

## Reactions of Trivinylborane with Diboron Tetrahalides: Properties of Some Dihalogenoboryl(vinylboryl)ethanes

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1:1 Addition of trivinylborane and diboron tetrachloride gives the adduct 1,2-bis(dichloroboryl)-1-(divinylboryl)-ethane  $(\text{CH}_2\text{:CH})_2\text{B}\cdot\text{CH}(\text{BCl}_2)\cdot\text{CH}_2\text{BCl}_2$  (I), which reacts with  $\text{BX}_3$  ( $\text{X} = \text{Cl}, \text{NMe}_3$ ) to give  $\text{X}_2\text{B}\cdot\text{CH}(\text{BCl}_2)\cdot\text{CH}_2\text{BCl}_2$ . Dehydroboration of (I) by addition of trimethylamine gives trimethylamine-divinylborane and pyrolysis gives 1,2-bisdichloroborylethylene. Similar 1:1 addition using diboron tetrafluoride gives an adduct with properties similar to (I).

1:2 Addition of trivinylborane and diboron tetrachloride gives  $(\text{CH}_2\text{:CH})\text{B}[\text{CH}(\text{BCl}_2)\cdot\text{CH}_2\text{BCl}_2]_2$ , unstable above  $-78^\circ\text{C}$ ; a similar adduct using diboron tetrafluoride has not been isolated. 1:3 addition does not occur with either tetrahalide.

WE have previously<sup>1</sup> reported briefly that the 1:1 addition of diboron tetrachloride to trivinylborane gives the compound  $(\text{CH}_2\text{:CH})_2\text{B}\cdot\text{CH}(\text{BCl}_2)\cdot\text{CH}_2\text{BCl}_2$  (I). We now report further studies on this compound, the results of the addition of an excess diboron tetrachloride, and the corresponding reactions with diboron tetrafluoride.

### EXPERIMENTAL AND RESULTS

All reactions were carried out in a vacuum system using quantities of *ca.* 1 mmol; reaction stoichiometries were established by material balance wherever possible since both reactants and products were air- and moisture-sensitive and reactive. The diboron tetrahalides and trivinylborane were prepared as described previously.<sup>2,3</sup> Boron, chlorine, and fluorine analyses were made by conventional methods. Quantitative cleavage of boron-carbon bonds by reaction with propionic acid at  $120^\circ$ , to yield hydrocarbon,<sup>4</sup> was used to identify boron-attached organo-groups, *e.g.* reaction of vinylboranes yielded a molar equivalent of ethylene for each vinyl group. I.r. spectra were recorded on a Perkin-Elmer 237 instrument,  $^1\text{H}$  n.m.r. spectra on a Varian Associates A60 machine, and mass spectra on a MS 902 spectrometer; all samples for spectra were prepared *in vacuo*.

In the following reactions quantities in brackets are mmol (unless otherwise stated) and data recorded are typical for several reactions in each case.  $^1\text{H}$  N.m.r.  $\tau$  values are relative to tetramethylsilane.

**1:1 Reaction of Trivinylborane and Diboron Tetrachloride: Identification and Reactions of 1,2-Bis(dichloroboryl)-1-divinylborylethane (I).**—Reaction of diboron tetrachloride (1.23) and trivinylborane (1.24) gave ethylene (0.06) as the only volatile product. Reaction of the nonvolatile product with propionic acid at  $120^\circ$  gave ethylene (2.43) and the residue, after degradation with alkaline peroxide, gave B, 12.88%; Cl, 55.3% [(I) requires B, 12.9%; Cl, 55.5%]. Direct aqueous hydrolysis of (I) (0.68) at  $60^\circ$ , gave ethylene (1.29) and subsequent pyrolysis at  $240^\circ$  gave ethane (0.55); direct reaction of (I) with hydrogen peroxide gave glyoxal (*o*-aminophenol and calcium oxide test<sup>5</sup>).

The i.r. spectrum of (I) showed a characteristic absorption at  $1580\text{ cm}^{-1}$  assigned to the C=C stretching frequency; the formation of (I) could be monitored by the disappearance of the characteristic peak in trivinylborane at  $750\text{ cm}^{-1}$ . The  $^1\text{H}$  n.m.r. spectrum of (I) in carbon tetrachloride showed the doublet  $\tau$  9.85 and triplet  $\tau$  9.30 expected for the ethane protons, and a broad multiplet  $\tau$  7.71; peak ratios for the spectrum were 1:2:6 respectively. The broad multiplet was attributed to polymerisation in carbon tetrachloride. Use of boron trichloride as a solvent caused reaction to occur (see below). However hydrogenation of (I) with Raney nickel allowed the  $^1\text{H}$  n.m.r. spectrum of the product to be examined in carbon tetrachloride; the doublet-triplet resonance due to the backbone protons was again observed, but the multiplet at  $\tau$  7.71 was now converted to a triplet at  $\tau$  9.04 and a quartet at  $\tau$  7.97 indicating formation of 1,2-bis(dichloroboryl)-1-diethylborylethane.

Compound (I) (0.63) was heated with bromine (1.18) to yield vinyl bromide (1.05) as a volatile product; (I) (0.80) with an excess of bromine (3.25) gave 1,1,2 tribromoethane (1.36).

Reaction of (I) (0.80) with an excess of boron trichloride gave a volatile product A, inseparable from the excess trichloride, and an involatile product B. The mixture of A and boron trichloride yielded ethylene (1.53) with propionic acid; the i.r. spectrum and mass spectrum of A indicated that it was divinylchloroborane. The involatile product, B, had i.r. and  $^1\text{H}$  n.m.r. spectra identical with those observed for 1,1,2 tris(dichloroboryl)ethane.<sup>6</sup> Reaction of B with propionic acid gave no ethylene. Reaction of (I) (0.80) and tris(dimethylamino)borane gave an inseparable, volatile mixture of a product C and excess tris(dimethylamino)borane, and an involatile product D. The mixture containing C and D was treated with propionic acid; C yielded ethylene (1.50) and D yielded only a small amount of ethylene (0.11). The mass spectrum of C indicated that it was divinyl(dimethylamino)borane.

Reaction of (I) (1.20) with trimethylamine (3.48) at  $120^\circ$  gave acetylene (1.05) and nonvolatile products; the latter after fractional sublimation yielded the following products. (i) A white crystalline solid E with an i.r. spectrum similar to that of trivinylborane-trimethylamine, but having a strong band at  $2360\text{ cm}^{-1}$ , assigned to B-H stretching; hydrolysis of E gave hydrogen and ethylene in the ratio

<sup>1</sup> A. K. Holliday and R. P. Ottley, *Chem. Comm.*, 1969, 336.

<sup>2</sup> A. G. Massey, D. S. Urch, and A. K. Holliday, *J. Inorg. Nuclear Chem.*, 1966, **28**, 365.

<sup>3</sup> A. K. Holliday and R. E. Pendlebury, *J. Organometallic Chem.*, 1967, **10**, 295.

<sup>4</sup> J. Crighton, A. K. Holliday, and N. R. Thompson, *Chem. and Ind.*, 1960, 347.

<sup>5</sup> F. Feigl and D. Goldstein, *Z. analyt. Chem.*, 1958, **163**, 30.

<sup>6</sup> T. D. Coyle and J. J. Ritter, *J. Organometallic Chem.*, 1968, **12**, 269.

1 : 2 and (qualitatively) trimethylamine, but no chloride; reaction of E with hydrogen chloride (2·15) yielded ethylene (2·07). (ii) A white solid with an i.r. spectrum identical with that of boron trichloride-trimethylamine. (iii) A brown unsublimed solid, which could not be quantitatively degraded by alkaline peroxide, with an unidentifiable i.r. spectrum. Reaction of 1,2-bis(dichloroboryl)ethylene (0·69) with trimethylamine gave, after pyrolysis at 120°, acetylene (0·66) and trimethylamine-boron trichloride.

Pyrolysis of (I) (0·80) at 220° gave boron trichloride, 1,2-bis(dichloroboryl)ethylene, and an involatile residue; reaction of propionic acid with the latter gave a mixture of hydrocarbons. The effect of time of heating on the yield of volatile products and hydrocarbons evolved with propionic acid is shown below.

Time of heating (hr.)	BCl <sub>3</sub>	C <sub>2</sub> H <sub>2</sub> (BCl <sub>2</sub> ) <sub>2</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2-3</sub> hydrocarbons
20	0·47	0·24	0·56	0·45	0·14
48	0·67	0·12	0·61	0·70	0·20

#### 1 : 2 Reaction of Trivinylborane and Diboron Tetrachloride.

—Reaction of diboron tetrachloride (1·66) and trivinylborane (0·84) at -78°, gave ethylene (0·05) as the only volatile product and a colourless crystalline solid (II). Reaction of (II) with an excess of propionic acid gave ethylene (0·80) and the residue after peroxide degradation gave B (Found: 12·05; Cl, 66·95%. C<sub>6</sub>H<sub>9</sub>B<sub>3</sub>Cl<sub>8</sub> requires B, 12·9; Cl, 67·75). Hydrolysis of (II) (0·67) gave ethylene (0·52) and ethane (0·90). At room temperature the reaction gave vinylchloroborane [i.r.; Found: B, 9·75; CH (as ethylene), 24·35; Cl, 64·95%. Calc. for C<sub>2</sub>H<sub>3</sub>BCl<sub>2</sub>: B, 10·1; CH, 24·9; Cl, 65·0]. Heating of (II) (0·80) for 24 hr. at 100° gave 0·74 vinylchloroborane. Treatment of (II) with an excess of boron trichloride at -78° for 7 days gave no reaction.

#### 1 : 3 Reaction of Trivinylborane and Diboron Tetrachloride.

—Diboron tetrachloride (3·05) and trivinylborane (1·00) gave, after 14 days at -78°, no material volatile at this temperature; hydrolysis to give hydrogen (0·73) indicated the presence of unchanged diboron tetrachloride. Similar reactions at room temperature all gave an involatile product which gave no hydrogen on hydrolysis, no reaction with propionic acid, and with an i.r. spectrum similar to that of 1,1,2-tris(dichloroboryl)ethane<sup>6</sup> [Found (after peroxide degradation): B, 12·0; Cl, 77·2%. Calc. for B<sub>3</sub>C<sub>2</sub>H<sub>3</sub>Cl<sub>6</sub>: B, 12·1; Cl, 78·0%].

#### 1 : 1 Reaction of Trivinylborane and Diboron Tetrafluoride.

—Diboron tetrafluoride (1·00) and trivinylborane (1·02) on reaction gave ethylene (0·03) as the only volatile product and a colourless nonvolatile oil (III); reaction of the latter with propionic acid gave ethylene (2·00) and a residue giving B, 17·0; F, 37·9%. C<sub>4</sub>H<sub>9</sub>B<sub>3</sub>F<sub>4</sub> requires: B, 17·35; F, 40·0%). Prolonged aqueous hydrolysis of (III) gave ethylene and ethane. Reaction of (III) (0·80) with boron trichloride (5·23) gave boron trifluoride (1·06), a mixture (4·09) of boron trichloride and divinylchloroborane (mass spectrum), and an involatile product yielding no ethylene with propionic acid (Found: B, 11·95; Cl, 77·2%. Calc. for C<sub>2</sub>H<sub>3</sub>B<sub>3</sub>Cl<sub>6</sub>: B, 12·1; Cl, 78·0%).

When (III) (0·96) was warmed slowly from -196° to

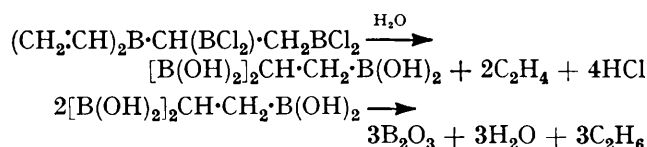
room temperature in presence of an excess of trimethylamine (3·47), uptake of the latter (1·96) gave an involatile white solid F and no volatile products; when the reaction mixture was warmed to 80° for 2 hr. a further uptake of trimethylamine (0·88) occurred to give another white solid (G). The solid (F) sublimed unchanged at 140°; the i.r. spectrum showed a C=C stretching peak at 1603 cm<sup>-1</sup> and the <sup>1</sup>H n.m.r. spectrum in carbon tetrachloride showed a multiplet at τ 2·7, a singlet at τ 6·9 and a broad resonance centred at τ 8·4; peak ratios were 2 : 6 : 8 : 1. Sublimation of G at 60° gave a product with the same i.r. spectrum as E which yielded hydrogen on hydrolysis; a further sublimate at 100° was not identified.

1 : 2 Reaction of Trivinylborane and Diboron Tetrafluoride. —After 14 days at -78°, diboron tetrafluoride (1·61) and trivinylborane (0·80) still contained unchanged tetrafluoride (0·93). After the mixture had warmed to room temperature and been set aside for 7 days, it gave vinyldifluoroborane (0·78) as the only volatile product.

#### DISCUSSION

The chemical and spectroscopic evidence clearly indicates that the 1 : 1 adduct of trivinylborane and diboron tetrachloride is the expected 1,2-bis(dichloroboryl)-1-divinylborylethane (CH<sub>2</sub>:CH)<sub>2</sub>B·CH(BCl<sub>2</sub>)·CH<sub>2</sub>·BCl<sub>2</sub> (I). Although its reactivity precluded a structural investigation of the corresponding 1 : 1 adduct with diboron tetrafluoride, the analysis and a study of its reactions clearly indicate it to have the analogous structure (CH<sub>2</sub>:CH)<sub>2</sub>B·CH(BF<sub>2</sub>)·CH<sub>2</sub>·BF<sub>2</sub> (III).

The reactions used to establish the structure of (I) show also that the two remaining vinyl groups are as readily protonated by propionic acid as in the original trivinylborane, whereas the bisdichloroborylethyl group is unaffected. Aqueous hydrolysis of (I) gave only 80% of the ethylene expected from the vinyl groups; subsequent pyrolysis of the hydrolysate gave ethane quantitatively:



This pyrolytic breakdown is characteristic of dihydroxyborylsubstituted ethanes.<sup>7,8</sup>

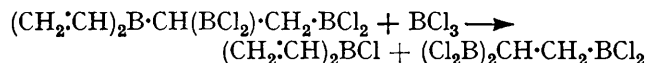
Although the i.r. spectrum of (I) showed the expected C=C stretching frequency at 1580 cm<sup>-1</sup>, the broad multiplet at τ 7·71 in the <sup>1</sup>H n.m.r. spectrum in carbon tetrachloride did not confirm the presence of vinyl groups. However, conversion of (I) into the 1-diethylborylethane Et<sub>2</sub>B·CH(BCl<sub>2</sub>)CH<sub>2</sub>·BCl<sub>2</sub> removed this broad multiplet and gave the expected triplet/quartet for the ethyl groups, the existing doublet and triplet resonances obtained for (I) in carbon tetrachloride remaining unchanged.

In an attempt to obtain a better <sup>1</sup>H n.m.r. spectrum of

<sup>7</sup> C. Chambers, A. K. Holliday, and S. M. Walker, *Proc. Chem. Soc.*, 1964, 286.

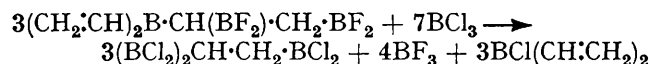
<sup>8</sup> A. K. Holliday, G. N. Jessop, and R. P. Ottley, *J. Organometallic Chem.*, 1968, 12, 269.

(I), the latter was dissolved in boron trichloride, but changes in the spectrum even below 0° clearly indicated that reaction had occurred. The identification of divinylchloroborane and 1,1,2-tris(dichloroboryl)ethane as the reaction products clearly indicated the reaction to be the exchange

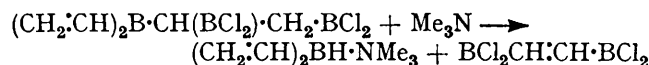


No evidence for the presence of either vinylchloroborane or the mixed compound  $\text{CH}_2\text{:CH}\cdot\text{BCH}(\text{BCl}_2)\cdot\text{CH}_2\cdot\text{BCl}_2$  was obtained at any stage; this implies that the exchange is that of divinylboryl and dichloroboryl groups rather than of single vinyl groups with chlorine atoms, and suggests ready fission of the divinylboryl group from the ethanic side chain.

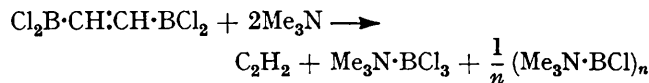
A similar exchange reaction with tris(dimethylamino)-borane, to yield dimethylaminodivinylborane, confirmed the lability of the divinylboryl group in (I). The products of the corresponding reaction of the fluoro-compound (III) with boron trichloride indicate exchange both of the divinylboryl group and of the difluoroboryl groups to give 1,1,2-tris(dichloroboryl)ethane, boron trifluoride, and divinylchloroborane, *i.e.*



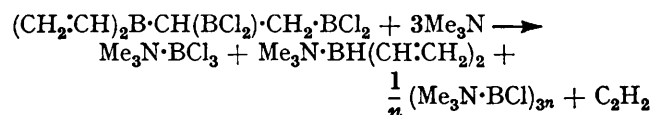
The i.r. spectrum of the solid E obtained as the product of the reaction of (I) with trimethylamine, indicated E to be trimethylamine-divinylborane  $\text{Me}_3\text{NBH}(\text{CH}\text{:CH}_2)_2$  and this was confirmed by the release of hydrogen and ethylene in a 1 : 2 ratio on hydrolysis. The appearance of this adduct suggests that in the presence of trimethylamine, (I) has undergone dehydroboration, the reaction being



However under the conditions of reaction of (I) with trimethylamine (120°), the other product of the above reaction, 1,2-bis(dichloroboryl)ethylene, also reacts with trimethylamine thus:

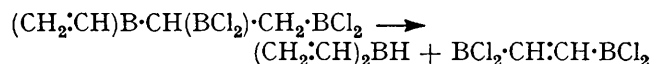


The overall reaction ratio of 1 : 3 in the reaction of (I) with trimethylamine, and the appearance of acetylene and trimethylamine-boron trichloride are thus accounted for:

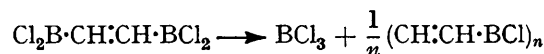


In the corresponding reaction of the fluoro-compound, (III), with trimethylamine, it was possible to distinguish two stages in the reaction, the first being uptake of two moles of trimethylamine to give a product  $(\text{CH}_2\text{:CH})_2\text{B}\cdot\text{CH}\cdot\text{BF}_2(\text{NMe}_3)\cdot\text{CH}_2\cdot\text{BF}_2(\text{NMe}_3)$  for which the  $^1\text{H}$  n.m.r. spectrum had a multiplet at  $\tau$  2.7 attributed to vinyl protons, a singlet at  $\tau$  6.9 attributed to methyl protons of trimethylamine, and a broad resonance at  $\tau$  8.4 attributed to the ethane protons. When the reaction mixture was further warmed additional uptake of a third molar equivalent of trimethylamine gave a solid which on sublimation yielded trimethylamine-divinylborane, *i.e.* underwent dehydroboration as did (I). The other product of this dehydroboration, 1,2-bis(difluoroboryl)ethylene has been shown to form only a simple 1 : 2 adduct with trimethylamine,<sup>9</sup> and hence no acetylene appeared in the reaction.

The appearance of 1,2-bis(dichloroboryl)ethylene as a product of the pyrolysis of (I) suggests that dehydroboration might be the initial stage in the decomposition, *i.e.*

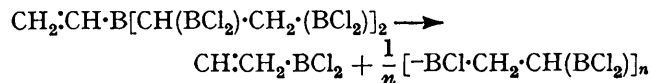


The divinylborane produced would be extremely unlikely to exist as an entity even at room temperature since polymerisation and hydroboration (*e.g.*  $\text{B-H} + \text{CH}_2\text{:CH-B} \longrightarrow \text{B-CH}_2\text{-CH}_2\text{-B}$ ) would be expected, and it is clear that this will occur under pyrolysis conditions. (The appearance of ethane from propionic acid treatment of the pyrolysis residue strongly supports the idea of  $\text{BCH}_2\cdot\text{CH}_2\text{B}$  formation). Moreover, under these conditions 1,2-bis(dichloroboryl)ethylene also decomposes<sup>10</sup> to give boron trichloride thus:



As the data show, increased times of heating increases the yield of boron trichloride and the amount of residue which yields ethylene with propionic acid, *i.e.* which contains  $\text{B-CH}\text{:CH-B}$  linkages.

Reaction of trivinylborane with 2-molar equivalents of diboron tetrachloride yields an addition product, stable only at low temperature, which contains only one vinyl group and may be formulated as  $\text{CH}_2\text{:CH-B}[\text{CH}(\text{BCl}_2)\cdot\text{CH}_2\cdot\text{BCl}_2]_2$  (II). The instability of (II) precluded further structural investigation; its decomposition, leading to the formation of vinylchloroborane as the only volatile and unidentifiable product, may be formulated as:

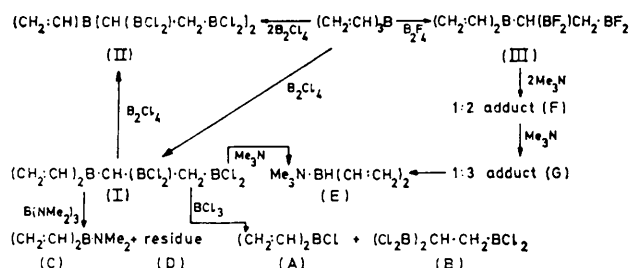


<sup>9</sup> C. Chambers, Ph.D. Thesis, University of Liverpool, 1964.

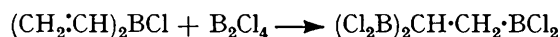
<sup>10</sup> C. Chambers and A. K. Holliday, *J. Chem. Soc.*, 1965, 3549.

There is no evidence that (II) can undergo exchange with boron trichloride, although its instability again precluded a study of any possible exchange at temperatures above 0°. On the hypothesis that the ready exchange reactions with  $\text{BX}_3$  of (I) and (III) occurs through exchange of divinylboryl groups rather than simple halogen-vinyl exchange, reaction of (II) with boron trichloride would not be expected.

The reactions discussed above are conveniently summarised in the following diagram:



It is clear that direct addition of 3 molar equivalents of diboron tetrachloride to trivinylborane does not occur; the appearance of 1,1,2-tris(dichloroboryl)ethane as a reaction product in this system is accounted for by the reaction of the divinylchloroborane [formed by decomposition of (II)] with the third molar equivalent of diboron tetrachloride:<sup>6</sup>



The generally more difficult addition of diboron tetrafluoride (as compared with diboron tetrachloride) to olefinic bonds accounts for the failure of the 1:2 trivinylborane-diboron tetrafluoride reaction mixture to form the fluoro-analogue of (II) at low temperatures. The appearance of vinyldifluoroborane from the reactions at room temperature, suggests that addition followed by decomposition may have occurred under these conditions.

Trivinylborane, unlike the adducts (I) and (III), does not appear to undergo ready exchange with other  $\text{BX}_3$  molecules, or dehydroboration. The increased reactivity of (I) and (III) is centred on the divinylboryl-saturated carbon-bond, and might be attributed to removal of  $\pi$ -electrons from this bond as a consequence of saturation of the vinyl bond by the added diboron tetrahalide. This assumes that delocalisation of the vinyl  $\pi$ -electrons to the boron occurs in trivinylborane, but there is no reliable evidence for this. Moreover, the reactivity of (I) is in marked contrast to that of 1,1,2-trisdichloroborylethane, which differs from (I) only in possessing a dichloroboryl group instead of a divinylboryl group. It is therefore possible to attribute the reactivity of the  $(\text{CH}_2\text{:CH})_2\text{B}-\text{C}-$  bond to a specific effect of the divinylboryl group, namely the withdrawal of electrons from the B-C bond *via* the vinylboron  $\sigma$ -bonds.

[0/1647 Received, September 25th, 1970]