63. *Diboron Tetrachloride–Olefin Compounds. Part III.*[1] *The Reaction of Diboron Tetrachloride with Trichloroethylene, Isobutene, and* cis- *and* trans-*But-2-ene.*

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Diboron tetrachloride is stabilised by addition of trichloroethylene; the nuclear magnetic resonance spectrum of the mixture indicates adduct formation, but no adduct was isolated. Diboron tetrachloride causes polymerisation of isobutene but forms stable 1 : 1 adducts with *cis*- and *trans*-but-2-ene. Both of these react with trimethylamine and ammonia in the same way as the ethylene adduct, but oxidation gives 2-chlorobutane and no free olefin. The wide melting ranges of these adducts are attributed to mixtures of rotational isomers, on the basis of their nuclear magnetic resonance spectra.

SINCE the isolation[2] of ethylene-1,2-bis(boron dichloride) $Cl_2B{\cdot}CH_2{\cdot}CH_2{\cdot}BCl_2$, the preparation and properties of other diboron tetrachloride–olefin adducts have been described,[3] *e.g.*, the stable but-2-ene adduct B_2Cl_4,CHMe:CHMe; but halogenoethylenes do not appear

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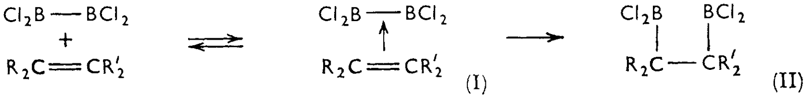
[1] Part I, *J.*, 1960, 43; Part II, *J.*, 1960, 2075.

[2] Urry, Kerrigan, Parsons, and Schlesinger, *J. Amer. Chem. Soc.*, 1954, **76**, 5299.

[3] Ceron, Finch, Frey, Kerrigan, Parsons, Urry, and Schlesinger, *J. Amer. Chem. Soc.*, 1959, **81**, 6368.

to react with diboron tetrachloride, although they stabilise it against decomposition to polymeric $(BCl)_n$ and boron trichloride.

The rapidity of the reaction of many olefins with diboron tetrachloride at low temperatures indicates that initial fission of the B–B bond and then addition is unlikely; more probably, the first stage is π-donation [4] from the olefin into the two vacant *p*-type orbitals of the boron atoms, and these being on adjacent bonded atoms constitute, in effect, a "vacant π-orbital." This would give a π-complex (I) which might either dissociate again or suffer fission of the B–B bond to give the structure (II), as found with ethylene ($R = R' = H$). The stability of the complex (I) with respect to dissociation into the reactants may be decreased (*a*) if there is repulsion or steric interference between the substituents, R and R′, and the chlorine atoms, and (*b*) if the π-donating ability of the olefin is reduced by the inductive or mesomeric effects of R or R′, either because of decreased electron density at the π-bond or because the latter is made asymmetrical when $R \neq R'$. The available evidence suggests that substituent effects are not critical when R = alkyl, but are important when R = halogen; stabilisation against decomposition in the latter case has, however, to be explained. We have therefore investigated the reaction of diboron tetrachloride with trichloroethylene, isobutene, and *cis*- and *trans*-but-2-ene; if double-bond character is lost [*i.e.*, if the adduct (II) is formed], these two isomers should give the same product.



(I) (II)

Trichloroethylene and diboron tetrachloride when mixed at −196° and warmed to −78° showed no evidence of solid adduct formation, and after several hours at 20° no reaction could be observed; but the expected rapid decomposition of diboron tetrachloride at this temperature did not occur. Fractionation of the mixture was impracticable, and excess of ammonia was therefore added; this reacts with diboron tetrachloride [5] and would also be expected to react with any stable olefin adduct without liberation of the free olefin.[1] A white solid was obtained, but all the trichloroethylene added was recovered, suggesting that a stable adduct had not been formed. However the ^1H nuclear magnetic resonance spectrum of the diboron tetrachloride–trichloroethylene mixture indicated that two-thirds of the latter had formed a substituted ethane and the remainder had formed an intermediate compound still retaining the double bond. Evidence for the substituted ethane was a multiplet absorption of chemical shift $\sim$183 c./sec. consisting of at least seven bands (all chemical shifts reported here are relative to water as external standard, positive values to the high-field side of the water band). This is consistent with the presence of two rotational isomers each containing a differently shielded hydrogen nucleus interacting with the boron magnetic nucleus ($I = \frac{3}{2}$) to give the observed fine structure. The remainder of the spectrum consisted of a single absorption in the olefinic region of chemical shift −59 c/sec. which could arise from an intermediate of type (I). Formation of either (I) or (II) would explain the observed stabilisation of the diboron tetrachloride; decomposition of the latter to $(BCl)_n$ and boron trichloride might occur by fission of the B–B bond, preceded by internal co-ordination (III), which would be prevented by filling of the vacant boron orbitals (hence the stability of, *e.g.*, the compound $B_2Cl_4,2NMe_3$).

In the reaction of isobutene and diboron tetrachloride, rapid polymerisation of the isobutene occurred; although variable amounts of diboron tetrachloride appeared to have reacted, no adduct was isolated.

Either *cis*- or *trans*-but-2-ene reacted readily with diboron tetrachloride at −78° to give a 1 : 1 addition compound; the reactions were completed in each case by repeated addition

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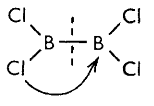
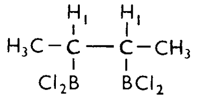
[4] Holliday and Massey, *J. Inorg. Nuclear Chem.*, 1960, in the press.

[5] Urry, Wartik, Moore, and Schlesinger, *J. Amer. Chem. Soc.*, 1954, **76**, 5293.

and removal of the butene, a procedure necessary in the case of the ethylene compound [2] to ensure complete reaction, and the only likely impurity, boron trichloride, was removed in this procedure. From either butene, the addition compound appeared as white crystals at —78°, and the chemical properties were identical, resembling those of the ethylene adduct. Thus, 1 mol. of either reacted with 2 mols. of trimethylamine to give a white solid which was thermally stable and not readily oxidised or hydrolysed, indicating the probable structure $Me_3N{\cdot}BCl_2{\cdot}CHMe{\cdot}CHMe{\cdot}BCl_2{\cdot}NMe_3$. 2 Mols. of hydrogen chloride added to this compound at room temperature—the corresponding reaction with the ethylene compound was complete only after heating. The addition did not liberate diboron tetrachloride–butene or other volatile products, and the product can be formulated as $[Me_3NH]_2[Cl_3B{\cdot}CHMe{\cdot}CHMe{\cdot}BCl_3]$. As with the ethylene compound, 1 mol. of the butene adduct reacted with 6 mols. of ammonia


(III)


$H_3C-\overset{H}{\underset{Cl_2B}{C}}-\overset{H}{\underset{BCl_2}{C}}-CH_3$
(IV)

$$nB_2Cl_4,C_4H_8 + 6nNH_3 \longrightarrow 4nNH_4Cl + [(BNH)_2,C_4H_8]_n$$

and the required amount of ammonium chloride was separated by sublimation from the other polymeric product. Reaction of either butene adduct with water or alkali at temperatures up to 100° did not give volatile products; *i.e.*, only the B–Cl bonds were attacked:

$$B_2Cl_4,C_4H_8 + 4H_2O \longrightarrow B_2(OH)_4,C_4H_8 + 4HCl$$

The product, like the corresponding ethylene compound, showed acid properties, enhanced by addition of mannitol. Neither butene adduct gave any reaction with ethylene; *i.e.*, the butene was not displaced.

The only observed reaction of diboron tetrachloride–ethylene which gives the free olefin is the oxidation by molecular oxygen, a reaction which is vigorous even at low temperatures.[1] A similar reaction with the butene adducts, releasing either *cis*- or *trans*-but-2-ene, might have helped in the elucidation of the reaction mechanism. Although, as before, oxygen did react with the butene adducts in a 1 : 1 ratio, the reaction was much less vigorous and either a long reaction time or heating was required to complete it. No free olefin was formed; the main product was hydrogen chloride, and a non-volatile polymer remained, in which most of the boron and chlorine were titratable on hydrolysis. A small amount of 2-chlorobutane was found; this could have been formed by reaction of any liberated but-2-ene and hydrogen chloride, and experiment showed that this reaction was catalysed by boron trichloride in presence of oxygen.

These reactions suggest that the butene adducts are identical, with no remaining double-bond character; *i.e.*, both have structure (II), like the ethylene adduct. The infrared spectra of the two butene adducts were identical, and both gave vapour-pressure values close to those reported for B_2Cl_4,C_4H_8 by Schlesinger *et al.*[3] But even after repeated fractionation (with no further change in the spectra), neither adduct melted sharply at the reported [3] temperature of —44·8°. Each preparation gave a product melting over a somewhat different temperature range; *e.g.*, the *cis*-adduct gave m. p. —19° to —22°; —42° to —48°, and the *trans*-adduct —56° to —60°; —25° to —62°. It was not possible therefore to correlate melting range with the particular isomer used.

In order to investigate these peculiarities further, and to confirm the ethane-type structure, the nuclear magnetic resonance spectra of various samples were examined. The ^1H spectra at 40·00 mc./sec. possessed no bands for olefinic-linked hydrogen, indicating that the double bond had been opened. Some of the high-field bands in the spectra of different samples differed in both chemical shift and intensity. However, a broad band at ~120 c./sec. was common to all the spectra and this was assigned to the single hydrogen atoms H_1 marked in formula (IV). The intensity of this band was lower than expected but it could be assigned with confidence since the hydrogen-1 spectrum of diboron tetrachloride–ethylene has a similar band, of this chemical shift and possessing no spin–spin interaction fine structure from the boron-11 nucleus. Such splittings are therefore assumed to be absent from the spectra of the butene adducts. The remaining bands of the spectrum corresponded to methyl-type hydrogen and in some cases extended over the range 145—183 c./sec. At 16·2 mc./sec. the spectra of some samples possessed at least four chemical shifts in the methyl region of the spectrum. None of these could be due to *cis*- or *trans*-butene impurities since there was no olefinic-linked hydrogen present, and the high-field bands of the but-2-ene compounds would also be readily recognisable. A freely rotating ethane-type structure would have resulted in a spectrum with a quartet for the lone hydrogen atoms and a doublet for the methyl groups with only two chemical shifts involved. Hindered rotation about the central C–C bond could give rise to three differently shielded methyl groups: further hindered rotation of the methyl groups themselves would result in a spectrum having more than three chemical shifts in the methyl region. Further evidence that this situation prevails is provided by the broad nature of the band of the lone hydrogen atoms. An examination of models of these compounds indicated that hindered rotation is possible; any remaining double-bond character would of course make it more likely. The varying intensities of some of the bands in the methyl region resulted from the presence of different amounts of the various rotational isomers in the different samples, and this would explain the melting-point peculiarities. The absence of an equilibrium mixture indicates that the populations of the isomers were controlled by some factor in their preparation and that, once formed, the energy barriers separating them were high enough to prevent interconversion at room temperature. This was further confirmed by examining the samples over the range −60° to +60°, no marked change in the spectra being observed.

Had the spectra of the *cis*- and *trans*-compounds been consistently different owing to the non-equivalence of the hydrogen atoms in hindered-rotation *meso*- and racemic forms,[6] it would have been possible to confirm that the diboron tetrachloride does not dissociate before addition of the olefin, and correlation with the expected isomers, diboron tetrachloride being assumed to be planar, would be further evidence for this structure.

EXPERIMENTAL

The preparation of diboron tetrachloride, and the methods used to study its reactions, have been described previously.[1] Trichloroethylene was dried (Na_2SO_4) and fractionated; it had v. p. 21 mm. at 0°. Pure samples of *cis*- and *trans*-but-2-ene were obtained from the National Chemical Laboratory. ^1H high-resolution nuclear magnetic resonance spectra were obtained at 40·00 mc./sec. by use of a Varian V-4300B spectrometer equipped with a field stabiliser.

In the following experiments, units are mmoles or mg.-atoms unless otherwise stated.

Reactions of Diboron Tetrachloride.—(i) *With trichloroethylene.* Diboron tetrachloride (1·44) and trichloroethylene (1·17) when warmed from −196° gave no solid product at −78°. After warming to 20° for 1 hr., excess of ammonia was added to give a white solid; trichloroethylene (1·17) was the only volatile product.

(ii) *With* cis- *or* trans-*but-2-ene.* In a typical experiment, *cis*-but-2-ene (2·12) was condensed on diboron tetrachloride (1·72), and the mixture warmed to −78°. Material volatile at this temperature was distilled off and returned to the reaction vessel several times, and finally the mixture was stored for ~18 hr. at −78°. The solid *product* then weighed 0·388 g. (= 1·76 of B_2Cl_4,C_4H_8) and *cis*-but-2-ene (0·42) was recovered. Hydrolysis of the product with excess of sodium hydroxide for 1 hr. at 100° gave Cl, 7·02 (B_2Cl_4,C_4H_8 requires Cl, 7·04); no butene was recovered.

Reactions of the But-2-ene Adducts with Trimethylamine and Ammonia.—In a typical experiment, excess of trimethylamine (2·76) was condensed on the adduct (0·97) at −196°; on warming, a vigorous reaction followed melting of the reactants. Trimethylamine (1·53) was recovered

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[6] Lee and Sutcliffe, *Trans. Faraday Soc.*, 1959, **55**, 880.

after 18 hr. at 20° and returned to the reaction vessel; after 1 minute's heating at 50°, trimethylamine (0·75) was recovered. The solid *product* weighed 0·339 g. (= 1·00 of $B_2Cl_4,C_4H_8,2NMe_3$); hydrolysis with boiling sodium hydroxide solution gave Cl, 3·90 ($B_2Cl_4,C_4H_8,2NMe_3$ requires Cl, 4·00). Treatment of the product with excess of methyl alcohol or water at 20° gave quantitative recovery of these reagents, but when the product (1·00) was treated with hydrogen chloride (3·60) at 20°, recovery of hydrogen chloride was 1·74, with no further uptake on heating, and no other volatile product; hydrolysis of the solid *product* gave Cl, 5·7 ($B_2Cl_4,C_4H_8,2NMe_3,2HCl$ requires Cl, 6·00).

Excess of ammonia (2·46) was condensed on the adduct B_2Cl_4,C_4H_8 (0·205), and the mixture warmed to 20°. After the vigorous reaction, ammonia (1·25) was recovered, but no other volatile product. The solid residue on heating gave a sublimate of ammonium chloride (0·80), leaving a white solid product. Hence reaction ratio, adduct : NH_3 used : NH_4Cl = 1 : 5·9 : 3·9.

Oxidation of the But-2-ene Adducts.—The reactions were carried out as previously described; [1] details are tabulated:

Time (hr.) and temp.	6 at 20°	125 at 20°, 0·25 at 50°	2 at 80°, 200 at 20°
B_2Cl_4,C_4H_8 used	0·28	0·50	0·62
O_2 used	0·21	0·51	0·63
Products: HCl	0·39	0·81	1·01
BCl_3	0·13	0·03	0·00
C_4H_9Cl	0·10	0·09	0·18
Residue: Cl^- (titrn.)	0·12	0·45	0·67
B (titrn.)	0·34	0·91	1·04

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