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THE CHEMISTRY OF TETRACHLORODIBORANE(4)
I. REACTIONS WITH CYCLIC OLEFINS

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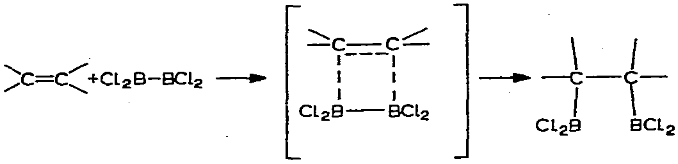
SUMMARY

Cis addition compounds are obtained from the reaction of tetrachlorodiborane(4) with an homologous series of cyclic olefins: cyclopentene, cyclobutene and cyclopropene. The stereochemistry of the adducts are deduced from chemical and spectroscopic properties. Reaction of 1-methylcyclopropene with B_2Cl_4 is complex and leads to olefin addition as well as random ring cleavage products.

INTRODUCTION

The stereochemistry of the tetrachlorodiborane(4) reaction with acetylenes and linear olefins has been well documented[1-3]. Unequivocal evidence exists which supports a *cis*-addition reaction pathway, presumably through a transition state or intermediate involving the overlap of the vacent *p*-orbital of each boron with the π bond of the hydrocarbon.



Recent literature reports seem to cast some doubt on the stereochemical course of B_2Cl_4 (I) addition to cyclic olefins. Zeldin, Gatti and Wartik reported that a *cis*-addition compound is the exclusive product from the reaction of (I) with cyclohexene[1]. This result is confirmed by Rudolf[2]. Similarly, norbornylene was shown to form only the *cis*-*exo*-1,2-bis(dichloroboryl) adduct[4]. At issue with these results is the report by Saha, Glicenstein and Urry that cyclopentane behaves uniquely to afford only the *trans* addition compound[5].

In order to reconcile this apparent discrepancy which may possibly be the

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result of an unusual change in mechanism as a function of ring size, we wish to report the results of our studies on the stereochemistry of the reaction of (I) with the homologous series of olefins: cyclopentene, cyclobutene and cyclopropene. The effect of methyl substitution on cyclopropene is also reported.

RESULTS

Reaction of (I) with cyclopentene (II)

Care was taken in this experiment to maintain the reaction conditions as close as possible to those reported previously[5]. Approximately equimolar quantities of (I) and (II) were allowed to react *in vacuo* at −78° for 30 h. The materials were warmed to room temperature and subsequent fractional condensation of volatile products through a −23° trap resulted in the isolation of the colorless addition compound (III).

The IR spectrum of (III) (Table 1) is in accord with spectra observed for the products of (I) with a variety of linear olefins[4]. In addition to the usual hydrocarbon absorptions, a strong broad band is noted at 930 cm^{-1} which is characteristic of BCl_2 stretching vibrations[6]. The shape and position of this absorption is apparently common to all hydrocarbons containing BCl_2 groups on adjacent carbon atoms[4]. The lack of an olefin stretching absorption in the 1650 cm^{-1} region, which is present in (II), indicates a ring saturated structure.

Evidence for the structural integrity of the ring is obtained by protonolysis with propionic acid[7]. The only volatile hydrocarbon that can be isolated after hydrolysis of (III) followed by treatment with the organic acid at 120° is cyclopentane.

It is well known that alkaline hydrogen peroxide oxidation of an organoborane stereospecifically cleaves the boron–carbon bond to yield an alcohol on hydrolysis[8]. When (III) is oxidized with an alkaline solution of H_2O_2, a high boiling liquid product is obtained after evaporation of the ether extract. A melting point range of 115–116.5° for the bis(*p*-nitrobenzoate) derivative of the diol corresponds to that reported for the *cis* compound (117°)[9]. The *trans*-diol derivative melts at 143°.

It is noteworthy that experiments at room temperature with an excess of olefin or (I) give identical results.

Reaction of (I) with cyclobutene (IV)

The product from the reaction of (I) with (IV) is a colorless, slightly volatile liquid (V) which can be purified by fractional condensation through a trap kept at −45°. As with (II), the reaction proceeds smoothly at −78° or at room temperature without color change.

The IR spectrum of (V) (Table 1) exhibits the usual strong and broad 920 cm^{-1} absorption indicating dichloroboryl substituents on the ring. No olefin band in the 1650 cm^{-1} region is observed.

The 60 MHz PMR spectrum of (V) contains two appreciably broadened multicenter signals at 2.43 ppm and 2.92 ppm with respective area ratio of 2/1. Based on the area ratio, the high field envelope of peaks has been assigned to ring methylene protons. This assignment is in accord with the proton spectra of the 2/1 adduct between (I) and 1,3-cyclohexadiene which has BCl_2 groups in essentially the same relative proximity to methylene protons[10]. The broadness of the peaks in both compounds and the general lack of resolution in the spectrum of (V) can be attributed both to interactions of the protons with magnetically active ^{10}B and ^{11}B nuclei and to quadrupole relaxation effects. Evidence for these interactions will be discussed later.

That the cyclobutyl ring is the basic structural unit in (V) is evidenced by the detection of only cyclobutane from protonolysis with propionic acid. Moreover, stereochemical details are revealed by oxidation of (V) with alkaline H_2O_2. A colorless liquid is obtained which, when derivatized with benzoyl chloride, gives a white solid with a melting point range (60–61°) indicative of the dibenzoate of the *cis*-diol (*cis* 61–61.5°, *trans* 112–113°)[11].

Reaction of (I) with cyclopropene (VI)

An equimolar mixture of (I) and (VI) in an inert solvent such as pentane is combined *in vacuo* at $-196°$. *Warning: this reaction is explosive in the absence of an inert solvent.* For best results, (I) is dissolved in the solvent prior to condensation of the hydrocarbon. If the reactants are allowed to warm slowly from $-196°$ to room temperature, the reaction proceeds smoothly without a color change. A colorless liquid product, (VII), is isolated by fractionation of the volatile materials through a $-45°$ bath. (VII) is low melting (-78 to $-78.8°$), slightly volatile [vp. (25°), 5.80 mm] and relatively stable towards decomposition at room temperature. Above 100° decomposition is rapid and evolves a mixture of BCl_3 and $HBCl_2$. The residue from decomposition is a non-volatile orange oil, presumably a polymer.

The IR spectra of (VII) (Table 1) suggests that olefin addition rather than a ring cleavage predominates. The C=C absorption at 1641 cm^{-1} in (VI) is absent in (VII). Furthermore, the weak bands at 3070 cm^{-1} and 3010 cm^{-1}, and the medium absorptions at 1200 cm^{-1} and 1020 cm^{-1} are characteristic of an in-tact cyclopropyl ring[12].

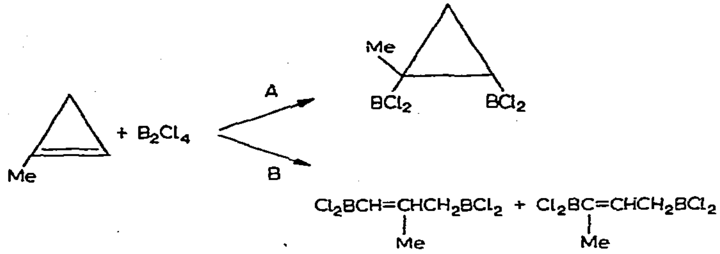
Attempts to substantiate the stereochemistry of (VII) by specific deboronation and protonolysis with organic acids were unsuccessful. Propene rather than cyclopropane is evolved regardless of acid or reaction conditions.

Oxidation with alkaline hydrogen peroxide did not afford the expected diol. Extraction of the aqueous solution with diethyl ether gives a viscous yellow oil which could not be completely characterized.

The proton NMR spectrum of (VII) (in CCl_4 at 60 MHz) is reproduced in Fig. 1. A complex multiplet envelop is observed at 1.5 ppm relative to TMS as an internal standard. Fig. 2 is a comparable spectrum on the HR 60 but irradiated at 9.251 MHz to decouple the ^{11}B nuclei. Interpretation of the spectra will be discussed later.

Reaction of (I) with 1-methylcyclopropane (VIII)

The reaction of (I) with (VIII) is extremely difficult to control even in the presence of relatively large quantities of inert solvent. To avoid a sudden large exothermic reaction, the reaction mixture is dissolved in pentane and warmed very slowly from $-196°$ to room temperature over a period of several days. The solution becomes turbid and pink at $-160°$. Fractional condensation through a $-45°$ bath yields a colorless liquid (IX). Both the large melting range (-120 to $-96°$) and the hysteresis



in the vapor pressure-temperature curve values indicate that the reaction material is not a single component product.

The IR spectrum (Table 1) suggests that the reaction proceeds by paths involving both olefin addition and ring cleavage. Besides the characteristic broad BCl_2 absorptions in the 910 cm^{-1} region, bands at 3040 cm^{-1} and 1605 cm^{-1} are interpreted as ring C–H stretching (Path A) and C=C stretching (Path B) respectively[12].

The proton NMR data are consistent with the formation of both saturated and unsaturated products. Multicenter patterns of broad peaks appear at 1.0–2.5 ppm (Me), 3.15 ppm (CH_2) and 6.0 ppm (C=CH).

Deboronation with propionic acid results in ring cleavage to give equimolar amounts of methylpropene, 1- and 2-butene. It is noteworthy that n-butane is not observed. Thus, secondary addition of (I) to the products of A or B is not appreciable.

DISCUSSION

The stereochemistry of B_2Cl_4 addition to cyclic olefins parallels comparable reactions with linear olefins and acetylenes. The experimental results presented here represent unequivocal evidence favoring a *cis*-addition mechanism, probably concerted, to four and five membered hydrocarbon rings. Larger cyclic olefins and bicyclic olefins have been shown to behave similarly[1,4]. In each case, the predominant product from specific oxidative cleavage of the B–C bond is the *cis*-diol, to the apparent exclusion of the *trans*-diol.

Attempts to support a *cis*-addition structure for the cyclopropyl derivative by chemical means were unsuccessful. For example, deboronation with propionic acid at elevated temperatures results in ring rupture and liberation of propene as the only volatile hydrocarbon. The cleavage reaction occurs regardless of the conditions or the organic acid used. Additionally, oxidative cleavage of the B–C bond with alkaline peroxide results in ring cleavage and polymer formation. The latter is a non-volatile oil whose polyol structure is suggested by the strong O–H stretching absorption between 3100–3500 cm^{-1}.

Some structural information for (VII) can be inferred from the IR spectrum (Table 1). The absence of a C=C stretching band at 1641 cm^{-1}, which is present in the olefin, implies that the compound is a saturated hydrocarbon. The prominent features of the spectrum which support a ring structure include (1) a very weak band at 3070 cm^{-1} which is assigned the asymmetric CH_2 stretching vibration in cyclopropyl rings, (2) the absorption at 3010 cm^{-1} which is characteristic of a ring methine (C–H) stretch and (3) the medium bands at 1200 cm^{-1} and 1020 cm^{-1} which are indicative of ring skeletal motions[12].

TABLE 1

IR SPECTRA OF B_2Cl_4–ADDITION COMPOUNDS

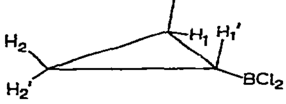
Compound	Frequencies (cm^{-1}) and relative intensities[a]
Cyclopentene–B_2Cl_4 (III)	2880 vs, 2800 s, 1440 s, 1375 m, 1305 m, 1265 m, 1210 m, 1110 sh, 1105 s, 1090 (sh) 1050 (sh), 1010 (br), 925 s (vbr), 860 m, 850 (sh), 835 s, 790 w
Cyclobutene–B_2Cl_4 (V)	3020 (sh), 2985 s, 2910 s, 1440 w, 1395 w, 1320 s, 1290 s, 1250 m, 1210 w, 1160 (sh), 1130 s (br), 1055 m, 1010 m (br), 920 s (vbr), 850 w, 790 m, 730 vw, 720 vw, 690 m
Cyclopropene–B_2Cl_4 (VII)	3070 vw, 3010 w, 2980 w, 2960 w, 2940 vw, 1500 w, 1362 vs, 1380 vs, 1280 vw, 1200 m, 1130 vs, 1082 vs, 1047 m, 994 s, (sh), 957 br, 920 (br), 890 (sh), 770 vw, 612 s, 541 w, 400 m
Methylcyclopropene–B_2Cl_4 (IX)	3040 w, 3000 (sh), 2980 s, 2930 s, 2870 w, 1605 m, 1430 s, 1385 vs, 1360 vs, 1285 vw, 1255 s, 1180 s, 1135 s (br), 1065 m, 1040 m, 1000 s, 920 s (vbr), 875 (sh), 780 m, 600 vs, 550 s, 535 m

[a] s: strong; m: medium; w: weak; v: very; br: broad; sh: shoulder.

Two properties suggest that (VII) is a unique structural isomer. First, a relatively narrow melting point range (−78° to −79°) is observed using a modified Stock-type melting point apparatus[13]. The relative invariability of the melting range with samples isolated from separate experiments (Table 2) indicates either a single component system or, more unlikely, a fortuitous and reproducible eutectic composition. Secondly, the linear relationship between the log P(mm) and $1/T$(°K) is reproducible from sample to sample regardless of heating or cooling. As little as a five percent mixture of known related isomers (products from the reaction of (I) with *cis*- and *trans*-2-butene) show a large melting point range (−40 to −49.5°) and deviations from linearity with hysteresis in the vapor pressure curve.

The most convincing evidence for structural assignment is obtained from the proton resonance spectrum. Theoretically, ^1H NMR should be capable of distinguishing between the *cis* (VIIA) and *trans* (VIIB) structures.

(VII A)



(VII B)

Isomer (VIIA) should exhibit a complex AA'BC spin–spin coupled system, whereas (VIIB) is expected to have considerably simpler AA'BB' coupling[14]. Regardless of the magnitude of the shifts or coupling constants, the spectrum of (VIIB) must be centro-symmetric. This is not so for (VIIA), an AA'BC molecule. In fact, based on accumulated literature data for substituted cyclopropanes, no reasonable values of chemical shifts, *geminal* coupling constants and across-ring *cis* and *trans* coupling constants in (VIIA) can reduce an AA'BC spectrum to AA'BB'[15]. It is noteworthy that similar arguments have been successfully applied to the structural assignments of 1,2-dichloro- and 1,2-diiodocyclopropane[16].

The proton spectrum of (VII) at 60 MHz (Fig. 1) consists of a complex multiplet envelope of overlapping peaks centered at 1.5 ppm. Although the pattern of peaks is apparently asymmetrical, or perhaps possibly pseudosymmetrical, it is not clear that the asymmetry is a result of a *cis* proton arrangement. For example, a *trans* isomer in which $J(H_1{-}^{11}B)$ is significant and appreciably larger than $J(H_2{-}^{11}B)$ could result in considerable broadening of portions of the spectrum which would apparently destroy true centrosymmetry. The effect of broadening attributed to both $H{-}^{11}B$ coupling and inefficient ^{11}B quadrupole relaxation has been widely reported for boranes, organoboranes and organodichloroboranes[17,4]. It is conceivable, therefore, that the spectrum in Fig. 1 consists of a symmetrical pattern of overlapping multiplets in which the lower field absorptions are assigned to H_1 of the *trans* compound. This hypothesis was tested by heteronuclear decoupling of the boron from the proton. Fig. 2 is the 60 MHz proton spectrum of (VII) in which simultaneous irradiation at 9.251 MHz has eliminated boron coupling. The principle feature of the spectrum is the lack of a center of symmetry. Clearly, the only assignment consistent with all the data is a *cis* structure.

Substitution of a methyl group contiguous to the double bond in cyclopropene alters both the rate and selectivity of the reaction. In addition to saturation

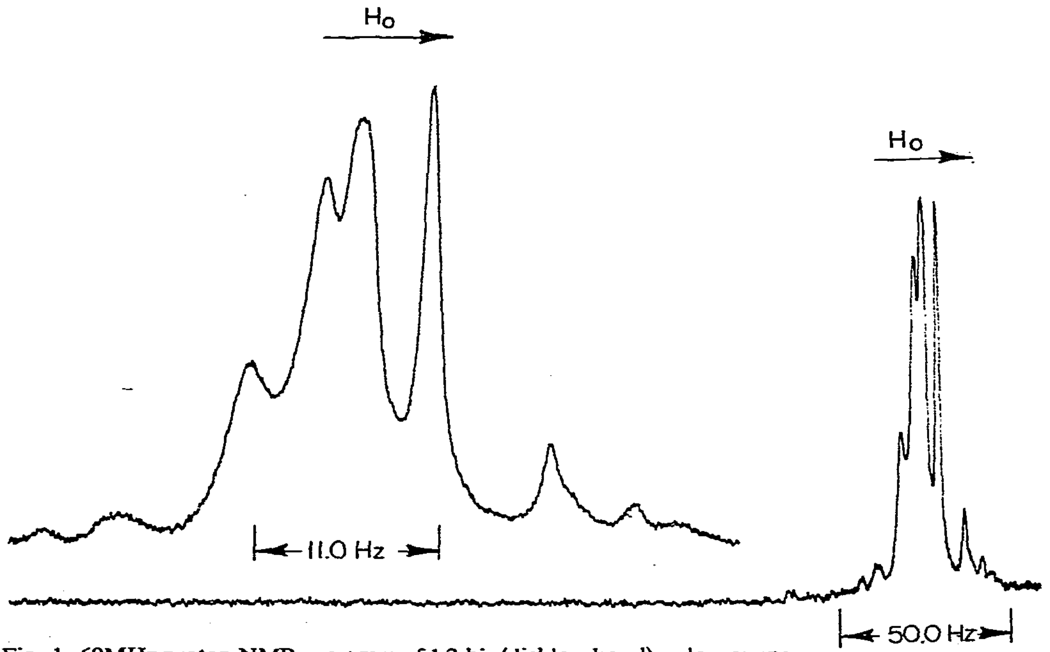


Fig. 1. 60MHz proton NMR spectrum of 1,2-bis(dichloroboryl)cyclopropane.

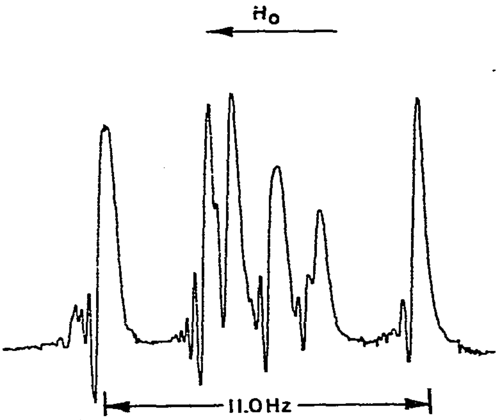


Fig. 2. 60MHz proton NMR spectrum of 1,2-bis(dichloroboryl)cyclopropane irradiated at 9.251 MHz.

of the ring, products are formed which result from a ring cleavage reaction. The reaction is extremely rapid and complete by the time the mixture, in pentane, is warmed to −162°. The fact that similar reactions of (I) with 2-butene, methylpropene or 1-butene occur normally and smoothly at room temperature without cleavage of adjacent carbon–carbon sigma bonds[1,4], suggests that the anomalous results are caused by additional ring strain owing to the presence of the methyl group. An alternative hypothesis could involve inductive release of the methyl group which appreciably enriches the "pi" character of the ring, thereby increasing the propensity of subhalide attack at adjacent positions to the pi bond[18,*].

EXPERIMENTAL

All organic and organoboron compounds were manipulated by conventional high-vacuum techniques. Extreme care was taken not to expose either reactants or products to moisture or oxygen. Perkin–Elmer 337 and 521 Grating Spectrometers were used to record IR spectra. All spectra were taken as neat smears on KBr plates. The proton resonance spectra were obtained on a Varian A60 spectrometer relative to TMS as an internal standard. Boron-11 decoupling was accomplished on a Varian HR60 spectrometer by simultaneous irradiation at 9.251 MHz. Liquid composition analyses of hydrocarbons were obtained with a Hewlett–Packard F&M 700 Chromatograph. Elemental analyses were reported by Schwarzkopf Microanalytical Laboratories.

(I) was synthesized by established electrical discharge methods[19]. (VI) was prepared from allyl chloride and sodamide by the method of Closs and Krantz[20]. The product was purified by fractional condensation. Similarly, (VIII) was obtained from either 1-chloro-2-butene or 3-chloro-2-methylpropene. (II) (Chemical Samples Co.) and (IV) (compliments of Dr. George Slavin, PIB) were purified by fractional condensation and dried prior to use by volatilization through a tower of 3A molecular sieves.

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[*] The reaction of (I) with cyclopropyl rings containing methyl substituents will be reported in Part II of this series.

Preparation of cis-1,2-bis(dichloroboryl)cyclopentane (III)

In a typical experiment a mixture of (I) (12.6 mmoles) and (II) (12.4 mmoles) were cocondensed in a vacuum ampoule. The mixture was warmed to −78° (dry ice/acetone bath) and stirred for 30 h. Fractional condensation through a −45° bath afforded a colorless, slightly volatile liquid, (III) (~1.8 g). The material trapped at −196° was a mixture of (I) and (II) contaminated with a small quantity of BCl_3. (Found: C, 26.3; H, 4.04; B, 9.64; Cl, 60.8; mol.wt., 231.6. $C_5H_8B_2Cl_4$ calcd.: C, 25.94; H, 3.48; B, 9.33; Cl, 61.25%; mol.wt., 221.) The IR spectrum is summarized in Table 1.

(III) (2.20 mmoles) was hydrolyzed with excess water at room temperature. The water and HCl were removed by pumping. The residues were heated *in vacuo* to 120° with anhydrous propionic acid (~5 ml) for 48 h. The mixture was cooled to −12° and the volatile materials were pumped through a caustic tower (KOH pellets) into a −196° trap. Both IR spectroscopy and gas-liquid phase chromatography verify that the condensible material is cyclopentane (1.56 mmoles).

(III) (10.8 mmoles; combined product from several experiments) was oxidized with 20 ml of aqueous 30% H_2O_2, 3 *M* in NaOH. The excess peroxide was destroyed with a platinum electrode. The aqueous solution was extracted with diethyl ether in a liquid–liquid extractor. A high boiling liquid product (0.82 g) was isolated after evaporation of ether. The bis(*p*-nitrobenzoate) derivative was prepared by refluxing the diol with excess *p*-nitrobenzoylchloride for 1 h. Excess water was added and the mixture was cooled to 0°. The precipitate was filtered and washed with 2% Na_2CO_3 (m.p. 115–116.5°; reported[9]: *cis*, 117°; *trans*, 143°). (Found: C, 57.0; H, 4.11. $C_{19}H_{16}N_2O_8$ calcd.: C, 57.00; H, 4.03%.)

Preparation of cis-1,2-bis(dichloroboryl)cyclobutane (V)

For example, (I) (4.21 mmoles) was combined with (IV) (5.10 mmoles) at −196°. The mixture was warmed slowly to room temperature over an 8 h period. Fractional condensation of products resulted in a colorless, slightly volatile liquid (V) at −45° and a mixture of unreacted starting materials at −196°. (Found: C, 22.7; H, 3.26; B, 9.88; mol.wt., 217.5. $C_4H_6B_2Cl_4$: C, 22.08; H, 2.76; B, 9.93%; mol.wt., 208.) See Table 1 for IR spectrum.

The PMR spectrum at 60 MHz consists of two envelopes; δ 2.43 (mc*, broad CH_2), δ 2.92 (mc, broad CH), area ratio, 2/1.

(V) (1.7 mmoles) was hydrolyzed and then heated to 110° with propionic acid for 2 days. The products were cooled to −20° and the more volatile components were pumped into a −196° trap. Only cyclobutane, as confirmed by comparison of IR, PMR and vapor pressures with that of the authentic sample (Isotropic Research, Ltd.) was obtained.

(V) (14.52 mmoles, combined from several experiments) was oxidized with 20 ml of 30% H_2O_2 in 3 *M* NaOH at room temperature. The excess peroxide was decomposed and the aqueous solution was extracted with diethyl ether. A colorless liquid (0.85 g) remained after evaporation of solvent. The dibenzoate derivative of the diol was prepared from benzoyl chloride (m.p. 60–61°; reported[11]: *cis*, 61–61.5°; *trans*, 112–113°). (Found: C, 73.1; H, 5.26. $C_{18}H_{16}O_4$ calcd.: C, 72.96; H, 5.44%.)

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* mc = multi-center.

TABLE 2

MELTING POINTS OF SEPARATE SAMPLES OF (VII)

Sample	Melting point range (°C)
1	−78.2 to −78.8
2	−78.0 to −78.8
3	−78.2 to −79.0
4	−78.0 to −78.6

Preparation of cis-1,2-bis(dichloroboryl)cyclopropane (VII)

(I) (10.5 mmoles) was condensed into a vacuum ampoule containing about 15 ml pentane. The mixture was warmed to room temperature to insure complete dissolution of (I). (VI) (10.3 mmoles) was then condensed at −196° onto the mixture. *Warning: the reaction is violently exothermic in the absence of an inert solvent.* The reactants were warmed slowly from −196° to room temperature over a period of several days. No color change was observed. The reaction product, (VII), was isolated and purified by repeated fractional condensations through a −45° trap. (VII) is a colorless, slightly volatile liquid which melts at −78° to −79°. (Found: C, 17.5, 17.6; H, 2.19, 2.06; B, 10.3, 10.9; Cl, 69.4, 69.4; mol.wt., 208. $C_3H_4B_2Cl_4$ calcd.: C, 17.7; H, 1.98; B, 10.6; Cl, 69.7%; mol.wt., 203.5) $P(\text{mm})[t(°\text{C})]$: 5.80(25.0); 7.95(30.3); 13.53(40.1); 22.11(50.9); 34.56(60.7); 54.15(70.1); 80.44(80.1); $\log P = 8.62 - 2173/T$ from 25–80°. The IR spectrum of (VII) is recorded in Table 1. The 60 MHz PMR spectrum is reproduced in Fig. 1. Fig. 2 is the spectrum of the ^{11}B decoupled sample which is obtained by irradiation of the 60 MHz proton resonances at 9.251 MHz.

(VII) (2.6 mmoles) was hydrolyzed with 5 ml H_2O. Subsequent treatment with anhydrous propionic or acetic acid under a variety of conditions gave propene as the only hydrocarbon product.

(VII) (4.83 mmoles) was treated with alkaline H_2O_2. The excess peroxide was destroyed prior to extraction with diethyl ether. Evaporation of the solvent gave a viscous yellow oil which reacted with benzoyl chloride to give an infusible solid (decompn. 250°).

Reaction with 1-methylcyclopropene (VIII)

(I) (6.54 mmoles) was condensed *in vacuo* with (VIII) (9.02 mmoles). The mixture was warmed to −80° and an immediate exothermic reaction took place with the emission of a bright green flash and the deposition of black solids on the walls of the ampoule. The reaction was rerun [(I) 3.23 mmoles, (VIII) 3.20 mmoles] in pentane (15 ml). The mixture was warmed to −160°. An immediate color change occurred and the solution turned turbid and pink. After several hours the temperature was raised to −126° (3 h), to −80° (12 h) and finally to room temperature. Fractionation through a −45° trap was sufficient to trap the less volatile materials (IX). The higher vapor pressure material (BCl_3 and pentane) was trapped at −196°. The residues in the ampoule were pale red solids. [Found: C, 23.0; H, 3.42; B, 10.1; Cl, 64.8. $C_4H_6B_2Cl_4$ calcd.: C, 22.08; H, 2.76; B, 9.93; Cl, 65.23%.] The IR spectrum is recorded in Table 1. PMR (CCl_4): δ 1.0–2.5 ppm, δ 3.15 (mc, CH_2), δ 6.0 (mc, C=CH), m.p. −120 to −96°.

Approximately 3 mmoles of (IX) were heated with propionic acid at 100° for 48 h. IR spectroscopy and chromatography of the volatile products indicate an equimolar mixture of 1- and 2-butene and methylpropene.

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