Anal. Calcd for $C_4H_{15}B_{11}S_2$: C, 19.5; H, 6.1. Found: C, 19.31; H, 6.1.

1,2-(2′-Chloro-1′,3′,2′-dithiabora)-*o*-carborane.—The acetonitrile–trichloroborane complex was formed by condensing 7.0 g (0.06 mol) of trichloroborane onto a solution of 3.0 g of acetonitrile in 50 ml of dry benzene at −80° and slowly warming the solution to room temperature. An additional 50 ml of benzene was added and the resulting slurry was heated to reflux. A solution of 1,2-bis(mercapto)-*o*-carborane in benzene (10.4 g in 25 ml) was added to the hot mixture and the reaction mixture was refluxed for 2 hr. The hydrogen chloride formed was collected as the triethylamine salt.

When the yellow reaction solution cooled to room temperature, excess $CH_3CN \cdot BCl_3$ precipitated. The clear solution was filtered away from the crystals with the aid of a fritted stick. (The entire experiment was conducted under N_2 atmosphere.) The solvent was removed under reduced pressure and the yellow residue was transferred to a sublimator in a nitrogen-filled drybox. Sublimation at 90° (0.25 mm) gave 12.5 g of a white crystalline material; mp 62.4–64.2°.

Anal. Calcd for $C_2H_{10}B_{11}S_2Cl$: C, 9.50; H, 3.96; B, 47.20; S, 25.40; Cl, 14.10. Found: C, 9.52; H, 4.19; B, 44.53; S, 25.00; Cl, 13.62.

Compound VII.—The acetonitrile–trichloroborane complex was prepared from 1.2 g (0.01 mol) of trichloroborane and 1.0 g (0.024 mol) of acetonitrile according to the procedure described above. A solution of 1,2-bis(mercapto)-*o*-carborane in benzene (0.029 mol in 50 ml) was added to the complex and the mixture was refluxed for 6 hr. Tetraethylammonium bromide (2.0 g, 0.0095 mol) in 10 ml of acetonitrile was added to the hot solution. A white precipitate formed when the solution cooled to room temperature. The product was recrystallized from a benzene–ethyl acetate mixture, washed with petroleum ether (bp 30–60°), and vacuum dried over P_2O_5; mp 320°.

Anal. Calcd for $C_{12}H_{40}B_{21}S_4N$: C, 26.05; H, 7.27; N, 2.53; B, 41.00; S, 23.20. Found: C, 25.81; H, 7.60; N, 2.64; B, 40.75; S, 21.30.

1,2(2′-Dimethylamino-1′,3′,2′-dithiabora)-*o*-carborane.—A tensimeter apparatus was charged with 0.57 g of dimethylaminoborane and 2.08 g (0.01 mol) of 1,2-bis(mercapto)-*o*-carborane and connected to the vacuum line. The entire system was evaluated and the stopcock was closed. The apparatus was submerged to the stopcock in an oil bath and the temperature was raised to 210°. An external source of nitrogen pressure was required to maintain equal mercury levels in the tensimeter. A measure of this pressure, corrected for temperature, was used to calculate the amount of hydrogen evolved in the reaction. The total volume of hydrogen evolved was 448 ml (STP) or 100% of theoretical maximum yield.

The white residue in the reaction tube was removed and the product was purified by sublimation at 140° (0.4–0.2 mm), mp 137–139°.

Anal. Calcd for $C_4H_{16}B_{11}S_2N$: C, 18.35; H, 6.13; N, 5.36. Found: C, 17.78; H, 6.12; N, 5.24.

Reaction of Diborane with 1,2-Bis(mercapto)-*o*-carborane.—A 50-ml reaction flask was charged with 2.35 g (0.01 mol) of 1,2-bis(mercapto)-*o*-carborane and 15 ml of dry diethyl ether. The flask was cooled to −196° and evacuated. Diborane (0.3 ml, 0.134 g) was condensed on the mixture and the flask was allowed to warm to −80°. After the cessation of hydrogen evolution (total hydrogen evolved amounted to approximately 0.02 mol) the ether was distilled from the white crystalline product. On warming the reaction flask to 50°, additional ether was evolved. The resulting product was insoluble in diethyl ether but soluble in petroleum ether; mp 42–50°. The infrared spectrum was in agreement with that expected for 1,2-(2′-hydro-1′,3′,2′-dithiabora)-*o*-carborane.

Carborane 1,2-Bis(phenylthiocarbamate.)—Phenyl isocyanate, 0.707 g, was dissolved in 10–15 ml of carbon tetrachloride and added to a solution of 1.5 g of 1,2-(2′-chloro-1′,3′,2′-dithiabora)-*o*-carborane in carbon tetrachloride. The mixture was refluxed for 30 min and cooled to 20°, and the resulting precipitate was collected, washed with petroleum ether (bp 30–60°), and dried in a nitrogen stream. A portion of this product was hydrolyzed and the water-insoluble fraction of the resulting materials was dried over P_2O_5. Recrystallization of this fraction from a benzene–hexane mixture (10:1) yielded white crystals; mp 131.0–132.5°.

Anal. Calcd for $C_{16}H_{22}B_{10}N_2S_2O_2$: C, 43.09; H, 4.94; B, 24.20; N, 6.28; S, 14.35. Found: C, 44.40; H, 5.30; B, 23.88; N, 6.28; S, 13.98.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF VIRGINIA, CHARLOTTESVILLE, VIRGINIA 22903

Carborane Formation in Alkyne–Borane Gas-Phase Systems. II. Slow Reactions of Tetraborane(10) and Pentaborane(11) with Acetylene, Methylacetylene, and Dimethylacetylene[1]

BY RUSSELL N. GRIMES, CHRISTOPHER L. BRAMLETT,[2] AND R. LEONARD VANCE

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The reactions of tetraborane(10) and pentaborane(11) with acetylene, methylacetylene, and dimethylacetylene have been examined in the vapor phase at 25–50° and the volatile products have been isolated and characterized. Alkyl derivatives of the *nido*-carboranes CB_5H_9, $C_2B_4H_8$, and $C_3B_3H_7$ are produced together with alkylboranes, hydrocarbons, and organoboron polymers, but the products and yields vary considerably with choice of reactants. In the B_4H_{10} reactions, carboranes account for all organoboron products, but B_5H_{11} gives alkylboranes plus small yields of carboranes. With either B_4H_{10} or B_5H_{11}, acetylene tends to give C_3B_3 rather than C_2B_4 carboranes, while the reverse is true in reactions with higher alkynes. Derivatives of CB_5H_9 are formed from B_4H_{10} but not from B_5H_{11}. Diboration of the alkyne triple bond is postulated to account for the carbon–carbon cleavage which is evidenced by reaction products of both boranes.

Introduction

The gas-phase interaction between tetraborane(10) and acetylene has been reported in an earlier paper[3] to take place explosively at 100° giving volatile *closo*-carboranes and to proceed slowly at 25–50° forming methyl

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(1) Presented in part at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., April 1967.

(2) Philip Francis du Pont Predoctoral Fellow, 1965–1967.

(3) R. N. Grimes and C. L. Bramlett, *J. Am. Chem. Soc.*, **89**, 2557 (1967).

TABLE I

VAPOR-PHASE REACTIONS OF B_4H_{10} AND B_5H_{11} WITH ALKYNES AT 50°[a]

Reactants, mmol (500-ml vol)		Time, hr	Mol % of volatile products[b,c]								Total volatile products, mmol[b]	Boranes obtained, mmol[e]
			2-CB_5H_9 derivatives		2,3-$C_2B_4H_8$[d] derivatives		2,3,4-$C_3B_3H_7$[d] derivatives		Other			
B_4H_{10}	3.56	3.8	4-CH_3	3.6	None		2-CH_3	26.7	None		0.041	B_4H_{10} 1.92
C_2H_2	3.28						2,3-$(CH_3)_2$	37.5				B_5H_9 0.095
							2,4-$(CH_3)_2$	32.2				B_6H_{12} 0.001
B_4H_{10}	0.89	8 days	4-CH_3	2.5	Parent	5.6	2-CH_3	20.4	None		0.196	B_4H_{10} None
C_2H_2	8.10[f]						2,3-$(CH_3)_2$	38.8				B_5H_9 0.020
							2,4-$(CH_3)_2$	32.2				B_6H_{12} 0.015
B_4H_{10}	16.71[g]	2.3	C-CH_3	3.6	2-CH_3	13.5	2-C_2H_5-3,4-$(CH_3)_2$	5.9	Propylene	71.1	0.562	B_4H_{10} 8.84
HC_2CH_3	16.75[g]		C,B-$(CH_3)_2$	2.1					Unidentified	1.8		B_2H_6 1.7
			C,B′-$(CH_3)_2$	2.0								B_5H_9 0.31
B_4H_{10}	2.70	2.5	None		2,3-$(CH_3)_2$	93.0	None		Unidentified	7.0	0.010	B_4H_{10} 1.77
$C_2(CH_3)_2$	2.70											B_2H_6 0.008
												B_5H_9 0.015
B_5H_{11}	0.93[h]	6.3	None		None		2-CH_3	16.3	2-$C_2H_5B_5H_8$	75.4	0.016	B_2H_6 0.28
C_2H_2	0.95[h]						2,4-$(CH_3)_2$	8.3				B_5H_9 0.45
B_5H_{11}	2.24	2.3	None		2-CH_3	9.3	None		Propylene	90.7	0.279	B_2H_6 1.10
HC_2CH_3	2.30											B_5H_9 0.245
B_5H_{11}	3.02	1.8	None		2,3-$(CH_3)_2$	17.8	None		*sec*-$C_4H_9B_5H_8$	28.4	0.197	B_2H_6 1.12
$C_2(CH_3)_2$	2.97								*n*-Butane	50.7		B_5H_9 0.264
									Unidentified	3.1		B_6H_{12} 0.054

[a] Typical experiments. In each case, reaction at 25° gave the same volatile products as at 50°. [b] Exclusive of boranes and H_2. [c] Carborane derivatives are indicated by their substituent groups. [d] Under a new numbering scheme proposed by the Nomenclature Committee of the Inorganic Division, American Chemical Society, Aug 1967, these carboranes would be given as 4,5-$C_2B_4H_8$ and 2,3,6-$C_3B_3H_7$, respectively. However, the currently accepted numbering (R. Adams, *Inorg. Chem.*, **2,** 1087 (1963)) is used in this paper. [e] No alkynes or $B\ H_{11}$ were recovered in any reaction except as noted. [f] A 4.53-mmol amount of C_2H_2 was recovered. [g] 2000 ml. [h] 125 ml.

and dimethyl derivatives of the *nido*-carborane[4] $C_3B_3H_7$ in small yields. It was noted that although borane–alkyne flash reactions give similar products regardless of the borane reactant, this is not true of the slower type of interaction. In the low-energy gas-phase systems, the products formed from alkynes with different boron hydrides (B_2H_6, B_4H_{10}, B_5H_9) are unexpectedly varied, ranging from alkylboranes and cyclic organoboranes[5,6] to several classes of carboranes.[3,7–10]

In order to explore further the general nature of the slow reactions, especially the formation of carborane cage systems, we have examined in detail the gas-phase reactions of B_4H_{10} and B_5H_{11} with several small alkynes. Attention was centered on the volatile products, since the accompanying nonvolatile solids and oils are usually amorphous or polymeric as well as unstable to air. The extreme sensitivity of gas chromatography, coupled with mass spectroscopic, infrared, and nmr techniques, permitted the isolation and structural characterization of virtually all volatile products.

Results

The volatile products from the six reactions studied are indicated in Table I (previously reported data[3] on the B_4H_{10}–C_2H_2 system are included for comparison) while the ^1H nmr τ and J values of $C_3B_3H_7$ derivatives are given in Table II. Since both B_4H_{10} and B_5H_{11} are unstable even in pure form at the temperatures used in this work, forming B_2H_6, B_5H_9, and higher boranes, we

TABLE II

^1H NMR CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR 2,3,4-TRICARBAHEXABORANE(7) DERIVATIVES[a,d]

Compound	τ, ppm	J, cps	Assignment
2-$CH_3C_3B_3H_6$	11.45	193	B(1)
	8.44		CH_3
	7.16	157	B(5), B(6)
	5.60		C(3)H or C(4)H
	3.85		C(4)H or C(3)H
2,3-$(CH_3)_2C_3B_3H_5$	11.20	179	B(1)
	9.78		CH_3
	8.23		CH_3
	7.10	156	B(5), B(6)
	4.53		C(4)H
2,4-$(CH_3)_2C_3B_3H_5$	11.40	179	B(1)
	9.25		2 CH_3
	7.00	157	B(5), B(6)
	4.20		C(3)H
2-C_2H_5-3,4-$(CH_3)_2C_3B_3H_4$[c]	10.05		CH_3
	9.50		C_2H_5
	∼9.0	130[b]	B(1)
	8.52		CH_3
	∼7.9	130[b]	B(5), B(6)

[a] Data on first three compounds are from recently obtained well-defined 60-Mc spectra which clearly show terminal B–H quartets. CH τ values are ∼0.2 ppm lower than previously reported.[10] [b] Estimated. [c] Obtained at 100 Mc. [d] Neat liquid samples at 25°.

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(4) The prefixes *nido* and *closo* designate open-cage and closed-cage carboranes, respectively, in accordance with the nomenclature system proposed by the Nomenclature Committee of the American Chemical Society, 1967.

(5) H. H. Lindner and T. Onak, *J. Am. Chem. Soc.*, **88,** 1886 (1966).

(6) D. T. Hurd, *ibid.*, **70,** 2053 (1948).

(7) H. G. Weiss and I. Shapiro, U. S. Patent 3,086,996 (1963).

(8) T. Onak, R. P. Drake, and G. B. Dunks, *Inorg. Chem.*, **3,** 1686 (1964).

(9) T. Onak, G. B. Dunks, J. R. Spielman, F. J. Gerhart, and R. E. Williams, *J. Am. Chem. Soc.*, **88,** 2061 (1966).

(10) C. L. Bramlett and R. N. Grimes, *ibid.*, **88,** 4269 (1966).

have arbitrarily excluded boranes from the relative-yield calculations.[11] The data reveal several trends worth noting.

(1) Carborane yields are much higher in the B_4H_{10} reactions than in those of B_5H_{11}; conversely, B_5H_{11} tends to give alkyl-substituted boranes whereas B_4H_{10} does not.

(2) With either borane, the use of higher alkynes in place of acetylene leads to a sharp decrease in the yield of $C_3B_3H_7$ derivatives and a corresponding increase in $C_2B_4H_8$ species. Thus, in 1:1 reactions with B_4H_{10}, acetylene gives derivatives of $C_3B_3H_7$ but essentially none of $C_2B_4H_8$, methylacetylene produces both carborane systems, and dimethylacetylene yields only the $C_2B_4H_8$ derivative. In the B_5H_{11} reactions the effect is similar except for the smaller over-all carborane yields.

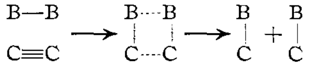
(3) The CB_5H_9 system is produced, in derivative form, in reactions of B_4H_{10} with all three alkynes but is not obtained from B_5H_{11}.

(4) Reaction of B_4H_{10} with a 9:1 excess of acetylene leads to an approximately ninefold increase in total carborane yield based on B_4H_{10} consumed (20-fold based on the starting quantity of B_4H_{10}) compared to the corresponding equimolar reaction.

Discussion

Little is established at present concerning the mechanisms of formation of carboranes from boranes in the gas phase. In the synthesis of 2,3-$C_2B_4H_8$ from B_5H_9 and C_2H_2, there is evidence that the acetylene unit remains intact without breakage of C–C or C–H bonds; thus C_2D_2 and B_5H_9 yield as a major product 2,3-$C_2D_2B_4H_6$ (*nido*-dicarbahexaborane-d_2) with both deuteriums attached to carbon.[12] Similar "alkyne-insertion" processes may well occur in the reactions discussed here, particularly in $C_2B_4H_8$ cage formation. However, carbon–carbon cleavage is clearly involved in the synthesis from C_2H_2 of at least some of the methylated C_3B_3 and CB_5 carboranes, *e.g.*, those containing odd numbers of carbons and those having methyl groups bound to boron.[13] Among these are the dimethyl derivatives of $C_3B_3H_7$ (which account for 70% of the volatile organoboron products of the C_2H_2–B_4H_{10} reaction) and several CB_5H_9 derivatives (Table I).

Although C—C cleavage has been observed at 215° in the synthesis[9] of B-methyl derivatives of 2-CB_5H_9 from C_2H_2 and B_5H_9, there seems to be no precedent for its occurrence in alkyne–borane vapor-phase systems at temperatures as low as 25–50°. It is interesting that a detailed study[5] of gas-phase reactions between B_2H_6 and various alkenes and alkynes gave no evidence of such cleavage at 75–90°, nor were carboranes produced (no reaction was reported below about 70°). The occurrence of C—C cleavage with B_4H_{10}, B_5H_{11}, and B_5H_9, but not with B_2H_6, suggests the involvement of direct B—B bonds (*i.e.*, those not involving H bridges). A diboration attack of B—B on C≡C may occur to give a four-center transition state resembling that proposed[14] for addition of H—B in hydroboration. The transition state, whose geometry seems likely to be planar, may break apart to produce fragments containing B—C links (bonds external to the ring are not shown)



The driving force for breakage of the C—C and B—B bonds in the transition state might well be related to the tendency of carbons to separate in the rearrangement[15,16] of *closo*-carboranes, particularly if the bonding in the four-center system is partially delocalized.

In further support of such a process it may be noted that (1) the mild reaction conditions tend to preclude drastic cleavage mechanisms and (2) only slight evidence of C—C cleavage is found in the reactions of methylacetylene and none at all with dimethylacetylene, suggesting steric interference with the cleavage process.

The tendency of B_5H_{11} to hydroborate, forming alkylboranes, and to hydrogenate the alkyne to the alkene (or even the alkane, as with dimethylacetylene) reflects an extremely facile loss of hydrogen by this unstable hydride. It is noteworthy, however, that whereas the reaction of B_5H_{11} with acetylene produces largely 2-ethylpentaborane(9), reaction of the same borane with ethylene[17] reportedly gives ethylpentaborane(11), dimethylenetetraborane, and ethyldiboranes, none of which was found in the present work. The possibility that ethylene is an important intermediate in the C_2H_2–B_5H_{11} reaction can therefore be ruled out. This result parallels the behavior of B_4H_{10}[18,19] and B_5H_9,[20] each of which reacts with ethylene in the gas phase to give organoboron products (mostly alkylboranes) which are distinct from those obtained with acetylene.

Experimental Section

Materials.—All reactants were chromatographically pure when used and were checked by infrared analysis. B_4H_{10} and B_5H_{11}

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(11) For consistency, most of these reactions were studied using equimolar alkyne–borane mixtures despite the low total yields of nonborane volatile products obtained under these conditions (~1–12.5% based on B_4H_{10} or B_5H_{11} consumed). However, the significance of the volatile products in regard to the over-all reaction mechanism is clear in the case of the C_2H_2–B_4H_{10} system, in which substantial yields of $C_3B_3H_7$ derivatives are obtained by the use of a high alkyne–borane mole ratio (Table I, reaction 2). (High carborane yields are also reported in reactions of B_5H_9 with alkynes in large excess.[8]) Although the sizable borane recoveries in the remaining reactions of B_4H_{10} and B_5H_{11} (Table I) suggest a comparable situation (*i.e.*, that a 1:1 reactant ratio is far from optimum for organoborane formation), no effort was made in the present investigation to maximize yields.

(12) (a) J. R. Spielman, R. Warren, G. B. Dunks, J. E. Scott, and T. Onak, *Inorg. Chem.*, **7**, 216 (1968); (b) D. A. Franz and R. N. Grimes, unpublished results. This appears to rule out a process of simple hydroboration (addition of two H–B to DCCD) followed by loss of H_2 (HD, D_2), which would lead to a mixture of $C_2D_2B_4H_6$, $C_2DHB_4H_6$, and $C_2H_2B_4H_6$. Since the last two are not observed, the addition mechanism is indicated.

(13) It may be noted that the evidence for C–C cleavage is independent of any assumptions concerning further structural details of these carboranes.

(14) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(15) W. N. Lipscomb, *Science*, **153**, 373 (1966).

(16) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1963.

(17) R. G. Maguire, I. J. Solomon, and M. J. Klein, *Inorg. Chem.*, **2**, 1133 (1963).

(18) B. C. Harrison, I. J. Solomon, R. D. Hites, and M. J. Klein, *J. Inorg. Nucl. Chem.*, **14**, 195 (1960).

(19) I. Shapiro, R. E. Williams, and S. G. Gibbins, *J. Phys. Chem.*, **65**, 1061 (1961).

(20) G. E. Ryschkewitsch, E. J. Mezey, E. R. Altwicker, H. H. Sisler, and A. B. Garrett, *Inorg. Chem.*, **2**, 893 (1963).

were prepared in quantities of several grams by allowing B_2H_6 (Olin Mathieson) at 600 psi to stand in a stainless steel cylinder at 35° for periods of 7–14 days,[21] followed by conventional fractionation on the vacuum line. B_4H_{10} was collected at −135° and B_5H_{11} at −78°. Acetylene and methylacetylene (both from Matheson) were fractionated through traps at −135 and at −95 and −150°, respectively. Dimethylacetylene (K & K) was purified using −63 and −95° traps.

Spectroscopy.—The instruments used included a Beckman IR-8 grating spectrophotometer, a CEC 21-103C mass spectrometer with digital readout, and Varian A-60 and HA-100 nmr spectrometers. Pyrex gas cells of 3.5–7.0 ml, fitted with salt windows, were used for infrared work.

General Procedure.—Each experiment was carried out by condensing measured quantities of reactants into an evacuated, degassed Pyrex bulb at −196°, sealing the bulb, and allowing it to stand at 25 or 50°. After completion of the reaction, the bulb was opened at its break-off tip and the volatile products were distilled into a vacuum system, initially at room temperature and finally at 80°. Highly volatile materials were removed by passage through a trap at −95° and purified by fractionation. All material condensing at −95° was gas chromatographed in a preparative-scale, air-free apparatus. Products emerging from the column were collected in traps cooled in liquid nitrogen; some compounds required repeated chromatography for complete purification. Three 9.5 ft × 0.25 in. columns were used at different times: 30% tricresyl phosphate, 30% Kel-F, and 30% Apiezon L grease, all on Chromosorb W solid support.[22] Yields were calculated from calibrated chromatographic peak areas or from direct gas measurement in the vacuum line.

Most of the reactions studied required repeated experiments in order to accumulate sufficient quantities of products for characterization. Each reaction was examined at both 25 and 50°, but the products in each case were qualitatively the same at the two temperatures. Since the 50° reactions were much more rapid, most experiments were run at that temperature.

Diborane and pentaborane(9) were identified in all reactions from their infrared spectra. Infrared data are given below only when previously unpublished, and data given in Table I are not repeated.

Tetraborane(10) and Acetylene.—The details have been reported previously.[3,10] In recent work, an unstable trace product (formerly conjectured to be the parent tricarbahexaborane(7)) has been isolated and clearly identified as hexaborane(12) from its infrared spectrum.[23]

Tetraborane(10) and Methylacetylene.—At 50° a white solid settled on the reactor bottom within 5 min, and after 1 hr a clear plastic-like material was observed over the entire surface, in addition to the white solid. After 2 hr no further change was noted. The same observations were made in the reaction at 25° over 14 days. On separation of the volatile products, propylene was identified from its infrared spectrum. $2\text{-}CH_3\text{-}2,3\text{-}C_2B_4H_7$ was characterized from ^1H and ^{11}B nmr, infrared, and mass spectra, and was identical with an authentic sample prepared[8] by pyrolysis of B_5H_9 with HC_2CH_3. The significant infrared bands (45 mm) are at 3010 (m), 2960 (s), 2920 (s), 2870 (m), 2600 (vs), 1925 (s), 1890 (sh), 1505 (sh), 1480 (vs), 1440 (s), 1380 (m), 1295 (w), 1150 (w), 1070 (s), 1030 (m), 963 (vs), 890 (m), 835 (s), 760 (sh), 730 (s), and 645 (s) cm^{-1}. $2\text{-}CH_3\text{-}2\text{-}CB_5H_8$ was identified from its mass spectrum, which matched the published data,[9] and its infrared spectrum, which contains no cage C–H stretch (3000-cm^{-1} region) but which has a strong bridge proton band at 1890 cm^{-1}. Two isomeric C,B-dimethyl derivatives of CB_5H_9 were characterized, but it was not possible to establish the locations of the B–CH_3 groups. The mass spectra of both isomers have sharp cutoffs at *m/e* 104, and the profiles are characteristic of *nido*-carboranes. Monoisotopic ^{11}B mass spectra of both isomers, calculated[24] assuming five B atoms, are very close to the monoisotopic spectrum of the known $2\text{-}CH_3\text{-}2\text{-}CB_5H_8$. Calculations assuming other than five B atoms did not give reasonable monoisotopic spectra. The infrared spectrum lacks cage C–H bands and shows strong B–CH_3 deformation near 1320 cm^{-1}. The infrared bands are, for isomer A (16 mm): 2960 (s), 2923 (s), 2870 (s), 2580 (vs), 1990 (s), 1560 (m), 1490 (vs), 1440 (vs), 1320 (s), 1240 (m), 1140 (w), 1105 (s), 995 (w), 960 (m), 910 (m), 870 (w), 820 (w), 695 (w) cm^{-1}; for isomer B (30 mm): 2950 (s), 2920 (s), 2865 (s), 2560 (s), 1980 (s), 1550 (m), 1475 (vs), 1440 (vs), 1318 (s), 1235 (s), 1140 (sh), 1105 (s), 990 (w), 960 (m), 910 (m), 870 (w), 825 (m), 690 (m) cm^{-1}.

$2\text{-}C_2H_5\text{-}3,4\text{-}(CH_3)_2\text{-}2,3,4\text{-}C_3B_3H_4$ was characterized from its infrared, ^1H nmr, and mass spectra. The parent peak is at *m/e* 132, and the calculated monoisotopic spectrum can be reconciled with the observed spectrum only when three borons are assumed. The infrared spectrum has neither cage C–H nor B–alkyl bands and is similar to the spectra[3] of known $C_3B_3H_7$ derivatives in the skeletal vibrational region. An alkyl $C_3B_3H_7$ derivative with four external carbons, none bonded to boron, is indicated. The ^1H nmr data (Table II) support the unsymmetrical $(CH_3)_2\text{-}C_2H_5C_3B_3H_4$ structure and confirm that no cage C–H group is present. The infrared bands (14 mm) are found at 2950 (s), 2920 (sh), 2870 (m), 2580 (vs), 1910 (m), 1580 (m), 1475 (m), 1460 (s), 1445 (s), 1380 (w), 1320 (w), 1250 (w), 1110 (w), 970 (w), and 925 (w) cm^{-1}.

Tetraborane(10) and Dimethylacetylene.—The reactions at 25 and 50° gave no solid deposits. Within 5 hr at 25°, and 20 min at 50°, liquid was observed condensing on the reactor walls and collecting at the bottom. On distilling off the volatiles, the liquid became viscous and finally solidified. The solid was not characterized. Except for traces of unidentified materials, the only volatile product was $2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_4H_6$, identified from its ^1H nmr,[25] infrared, and mass spectra. The infrared absorptions (40 mm) are at 2960 (sh), 2908 (vs), 2860 (s), 2560 (s), 1920 (s), 1450 (vs), 1370 (m), 1155 (m), 960 (s), 890 (s), 838 (s), 785 (w), 740 (s), 715 (sh), and 640 (s) cm^{-1}.

Pentaborane(11) and Acetylene.—At 25 and 50° a white, nonvolatile solid collected on the bottom half of the reactor; its appearance and properties were very similar to the solid obtained in the B_4H_{10}–C_2H_2 reaction. $2\text{-}CH_3\text{-}2,3,4\text{-}C_3B_3H_6$ and $2,4\text{-}(CH_3)_2\text{-}2,3,4\text{-}C_3B_3H_5$ were identified from their infrared spectra and vpc retention times, which are identical with those of the known compounds.[3] $2\text{-}C_2H_5B_5H_8$ (2-ethylpentaborane(9)) was characterized from its infrared spectrum.[26]

Pentaborane(11) and Methylacetylene.—In the 25 and 50° reactions a white solid collected in the bottom of the reactor and a transparent solid formed over the entire surface. Both materials were nonvolatile and appeared similar to those formed in the B_4H_{10}–HC_2CH_3 reaction, except that relatively less of the white solid and more of the clear material was noted in the B_5H_{11} reaction. Propylene and $2\text{-}CH_3\text{-}2,3\text{-}C_2B_4H_7$ were identified from their infrared spectra (see above).

Pentaborane(11) and Dimethylacetylene.—In experiments at both 25 and 50°, droplets of a greenish yellow, viscous liquid collected at the bottom of the reactor. As the volatiles were distilled out, the liquid solidified, giving a crystalline appearance which remained unchanged on prolonged pumping under vacuum at 80°. *n*-Butane, B_6H_{12}, and $2,3\text{-}(CH_3)_2\text{-}2,3\text{-}C_2B_4H_6$ were identified from their infrared spectra. *sec*-Butylpentaborane(9) was characterized from its infrared and mass spectra as follows. A sharp cutoff, indicative of a parent peak, appears in the mass spectrum at *m/e* 120, with no significant intensities at higher mass numbers. The infrared spectrum contains bands char-

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[21] We are indebted to W. V. Hough of the Callery Chemical Co. for suggesting this method.

[22] Retention volumes and other chromatographic parameters are available on request.

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acteristic of B_5H_9, especially at 892 (s), 1010 (m), 1385 (s), 1595 (m), and 1800 (m) cm^{-1}, in addition to absorptions attributable to B–H stretch and alkyl groups, at 2950 (vs), 2900 (s), 2860 (s), 2590 (vs), 1445 (s), 1165 (w), 1070 (w), 940 (w), 838 (w), 785 (m), 685 (w), and 630 (w) cm^{-1}. The single sharp spike at 2590 cm^{-1} eliminates BH_2 groups, and alkyl substituents other than butyl (*e.g.*, diethyl, ethyldimethyl) are precluded by the absence of bands in the 1280–1350-cm^{-1} range characteristic of B–CH_3 and B–C_2H_5 deformation. *sec*-Butyl and *n*-butyl ligands are not distinguishable by these data, but the *sec*-butyl structure is much more probable in view of the facile preparation from dimethylacetylene and the reported synthesis of 2-*sec*-butyl pentaborane(9) from B_5H_9 and 2-butene.[20]

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS 02138

Molecular and Crystal Structure of 1,7-Dimethyl-1,7-dicarbaclovooctaborane(8)

BY HASKELL HART AND WILLIAM N. LIPSCOMB

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The molecular structure of 1,7-dimethyl-1,7-dicarbaclovooctaborane(8), $B_6H_6C_2(CH_3)_2$, has C_2 symmetry. The B_2C_2 unit is nearly, but distorted from, the idealized D_{2d} geometry found earlier for B_8Cl_8 and recently for $B_8H_8^{2-}$. Molecular orbital calculations suggest that outermost electrons are most available on BH units 2 and 8 (connected to one C and three other B), next on BH units 5 and 6 (connected to one C and four other B), and least on BH units 3 and 4 (connected to two C and three other B) in the ground state. The crystal structure at −50° has the space group C2/c, four molecules in a unit cell having parameters $a = 15.243$, $b = 5.89$, $c = 12.740$ Å, and $\beta = 131.39°$, a calculated density of 0.968 g/cm³, and a final value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.11$ for 491 X-ray reflections.

The gas-phase reaction[1] of B_6H_{10} and dimethylacetylene and the pyrolysis[2] of $B_7C_2H_{11}(CH_3)_2$ in diphenyl ether yield $B_6H_6C_2(CH_3)_2$ along with other carboranes. Prior to our preliminary report,[3] the structure of $B_6H_6C_2(CH_3)_2$ was uncertain. The earlier interpretation[1] of the 12.8-Mc ^{11}B nuclear magnetic resonance (nmr) spectrum was based upon a chemically reasonable distortion of the polyhedron which was established earlier[4] in B_8Cl_8 and recently[5] in $B_8H_8^{2-}$ to have idealized symmetry D_{2d}. However, this interpretation requires that two different types of boron atoms have coincident ^{11}B nmr resonances. Confirmation of this coincidence at 19.3 Mc led[2] to some favoritism for a structure based, when idealized, upon an Archimedian antiprism of D_{4d} symmetry for an equal-atom structure. On the other hand, the theoretical treatment by Hoffmann and Lipscomb[6] of B_8H_8 of D_{2d} symmetry indicated an unfilled singly degenerate level immediately above the filled levels, thus providing a reasonable basis for prediction of a $B_8H_8^{2-}$ structure of D_{2d} symmetry. The possibilities of distortions, an intermediate structure, or a dynamical fluctuating structure (unlikely at room temperature) between the two idealized extremes based upon equal-atom D_{2d} and D_{4d} structures have all been discussed[6] as part of the structural ambiguities of this B_6C_2 polyhedron. We show here that small distortions do indeed occur toward such an intermediate structure. Also, the attachment of methyl groups to the C atoms allows us to establish with certainty the positions of the C atom in the B_6C_2 molecule.

Structure Determination

Single crystals about 0.5 × 0.5 × 1 mm were grown from the neat liquid (mp −39 to −40°) which had been sealed into glass capillaries. The crystal was maintained at approximately −50° by means of a stream of cold gaseous nitrogen.[7] Extinction of $h0l$, when h or l is odd, and of hkl, when $h + k$ is odd, are consistent with space groups Cc or C2/c. Monoclinic unit cell parameters, calibrated by least squares from a superimposed powder diffraction pattern of Al ($a = 4.0493$ Å) are $a = 15.243 \pm 0.003$ Å, $c = 12.740 \pm 0.002$ Å, and $\beta = 131.39 \pm 0.03°$, as determined from a Weissenberg $h0l$ zone taken with the aid of Cu Kα radiation (λ 1.54178 Å). The two estimates of $b = 5.88$ and 5.90 Å (average 5.89 Å) were made[8] from a precession photograph of the $hk0$ zone taken with the aid of MoKα radiation (λ 0.71069 Å). This separate determination of $b = 5.89 \pm 0.01$ Å was necessary because the crystals grew so that the b axis was consistently along the capillary axis.

Weissenberg multiple films were taken of hkl data for $0 \leqslant k \leqslant 4$ with Ni-filtered Cu Kα radiation, and

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