-8-$BrC_2B_7H_7$	52.0	204
1,6-$(CH_3)_2$-8-$BrC_2B_7H_6$	44.0	218
4,5,7,8-$Br_4C_2B_7H_5$	75.8	430
1-CH_3-4,5,7,8-$Br_4C_2B_7H_4$	78.6	444
1,6-$(CH_3)_2$-4,5,7,8-$Br_4C_2B_7H_3$	81.1	458

[a] Yield based on starting carborane consumed.

The first trap contained a trace of unreacted 1-CH_3-1,6-$C_2B_7H_8$. The second trap contained material identified as 1,8-$(CH_3)_2$-1,6-$C_2B_7H_7$ (Table I).

3. **1,6,8-$(CH_3)_3$-1,6-$C_2B_7H_6$.**—In a reaction conducted as in section 1 above (Table II), the −145 and −196° traps contained 1.0 mmol of CH_3Cl and 1.6 mmol of HCl, respectively. The contents of the −80° trap were passed through the vpc column operating at 155° and only one fraction was collected. This material was identified as 1,6,8-$(CH_3)_3$-1,6-$C_2B_7H_6$ (Table I).

4. **8-C_2H_5-1,6-$C_2B_7H_8$.**—To the reaction vessel described in section 1 above 3–5 mg of $AlCl_3$ was added by sublimation followed by the addition of 0.5297 g (4.86 mmol) of 1,6-$C_2B_7H_9$ and 7.6 mmol of ethylene and sealing. The vessel was allowed to warm slowly to room temperature at which time the mixture became amber. The vessel was then heated at 100° for 36 hr. The reaction mixture was passed through traps cooled at −80 and −196°. The −196° trap contained 2.4 mmol of ethylene identified by its infrared spectrum. The reaction vessel contained approximately 100 mg of red-brown tarry material which was not characterized. The contents of the −80° trap were passed through the vpc column operating at 160° and two fractions were collected. The first trap contained 0.3542 g (3.25 mmol) of 1,6-$C_2B_7H_9$. The second trap contained material identified as 8-C_2H_5-1,6-$C_2B_7H_8$ (Table I).

5. **1-CH_3-8-C_2H_5-1,6-$C_2B_7H_7$.**—In a reaction conducted as in section 4 above (Table II), the −196° trap contained 2.9 mmol of ethylene. The contents of the −80° trap were passed through the vpc column operating at 160° and two fractions were collected. The first fraction consisted of 0.2163 g (1.76 mmol) of 1-CH_3-1,6-$C_2B_7H_8$. The second fraction was identified as 1-CH_3-8-C_2H_5-1,6-$C_2B_7H_7$ (Table I).

6. **1,6-$(CH_3)_2$-8-C_2H_5-1,6-$C_2B_7H_6$.**—In a reaction conducted as in section 4 above (Table II), the −196° trap contained 1.6 mmol of ethylene. The contents of the −80° trap were passed through the vpc column operating at 160° and two fractions were collected. The first trap contained 0.1435 g (1.04 mmol) of 1,6-$(CH_3)_2$-1,6-$C_2B_7H_7$. The second trap contained material identified as 1,6-$(CH_3)_2$-8-C_2H_5-1,6-$C_2B_7H_6$ (Table I).

7. **8-Br-1,6-$C_2B_7H_8$.**—Into a 60-ml tube fitted with a ground-glass joint to a stopcock and containing a magnetic stirring bar was placed 4 mg of aluminum foil, 2.0 ml of dry carbon disulfide, and 0.3224 g (2.01 mmol) of bromine and the mixture was allowed to remain at room temperature. After 2 hr, 0.2150 g (1.97 mmol) of 1,6-$C_2B_7H_9$ was added. The reaction tube was placed into a −80° bath which was allowed to come to −20° over a 3-hr period with stirring. The contents were then passed through traps cooled at −35, −80, −120, and −196°. The −80° trap contained a trace of 1,6-$C_2B_7H_9$. The −120° trap contained CS_2 and a trace of Br_2. The −196° trap contained 0.98 mmol of hydrogen bromide which was identified by its infrared spectrum. The reaction tube contained a small amount of solid residue which was not characterized. The −35° trap contained material identified as 8-Br-1,6-$C_2B_7H_8$ (Table I).

8. **1-CH_3-8-Br-1,6-$C_2B_7H_7$.**—In a reaction conducted as in section 7 above (Table II) the contents of the tube were passed through −25, −80, −140, and −196° traps. The −80° trap contained a trace of 1-CH_3-1,6-$C_2B_7H_8$. The −140° trap contained 1.3 mmol of HBr. The contents of the −25° trap were identified as 1-CH_3-8-Br-1,6-$C_2B_7H_7$ (Table I).

9. **1,6-$(CH_3)_2$-8-Br-1,6-$C_2H_7H_6$.**—In a reaction conducted as in section 7 above (Table II), the contents of the tube were passed through −20, −80, −140, and −196° traps. The −80° trap contained a trace of 1,6-$(CH_3)_2$-1,6-$C_2B_7H_7$. The −140° trap contained CS_2 and Br_2. The −196° trap contained 2.4 mmol of HBr. The −20° trap contained white crystals, which were identified as 1,6-$(CH_3)_2$-8-Br-1,6-$C_2B_7H_6$ (Table I).

TABLE II

REACTION CONDITIONS

Starting carborane	Amt of carborane, g (mmol)	Amt of reagent,[a] mmol	Time, hr	Temp, °C	Product
1,6-$C_2B_7H_9$	0.1681 (1.54)	A 3.1	36	*b*	8-$CH_3C_2B_7H_8$
	0.5297 (4.86)	B 7.6	36	100	8-C_2H_5-$C_2B_7H_8$
	0.2150 (1.97)	C 2.0	3	−20	8-$BrC_2B_7H_8$
	0.0909 (0.83)	C 6.3	32	100	4,5,7,8-$Br_4C_2B_7H_5$
1-CH_3-1,6-$C_2B_7H_8$	0.5176 (4.20)	A 5.2	19	50	1,8-$(CH_3)_2C_2B_7H_7$
	0.4583 (3.73)	B 7.8	36	100	1-CH_3-8-$C_2H_5C_2B_7H_7$
	0.1338 (1.08)	C 1.4	3	*b*	1-CH_3-8-$BrC_2B_7H_7$
	0.2091 (1.70)	C 8.4	32	100	1-CH_3-4,5,7,8-$Br_4C_2B_7H_4$
1,6-$(CH_3)_2$-1,6-$C_2B_7H_7$	0.2381 (1.74)	A 3.0	19	50	1,6,8-$(CH_3)_3C_2B_7H_6$
	0.4243 (3.10)	B 8.0	36	100	1,6-$(CH_3)_2$-8-$C_2H_5C_2B_7H_6$
	0.2810 (2.05)	C 2.5	3	*b*	1,6-$(CH_3)_2$-8-$BrC_2B_7H_6$
	0.1815 (1.33)	C 6.4	32	100	1,6-$(CH_3)_2$-4,5,7,8-$Br_4C_2B_7H_3$

[a] A, CH_3Cl; B, C_2H_4; C, Br_2. [b] Room temperature.

10. **4,5,7,8-Br_4-1,6-$C_2B_7H_5$.**—Into a 50-ml bulb fitted with a breakoff which could be attached through a ground-glass joint directly to a sublimer were placed 1.0029 g (6.26 mmol) of Br_2 and 0.0909 g (0.83 mmol) of 1,6-$C_2B_7H_9$. The bulb was sealed and allowed to warm to room temperature (during which time a vigorous, exothermic reaction occurred), followed by heating at 100° for 32 hr. The contents were caused to pass a cold finger cooled with running water and −80 and −196° traps. The −80° trap contained a trace of Br_2. The −196° trap contained 4.8 mmol of HBr. The reaction flask was heated to 80° which caused a pale yellow solid to sublime to the cold finger. This material was removed from the cold finger in a nitrogen-filled dry box and identified as 4,5,7,8-Br_4-1,6-$C_2B_7H_5$ (Table I).

11. **1-CH_3-4,5,7,8-Br_4-1,6-$C_2B_7H_4$.**—In a reaction conducted exactly as in section 10 above (Table II), the −80° trap contained a small amount of Br_2. The −196° trap contained 4.4 mmol of HBr. The pale yellow material collected on the cold finger was identified as 1-CH_3-4,5,7,8-Br_4-1,6-$C_2B_7H_4$ (Table I).

12. **1,6-$(CH_3)_2$-4,5,7,8-Br_4-1,6-$C_2B_7H_3$.**—In a reaction con-

ducted exactly as in section 10 above (Table II), the −80° trap contained Br_2. The −196° trap contained 4.8 mmol of HBr. The pale yellow material collected on the cold finger was identified as 1,6-$(CH_3)_2$-4,5,7,8-Br_4-1,6-$C_2B_7H_5$ (Table I).

13. Attempted Rearrangement of 1,6-$(CH_3)_2$-8-Br-1,6-$C_2B_7H_6$.—To the side arm of a 50-ml bulb similar to that used in expt 1 above was added 100 mg of hexamethylenetetramine, which was sublimed *in vacuo* to the main body of the bulb, and the side arm then was sealed off. The bulb was cooled to −196° and 0.1922 g (0.90 mmol) of 1,6-$(CH_3)_2$-8-Br-1,6-$C_2B_7H_6$ was added. The bulb was sealed and heated at 80° for 24 hr. The contents were sublimed at room temperature to a −80° cold finger. The infrared, ^1H, and ^{11}B nmr spectra of the product were identical with those of the starting material.

Results and Discussion

Electrophilic substitution reactions of 1,6-$C_2B_7H_9$ and its C-methyl and C,C′-dimethyl derivatives with methyl chloride, ethylene, or bromine occur at the 8 or apex position, producing the methyl, ethyl, and bromo derivatives, respectively. By using an excess of bromine tetrabromo derivatives were produced.

$$\text{1,6-}C_2B_7H_9 + CH_3Cl \xrightarrow{AlCl_3} \text{8-}CH_3C_2B_7H_8 + HCl$$

$$\text{1,6-}C_2B_7H_9 + C_2H_4 \xrightarrow{AlCl_3} \text{8-}C_2H_5C_2B_7H_8$$

$$\text{1,6-}C_2B_7H_9 + Br_2 \xrightarrow[CS_2]{AlBr_3} \text{8-}BrC_2B_7H_8 + HBr$$

$$\text{1,6-}C_2B_7H_9 + Br_2\ (\text{excess}) \longrightarrow \text{4,5,7,8-}Br_4C_2B_7H_5 + 4HBr$$

$$\text{1,6-}C_2B_7H_9 + Br_2\ (\text{excess}) \xrightarrow{AlBr_3} \text{mixture}$$

An attempt to rearrange 1,6-$(CH_3)_2$-8-Br-1,6-$C_2B_7H_6$ using hexamethylenetetramine as catalyst[10] failed and the starting material was recovered nearly quantitatively. Attempts to prepare a perbromo derivative of 1,6-$C_2B_7H_9$ produced mixtures of brominated products.

The results of these experiments indicate that the electrophile attacks the 8 position of 1,6-$C_2B_7H_9$ preferentially. Apparently, in the experiment using excess bromine, a bromine atom substitutes first at the 8 position followed by further substitution at the 4, 5, 7 positions. However, the possibility of rearrangement of the bromine atom at the 8 position followed by subsequent substitutions and rearrangements to yield the tetrabromo product observed cannot be ruled out.

Nuclear Magnetic Resonance and Mass Spectra. 8-CH_3-1,6-$C_2B_7H_8$.—The 32.1-MHz ^{11}B nmr spectrum of 8-CH_3-1,6-$C_2B_7H_8$ (Figure 2A) consisted of a singlet and two doublets of relative areas 1:2:4, respectively. The collapse of the low-field doublet of the parent carborane (Figure 3) indicates substitution at the 8 position. The ^{11}H nmr spectrum consisted of two broad singlets at τ 4.85 of relative area 2 assigned to the cage C–H resonance and at τ 8.69 of relative area 3 assigned to the methyl CH resonance. Chemical shifts are relative to internal tetramethysilane (TMS). The mass spectrum exhibited a sharp cutoff at *m/e* 124 which corresponds to the $^{12}C_3{}^{11}B_7{}^1H_{11}{}^+$ ion.

1,8-$(CH_3)_2$-1,6-$C_2B_7H_7$.—The 32.1-MHz ^{11}B nmr spectrum of 1,8-$(CH_3)_2$-1,6-$C_2B_7H_7$ (Figure 2B) consisted of a singlet and two doublets of relative areas 1:2:4, respectively. The ^{11}H nmr spectrum consisted of broad singlets at τ 4.93 of relative area 1 assigned to the single-cage CH resonance, at τ 7.57 of relative area 3 assigned to the resonance due to the methyl group attached to the cage carbon, and at τ 8.72 of relative area 3 assigned to the resonance due to the methyl group attached to boron. The mass spectrum exhibited a sharp cutoff at *m/e* 138 which corresponds to the $^{12}C_4{}^{11}B_7{}^1H_{13}{}^+$ ion.

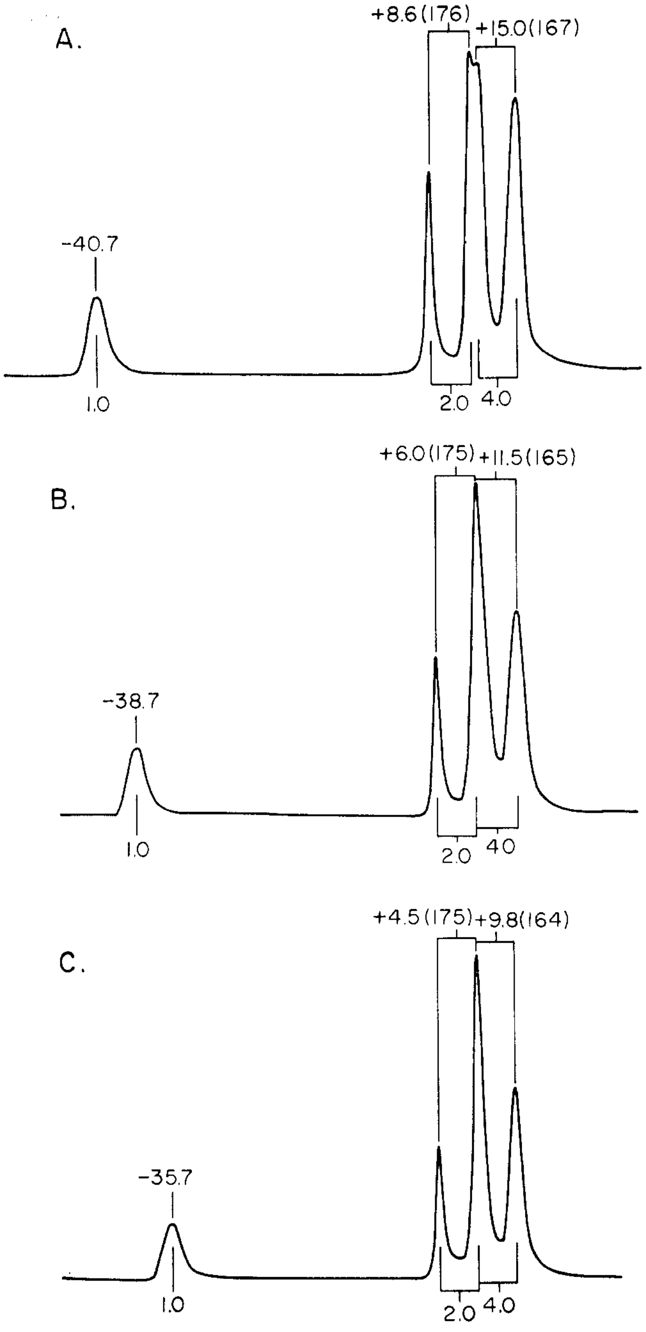

Figure 2.—The 32.1-MHz ^{11}B nmr spectra of 8-CH_3-1,6-$C_2B_7H_8$ (A), 1,8-$(CH_3)_2$-1,6-$C_2B_7H_7$ (B), and 1,6,8-$(CH_3)_3$-1,6-$C_2B_7H_6$ (C). [Chemical shifts (ppm, relative to $BF_3 \cdot O(C_2H_5)_2$) and coupling constants (cps) are indicated. Relative areas appear beneath the peaks.]

1,6,8-$(CH_3)_3$-1,6-$C_2B_7H_6$.—The 32.1-MHz ^{11}B nmr spectrum of 1,6,8-$(CH_3)_3$-1,6-$C_2B_7H_6$ (Figure 2C) con-

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(10) A. B. Burg and J. S. Sandhu, *J. Am. Chem. Soc.*, **87**, 3787 (1965).

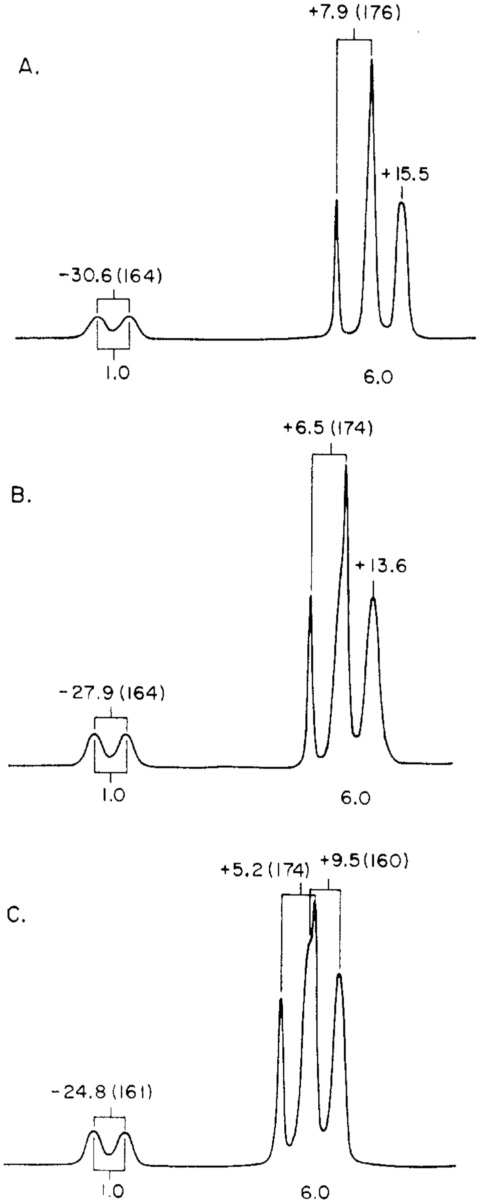

Figure 3.—The 32.1-MHz ^{11}B nmr spectra of 1,6-$C_2B_7H_9$ (A), 1-CH_3-1,6-$C_2B_7H_8$ (B), and 1,6-$(CH_3)_2$-1,6-$C_2B_7H_7$ (C).

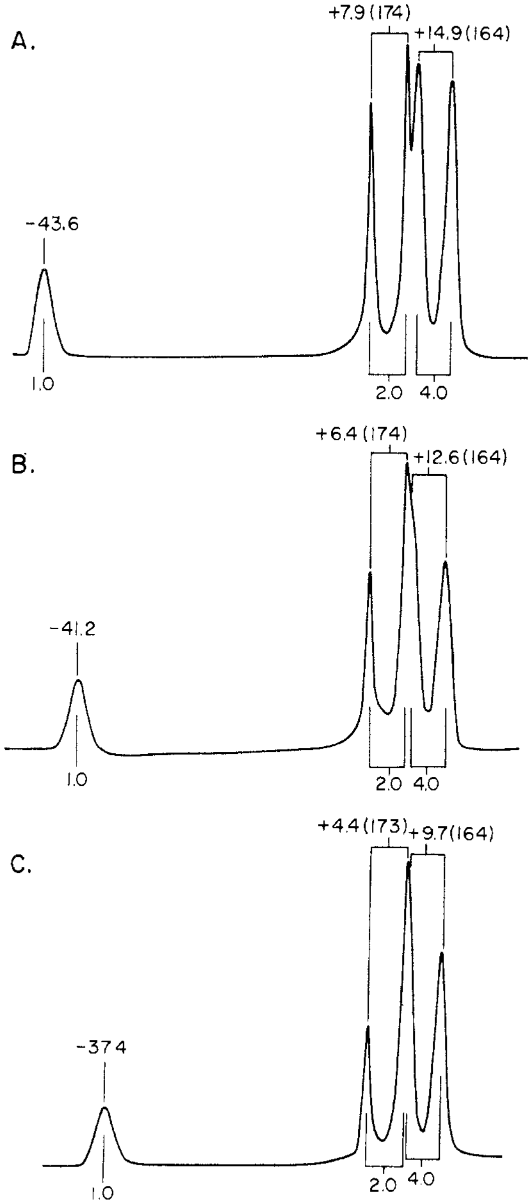

Figure 4.—The 32.1-MHz ^{11}B nmr spectra of 8-C_2H_5-1,6-$C_2B_7H_8$ (A), 1-CH_3-8-C_2H_5-1,6-$C_2B_7H_7$ (B), and 1,6-$(CH_3)_2$-8-C_2H_5-1,6-$C_2B_7H_6$ (C).

sisted of a low-field singlet and two doublets of relative areas 1:2:4, respectively. The ^{1}H nmr spectrum consisted of two singlets; one at τ 7.62 of relative area 2, which was assigned to the resonance due to the two identical methyl groups attached to cage carbon atoms, and one at τ 8.80 of relative area 1 which was assigned to the methyl group attached to boron. The mass spectrum exhibited a sharp cutoff at *m/e* 152 which corresponds to the $^{12}C_5{}^{11}B_7{}^1H_{15}{}^+$ ion.

8-C_2H_5-1,6-$C_2B_7H_8$.—The 32.1-MHz ^{11}B nmr spectrum of 8-C_2H_5-1,6-$C_2B_7H_8$ (Figure 4A) consisted of a low-field singlet and two doublets of relative areas 1:2:4, respectively. The ^{1}H nmr spectrum consisted of a broad singlet of relative area 2 at τ 4.90 and a broad multiplet of three major peaks of relative area 5 and centered at τ 8.65. They were assigned to the cage CH resonance and to the ethyl group attached to boron, respectively. The mass spectrum exhibited a sharp cutoff at *m/e* 138 which corresponds to the $^{12}C_4{}^{11}B_7{}^1H_{13}{}^+$ ion.

1-CH_3-8-C_2H_5-1,6-$C_2B_7H_7$.—The 32.1-MHz ^{11}B nmr spectrum of 1-CH_3-8-C_2H_5-1,6-$C_2B_7H_7$ (Figure 4B) consisted of a low-field singlet and two doublets of relative area 1:2:4, respectively. The ^{1}H nmr spectrum consisted of a singlet of relative area 1 at τ 5.10 which was assigned to the single-cage CH resonance, a singlet of relative area 3 at τ 7.60 which was assigned to the resonance of the methyl group attached to the cage carbon atom, and a multiplet of relative area 5 at τ 8.70 which was assigned to the ethyl group attached to boron. The mass spectrum exhibited a cutoff at *m/e* 152 which corresponds to the $^{12}C_5{}^{11}B_7{}^1H_{15}{}^+$ ion.

1,6-$(CH_3)_2$-8-C_2H_5-1,6-$C_2B_7H_6$.—The 32.1-MHz ^{11}B nmr spectrum of 1,6-$(CH_3)_2$-8-C_2H_5-1,6-$C_2B_7H_6$ (Figure 4C) consisted of a low-field singlet and two doublets of relative area 1:2:4, respectively. The ^{1}H nmr

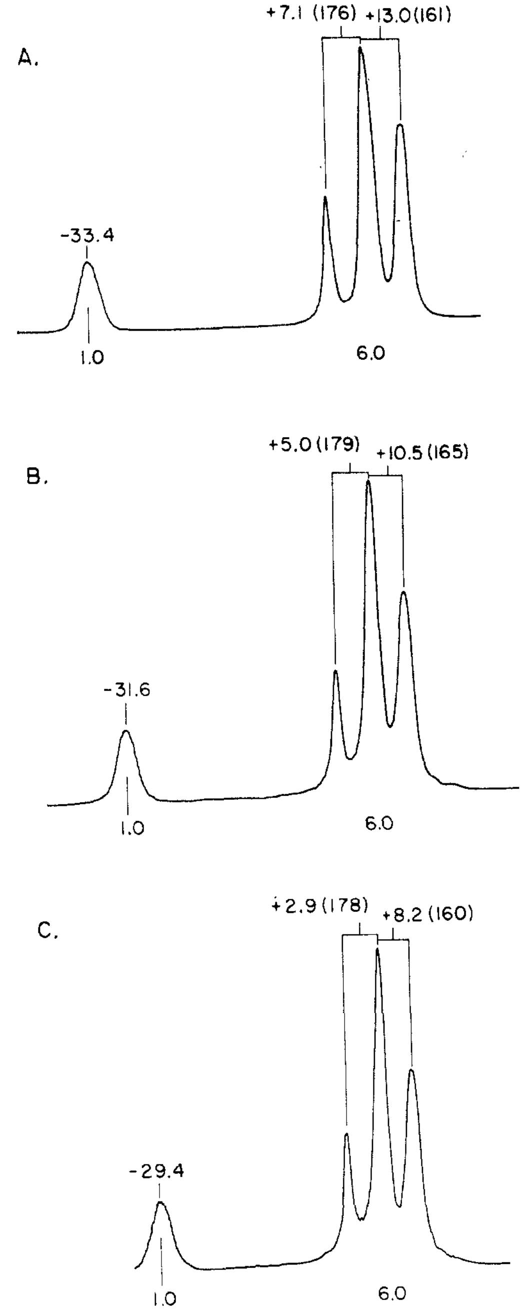

Figure 5.—The 32.1-MHz ^{11}B nmr spectra of 8-Br-1,6-$C_2B_7H_8$ (A), 1-CH_3-8-Br-1,6-$C_2B_7H_7$ (B), and 1,6-$(CH_3)_2$-8-Br-1,6-$C_2B_7H_6$ (C).

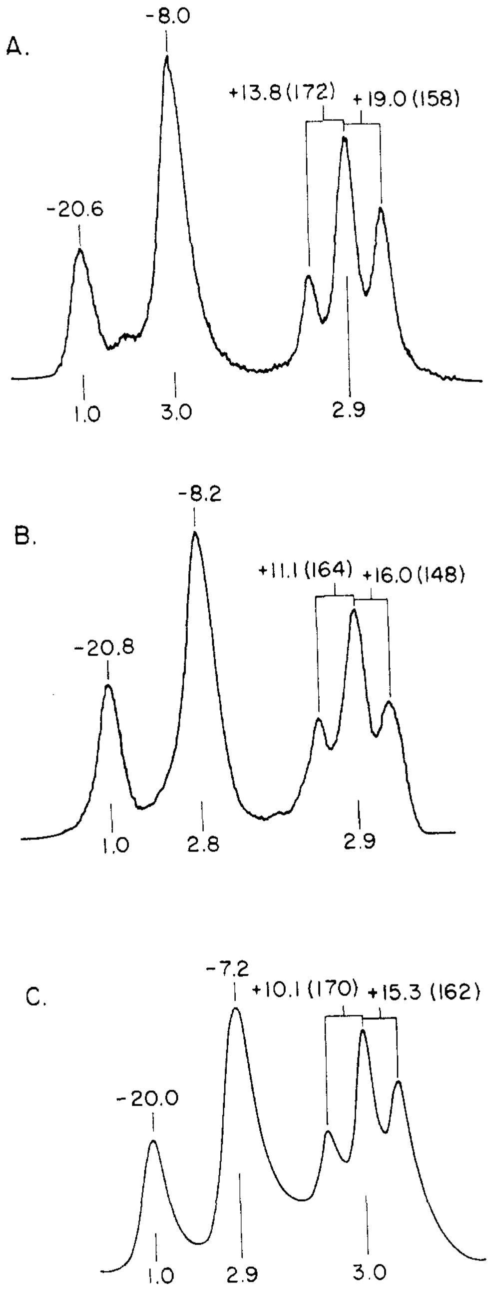

Figure 6.—The 32.1-MHz ^{11}B nmr spectra of 4,5,7,8-Br_4-1,6-$C_2B_7H_5$ (A), 1-CH_3-4,5,7,8-Br_4-1,6-$C_2B_7H_4$ (B), and 1,6-$(CH_3)_2$-4,5,7,8-Br_4-1,6-$C_2B_7H_3$ (C).

spectrum consisted of a singlet of relative area 6 at τ 7.65 which was assigned to the resonance of the two identical methyl groups attached to cage carbon atoms and a multiplet of relative area 5 at τ 8.75 which was assigned to the resonance of the ethyl group attached to boron. The mass spectrum exhibited a cutoff at *m/e* 166 which corresponds to the $^{12}C_6{}^{11}B_7{}^1H_{17}{}^+$ ion.

8-Br-1,6-$C_2B_7H_8$.—The 32.1-MHz ^{11}B nmr spectrum of 8-Br-1,6-$C_2B_7H_8$ (Figure 5A) consisted of a low-field singlet of relative area 1 and two overlapping doublets of relative area 6. The ^1H nmr spectrum consisted of a broad singlet at τ 4.65 which was assigned to the cage CH resonance. The mass spectrum exhibited a cutoff at *m/e* 190 which corresponds to the $^{81}Br^{12}C_2{}^{11}B_7{}^1H_8{}^+$ ion.

1-CH_3-8-Br-1,6-$C_2B_7H_7$.—The 32.1-MHz ^{11}B nmr spectrum of 1-CH_3-8-Br-1,6-$C_2B_7H_7$ (Figure 5B) consisted of a low-field singlet of relative area 1 and two overlapping doublets of relative area 6. The ^1H nmr spectrum consisted of a broad singlet of relative area 1 at τ 4.81 which was assigned to the cage CH resonance and a singlet of relative area 3 at τ 7.61 which was assigned to the resonance of the methyl group attached to the cage carbon atom. The mass spectrum exhibited an *m/e* cutoff at 204 which corresponds to the ^{81}Br-$^{12}C_3{}^{11}B_7{}^1H_{10}{}^+$ ion.

1,6-$(CH_3)_2$-8-Br-1,6-$C_2B_7H_6$.—The 32.1-MHz ^{11}B nmr spectrum of 1,6-$(CH_3)_2$-8-Br-1,6-$C_2B_7H_6$ (Figure 5C) consisted of a low-field singlet of relative area 1 and two overlapping doublets of relative area 6. The

TABLE III

INFRARED SPECTRA[a]

8-$CH_3C_2B_7H_8$	2950 w, 2610 vs, 1320 m, 1180 m' 1115 m, 1030 m, 955 w, 880 w
1,8-$(CH_3)_2C_2B_7H_7$	3010 w, 2950 s, 2600 vs, 1300 s, 1220 m, 1180 vs, 1120 vs, 1060 m, 920 s, 875 w, 800 w
1,6,8-$(CH_3)_3C_2B_7H_6$	2950 vs, 2600 vs, 1310 s, 1210 w, 1175 s, 962 m, 920 m, 840 m
8-$C_2H_5C_2B_7H_8$	3010 w, 2950 vs, 2600 vs, 1450 s, 1410 m, 1360 m, 1280 m, 1160 s, 1110 vs, 1090 s, 1030 m, 950 m, 880 m, 795 m, 785 m
1-CH_3-8-$C_2H_5C_2B_7H_7$	3010 w, 2950 vs, 2900 s, 2600 vs, 1450 s, 1370 m, 1300 m, 1180 m, 1150 s, 1110 s, 1060 m, 910 m, 870 m, 795 m
1,6-$(CH_3)_2$-8-$C_2H_5C_2B_7H_6$	2940 vs, 2900 s, 2600 vs, 1450 s, 1370 m, 1290 m, 1190 m, 1160 s, 1110 w, 1060 w, 965 m, 905 m, 870 w, 840 m, 795 w, 745 w
8-$BrC_2B_7H_8$	3040 m, 2610 vs, 1160 s, 1110 s, 1090 s, 965 s, 850 s, 820 m, 785 m, 780 m
1-CH_3-8-$BrC_2B_7H_7$	3050 m, 2900 w, 2600 vs, 1440 m, 1280 w, 1160 m, 1110 s, 1060 m, 1040 s, 885 s, 855 s, 825 m, 790 m
1,6-$(CH_3)_2$-8-$BrC_2B_7H_6$[b]	2870 vs, 2600 vs, 1440 vs, 1370 s, 1300 w, 1140 w, 1090 m, 1060 s, 960 m, 920 w, 890 w, 870 s, 850 m, 829 s, 783 m, 738 w, 720 w
4,5,7,8-$Br_4C_2B_7H_5$[b]	3050 w, 2910 vs, 2600 m, 1460 s, 1370 s, 1160 s, 1120 s, 1070 s, 1040 m, 975 m, 915 m, 850 m, 805 m, 725 m
1-CH_3-4,5,7,8-$Br_4C_2B_7H_4$[b]	3060 w, 2900 vs, 2600 s, 1460 s, 1370 s, 1160 vs, 1110 vs, 1030 vs, 1010 vs, 965 vs, 900 s, 855 s, 835 m, 755 m, 710 w
1,6-$(CH_3)_2$-4,5,7,8-$Br_4C_2B_7H_3$[b]	2900 vs, 2600 s, 1460 s, 1370 s, 1150 s, 1100 s, 1080 s, 1010 s, 965 s, 910 m, 855 m, 835 m, 808 m, 764 m, 695 m

[a] Relative intensities: vs, very strong; s, strong; m, medium; w, weak. [b] Nujol mull.

^1H nmr spectrum consisted of a very sharp singlet at τ 7.60 which was assigned to the resonance of the methyl groups attached to cage carbon atoms. The mass spectrum exhibited a cutoff at *m/e* 218 which corresponds to the $^{81}Br^{12}C_4{}^{11}B_7{}^1H_{12}{}^+$ ion.

4,5,7,8-Br_4-1,6-$C_2B_7H_5$.—The 32.1-MHz ^{11}B nmr spectrum of 4,5,7,8-Br_4-1,6-$C_2B_7H_5$ (Figure 6A) consisted of a broad singlet of relative area 1.0 at -20.6 ppm which was assigned to the resonance of the 8-boron atom, and a broad singlet of relative area 3.0 at -8.0 ppm which was assigned to the 4,5,7-boron atoms. This peak is broadened due to the nonequivalence of the 4-boron atom. Two overlapping doublets of total relative area 2.9 at $+13.8$ and $+19.0$ ppm are assigned to the 9- and 2,3-boron atoms, respectively. The ^1H nmr spectrum consisted of a broad singlet at τ 5.66 assigned to the slightly nonequivalent cage CH resonances. The mass spectrum exhibited a cutoff at *m/e* 430 which corresponds to the $^{81}Br_4{}^{12}C_2{}^{11}B_7{}^1H_5{}^+$ ion.

1-CH_3-4,5,7,8-Br_4-1,6-$C_2B_7H_4$.—The 32.1-MHz ^{11}B nmr spectrum of 1-CH_3-4,5,7,8-Br_4-1,6-$C_2B_7H_4$ (Figure 6B) consisted of two low-field singlets and two overlapping doublets of relative areas 1:2.8:2.9, respectively. The assignments of these peaks are similar to those of 4,5,7,8-Br_4-1,6-$C_2B_7H_5$ above. The ^1H nmr consisted of a broad singlet of relative area 1 at τ 5.50 and a sharp singlet of relative area 3 at τ 7.92 which were assigned to the cage CH and the methyl group attached to cage carbon atoms, respectively. The mass spectrum exhibited a cutoff at *m/e* 444 which corresponds to the $^{81}Br_4{}^{12}C_3{}^{11}B_7{}^1H_7{}^+$ ion.

1,6-$(CH_3)_2$-4,5,7,8-Br_4-1,6-$C_2B_7H_3$.—The 32.1-MHz ^{11}B nmr spectrum of 1,6-$(CH_3)_2$-4,5,7,8-Br_4-1,6-$C_2B_7H_3$ (Figure 6C) consisted of two singlets of relative areas 1 and 2.9 and two overlapping doublets of relative area 3.0. The assignments are similar to those for 4,5,7,8-Br_4-1,6-$C_2B_7H_5$ above. The ^1H nmr spectrum consisted of a singlet at τ 8.13 which was assigned to the resonance of the methyl groups attached to cage carbon atoms. The mass spectrum exhibited a cutoff at *m/e* 458 which corresponds to the $^{81}Br_4{}^{12}C_4{}^{11}B_7{}^1H_9{}^+$ ion. The observed precise mass measurement was 457.8035 while the calculated mass was 457.8009.

The infrared spectra of the products produced in this study are presented in Table III.

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