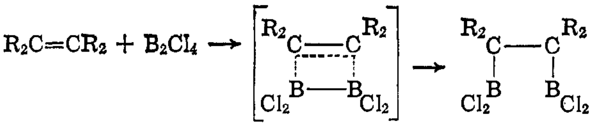
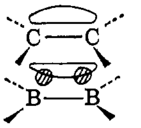
same retention time as an authentic sample of *meso*-2,3-butanediol. These results are precisely those to be expected from the *cis* addition of B_2Cl_4 to the two butenes involved; with *trans*-2-butene, the *dl* mixture should be observed, and, with *cis*-2-butene, the *meso* compound.

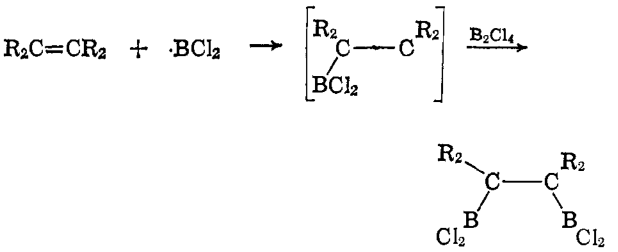
The three cases cited above point convincingly to a bimolecular addition reaction involving one molecule of B_2Cl_4 and one molecule of olefinic or acetylenic compound in the activated complex.



The favored orientation in the suggested transition state would seem to require that B_2Cl_4 assume a near-planar configuration, the driving force for which is the maximum orbital overlap between the vacant p orbitals on the boron atoms and the basic site of the pπ orbital on the hydrocarbon.

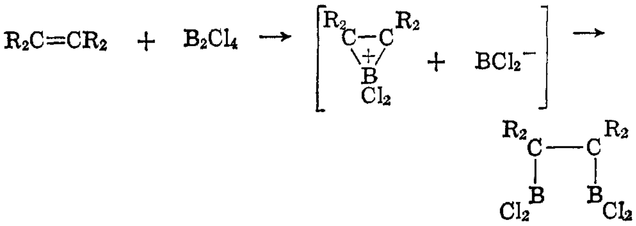


In contrast to the above mechanism, which must give rise to a *cis* product, a process involving prior homolytic cleavage of the boron–boron bond to generate free dichloroboryl radicals would, because of the opportunity for free rotation about the carbon–carbon single bond, not be expected to proceed in a stereospecific manner.



Further, bond energy considerations do not favor dissociation as an initiating step ($\Delta H°_{B-B}$ = 79.0 kcal/mole[7]).

A third possibility, which implies the formation of a cyclic organoboronium ion followed by addition of BCl_2^-, may be described as



This mechanism appears quite unlikely in that it should result in cleanly *trans* addition, as noted for the bromination of maleic and fumaric acids.[8]

Very shortly after the investigations described above had been completed, the authors were given the opportunity to examine a manuscript by Rudolph[9] describing an independent attack on the problem of the stereochemistry of B_2Cl_4 addition to olefinic and acetylenic compounds. One of Rudolph's proofs, that involving the addition of B_2Cl_4 to *cis*- and *trans*-2-butenes, is identical with ours in all but superficial details. We find ourselves in complete agreement with his conclusions on the general problem.

Acknowledgment. We are indebted to Professor G. K. Helmkamp of the University of California, Riverside, Calif., for supplying samples of *d*-(−)-2,3-butanediol and *meso*-2,3-butanediol and to Mr. Raymond Plepys for performing the glpc analyses relating to these diols. M. Z. wishes to thank the National Institutes of Health for a Public Health Service Predoctoral Fellowship.

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[7] S. R. Gunn, L. G. Green, and A. I. Von Egidy, *J. Phys. Chem.*, **63**, 1787 (1959).

[8] I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937).

[9] R. W. Rudolph, *ibid.*, **89**, 4216 (1967).

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Received May 19, 1967

Rearrangements in the Icosahedral Carboranes

Sir:

The use of labels, such as halogen substituents, on various positions of carboranes (here, the $B_{10}H_{10}C_2H_2$ type) provides a powerful tool for the study of the isomeric rearrangements of these compounds. We report here some preliminary indications of a complex set of factors which influence the pathways of these rearrangements.

It has been proposed[1] that the icosahedral carboranes pass through a cuboctahedral intermediate, for example, in the rearrangement of *o*-$B_{10}H_{10}C_2H_2$ to *m*-$B_{10}H_{10}C_2H_2$ (Figure 1, lower left). A second suggestion[2] is that the rearrangement involves mutual rotation of two pentagonal pyramids in the molecule. Under conditions in which rearrangement stops when a *meta* derivative is formed ($\sim$400°) Zakharkin and Kalinin[3a] have reported recently that a few more *meta* products were observed in the isomerization of halogenated carboranes than they could account for by the cuboctahedral pathway, and hence favored the pentagonal pyramid rearrangement. We show here that *all possible* isomers of B-monobromo-*o*-carborane are observed during the isomerization of 9-bromo-*o*-carborane as starting material in the temperature range 395–425°, and that all possible B-monobromo-*m*-carborane isomers are observed in the final reaction products.[3b] We confirm that the reactions stop when the *meta* derivatives are formed. We find that the *ortho* products, however, continue to rearrange in this temperature range.

The experimental data (Figure 2) for the isomerization of 9-bromo-*o*-carborane show seven isomers plus start-

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[1] (a) A. Kaczmarczyk, R. D. Dobrott, and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **48**, 729 (1962); (b) R. Hoffmann and W. N. Lipscomb, *Inorg. Chem.*, **2**, 231 (1963); (c) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin Co., New York, N. Y., 1963, p 191.

[2] D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963).

[3] (a) L. I. Zakharkin and V. N. Kalinin, *Dokl. Akad. Nauk SSSR*, [3] **169**, 590 (1966); (b) our analytical techniques have enabled us in several other cases, namely 9,12-dibromo-*o*-carborane, 8,9,12-tribromo-*o*-carborane, and 8,9,10,12-tetrachloro-*o*-carborane, to observe larger numbers of isomers than have been reported by these workers.

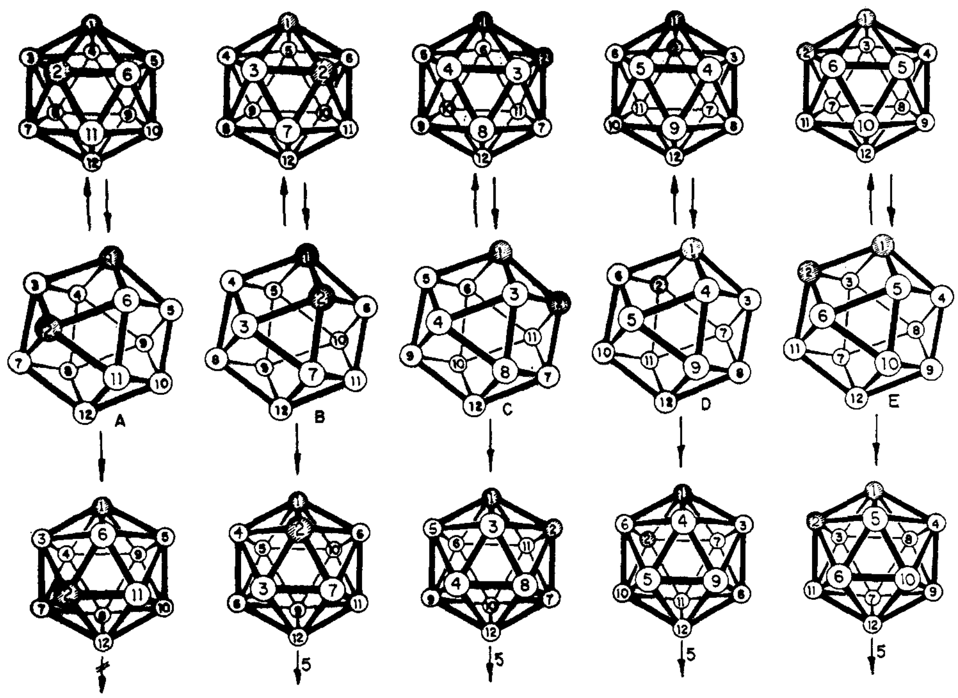

Figure 1. Cuboctahedral rearrangement processes. The five unique planar projections of the starting material (first line) lead to the five intermediates (second line) which open the icosahedron to a cuboctahedron in all possible ways. In the cuboctahedral intermediates triangle rotations may be permitted; these rotations occur more easily if fewer B–C bonds are broken. The products in the last line are those illustrated if no triangle rotations occur. The *meta* isomer (lower left) does not rearrange further at these temperatures (395–425°), but each of the four *ortho* products undergoes further rearrangements to five other cuboctahedra if no triangle rotations occur, and more if some of these rotations do occur.

ing material at some intermediate point in the conversion. The four *ortho* isomers are identified by their disappearance upon allowing the reaction to go to completion. The identities of 9-bromo-*m*-carborane (9-Br-*m*) and 9-bromo-*o*-carborane (9-Br-*o*) which are obtained by electrophilic bromination of the corresponding carboranes ($B_{10}C_2H_{12}$) are established by X-ray diffraction studies of the related dibromo derivatives.[4] The identities of the other isomers within each of the *ortho* and *meta* series are based upon their elution time, which is presumably related to their relative dipole moments which were estimated from those of known closely related compounds.[5] The striking features of the rearrangements are the initial cascade of *ortho* products from 9-Br-*o* toward 8-Br-*o*, and to some extent toward 4-Br-*o*, before the formation of large amounts of *meta* products, and the nonrandom nature of the final products after long times.[6] A satisfactory explanation must therefore demonstrate extensive nonrandom *ortho–ortho* conversions (yielding little 3-Br-*o* derivative), while *meta* products are produced in a distribution in which amounts of 4-Br-*m* exceed those of 5-Br-*m* derivatives.[6a]

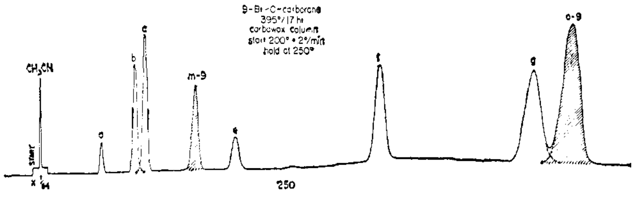

Figure 2. Vapor phase chromatogram of products obtained by isomerization of neat 9-bromo-*o*-carborane for 17 hr at 395° at 0.5–1.0 atm. Dipole moment estimates suggest that peaks a, b, and c are 2-Br-*m* (1%), 4-Br-*m* (7%), and 5-Br-*m* (9%), and that peaks e, f, and g are 3-Br-*o* (3%), 4-Br-*o* (13%), and 8-Br-*o* (22%), respectively. Values of 9-Br-*m* and 9-Br-*o* are 8 and 37%, respectively.

Extensive computations with the pentagonal pyramid rearrangement and with rotation in the icosahedron of some or all triangles of B_3, B_2C, or BC_2 units by 120° have failed to reproduce the major trends in these data. However, a physically plausible extension of the cuboctahedral pathway in which rearrangements may occur in regions furthest from carbon in this intermediate, suggested earlier but without details,[7] gives a good account of the data. All possible cuboctahedra from a single starting molecule are shown in Figure 1, second row. The intermediate cuboctahedron A accounts for *ortho–meta* conversions while the intermediates BCDE account for *ortho–ortho* interconversions; products are shown in the third line of Figure 1. However, for 9-Br-*o* starting material, only the 9-Br-*m* product plus exclusive return to 9-Br-*o* are predicted by these pathways. It is therefore necessary to allow rotation of triangles in the cuboctahedral intermediates,[8] preferentially

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(4) (a) J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, **5**, 1471 (1966); (b) H. A. Beall and W. N. Lipscomb, *ibid.*, **6**, 874 (1967).

(5) (a) A. W. Laubengayer and W. R. Rysz, *ibid.*, **4**, 1513 (1965); (b) R. Maruca, H. Schroeder, and A. W. Laubengayer, *ibid.*, **6**, 572 (1967).

(6) (a) Random values are 40% for 4-Br-*m* and 20% for each of the other three *meta* products. (b) Our arbitrary choice of equal rates, *R*, for the disappearance of *ortho* isomers is an assumption to which the final distribution of *meta* isomers is not very sensitive. Further studies are being made of intermediate distributions as functions of these various initial rates.

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

(8) It should be noted that the rotation of a triangle by 60° in the cuboctahedral intermediates involves the transformation from cubic close packing to hexagonal close packing. Further rotation by 60° returns HCP to CCP.

those triangles furthest from the C atoms, and also to give different weights to the *ortho–meta* path (A) than to the *ortho–ortho* paths (BCDE) in order to fit the unusual features of the observed product distribution. For example, if rotation by 120° of those triangles which break the fewest B–C bonds is allowed to occur preferentially (4, 8, 9; 7, 8, 12; 5, 9, 10; 10, 11, 12 in A; 8, 9, 12 in B and D; and 9, 10, 12 in C and E) and if path A is given $10\%^{6b}$ of the weight and the other 90% is divided equally among BCD and E, the calculated yields are 63, 31, 1, 0, 1, 3, 1, and 0% after one step and 0, 0, 0, 0, 23, 28, 35, and 14% after many steps of this mechanism (products are listed in the order 9-Br-*o*, 8-Br-*o*, 4-Br-*o*, 3-Br-*o*, 9-Br-*m*, 5-Br-*m*, 4-Br-*m*, 2-Br-*m*). Yields for intermediate times are reproduced almost as well.

Other derivatives (such as 8-Br-*o*, 4-Br-*o*, and 3-Br-*o*, separated from isomerization mixtures of 9-Br-*o*) have also been subjected to these rearrangements. The same general mechanism is found to apply but with some small changes in the weighting of the *ortho–meta* pathways and with some other changes in the restrictions of triangle rotations probably associated in an interesting way with differences in bonding in these isomers.

Further studies are under way on more complex systems, and at higher temperatures, at which *para* compounds are produced upon further transformations of *meta* isomers.

Table I. Yields (per cent) for the Rearrangements of 9-Bromo-*o*-carborane at 420–425°

Product	Time, min			
	30	60	210	330
9-Br-*o*	68	52	20	0
8-Br-*o*	21	23	14	0
4-Br-*o*	3	8	8	0
3-Br-*o*	0	1	4	0
9-Br-*m*	3	6	15	24
5-Br-*m*	4	7	18	28
4-Br-*m*	1	3	17	35
2-Br-*m*	0	0	4	13

Acknowledgment. We wish to thank the Office of Naval Research for support and H. Schroeder for chemicals.

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Received June 7, 1967

Structure of the Carborane $B_6H_6C_2(CH_3)_2$

Sir:

Of the polyhedral carborane structures, $B_6H_6C_2H_2$, which we study here as its C,C′-dimethyl derivative, is of uncertain structure. The interpretation[1] of the ^{11}B nuclear magnetic resonance (nmr) spectrum on the basis of the polyhedron established[2] to have D_{2d} symmetry in B_8Cl_8 requires that two different types of B atoms in $B_6H_6C_2(CH_3)_2$ have a coincident ^{11}B resonance in the spectrum taken at 12.8 Mc. This coincidence remains in the 19.3-Mc ^{11}B nmr spectrum, which led to some favoritism[3] for the structure derived from the Archimedian antiprism of D_{4d} symmetry for an equal-atom structure; however, the ambiguity of this conclusion was recognized, and study of the ^{11}B nmr spectrum at still higher resolution was recommended.[3] A dynamical structure, fluctuating between these, is also a possibility,[4] but now seems less likely in view of the higher temperatures normally required for polyhedral carborane rearrangements. Also, and finally, one type of intermediate structure which has only one square face is plausible,[4] and we shall show that the actual structure has very slight distortions toward this intermediate. Also, we establish with certainty the positions of the carbon atoms in the B_6C_2 polyhedron.

Results were obtained from three-dimensional X-ray diffraction data obtained from a single crystal at about −50°. The space group is C2/c, and there are four molecules in a unit cell having parameters $a = 15.24$, $b = 5.89$, $c = 12.74$; $\beta = 131.4°$. The structure, solved from Sayre's equations[5] (in a modified form of the multiple-solution program of Long[6]), has yielded a value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.11$ for 491 observed reflections. The molecule (Figure 1) has C_2 symmetry, coincident with a crystallographic C_2 axis. The B_6C_2 polyhedron is based upon the same idealized polyhedron as was found in B_8Cl_8, and shown[4] to have satisfactory molecular orbitals for both B_8H_8 (D_{2d}) and $B_8H_8^{2-}$ (D_{2d}). The C atoms are separated from one another and in the positions expected for greatest stability in their interactions with the molecular orbitals. Thus it is probable that less stable isomers can occur if preparative methods are less drastic. The distances are comparable in a general way with those[2] in the B_8Cl_8 polyhedron: bonds at atomic sites having smaller number of coordination tend to be shorter, and the shortest distances are the 1, 2 and 7, 8 distances, whereas the longest distances are between adjacent pairs among the 3, 4, 5, and 6 atoms in both B_8Cl_8 and $B_6H_6C_2(CH_3)_2$.

The smaller covalent radius of C is probably a major factor which appears to shorten distances near carbon atoms. The larger nuclear charge on C, as compared to B, appears to withdraw electrons from the adjacent B atoms, and the relatively long B_3–B_4 distance of 1.89 ± 0.01 A is directly comparable with less precisely established distances of 1.89 ± 0.04 A in m-$B_{10}Br_2H_8C_2H_2$[7] and 1.89 ± 0.06 A in m-$B_{10}Cl_{10}C_2H_2$[8] for a bond between B atoms each joined to two C atoms. However, in the molecule $B_7H_7C_2(CH_3)_2$ of C_{2v} symmetry (like $B_9H_9^{-2}$ of D_{3h} symmetry) this type of B–B distance is

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

[2] (a) R. A. Jacobson and W. N. Lipscomb, *J. Chem. Phys.*, **31**, 605 (1959); (b) R. A. Jacobson and W. N. Lipscomb, *J. Am. Chem. Soc.*, **80**, 5571 (1958); (c) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin Co., New York, N. Y., 1963, p 23; (d) G. S. Pawley, *Acta Cryst.*, **20**, 631 (1966).

[3] F. N. Tebbe, P. M. Garrett, D. C. Young, and M. F. Hawthorne, *J. Am. Chem. Soc.*, **88**, 609 (1966).

[4] W. N. Lipscomb, *Science*, **153**, 373 (1966). The unpublished molecular orbital studies of B_8H_8 (D_{2d}) and $B_8H_8^{2-}$ (D_{2d}) referred to here were carried out by R. Hoffmann.

[5] D. Sayre, *Acta Cryst.*, **5**, 60 (1952).

[6] R. E. Long, "A Program for Phase Determination by Reiterative Application of Sayre's Equation," Ph.D. Thesis (Part III), University of California at Los Angeles, 1965.

[7] H. A. Beall and W. N. Lipscomb, *Inorg. Chem.*, **6**, 874 (1967).

[8] J. A. Potenza and W. N. Lipscomb, *Proc. Natl. Acad. Sci. U. S.*, **56**, 1917 (1966).