

THE CHEMISTRY OF TETRACHLORODIBORANE(4) II*. REACTIONS WITH SATURATED RING HYDROCARBONS

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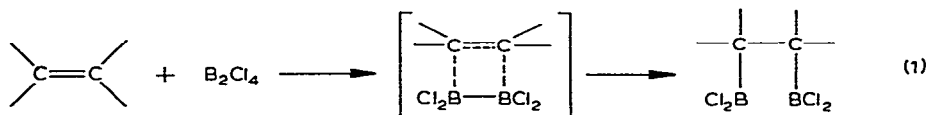
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SUMMARY

Tetrachlorodiborane(4) reacts with cyclopropane, methylcyclopropane and dimethylcyclopropanes to give ring cleavage addition compounds. IR and NMR data support structures with dichloroboryl groups in the 1,3 position of the hydrocarbon chain. Some evidence is presented to support a stereospecific reaction which involves a 4-centered transition state comparable to that which has been postulated for subchloride addition to olefins. No reaction occurs with 1,1-dichlorocyclopropane or cyclobutane.

INTRODUCTION

Tetrachlorodiborane(4), B_2Cl_4 (I), is known to react with a wide variety of unsaturated hydrocarbons; linear and cyclic olefins, dienes, acetylenes and polynuclear aromatics¹⁻³. The structures of some of these adducts, as deduced from spectroscopic and chemical properties, point unambiguously to a mechanism which involves a stereospecific insertion of the boron subhalide into the π bond presumably through a four-centered concerted transition state or π -complex intermediate³⁻⁶ [cqn. (1)].



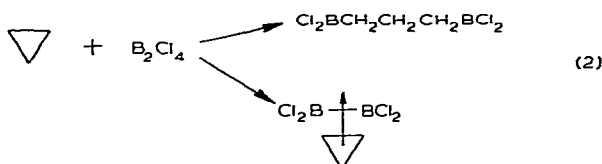
Substantiated examples of comparable insertions into carbon-carbon σ bonds are non-existent. Saturated hydrocarbons, both normal or branched, remain unchanged even when heated with (I) for extended periods of time. Only the usual decomposition products of (I) are observed⁷.

Curiously, the reaction between (I) and cyclopropane, first reported by Schle-

* For Part I see ref. 6.

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singer and coworkers¹, represents a possible exception; however, aside from the report of some physical properties, neither the nature of the reaction nor the structure of the products is postulated. Whether the reaction involves cleavage of the ring [eqn. (2)] or the formation of a molecular association complex resulting from the interaction of the vacant *p* orbitals of the borons with electron density on the ring has not been resolved.



As part of our program to study the chemistry of catenated boron halides⁶, we have examined the reactions of (I) with cyclopropane and some of its derivatives: methylcyclopropane, *cis*- and *trans*-1,2-dimethylcyclopropane, 1,1-dimethylcyclopropane, 1,1,2,2-tetramethylcyclopropane and 1,1-dichlorocyclopropane. The behavior of (I) with cyclobutane is also noted.

EXPERIMENTAL

All reactions were carried out in vacuum. Conventional greaseless vacuum line facilities were employed⁸. All products were manipulated either on the vacuum system or in moisture-oxygen free environments. IR spectra were recorded with a Perkin-Elmer 337 Grating Spectrometer. All spectra were taken as neat smears on KBr plates. ¹H-NMR spectra were obtained in CCl₄ relative to TMS as an internal reference on a Varian A60 Spectrometer. Liquid composition analyses were obtained with a Hewlett-Packard F & M 700 Chromatograph. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratories.

(I) was synthesized by established electric discharge methods⁹. Cyclopropane (Matheson Gas), methylcyclopropane, 1,1-dimethylcyclopropane, *cis*- and *trans*-1,2-dimethylcyclopropane, 1,1,2,2-tetramethylcyclopropane (Chemical Samples), 1,1-dichlorocyclopropane (K & K) and cyclobutane (Isotropic Research, Ltd.) were purchased in their purest form and were dried by vaporization *in vacuo* through a 2.5 ft tower of 3-A molecular sieves.

Reaction of (I) with cyclopropane (II)

In a typical experiment (I) (18.7 mmoles) was condensed at -196° into a reaction ampul containing (II) (10.2 mmoles). The reactants were warmed to room temperature and allowed to stand for 48 h. The ampul was opened *in vacuo* and the contents were fractionally condensed through traps kept at -52° and -196° . Unreacted (I) (8.3 mmoles) was recovered at -196° ; C₃H₆/B₂Cl₄ consumed, 1.02. The material collect at -52° is a colorless, slightly volatile liquid (III) which has a melting point range from -69.8 to -69.2° (reported¹ -69.2°). [Found: C, 17.8; H, 3.07; B, 10.4; Cl, 68.8; mol.wt. (vapor density), 211; v.p. (25°), 5.5 mm (reported¹ 5.6 mm). C₃H₆B₂Cl₄ calcd.: C, 17.53; H, 2.94; B, 10.53; Cl, 69.01%; mol.wt., 205.] IR (KBr

smear): 2970 vs, 2940 s, 2865 vs, 1455 s, 1370 m, 1330 m, 1305 m, 1240 m, 1140 (br), 1095 (br), 1030 (br), 1005 m, 940 (sh), 920 s(vbr), 882 m, 788 vs, 653 w cm^{-1} . NMR (CCl_4): δ 1.08 (t, 2, J 7.0 Hz, $\text{CH}_2\text{-B}$); δ 2.09 ppm (quintet, 1, J 7.0 Hz, $\text{CH}_2\text{-C}$).

(III) (3.09 mmoles) was heated at 100° for 48 h with glacial acetic acid (5 ml). The ampul was cooled to 0° and the volatile materials were pumped through a column containing KOH pellets into a liquid N_2 trap. The -196° material was identified as propane* (2.5 mmoles) by IR and vapor pressure comparisons with the pure material.

(III) (8.96 mmoles) was hydrolyzed with excess H_2O . The products, HCl and H_2O , were removed under vacuum. Alkaline 30% H_2O_2 (20 ml, 3 M NaOH) was added to the white solid residues and the mixture was stirred at 0° for several hours¹². The excess peroxide was destroyed by insertion of a Pt electrode into the solution. The organic materials were extracted with diethyl ether (100 ml) in a liquid-liquid extractor. The ether solution was then dried over anhydrous CaCl_2 , concentrated and preparatively chromatographed. The IR and NMR spectra of the major eluted material are identical with that of a pure sample of 1,3-propanediol (Chemical Samples Co.); n_D^{25} 1.4390 (pure diol 1.4389).

Reaction of (I) with methylcyclopropane (IV)

(I) (10.1 mmoles) and (IV) (16.50 mmoles) were condensed into a vacuum ampul. The mixture was kept at room temperature for 48 h. A colorless liquid product, (V), was isolated by trap to trap distillation, (V) being retained at -45° . (Found: C, 21.5; H, 4.11; B, 10.3; Cl, 63.9. $\text{C}_4\text{H}_8\text{B}_2\text{Cl}_4$ calcd.: C, 21.89; H, 3.67; B, 9.85; Cl, 64.60 %.) IR (KBr smear): 2960 s, 2920 (sh), 2885 s, 2875 (sh), 1425 s, 1350 m, 1300 m, 1280 m, 1210 s, 1130 (br), 1085 (br), 980 (sh), 925 (vbr), 835 (br), 795 m, 780 w cm^{-1} .

(V) was deboronated with propionic acid at 110° for 3 days. The more volatile materials were pumped through a caustic tower (KOH pellets) into a -196° bath. The isolated products were not subjected to further separation; however, a vapor phase IR spectrum indicated a mixture of n-butane and methylpropane.

Reaction of (I) with cis-1,2-dimethylcyclopropane (VI)

In a typical experiment, (VI) (15.6 mmoles) was condensed *in vacuo* with (I) (14.9 mmoles) at -196° . The mixture was stirred at room temperature for 3 days. The volatile materials were fractionated through -45° and -196° traps. The latter trap retained the unreacted hydrocarbon (0.66 mmoles); hydrocarbon/ B_2Cl_4 consumed, 1.00. A colorless, slightly volatile liquid, (VII), was isolated at -45° . (Found: C, 26.0; H, 4.16; B, 9.11; Cl, 60.8. $\text{C}_5\text{H}_{10}\text{B}_2\text{Cl}_4$ calcd.: C, 25.71; H, 4.32; B, 9.26; Cl, 60.71 %.) IR (KBr smear): 2960 s, 2910 (sh), 2880 vs, 1510 w, 1465 s, 1390 s, 1380 m, 1350 m, 1310 w, 1305 m, 1275 s, 1235 m, 1220 m, 1090 (vbr), 930 (vbr), 800 (sh), 890 m, 680 w, 640 m cm^{-1} .

(VII) (3.08 mmoles) was treated with propionic acid (6 ml) and heated in vacuum at 120° for 3 days. The mixture was cooled to -20° while the volatile components were removed by pumping through a caustic tower into a -196° trap. The

* GLC of the residual acetic acid solution indicates the presence of dissolved propane. Thus the protonolysis of (III) occurs with a minimum of 80% yield. Actual yields should be substantially above this value and would be consistent with similar acid deboronation reactions of organodibromoboranes¹⁰ and organoboranes¹¹.

contents of the trap (2.06 mmoles*) were analyzed for composition by GLC: methylbutane 72%, n-pentane 28%*.

In a similar experiment, (VII) (2.68 mmoles) was deboronated with excess propionic acid at 120° for 2 days to give a hydrocarbon mixture (1.81 mmoles) with composition: methylbutane 74%, n-pentane 26%*.

(VII) (53 mmoles; combined from 4 separate experiments) was hydrolyzed *in vacuo* with 30 ml degassed distilled water. After the evaporation of the water and HCl, alkaline H₂O₂ (50 ml 3 M NaOH, 30% H₂O₂) was added slowly with stirring at 0°. The aqueous solution was exhaustively extracted with diethyl ether in a liquid-liquid extractor. The ether solution was dried by passing the liquid through a column of freshly activated Linde 3-A molecular sieves. The resulting diols (VIIA) are extremely hygroscopic and must be kept under ether over a drying agent until separation by distillation. Ether was removed by evaporation just prior to fractional distillation. Fractional distillation of the product (~10 ml) was carried out on an annular teflon spinning band distillation column (Nestler-Faust). Combined cuts were taken between 111–115° (at 25 mm, ~2 ml); n_D^{20} 1.4322; reported^{13,14} for 2,4-pentanediol: *meso* 109–109.5° at 22.5 mm, n_D^{20} 1.4327; *dl* 111–112° at 22.5 mm, n_D^{20} 1.4378. This lower boiling fraction was stirred with a pyridine solution of 3,5-dinitrobenzoyl chloride (3 g in 20 ml) at 0° for 1 h. Excess water was added and the precipitate was washed with 2% aqueous Na₂CO₃, then with small portions of H₂O. The solids were recrystallized from acetone (m.p. 188–189°, reported¹⁴: *meso* 190°, *dl* 179°). (Found: C, 46.2; H, 3.31. C₁₉H₁₆N₄O₁₂ calcd.: C, 46.35; H, 3.28%.) Approximately 6 ml of (VIIA) distilled between 135–138° at 25 mm. This material was not characterized further and was presumed from the boiling point to be 2-methyl-1,3-butanediol [reported¹⁴: b.p. 114–116 (6–7 mm), 68° (0.8 mm)] which results from the unsymmetrical cleavage reaction.

Reaction of (I) with *trans*-1,2-dimethylcyclopropane (VIII)

Typically, (I) (4.80 mmoles) and (VIII) (4.80 mmoles) were condensed at –196° *in vacuo*. The mixture was warmed to room temperature and allowed to stand for 48 h. On fractional condensation, a colorless liquid (IX) was collected at –23°. (Found: C, 25.5; H, 3.88; B, 10.1; Cl, 61.0. C₅H₁₀B₂Cl₄ calcd.: C, 25.71; H, 4.32; B, 9.26; Cl, 60.71%.) IR (KBr smear): 2960 vs, 2940 (sh), 2870 vs, 1460 s, 1365 m, 1310 w, 1305 m, 1275 s, 1235 m, 1220 m, 1080 (vbr), 1035 (sh, br), 1005 m, 950 (sh), 925 (vbr), 885 m, 880 (sh), 685 m, 640 w cm^{–1}. NMR (CCl₄): multiplets from 0.8–2.6 ppm.

(IX) (2.10 mmoles) was treated with propionic acid (5 ml) at 110° for 5 days in vacuum. The ampul was cooled to –20° and the more volatile materials (1.84 mmoles) were passed through a caustic tower and condensed at –196°. GLC: methylbutane 75%, n-pentane 25%. The hydrocarbon composition of the propionic acid solution is 72% and 28% respectively*,**

Similarly, (IX) (2.02 mmoles) was deboronated at 120° for 3 days with propionic acid. GLC of the hydrocarbon mixture (1.57 mmoles): methylbutane 72%, n-pentane 28%.

* As with (III), this quantity of hydrocarbon mixture represents isolated material. GLC of the propionic acid solution indicates methylbutane and n-pentane in the ratio 75/25 in the first run and 78/22 in the second run (see Table 3).

** See footnote p. 261.

The peroxide oxidation reaction was carried out in a like manner as described above with approximately 50 mmoles of (IX) (combined product from 5 separate runs), and 50 ml of 30% alkaline hydrogen peroxide. The diols were extracted with ether. On distillation, the fraction collected at 112–114° crystallized in the receiver (m.p. 50–51.5°, reported: 53°¹³, 48–49°¹⁴; m.p. dibenzoate, 180–181°; reported¹⁴: *dl* 179, *meso* 190°). (Found: C, 46.6; H, 3.50. C₁₉H₁₆N₂O₁₂ calcd.: C, 46.35; H, 3.28%.)

Reaction of (I) with 1,1-dimethylcyclopropane (X)

(X) (5.23 mmoles) and (I) (6.10 mmoles) were combined in a vacuum ampul at –196°. The mixture was warmed to room temperature and stirred for 3 days. Fractional condensation gave the product (XI) at –45° and unreacted (I) at –196° (0.88 mmole); hydrocarbon/B₂Cl₄ 1.02. (Found: C, 26.1; H, 4.16; B, 9.11; Cl, 61.2. C₅H₁₀B₂Cl₄ calcd.: C, 25.71; H, 4.32; B, 9.26; Cl, 60.71%.) IR (KBr smear): 2960 s, 2900 (sh), 2880 vs, 1630 w, 1465 s, 1390 s, 1370 s, 1345 w, 1310 m, 1270 s, 1220 s, 1090 (br), 1035 (sh), 925 s(vbr), 880 m, 790 (sh), 775 s, 670 m, 625 m cm^{–1}.

(XI) (2.95 mmoles) was heated to 120° for 2 days with 5 ml of propionic acid. GLC of recovered hydrocarbons (2.12 mmoles): neopentane 38%, methylbutane 62%.

Similarly, (XI) (2.78 mmoles) was heated to 120° for 2 days with excess propionic acid. GLC of recovered hydrocarbons (2.13 mmoles): neopentane 35%, methylbutane 65%; the hydrocarbon composition of the propionic acid solution was 40% and 60%, respectively.

Reaction of (I) with 1,1,2,2-tetramethylcyclopropane (XII)

(I) (6.81 mmoles) was combined with (XII) (7.15 mmoles) *in vacuo* and kept at room temperature for 12 days. The product (XIII) which has a relatively low vapor pressure, can be isolated by first pumping off the volatile materials and then transferring the residual liquid to a 0° trap with gentle warming. (Found: C, 31.9; H, 5.45; Cl, 54.6. C₇H₁₄B₂Cl₄ calcd.: C, 32.14; H, 5.39; Cl, 54.20%.) IR (KBr smear): 2960 vs, 2880 s, 2860 (sh), 1460 m, 1385 s, 1370 m, 1300 w, 1275 m, 1220 m, 1170 m, 1080 (vbr), 925 s(vbr), 780 (br), 705 m cm^{–1}.

(XIII) (3.3 mmoles) was heated with propionic acid (10 ml) at 110° for 2 days. The solution was neutralized with aqueous NaOH and extracted with toluene. GLC: 2,2,3-trimethylbutane 85%, 2,4-dimethylpentane 15%. A similar reaction with 2.9 mmoles of (XIII) gave 81% and 19% respectively of the hydrocarbon mixture.

Behavior of (I) with 1,1-dichlorocyclopropane (XIV)

(XIV) (11.2 mmoles) and (I) (9.65 mmoles) were condensed in a vacuum ampul and kept at room temperature for 6 days without a color change. No products were isolated on fractionation through a –45° trap. The reactants were recombined and heated to 60° for 24 h. No reaction products could be isolated. The recombined materials were allowed to stand for 3 months without formation of products. (I) and (XIV) cannot be separated by conventional vacuum line manipulations, however, a comparison of the vapor phase IR of the mixture with a mixture of the authentic starting materials indicates neither reaction nor appreciable B₂Cl₄ decomposition.

Behavior of (I) with cyclobutane (XV)

(I) (10.8 mmoles) and (XV) (18.5 mmoles) were kept at room temperature for

19 days. The solution turned orange-yellow. Fractionation through -45° and -78° failed to separate reactants or any reaction products. A large quantity of yellow solids and viscous orange oil remained in the reaction vessel. The IR of the volatile materials indicated a mixture of (I) and (XV). The reactants were recombined and heated to 70° in vacuum for 3 days. No volatile products were isolated.

RESULTS AND DISCUSSION

The reaction of B_2Cl_4 with cyclopropane and its methyl derivatives occurs quantitatively at room temperature in the absence of solvents and with little decomposition of either the subhalide or the reaction products. In general the products may be classified as 1/1 addition compounds where the dichloroboryl groups are located at the 1,3 positions of a propane framework. The structure of these compounds have been deduced by interpretation of IR and NMR spectra and chemical properties.

IR and NMR spectra

Although exceedingly complex, the IR spectra of the addition compounds, (III), (V), (VII), (IX) and (XI) (see Experimental) have a number of similar features which suggest a ring cleavage product. Characteristic absorptions, indicative of $-CH_2-$ in an acyclic hydrocarbon structure, appear just below 3000 cm^{-1} and in the region from 1460 cm^{-1} to 1425 cm^{-1} (Table 1)¹⁵. Generally, all the addition adducts lack a band at or near 3050 cm^{-1} whose presence is diagnostic of the asymmetric CH_2 stretching vibration in cyclopropyl derivatives*.

(III), (V), (VII), (IX) and (XI) have common strong and broad absorptions in the region between $900\text{--}1100\text{ cm}^{-1}$. The band positions and shapes are generally recognized as vibrations belonging to the planar site symmetry around boron. Based on the IR analysis of CH_3BCl_2 by von Becker** and the reported assignments for $HC\equiv CBCl_2$ by Ritter¹⁷, the higher frequency band near 1090 cm^{-1} (Table 1) is assigned to the B-C symmetrical stretching vibration whereas the band at lower frequency $920\text{--}930\text{ cm}^{-1}$, is attributed to the BCl_2 asymmetric stretching mode.

All the addition compounds except (III) exhibit proton resonance spectra which are extremely complex (Fig. 1) presumably because of spin-spin splitting, overlapping of peaks due to the presence of product mixtures and magnetic interaction with boron nuclei. The spectrum of (III), (Fig. 1a), however is relatively simple and points conclusively to the propane structure, $Cl_2BCH_2CH_2CH_2BCl_2$. Two multiplet signals are observed; the triplet at 1.08 ppm assigned to the four terminal methylene protons and the quintet at 2.09 ppm attributed to the pair of internal protons have an area ratio of 1/2, respectively.

It is interesting and noteworthy that a comparison of the NMR spectrum of (III) with some structurally related molecules (Table 2) reveals little correlation between the proton shift (*i.e.*, the shielding effect of the BCl_2 group) with the number and

* See ref. 15. Additionally 1,2-bis(dichloroboryl)cyclopropane has a comparable absorption at 3070 cm^{-1} (see ref. 6).

** See ref. 16. The IR active fundamental that corresponds to this absorption is not a pure B-C stretch but belongs to the A_1 irreducible representation which involves a combination of B-C stretch and BCl_2 angle deformation.

proximity of the borons. For methylene protons adjacent to BCl_2 , resonance occurs between 1.08 and 2.71 ppm whereas for methine protons the shifts vary from 1.92 to 3.65 ppm.

TABLE 1

IR FREQUENCIES AND ASSIGNMENTS FOR B_2Cl_4 -CYCLOPROPANE ADDITION COMPOUNDS

Hydrocarbon	B_2Cl_4 adduct frequencies and assignments (cm^{-1})				
	$\nu_{\text{asym}}(\text{CH}_2)$	$\nu_{\text{sym}}(\text{CH}_2)$	$\nu_{\text{def}}(\text{CH}_2)$	$\nu_{\text{asym}}(\text{BCl}_2)$	$\nu_{\text{sym}}(\text{BCl}_2)$
Cyclopropane	2940	2865	1455	1095	920
Methylcyclopropane	2960	2885	1425	1085	925
<i>cis</i> -1,2-Dimethylcyclopropane	2960	2880	1465	1090	930
<i>trans</i> -1,2-Dimethylcyclopropane	2960	2870	1460	1080	925
1,1-Dimethylcyclopropane	2960	2880	1465	1090	925
1,1,2,2-Tetramethylcyclopropane	2960	2880	1460	1080	925
CH_3BCl_2				1090	1063
$\text{HC}\equiv\text{CBCl}_2$				995, 960	1115, 1076

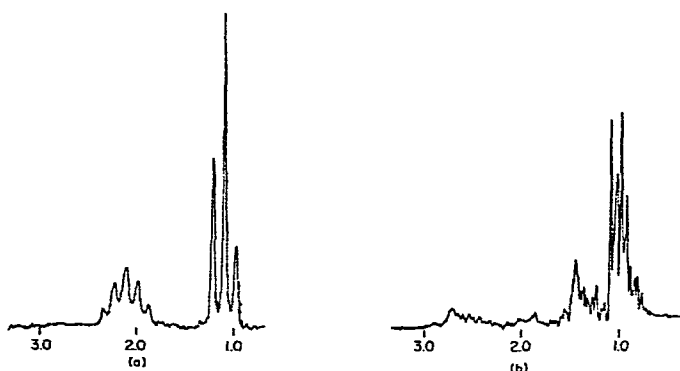


Fig. 1. Proton resonance spectra at 60 MHz of (a) product from cyclopropane and B_2Cl_4 and (b) product from *cis*-1,2-dimethylcyclopropane and B_2Cl_4 .

TABLE 2

CHEMICAL SHIFTS OF SOME B_2Cl_4 ADDITION COMPOUNDS

Compound	Chemical shift, δ (ppm)		
	$\text{CH}_2\text{-B}$	CH-B	$\text{CH}_2\text{-C}$
$\text{Cl}_2\text{BCH}_2\text{CH}_2\text{CH}_2\text{BCl}_2$	1.08		2.09
$\text{Cl}_2\text{BCH}_2\text{CH}(\text{BCl}_2)_2^5$	2.25	2.90	
$\text{Cl}_2\text{BCH}_2\text{CH}(\text{SnCl}_3)(\text{BCl}_2)^5$	2.71	3.65	
$\text{CH}_2\text{CH}_2[\text{CH}(\text{BCl}_2)]_2^6$		2.92	2.43
$\text{CH}_2\text{CH}_2[\text{CH}(\text{BCl}_2)]_4^2$		1.92, 3.78	2.92, 2.02

Product distribution and reaction mechanism

For all disubstituted cyclopropyl derivatives σ bond cleavage occurs at two different ring positions. In the absence of steric or electronic influences a statistical distribution between symmetrical and unsymmetrical cleavage products is expected. Estimates of the product distribution can be obtained by analysis of the hydrocarbon mixture which results from specific deboronation of the organodichloroborane with an organic acid at elevated temperatures*. The results of deboronation with propionic acid are summarized in Table 3 and suggest that the operating mechanism of B_2Cl_4 addition to the ring is more sensitive to steric than electronic factors. For example, in spite of the appreciable inductive influence of the methyl groups on adjacent bonds in (X), there is a slight statistical preference for the symmetrical cleavage product. Significantly, with (XII), the inductive effect favors a symmetrical product; however, predominant steric control is evident from the relatively small quantity of 2,4-dimethylpentane.

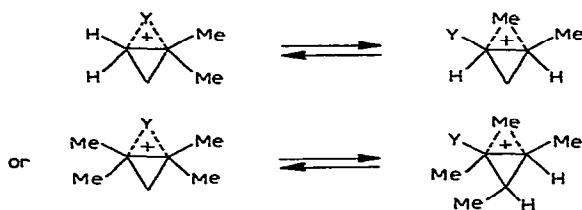
TABLE 3

PRODUCT DISTRIBUTION OF HYDROCARBONS ISOLATED FROM DEBORONATION OF B_2Cl_4 -CYCLOPROPANE ADDITION COMPOUNDS WITH PROPIONIC ACID

No.	Hydrocarbon	% Symmetrical	% Unsymmetrical
(VI)		28 (25) ^a 26 (22)	72 (75) 74 (78)
(VIII)		25 (28) 28	75 (72) 72
(X)		38 35 (40)	62 65 (60)
(XII)		15 19	85 81

^a Numbers in parentheses represent hydrocarbon composition retained in the propionic acid solution.

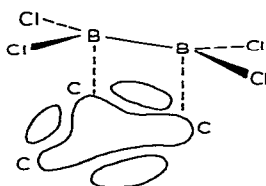
The fact that n-pentane and 2,3-dimethylpentane are not detected as deboronation products from adducts with (X) and (XII) respectively, argues against a broadside electrophilic addition mechanism involving transition states such as



which has been postulated for the addition of Br_2 to (X)¹⁸.

* See footnote p. 261.

Some experimental evidence exists which indicates that the ring cleavage reactions follows, at least in part, a stereospecific pathway. Peroxide oxidation of the bis(dichloroboryl) compound from symmetrical cleavage of (VI) and (VIII) produces only *racemic*- and *meso*-diols respectively. This stereospecificity implies that the reaction occurs in a concerted manner presumably through a four-centered transition state related to the one postulated for the addition of (I) to olefins^{3,4}. As with olefins, there is an inherent affinity of the vacant *p* orbitals on the boron atoms in (I) for the available electron density on the ring. One such type of interaction consistent with the above data is depicted below using the Sugden-Walsh^{19,20} trigonally hybridized model for cyclopropane bonding. In the transition state, a planar (or near planar) molecule of (I) can be considered approaching the highest occupied three-center molecular orbital of the ring such that minimum interaction between ring substituents and the halogen atoms occurs.



There have been conflicting reports of the behavior of (I) with chlorinated hydrocarbons. Some researchers find that (I) remains stable and inert in the presence of vinyl chloride and 1,1,2-trichloroethylene even after extended periods of contact^{1,21}. On the other hand, there are reports of substitution as well as addition to the halogenated olefins^{17,22,23}. The present study finds that (I) is not affected by 1,1-dichlorocyclopropane whether standing at room temperature for 3 months or at 60° for 24 h. Aside from a slight yellow coloration and nominal subhalide decomposition (indicated by the presence of small quantities of BCl₃) no reaction products could be isolated or detected*.

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* Ritter¹⁷ reports that chlorocyclopropane gives no evidence of reaction after 5 months at 25°; however, 5 days at 105° causes noticeable changes in the proton NMR. Three oils are isolated from the reaction mixture and their chemical properties seem to indicate ring cleavage compounds.

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