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ADDITION OF DIBORON TETRACHLORIDE TO SOME CYCLIC OLEFINS AND DIENES

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INTRODUCTION

Diboron tetrachloride rapidly adds to ethylene, at −79°, to form 1,2-bis(dichloroboryl)ethane, as previously described[1]. The stoichiometry of this reaction is shown in eqn. (1). Since the addition is similar to Brown's hydroboration[2], diboration would be a suitable name for this reaction.

$$B_2Cl_4 + CH_2{=}CH_2 \xrightarrow[12\,h]{-79°} Cl_2B{-}CH_2CH_2{-}BCl_2 \qquad (1)$$

RESULTS AND DISCUSSION

Diboron tetrachloride reacts with cyclopentene in a 1 : 1 molar ratio to give a quantitative yield of 1,2-bis(dichloroboryl)cyclopentane. Some of the properties of this compound are listed in Table 1. Hydrolysis, with excess water, evolved 99.23% of the chlorine as hydrogen chloride. The resulting white, solid residue has been shown to be 1,2-bis(dihydroxyboryl)cyclopentane by analysis. Oxidation of this

TABLE 1

SOME PHYSICAL CONSTANTS OF DIBORATION PRODUCTS OF CYCLIC OLEFINS AND CYCLIC DIENES

Compound	*Formula*	*M.p.(°C)*	*A*[a]	*B*[a]	*Valid range (°C)*[a]
1,2-bis(dichloroboryl)-cyclopentane	1,2-$(Cl_2B)_2C_5H_8$	−54	7.430	2229	20–95
4,5-bis(dichloroboryl)-cyclohexene	4,5-$(Cl_2B)_2C_6H_8$		5.586	1633	20–100
4,5-bis(dimethylboryl)-cyclohexene	4,5-$[(CH_3)_2B]_2C_6H_8$		7.591	1446	−78–0
1,2,4,5-tetrakis-(dichloroboryl)-cyclohexane	1,2,4,5-$(Cl_2B)_4C_6H_8$	108			

[a] For the vapor pressure equation: $\log_{10}p_{mm} = A - B/T$.

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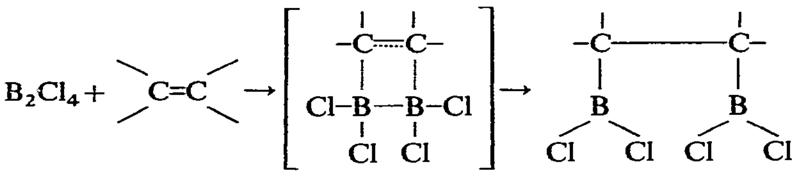
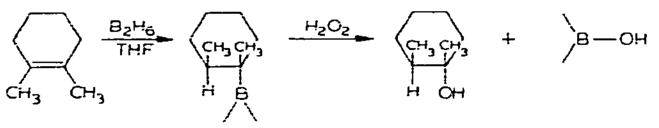
compound with 30% hydrogen peroxide in the presence of base yields a 1,2-cyclopentanediol. Gas-chromatographic comparison of this diol with authentic samples of *cis*- and *trans*-1,2-cyclopentanediol[3] shows the oxidation product to be exclusively the *trans*-1,2-cyclopentanediol. If the oxidation is stereospecific, as reported for the monoboron compounds[4], then the dichloroboryl groups in the prepared 1,2-bis(dichloroboryl)cyclopentane apparently are *trans*.

The diboration reaction can be visualized as occurring by at least three different mechanisms, homolytic cleavage, heterolytic cleavage, and a four-centered reaction. Homolytic cleavage of the boron–boron bond followed by addition of the dichloroboryl radicals to the unsaturated carbon–carbon bond would be expected to yield a mixture of *cis* and *trans* addition products[5]. Heterolytic cleavage of the boron–boron bond to form the dichloroboryl anion and cation, with subsequent ionic addition to the unsaturated site would produce mainly *trans* addition products[6]. A four-centered reaction should give *cis* addition products, as shown in eqn. (2). Therefore, the steric evidence obtained in the present work would argue against the four centered addition.



(2)

The evidence for the ionic addition is not conclusive since Brown's study on the stereospecificity of the hydrogen peroxide oxidation involved compounds formed by hydroboration, as may be seen in eqn. (3). These compounds are unlike the compounds



(3)

presently being studied in that they have no electron-withdrawing groups on the carbon β to the boron. Hawthorne and DuPont[7] have observed that such groups do affect the reactions of organoboranes. They showed that the hydrolysis of (β-chloroethyl)dichloroborane produces ethene, boric acid and three moles of hydrogen chloride. Hydrolysis of the unsubstituted ethyldichloroborane gives ethylboronic acid and two moles of hydrogen chloride as would normally be expected.

To continue the investigation of the diboration mechanism, the treatment of diboron tetrachloride with 2-butyne was studied. The product expected from *cis*-boration would be 2,3-bis(dichloroboryl)-*cis*-2-butene, that from *trans*-diboration 2,3-bis(dichloroboryl)-*trans*-2-butene. Spectroscopic methods would serve to distinguish which isomer is formed. Unfortunately, when diboron tetrachloride is allowed to react with excess 2-butyne, the halide serves as a catalyst for the trimerization of the 2-butyne, and hexamethylbenzene is the only volatile product of the reaction which has been identified.

Diboron tetrachloride also catalyzes the polymerization of conjugated cyclic dienes. Immediately upon mixing diboron tetrachloride with excess 1,3-cyclohexadiene, at −79°, a yellow color is formed which gradually fades. The major product of this reaction is a very viscous liquid. Polymerization continues if more diene is condensed onto this liquid.

Zeldin and Wartik in studying this same reaction isolated an orange oil which they purified further to an orange crystalline solid. This they identified as the 1,2,3,4-tetrakis(dichloroboryl)cyclohexane by analysis, infrared and nuclear magnetic resonance spectra[8]. In this work they used a large excess of diboron tetrachloride, the reverse of conditions employed in the present work. Apparently the polymerization reaction we have observed is much favored over the addition reaction and the stoichiometry must be adjusted to minimize the possibility of polymerization of the conjugated dienes. Diboron tetrachloride also polymerizes cyclooctatetraene and cyclopentadiene. The polymer formed in the case of cyclopentadiene is not the typical Diels–Alder adduct. Further work on the nature of this polymer is in progress.

One obtains typical diborations if non-conjugated cyclic dienes are used. The diboration of 1,4-cyclohexadiene yields a mixture of the 1 : 1 product, 4,5-bis(dichloroboryl)cyclohexene, and the 2 : 1 product, 1,2,4,5-tetrakis(dichloroboryl)cyclohexane. One can obtain the 4,5-bis(dichloroboryl)cyclohexene as the major product by using an excess of the 1,4-cyclohexadiene. The 1,2,4,5-tetrakis(dichloroboryl)cyclohexane is the major product if 1,4-cyclohexadiene is allowed to react with an excess of the diboron tetrachloride. Treating one mole of 4,5-bis(dichloroboryl)cyclohexene with excess dimethylzinc gives an 84% yield of a colorless liquid, 4,5-bis(dimethylboryl)cyclohexene. All of these compounds form the expected trimethylamine complexes, wherein each of the acidic borons is complexed with an amine. Table 1 lists some properties of these compounds.

EXPERIMENTAL

Most of the reactions were carried out on a standard vacuum line equipped with mercury float valves (see *e.g.* ref. 9).

Reagents

2-*Butyne*, obtained from Farchan Research Laboratories, Wickliffe, Ohio, was purified by fractional condensations through U-tube traps maintained at −63, −79, and −196°. The material retained in the −79° trap was used. The 1,3-*cyclohexadiene* and the 1,4-*cyclohexadiene* were used as supplied by Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. *Cyclooctatetraene*, as obtained from the K&K Laboratories, Inc., Jamaica, New York, was assumed to be pure. *Cyclopentadiene* was obtained from the Aldrich Chemical Company, Inc., as the dimer. The dimer was heated at 200° until it depolymerized, then cooled, and the cyclopentadiene distilled off at 41–42°. Prior to use it was stored at −20°. *cis*- And *trans*-1,2-*cyclopentanediol* were synthesized using the method of Owen and Smith[3]. Research grade *cyclopentene* was obtained from Phillips Petroleum Company, Bartlesville, Oklahoma, and used without further purification. *Diboron tetrachloride* was prepared as described by Urry, Wartik, Moore and Schlesinger[10]. The 30% *hydrogen peroxide* and the *sodium hydroxide* used were Mallinckrodt Analytical Reagent grade. *Trimethylamine*, obtained from the Matheson Company, Joliet, Illinois, was further purified by repeated vacuum distillation through a series of U-tube traps held at −95, −112, and −96°. The material retained at −112° was assumed to be pure trimethylamine when it exhibited a −79° vapor pressure of 6.6 mm. *Dimethylzinc* was obtained from the K&K Laboratories, Inc. and purified by fractional condensation through U-tube traps maintained at −63, −79, and −196°. The material retained in the −79° trap had a vapor pressure of 125 mm at 0°, and thus was tensiometrically pure.

Analytical procedures

Carbon and hydrogen content was determined by standard microanalytical methods.

Chloride analyses were carried out using a Fisher Titrimeter, Model 36, fitted with a silver electrode. The titrant used was 0.1 *N* silver nitrate. After basic hydrolysis of the boron–chlorine bonds, the solution was neutralized with acetic acid, and then titrated to −465 mv.

Boron was determined using the method of Schram and Urry[11].

Titration of organoboranes with trimethylamine to determine the boron content was effected as follows: A measured amount of trimethylamine was condensed, at −196°, into a reaction flask containing one mole of organoborane dissolved in cyclopentane. The −196° bath was replaced with a −79° bath, and the contents of the reaction flask stirred at this temperature for 1 h. The temperature was slowly raised to 0°, and at this temperature all the volatiles removed and fractionally condensed to recover the unreacted trimethylamine. The number of moles of trimethylamine that react per mole of organoborane indicates the number of acidic boron atoms per molecule of the organoborane.

Oxygen was determined by usual microanalytical procedures.

Preparation of 1,2-*bis(dichloroboryl)cyclopentane*

Cyclopentene (20.49 mmoles) was condensed into a reaction vessel maintained at −79°, containing diboron tetrachloride (9.92 mmoles). A white solid formed immediately. The reactants were stirred at this temperature for 20 h, during which time the solid disappeared. The temperature was allowed to rise to −15°, and the materials volatile at this temperature removed. The volatile material was pure cyclopentene (10.57 mmoles). Therefore, 9.92 mmoles of cyclopentene reacted with 9.92 mmoles of diboron tetrachloride. The colorless liquid in the reaction vessel passes through a 0° trap, but is retained in a U-tube trap maintained at −15°. Upon hydrolysis, with excess water, of 0.2998 g of the product 5.14 meq. of hydrogen chloride were evolved. This is in good agreement with the expected 5.18 meq. from the hydrolysis of 1,2-bis(dichloroboryl)cyclopentane. The white, solid material from the hydrolysis was dried *in vacuo*. (Found: C, 38.14; H, 7.69; B, 14.00; mol.wt., 156.2. $C_5H_{12}B_2O_4$ calcd.: C, 38.04; H, 7.67; B, 13.72%; mol.wt., 157.7.) The analysis is in good agreement with the results expected from 1,2-bis(dihydroxyboryl)cyclopentane.

TABLE 2

VAPOR PRESSURES OF 1,2-BIS(DICHLOROBORYL)CYCLOPENTANE

t(°C)	30.3	47.2	57.6	67.4	75.7	86.2
p (obsd.) (mm)	1.03	2.29	3.89	5.97	8.92	13.93
p (calcd.)[a] (mm)	0.97	2.44	3.86	6.14	8.79	13.93

[a] The calculated values were obtained from the equation: $\log_{10}p_{mm} = 7.340 - 2228.6/T$.

Vapor pressures were determined on a sample of 1,2-bis(dichloroboryl)cyclopentane prepared as described above. These are recorded in Table 2.

Oxidation of 1,2-*bis*(*dihydroxyboryl*)*cyclopentane*

A sample of 1,2-bis(dihydroxyboryl)cyclopentane (0.63 g; 4.0 mmoles) was dissolved in 6 ml of 95% ethanol to form a colorless solution. Sodium hydroxide (0.35 g) was added with stirring. The resulting alkaline solution was pale yellow in color. Hydrogen peroxide (0.5 ml, 30%) was added, with stirring, over a period of 5 min. A thick precipitate formed. When the vigorous reaction subsided, 20 ml of water were added to the reaction flask. The water then was evaporated from the solution until a damp white solid remained. This residue was extracted numerous times with 5-ml portions of ethyl ether. The ether layers were combined, evaporated to about 40 ml, dried over anhydrous magnesium sulfate, filtered, and evaporated to 0.5 ml. Samples of this solution were injected into an Aerograph "Autoprep", model A-700 gas chromatograph fitted with a 20 M carbowax column. Retention times of this sample were compared with that of known *cis*- and *trans*-1,2-cyclopentanediol. Under the following conditions the retention time for *cis*-1,2-cyclopentanediol is 8.5 min, that of the *trans*-1,2-cyclopentanediol is 13 min. Flow rate: 25 cc/min. Column temperature: 168°. Injector temperature 227°. Detector temperature: 254°. Sensitivity: 1. Filament: 157 ma. The *cis*-diol was identified further by its immediate reaction with a saturated basic-boric acid solution to form the borate ester. The unknown had a retention time of 13 minutes, and therefore was identified as *trans*1,2-cyclopentanediol. There was no detectable amount of *cis*-1,2-cyclopentanediol in the sample examined.

Preparation of 4,5-*bis*(*dichloroboryl*)*cyclohexene*

Diboron tetrachloride (1.44 mmoles) was condensed into a reaction vessel containing 1,4-cyclohexadiene (2.68 mmoles) maintained at −196°. The reactants then were allowed to warm to −30°. After 1 h, the temperature was raised to −10°. The reactants were stirred at this temperature for 23 h, then warmed to room temperature. The reaction mixture was fractionally condensed through U-tube traps maintained at 0° and −196°. The material in the −196° trap was identified as mainly excess cyclohexadiene, with a trace of diboron tetrachloride. The product was retained in the 0° trap. This was divided into five portions. An analysis was performed on one portion. (Found: C, 29.76; H, 3.57; Cl, 57.98. $C_6H_8B_2Cl_4$ calcd.: C, 29.59; H, 3.31; Cl, 58.21%.)

TABLE 3

VAPOR PRESSURE OF 4,5-BIS(DICHLOROBORYL)CYCLOHEXENE

t (°C)	31.8	50.05	66.0	77.8	89.4
p (obsd.) (mm)	1.78	3.35	5.99	8.29	12.79
p (calcd.)[a] (mm)	1.69	3.46	6.08	8.53	11.96

[a] The calculated values were obtained from the equation: $\log_{10}p_{mm} = 5.5858 - 1633.3/T$.

Trimethylamine (3.51 mmoles) reacts with 1.77 mmoles of 4,5-bis(dichloroboryl)cyclohexene. This is a molar ratio of 1.98 : 1, indicating two acidic boron atoms per molecule. Nuclear magnetic resonance spectroscopy indicates the presence of three types of hydrogens in the ratio of 1 : 2 : 1 at δ 2.68, 3.00 and 6.25 ppm respectively. The infrared spectrum for this compound indicates presence of a cyclohexene ring. The vapor pressures for this compound are recorded in Table 3.

Preparation of 4,5-*bis(dimethylboryl)cyclohexene*

Cyclopentane, approximately 1 ml, was condensed, at −196°, into a reaction flask containing 4,5-bis(dichloroboryl)cyclohexene (1.139 mmoles), followed by the addition of dimethylzinc (6.381 mmoles). The reactants were warmed to −45°. After 1 h the temperature was raised to −23°. This temperature was maintained for 3 h, then the reaction mixture was allowed to come to room temperature. The volatile materials were pumped off, and fractionally condensed through U-tube traps maintained at −95, −112 and −196°. The product, a colorless liquid, was retained in the −112° trap. Excess dimethylzinc was stopped in the −95° trap. The titration of 0.9537 mmoles of product took 1.858 mmoles of trimethylamine. This indicates two acidic boron atoms per molecule. Molecular weight, determined by vapor density, was 157.8; calculated for $C_{10}H_{20}B_2$ 161.9. Vapor pressures were determined on a sample of the product; they are recorded in Table 4.

TABLE 4

VAPOR PRESSURES OF 4,5-BIS(METHYLBORYL)CYCLOHEXENE

t (°C)	−79	−63.5	−45.2	−30.6	−22.9	−10	0
p (obsd.) (mm)	1.5	4.710	16.69	41.02	61.16	119.1	189.7
p (calcd.)[a] (mm)	1.453	4.782	16.82	39.75	65.30	119.5	188.3

[a] The calculated values were obtained from the equation: $\log_{10}p_{\text{mm}} = 7.5350 - 1437.2/T$.

Preparation of 1,2,4,5-*tetrakis(dichloroboryl)cyclohexane*

1,4-Cyclohexadiene (10.9 mmoles) was condensed, at −196°, into a reaction vessel containing diboron tetrachloride (24.0 mmoles). The reactants were warmed to −79°. After 10 h, the temperature was raised to 0°, and the excess diboron tetrachloride removed. The reaction product then was warmed to room temperature, and the volatiles removed. A small amount of 4,5-bis(dichloroboryl)cyclohexene was recovered. The white, crystalline product, remaining in the reaction flask, was purified by sublimation at 80°, *in vacuo* (10^{-5} mm). The product was divided into four samples. Trimethylamine (0.9183 mmoles) reacted with 0.2272 mmoles of the sample. This corresponds to a mole ratio of amine/organoborane of 4.04 : 1. (Found: C, 18.73; H, 2.36; Cl, 68.52. $C_6H_8B_4Cl_8$ calcd.: C, 17.70; H, 1.98; Cl, 69.68%.)

Hydrolysis, with excess water of 1,2,4,5-tetrakis(dichloroboryl)cyclohexane, *in vacuo*, yields a white solid. (Found: C, 28.99; H, 6.14; O, 48.20. $C_6H_{16}B_4O_8$ calcd.: C, 27.77; H, 6.22; O, 49.33%.)

Reaction of diboron tetrachloride with 1,3-*cyclohexadiene*

A sample of 1,3-cyclohexadiene (3.038 mmoles) was condensed, at −196°, into a reaction vessel containing diboron tetrachloride (1.99 mmoles). The temperature gradually was raised to −79°, and maintained there for $1\frac{1}{2}$ h. The temperature then was raised to −22.9° for $1\frac{3}{4}$ h, followed by 7 h at −10°, 1 h at 0° and finally to room temperature. After this treatment a −15° bath was placed on the reaction vessel. The materials volatile at this temperature were fractionally condensed through U-tube traps maintained at −79 and −196°. Boron trichloride (0.063 mmoles) and 1,3-cyclohexadiene (0.295 mmoles) were recovered. A colorless, viscous material remained in the reaction flask.

Pure 1,3-cyclohexadiene (14.88 mmoles) was condensed, at −196°, onto the viscous liquid. The temperature was gradually raised to 0° ,and held there for 12 h. The mixture was first brown in color, then became light yellow. After cooling the reaction vessel to −79°, the volatiles were collected and fractionated. Only a small fraction of the added 1,3-cyclohexadiene (0.3453 mmoles) was recovered.

Reaction of diboron tetrachloride with cyclopentadiene

Diboron tetrachloride (1.972 mmoles) was condensed, at −79°, into a reaction vessel equipped to stir *in vacuo*. Cyclopentadiene (3.979 mmoles) was condensed, at −196°, into an adjacent U-tube trap. The −196° on the U-tube then was replaced with a −45° bath, and the cyclopentadiene allowed to diffuse slowly from the U-tube trap into the reaction vessel maintained at −79°. A yellow color immediately formed in the reaction vessel. When all the cyclopentadiene had been added to the diboron tetrachloride, the −79° bath on the reaction vessel was replaced with a −45° bath. After 7 h at this temperature all material volatile at this temperature was removed. Fractional condensations through U-tube traps maintained at −45, −63, −79 and −196° showed that the volatiles consisted of traces of boron trichloride, diboron tetrachloride and hydrogen chloride. A reddish-brown, transparent polymer remained in the reaction vessel. The polymer does not appear to be the typical Diels–Alder polymer of cyclopentadiene.

Reaction of diboron tetrachloride with 2-butyne

2-Butyne (13.48 mmoles) and diboron tetrachloride (6.51 mmoles) were separately condensed, at −196°, into a reaction vessel equipped to stir *in vacuo*. The reactants were warmed to −79°, and maintained at this temperature for 12 h. A yellow solid precipitated. The temperature was then raised to −20° for 1 h, and finally to 0°. A light orange solid was observed in the reaction vessel. The volatiles were pumped off, then methanol condensed into the reaction vessel. The resulting slurry was filtered. The precipitate left on the filter was identified as hexamethylbenzene by mass spectrometric analysis.

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SUMMARY

The study of the reaction of diboron tetrachloride with unsaturated hydrocarbons has been extended to include some cyclic olefins and dienes. Addition of diboron tetrachloride to cyclopentene yields the expected product, 1,2-bis(dichloroboryl)cyclopentane. Hydrolysis of this yields the 1,2-diboronic acid of cyclopentane,

which upon oxidation by alkaline hydrogen peroxide apparently yields only the *trans*-1,2- cyclopentanediol. Diboration of non-conjugated cyclic dienes can be effected in a stepwise fashion. Thus, the addition of diboron tetrachloride to 1,4-cyclohexadiene results in either 4,5-bis(dichloroboryl)cyclohexyne or 1,2,4,5-tetrakis(dichloroboryl)-cyclohexane. When conjugated cyclic dienes are treated with diboron tetrachloride polymerization of the diene is the principal result. Similarly, 2-butyne is trimerized to form hexamethylbenzene upon treatment with diboron tetrachloride.

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