that all possible trigonal-bipyramidal isomers are present, although nmr work has shown no sign of PF_3 nonequivalence.[28] On the basis of the calculated 21% *cis*, 23% *trans*, and 56% *vic* isomer composition,[16] an average angle of about 128° is estimated to correspond to the 98 Hz $^{31}P-^{31}P$ coupling.

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The Polyhedral $B_6C_2H_8$, $B_7C_2H_9$, and $B_8C_2H_{10}$ Carboranes and Their C-Monomethyl and C-Monophenyl Derivatives

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The pyrolysis of 1,3-$B_7C_2H_{13}$ at 215° in the absence of diborane yields the $B_6C_2H_8$, $B_7C_2H_9$, and 1,6-$B_8C_2H_{10}$ carboranes, while in the presence of diborane the yield of 1,6-$B_8C_2H_{10}$ is considerably enhanced. Isomerization of 1,6-$B_8C_2H_{10}$ to the 1,10-$B_8C_2H_{10}$ isomer occurs at 300°. Pyrolysis of 1,3-$NaB_7C_2H_{12}$ at 200° yields 1,7-$B_7C_2H_9$. The C-monomethyl and C-monophenyl derivatives of these carboranes are also described.

Recently, the preparation and characterization of the C,C′-dimethyl derivatives of 1,7-dicarba-*closo*-octaborane(8), 1,7-$B_6C_2H_8$, 1,7-dicarba-*closo*-nonaborane(9), 1,7-$B_7C_2H_9$, 1,6-dicarba-*closo*-decaborane(10), 1,6-$B_8C_2H_{10}$, and 1,10-dicarba-*closo*-decaborane(10), 1,10-$B_8C_2H_{10}$, were reported.[1,2] The results of X-ray diffraction studies and theoretical treatments of the C,C′-dimethyl derivatives of 1,7-$B_6C_2H_8$ and 1,7-$B_7C_2H_9$ have been reported[3,4] by Lipscomb and coworkers. Dunks and Hawthorne[5] have reported the low-pressure pyrolysis of 1,3-$B_7C_2H_{13}$ at 360° to give a 60% yield of 1,7-$B_6C_2H_8$. This paper describes the preparation and characterization of the 1,7-$B_6C_2H_8$, 1,7-$B_7C_2H_9$, 1,6-$B_8C_2H_{10}$, and 1,10-$B_8C_2H_{10}$ carboranes and their C-monomethyl and C-monophenyl derivatives.

Results and Discussion

Pyrolysis of 1,3-$B_7C_2H_{13}$.—The thermal decomposition of 1,3-dicarba-*nido*-nonaborane(13) near 215° in diphenyl ether solution produced 1,7-$B_6C_2H_8$, 1,7-$B_7C_2H_9$, and 1,6-$B_8C_2H_{10}$ carboranes. The corresponding C-monomethyl derivatives were obtained by the same route while the C-monophenyl derivatives were obtained using benzene solvent. Yield and characterization data are presented in Table I. The almost equivalent yields of 1,7-$B_6C_2H_8$ and 1,6-$B_8C_2H_{10}$ carboranes and the low yield of 1,7-$B_7C_2H_9$ suggests that the predominant reaction is a disproportionation of 1,3-$B_7C_2H_{13}$ (eq 1) and that 1,7-$B_7C_2H_9$ arises from the elimination of hydrogen from 1,3-$B_7C_2H_{13}$ (eq 2).

$$2(1,3\text{-}B_7C_2H_{13}) \longrightarrow 1,7\text{-}B_6C_2H_8 + 1,6\text{-}B_8C_2H_{10} + 4H_2 \quad (1)$$

$$1,3\text{-}B_7C_2H_{13} \longrightarrow 1,7\text{-}B_7C_2H_9 + 2H_2 \quad (2)$$

When a continuous stream of diborane was passed through a diphenyl ether solution of 1,3-$B_7C_2H_{13}$ at 215°, the yield of 1,6-$B_8C_2H_{10}$ increased at the expense of 1,7-$B_6C_2H_8$ and 1,7-$B_7C_2H_9$. With excess diborane, 1,6-$B_8C_2H_{10}$ was the predominant product along with only trace amounts of 1,7-$B_6C_2H_8$ and 1,7-$B_7C_2H_9$ and a low yield of 1,7-$B_{10}C_2H_{12}$ (eq 3). Hydroboration of pure

$$1,3\text{-}B_7C_2H_{13} + B_2H_6 \longrightarrow 1,6\text{-}B_8C_2H_{10} + 1,7\text{-}B_{10}C_2H_{12} \quad (3)$$

1,6-$B_8C_2H_{10}$ under the same conditions produced 1,7-$B_{10}C_2H_{12}$ in moderate yield[1] and this may account for its appearance among the pyrolysis reaction products. The yield data for the pyrolysis of 1,3-$B_7C_2H_{13}$ and its C-monomethyl and C-monophenyl derivatives in the presence of diborane are presented in Table I. 1-C_6H_5-1,6-$B_8C_2H_9$ could not be successfully prepared by pyrolysis of 1-C_6H_5-1,3-$B_7C_2H_{12}$ in the presence of added diborane.

Thermal rearrangement of 1,6-$B_8C_2H_{10}$ occurs above 300° to give a nearly quantitative yield of the 1,10-$B_8C_2H_{10}$ isomer.[1] The yield and characterization data for 1,10-$B_8C_2H_{10}$ and its C-monomethyl and C-monophenyl derivatives are presented in Table I.

Isomers of Substituted 1,6-$B_8C_2H_{10}$ Carboranes.—The infrared and ^1H nmr spectra of 1,7-$B_6C_2H_8$, 1,7-$B_7C_2H_9$, 1,6-$B_8C_2H_{10}$, and 1,10-$B_8C_2H_{10}$ and their C-monomethyl

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TABLE I

YIELD AND CHARACTERIZATION DATA FOR $B_6C_2H_8$, $B_7C_2H_9$, 1,6-$B_8C_2H_{10}$, AND 1,10-$B_8C_2H_{10}$ AND THEIR C-MONOMETHYL AND C-MONOPHENYL DERIVATIVES

			Yield, %			Analyses, %					
						Calcd			Found		
Compound	Mp, °C	Bp, °C	*a*	*b*	*c*	C	H	B	C	H	B
$B_6C_2H_8$	29.0–30.0		25	0		*d*					
$B_7C_2H_9$	108.5–109.5		4	Trace	38	*e*					
1,6-$B_8C_2H_{10}$	145.0–146.0		19	29		19.91	8.29	71.80	20.26	8.34	72.18
1,10-$B_8C_2H_{10}$	161.0–162.0		98[f]			19.91	8.29	71.80	19.64	8.56	72.13
$B_6C_2H_7CH_3$		101–102	24	0		32.45	9.08	58.47	32.21	9.06	58.25
$B_7C_2H_8CH_3$		138–139	1.5	Trace	56	*g*					
1,6-$B_8C_2H_9CH_3$		164–165	18	33		*h*					
1,10-$B_8C_2H_9CH_3$	39.5–40.5		98[f]			26.75	8.98	64.27	26.18	8.88	63.72
$B_6C_2H_7(C_6H_5)$		233–234	19			55.54	6.94	37.52	55.46	7.18	37.14
$B_7C_2H_8(C_6H_5)$	37.0–38.0		4			*i*					
1,6-$B_8C_2H_9(C_6H_5)$	50.8–51.5		20	*j*		48.45	7.13	44.05	48.82	7.40	43.83
1,10-$B_8C_2H_9(C_6H_5)$	42.0–43.0		98[f]			48.85	7.13	44.05	48.51	7.37	43.81

[a] When prepared in the absence of diborane. [b] When prepared in the presence of diborane. [c] Pyrolysis of $NaB_7C_2H_{12}$ and $NaB_7C_2H_{11}(CH_3)$. [d] Mass spectrum calcd for $^{11}B_6{}^{12}C_2{}^1H_8$, 98.1184; found, 98.1177. [e] Mass spectrum calcd for $^{11}B_9{}^{12}C_2{}^1H_9$, 110.1356; found, 110.1356. [f] Prepared from its 1,6 isomer. [g] Mass spectrum calcd for $^{11}B_7{}^{12}C_3{}^1H_{11}$, 124.1512; found, 124.1508. [h] Mass spectrum calcd for $^{11}B_8{}^{12}C_3{}^1H_{12}$, 136.1681; found, 136.1681. [i] Mass spectrum calcd for $^{11}B_7{}^{12}C_8{}^1H_{13}$, 186.1669; found, 186.1665. [j] Phenyl derivative could not be hydroborated.

and C-monophenyl derivatives are presented in Tables II and III. Characteristic ^{11}B nmr spectra of these compounds are presented elsewhere as the C,C′-dimethyl derivatives.[1] The nonequivalence of carbon in the 1 and 6 positions of 1,6-$B_8C_2H_{10}$ is clearly demonstrated by its infrared and ^1H nmr spectra and the ^{11}B nmr spectrum of the C,C′-dimethyl derivative.[1] The infrared spectrum of 1,6-$B_8C_2H_{10}$ contains two carborane C–H absorptions at 3120 and 3070 cm^{-1} and the ^1H spectrum contains two resonances of equal area at τ 4.8 and 8.1, relative to tetramethylsilane. The 1,10-$B_8C_2H_{10}$, 1-C_6H_5-1,10-$B_8C_2H_9$, and 1-CH_3-1,10-$B_8C_2H_9$ carboranes have carborane C–H resonances in their ^1H nmr spectra at τ 3.1, 3.3, and 3.5, respectively. Hence, the 1,6-$B_8C_2H_{10}$ carborane C–H resonance at τ 4.8 in its ^1H nmr spectrum may be assigned with some assurance to the 1-position carborane C–H, and the resonance at τ 8.1 can be assigned to the 6-position carborane C–H. This information was most helpful in establishing isomer structures in the C-monosubstituted 1,6-$B_8C_2H_{10}$ carboranes. In the case of crude C-monophenyl-substituted 1,6-$B_8C_2H_{10}$, a single carborane C–H resonance in its ^1H nmr spectrum at τ 8.0 was observed which implies that the phenyl group is exclusively substituted in the 1 position. This is further supported by its infrared spectrum which contains a single carborane C–H absorption at 3020 cm^{-1}. Moreover, no separation was observed when C-monophenyl-substituted 1,6-$B_8C_2H_{10}$ was subjected to vapor-phase chromatography at 100° on a $^1/_8$ in. × 50 ft Apiezon L column. However, crude C-monomethyl-substituted 1,6-$B_8C_2H_{10}$ was easily separated into two components of areas 2:1 when subjected to vapor-phase chromatography at 100° on a $^1/_8$ in. × 50 ft Apiezon L column. All attempts to separate and collect these two components using preparative-scale vapor-phase chromatography failed. The infrared spectrum of crude C-monomethyl-substituted 1,6-$B_8C_2H_{10}$ contained two carborane C–H absorptions at 3120 and 3050 cm^{-1}, which gives additional support that there are two isomers present. The ^1H nmr spectrum of the mixture of C-monomethyl-substituted 1,6-$B_8C_2H_{10}$ contains four C–H resonances. The C-methyl resonances occur at τ 7.2 and 8.7 and are of relative area 2:1, respectively. The carborane C–H resonances occur at τ 8.1 and 4.8 and are of relative area 2:1, respectively. Since the 1-position carborane C–H resonance of 1,6-$B_8C_2H_{10}$ occurs at τ 4.8 and the carborane C–H resonance in the 6 position of C-monophenyl and unsubstituted 1,6-$B_8C_2H_{10}$ carboranes occurs near τ 8.0, it seems probable that the 1-CH_3-1,6-$B_8C_2H_9$ and 6-CH_3-1,6-$B_8C_2H_9$ isomers are 2:1 in relative abundance, respectively. Pyrolysis of 1-CH_3-1,3-$B_7C_2H_{12}$ in both the absence and the presence of diborane produced the same relative abundance of isomers of the C-monomethyl-substituted 1,6-$B_8C_2H_{10}$.

Pyrolysis of $NaB_7C_2H_{12}$.—The pyrolysis of the sodium salt of the 1,3-$B_7C_2H_{12}^-$ ion[1] in diphenyl ether solution at 200° yields 1,7-$B_7C_2H_9$, sodium borohydride, and unidentified yellow solids. The sodium borohydride produced was identified by its infrared and ^{11}B nmr spectra and attempts to identify the yellow residue proved unsuccessful. The yields of 1,7-$B_7C_2H_9$ and its C-methyl derivative were 38 and 56%, respectively. The pyrolysis of the sodium salt of the 1,3-$B_7C_2H_{11}^{2-}$ ion[6] under the same conditions as those employed with the monoanion gave 1,7-$B_7C_2H_9$ in 20% yield and sodium borohydride.

Experimental Section

Materials.—1,3-Dicarba-*nido*-nonaborane(13) and its 1-methyl and 1-phenyl derivatives were prepared by literature methods.[1,7] Diphenyl ether was distilled under vacuum from calcium hydride, and all other solvents and reagents were reagent grade and used without further purification. Diborane was generated by the method of Brown.[8]

Methods.—The ^{11}B nmr spectra of the compounds reported here were recorded and were found to be sufficiently similar to the ^{11}B nmr spectra of the C,C′-dimethyl derivatives that they did not warrant reproduction here. The ^{11}B nmr spectra of the C,C′-dimethyl derivatives are reported elsewhere.[1] Infrared spectra were obtained on a Beckman IR-5 spectrophotometer and are presented in Table II. Proton nmr spectra were re-

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[6] M. F. Hawthorne and T. A. George, *J. Am. Chem. Soc.*, **89**, 7114 (1967).

[7] P. M. Garrett, T. A. George, and M. F. Hawthorne, *Inorg. Chem.*, **8**, 2008 (1969).

[8] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

TABLE II

INFRARED SPECTRA OF $B_6C_2H_8$, $B_7C_2H_9$, 1,6-$B_8C_2H_{10}$, AND 1,10-$B_8C_2H_{10}$ AND THEIR C-MONOMETHYL AND C-MONOPHENYL DERIVATIVES

$B_6C_2H_8$[a]	3080 w, 2925 s, 2580 s, 1458 m, 1375 m, 1205 m, 1122 s, 1045 s, 988 m, 974 m, 853 w, 822 m
$B_6C_2H_7CH_3$[b]	3000 w, 2955 w, 2600 s, 1450 w, 1169 w, 1115 m, 1056 m, 975 m, 925 m, 836 w, 814 w, 752 w, 703 w, 668 w
$B_6C_2H_7(C_6H_5)$[b]	3060 w, 2565 s, 1518 w, 1487 m, 1441 w, 1391 m, 1362 m, 1320 m, 1235 m, 1175 m, 1111 m, 1078 m, 1033 m, 1012 m, 945 w, 927 w, 828 m, 780 w, 745 m, 693 s
$B_7C_2H_9$[a]	3075 w, 2875 s, 2570 s, 1450 s, 1365 s, 1145 m, 1122 s, 1097 m, 1058 w, 953 w, 979 w, 902 w, 776 w, 721 w
$B_7C_2H_8CH_3$[b]	3100 w, 2580 s, 1450 m, 1295 w, 1113 s, 1068 m, 971 m, 893 m, 853 m, 803 m, 787 m, 670 m
$B_7C_2H_8(C_6H_5)$[a]	3090 w, 2580 s, 1575 w, 1448 m, 1362 w, 1132 m, 1087 s, 965 w, 892 w, 858 m, 809 w, 787 m, 752 s, 692 s
1,6-$B_8C_2H_{10}$[a]	3120 w, 3070 w, 2950 s, 2620 s, 1455 s, 1375 s, 1157 m, 1118 s, 1084 s, 995 s, 975 w, 942 s, 872 m, 853 m, 810 w, 672 s
1,6-$B_8C_2H_9CH_3$[b,c]	3120 w, 3050 w, 2950 w, 2580 s, 1450 m, 1105 s, 1022 s, 958 s, 909 m, 893 w, 864 m, 689 s
1,6-$B_8C_2H_9(C_6H_5)$[a]	3020 w, 2925 s, 2600 s, 1590 w, 1445 m, 1107 s, 1078 s, 985 m, 932 m, 917 m, 898 m, 883 m, 863 m, 757 s, 693 s
1,10-$B_8C_2H_{10}$[a]	3120 w, 2930 s, 2585 s, 1450 s, 1375 m, 1237 w, 1195 w, 1147 s, 1052 w, 965 s, 950 s, 888 m, 847 w, 825 s, 781 s, 748 w, 721 w, 671 s
1,10-$B_8C_2H_9CH_3$[b]	3090 w, 2920 s, 2530 s, 1450 s, 1173 s, 1088 s, 980 m, 962 m, 932 m, 894 m, 862 s, 811 s, 742 w, 687 s
1,10-$B_8C_2H_9(C_6H_5)$[a]	3120 w, 2935 s, 2615 s, 1595 w, 1500 m, 1453 m, 1379 m, 1144 m, 1100 s, 934 w, 908 w, 857 w, 806 w, 755 s, 694 s

[a] Nujol mull. [b] Neat film. [c] Combined 1-methyl and 6-methyl isomers.

TABLE III

THE ^{1}H NMR SPECTRA OF $B_6C_2H_8$, $B_7C_2H_9$, 1,6-$B_8C_2H_{10}$, AND 1,10-$B_8C_2H_{10}$ AND THEIR C-MONOMETHYL AND C-MONOPHENYL DERIVATIVES

	Chemical shifts, τ[a]		
	CH_3	H	^{1}H
$B_6C_2H_8$		5.2 (1)	5.2
$B_6C_2H_7CH_3$	7.9 (3)	5.1 (1)	
$B_6C_2H_7(C_6H_5)$		5.0 (1)	
$B_7C_2H_9$		4.4 (1)	4.4
$B_7C_2H_8CH_3$	7.5 (3)	4.7 (1)	
$B_7C_2H_8(C_6H_5)$		4.6	
1,6-$B_8C_2H_{10}$		8.1 (1)	4.8 (1)
1-CH_3-1,6-$B_6C_2H_9$[b]	7.2 (3)	8.1 (1)	
6-CH_3-1,6-$B_8C_2H_9$[b]	8.7 (3)	4.8 (1)	
1-C_6H_5-1,6-$B_8C_2H_9$		8.0	
1,10-$B_8C_2H_{10}$		3.1 (1)	3.1
1-CH_3-1,10-$B_8C_2H_9$	7.2 (3)	3.5 (1)	
1-C_6H_5-1,10-$B_8C_2H_9$		3.3	

[a] Chemical shifts relative to tetramethylsilane and relative areas are in parentheses. Spectra were recorded in carbon disulfide solution. [b] The spectra of these two isomers were recorded as a mixture.

corded on a Varian Associates A-60 spectrometer and the chemical shifts were measured relative to internal tetramethylsilane. The mass spectra were measured on a GEC-AEI, Ltd., Model MS-9 mass spectrometer. All melting points and nmr spectra were made in sealed capillaries and elemental analyses were conducted by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y.

Vapor-phase chromatography (vpc) was performed with an Aerograph vapor-phase chromatograph, Model A-350-B, using 10-ft, $^3/_8$-in. o.d. preparative, or $^1/_4$-in. o.d. analytical, or $^1/_8$ in. × 50 ft columns packed with 20% Apiezon L on 60/80 HMDS Chromosorb P. Spinning-band distillations were carried out with a 3-ft Nester-Faust column. The vacuum-jacketed Vigreux column employed was of 40-cm length and 1.5-cm i.d.

All reactions were conducted under an atmosphere of nitrogen and subsequent manipulations were carried out with standard vacuum-line techniques or under a nitrogen atmosphere. The analytically pure carboranes were transferred under high vacuum from the vpc collection U tube into another U tube containing a small portion of Fisher Scientific Co. Type 4A Molecular Sieve.

Pyrolysis of 1,3-Dicarba-*nido*-nonaborane(13) in Diphenyl Ether.—Into a 250-ml three-necked flask equipped with a magnetic stirrer, Dry Ice reflux condenser, and a nitrogen inlet was placed 125 ml of diphenyl ether containing 10.0 g (88.6 mmol) of freshly sublimed $B_7C_2H_{13}$. This solution was heated under a nitrogen atmosphere at 225 ± 5° for 40 min. After cooling, the products were distilled from the solvent under nitrogen on a spinning-band column with 0° water in the reflux condenser. The products solidified in the still head and were washed from the still head with pentane after removing the original distillation pot. The volume of the pentane was reduced by distilling away the pentane under high vacuum using a vacuum-jacketed Vigreux column topped with a small sublimer cooled to $-80°$. The products were separated by preparative vpc by employing a preparative Apiezon L column at 135° and collecting the fractions at $-80°$ in U tubes fitted at one end with a stopcock. The yields were: $B_6C_2H_8$, 2.2 g or 25%; $B_7C_2H_9$, 0.4 g or 4%; 1,6-$B_8C_2H_{10}$, 2.0 g or 19%. Analytically pure samples were obtained by vpc on an analytical Apiezon L column at 100°.

Pyrolysis of 1-Methyl-1,3-dicarba-*nido*-nonaborane(13) in Diphenyl Ether.—The same apparatus was used here as in the above experiment. The reaction flask was charged with 8.8 g (69.3 mmol) of freshly distilled $B_7C_2H_{12}(CH_3)$ and 125 ml of diphenyl ether. The system was flushed with nitrogen and the solution heated at 220 ± 5° for 40 min. After cooling, the dark red-brown solution was transferred to a spinning-band column and the products were distilled at atmospheric pressure under nitrogen. Two fractions were collected. The first at 100° consisted of nearly pure $B_6C_2H_7(CH_3)$. The second fraction was collected between 120 and 165° and consisted of $B_6C_2H_7(CH_3)$, $B_7C_2H_8(CH_3)$, and 1,6-$B_8C_2H_9(CH_3)$. A third fraction collected above 165° consisted almost entirely of diphenyl ether. The components of the second fraction were separated by preparative vpc using a preparative Apiezon L column at 140°. The first cut and the $B_6C_2H_7(CH_3)$ from the vpc separation of the second cut were combined giving the following yields: $B_6C_2H_7(CH_3)$, 1.8 g or 24%; $B_7C_2H_8(CH_3)$, 0.13 g or 1.5%; 1,6-$B_8C_2H_9(CH_3)$, 1.7 g or 18%. Analytically pure samples were obtained by vpc on an analytical Apiezon L column at 125°.

Pyrolysis of 1-Phenyl-1,3-dicarba-*nido*-nonaborane(13) in Benzene.—Into a 1-l. magnetically stirred autoclave was placed 25 g (0.132 mol) of freshly sublimed $B_7C_2H_{12}(C_6H_5)$ and 150 ml of benzene. After flushing the autoclave with nitrogen, the temperature was brought up to and maintained at 225 ± 10° for 40 min. The reaction was then cooled by passing water through the internal cooling coils. *Caution:* the reaction upon first reaching temperature was very exothermic and internal cooling coil water had to be available. After cooling to room temperature, the hydrogen pressure was released, the autoclave was opened, and the dark red-brown solution was transferred to a spinning-band distillation column. The bulk of the benzene was distilled off at atmospheric pressure under nitrogen. The residual benzene was distilled away under high vacuum and the products were alembically[9] distilled under high vacuum using tap water in the cooling jacket. The products were separated by preparative vpc using a $^3/_8$ in. × 20 ft SE-30 column at 210°. The products were collected at −80° in U tubes fitted with a stopcock. The yields of the products collected were as follows: $B_6C_2H_7(C_6H_5)$, 4.3 g or 19%; $B_7C_2H_8(C_6H_5)$, 0.95 g or 4%; 1,6-$B_8C_2H_9(C_6H_5)$, 5.3 g or 20%. Analytically pure samples were obtained by vpc on an analytical Apiezon L column at 195° for $B_6C_2H_7(C_6H_5)$ and $B_7C_2H_8(C_6H_5)$ and 210° for 1,6-$B_8C_2H_9(C_6H_5)$.

Pyrolysis of 1,3-Dicarba-*nido*-nonaborane(13) in Diphenyl Ether Solution in the Presence of Diborane.—The reaction vessel for the pyrolysis consisted of a 500-ml four-necked flask which was equipped with a mechanical stirrer, Dry Ice reflux condenser, thermometer, diborane inlet extending into the flask, and nitrogen inlet which also served as a vent for the excess diborane and hydrogen. The vented gases were passed through an acetone trap. Into the flask was placed 12.0 g (0.106 mol) of freshly sublimed $B_7C_2H_{13}$, 225 ml of diphenyl ether, and 0.5 ml of isopentane.[10] After the system was flushed with nitrogen, the reaction vessel was rapidly brought up to and maintained at 215 ± 5° for 45 min with stirring. Addition of a 5 molar excess of diborane to $B_7C_2H_{13}$ was started when the temperature reached 190° and was added at such a rate that it required 45 min to complete the addition. After cooling to room temperature, the dark brown solution was transferred to a spinning-band distillation column and the products were distilled from the solvent at atmospheric pressure under nitrogen. The condenser water was maintained at 0°. The solidified products were removed from the still head by removing the original distillation pot and washing out the products with pentane. With a vacuum-jacketed Vigreux column topped with a sublimer maintained at −80°, the pentane was removed and the bulk of the 1,6-$B_8C_2H_{10}$ was sublimed and collected. The remaining 1,6-$B_8C_2H_{10}$ and 1,7-$B_{10}C_2H_{12}$ were separated by preparative vpc using a preparative Apiezon L column at 140°. The sublimed 1,6-$B_8C_2H_{10}$ contained a trace of $B_7C_2H_9$. The yield of the two 1,6-$B_8C_2H_{10}$ fractions was 3.7 g or 29% and the 1,7-$B_{10}C_2H_{12}$ was 0.4 g or 2%.

Pyrolysis of 1-Methyl-1,3-dicarba-*nido*-nonaborane(13) in Diphenyl Ether Solution in the Presence of Diborane.—The apparatus used here was the same as that used for the pyrolysis of $B_7C_2H_{13}$. Into the reaction flask was placed 10.0 g (79.0 mmol) of $B_7C_2H_{12}(CH_3)$ and 225 ml of diphenyl ether. The system was flushed with nitrogen and rapidly heated to 220 ± 5° for 45 min. Diborane addition was started at 190° and a 5 molar excess of diborane to $B_7C_2H_{12}(CH_3)$ was added as evenly as possible over this heating period. After cooling, the dark brown solution was transferred to a spinning-band distillation column and the products were distilled at atmospheric pressure under nitrogen. Three cuts were taken (100–152, 152–165, 165–200°) the second of which gave nearly pure 1,6-$B_8C_2H_9(CH_3)$. The first fraction consisted of 1,6-$B_8C_2H_9(CH_3)$ with a small amount of $B_7C_2H_8(CH_3)$ and the third fraction consisted of 1,6-$B_8C_2H_9(CH_3)$, 1,7-$B_{10}C_2H_{11}(CH_3)$, and some diphenyl ether. The first and third fractions were separated by preparative vpc using an Apiezon L column at 180°. The two 1,6-$B_8C_2H_9(CH_3)$ fractions were combined giving the following yields: $B_7C_2H_8(CH_3)$, trace; 1,6-$B_8C_2H_9(CH_3)$, 3.5 g or 33%; 1,7-$B_{10}C_2H_{11}(CH_3)$, 0.96 g or 8%.

Preparation of 1,10-$B_8C_2H_{10}$. General Procedure.—Into a thick-walled tube was placed 4.0 g of 1,6-$B_8C_2H_{10}$ which was sealed off under high vacuum. The sample was heated at 350 ± 10° for 12 hr in a bomb partially filled with diphenyl ether. After cooling, the tube was opened in the air and was rapidly transferred to a sublimer. No hydrogen pressure was observed when the tube was opened. The product was sublimed at room temperature to a −80° cold finger. The yield of 1,10-$B_8C_2H_{10}$ was 3.9 g or 98%. Analytically pure samples were obtained for the 1,10-$B_8C_2H_{10}$ and its 1-phenyl and 1-methyl derivatives by vpc on an analytical Apiezon L column at 110, 210, and 140°, respectively.

Preparation of 1,7-$B_7C_2H_9$.—In a typical preparation, 4.0 g (35.0 mmol) of freshly sublimed 1,3-$B_7C_2H_{13}$ was dissolved in 50 ml of diethyl ether and was slowly added with stirring to 1.5 g (37.0 mmol) of 60% sodium hydride dispersion in mineral oil. The reaction mixture was stirred an additional 5 min under nitrogen after addition of the carborane was complete. The ether solution was filtered and the solvent was evaporated under high vacuum to produce a thin oil. To this solution was added 75 ml of diphenyl ether and the resulting solution was heated at 200 ± 10° for 17 hr under a nitrogen atmosphere using 8° water in the condenser.[11] After cooling, the residual diethyl ether and the product were distilled from the diphenyl ether under high vacuum at 70°. Purification was accomplished by high-vacuum fractionation employing a vacuum-jacketed Vigreux column topped with a sublimer maintained at −80°. The 1,7-$B_7C_2H_9$ was sublimed at 25° to a −80° cold finger and weighed 1.5 g (38%), mp 106–108°. The same procedure was used for the C-methyl derivative.

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[9] *Inorg. Syn.*, **10**, 103 (1967).

[10] The purpose of the isopentane was to wash sublimed carborane out of the condenser.

[11] Addition of a small amount of diethyl ether may be required to maintain a brisk reflux and wash sublimed material into the reaction flask.