Formation of Open-Cage and Closed-Cage Carboranes from Tetraborane(10) and Acetylene

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Abstract: The vapor-phase reaction of tetraborane(10) and acetylene has been examined at 25, 50, and 100°, and the volatile products were isolated and structurally characterized. At 25 and 50°, methyl derivatives of tricarbahexaborane(7) and monocarbahexaborane(9) are formed. At 100° a flash reaction takes place in which nine volatile products are obtained, all of which are closed-cage carboranes having three to eight boron atoms. Pyrolysis of the 2-methyl and 2,4-dimethyl derivatives of 2,3,4-tricarbahexaborane(7) yields no carboranes, but the 2,3-dimethyl derivative produces new dimethyl derivatives of 2,4-dicarbaclovoheptaborane(7) and tricarbahexaborane(7) in small yields. Comparison of these results with earlier work from several laboratories permits some tentative conclusions concerning carborane formation in vapor-phase alkyne–borane reactions.

In recent years a number of carborane cage compounds have been synthesized by direct reactions of unsaturated hydrocarbons with boranes in the vapor phase. Several observations concerning these reaction systems now seem to have general significance:[2] (1) while alkynes often lead to carborane formation, alkenes do not; (2) formation of closed-cage species (the $C_2B_nH_{n+2}$ series) is favored in high-energy situations such as electric discharges[3-6] or flash reactions;[5,6] (3) synthesis of open-cage carboranes containing hydrogen bridges, *e.g.*, CB_5H_9,[7] $C_2B_4H_8$,[8] $C_3B_3H_7$,[9] or alkyl derivatives of these, occurs under comparatively mild conditions (thermally induced reactions at 25 to 215°); (4) formation of methyl-substituted carboranes from acetylene is common in both high-energy and low-energy reactions;[5-7,9] (5) methyl substitution occurs predominantly in boron cage positions in the high-energy syntheses, but C-methylation is frequently observed in low-energy reactions.

Previous reports of carborane formation from boranes in the vapor phase have involved B_2H_6,[5,6] B_5H_9,[3,4,7,8] or B_6H_{10}[10] as reactants. The action of B_4H_{10} on ethylene has been studied,[11,12] but no carboranes are produced and the principal product is 2,4-dimethylenetetraborane. In this paper we describe an investigation of the vapor-phase interaction between B_4H_{10} and acetylene in which both open- and closed-cage carboranes were obtained under varying conditions.[13] The results of this study lend further support to the above generalizations and offer some insight into the nature of the carborane-forming processes in these systems.

Results and Discussion

Reactions at 25 and 50°. The gas-phase reaction between chromatographically pure B_4H_{10} and C_2H_2 in a 1:1 mole ratio takes place slowly at room temperature, and more rapidly at 50°, to give a white, nonvolatile organoboron polymer and several volatile carboranes, all having open-cage structures (Table I). In addition to B_5H_9 and an unstable material which may be the parent 2,3,4-tricarbahexaborane(7), the products are the 2-methyl, 2,3-dimethyl, and 2,4-dimethyl derivatives of 2,3,4-tricarbahexaborane(7), the infrared spectra of which are presented in Table II, plus 4-methyl-2-carbahexaborane(9). (The last-mentioned compound has been previously reported[7] as a product of the reaction of B_5H_9 with C_2H_2 at 215°.) No other volatile materials have been detected in significant amounts despite the use of sensitive chromatographic methods, and the same products were obtained at 50 as at 25°.

The white solid is highly reactive toward both dry air, in which it inflames, and moisture, which rapidly degrades it to boric acid. Infrared analysis indicates the presence of both CH and BH_2 groups and strongly suggests a polymeric structure. The formation of this material is not wall catalyzed, since it is produced homogeneously throughout the reactor and settles to the bottom, and it appears to be the major product of a gas-phase hydroboration attack of acetylene on B_4H_{10} in which the volatile carboranes are side products.

These results for the B_4H_{10}–C_2H_2 system are in sharp contrast to those recently reported for the B_2H_6–C_2H_2 gas-phase reaction,[14] in which ethyldiborane and 1,1-diethyldiborane were the major volatile products at 85° and no carboranes were found. Thus it is clear that none of the carborane products obtained in the present work could have resulted from direct interactions between C_2H_2 and B_2H_6 (some of which is always present as a decomposition product in B_4H_{10} vapor). Moreover, since other experiments[15] have established that neither B_5H_9 nor B_5H_{11} combines with C_2H_2 at room

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[1] Philip Francis du Pont Predoctoral Fellow, 1965–1967.

[2] Although both open- and closed-cage carboranes have been prepared by other methods, we wish to restrict this discussion to direct gas-phase reactions between hydrocarbons and boranes.

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

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

[5] R. N. Grimes, *ibid.*, **88**, 1070 (1966).

[6] R. N. Grimes, *ibid.*, **88**, 1895 (1966).

[7] T. P. Onak, G. B. Dunks, J. R. Spielman, F. J. Gerhart, and R. E. Williams, *ibid.*, **88**, 2061 (1966).

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

[9] C. L. Bramlett and R. N. Grimes, *J. Am. Chem. Soc.*, **88**, 4269 (1966).

[10] R. E. Williams and F. J. Gerhart, *ibid.*, **87**, 3513 (1965).

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

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

[13] A preliminary report on a portion of this work has appeared; see ref 9.

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

[15] R. L. Vance and R. N. Grimes, unpublished results.

Table I. Reactions of B_4H_{10} with C_2H_2[a]

Reactants, mmoles (500-ml flask)		Temp, °C	Reaction time, hr	Reactants recovered, mmoles		Mole % of volatile products[b,c]															Total volatile products, mmoles
						2,3,4-$C_3B_3H_7$ deriv				1,5-$C_2B_3H_5$ deriv	1,6-$C_2B_4H_6$ deriv	2,4-$C_2B_5H_7$ deriv					Other				
B_4H_{10}	C_2H_2			B_4H_{10}	C_2H_2	1a	1b	1c	1d	2a	3a	4a	4b	4c	4d	4e	5a	6a	7a	7b	
3.33	3.37	25	140	1.68	0.0	3	15	21	18	0	0	0	0	0	0	0	2	41	0	0	0.097
3.60	7.20	25	192	0.88	0.0	...[d]	15	26	18	0	0	0	0	0	0	0	4	37	0	0	0.114
0.89[e]	0.82[e]	50	3.8	0.48	0.0	...[d]	7	14	6	0	0	0	0	0	0	0	...[d]	70	0	0	0.034
3.58	3.58	100	...[f]	0.0	0.10	0	0	0	0	4	4	35	9	17	9	4	0	0	11	7	0.116
0.98	1.92	100	...[g]																		

[a] Typical experiments; gas phase. [b] Exclusive of H_2. [c] Key: 1a = $C_3B_3H_7$(?), 1b = 2-$CH_3C_3B_3H_6$, 1c = 2,3-$(CH_3)_2C_3B_3H_5$, 1d = 2,4-$(CH_3)_2C_3B_3H_5$, 2a = 2-CH_3-1,5-$C_2B_3H_4$, 3a = 1,6-$C_2B_4H_6$, 4a = 2,4-$C_2B_5H_7$, 4b = 1-CH_3-2,4-$C_2B_5H_6$, 4c = 2-CH_3-2,4-$C_2B_5H_6$, 4d = 3-CH_3-2,4-$C_2B_5H_6$, 4e = 5-CH_3-2,4-$C_2B_5H_6$, 5a = 4-CH_3-2-CB_5H_8, 6a = B_5H_9, 7a = $C_2B_8H_{10}$, 7b = B-$CH_3C_2B_8H_9$. [d] Trace. [e] 125-ml flask. [f] Flashed after 6 min at 100°. [g] Exploded violently after 5 min at 100°.

Table II. Gas Infrared Spectra of Tricarbahexaborane(7) Derivatives[a]

2-CH_3-$C_3B_3H_6$	2,3-$(CH_3)_2$-$C_3B_3H_5$	2,4-$(CH_3)_2$-$C_3B_3H_5$
3070 sh	3010 sh	3030 m
3030 m	3000 sh	2950 vs
2960 s	2950 vs	2910 m
2920 s	2920 vs	2880 m
2870 s	2870 m	2590 vs
2590 vs	2830 sh	1980 w
1900 m, b	2590 vs	1950 m, b
1840 sh	1975 w	1500 m
1530 s	1920 m	1455 s
1440 s	1870 m	1360 m
1328 m	1585 w	1290 w
1225 m	1470 vs	1140 sh
1065 m	1450 sh	1110 m
1020 w	1390 m	1060 m
990 sh	1320 m	1000 w, b
950 m	1210 m	945 w
905 w	1160 w	815 s
825 m	1125 m	790 m
765 m	1065 w	735 w
690 m	990 sh	
615 m	940 s	
	880 w	
	835 m	
	755 m	
	725 m	

[a] In cm^{-1} at 25 mm pressure.

temperature to give more than traces of the tricarbahexaborane(7) products in Table I, it is apparent that the two pentaboranes, as such, are not significant intermediates in the formation of the $C_3B_3H_7$ derivatives from B_4H_{10}. We conclude, then, that formation of the $C_3B_3H_7$ products is initiated by a direct attack of C_2H_2 on B_4H_{10} itself or on a fragment formed therefrom (B_3H_7 is a reasonable possibility).

Reaction at 100°. The interaction between B_4H_{10} and C_2H_2 at 100° is of an entirely different nature from that occurring at 25 or 50°. Within a few minutes an equimolar mixture flashes, yielding dark gray solids and a series of nine volatile closed-cage carboranes having no hydrogen bridges (Table I). With the exception of 2-$CH_3C_2B_5H_6$, $C_2B_8H_{10}$, and B-$CH_3C_2B_8H_9$, the same species have also been produced in electric discharges of B_2H_6–C_2H_2 mixtures,[6] which implies somewhat similar mechanisms. It is notable, however, that among the products obtained in the present study there is no indication of the 1,2-$C_2B_3H_5$ methyl derivatives[5,6,16] which were significant products of the B_2H_6–C_2H_2 discharge reaction.

Pyrolysis of Tricarbahexaborane(7) Derivatives. In order to examine the possibility that the alkylated $C_3B_3H_7$ species which form at low temperatures might be intermediates in the synthesis of closed-cage carboranes at 100°, vapor-phase pyrolysis experiments have been carried out on the three $C_3B_3H_7$ methyl derivatives obtained in the B_4H_{10}–C_2H_2 reaction at 25°. All three compounds are completely stable at 100°, and neither 2-$CH_3C_3B_3H_6$ nor 2,4-$(CH_3)_2$-$C_3B_3H_5$ is affected by heating at 250° for several days, although the latter substance decomposes at 350° to hydrogen and nonvolatile solids. The 2,3-dimethyl derivative, on the other hand, at 250° gives traces of a dimethyl-2,4-dicarbaclovoheptaborane(7) plus a B,C-dimethyl derivative of $C_3B_3H_7$, and at 300° yields a small quantity of a second $(CH_3)_2C_2B_5H_5$ product which appears to be alkylated at the B(1) and B(7) positions.

Clearly the $C_3B_3H_7$ derivatives are not significant precursors of the closed-cage molecules which form in the 100° reaction.[17] Indeed it is not surprising that the $C_3B_3H_7$ cage system appears to have far less tendency to form closed-cage carboranes on pyrolysis than does the structurally similar (and isoelectronic) $C_2B_4H_8$.[8,18] This is to be expected from the accepted valence theory for the polyhedral carboranes, which requires two cage carbon atoms and therefore necessitates the formal "ejection" of one carbon from the $C_3B_3H_7$ framework before closure can be completed.

While a detailed clarification of the reaction mechanisms involved in acetylene–borane interactions is not yet available, a comparison of the results of this work with those from earlier investigations does permit some tentative observations. First, it is now evident that, in the low-energy reactions, the nature of the products obtained is strongly dependent on the specific borane starting material. As the data in Table III indicate, the four boranes whose gas-phase reactions with acetylene have been studied under moderate conditions give almost totally different sets of products.[18a] This is certainly reasonable from the viewpoint that the experimental conditions in each case do not presage extensive

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(16) R. N. Grimes, *J. Organometal. Chem.* (Amsterdam), in press.

(17) The possibility of interaction between the $C_3B_3H_7$ derivatives and C_2H_2 was eliminated by appropriate control experiments in which no reaction was observed.

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

(18a) NOTE ADDED IN PROOF. Results obtained in this laboratory on the B_5H_{11}–C_2H_2 system fit the pattern indicated in Tables III and IV. At 25° the major product is 2-$C_2H_5B_5H_8$, while the 100° flash reaction virtually duplicates the results of the 100° B_4H_{10}–C_2H_2 reaction.

disintegration of the borane framework, and the organoboron products evidently retain many of the B–H and/or B–B bonds present in the borane reactant.

Table III. Low-Energy Borane–Acetylene Reactions[a]

Borane reactant	Temp,[b] °C	Volatile organoboron products	Ref
B_2H_6	70	$C_2H_5B_2H_5$ + 1,1-$(C_2H_5)_2B_2H_4$	14
B_4H_{10}	25–50	Three methyl derivatives of 2,3,4-$C_3B_3H_7$ + small amount of 4-CH_3-2-CB_5H_8	This work
B_5H_9	215	2,3-$C_2B_4H_8$ + three methyl derivatives of 2-CB_5H_9	7, 8
B_6H_{10}[c]	200	$(CH_3)_2C_2B_6H_6$	10

[a] Vapor phase. [b] Temperatures cited are the lowest at which reaction was reported to occur. [c] Reaction with $(CH_3)_2C_2$.

In considering the rapid, high-energy interactions between acetylene and boranes, however, one is led to a different conclusion. Although some variation in product mixtures is evident in the three systems that have been studied (Table IV), *all* of the volatile organoboron products so far identified in these reactions are closed-cage carboranes. It should be noted further that two cage systems, 1,6-$C_2B_4H_6$ and 2,4-$C_2B_5H_7$, are predominant in each case. At least insofar as these three reaction systems are concerned, it is apparent that the specific cage structure of the borane reactant is not a major factor in determining final product structures, and that mechanisms involving severe disruption of the borane framework must be dominant. In this situation it may be assumed that the final product distribution is largely determined by the relative thermodynamic stabilities of the carborane cage systems.

Table IV. High-Energy Borane–Acetylene Reactions[a]

Borane reactant	Reaction conditions	Volatile organoboron products	Ref
B_2H_6	Flash or glow discharge	1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, and methyl derivatives of these; + $(CH_3)_2$-1,2-$C_2B_3H_5$ (two isomers); + higher carboranes	5, 6, 16
B_4H_{10}	Flash	1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, and methyl derivatives of these; + $C_2B_8H_{10}$ and B-$CH_3C_2B_8H_9$	This work
B_5H_9	Glow discharge	1,5-$C_2B_3H_5$, 1,6-$C_2B_4H_6$, 1,2-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, plus unidentified products	3, 4

[a] Vapor phase.

In summary, it is reasonable to expect that still untried high-energy vapor-phase interactions between boranes and acetylene will yield a series of closed-cage carboranes and derivatives similar to those in Table IV.[18a] As a consequence, the remaining undiscovered carborane systems will most probably be synthesized under relatively mild, controlled reaction conditions which favor at least partial retention of the original borane cage structure and which limit the extent of cage rearrangement in the products.

Experimental Section

Materials. B_4H_{10} was prepared from B_2H_6 (Olin Mathieson) by the hot-cold reactor method of Klein, *et al.*,[19] and was purified by repeated fractionation through traps at −95 and −135°; the purity was monitored by gas chromatography and infrared spectra. C_2H_2 (Matheson) was purified by passage through a −135° trap several times and was checked by infrared analysis.

Procedures. All reactions were carried out in sealed Pyrex bulbs equipped with break-off tips. Volatile products were separated by preparative-scale gas chromatography under air-free conditions using either a 9.5 ft × 0.25 in. column of tricresyl phosphate on Chromosorb W or a 9.5 ft × 0.25 in. column of Kel-F on Chromosorb W. Purification of individual products was effected by repeated passages through the column when necessary.

Spectroscopy. Infrared spectra were obtained on a Beckman IR-8 grating spectrophotometer. Gas infrared spectra were measured in a 3.5-ml, 9-cm Pyrex cell with NaCl windows. Mass spectra were recorded on a CEC 21-103C spectrometer with digital readout, proton nmr spectra were obtained on a Varian A-60 instrument, and ^{11}B nmr spectra were measured with a Varian HR-100 spectrometer at 32.2 Mc.

Reactions of Tetraborane(10) with Acetylene. Measured quantities of tetraborane(10) and acetylene were condensed into an evacuated 125- or 500-ml flask cooled in liquid nitrogen, after which the reactor was sealed and the reaction allowed to proceed to the desired temperature (Table I). At 25°, reaction was evidenced after 1 to 2 hr by the accumulation of a white solid at the bottom. At 50° the same effect was noted within 2 to 3 min. In the experiments at 100°, typically within 6 min a flash was observed with instantaneous formation of large quantities of dark solids, which were not investigated. No breakage of the reactor was observed when the C_2H_2:B_4H_{10} ratio was 1.0 or less, but when a 2:1 ratio was used the result was a violent explosion (Table I).

Following each experiment most of the unreacted B_4H_{10} and C_2H_2 was removed by passage through a trap at −95°, after which the volatile products were separated by chromatography as described above. 2-$CH_3C_3B_3H_6$, 2,3-$(CH_3)_2C_3B_3H_5$, and 2,4-$(CH_3)_2$-$C_3B_3H_5$ were structurally characterized by means of their ^1H and ^{11}B nmr, infrared, and mass spectra as reported earlier.[9] An additional product which has an infrared spectrum similar to the three $C_3B_3H_7$ derivatives, except for the bands attributable to methyl groups, is possibly the parent $C_3B_3H_7$, but further investigation of this material was hampered by its instability even at room temperature. 4-$CH_3CB_5H_8$ was identified from its mass spectrum, which is in precise agreement with the published spectrum[7] and is clearly distinguishable from the other known carborane fragmentation patterns.

Several attempts to remove the white polymer from the reactor in order to obtain an infrared spectrum were unsuccessful, even in dry argon, due to reaction with traces of oxygen or moisture. This problem was finally circumvented by allowing the reaction between B_4H_{10} and C_2H_2 to proceed in a gas infrared cell in such a manner that the solid collected on the NaCl windows. All volatile materials were then removed, and the spectrum of the solid was recorded. The only well-defined bands are at 2900 and 2500 cm^{-1}, but a series of broad absorptions appears between 700 and 1500 cm^{-1}. The spectrum was unchanged after the cell had stood 13 days at room temperature.

Of the products obtained in the 100° flash reaction, the following were identified by comparison of their infrared and mass spectra[3-6] with those of authentic samples: 2-CH_3-1,5-$C_2B_3H_4$, 1,6-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, 1-CH_3-2,4-$C_2B_5H_6$, 3-CH_3-2,4-$C_2B_5H_6$, and 5-CH_3-2,4-$C_2B_5H_6$. 2-CH_3-2,4-$C_2B_5H_6$, which is the only other possible monomethyl derivative[20] of 2,4-$C_2B_5H_7$, was characterized from its mass spectrum (high-mass cutoff = *m/e* 100, and the calculated boron-11 monoisotopic fragmentation pattern closely resembles the patterns of known $C_2B_5H_7$ derivatives) and its infrared absorption bands, which appear at 2925 (s), 2870 (m), 2590 (vs), 1440 (m, b), 1195 (s), 1110 (m), 1025 (m), 955 (w), 890 (w), 850 (w), 780 (w), and 710 (m) cm^{-1}. Absence of bridge hydrogens is indicated by the lack of absorptions between 1500 and 2500 cm^{-1}. The existence of a band at 1440 cm^{-1}, while none is found near 1320 cm^{-1},

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(19) M. J. Klein, B. C. Harrison, and I. Solomon, *J. Am. Chem. Soc.*, 80, 4149 (1958).

(20) Excluding optical isomers.

is indicative of a C-methyl rather than a B-methyl group, and the spectrum in the cage vibrational region (700 to 1200 cm^{-1}) is similar to the spectra[6] of 2,4-$C_2B_5H_7$ and its derivatives.

Identification of $C_2B_8H_{10}$ was accomplished from its mass spectrum (high-mass cutoff = *m/e* 122, and the fragmentation pattern is characteristic of a closed-cage carborane[21]) and the infrared spectrum, which discloses no alkyl substituents or bridge hydrogens. Bands are observed at 3090 (w), 2590 (vs), 1310 (w, b), 1125 (s), 1110 (sh), 1040 (w), 970 (m), 960 (m), 945 (m), 880 (m), 815 (m), 775 (s), and 660 (s) cm^{-1}. Since the spectrum of authentic C,C'-$(CH_3)_2$-1,6-$C_2B_8H_8$ is similar in the cage vibrational region, while that of C,C'-$(CH_3)_2$-1,10-$C_2B_8H_8$ is quite different,[22] it seems likely that the $C_2B_8H_{10}$ product described here is the 1,6 isomer.

Characterization of the B-methyl derivative of $C_2B_8H_{10}$ was similarly based on infrared and mass spectra. The high-mass cutoff is at *m/e* 136, and the fragmentation pattern is very close to that of the $C_2B_8H_{10}$ described above. The infrared bands are at 2940 (w), 2585 (vs), 1315 (s), 1170 (m), 1130 (s), 1090 (w), 1030 (w, b), 970 (w, b), and 670 (m) cm^{-1}. B-Methyl deformation is indicated by the characteristic band at 1315 cm^{-1} and the absence of a significant absorption near 1450 cm^{-1} (C–CH_3 deformations).

Pyrolysis of Tricarbahexaborane(7) Derivatives. 2-$CH_3C_3B_3H_6$ (0.03 mmole) was sealed in a 7-ml reactor and heated 5 days at 250°, at the end of which all of the starting material was recovered unchanged. Similarly, 2,4-$(CH_3)_2C_3B_3H_5$ (0.01 mmole) in a 15-ml tube did not react in 16 hr at 250°. The same sample was replaced in the reactor and heated 19 hr at 350°, after which only nonvolatile solids and H_2 remained.

2,3-$(CH_3)_2C_3B_3H_5$ (0.100 mmole) in a 10-ml tube failed to react at 100° over a 20-hr period. The same sample in 120 hr at 250° gave cleanly, with no solids, 0.016 mmole of a dimethyl derivative of 2,4-$C_2B_5H_7$. The mass spectrum of this compound has a high-mass cutoff at *m/e* 114, and the calculated boron-11 monoisotopic spectrum is characteristic of the 2,4-$C_2B_5H_7$ cage structure. The infrared spectrum has bands indicating C–H, B–H, C–CH_3, and B–CH_3 groups, and the cage vibrational bands are similar to those of known 2,4-$C_2B_5H_7$ derivatives.[6] Also obtained in the same pyrolysis was 0.012 mmole of a product characterized as a B,C-dimethyl derivative of 2,3,4-$C_3B_3H_7$. The mass spectrum has a high-mass cutoff at *m/e* 104 and the fragmentation pattern closely matches those of the known derivatives of $C_3B_3H_7$.[9] Moreover, calculated boron-11 monoisotopic spectra can be fitted to the observed data only when three borons or fewer are assumed. The infrared spectrum contains, in addition to C–H, B–H, and bridge proton bands, absorptions at 1450 and 1320 cm^{-1} which are characteristic of C–CH_3 and B–CH_3 deformations, respectively.

The same starting material (2,3-$(CH_3)_2C_3B_3H_5$, 0.045 mmole) was heated to 300° for 7 days, after which chromatographic and infrared analyses disclosed the same two products as were obtained at 250° (see above), plus an additional product which is probably 1,7-$(CH_3)_2$-2,4-$C_2B_5H_5$. Identification was by means of the mass spectrum (high-mass cutoff at *m/e* 114) and the infrared spectrum, which contains no C–CH_3 deformation bands but has a very strong absorption at 1320 cm^{-1}, the B–CH_3 deformation frequency. In addition, the cage vibrational region is remarkably similar to that in 1-CH_3-2,4-$C_2B_5H_6$ (the monoapically substituted derivative),[6] which is taken as a strong indication that this product is the 1,7 (diapically substituted) derivative.

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[21] A compact, stable framework which resists breakdown is indicated by the fact that the peaks in the parent group (fragments formed by loss of H only) are the most intense in the spectrum; see ref 3, 4, 7, and 16.

[22] The spectra of the dimethyl derivatives of $C_2B_8H_{10}$ were provided by Professor M. F. Hawthorne, University of California, Riverside, Calif.