rule" is not operative and confirm the *cis* structure.[10]

A somewhat more devious method was necessary to show that B_2Cl_4 adds to the 2-butenes in a *cis* manner. In the case of *trans*-2-butene (IV), *cis* addition predicts a racemic product; for *cis*-2-butene (VI), the *meso* isomer would be expected. Conversion of the bis(dichloroboryl) isomers to their corresponding 2,3-butanediols by basic hydrolysis and oxidation with 30% H_2O_2 was found to be the best expedient for identification of the isomers. The oxidation of the C–B bond proceeds with retention of configuration.[11] Thus, the configuration of the diols corresponds to that of the bis(dichloroboryl) precursors.

The isomers of 2,3-butanediol obtained from the addition and oxidation reaction series were identified by comparison with authentic samples which were isolated from Aldrich Chemical Co. 2,3-butanediol by preparative scale vpc. Analysis by vpc (Beckman GC-4, 100°, 20% Carbowax) showed that addition of B_2Cl_4 to IV followed by hydrolysis and oxidation yielded racemic 2,3-butanediol (V) exclusively; *meso*-2,3-butanediol (VII) was the only product when VI was used. The infrared spectra of all samples of VII did not display bands at 968 and 817 cm^{-1} which were found in the spectra of V. The remainder of the infrared spectrum was identical for both the racemic and the *meso* compounds. Finally, the melting points of the bis(*p*-nitrobenzoate) derivatives corresponded to those expected for *cis* addition: from the IV reaction series, mp 128–129°, lit.[12] for V-bis(*p*-nitrobenzoate) mp 128–128.5°; from the VI reaction series, mp 192–193°, lit.[12] for VII-bis(*p*-nitrobenzoate), mp 193–193.5.

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(10) Recently, P. L. Timms [*J. Am. Chem. Soc.*, **89**, 1629 (1967)] assigned a *cis* structure to $C_2B_2F_6$ partly on the basis of a *cis* structure for $C_2H_2 \cdot B_2Cl_4$. However, the latter structure had not been established at that time. Timm's data do not exclude the asymmetric structure $F_2C{=}C(BF_2)_2$ from consideration.

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

(12) F. M. Robertson and A. C. Neish, *Can. J. Res.*, **26B**, 737 (1948).

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Stereochemical Investigations of the Addition of Diboron Tetrachloride to Unsaturated Organic Molecules

Sir:

Earlier studies[1] carried out in this laboratory were consistent with the assumption that the addition of B_2Cl_4 to unsaturated organic compounds proceeds *via cis* addition. We now wish to report the results of investigations which provide virtually incontrovertible support for this assumption. Three different addition reactions, all of which appear to involve the same stereochemistry, were studied. These were the addition of B_2Cl_4 to (1) 2-butyne, (2) cyclohexene, and (3) *cis*- and *trans*-2-butene.

The 1:1 adduct between B_2Cl_4 and 2-butyne, formed by allowing a mixture of the reagents to stand at −80° for several hours, at 23° overnight, and at room temperature for 10 days in the dark, was hydrolyzed by treatment with aqueous potassium hydroxide at 180° for 15 min, and the infrared spectrum of the volatile hydrocarbon formed was found to correspond to that of *cis*-butene.[2] When the sample was subjected to glpc analysis (30% hexamethylphosphoric triamide on Fisher Columnpac at 0°) only one peak at 36 min was observed. Authentic samples of *cis*-2-butene and *trans*-2-butene gave retention times of 36 and 32 min, respectively. If the stereochemistry of hydrolysis at each of the neighboring boron–carbon bonds is the same, the recovery of 100% pure *cis*-2-butene can best be interpreted in terms of a *cis* configuration for the original bis(dichloroboryl) adduct.

The 1:1 adduct between B_2Cl_4 and cyclohexene was prepared by allowing approximately equimolar quantities of the reagents to stand in a sealed tube for 12 hr. After hydrolysis of this adduct to the corresponding bis(boronic acid) and evaporation of the HCl and excess water, the resulting solid was oxidized with alkaline 30% hydrogen peroxide at 0° for 12 hr. Destruction of the excess peroxide was accomplished by means of a platinum electrode, after which the solution was subjected to repeated extraction with diethyl ether. Removal of the solvent by vacuum evaporation left a white solid melting at 96.9–97.7° (lit. value[3] for cyclohexane-*cis*-1,2-diol, mp 94–98°; for the corresponding *trans*-1,2 diol, the value[3] is 104°). The melting point of the bis(*p*-nitrobenzoate) derivative was 149° (reported value[4] for the *cis* derivative is 149° and for the *trans* 129°). Since alkaline peroxide oxidation of the boron–carbon bond is reported[5] to proceed stereospecifically with retention of configuration, the initially formed bis(dichloroboryl)cyclohexane must be assumed to have a *cis* orientation.

The 1:1 adducts of *cis*-2-butene and *trans*-2-butene with B_2Cl_4 were prepared by allowing approximately equimolar mixtures of the reagents to warm slowly to room temperature in sealed glass ampoules. Each of the two adducts was hydrolyzed with excess water, made alkaline with NaOH, and then treated with 30% hydrogen peroxide.[6] Following destruction of the residual peroxide with a platinum electrode, the resulting diols were recovered by means of continuous ether extraction. Analysis of the oxidation products was accomplished on a Perkin-Elmer F11 glpc equipped with a 100 ft × 0.01 in. capillary column operated in the vicinity of 90° and coated with 1,2,3-tris(2-cyanoethoxy)propane. The diol resulting from B_2Cl_4–*trans*-2-butene exhibited only one peak, which corresponded in retention time exactly with that of an authentic sample of *d*-(−)-2,3-butanediol and which occurred 2.2 min before the peak produced by an authentic sample of *meso*-2,3-butanediol. The oxidation product resulting from B_2Cl_4–*cis*-2-butene produced only one peak, which had exactly the

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(1) M. Zeldin and T. Wartik, *J. Am. Chem. Soc.*, **88**, 1336 (1966).

(2) "Catalog of Infrared Spectral Data," API Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., 1960.

(3) F. D. Gunstone and L. J. Morris, *J. Chem. Soc.*, 487 (1957); N. A. Milas and S. Sussman, *J. Am. Chem. Soc.*, **59**, 2345 (1937).

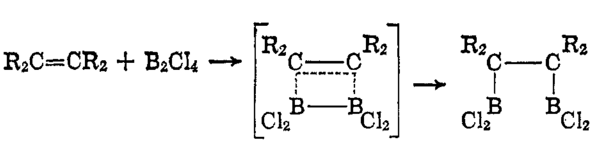
(4) J. S. E. Holker, K. U. Holker, A. McGookin, A. Robertson, K. Sargeant, and D. E. Hathway, *J. Chem. Soc.*, 3746 (1957).

(5) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **81**, 247 (1959).

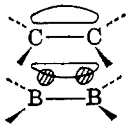
(6) D. J. Pasto (*ibid.*, **86**, 3039 (1964)) has suggested that, under conditions similar to those employed here, monoalcohols, glycols, and olefins can be formed from vicinal diboro compounds, and he assumed that a bridged boron intermediate played an important role. In our studies, we observed only glycols.

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.

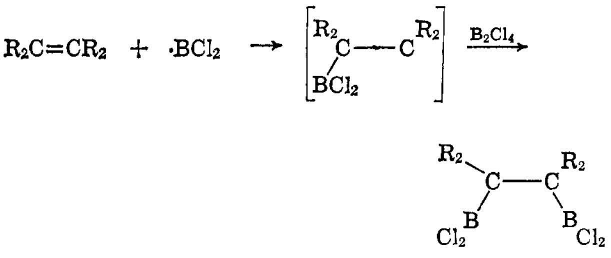
The three cases cited above point convincingly to a bimolecular addition reaction involving one molecule of B_2Cl_4 and one molecule of olefinic or acetylenic compound in the activated complex.



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.

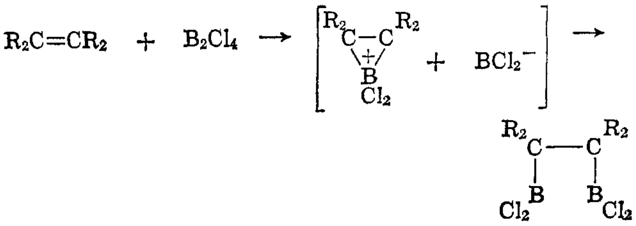


In contrast to the above mechanism, which must give rise to a *cis* product, a process involving prior homolytic cleavage of the boron–boron bond to generate free dichloroboryl radicals would, because of the opportunity for free rotation about the carbon–carbon single bond, not be expected to proceed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