a variation in the enthalpy change of reaction 6 from −25 to −37 kcal. Such limits appear to be reasonably cautious. Combining these with the uncertainty in the energy expended in lattice expansion, it appears appropriate to set limits of about ±8 kcal on this value of −31 kcal/mol for the minimum hydrogen-bond energy of $B_2H_7^-$.

The large magnitude of the $B_2H_7^-$ hydrogen-bond energy (second only to the FHF^- at −37 kcal)[18] may be taken to mean that the lone pair of electrons usually considered to be necessary for hydrogen bonding may actually be destabilizing in their effect on the hydrogen-bond energy. In the molecular orbital approach to hydrogen bonding,[19] only an orbital, either vacant or filled, is necessary for the hydrogen-acceptor atom. If the available orbital is filled with an electron pair, this pair will end up in a nonbonding molecular orbital. The present datum for the H-bond energy of the $B_2H_7^-$ species makes it appear that the "nonbonding" orbital may actually be antibonding in character. The only other hydrogen-bond energies for electron-deficient systems which are currently available are −17.5 kcal/H bond for diborane[16] and an estimate by Coates[20] of −15 to −20 kcal/H bond for the $(C_2H_5)_2$-AlH polymer. These values are much larger than the value for other H bonds in neutral species and again imply that the lone electron pairs contributed to hydrogen bonds may be antibonding in character.

Acknowledgment.—We are grateful to the National Science Foundation for support of this work.

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[18] S. A. Harrell and D. H. McDaniel, *J. Am. Chem. Soc.*, **86**, 4497 (1964).

[19] G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

[20] G. E. Coates, "Organo-Metallic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1960, p 142.

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High-Yield Synthesis of the Smaller *closo*-Carboranes $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$

BY J. F. DITTER

Received January 22, 1968

Under conditions of relatively high temperature, low pressure, and short residence time the *nido*-carborane 4,5-$C_2B_4H_8$ is converted in nearly 100% yield to the three *closo*-carboranes 1,5-$C_2B_3H_5$, 1,6- (and a little 1,2-) $C_2B_4H_6$, and 2,4-$C_2B_5H_7$. Conditions have not yet been completely optimized, but at 450–460° at 10 mm pressure for 1–3 sec (continuous flow system) 25–30% of the $C_2B_4H_8$ is converted approximately as follows: 40% $C_2B_3H_5$, 20% $C_2B_4H_6$, and 40% $C_2B_5H_7$, based on moles of $C_2B_4H_8$ consumed. The mechanism of formation of $C_2B_3H_5$ and $C_2B_5H_7$ appears to be *via* disproportionation of two $C_2B_4H_8$ molecules, while $C_2B_4H_6$ probably forms by simple loss of hydrogen from the $C_2B_4H_8$ parent.

Introduction

The first *closo*-carboranes discovered,[1–4] 1,5-$C_2B_3H_5$, 1,6- (and 1,2-) $C_2B_4H_6$, and 2,4-$C_2B_5H_7$, with the respective systematic names *closo*-1,5-dicarbapentaborane-5, *closo*-1,6-dicarbahexaborane-6, and *closo*-2,4-dicarbaheptaborane-7, were initially produced only in trace amounts from B_5H_9 and HCCH in a silent electric-discharge apparatus, and their derivative chemistry consequently has suffered from the lack of ready availability. In striking contrast the initially realized yields of the icosahedral *closo*-dicarbadodecaborane-12 $C_2B_{10}H_{12}$, which was discovered and characterized[5–16] independently of the small *closo*-carboranes, were much greater. Consequently its derivative chemistry, including the production of superior polymers by incorporation of $-C_2B_{10}H_{10}-$ moieties into silicones, has far outdistanced the derivative chemistry of $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$.[17] As to the compounds in the $C_2B_nH_{n+2}$ *closo*-carborane series lying between $C_2B_5H_7$ and $C_2B_{10}H_{12}$, routes to at least one isomer of each species have been discovered within the past 5 years. These include $C_2B_6H_8$,[18,19]

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[1] C. D. Good and R. E. Williams, U. S. Patent 3,030,289 (1959); *Chem. Abstr.*, **57**, 12534*b* (1962).

[2] R. E. Williams, C. D. Good, and I. Shapiro, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1961, p 14N.

[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] T. L. Heying, J. W. Ager, S. L. Clark, D. J. Mangold, H. L. Goldstein, M. Hillman, R. J. Polak, and J. W. Szymanski, *Inorg. Chem.*, **2**, 1089 (1963).

[6] T. L. Heying, J. W. Ager, S. L. Clark, R. P. Alexander, S. Papetti, J. A. Reid, and S. I. Trotz, *ibid.*, **2**, 1097 (1963).

[7] M. M. Fein, J. Bobinski, N. Mayes, N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1111 (1963).

[8] M. M. Fein, D. Grafstein, J. E. Paustian, J. Bobinski, B. M. Lichstein, N. Mayes, N. N. Schwartz, and M. S. Cohen, *ibid.*, **2**, 1115 (1963).

[9] D. Grafstein, J. Bobinski, J. Dvorak, H. Smith, N. Schwartz, M. S. Cohen, and M. M. Fein, *ibid.*, **2**, 1120 (1963).

[10] D. Grafstein, J. Bobinski, J. Dvorak, J. E. Paustian, H. F. Smith, S. Karlin, C. Vogel, and M. M. Fein, *ibid.*, **2**, 1125 (1963).

[11] D. Grafstein and J. Dvorak, *ibid.*, **2**, 1128 (1963); U. S. Patent 3,226,429 (1961).

[12] H. Schroeder, T. L. Heying, and J. R. Reiner, *ibid.*, **2**, 1092 (1963).

[13] H. Schroeder and G. D. Vickers, *ibid.*, **2**, 1317 (1963).

[14] S. Papetti and T. L. Heying, *ibid.*, **2**, 1105 (1963).

[15] L. I. Zakharkin, V. I. Stanko, V. A. Brattsev, Yu. A. Chapovskii, and O. Yu. Ochlobystin, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 2238 (1963); *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 2074 (1963).

[16] V. I. Stanko, Yu. A. Chapovskii, V. A. Brattsev, and L. I. Zakharkin, *Usp. Khim.*, **34**, 1011 (1965); *Russ. Chem. Rev.*, 424 (1965); *Chem. Abstr.*, **63**, 9429*c* (1965).

[17] S. Papetti, B. B. Schaeffer, A. P. Gray, and T. L. Heying, *J. Polymer Sci.*, **4**, 1623 (1966).

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

[19] F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *ibid.*, **88**, 609 (1966).

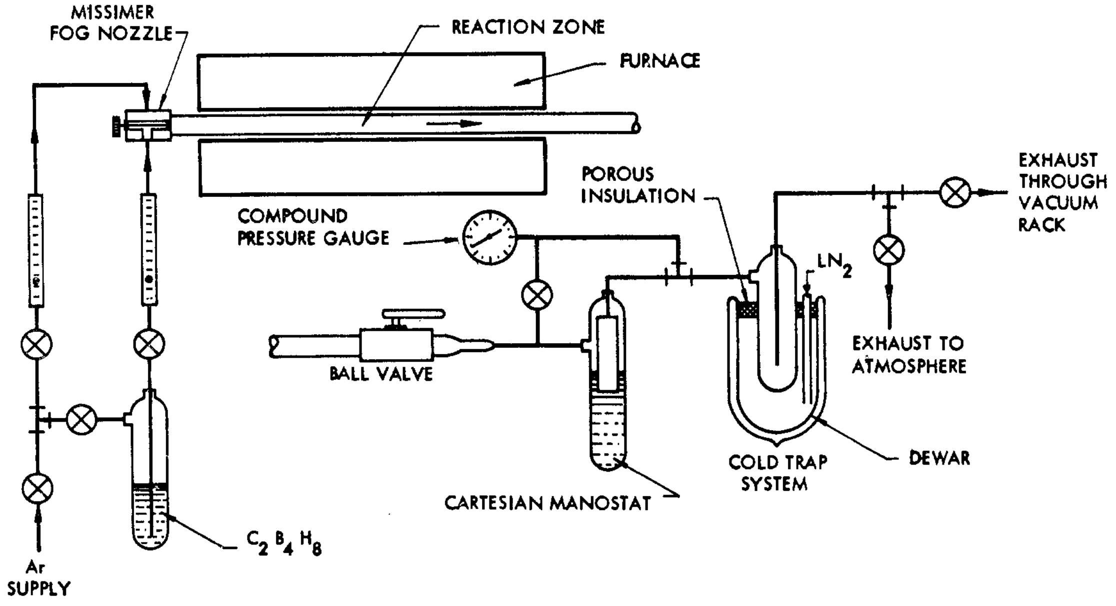

Figure 1.—Schematic diagram of $C_2B_4H_8$ pyrolysis apparatus.

$C_2B_7H_9$,[19] $C_2B_8H_{10}$,[19] and $C_2B_9H_{11}$.[20] Also of importance in this respect have been a greatly improved route to the synthesis of $C_2B_5H_7$[21] and the recent synthesis of the parent *closo*-carborane, $C_2B_{10}H_{12}$, from the borohydride ion and diborane.[22,23] For a general review in this field the reader is referred to the paper by Köster and Grassberger.[24]

The aforementioned high-yield route to $C_2B_5H_7$ was secured by first preparing the *nido*-carborane $C_2B_4H_8$[21,25] from B_5H_9 and C_2H_2 in about 40% yield, and then converting it to $C_2B_5H_7$ by pyrolysis, again in about 40% yield. The fact that the transformation of $C_2B_4H_8$ into $C_2B_5H_7$ repeatedly occurred in yields approaching but never exceeding 50% led us to suspect that the reaction was a disproportionation of two $C_2B_4H_8$ molecules into a molecule of $C_2B_5H_7$ and one of $C_2B_3H_5$ and that the $C_2B_3H_5$ was never observed as a product simply because it decomposed. $C_2B_3H_5$ is unstable at 340°,[26] whereas $C_2B_5H_7$ readily survives. The same situation would prevail with $C_2B_4H_6$, which would form by loss of H_2 but would also be unstable in the reaction zone. Support for these postulates is found with another *nido*-carborane, $(CH_3)_2C_2B_7H_{11}$,[27] which is known to decompose into $(CH_3)_2C_2B_8H_8$ and $(CH_3)_2C_2B_6H_6$ by disproportionation and into $(CH_3)_2C_2B_7H_7$ by simple loss of hydrogen.

These speculations coupled with the knowledge that almost all high-yield borane–carborane pyrolysis-induced interconversions are best carried out under high-temperature, short-term conditions rather than low-temperature, long-term conditions led to the present investigation of the pyrolysis of $C_2B_4H_8$. The experiments demonstrated indeed that the cumulative yield of the smaller *closo*-carboranes, based on $C_2B_4H_8$ consumed, is nearly quantitative under high-temperature, short-term pyrolysis conditions, with the following approximate yields: 40% $C_2B_5H_7$ (as before), 40% $C_2B_3H_5$ (as might have been anticipated), and 20% $C_2B_4H_6$.

Experimental Section

Reagents.—The $C_2B_4H_8$ used in these experiments was prepared[21,25] in large batches by reaction of acetylene and pentaborane-9 (8:1 ratio, initial pressure of 2 atm absolute) in 34-l. stainless steel tanks maintained at 215–225° for about 48 hr. At the end of this time, if no make-up acetylene was added, the pressure in the reactor generally stood at about 0.5 atm absolute. The products were vacuum pumped from the tanks and fractionated through traps at $-120°$, which removed the $C_2B_4H_8$ and allowed the more volatile hydrocarbons (ethylene, unreacted acetylene, etc.) to pass. The $C_2B_4H_8$, with benzene as the principal contaminant, was then purified by vapor-phase chromatography on a 0.75-in. diameter by 20-ft long column containing Apiezon N on Chromosorb P at a column temperature of about 65°.

Experimental Apparatus.—A schematic diagram of the equipment used to effect pyrolysis of the $C_2B_4H_8$ is shown in Figure 1. The reaction chamber, about 65 cc in volume, consisted of a 0.75-in. o.d. stainless steel tube heated over a length of 13 in. The reactant carborane (and diluent, when used) was metered into the reaction chamber *via* precalibrated flow meters through a fog nozzle just upstream of the furnace. At this point the temperature was estimated to be about 100°, high enough to prevent condensation of the reactant but not so hot as to initiate its decomposition prematurely. In all experiments in which the reaction pressure was to exceed the vapor pressure of $C_2B_4H_8$ (0.25 atm or above), the $C_2B_4H_8$ was metered in as a liquid, while below that pressure it was metered in as a vapor. The pressure in the reaction chamber was controlled by a glass Cartesian diver manostat located between the reaction zone and the cold trap (see Figure 1).

Temperature Control.—The furnace temperature in most of the experiments was controlled by a Gardsman Model J "on–off"

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(20) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **86**, 4222 (1964).

(21) T. P. Onak, F. J. Gerhart, and R. E. Williams, *ibid.*, **85**, 3378 (1963).

(22) M. D. Marshall, R. M. Hunt, G. T. Hefferan, R. M. Adams, and J. M. Makhlouf, *ibid.*, **89**, 3361 (1967).

(23) J. M. Makhlouf, W. V. Hough, and G. T. Hefferan, *Inorg. Chem.*, **6**, 1196 (1967).

(24) R. Köster and M. A. Grassberger, *Angew. Chem. Intern. Ed. Engl.*, **6**, 218 (1967).

(25) T. P. Onak, R. E. Williams, and H. G. Weiss, *J. Am. Chem. Soc.*, **84**, 2830 (1962).

(26) T. P. Onak, *Advan. Organometal. Chem.*, **3**, 263 (1965).

(27) F. N. Tebbe, P. M. Garrett, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **88**, 507 (1966).

Table I

Experimental Data on the Pyrolysis of $C_2B_4H_8$

Run no.	Temp, °C	Reactor press. (abs), atm	$C_2B_4H_8$ input, cc (STP)	$C_2B_4H_8$ concn, %	Nominal residence, sec	Duration of run, sec	Fraction of $C_2B_4H_8$ consumed	Moles of product per mole of $C_2B_4H_8$ consumed				
								1,5-$C_2B_3H_5$	1,6-$C_2B_4H_6$	1,2-$C_2B_4H_6$	2,4-$C_2B_5H_7$	Total
1	600	1	111	17.0	2.8	90	0.955	0.054	0.147	0.004	0.160	0.365
2	600	2	111	9.3	3.1	90	1.00	0.080	0.186	0.003	0.200	0.469
3	600	3	111	6.3	3.1	90	1.00	0.096	0.200	0.007	0.202	0.505
4	600	0.5	111	29.1	2.4	90	1.00	0.150	0.235	0.004	0.161	0.550
5	600	1	88	17.0	5.1	120	0.99	0.116	0.275	0.003	0.237	0.631
6	600	0.5	148	28.9	2.3	120	1.00	0.127	0.257	0.004	0.234	0.622
7	600	0.25	111	44.7	1.8	90	1.00	0.132	0.224	0.002	0.223	0.581
8	600	0.25	85	69.7	1.2	30	1.00	0.145	0.225	0.002	0.225	0.597
9	600	0.25	85	69.7	1.2	30	1.00	0.099	0.167	0.004	0.153	0.423
10	700	0.25	85	69.4	1.0	30	0.99	0.069	0.084	0.002	0.144	0.299
11	550	0.25	85	69.4	1.3	30	0.90	0.182	0.203	0.003	0.260	0.648
12	500	0.25	85	69.2	1.4	30	0.89	0.212	0.176	0.006	0.292	0.686
13	450	0.25	85	69.2	1.5	30	0.21	0.203	0.059	0.025	0.271	0.558
14	500	0.25	54	66.7	2.1	30	0.86	0.246	0.185	0.004	0.328	0.763
15	500	0.25	34	65.1	6.3	60	0.99	0.153	0.134	Trace	0.235	0.522
16	500	0.25	60	64.5	19.6	300	0.98	0.191	0.172	Trace	0.314	0.677
17	500	0.25	85	94.2	1.9	30	0.86	0.237	0.167	0.007	0.306	0.717
18	450	0.25	60	64.5	2.1	300	0.57	0.229	0.097	0.007	0.331	0.664
19	675	0.25	85	69.7	1.2	30	1.00	0.070	0.108	0	0.168	0.346
20	725	0.25	85	69.4	1.1	30	1.00	0.035	0.025	0	0.140	0.200
21	475	0.25	85	69.4	1.4	30	0.40	0.275	0.125	0.014	0.351	0.765
22	700	0.25	167	66.3	2.7	15	0.99	0.081	0.111	0	0.188	0.380
23	500	3	85	17.1	4.0	30	0.98	0.198	0.176	Trace	0.339	0.713
24	461	10 mm	20	100	2.9	180	0.41	0.391	0.195	0.001	0.399	0.986
25	467	10 mm	20	100	2.8	180	0.55	0.338	0.178	0.013	0.311	0.840
26	459	10 mm	20	100	2.9	180	0.37	0.386	0.191	0.024	0.396	0.997
27	452	10 mm	23	100	2.9	180	0.23	0.396	0.159	0.039	0.415	1.009
28	446	10 mm	20	100	2.9	180	0.24	0.410	0.152	0.033	0.380	0.975
29	456	10 mm	4	100	14.4	180	0.82	0.071	0.043	Trace	0.077	0.141
30	449	10 mm	37	100	0.26	30	0.16	0.154	0.037	0.027	0.171	0.389
31	449	10 mm	51	100	0.38	60	0.15	0.331	0.111	0.058	0.507	1.007
32	449	10 mm	37	100	0.52	60	0.22	0.372	0.122	0.051	0.440	0.985
33	449	10 mm	28	100	0.69	60	0.32	0.379	0.117	0.027	0.436	0.959
34	448	10 mm	32	100	0.91	90	0.37	0.352	0.155	0.021	0.475	1.003

controller coupled through a Variac. The sensing thermocouple with a cold-junction compensation was inserted in the annular space between the tube furnace and the reactor. In later experiments, where more precise control was desired, we measured the temperature with a precision potentiometer and manually controlled the furnace by fine-positioning of a Variac dial.

The cold-trap temperature was regulated by means of a copper–constantan thermocouple and a West controller, which operated a solenoid valve through which liquid nitrogen flowed on demand. This allowed us to set the trap temperature, when needed, above the condensation point of argon, which boils at −185° at 1 atm.

Analyses.—To measure the amount of condensable product from a given run, we vacuum transferred it from the original trapping system to a calibrated volumetric bulb and measured its pressure; we then transferred it to an evacuated 1-l. bulb equipped with a silicone plug (Figure 2). All samples were of such volume as to be completely vaporized in the 1-l. bulb. To this bulb was then added argon gas until the total pressure reached about 780 mm. After allowing time for complete diffusion of gases in the 1-l. bulb, a 20-cc aliquot was extracted by means of a hypodermic syringe inserted through the silicone plug. The contents of the syringe were then emptied into a gas chromatograph equipped with a $^3/_8$-in. by 20-ft column of Apiezon N on Chromosorb P, held generally at a temperature around 100°. The carrier gas was helium, flowing at 85 cc/min; the detector was a thermal conductivity cell (katharometer). Elution times (approximate) were as follows: argon, 2.5 min; 1,5-$C_2B_3H_5$, 5 min; 1,6-$C_2B_4H_6$, 7 min; 1,2-$C_2B_4H_6$, 8.5 min; 2,4-$C_2B_5H_7$, 13 min; 4,5-$C_2B_4H_8$, 16 min. Initial identifications were made with a mass spectrometer, and percentages were determined by measuring the gas chromatography traces with a planimeter. The data obtained in these experiments are based on the assumption of equal sensitivities toward the thermal conductivity cell, although we know various carboranes indicated slight differences in sensitivities, particularly with respect to the *nido*-carborane $C_2B_4H_8$, which had a slightly higher sensitivity than any of the *closo*-carboranes.

Discussion of Experimental Results

The data for this work are contained in 34 experiments (Table I) run over a fairly wide range of temperatures and residence times and at several selected pressures and argon concentrations. Most of the data were obtained at 0.25 atm pressure because it happened to be convenient and because early runs at several pressures did not indicate any gross differences due to pressure changes (excepting at very low pressures, as discussed later). The run times generally were short, as low as 30 sec for about one-third of the runs, and consequently errors in total recovery data and in per cent conversion due to surges of the reactant at the beginning of some of the runs were fairly substantial in magnitude. The yield data, however, were internally consistent to a remarkable degree, considering the wide ranges of residence times, dilution, etc. Run no. 30 (see Table I) gave anomalously low yield data for reasons unknown, and run no. 29, wherein the residence time in the furnace was excessively long (14

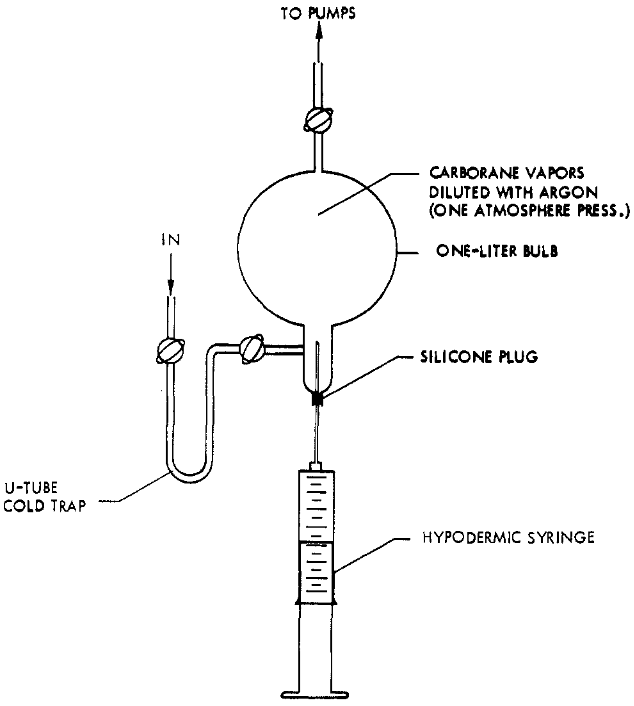

Figure 2.—Apparatus for extracting vapor samples for gas chromatographic analyses.

sec), showed a high percentage conversion of $C_2B_4H_8$ and a low percentage of recoverable product (14%). Obviously, the useful products have to be removed as quickly as possible from the reaction zone to minimize further interaction and consequent loss. This problem is reminiscent of similar ones encountered in boron hydride syntheses.

The largest and most consistent set of runs (no. 7–22 in Table I) was made at 0.25 atm, and although the yields are not as high as in later runs at 10 mm, the data reveal some interesting things about the types of reactions that occur. Yield data for the individual *closo*-carborane products are plotted in Figures 3–5, while total yield and per cent conversion are shown in Figure 6. Figure 7 is a composite of Figures 3–6 but with all of the data points deleted for clarity. As seen in Figures 3 and 5 the yields of $C_2B_3H_5$ and $C_2B_5H_7$ (*based on moles of* $C_2B_4H_8$ *consumed*) decrease linearly as the temperature increases, indicating that the rates of decomposition of the two products are more rapid than the rates of formation. The fact that the $C_2B_3H_5$ and $C_2B_5H_7$ plots are parallel suggests strongly that both are formed from the same (disproportionation) reaction, *i.e.*

$$2C_2H_4B_8 \longrightarrow C_2B_3H_5 + C_2B_5H_7 + H_2$$

The fact that the $C_2B_5H_7$ yield is always slightly higher than that of $C_2B_3H_5$ would again seem to be a reflection of the relative stabilities of the two compounds.

The plot of the $C_2B_4H_6$ yield *vs.* temperature (Figure 4), on the other hand, is radically different from the other two. Initially the yield increases with temperature, but then at higher temperatures it drops off as the effects of decomposition become predominant. From the shape of the curve it is obvious that the reaction mechanism whereby $C_2B_4H_6$ is formed is different from the disproportionation reaction by which $C_2B_3H_5$ and $C_2B_5H_7$ are formed. A simple explanation would be the loss of hydrogen from $C_2B_4H_8$, *i.e.*

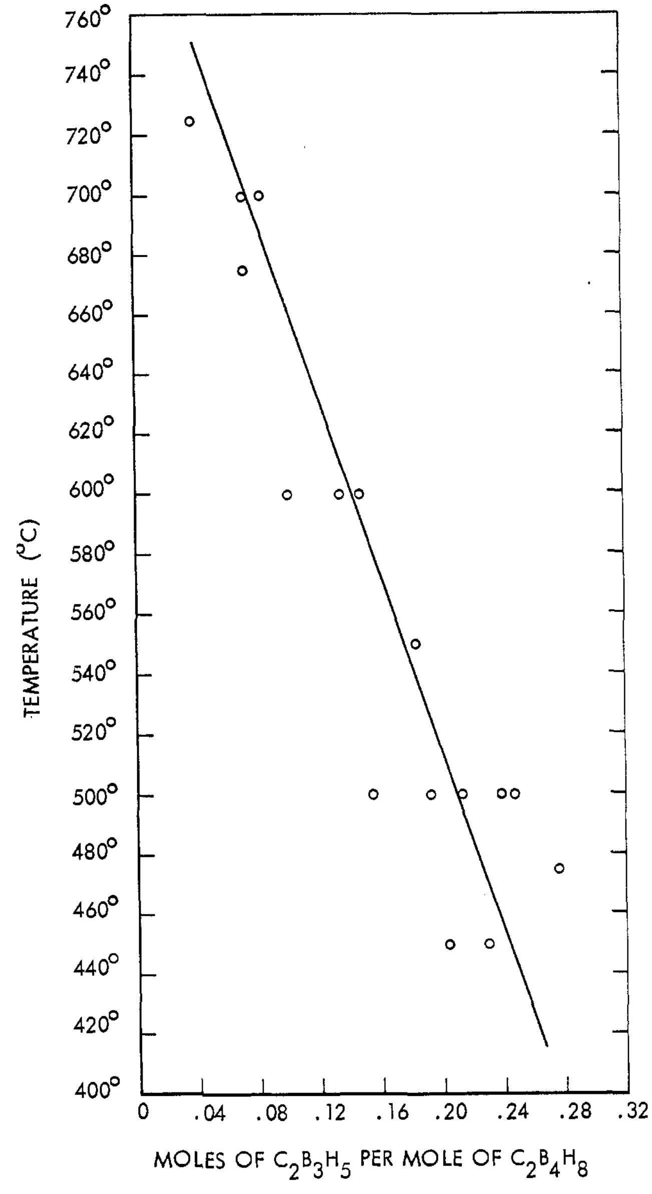

Figure 3.—Yield of $C_2B_3H_5$ as a function of temperature.

$$C_2B_4H_8 \longrightarrow C_2B_4H_6 + H_2$$

In most of the runs, the symmetrical 1,6 isomer is the predominant one, but this again most probably simply reflects relative stabilities inasmuch as the unsymmetrical isomer, 1,2-$C_2B_4H_6$, is known to undergo rapid rearrangement to the symmetrical 1,6-$C_2B_4H_6$[28] at elevated temperatures. With very short residence times and at reasonably low temperatures (no. 30–34), the 1,2 isomer was found in somewhat higher percentages. This suggests either that the two isomers are formed initially in equal abundance (statistical probability) or that the 1,2 compound is formed first and it in turn generates the 1,6 species by rearrange-

(28) J. R. Spielman and J. E. Scott, *J. Am. Chem. Soc.*, **87**, 3512 (1965).

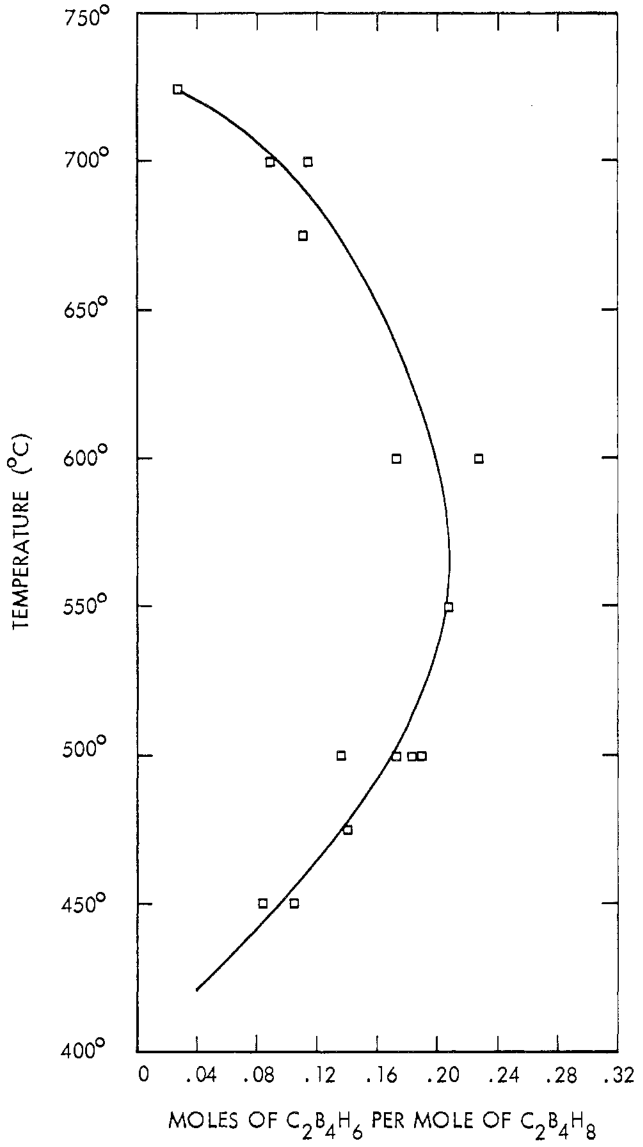

Figure 4.—Yield of $C_2B_4H_6$ (symmetrical plus unsymmetrical) as a function of temperature.

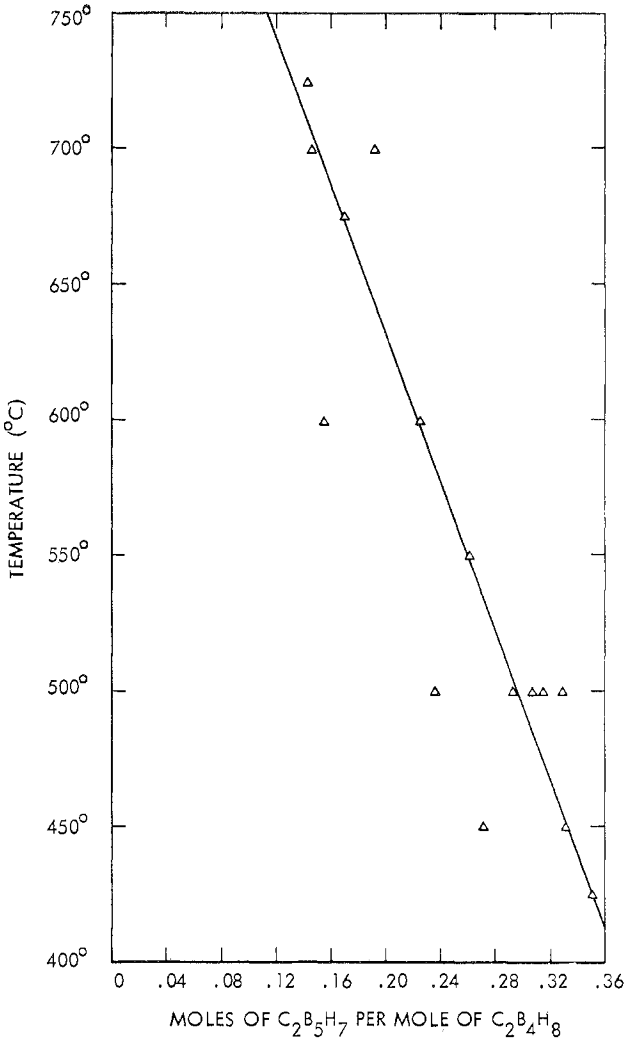

Figure 5.—Yield of $C_2B_5H_7$ as a function of temperature.

ment. Since the two carbon atoms are adjacent in the precursor $C_2B_4H_8$ molecule, it is not unreasonable to suppose that the 1,2 precedes the 1,6 isomer in the reaction sequence.

In Figure 6 the curve which shows total recoverable products ($C_2B_3H_5$ + $C_2B_4H_6$ + $C_2B_5H_7$) was constructed simply by adding up the values of the curves in Figures 3–5. It was not obtained by plotting experimentally measured volumes (total volumes of condensables minus the volume of unreacted $C_2B_4H_8$) because these data were not sufficiently consistent to determine the shape or position of the curve with any degree of accuracy. Similarly, since the $C_2B_4H_8$ conversion data (also plotted in Figure 6) deviated considerably from the "norm" in some runs, the position of the curve plotted in Figure 6 is only approximate.

In this set of experiments, *i.e.*, under 0.25 atm pressure and with argon diluent, the maximum yield of products (68%) occurs at about 470°, as shown in Figure 6. At this temperature the two curves, one indicating total yield and the other indicating $C_2B_4H_8$ consumed, intersect (coincidentally). If the temperature is raised to 575° or above, assuming no drastic reduction in residence time, all of the $C_2B_4H_8$ is consumed in the reaction while the total yield drops to about 60%. In addition the product distribution also changes substantially; *e.g.*, at 475° the individual yields of $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$ are about 22, 14, and 32%, respectively, while at 575° these figures change to 15, 21, and 23%.

Initial experimentation at relatively high pressures (runs 1–6 in Table I) had indicated no great influence of pressure on total yield, but when we conducted the experiments at very low pressures (10 mm) and with no diluent, the yields increased substantially. Runs 24–34 show (last column) that the yields, based on $C_2B_4H_8$ consumed, are close to 100%, at least for reaction zone temperatures in the vicinity of 450–460° and residence times on the order of a few seconds or less. Under these conditions the consumption of $C_2B_4H_8$ reactant is 25–30%, while the product distribution of $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$ is on the order of 40, 20, and 40%, respectively.

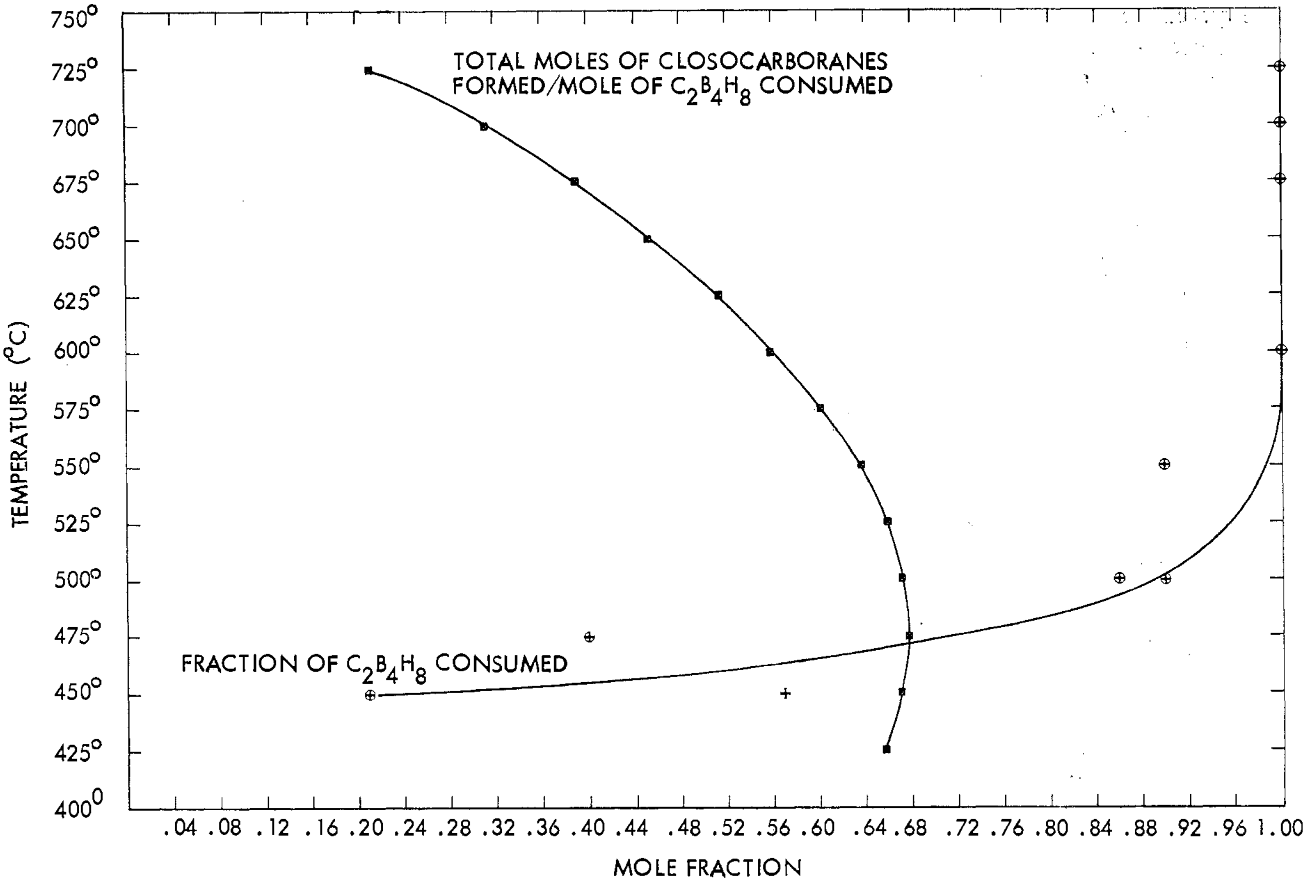

Figure 6.—Total *closo*-carborane yield and fraction of $C_2B_4H_8$ consumed as function of temperature.

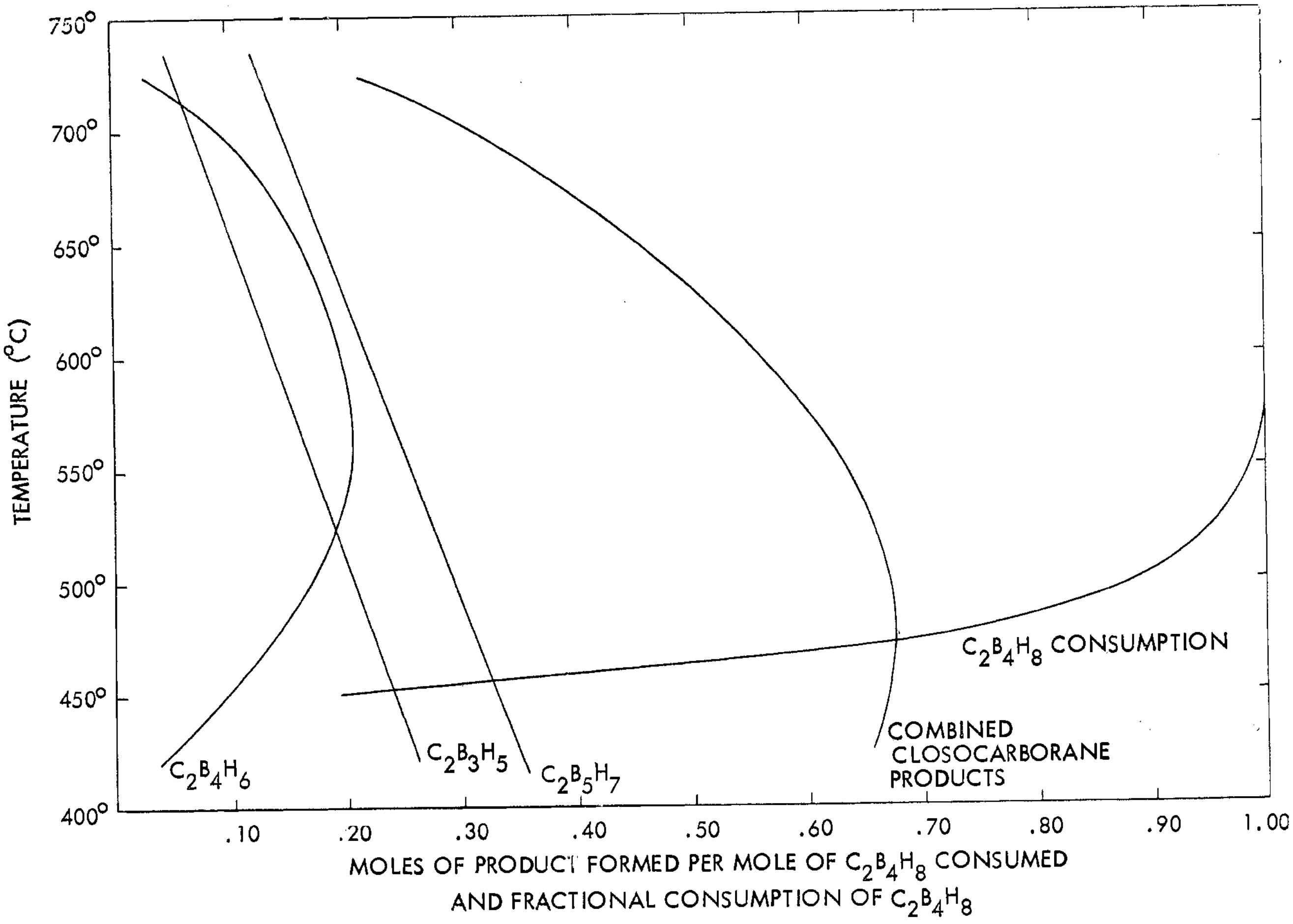

Figure 7.—Composite picture of $C_2B_4H_8$ pyrolysis data obtained at 0.25 atm pressure (with argon diluent).

The system as described is a good one for synthesizing laboratory-scale quantities of the smaller *closo*-carboranes. Even at 10 mm operating pressure it was capable of producing about 3 g/hr of the combined products $C_2B_3H_5$, $C_2B_4H_6$, and $C_2B_5H_7$. One very important feature of this nearly quantitative process is its relative cleanliness. Solid residues do not build up in the reactor chamber, and the equipment does not require the frequent disassembly and cleaning that has been our experience with the batch process.

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The Preparation of B-Methyl Derivatives of $C_2B_4H_8$. The Correlation of Proton Nuclear Magnetic Resonance Chemical Shift Measurements in $C_2B_4H_8$ Derivatives by Employing "Ring-Current" Contributions

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By the reaction of methylpentaborane with acetylene and 2-butyne, all of the B-methyl derivatives of 2,3-$C_2B_4H_8$ and of 2,3-$(CH_3)_2$-2,3-$C_2B_4H_6$, respectively, have been prepared. The proton nmr of the terminal substituents on boron are correlated by an empirical consideration of ring-current contributions. In this approach the relative magnitude, as well as the direction, of the chemical shifts can be reasonably predicted.

Introduction

Although some C-alkyl derivatives of $C_2B_4H_8$ are known, no boron-substituted derivatives have heretofore been reported except for B-deuterio compounds.[1,2] In the present study the 1-, 4-, and 5-methyl derivatives are reported and the observed proton nmr resonances correlated. Earlier, it had been suggested that a ring current might be one of several effects to account for the high-field position of the $C_2B_4H_8$ apical boron in the ^{11}B nmr.[3] A quantitative approach has been taken in this paper and can satisfactorily account for the magnitude of the chemical shifts for boron-attached hydrogens and alkyl derivatives.

Experimental Section

Materials.—1-Methyl- and 2-methylpentaboranes were prepared using previously reported procedures.[4] Acetylene (Airco) was vacuum fractionated through a trap at −100° to remove acetone. 2-Butyne (Columbia) was used without further purification. All chemicals were handled in standard high-vacuum equipment.

Mass spectra were recorded using a Consolidated Electrodynamics Corp. 21-620 mass spectrometer.

Infrared spectra were recorded by a Beckman IR-5 spectrophotometer and also, in the case of the B-methyl derivatives of $C_2B_4H_8$, by a Beckman IR-12 spectrophotometer.

Gas Chromatography.—A 30% Apiezon L on firebrick column operating at 100° was used in the final purification of the products from the acetylene experiment and a 30% Kel-F on firebrick column was used for the products from the 2-butyne experiment.

Nuclear Magnetic Resonance.—Boron-11 nmr spectra (Table I) were obtained at 12.8 Mc with a Varian V-4300 high-resolution spectrometer and also at 32.1 Mc with a Varian HA-100 spectrometer. Proton nmr spectra (Table II) were obtained using a Varian A-60 spectrometer.

B-Methyl Derivatives of $C_2B_4H_8$.—A mixture of 1-methylpentaborane (16 mmol) and acetylene (185 mmol) was sealed in a 2-l. flask and heated to 220° for 68 hr and then to 250° for 20 hr. The volatile fraction was distilled away from the large amount of dark brown solids that had formed and was vacuum fractionated through traps at −20, −100, and −190°. The contents of the −100° trap were gas chromatographed at 100° to yield 1.25 mmol (7.8%) of 2,3-dicarbahexaborane(8) (retention volume 1.00), 0.70 mmol (4.4%) of 1-methyl-2,3-dicarbahexaborane(8) (retention volume 1.41), and 1.0 mmol (6.3%) of a mixture of 4-methyl-2,3-dicarbahexaborane(8) and 5-methyl-2,3-dicarbahexaborane(8) (retention volume 1.78) in a mole ratio of 2:1. The mass spectra of the latter two fractions exhibited a sharp cutoff at m/e 90, corresponding to the $^{12}C_3{}^{11}B_4{}^1H_{10}$ parent ion. The identification of the last fraction as an inseparable mixture of the 4- and 5-methyl isomers was obvious from a complete analysis of both the 12.8- and 32.1-Mc ^{11}B nmr spectra and also of the proton nmr spectra.

The infrared spectrum of the purified 1-methyl-2,3-dicarbahexaborane(8) exhibited bands at (cm^{-1}): 2982 m (C–H stretch), 2950 m (C–H stretch), 2880 m (C–H stretch), 2634 vs (terminal B–H stretch), 1967 m (bridge hydrogen symmetric stretch), 1500 s (bridge hydrogen asymmetric stretch), 1345 m, 1210 m, 1165 w, and 925 m.[5] The infrared spectrum of the mixture of basal boron-substituted isomers was similar to but not identical with that of the 1-methyl isomer. Unfortunately, the unavailability of pure basal isomers or of mixtures of different com-

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[1] J. R. Spielman, R. Warren, G. B. Dunks, J. E. Scott, and T. Onak, *Inorg. Chem.*, **7**, 216 (1968).

[2] T. Onak and G. B. Dunks, *ibid.*, **5**, 439 (1966).

[3] W. E. Streib, F. P. Boer, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 2331 (1963).

[4] T. Onak, G. B. Dunks, I. W. Searcy, and J. Spielman, *Inorg. Chem.*, **6**, 1465 (1967), and references therein.

[5] Since it was difficult to remove the last traces of benzene, a side product of the reaction, from the 1-methyl derivative, compensation techniques were used to subtract out benzene infrared contributions.