Carboranes from Diborane and Acetylene in an Electric Discharge

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Abstract: Circulation of diborane–acetylene mixtures in helium through an electric discharge yields carboranes as the major volatile products, including 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, and at least six B-methylated derivatives of these plus C,3-$(CH_3)_2$-1,2-$C_2B_3H_3$. Isolation of the products in pure form followed by nuclear magnetic resonance, infrared, and mass spectroscopic studies has permitted their structural characterization. The significance of the predominance of carboranes, especially B-methylated carboranes, among the reaction products is examined. The stability of C,3-$(CH_3)_2$-1,2-$C_2B_3H_3$ relative to its rearrangement to 1,2-$(CH_3)_2$-1,5-$C_2B_3H_3$ is discussed. Comparison of the infrared and nuclear magnetic resonance data for the ten carborane products has allowed improved correlation between the spectra and structural features.

Reactions in electric discharges have been important in the discovery of many boron hydrides and carboranes (*e.g.*, B_9H_{15},[1] $B_{10}H_{16}$,[2] $B_{20}H_{16}$,[3] B_6H_{12},[4] B_8H_{12},[5] 1,5-$C_2B_3H_5$,[6] 1,6-$C_2B_4H_6$,[7] 1,2-$C_2B_4H_6$,[7] and 2,4-$C_2B_5H_7$[6]), all of the carboranes listed having been first isolated as products of electric-discharge reactions of acetylene–pentaborane(9) mixtures. Because of the high reactivity and structural simplicity of diborane relative to the higher boranes, it was of interest to examine the reaction of diborane with acetylene under high-energy electric-discharge conditions in which the formation of stable carborane cage molecules as end products was expected to be favored. Vapor-phase chromatography offered a feasible method for resolving the anticipated mixtures of volatile products into pure components and thus avoiding the difficulties encountered in fractionation procedures.

Results

The rapid circulation of mixtures of acetylene and diborane diluted in helium through an ac discharge between copper electrodes yielded, in repeated experiments with varying conditions, volatile products of which 62 to 99 mole % were carborane species (Table I). When the applied voltage was sufficiently high to induce flash reaction, virtually all of the volatile products were carboranes, and no boranes, alkylboranes, or hydrocarbons, except for traces of *n*-butane, were detected. In experiments in which diborane was initially in excess, approximately 10 to 15% of the acetylene consumed was converted into volatile carboranes, most of the remainder forming nonvolatile solids.

Table I. Products of B_2H_6–C_2H_2 Discharge Reactions[a]

Type of discharge	Reactants, mmoles B_2H_6	Reactants, mmoles C_2H_2	Total volatile products, mmoles[b]	Mole % of volatile products[b] Carboranes I	II	III	IV	V	VI	VII	VIII	IX	X	Unidentified[c]	Boranes	Other
Cu electrodes[h] (flash reaction)	3.62	3.56	0.19	10.9	0.9	10.9	20.7	17.8	6.6	7.4	7.1	3.9	0.6	12.3	0.0	0.9
	1.74	1.74	0.13	11.2	2.2	11.3	15.9	19.0	10.2	6.0	4.7	4.3	1.3	13.4	0.0	0.5
Cu electrodes[h] (glow, 0.5 hr)	2.25	1.09	0.052	13.7	11.0	3.1	10.1	5.7	3.2	1.5	6.7	2.4	1.2	18.1	23.3[d]	0.0
	2.35	1.14	0.030	8.4	8.8	4.8	11.7	6.3	1.8	5.0	10.1	2.5	1.5	14.5	24.6[d]	0.0
	2.23	1.14	0.085[g]	9.4	22.4	2.9	3.6	6.8	1.7	3.0	4.6	2.2	1.5	3.4	27.9[e]	10.6[f]
Electrodeless (glow, 1.0 hr)[i]	2.30	1.14	0.015	tr	1.9	12.4	7.9	2.6	0.0	0.0	0.0	0.0	0.0	0.0	75.2[d]	tr[j]
	2.29	1.13	0.059[g]	tr	1.2	5.5	3.0	1.5	0.0	0.0	0.0	0.0	0.0	0.0	88.8[d]	tr[j]

[a] Data from typical experiments. [b] Exclusive of H_2. [c] Products of lower volatility having typical carborane infrared spectra but not characterized. [d] B_5H_9. [e] 20.7 B_5H_9, 7.2 B_4H_{10}. [f] 2.1 C_4H_{10} + C_6H_6, C_4H_2, and unidentified substances. [g] Condensed in −135° trap during discharge period. [h] 1200 v ac. [i] 11,500 v ac. [j] tr = trace.

The major volatile carborane products have been isolated and structurally characterized from their mass spectra (Table II), infrared absorptions (Table III), and ^{11}B and ^{1}H nmr spectra (Tables IV and V) and include the following:[8] C,3-dimethyl-1,2-dicarbaclovopentaborane(5)[9] (I), 1,5-dicarbaclovopentaborane(5)[6]

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[1] W. V. Kotlensky and R. Schaeffer, *J. Am. Chem. Soc.*, **80**, 4517 (1958).

[2] R. Grimes, F. E. Wang, R. Lewin, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, 47, 996 (1961).

[3] L. B. Friedman, R. D. Dobrott, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 3505 (1963).

[4] Mass spectrometric evidence for B_6 and B_7 hydrides obtained in the silent discharge of B_2H_6 has been reported (S. G. Gibbons and I. Shapiro, *ibid.*, **82**, 2968 (1960)), but no compounds were isolated.

[5] R. E. Enrione, F. P. Boer, and W. N. Lipscomb, *Inorg. Chem.*, **3**, 1659 (1964).

[6] I. Shapiro, C. D. Good, and R. E. Williams, *J. Am. Chem. Soc.*, **84**, 3837 (1962).

[7] I. Shapiro, B. Keilin, R. E. Williams, and C. D. Good, *ibid.*, **85**, 3167 (1963).

[8] For a description of the cage numbering system for carboranes, see R. Adams, *Inorg. Chem.*, **2**, 1087 (1963).

[9] R. N. Grimes, *J. Am. Chem. Soc.*, **88**, 1070 (1966).

Table II. Chromatographic Retention Volumes and Mass Spectroscopic Data

Compd	R_v[a]	Parent peak, m/e	Parent ion
II	0.5	62[b]	$^{12}C_2{}^{11}B_3H_5^+$
V	0.9	76	$^{12}C_3{}^{11}B_3H_7^+$
III	1.3	74[b]	$^{12}C_2{}^{11}B_4H_6^+$
I	1.7	90	$^{12}C_4{}^{11}B_3H_9^+$
X	2.3	Not taken	
VI	3.1	88	$^{12}C_3{}^{11}B_4H_8^+$
IV	5.1	86	$^{12}C_2{}^{11}B_5H_7^+$
IX	8.0	100	$^{12}C_3{}^{11}B_5H_9^+$
VII	9.2	100	$^{12}C_3{}^{11}B_5H_9^+$
VIII	9.7	100	$^{12}C_3{}^{11}B_5H_9^+$

[a] Relative to B_4H_{10}, 25° column. [b] Reported previously.[6,7]

Table III. Infrared Absorption Spectra of Carborane Products (cm^{-1})[a]

I (40 mm)	II (36 mm)	III (50 mm)	IV (27 mm)	V (52 mm)	VI (40 mm)	VII (25 mm)	VIII (35 mm)	IX (33 mm)	X (25 mm)
2960 sh				3000 sh			2970 sh		
				2960 m	2950 m		2930 m	2930 m	2910 s
2900 s				2890 m	2895 m	2900 m,b	2880 m	2885 s	2850 m
2860 sh				2800 sh	2830 sh	2820 sh	2820 sh	2810 sh	
2570 vs	2590 vs	2645 vs	2600 vs	2590 vs	2620 vs	2590 vs	2590 vs	2595 vs	2575 vs
					2570 m				
				1750 w	1870 vw				1570 w,b
1450 m				1450 w	1470 sh	1450 m,b	1450 m,b	1450 m,b	1450 m
1320 vs		1310 sh		1330 vs	1330 vs	1330 s	1340 s	1330 s	1325 s
	1232 m	1290 m		1285 sh			1290 sh		
	1224 m	1280 m	1270 w,b	1278 m	1272 sh	1270 w	1280 s		
1265 s	1214 m	1265 m	1220 m	1270 m	1268 s		1272 sh	1250 s	1260 vw
	1205 sh		1209 s	1235 w		1210 m			1205 sh
1195 s	1200 sh	1195 sh	1200 sh	1195 s	1190 m,b	1190 sh			
		1170 vs,b	1175 sh	1170 sh		1180 s	1175 m	1175 sh	1182 s
			1150 w	1110 sh	1155 s	1110 w	1145 m	1150 s	
1110 s	1100 vs,b		1075 sh	1100 vs	1120 m	1072 m			1100 s
			1062 s						
1050 w			1050 s				1050 s	1050 s	
1015 sh,w			1038 sh	1015 w,b	1030 w,b	1030 m			1030 w
980 w		930 sh	940 w,b	970 s				960 w,b	983 m
950 sh	918 m,b	920 m	912 w		936 m		935 sh		
940 m	902 s		900 sh	902 vs			905 m	895 w,b	885 m
906 w	890 m	810 w	870 w	893 s	884 m	882 w	840 w	860 sh	850 w
880 w,b	800 w,b	750 w	795 m,b	842 w			795 sh	800 w,b	
800 w,b	785 w	740 m							
	760 w,b	700 w,b							

[a] Spectra of I,[9] II,[6] and III[7] have been reported previously. s = strong, m = medium, w = weak, sh = shoulder, b = broad.

(II), 1,6-dicarbaclovohexaborane(6)[7] (III), 2,4-dicarbaclovoheptaborane(7)[6] (IV), 2-methyl-1,5-dicarbaclovopentaborane(5) (V), 2-methyl-1,6-dicarbaclovohexaborane(6) (VI), 1-methyl-2,4-dicarbaclovoheptaborane(7) (VII), 3-methyl-2,4-dicarbaclovoheptaborane(7) (VIII), and 5-methyl-2,4-dicarbaclovoheptaborane(7) (IX). An additional isolated trace product is probably 2,3-dimethyl-1,5-dicarbaclovopentaborane(5) (X).

Except for pentaborane(9), no products other than carboranes were detected in experiments at room temperature using copper electrodes. However, when a trap at −135° was maintained just downstream from the discharge, detectable quantities of tetraborane(10), pentaborane(9), diacetylene, *n*-butane, and benzene, together with traces of unidentified materials, were trapped out in addition to the carborane products. Experiments conducted in an electrodeless discharge produced both smaller quantities of volatile products and lower yields of carboranes relative to the results obtained with copper electrodes (Table I).

Experimental Section

Discharge Apparatus. The 4.5-l. greaseless reaction system was constructed of Pyrex and was connected through a mercury float valve to a conventional high-vacuum apparatus. A magnetically driven copper and stainless steel propeller with which gases could be circulated at velocities up to 75 cc/sec was enclosed in the discharge system. A U-tube trap located adjacent to the discharge tube on the downstream side permitted condensation of gases by the use of appropriate cold baths when desired. The pressure in the system was monitored on a conventional mercury manometer.

The discharge tubes employed were of two types. That used for most of the work contained copper disk electrodes 2 cm in diameter and placed parallel to the direction of gas flow 1.5 cm apart. In a few experiments the copper electrodes were replaced by a Pyrex ozonizer tube[10] in which a potential was maintained between an inner tube filled with copper sulfate solution and an outer layer of aluminum foil covered with asbestos. In all experiments the discharge apparatus was connected through a 12-kv transformer and a rheostat to a 110-v ac source.

Materials. B_2H_6 (Olin Mathieson) and C_2H_2 (Matheson) were purified by repeated fractionation through a −135° trap and stored at −196° until use. The purity of these materials was checked periodically by infrared analysis.

Procedure. Measured quantities of B_2H_6[11] and C_2H_2 were distilled into the reactor and condensed at −196°. Helium was introduced to a pressure of approximately 55 mm and the mercury valve was closed. The reactants were warmed to room temperature and the mixture was precirculated at 50 cc/sec for 30 min before starting the discharge. In most experiments the voltage across the electrodes was maintained at 1000 to 1500 v for 30 min with a flow rate of 50 to 60 cc/sec, under which conditions a steady glow was observed between the electrodes. When the B_2H_6:C_2H_2 ratio was smaller than ~1.0, flash reactions invariably occurred, but a

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(10) W. Jolly in "Technique of Inorganic Chemistry," Vol. I, H. B. Jonassen and A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1963, Chapter 5.

(11) Mixtures of B_2H_6 and C_2H_2 undiluted by an inert gas are hazardous; explosions have been observed[12] at 100°. At no time in the present study were B_2H_6 and C_2H_2 vapors in contact except in the presence of large (>50%) quantities of helium.

(12) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p 150.

Table IV. ^{11}B Nmr Chemical Shifts and Coupling Constants[a]

Compound	δ,[b] J (cps)	Rel peak area	Assignment[c]
I	−6.2	1	B(3)–CH_3
	−7.8, 174	1	B(4)–H
	−34.9, 184	1	B(5)–H
II	+17, 184		B–H
III	+37, 188		B–H
IV	+13.1, 186	1	B(3)–H
	+16.1, 170	2	B(5)–H, B(6)–H
	+41.6, 178	2	B(1)–H, B(7)–H
V	+9.6	1	B(2)–CH_3
	+11.5, 182	2	B(3)–H, B(4)–H
VI	+24.0	1	B(2)–CH_3
	+31.2, 184	2	B(3)–H, B(5)–H
	+37.4, 184	1	B(4)–H
VII	+9.0, 188	1	B(3)–H
	+12.9, 177	2	B(5)–H, B(6)–H
	+28.7	1	B(1)–CH_3
	+44.4, 185	1	B(7)–H
VIII	+4.4	1	B(3)–CH_3
	+15.1, 175	2	B(5)–H, B(6)–H
	+38.6, 178	2	B(1)–H, B(7)–H
IX	(+9.0)[d]	1	B(5)–CH_3
	+12.1, 182	1	B(3)–H
	(+15.8),[e] (184)	1	B(6)–H
	+39.2, 174	2	B(1)–H, B(7)–H

[a] Chemical shifts and coupling constants for I,[9] II,[7] III,[7] and IV[13] have been reported previously. [b] Ppm relative to $B(OCH_3)_3$; estimated values in parentheses. [c] Boron cage atoms numbered by standard system.[8] [d] Shoulder. [e] Lower member of doublet visible only as shoulder.

Table V. ^{1}H Nmr Chemical Shifts and Coupling Constants[a]

Compound	δ,[b] J (cps)	Rel peak area	Assignment[c]
I	−4.50	1	H–C
	−3.4, 175	1	H–B(4)[d]
	(−1.9), 182[e]	1	H–B(5)[d]
	−0.3 (broad)	6	2 CH_3
II	−4.6	2	H–C
	−2.9, 186	3	H–B
III	−3.1	2	H–C
	−1.9, 185	4	H–B
IV	−5.30	2	H–C(2), H–C(4)
	−4.74, 180	1	H–B(3)
	(−4.0), (170)[f]	~2	H–B(5), H–B(6)[d]
	−0.28, 175	2	H–B(1), H–B(7)[d]
V	−4.98	2	H–C(1), H–C(5)
	−3.75, 191	2	H–B(3), H–B(4)
	+0.13	3	CH_3
VI[g]	−2.95	2	H–C(1), H–C(6)
	−1.88, 180[e]	2	H–B(3), H–B(5)
	−0.53	3	CH_3
VII	−5.43	2	H–C(2), H–C(4)
	(−4.7), (180)[h]	~1	H–B(3)
	(−4.0), (170)[h]	~2	H–B(5), H–B(6)
	−0.13, 175	1	H–B(7)
	+0.24	3	CH_3
VIII	−4.77	2	H–C(2), H–C(4)
	(−3.9), (170)[h]	~2	H–B(5), H–B(6)[d]
	−0.7	3	CH_3
	0.0, 176	2	H–B(1), H–B(7)[d]
IX[i]	−4.8 (broad)	2	H–C(2), H–C(4)
	−0.5	3	CH_3
	0.0, 175[h]	~2	H–B(1), H–B(7)

[a] Chemical shifts and coupling constants for II,[7,16] III,[7,16] and IV[18] have been reported previously. [b] Ppm relative to tetramethylsilane; negative values are at low field; estimated values in parentheses. [c] Cage atoms numbered by standard system.[8] [d] Assignment based on comparison of J values with ^{11}B nmr spectrum. [e] The second highest-field member of the quartet was hidden by the CH_3 peak. [f] Only the lowest peak in the quartet was clearly distinguishable. [g] The H–B(4) quartet was not observed. [h] Broad and weak quartet. [i] The H–B(3) and H–B(6) quartets were not observed.

glow discharge was always achieved when the ratio was 2.0 or higher. During the reaction period yellow-to-brown solid deposits formed continuously on the reactor walls and the pressure increased slightly (*ca.* 10%). In some experiments the U-tube trap was maintained at −135°, a temperature sufficiently cold to trap most products but which permitted B_2H_6 and C_2H_2 to remain in the vapor state.

At the end of the discharge period the trap was cooled to −196° and circulation was continued until all condensable material had been trapped out. After pumping off noncondensable gases through another −196° trap, the volatile condensable materials were distilled several times through a trap at −135° which permitted only B_2H_6 and C_2H_2 to pass through (infrared analysis of material not condensing at −135° disclosed only starting materials).

The reaction products were separated by vapor-phase chromatography (Table II) on an 8.5 ft × 0.25 in. column packed with 30% tricresyl phosphate on Chromosorb W. Individual compounds were collected in liquid nitrogen traps as they emerged from the column. Complete separation of products having similar retention times in some cases required repeated passes through the column, but traces of unreacted B_2H_6 and C_2H_2, by virtue of their high volatilities, were easily separated from the products.

Gas samples were measured in a calibrated volume equipped with a manometer, and yields were calculated from chromatogram peak areas after calibration for individual compounds.

Infrared spectra were obtained in the gas phase on a Perkin-Elmer Model 337 grating spectrophotometer, using a 3.5-cc Pyrex cell with a 9-cm path length, fitted with NaCl windows and a cold finger for sample condensation. Strong absorption spectra were obtained with this cell even on samples as small as a few micromoles. Mass spectra were run on a CEC 21-103C mass spectrometer, ^{1}H nmr spectra were recorded at 60 Mc on a Varian A-60 spectrometer, and ^{11}B nmr spectra were measured with a Varian HR-60 spectrometer at 19.3 Mc. All nmr data were obtained from pure liquid samples at room temperature.

Interpretation of Spectra

Comparison of the gas-phase infrared spectra of pure products I–X (Table III) reveals remarkable similarity and discloses several common features. All of the spectra contain strong, sharp absorptions near 2500 cm^{-1}, the B–H stretching frequency. None shows any appreciable absorptions in the 1500–2500-cm^{-1} region, indicating an absence of hydrogen bridges and suggesting closed cage structures. All except II, III, and IV exhibit strong bands near 3000 cm^{-1} (C–H stretch) and 1200–1500 cm^{-1} (CH_3 deformation modes). Only a few additional bands, most of them appearing in the 900–1200-cm^{-1} region, are found in any of the spectra.

The known carboranes II, III, and IV are readily identified from their published[6,7,13] infrared, ^{11}B nmr, and mass spectra. The infrared spectra of the remaining compounds are indicative of alkylcarboranes, particularly when their close resemblance to the spectra of the parent carboranes II, III, and IV is considered.

As we indicated in a previous communication,[9] compound I is apparently either 1,3- or 2,3-dimethyl-1,2-dicarbaclovopentaborane(5), the only ambiguity being in the location of the C-bonded methyl group.[14]

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(13) T. P. Onak, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **85**, 3378 (1963).

(14) The unlikely structure 1,2-dimethyl-2,3-dicarbaclovopentaborane-(5) would require that one or both of the two high-field resonances in the ^{11}B nmr spectrum of I be assigned to apical boron(s). Either assignment is improbable in view of the ^{11}B spectra of the other known borane and carborane cage molecules (see ref 9). In the 1,2 isomer, the unique (among carboranes) four-coordinated apical boron would be expected to show one very low-field doublet, as is actually observed in the ^{11}B spectrum of I.

The latter structure is preferred because of the similar chemical shifts of protons bonded to cage carbons in the ^{1}H nmr spectra of I and II, the implication being that the CH group in I is apical. However, the 1,3-substituted structure certainly cannot be excluded at present.

V and VI are established by the data in Tables II–V as B-methyl derivatives of 1,5-$C_2B_3H_5$ and 1,6-$C_2B_4H_6$, respectively, and VII, VIII, and IX are clearly B-methylated CH_3-2,4-$C_2B_5H_6$ isomers. VIII is shown by its ^{11}B nmr spectrum to be methylated at the 3 (unique boron) position, since the doublet arising from that boron in the parent compound 2,4-$C_2B_5H_7$ (IV) collapses to a singlet in VIII. The positions of substitution on VII and IX are not immediately obvious, however, since unequivocal assignment of the two highest-field doublets in the ^{11}B nmr spectrum of IV has not previously been possible. Nevertheless, comparison of the ^{11}B and ^{1}H nmr spectra of IV, VII, VIII, and IX permits reasonably certain identification of VII and IX based on the following considerations.

(1) The electronic environment, and hence the ^{11}B nmr chemical shift, of B(3) in 2,4-$C_2B_5H_7$ would be expected to be influenced more directly by methylation at the adjacent (1 and 7) borons than by methylation at the more distant (5 and 6) boron atoms. The data in Table IV reveal that δ for B(3) is shifted (compared to 2,4-$C_2B_5H_7$) by 4.1 ppm in VII but by only 1.0 ppm in IX, suggesting that VII is the 1-methyl isomer and IX the 5-methyl isomer, and that the high-field doublet in 2,4-$C_2B_5H_7$ arises from B(1) and B(7). Consistent with this analysis is the fact that the high-field doublet in VIII, the 3-methyl isomer, is shifted more with respect to 2,4-$C_2B_5H_7$ than is the low-field doublet (3.0 and 1.0 ppm, respectively), again suggesting that the high-field resonance originates from B(1) and B(7).

(2) Methyl substitution at B(1) or B(7) leaves the cage carbon atoms chemically equivalent, while substitution at B(5) or B(6) renders the carbons nonequivalent. The broad proton nmr signal from the cage C–H groups in IX is more indicative of nonequivalent protons than is the characteristically sharp C–H resonance signal in the spectrum of VII. The identification of IX as the 5-substituted isomer is therefore supported.

The structure 2,3-$(CH_3)_2$-1,5-$C_2B_3H_3$ is tentatively assigned to X, a product obtained only in trace quantities, based on a comparison of its infrared spectrum (Table III) with those of the B_3 carboranes I, II, and V and on its volatility and vpc retention time.

Discussion

Under the conditions used in this study, the major volatile end products of the reaction between diborane and acetylene in a high-energy electric discharge are carboranes. That boron hydrides and hydrocarbons are formed in appreciable quantities during the reaction is evidenced by the condensation of these materials when the reaction mixture is continuously circulated through a cold trap. In the absence of such a trap, however, few noncarborane volatile products are obtained. It is evident that of the many species produced in the reaction, for the most part only closed-cage molecules survive repeated passage through the discharge, a result attributable to the remarkable stability of these structures. Such features as hydrogen bridges and BH_2 groups, present in boranes and in other possible intermediate species such as hydrocarboranes, are lost through rearrangement and reaction to form the volatile carboranes and nonvolatile residues.

The series of carboranes obtained is qualitatively the same regardless of experimental conditions tried, although the relative yields of individual carboranes vary somewhat as factors such as the type of discharge, applied potential, and concentrations of starting materials are changed (Table I). Thus the nature of the carboranes formed does not appear to be greatly dependent on reaction conditions within the limits of this investigation.

The principal structural relationships between the ten characterized carborane products may be summarized as follows: (1) All are closed-cage molecules having two skeletal carbons and from three to five boron atoms; (2) the three known stable parent carboranes in this range, 1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, and 2,4-$C_2B_5H_7$, are included; (3) six products are methylated derivatives of these three parent carboranes; (4) the five monomethyl derivatives are alkylated at boron positions only, and include all of the possible B-monomethyl derivatives of the above parent carboranes; (5) one of the dimethyl derivatives (I) is the first B_3 carborane having adjacent cage carbon atoms and is the only C-alkylated product found in this study.

The predominance of methylated species among the volatile products is a somewhat surprising result since the only carbon compound initially present is acetylene. The mechanism(s) responsible for methylation is unclear, but a hydroboration attack on acetylene may be involved. This phenomenon appears to have general significance since the vapor-phase reaction of acetylene with pentaborane(9) at elevated temperatures yields a series of B-methylated organoboranes in appreciable yields.[15]

A closely related problem concerns the attachment of the alkyl groups at boron positions only (except in I, where both B and C substitution are noted). This is again consistent with results observed in high-temperature borane–acetylene reactions.[15] It is unlikely that methyl groups once bonded to cage carbon atoms have any appreciable tendency to migrate to boron positions, since reported preparations of alkyl carboranes from substituted acetylenes invariably yielded only C-alkylated products,[16,17] even in high-temperature reactions. It is assumed, then, that the B-methyl groups observed in this study arise from B–C linkages formed initially, a sequence consistent with the suggestion that hydroboration of acetylene is an important early step in the reaction.

Compound I requires special comment. As was previously pointed out,[9] the failure to detect among the discharge products either the parent compound 1,2-$C_2B_3H_5$ or any derivative of it other than I seems to suggest that the presence of the methyl groups on I

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(15) (a) T. P. Onak, G. B. Dunks, J. R. Spielman, F. J. Gerhart, and R. E. Williams, presented at the Western Regional Meeting of the American Chemical Society, Los Angeles, Calif., Nov 1965; (b) R. N. Grimes, unpublished results.

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imparts some stability to the adjacent-carbon structure with respect to rearrangement to the isomer having nonadjacent carbons. Both theoretical[18-21] and experimental[13,22,23] considerations have indicated that the more stable carborane structures are those in which the cage carbons are nonadjacent. Therefore the apparent reluctance of I to rearrange to the 1,5 isomer [1,2-dimethyl-1,5-dicarbaclovopentaborane(5)], either in the discharge or under moderate conditions, is intriguing.[24] It is conceivable that such an isomerization involves an intermediate with a sterically unfavorable configuration which hinders rearrangement. However, although steric effects have recently been observed in the rearrangement[25] of *o*-carborane(12) to neocarborane(12), which is facilitated by the replacement of the C-hydrogen atoms by large substituted silyl groups, the importance of such effects in the case of the much smaller methyl substituents is not obvious. Possibly a more likely explanation is that alkylation in I alters the electronic situation in the cage so as to stabilize the adjacent-carbon structure. Studies on I currently in progress are expected to yield information on possible thermal or base-catalyzed isomerization.

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Photoinduced Nucleophilic Substitution in Halogenated Clovoboranes

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Abstract: Irradiation of polyhalogenated $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$ derivatives in aqueous solutions containing CN^-, N_3^-, or OCN^- ions results in replacement of halogen by the appropriate nucleophile. Up to nine halogens were replaced with CN groups, while the introduction of more than two N_3 or OCN groups was prevented, respectively, by competing photolytic or hydrolytic reactions of the new substituent. The results are consistent with a photoinduced heterolysis of the boron–halogen bond followed by addition of an anion to the resulting electron-deficient species, steric factors being important. This mechanism is supported by halogen-exchange experiments.

The clovoboranes, $B_{10}H_{10}^{2-}$ and $B_{12}H_{12}^{2-}$, have displayed a remarkably broad spectrum of derivative chemistry. For instance, the introduction of chloromethyldimethylamino,[1] amino,[2] acyl,[3] hydroxy,[3] alkoxy,[3] alkyl,[3] mercapto,[3] alkylthio,[3,4] diazonium,[5] carbonyl,[5,6] and halo[7] substituents has been reported. However, only halogenation proceeded beyond the disubstitution stage to afford readily poly- and perhalogenated cages. The availability of such derivatives suggested their use as starting materials for the synthesis of otherwise inaccessible, substituted clovoboranes. The direct replacement of halogen by nucleophiles, a valuable synthetic tool in organic as well as boron chemistry, was inapplicable in view of the reported and confirmed inertness of halogenated clovoboranes.[7] Cripps' discovery that $B_{12}Cl_{12}^{2-}$ yields chloride ion on irradiation led to a study in the course of which it was found that *such substitution is effected readily when aqueous solutions of halogenated clovoboranes are irradiated in the presence of nucleophiles*[8] (eq 1, X = Cl,

$$B_{12}X_{12}^{2-} + nY^- \xrightarrow[H_2O]{h\nu} B_{12}X_{12-n}Y_n^{2-} + nX^- \qquad (1)$$

Br; $Y^- = CN^-$, N_3^-, etc.). It was of interest, therefore, to determine the synthetic scope of this reaction and its mechanistic implications.

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