

The $B_6C_2H_8$, $B_7C_2H_9$, and $B_8C_2H_{10}$ Carborane Systems

Sir:

We wish to report the synthesis and tentative structural assignments of $B_7C_2H_9$ and two isomeric $B_8C_2H_{10}$ carborane systems. In addition, an improved synthesis of the $B_6C_2H_8$ carborane¹ is presented. The results described here were principally obtained with the C,C'-dimethyl derivatives of each carborane system. However, the preparation of these carboranes appears to be of general applicability, and further work with other derivatives is in progress. The availability of these materials completes the series $B_nC_2H_{n+2}$ from $n = 3$ to 10.

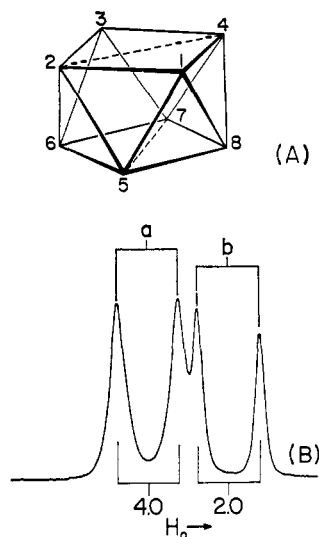


Figure 1. (A) Archimedean antiprism geometry for the $B_6C_2H_8$ carborane system. Closure of the faces along the dotted lines produces the bisdisphenoid¹ structure. (B) The 19.3-Mc/sec ^{11}B nmr spectrum of $B_6C_2H_8(CH_3)_2$. Chemical shifts, ppm (with reference to $BF_3O(C_2H_5)_2$), and coupling constants (cps) for the indicated peaks are (a) -7.22 (168) and (b) $+4.14$ (170). Integrated areas are indicated beneath the peaks.

The dicarbanoborane(13) derivative,² $B_7C_2H_{11}(CH_3)_2$, was pyrolyzed at temperatures near 200° in diphenyl ether solvent. The reaction products consisted of hydrogen, $B_6C_2H_6(CH_3)_2$, $B_7C_2H_8(CH_3)_2$, and a single $B_8C_2H_8(CH_3)_2$ isomer. When the pyrolysis reaction was conducted in the presence of B_2H_6 , the yield of $B_8C_2H_8(CH_3)_2$ was enhanced at the expense of the lower carboranes, and 1,7-dimethyl-1,7-dicarbaclododecaborane(12) appeared in low yield. The relevant yield and characterization data are presented in Table I. The mass spectrum of each carborane contained a parent peak which corresponded to the proper $^{11}B_n^{12}C_2^{1}H_n(^{12}C^1H_3)_2$ formulation. These results suggest that the B_7 tetrahydrocarborane disproportionates to form comparable amounts of the B_6 and B_8 carborane systems in the absence of B_2H_6 . In the presence of B_2H_6 , the pyrolysis reaction intermediates apparently intercept the added hydride to give enhanced yields of B_8 and B_{10} carboranes.

The carborane products were easily separated by conventional fractional distillation or by preparative vpc.

(1) R. E. Williams and F. J. Gerhart, *J. Am. Chem. Soc.*, **87**, 3513 (1965).

(2) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *ibid.*, **88**, 607 (1966).

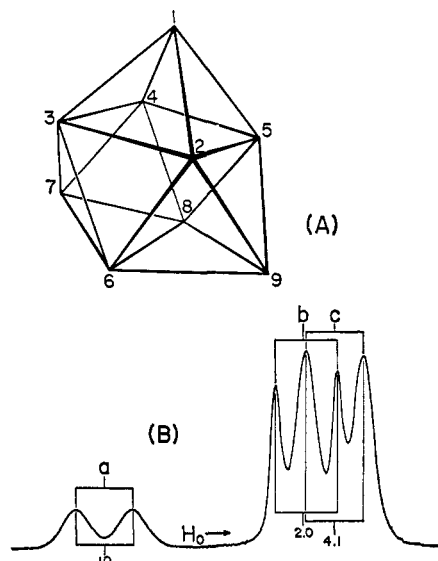


Figure 2. (A) The tricapped trigonal prism geometry. (B) The 19.3-Mc/sec ^{11}B nmr spectrum of $B_7C_2H_7(CH_3)_2$. Chemical shifts, ppm (with reference to $BF_3O(C_2H_5)_2$), and coupling constants (cps) for the indicated peaks are (a) -25.5 (160), (b) $+4.50$ (173), and (c) $+8.90$ (163). Integrated areas are indicated beneath the peaks.

Thermal rearrangement of the $B_8C_2H_8(CH_3)_2$ carborane obtained from the pyrolysis reaction occurred at temperatures near 350° (10 hr) and produced a second $B_8C_2H_8(CH_3)_2$ isomer in 95% yield. Boron-11 nmr evidence bearing upon the structures of the B_6 , B_7 , and the two B_8 carborane systems follows.

$B_6C_2H_6(CH_3)_2$. The $B_6C_2H_6(CH_3)_2$ obtained in this study was shown to be identical with the compound reported by Williams and Gerhart¹ although some discrepancies exist in the previously reported ^{11}B nmr spectrum (12.8 Mc/sec) and melting point.³ Figure 1 presents the 19.3-Mc/sec ^{11}B nmr spectrum of $B_6C_2H_6(CH_3)_2$. The two sets of doublets of relative intensities 4:2 observed in this spectrum are in agreement with the Archimedean antiprism structure shown in Figure 1 with carbon atoms at the 1,3 positions. Distortion of this system by compression along the dotted lines ultimately yields the bisdisphenoid^{1,4} geometry which would require three sets of doublets of relative intensities 2:2:2 at very high resolution. Since the spectrum obtained (19.3 Mc/sec) indicates only two types of boron atoms, the antiprism structure is suggested. However, very high-resolution nmr spectra may prove that the doublet of intensity 4 is actually composed of two overlapped doublets of intensity 2, in which case a distorted antiprism or bisdisphenoid structure would be required. The proton nmr spectrum of either the antiprism or the bisdisphenoid

(3) The previously reported chemical shifts in the ^{11}B nmr spectrum of $B_6C_2H_6(CH_3)_2$ appear to be offset to low field by about 6 ppm. Comparison of the product obtained in this study with a sample kindly supplied by Dr. R. E. Williams confirms this situation. The melting point of highly purified $B_6C_2H_6(CH_3)_2$ prepared in this laboratory was -40.4 to -39.4° , which may be compared with the previously reported mp of -58 to -63° . Retention times were identical with both samples using an Aerograph Model A350-B gas chromatograph employing a 0.25 in. \times 10 ft 20% carbowax on 45/60 HMDS Chromosorb P column operating at 143° . The retention time of $B_6C_2H_6(CH_3)_2$ under these conditions is 1.62 with respect to benzene.

(4) A. F. Wells, "Structural Inorganic Chemistry," 3rd ed, Oxford University Press, London, 1962, p 100.

Table I. Yield and Characterization Data for $B_nC_2H_{n+2}$ Species

Compound	Mp, °C	Bp, °C (mm)	Yield, ^b %	Yield, ^c %	Analyses, %					
					Calcd			Found		
					C	H	B	C	H	B
$B_8C_2H_8(CH_3)_2$	(-40.4)-(-39.4) ^a	62 (134)	30	0	38.43	9.68	51.89	37.42	9.82	52.10
$B_7C_2H_7(CH_3)_2$	(-22)-(-21.3) ^a		7	0	35.11	9.58	55.31	35.14	9.74	55.76
$1,6-B_8C_2H_8(CH_3)_2$	1.0-1.6 ^a	73 (32)	28	41	32.32	9.49	58.18	31.97	9.69	57.84
$1,10-B_8C_2H_8(CH_3)_2$	26.5-27.5 ^a		95 ^d	..	32.32	9.49	58.18	33.35	9.67	57.63
$1,7-B_{10}C_2H_{10}(CH_3)_2^e$	170		0	8	27.89	9.36	62.75	27.80	9.21	62.61

^a In sealed capillary. ^b When prepared in the absence of diborane. ^c When prepared in the presence of diborane. ^d Prepared from 1,6- $B_8C_2H_8(CH_3)_2$. ^e Although several C-substituted derivatives of 1,7- $B_{10}C_2H_{12}$ have been reported [D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963)], the 1,7-dimethyl-derivative has not been previously characterized. We thank F. P. Olsen for a sample of the authentic material.

structure should contain a single methyl proton resonance. Only one line is observed at τ 7.84.

$B_7C_2H_7(CH_3)_2$. The 19.3-Mc/sec ^{11}B nmr spectrum of $B_7C_2H_7(CH_3)_2$ is presented in Figure 2. Three types of boron atoms are evident in the ratios 1:2:4. The doublet of area 1 at lowest field may be assigned to a boron atom in an apical position⁵ as in $B_{10}H_{10}^{-2}$. Such an assignment and the available data suggest the

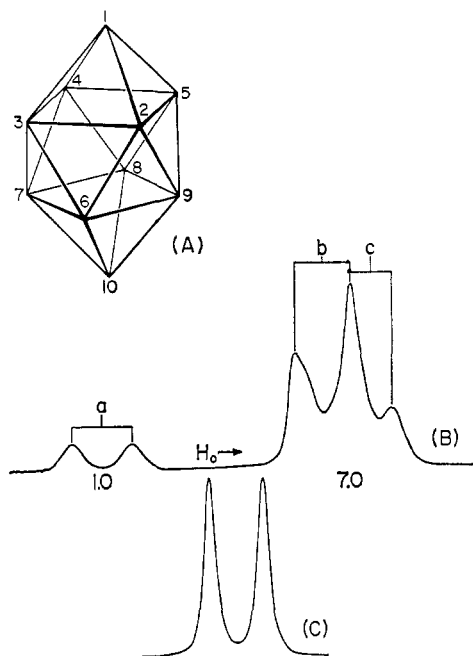


Figure 3. (A) The biccapped Archimedean antiprism geometry. (B) The 19.3-Mc/sec ^{11}B nmr spectrum of the proposed 1,6 isomer of $B_8C_2H_8(CH_3)_2$. Chemical shifts, ppm (with reference to $BF_3O(C_2H_5)_2$), and coupling constants (cps) for the indicated peaks are (a) -19.8 (178), (b) +15.3 (apparent, 167), and (c) +22.9 (apparent, 128). Integrated areas are indicated beneath the peaks. (C) The 19.3-Mc/sec ^{11}B nmr spectrum of the proposed 1,10 isomer of $B_8C_2H_8(CH_3)_2$. The chemical shift (with reference to $BF_3O(C_2H_5)_2$) and coupling constant are +10.3 ppm and 162 cps, respectively.

triccapped trigonal prism structure shown in Figure 2 with an apical boron at the 9-position. Such a structure places the two carbon atoms in nonadjacent apical positions at sites 1 and 7 with a coordination number of 5. This structure requires the two methyl group resonances to be equivalent in the proton nmr spectrum, and only one line is observed at τ 7.50.

(5) W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **81**, 5833 (1959).

$B_8C_2H_8(CH_3)_2$ Isomers. Figure 3 presents the 19.3-Mc/sec ^{11}B nmr spectrum (B) of the $B_8C_2H_8(CH_3)_2$ isolated from the initial pyrolysis reaction and the spectrum (C) of the isomer which results from thermal rearrangement. The low-field doublet of area 1 in spectrum B suggests a single apical boron atom⁵ and would place one carbon atom at the opposite apical position of a $B_{10}H_{10}^{-2}$ polyhedron. Since it is unlikely that the two carbon atoms are nearest neighbors, the second carbon atom may be placed in the second equatorial belt removed from the apical carbon atom. Such a 1,6 arrangement of carbon atoms should give nonequivalent methyl proton resonances as observed. The two methyl resonances appear as sharp singlets of equal intensity at τ 7.19 and 8.68.

The spectrum C (Figure 3) is a sharp doublet which suggests the equivalence of all eight boron atoms. If the $B_{10}H_{10}^{-2}$ polyhedron is again employed as the framework model, the carbon atoms are uniquely placed at the apical (1,10) positions. The methyl proton resonances were observed as one sharp singlet at τ 7.22, and this result is in agreement with the 1,10 carbon assignment. The observed thermal rearrangement thus constitutes a polyhedral rearrangement of the 1,6 isomer to the 1,10 isomer. The latter material is expected to be the most stable isomer of the $B_8C_2H_{10}$ system owing to the favorable coordination numbers of 5 and 6 for carbon and boron, respectively.¹

The work briefly described here is being extended to other members of the B_6 , B_7 , and B_8 carborane systems along with derivative and reaction chemistry.

Acknowledgment. This research was supported by the National Cancer Institute, U. S. Public Health Service, under Grant CA-06773MCHB. The authors express their thanks for this support.

(6) Alfred P. Sloan Research Fellow.

Fred N. Tebbe, Philip M. Garrett
Donald C. Young, M. Frederick Hawthorne⁶
Department of Chemistry, University of California
Riverside, California
Received November 8, 1965

Concerning the Photolysis of the Sodium Salt of (Δ^2 -2,3-Diphenylcyclopropenyl)carboxaldehyde Tosylhydrazone

Sir:

Recently we reported that the photolysis of the title compound provided diphenyltetrahedrane in 0.1% yield.¹ However, we must retract our claim for the

(1) S. Masamune and M. Kato, *J. Am. Chem. Soc.*, **87**, 4190 (1965).