625. *The Reactions of Diboron Tetrahalides with Acetylene. Part I. The Preparation and Properties of* 1,2-*Bisdichloroborylethylene*

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Direct reaction of diboron tetrachloride with an excess of acetylene gives the 1,2-bisdichloroborylethylene, $Cl_2B\cdot CH{:}CH\cdot BCl_2$. Protonolysis yields ethylene quantitatively, as does heating of the hydrolysis product $(HO)_2B\cdot CH{:}CH\cdot B(OH)_2$. Pyrolysis gives boron trichloride, and the latter is also obtained as the adduct Cl_3B,NMe_3 by addition of trimethylamine; dimethylamine gives the compound $B(NMe_2)_3$. Bromine adds quantitatively to the double bond, while oxygen breaks the B–C bonds, giving carbon monoxide and boron trichloride.

The reaction of acetylene with diboron tetrachloride has been reported [1] to give only the 1 : 1 adduct B_2Cl_4,C_2H_2 at $-45°$; the structure $Cl_2B\cdot CH{:}CH\cdot CBl_2$ has been assigned on the basis of infrared spectral evidence.[2] We have re-investigated the reaction of diboron tetrachloride with acetylene, and can now report some chemical properties of the product.

Experimental and Results

Diboron tetrachloride was prepared as previously described; [3] the purity of the acetylene was checked by infrared spectroscopy. Analyses were carried out as previously described,[3] and apart from titrations of hydrolysed residues, all manipulations and reactions were carried out *in vacuo* with quantities of the order of 1 mmole. Units are mmoles unless otherwise stated.

Diboron Tetrachloride–Acetylene Reactions.—In a typical reaction, diboron tetrachloride (1·21) and acetylene (2·31) were allowed to react at 20° for 18 hr.; fractionation then gave

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[1] P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. Parsons, G. Urry, and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 1959, **81**, 6368.

[2] J. Frey, Ph.D. Thesis, Chicago, 1960.

[3] A. K. Holliday and A. G. Massey, *J.*, 1960, 43.

acetylene (1·26), boron trichloride (0·12), and 0·197 g. of a volatile *product* [Found, after hydrogen peroxide degradation: B, 11·6; Cl, 77·8%; *M* (vapour density), 208, 209. Calc. for B_2Cl_4,C_2H_2: B, 11·4; Cl, 74·8%; *M*, 190) (0·197 g., 1·05 mmoles). The residue gave a red colour with calcium oxide and *o*-aminophenol (test for glyoxal). After corrections had been made for diboron tetrachloride lost as boron trichloride, the ratios $B_2Cl_4 : C_2H_2$: product were 1·09 : 1·05 : 1·05; in two other experiments the ratios were 1·14 : 1·08 : 1·07 and 0·98 : 1·05 : 0·98, respectively. The vapour pressures at 25, 50, and 80° followed the equation $\log p(\text{mm.}) = 7{\cdot}66 - 1995/T^1$.

Protonolysis and Hydrolysis.—The compound, B_2Cl_4,C_2H_2 (0·67), when heated with anhydrous propionic acid at 120° gave ethylene (0·68). Hydrolysis of the compound (1·20, 0·227 g.) with water at 100° for 2 hr. gave an aqueous distillate containing hydrogen chloride (4·88); the white solid residue weighed 0·136 g. [Calc. for $B_2(OH)_4,C_2H_2$: 0·138 g.]. The solid residue after hydrolysis of another sample (1·50) of the compound, on being heated for 4 days at 240°, gave ethylene (1·29) and a white anhydrous residue which showed no change in weight on ignition (Found: B, 29·2. Calc. for B_2O_3: B, 31·0%).

Reactions with Trimethylamine, Dimethylamine, and Ammonia.—The compound (0·97) and trimethylamine (2·54) were condensed together and warmed to 20°, when a vigorous reaction occurred; after 1 hr. the only volatile material found was excess trimethylamine (1·44). Heating of the solid residue effected partial separation of a white sublimate (Found: B, 5·5; Cl, 58·4. Calc. for $Me_3N{\cdot}BCl_3$: B, 6·1; Cl, 60·2%) which had an infrared spectrum identical with that of trimethylamine–boron trichloride. In other reactions at 20°, values for the ratio $B_2Cl_4,C_2H_2/NMe_3$ were 1 : 1·17. 1 : 1·16, and 1 : 0·99 and at 100° for 3 hr., 1 : 1·17. From two further experiments using B_2Cl_4,C_2H_2 (1·26, 1·32) and excess trimethylamine, the residues after hydrolysis with aqueous sodium hydroxide at 100° and evaporation to dryness gave, with anhydrous propionic acid at 120°, only ethylene (1·09, 0·98).

The compound (0·37) and dimethylamine (4·60) after 3 days at 20° gave excess dimethylamine (1·88) and only one volatile product (0·46); in another experiment, treatment of the latter (0·55) with alkali gave dimethylamine (1·58), and the infrared spectrum was identical with that of trisdimethylaminoborane $(Me_2N)_3B$. Using B_2Cl_4,C_2H_2 (1·35) and dimethylamine (17·47) for 21 hr. at 110° gave $(Me_2N)_3B$ (0·79) and excess dimethylamine (7·63).

The compound (1·28) and ammonia (9·97), on being heated for 5 hr. at 100°, gave only excess ammonia (2·33) as volatile material; heating of the residue gave a sublimate identified as ammonium chloride.

Pyrolysis.—The compound (1·45) after being heated for 18 hr. at 160° gave B_2Cl_4,C_2H_2 (undecomposed) (0·33), hydrogen chloride (0·20), and boron trichloride (0·73). The residue took up trimethylamine (0·30); hence [$BCl_3 + B_2Cl_4,C_2H_2$ unreacted $+ NMe_3$ taken up] = 1·35. In another experiment the compound (1·63) after 20 hr. at 110° gave B_2Cl_4,C_2H_2 (undecomposed, not determined), hydrogen chloride (0·17), and boron trichloride (0·28); the remaining non-volatile residue when heated with an excess of propionic acid gave ethylene (1·53). In a third experiment, the residue from the decomposition of the compound (1·42) (for 30 hr. at 110°) took up bromine (1·40).

Oxidation.—The compound and oxygen were warmed from liquid-nitrogen temperature to 20°, set aside, and the volatile products removed. Results are given in the Table; ignition occurred in experiments 1, 3, and 4.

Experiment:	1	2	3	4
Time, hr.	0·5	1·0	2·0	18
B_2Cl_4,C_2H_2 added	1·39	1·37	0·22	0·93
reacted	0·61	1·11	0·22	0·90
O_2 added	0·63	0·78	0·42	1·03
reacted	0·31	0·55	0·31	1·01
Products: CO	0·15	0·25	0·17	0·48
HCl ($=H_2O$) *	0·18	0·48	0·35	0·60
BCl_3 found	0·37	1·00	0·18	0·41
BCl_3 (corr.) †	0·43	1·16	0·30	0·61
Residue: B found	0·70	0·87	0·35	1·03
corr.†	0·64	0·70	0·23	0·80
Cl	0·83	1·02	0·18	0·82

* The reaction $BCl_3 + 3H_2O \longrightarrow B(OH)_3 + 3HCl$ is assumed, and values marked † are corrected for this.

DISCUSSION

Optimum conditions for the preparation of 1,2-bisdichloroborylethylene are those used in the Experimental section, *viz.*, a temperature near 20° and addition of an excess of acetylene to diboron tetrachloride. At the temperature of —40° previously[1] used, reaction was very slow and the considerable decomposition of the diboron tetrachloride over the long period required reduced the yield; at 20°, reaction was rapid, and the tetrachloride (normally unstable at this temperature) was sufficiently stabilised by presence of acetylene[4] to prevent much loss. Unless an appreciable excess of acetylene was used, the reaction ratio $B_2Cl_4 : C_2H_2$ considerably exceeded 1 : 1, the product contained more boron and chlorine than required for B_2Cl_4,C_2H_2, and the measured molecular weight was too high. Even under optimum conditions, a reaction ratio slightly greater than 1 : 1 was found; but the product, after fractionation, had a vapour pressure–temperature curve the same as that previously reported[1] and the molecular weight, though slightly high, was also very close to that previously found. These observations are to be explained by the presence in the 1,2-bisdichloroborylethylene of 1,2-tetrakisdichloroborylethane $(Cl_2B)_2CH{\cdot}CH(BCl_2)_2$ with a $B_2Cl_4 : C_2H_2$ ratio of 2 : 1. The properties of this compound have been briefly reported;[5] the high-field peak to which it gives rise in the proton nuclear magnetic resonance spectrum is never entirely absent from the spectrum of the ethylene derivative, which is characterised by a strong low-field band at —309 c./sec. The relative intensities of the peaks suggest (as does the molecular weight) that the ethylene derivative, prepared under optimum conditions and fractionated, still contains about 5% of the tetraborylethane derivative. This quantity is insufficient to affect the boron and chlorine analyses, or the stoicheiometry of the reactions, to any significant extent.

Formulation of the adduct B_2Cl_4,C_2H_2 as 1,2-bisdichloroborylethylene was supported by the appearance of glyoxal after hydrogen peroxide degradation, and the quantitative evolution of ethylene after prolonged heating with propionic acid. The compound inflamed in air and was very sensitive to hydrolysis; consequently, hydrogen chloride tended to appear whenever the compound was placed in a reaction vessel which had not been exposed previously to a water-sensitive boron compound. The hydrolysis gave a quantitative yield of hydrochloric acid and no hydrocarbon or hydrogen was formed, indicating the reaction

$$Cl_2B{\cdot}CH{:}CH{\cdot}BCl_2 + 2H_2O \longrightarrow (HO)_2B{\cdot}CH{:}CH{\cdot}B(OH)_2 + 4HCl$$

The corresponding ethanediboronic acid, $(HO)_2B{\cdot}CH_2{\cdot}CH_2{\cdot}B(OH)_2$, only lost water reversibly on heating;[3] the ethylenediboronic acid decomposed to give an 86% yield of ethylene, based on the equation

$$(HO)_2B\ CH{:}CH\ B(OH)_2 \longrightarrow B_2O_3 + C_2H_4 + H_2O$$

and a residue of boric oxide was left.

Attemps to hydrogenate 1,2-bisdichloroborylethylene (to form the corresponding ethane derivative) using hydrogen and palladised asbestos, lithium hydride, or diborane, were unsuccessful; but bromine added on quantitatively at ordinary temperature. The product, presumably $Cl_2B{\cdot}CHBr{\cdot}CHBr{\cdot}BCl_2$, was not characterised, and it did not yied 1,2-dibromoethane in amounts sufficient for separation and identification when treated with propionic acid.

Trimethylamine adds on to both boron atoms of the compound $Cl_2B{\cdot}CH_2{\cdot}CH_2{\cdot}BCl_2$ to give a stable 2 : 1 adduct.[3] With the compound $Cl_2B{\cdot}CH{:}CH{\cdot}BCl_2$, reaction with trimethylamine was vigorous, but the mean reaction ratio $B_2Cl_4,C_2H_2 : NMe_3$ for four experiments at room temperature was 1 : 1·11, and 1 : 1·17 for an experiment at 100°. The production of some trimethylamine–boron trichloride, and the preservation of the

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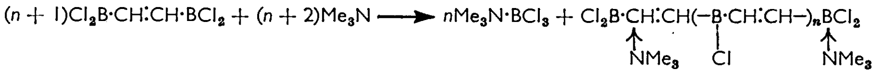
[4] J. Feeney, A. K. Holliday, and F. J. Marsden, *J.*, **1961**, 356.

[5] C. Chambers, A. K. Holliday, and S. M. Walker, *Proc. Chem. Soc.*, **1964**, 286.

$>B\cdot CH{:}CH\cdot B<$ bond system in the non-volatile reaction residue (as indicated by evolution of ethylene with propionic acid), suggest a reaction of the type



$$(n+1)Cl_2B\cdot CH{:}CH\cdot BCl_2 + (n+2)Me_3N \longrightarrow nMe_3N\cdot BCl_3 + \underset{\substack{\uparrow\\ NMe_3}}{Cl_2B}\cdot CH{:}CH(-\underset{\substack{|\\ Cl}}{B}\cdot CH{:}CH-)_n\underset{\substack{\uparrow\\ NMe_3}}{BCl_2}$$

with *n* having possible values in the range 5—10. The reactions of 1,2-bisdichloroborylethane with dimethylamine and ammonia had the limiting values $B_2Cl_4,C_2H_4 : HNMe_2 = 1 : 8$ and $B_2Cl_4,C_2H_4 : NH_3 = 1 : 6$, respectively.[3] With 1,2-bisdichloroborylethylene, these reaction ratios were approached only by using a large excess of base and either long reaction times at ordinary temperatures or shorter times at ~100°. The values obtained were $B_2Cl_4,C_2H_2/HNMe_2 = 1 : 7{\cdot}3$ and $B_2Cl_4,C_2H_2/NH_3 = 1 : 5{\cdot}9$. The expected reactions are then

$$Cl_2B\cdot CH{:}CH\cdot BCl_2 + 8HNMe_2 \longrightarrow (Me_2N)_2B\cdot CH{:}CH\cdot B(NMe_2)_2 + 4Me_2NH_2Cl$$

$$nCl_2B\cdot CH{:}CH\cdot BCl_2 + 6nNH_3 \longrightarrow [-HN{:}B\cdot CH{:}CH\cdot B{:}NH-]_n + 4nNH_4Cl$$

The reaction with ammonia yielded a non-volatile residue and some ammonium chloride, as the equation requires; but with dimethylamine, appreciable (and variable) amounts of trisdimethylaminoborane $(Me_2N)_3B$ were obtained from the vigorous reaction.

1,2-Bisdichloroborylethylene decomposed very slowly at room temperature, and the rate of decomposition became rapid only above about 110°, when a yellow non-volatile oil was formed and boron trichloride was evolved in amounts varying between 50 and 75% of that required by the equation

$$nCl_2B\cdot CH{:}CH\cdot BCl_2 \longrightarrow nBCl_3 + (Cl\dot{B}\cdot CH{:}CH\cdot)_n$$

Addition of trimethylamine to the oil gave an uptake approximately equal to the deficiency of boron trichloride as required by the above equation, suggesting presence in the oil of either occluded boron trichloride or of undecomposed 1,2-bisdichloroborylethylene. Reaction of the oil with both bromine and propionic acid indicated the expected preservation of the $>B\cdot CH{:}CH\cdot B<$ bond system.

When 1,2-bisdichloroborylethylene was treated with oxygen at 20°, a vigorous reaction began after a few seconds, with the reacting materials in violent turbulent motion; the reaction seemed to subside and then recommenced, and the cycle was repeated several times in some experiments, while in others a red flash followed by a flame appeared to terminate the cycle at an early stage. Despite these appearances, reaction (as measured by disappearance of 1,2-diborylethylene) was still slow, and the Table shows that some reacting substances remained, even after 18 hr. The progress of the reaction did not appear to be much affected by the amount of oxygen added, or by the incidence of ignition in the early stages. As reaction proceeded, the two ratios, (B_2Cl_4,C_2H_4 reacted) : (O_2 reacted) and (BCl_3 formed)/(O_2 reacted), both fell, and the ratio (CO formed) : (O_2 reacted) remained approximately constant at about 1 : 2. An oxidation mechanism similar to that suggested[3] for 1,2-bisdichloroborylethane at temperatures around 0° will partly explain these results, *viz.*, co-ordination of oxygen to form a $>B\cdot O\cdot O\cdot B<$ linkage, with displacement of the hydrocarbon (in this case, acetylene) which then oxidises, with or without ignition, to form carbon monoxide and water.

In the early stages of reaction the exothermic oxidation must cause concomitant pyrolysis of unoxidised 1,2-bisdichloroborylethylene; the pyrolysis product $(Cl\dot{B}\cdot CH{:}CH\cdot)_n$ may itself undergo oxidation yielding $(BCl)_n$ residue, carbon monoxide, water, and carbon, but no further boron trichloride, so that the overall oxidation process is essentially

$$nCl_2B\cdot CH{:}CH\cdot BCl_2 \xrightarrow{O_2} (BCl)_n + nBCl_3 + CO,\ C,\ H_2O$$

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