Table I. Photolysis of $C_2B_4H_8$ [a]

Expt. no.	$C_2B_4H_8$, mmoles	Added gas, mmoles	$C_2B_4H_8$ consumed, mmole	Products, mole % of $C_2B_4H_8$ consumed		
				$C_2B_3H_5$	$1,6-C_2B_4H_6$	$1,2-C_2B_4H_6$
1	1.010	None	0.292	17.1	22.3	14.0
2	0.544	B_5H_9 (0.544)	0.204	15.2	23.5	13.7
3	1.082	B_2H_6 (1.093)	0.423	0.9	15.8	11.5
4	1.141	C_2H_2 (2.237)	0.321	21.0	16.8	6.7
5	0.951	H_2 (10)	0.407	18.0	24.4	17.2
6	1.072	N_2 (11)	0.391	12.2	19.7	10.3

[a] 2-hr. periods, $60°$.

The $C_2B_4H_8$ was prepared from C_2H_2 and B_5H_9 by previously described methods.[3] Samples were condensed into a 4.0 × 30 cm. fused silica tube sealed with a Teflon needle valve and clamped in front of a 360-w., quartz, medium pressure, mercury arc lamp[4] for irradiation. The tube was placed in the same position in front of the lamp for each experiment and an arrangement was made for cooling the tube in a stream of tap water for some of the experiments. The products were separated by high vacuum distillation and vapor phase chromatography (10-ft. column, 30% Kel-F on firebrick) and identified by their retention volumes[3] and infrared spectra.[1,2]

In a typical experiment 1.385 mmoles of $C_2B_4H_8$ was irradiated for 2.0 hr. at $23°$. During this time 0.295 mmole of material was consumed, giving (in mmoles) H_2, 0.139; B_2H_6, 0.042; B_5H_9, 0.032; $C_2B_3H_5$, 0.067; $1,6-C_2B_4H_6$, 0.058; and $1,2-C_2B_4H_6$, 0.036. Changing the temperature (0 to $60°$) did not alter the yield of carboranes or appreciably change the distribution of products. Longer irradiation time resulted in decreased yield of product, especially $1,2-C_2B_4H_6$, and the rate of $C_2B_4H_8$ consumption decreased, probably because the coating which formed on the tube absorbed light.

If some reactive intermediate is produced in the course of this reaction, it might react with other gases giving a change in the distribution of products or different products. Several experiments are outlined in Table I in which various gases were added to the tube. These experiments were all done without controlling the temperature of the reaction; however, the temperature came to about $60°$. The effects are rather minor, except in experiment 3, where the yield of $C_2B_3H_5$ decreased. In this case 40% of the B_2H_6 was not recovered and, in a separate experiment, approximately the same proportion of B_2H_6 was consumed when it was irradiated alone under the same conditions.

Apparently no $C_2B_5H_7$ was produced in this work. Since it is difficult to separate from the recovered $C_2B_4H_8$, the n.m.r. spectrum, infrared spectrum, and gas density of the recovered starting material were carefully checked, but no evidence was found for $C_2B_5H_7$.

An attempt was made to produce carboranes by irradiating a mixture of B_5H_9 and C_2H_2. When 1.50 mmoles of B_5H_9 and 7.50 mmoles of C_2H_2 were irradiated for 18.5 hr., 0.21 mmole of B_5H_9 and 0.29 mmole of C_2H_2 were consumed, but no other volatile material was recovered.

(4) G. W. Gates and Co., Franklin Square, L. I., N. Y., Model No. 420-U1.

John R. Spielman, James E. Scott, Jr.

Department of Chemistry
California State College at Los Angeles
Los Angeles, California 90032

A Six-Boron Carborane, $(CH_3)_2C_2B_6H_6$, and $B_6H_{10}-P(C_6H_5)_3$ from Hexaborane(10)

Sir:

The carborane containing six boron atoms, $C_2B_6H_8$ (dicarbaclovooctaborane(8)), was expected to be thermally quite stable; B_6H_{10} and acetylene(s) were considered the most likely candidate reagents for its synthesis. Accordingly, several hundred millimoles of B_6H_{10} were prepared[1] and a number of reactions which paralleled the successful synthesis of carboranes from B_5H_9[4-8] and $B_{10}H_{14}$[9,10] were undertaken. B_6H_{10} was therefore treated with acetylene at elevated temperatures in the presence and absence of several Lewis bases and with Lewis bases alone. Although trace amounts of the six-boron carborane were prepared by heat treatment, the subsequent utilization of ultraviolet irradiation resulted in a "reasonable yield" synthesis.

$B_6H_{10}-CH_3C{\equiv}CCH_3$. The mass spectrum of the least volatile fractions isolated from the reactions of a

(1) B_6H_{11} was prepared[2] from B_2H_6 and converted to B_6H_{10}.[3]

(2) A. B. Burg and H. I. Schlesinger, J. Am. Chem. Soc., 55, 4009 (1933).

(3) M. W. Forsyth, M. V. Hough, M. D. Ford, G. T. Hefferan, and J. L. Edwards, Abstracts, 135th National Meeting of the American Chemical Society, Boston, Mass., April 1959, p. 40M.

(4) R. E. Williams, C. D. Good, I. Shapiro, and B. Keilin, Abstracts, 140th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1961, p. 14N; I. Shapiro, C. D. Good, and R. E. Williams, J. Am. Chem. Soc., 84, 3837 (1962); I. Shapiro, B. Keilin, R. E. Williams, and C. D. Good, ibid., 85, 3167 (1963).

(5) C. D. Good and R. E. Williams, U. S. Patent 3,030,289 (1962).

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

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

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

(9) T. L. Heying, H. Schroeder, et al., ibid., 2, 1087, 1089, 1092, 1097, 1105, 1107, 1317 (1963).

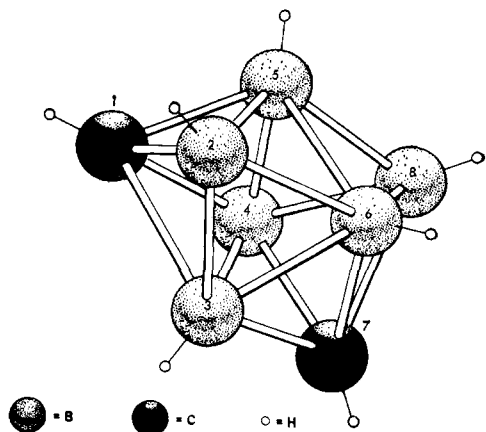(10) M. M. Fein, D. Grafstein, et al., ibid., 1111, 1115, 1120, 1125, 1128 (1963).

Figure 1. Predicted structure for the most stable $C_2B_6H_8$ isomer.

mixture of $(CH_3)_2C_2{}^{11}$ and B_6H_{10} (4:1) at 200° for 1 hr. in the gas phase revealed unambiguously the synthesis of the six-boron carborane $(CH_3)_2C_2B_6H_6$. The parent group of peaks in the mass spectrum is reproduced in Table I. The monoisotopic spectrum may be obtained with negligible residues only when six boron nuclei are assumed; the m/e peak at 127 is exactly the amplitude necessary from the presence of C^{13} in natural abundance, and the parent fragment $(CH_3)_2$-$C_2B_6H_6{}^+$ is the most abundant "fragment" in keeping with the mass spectra of the other carboranes and in contradistinction to the mass spectra of boron hydrides, alkylboron hydrides, and to a lesser extent hydrocarboranes. The yield of $(CH_3)_2C_2B_6H_6$ was quite low (<2%), and $(CH_3)_2C_2B_5H_5$ as well as $(CH_3)C_2B_4H_6$ were produced; however, the existence of the six-boron carborane was established.

Table I. Partial Mass Spectrum of $(CH_3)_2C_2B_6H_6$

m/e	Ion intensity
119	9.6
120	15.0
121	24.6
122	38.7
123	57.0
124	82.2
125	100.0
126	60.4
127i	5.0

Guided by and following the successful experiments of Spielman and Scott,[13] we treated mixtures of B_6H_{10} and $(CH_3)_2C_2$ (1:15) with ultraviolet irradiation[14] in the gas phase for 2 hr. at 60°, 12 min. at 35°, and 1 min. at 35°; the B_6H_{10} disappeared and $(CH_3)_2$-$C_2B_6H_6$ was isolated in every case with the identical mass spectrum previously obtained (Table I). The highest yield (~12%) was realized from the 12-min.

(11) Dimethylacetylene is always utilized in our exploratory experiments since higher yields are realized[6-8] and since acetylene is known to produce both carboranes and dimethylcarboranes via different reaction paths.[12]

(12) R. Koster and G. W. Rotermund, Tetrahedron Letters, No. 25, 1667 (1964); Angew. Chem., Intern. Ed., 3, 515 (1964).

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

(14) The Southern New England Ultraviolet Co., Middletown, Conn.; 200-w. (1.65 × 10¹⁶ photons sec.⁻¹ cm.⁻¹).

experiment. $(CH_3)_2C_2B_6H_6$ has a melting range -58 to $-63°$ and exhibits a structurally unrevealing 12.8 Mc. B^{11} n.m.r. spectrum (a skewed triplet; δ (± 2) $+5$, -7, and -21 relative to $BF_3OEt_2 = 0$) in the chemical shift range characteristic of carboranes.

A material exhibiting almost the identical mass spectrum was isolated in trace amounts and may be the 1,2 isomer of $(CH_3)_2C_2B_6H_6$.

$(CH_3)_2C_2B_6H_6$. The following regularities have been observed with respect to the structures of the carboranes: (a) the carboranes thus far discovered are constructed of two CH and a number of BH groups placed about the vertices of polyhedra with triangular faces; (b) when a choice exists, the CH groups occupy the vertices with the least number of neighboring nuclei; (c) the most stable isomers have nonadjacent carbon nuclei; and (d) (tentative) stability is maximized when the carbons have five neighboring nuclei and the borons have six neighboring nuclei.

These empirical rules allowed us to predict the correct structure for $C_2B_5H_7{}^7$ (three were compatible with the B^{11} n.m.r. spectrum) and prompt us to predict that the most stable structures for $C_2B_6H_8$ will be the 1,2 and 1,6 isomers assembled about the vertices of a disbisphenoid[15] (Figure 1).

The preceding generalities account for the structures and increasing thermal stability[16] of the series[1,5] $C_2B_3H_5$,[4] $1,2$-$C_2B_4H_6$,[4] $1,6$-$C_2B_4H_6$,[4] and $2,4$-$C_2B_5H_7$,[7,17] for which structures were predicted and the doubtful confirmed.[18,19] The relative instability of the predicted structure for $C_2B_9H_{11}{}^{20}$ is also in order; it follows that the nonisolated $1,10$-$C_2B_8H_{10}$ should be the most stable carborane in the series $C_2B_3H_5$ to $C_2B_{10}H_{12}$.[21]

B_6H_{10}—Lewis Base(s). Although B_6H_{10} is stable indefinitely in cineole at room temperature, reaction takes place at 100° to produce a colorless gel which has not been characterized. B_6H_{10} reacts with pyridine and acetonitrile during warming from $-196°$ to room temperature within a period of 12 hr.; orange-colored mixtures are formed from which the B_6H_{10} is not recoverable. The reaction of B_6H_{10} and $(C_6H_5)_3P$ in contrast takes place quantitatively in benzene or chloroform in a 1:1 ratio with no loss of hydrogen; either reagent introduced in excess may be recovered. The probable product, B_6H_{10}-$P(C_6H_5)_3$, is a white, air-stable substance with a melting point of 168–171° dec. B_6H_{10}-$P(C_6H_5)_3$ reacts with excess dimethylacetylene in the liquid phase at 100° within a period of 12 hr. The prospective carborane $(CH_3)_2C_2B_6H_6$ was

(15) The disbisphenoid is chosen (see A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford University Press, London, 1962, p. 100) so that it may be distinguished from the several other dodecahedra.

(16) Determined by T. P. Onak, private communication.

(17) In a related program two isomers of $(CH_3)_2C_2B_5H_5$ have been produced in small amount; the second isomer is predicted to have the 2,3 geometry.

(18) R. A. Beaudet and R. L. Poynter, J. Am. Chem. Soc., 86, 1258 (1964).

(19) R. A. Beaudet has confirmed the unsymmetrical $C_2B_4H_8$; private communication.

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

(21) If regularity d is correct $B_{12}H_{12}{}^{2-}$ would be expected to be a more stable $B_nH_n{}^{2-}$ species than $B_{10}H_{10}{}^{2-}$; species such as $B_{11}H_{11}{}^{2-}$ and $B_9H_9{}^{2-}$ as well as $B_6H_6{}^{2-}$ should be less stable. Such results have been reported.[22,23]

(22) E. L. Muetterties, Chemistry Lecture, California Institute of Technology, Pasadena, Calif., May 26, 1965.

(23) J. L. Boone, J. Am. Chem. Soc., 86, 5036 (1964).

not isolated. B_6H_{10} reacts cleanly with $(CH_3)_2S$ to produce a white product.

Robert E. Williams, F. James Gerhart

Space-General Corporation
El Monte, California

The Activation Volumes in the Solvolysis of exo- and endo-2-Norbornyl Brosylate

Sir:

It has been known for many years that ionization is accompanied by a net decrease in volume, typically of about 20 cm.^{3}/mole, due to the very large forces exerted by the ions on surrounding molecules (electrostriction).[1] The magnitude of this volume change, ΔV, is dependent on the solvent, the temperature, the pressure, and the magnitude (and possibly the sign) of the charge; the same remarks apply to the activation volumes, ΔV^*, of reactions in which ionization represents the rate-controlling step. Drude and Nernst[2] showed that ΔV is furthermore affected by the degree of dispersion of the charge: for n charges of q it is twice as great as that for $2n$ charges of $^1/_2q$.[3] It occurred to us that for this reason knowledge of ΔV^* might provide an added insight into the nature of the transition states leading to classical and nonclassical carbonium ions.

The carbonium ions formed from *endo-* and *exo-*2-norbornyl derivatives have been much discussed. The latter substrates generally are solvolyzed 10^{2-3} times faster than the former, and two schools of thought have developed to explain this difference. According to one of these,[4] the cation formed from the *exo* compounds is stabilized by resonance, permitting relief of steric strain and involving delocalization of the positive charge to the C-1 carbon atom, and possibly the C-6 atom as well; this delocalization is presumed also to lower the free energy of the transition state preceding the ion. Such participation would not be possible in the *endo* transition state, since the developing p-orbital is not suitably oriented. The alternative point of view is that the *exo-*2-norbornyl derivatives solvolyze at normal rates and that their isomers are retarded by steric interference of the *endo* hydrogen atoms with ionization.[5] Besides solvolysis rates, the criteria used to date have included product composition,[6] stereo-

(1) See, *e. g.*, S. D. Hamann, "Physico-Chemical Effects of Pressure," Academic Press, Inc., New York, N. Y., 1957, Chapters VIII and IX.

(2) P. Drude and W. Nernst, *Z. phys. Chem.*, **15**, 79 (1894).

(3) Experimental support for this contention is provided by inspection of a list of values of ΔV for the ionization of various acids (for a recent compilation, see L. G. Hepler, *J. Phys. Chem.*, **69**, 965 (1965)). Thus, for dibasic acids ΔV_2 is invariably greater by nearly 10 cm.^{3}/mole than ΔV_1; for citric acid, $\Delta V_3 > \Delta V_2 > \Delta V_1$; $\Delta V_{H_2O} > \Delta V_{phenol} > \Delta V_{RCOOH}$; $\Delta V_{phenol} > \Delta V_{p-NO_2-phenol}$, etc. Similar but more limited observations apply to the ionization of amines.

(4) S. Winstein and D. S. Trifan, *J. Am. Chem. Soc.*, **71**, 2953 (1949); S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, **87**, 377 (1965).

(5) H. C. Brown in "The Transition State," Special Publication No. 16, The Chemical Society, London, 1962, p. 155; H. C. Brown, F. J. Chloupek, and M.-H. Rei, *J. Am. Chem. Soc.*, **86**, 1248 (1964).

(6) H. C. Brown and H. M. Bell, *ibid.*, **85**, 2324 (1963); S. Winstein, A. H. Lewin, and K. C. Pande, *ibid.*, **85**, 2423 (1963).

chemistry,[4] the spectral properties of a number of stable carbonium ions,[7] the effect of substituents on solvolysis rates,[8] empirical calculations of the rate constants,[9] and the rates of model compounds.[10]
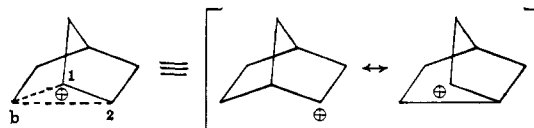
A nonclassical transition state is by definition characterized by a diffuse charge, and hence its formation would presumably involve a smaller volume change than a normal, classical transition state. Since $\Delta V^* = -RT(\partial \ln k/\partial p)$, this means that solvolysis of *exo-*2-norbornyl brosylate should be accelerated by the application of pressure, but less so than that of cyclopentyl brosylate, the model compound used in this study. The magnitude of this difference may be estimated as follows. If it is assumed that half of the electrostriction is due to the cation, and that half of this is lost due to the distribution of the positive charge between (at least) two sites, $\Delta V^*_{exo} - \Delta V^*_{CyPe}$ is expected to be about 4 cm.^{3}/mole (about $^1/_4\Delta V^*_{CyPe}$). In practice, the difference would be somewhat smaller as the two sites are not infinitely far apart and not yet completely equivalent, as assumed in the derivation by Drude and Nernst. No difference is expected between ΔV^*_{CyPe} and ΔV^*_{endo}. When the alternative point of view is examined, it is anticipated that the *endo* isomer, its ionization retarded because of steric hindrance, will be characterized by a volume diminution greater than that of cyclopentyl brosylate; in accordance with the Hammond postulate, the incipient ions should be more highly developed and thus have a greater effect on the surrounding solvent. No difference is now expected between ΔV^*_{CyPe} and ΔV^*_{exo}.

A difference of several cm.^{3} is a small one to look for. None of the additional factors that might affect the magnitude of the activation volumes (the temperature, the solvent, and the anion) were therefore varied in these experiments; the cations were the only variables. The rate constants were measured by means of the standard titrimetric method[11] with excellent precision (1–2%). The usual high-pressure apparatus was used[12] and the results obtained are well outside the limits imposed by the experimental technique (see Table I and Figure 1). The data show that at atmospheric pressure[13] $\Delta V^*_{exo} - \Delta V^*_{CyPe} = 3.5 \pm 1$ ml., a value which is in accord with the view that the *exo* transition state is characterized by participation. The alternative prediction that $\Delta V^*_{CyPe} - \Delta V^*_{endo} > 0$ is not borne out. At atmospheric pressure the two are equal, and at higher pressures the activation volume

(7) M. Saunders, P. von R. Schleyer, and G. A. Olah, *ibid.*, **86**, 5680 (1964); P. von R. Schleyer, D. C. Kleinfelter, and H. G. Richey, *ibid.*, **85**, 479 (1963).

(8) P. von R. Schleyer, M. M. Donaldson, and W. E. Watts, *ibid.*, **87**, 375 (1965); H. C. Brown and M.-H. Rei, *ibid.*, **86**, 5008 (1964).

(9) P. von R. Schleyer, *ibid.*, **86**, 1854, 1856 (1964).

(10) H. C. Brown and F. J. Chloupek, *ibid.*, **85**, 2322 (1963).

(11) S. Winstein and D. Trifan, *ibid.*, **74**, 1147, 1154 (1952); H. C. Brown and G. Ham, *ibid.*, **78**, 2735 (1956).

(12) W. le Noble, *ibid.*, **85**, 1470 (1963).

(13) At higher pressures all activation volumes and the differences between them rapidly diminish; this curvature, commonly observed in such plots, shows that a relatively dense transition state is also relatively incompressible.