Acknowledgment. The very helpful advice and encouragement offered by Professor W. Weltner, Jr., in the early stages of this work is acknowledged.

(14) NOTE ADDED IN PROOF. Recent work on the polarization of the electronic bands of the benzyl radical indicates that the assignments quoted above might not be correct: P. M. Johnson and A. C. Albrecht, Symposium on Molecular Structure and Spectroscopy, Columbus, Ohio, Sept 6–10, 1966, Abstract G3.

C. L. Angell, E. Hedaya, D. McLeod, Jr.
Union Carbide Research Institute
Tarrytown, New York 10591

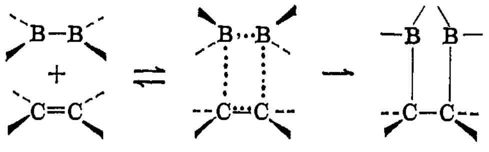
Received May 6, 1967

The Mechanism of Addition of Diboron Tetrachloride to Unsaturated Organic Compounds

Sir:

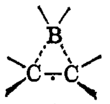
Holliday, *et al.*,[1,2] have postulated that diboron tetrachloride, B_2Cl_4, adds to unsaturated molecules through initial "π donation" from the unsaturated linkage to the two vacant p-type orbitals of the adjacent boron atoms in diboron tetrachloride. Subsequent B–B fission would result in *cis* addition of the $-BCl_2$ moieties across the unsaturated bond. Recently, Zeldin and Wartik[3] assumed *cis* addition of B_2Cl_4 to the π bonds of the conjugated systems in 1,3-cyclohexadiene and naphthalene. The rapidity of the reaction of many unsaturated species with diboron tetrachloride,[1–5] even at low temperatures, weighs against B–B bond rupture prior to addition. Nevertheless, the intuitively favored mechanism, the formation of an intermediate "π complex" leading to *cis* addition, has not been proven correct. In fact, Urry[6,7] has found the question of mechanism "somewhat puzzling" since, when cyclopentene is "diborated," the *trans*-bis(dichloroboryl) adduct is apparently formed.

In the present study the stereochemistry of certain B_2Cl_4 addition reactions was found to be stereospecific for *cis* addition. Such addition is consistent with a four-center transition state.

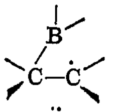


cis addition

Alternatively, B_2Cl_4 might dissociate prior to reaction. However, reasonable schemes involving $\cdot BCl_2$ would not be stereospecific for *cis* addition but present either (1) a bridged intermediate such as i which forces the second $\cdot BCl_2$ to add *trans*, or (2) a freely rotating intermediate such as ii which would allow random addition of the second $\cdot BCl_2$ and give no stereospecificity.



i



ii

When B_2Cl_4 and C_2H_2 were mixed as gases at 25° a pure compound identical with the originally reported $C_2H_2 \cdot B_2Cl_4$ was cleanly formed, as demonstrated by melting-point and vapor pressure checks. Since the *trans* form of $C_2H_2 \cdot B_2Cl_4$, *trans*-$(Cl_2B)HC{=}CH(BCl_2)$ [I (C_{2h})], possesses a center of symmetry, the "mutual exclusion rule"[8] should be obeyed in the infrared and Raman spectra of I. A comparison of the vibrational spectra (Table I) eliminates I because of the close agreement between infrared and Raman frequencies.

Table I. Infrared and Raman Spectra[a] of $(Cl_2B)HCCH(BCl_2)$

Frequency, cm^{-1}, and relative intensity Raman (liquid)	Infrared (gas)	Tentative assignment
109 s		ρ(BC)
159 s		ω(BC)
255 m		$\rho(BCl_2)$
274 m		$\omega(BCl_2)$
317 m, dp	332 vw	$\delta(BCl_2)$
371 m, p		$\delta(BCl_2)$
473 w		$\omega(BCl_2)$
496 m, p		$\omega(BCl_2)$
530 s	570 vw	δ(BCB)
680 w	694 m	ω(CH)
926 w	947 vs	$\nu(^{11}BCl)$
	984 s	$\nu(^{10}BCl)$
1025 w	1030 s	ν(BC)
1060 w	1068 s	$\nu(^{11}BC)$
	1089 w	$\nu(^{10}BC)$
1186 m	1193 vw	δ(CH)
	1322 vw	
1376 w, dp	1382 s	δ(CH)
1544 s, p	1598 s	ν(CC)
2915 w		Combination
2971 m, p		ν(CH)
3015 w, p	3010 vw 3028 vw	ν(CH)

[a] ν = stretch, δ = deformation, ω = wag, ρ = rock, v = very, s = strong, m = medium, w = weak, p = polarized, dp = depolarized; infrared determined between 4000 and 200 cm^{-1}. The slight shifts in line positions between the infrared and Raman spectra can be attributed to the necessity of determining the spectra in different phases.

The only alternative[9] is *cis*-1,2-bis(dichloroboryl)ethylene, *cis*-$(Cl_2B)HC{=}CH(BCl_2)$ [III (C_{2v})]. The presence of an infrared active C=C stretch alone is good evidence for III. However, the complementary Raman data listed in Table I show that the "mutual exclusion

---

(1) A. K. Holliday and A. G. Massey, *J. Inorg. Nucl. Chem.*, **18**, 108 (1961).

(2) J. Feeney, A. K. Holliday, and F. J. Marsden, *J. Chem. Soc.*, 356 (1961).

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

(4) G. Urry, J. Kerrigan, T. D. Parsons, and H. I. Schlesinger, *ibid.*, **76**, 5299 (1954).

(5) P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. Parsons, G. Urry, and H. I. Schlesinger, *ibid.*, **81**, 6368 (1959).

(6) G. Urry in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., John Wiley and Sons, Inc., New York, N. Y., p 359.

(7) H. K. Saha, L. J. Glicenstein, and G. Urry, *J. Organometal. Chem.* (Amsterdam), **8**, 37 (1967).

(8) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1945.

(9) Even though the asymmetric isomer, $(Cl_2B)_2C{=}CH_2$ [II (C_{2v})], might be consistent with the spectroscopic data it can be eliminated since X-ray [M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, **36**, 605 (1959)] crystallography has shown that B_2Cl_4 adds across the unsaturated linkage. Also, the hydrogen atom migration necessary to form II is improbable.

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.

Acknowledgments. The author wishes to thank R. C. Taylor and H. Clark of the University of Michigan for graciously obtaining the Raman spectrum of $C_2H_2 \cdot B_2Cl_4$.

[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).

R. W. Rudolph
Frank J. Seiler Research Laboratory, Office of Aerospace Research
U. S. Air Force Academy, Colorado 80840

Received May 8, 1967

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

[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.