

two species are present for which n.m.r. data were not previously available. We find that phenyl dichlorophosphate,  $\text{OPCl}_2(\text{OC}_6\text{H}_5)$ , exhibits a chemical shift<sup>4</sup> of  $-1.5$  p.p.m. with respect to  $85\%$   $\text{H}_3\text{PO}_4$ . This means that the resonance peak for this compound can be resolved from the peak corresponding to  $\text{OPCl}_3$  with only the utmost difficulty. Diphenyl monochlorophosphate,  $\text{OPCl}(\text{OC}_6\text{H}_5)_2$ , exhibits a chemical shift of  $+6.2$  p.p.m. with respect to  $85\%$   $\text{H}_3\text{PO}_4$ .

When plotted in the same manner as Fig. 1, the system  $\text{OPCl}_3\text{-P}(\text{OC}_6\text{H}_5)_3$  appears appreciably different from the system  $\text{OPCl}_3\text{-PBr}_3$ . Completely random reorganization at  $R = \text{Cl/P} = 1.50$  should lead to  $6.25\%$  of the total phosphorus in each of the four simple compounds and  $18.75\%$  in each of the four mixed species. The experiment showed these various percentages of total phosphorus in the simple compounds:  $\text{PCl}_3$ , 6.5;  $\text{P}(\text{OC}_6\text{H}_5)_3$ , 0;  $\text{OPCl}_3$ , 1.8; and  $\text{OP}(\text{OC}_6\text{H}_5)_3$ , 12.3—with the mixed species giving:  $\text{PCl}_2\text{-}$

(4) J. R. Van Wazer, C. F. Callis, J. N. Shooley and R. C. Jones, *THIS JOURNAL*, **78**, 5715 (1956).

$(\text{OC}_6\text{H}_5)$ , 30.6;  $\text{PCl}(\text{OC}_6\text{H}_5)_2$ , 12.6;  $\text{OPCl}_2(\text{OC}_6\text{H}_5)$ , 16.0; and  $\text{OPCl}(\text{OC}_6\text{H}_5)_2$ , 20.2. From these data, a value was obtained for the form of  $K_1$  shown in eq. 4

$$K = \frac{[\text{PCl}(\text{OC}_6\text{H}_5)_2][\text{OPCl}_2(\text{OC}_6\text{H}_5)]}{[\text{PCl}_2(\text{OC}_6\text{H}_5)][\text{OPCl}(\text{OC}_6\text{H}_5)_2]} = 0.3 \quad (4)$$

Within the accuracy of measurement, the values of the dissociation constants of monophenyl dichlorophosphate and diphenyl monochlorophosphate cannot be differentiated from the theoretical value<sup>5</sup> of one-third, corresponding to completely random reorganization.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY AND THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

## Diboron Tetrachloride and Tetrafluoride as Reagents for the Synthesis of Organoboron Compounds. II. The Behavior of the Diboron Tetrahalides toward Unsaturated Organic Compounds<sup>1</sup>

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The study of the reactions of diboron tetrachloride with unsaturated hydrocarbons has been extended to the corresponding reactions of diboron tetrafluoride and to those of vinyl halides and other halogen derivatives of ethylene, to propene, to cyclopropane, to butene-2, to acetylene, to allyl halides, to butadiene and to 4-chlorobutene-1. Several new compounds are described and the effect of substitution of halogen atoms for the hydrogen atoms of unsaturated hydrocarbons is pointed out and discussed briefly.

It has been shown<sup>2</sup> previously that diboron tetrachloride reacts with ethylene at low temperature ( $-80^\circ$ ) to form 1,2-bisdichloroboryl-ethane  $\text{Cl}_2\text{BC}_2\text{H}_2\text{BCl}_2$ .<sup>3</sup> The present paper shows that diboron tetrachloride reacts in similar fashion with propene, cyclopropane, butene-2, acetylene, butadiene, allyl halides and 4-chlorobutene-1. But the corresponding reaction with vinyl halides or other haloethylenes does not occur even at temperatures well over  $25^\circ$ . It is further noteworthy that the adducts<sup>4</sup> of diboron tetrahalides and vinyl

halides are far less stable than the adducts involving the unsubstituted unsaturated hydrocarbons or that involving 4-chlorobutene-1. The failure of the haloethylenes to undergo the reaction in question is analogous to the relatively low reactivity of these compounds toward electrophilic reagents in general, as is also the renewed reactivity when the substituting  $\text{BCl}_2$  group is not attached to a carbon atom directly adjacent to the double bond.

One mole of acetylene adds only one mole of diboron tetrachloride, although the resulting "adduct"  $\text{Cl}_2\text{BC}_2\text{H}_2\text{BCl}_2$  still contains doubly bonded carbon atoms. One mole of butadiene may, on the other hand, add either one or two moles of  $\text{B}_2\text{Cl}_4$ . Evidently the presence of  $\text{BCl}_2$  groups attached to carbon atoms adjacent to double bonds has the same effect in decreasing the reactivity of the double bond as do halogen atoms similarly located; as in the case of halogen atoms the inhibiting effect of  $\text{BCl}_2$  groups is either lacking or is much less pronounced if the substituting groups are attached to carbon atoms not adjacent to double bonds.

The corresponding reactions of diboron tetrafluoride<sup>5</sup> are in general similar to those of the

(1) This paper is based largely on Annual Reports submitted to the Office of Naval Research in connection with Contracts N6-ori-020100 Project NR356-255 and Nonr2121(02) Project NR052-255. These reports cover the years ending June 30 or July 31, 1954, 1956 and 1957, and are entitled "Hydrides and Borohydrides of Light Weight Elements and Related Compounds." In addition certain parts have been taken from a thesis submitted to the Department of Chemistry, University of Chicago, by John Frey in part fulfillment of the requirements for the degree of Doctor of Philosophy.

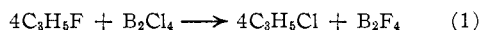
(2) G. Urry, J. Kerrigan, T. D. Parsons and H. I. Schlesinger, *THIS JOURNAL*, **76**, 5299 (1954).

(3) The structure indicated by this formula was originally based on chemical evidence; it has since been confirmed by E. B. Moore and W. W. Lipscomb, *Acta Cryst.*, **9**, 688 (1956).

(4) The products of the reactions herein described are, strictly speaking, not adducts, since in their formation the boron to boron bonds of the tetrahalides are severed. The term is nevertheless used as a matter of convenience.

(5) A. Finch and H. I. Schlesinger, *THIS JOURNAL*, **80**, 3573 (1958).

tetrachloride except that the former reacts much more slowly and that the "adducts" it forms are much more stable. For this reason it occasionally proved desirable to prepare the bis-difluoroboryl derivatives by treatment of the corresponding chloro derivatives with antimony trifluoride. In the case of the allyl "adducts" two complicating factors were noted. The first was the catalytic effect of the tetrafluoride on the polymerization and decomposition of the allyl compounds, as illustrated in experiment 9 of the section entitled "Experimental"; the other disturbing factor was that the reaction between allyl fluoride and diboron tetrachloride proceeds largely according to the equation (see experiment 8)



The 1,2-bisdimethylboryl derivatives of cyclopropane, propene and butene-2 have been prepared by treatment of the corresponding chloro derivatives with dimethylzinc.<sup>6</sup> These compounds were made in the hope that their decomposition products would be easier to isolate, to purify and to interpret than those previously obtained by the decomposition of 1,2-bisdimethylborylethane.<sup>2</sup> However, the same difficulties were encountered as in the previous work. For this reason only a few details of preparation and some of the physical properties of the compounds obtained are reported below. One point, however, deserves special mention, namely, that the decomposition of 1,2-bisdimethylborylethane is markedly catalyzed by traces of zinc compounds. This observation may be of value to further work with the alkyl derivatives in question, since it explains the variation in the stability of different samples of these compounds.

### Apparatus and Materials

All reactions were carried out in the absence of air and moisture, for which purpose we used standard vacuum lines having one manifold equipped with mercury float valves and one fitted with stopcocks. For determination of melting points appropriate vapor tension thermometers were used.<sup>7</sup>

The olefins were commercial samples, obtained from the Matheson Company and were purified by distillation in the vacuum line. Allyl chloride was taken from a sample of unknown manufacturer and was purified in similar fashion. Allyl fluoride was prepared by the reaction of allyl iodide with silver fluoride. It was purified according to the method of Meslans.<sup>8</sup>

The first step in the preparation of 4-chlorobutene-1 was the partial dehydration of toluene-*p*-sulfonic acid monohydrate as described by Birch and McAllen.<sup>9</sup> The crude product was distilled in a Podbielniak column. The fraction collected at 110–114.5° then was converted to the chlorobutene by use of phosphorus trichloride according to the procedure of A. Juvala.<sup>10</sup> Distillation of the product yielded 3 fractions. The middle fraction of boiling point 74° was used.

Diboron tetrachloride was obtained as described by Urry, Wartik, Moore and Schlesinger.<sup>11</sup> The tetrafluoride was prepared from the tetrachloride by treatment with antimony trifluoride.<sup>5</sup>

(6) For the procedure see ref. 2. The 1,2-bisdimethylboryl derivatives obtained from allyl chloride and from acetylene were too unstable for isolation.

(7) See, for example, "Vacuum Manipulation of Volatile Compounds," R. T. Sanderson, John Wiley and Sons, Inc., New York, N. Y., 1948.

(8) M. Meslans, *Ann. Chim.*, [7] 1, 374 (1894).

(9) S. F. Birch and D. T. McAllen, *J. Chem. Soc.*, 2561 (1951).

(10) A. Juvala, *Ber.*, 63, 1989 (1930).

(11) G. Urry, T. Wartik, E. H. Moore and H. I. Schlesinger, *THIS JOURNAL*, 76, 5293 (1954).

### Procedure

The procedure employed in this investigation was so nearly the same for all of the compounds which were involved that a general description is adequate. The diboron tetrahalide and the unsaturated organic compound were separately distilled from the vacuum line into a suitable reaction vessel maintained at  $-80^\circ$  and so constructed that its contents could be stirred without exposure to air or moisture. After thorough mixing of the contents had been achieved, the reaction mixture was warmed slowly until reaction set in, as indicated by a drop in the pressure. After the pressure drop had ceased, or had become very slow, the volatile reaction products were fractionated in a series of traps at  $-45^\circ$ ,  $-80^\circ$ ,  $-112^\circ$  and  $-196^\circ$ . In except a few experiments the unsaturated organic compound was present in excess in the original reaction mixture because that procedure made fractionation easier and tended to prevent spontaneous decomposition of the diboron tetrachloride. The quantity of the latter used in each experiment varied considerably within the limits of about 1.5 to 5 mmoles; the amount of the unsaturated compound varied from about 3 to 10 mmoles. These variations are not significant; they are mentioned merely to indicate the scale of the experiments.

In general the stoichiometry of the reaction and the experimentally determined vapor densities (molecular weights) of the reaction product were sufficient to establish the empirical formulas of the compounds isolated. When additional data were considered desirable they are supplied in the "Experimental" section.

The bisdimethylboryl derivatives of cyclopropane, propene and butene-2 were prepared by action of dimethylzinc on the corresponding dichloro derivatives. The reagents were mixed in approximately the theoretical 2/1 molar ratio, a few cc. of isopentane was added, whereupon the mixture was allowed to stand first for about 5 hr. at  $-45^\circ$  and then for a similar period at  $-23^\circ$ . The volatile reaction product was purified by fractional condensation. The cyclopropane and the propene derivatives were condensed at  $-45^\circ$ , that of butene-2 at  $-63^\circ$ .

### Results

The experimental data for the reactions of the unsaturated organic compounds with the two diboron tetrahalides are recorded in Table I. In it, the first column contains an "experiment number" for reference to the section entitled "Experimental." Column 2 contains the formula of the organic compound allowed to react with the tetrahalide; the symbol Un is an abbreviation for "unsaturated compound." The symbols Cl and F in column 3 stand for reactions involving diboron tetrachloride and diboron tetrafluoride, respectively. The reaction mixture (Rx. mixt.) in column 4 represents the ratio "moles Un taken/moles  $\text{B}_2\text{X}_4$ " ( $\text{X} = \text{Cl}$  or  $\text{F}$ ). The data of columns 5 and 6 are included to show the differences in the qualitatively observed rates of reaction. Column 7 records the molar ratio in which the unsaturated organic compound united with the tetrahalide. Column 8 records the molecular weight calculated from the observed vapor densities.

Table II presents additional data about the compounds prepared and isolated. To save space the formulas of the compounds in the first column are represented as "adducts" of  $\text{B}_2\text{Cl}_4$  or  $\text{B}_2\text{F}_4$  or  $\text{B}_2(\text{CH}_3)_4$  with the unsaturated compound, rather than as  $\text{BCl}_2$ ,  $\text{BF}_2$  or  $\text{B}(\text{CH}_3)_2$  derivatives. Columns 4 and 5 contain values for the constants for the equations  $\log p_{\text{mm.}} = A - B/T$  according to which values for the vapor tensions of the compounds may be calculated to within a few per cent. of the observed values.

### Experimental

**Experiment 3.**—Under the conditions required to complete the reaction some decomposition (about 8%) of the di-

TABLE I  
 REACTIONS OF UNSATURATED HYDROCARBONS

1 Expt.	2 Un	3 X	4 Rx mixt.	5 Rx temp., °C.	6 Rx time, hr.	7 Un/B <sub>2</sub> X <sub>4</sub>	8 Mol. wt.	9 Mol. wt. calcd.
1	C <sub>3</sub> H <sub>6</sub>	Cl	3.4	-45	Fast	0.91	193	205
2	(CH <sub>2</sub> CH) <sub>2</sub>	Cl	1.6	-40	8	0.95	221	220
3	(CH <sub>2</sub> ) <sub>3</sub>	Cl	1.9	0	20	1.0	206	205
4	C <sub>2</sub> H <sub>4</sub>	F	..	-23	..	..	127	126
5	(CH <sub>2</sub> CH) <sub>2</sub>	F	4.2	90	Slow	..	154	153
6	C <sub>3</sub> H <sub>5</sub> Cl	Cl	1.4	-45	48	1.0	..	..
				-23				
7	C <sub>3</sub> H <sub>5</sub> Cl	F	2.5	-45	25	1.25	..	..
8	C <sub>3</sub> H <sub>5</sub> F <sup>a</sup>	Cl	4.04	-80	..	..	..	..
9	C <sub>3</sub> H <sub>5</sub> F	F	0.24	-80	48	..	..	..
10	C <sub>4</sub> H <sub>7</sub> Cl	Cl	0.71	-45 to +25	7	0.91	..	..
						1.1		
11	C <sub>4</sub> H <sub>7</sub> Cl	F	1.63	+100	24	0.9	214	188
12	C <sub>2</sub> H <sub>2</sub>	Cl	1.0	-45 120	24	.9	210	190(98°)
13	C <sub>2</sub> H <sub>2</sub>	F	1.0	140	24	.8	124	124
14	C <sub>3</sub> H <sub>6</sub>	Cl	2.6	-60	16	.9	..	..
15	C <sub>4</sub> H <sub>6</sub>	Cl	0.4	-45	20	2.1	..	..

<sup>a</sup> In a second experiment this ratio was 0.28. In that experiment all of the fluoride was converted to boron trifluoride.

 TABLE II  
 SUMMARY OF PHYSICAL PROPERTIES OF B<sub>2</sub>Cl<sub>4</sub> AND B<sub>2</sub>F<sub>4</sub>  
 ADDUCTS

Compound	M.p., °C.	B.p., °C.	A	B	H	Tr. const.
B <sub>2</sub> Cl <sub>4</sub> ·C <sub>2</sub> H <sub>4</sub> <sup>a</sup>	-28.5	142	8,230	2220	10,140	24.4
B <sub>2</sub> Cl <sub>4</sub> ·CH <sub>2</sub> CHCH <sub>3</sub>	-130	165	7,701	2105	9,600	22.1
B <sub>2</sub> Cl <sub>4</sub> ·(CH <sub>3</sub> CH) <sub>2</sub>	-44.8	171	8,147	2339	10,700	24.1
B <sub>2</sub> Cl <sub>4</sub> ·(CH <sub>2</sub> ) <sub>3</sub>	-69.2	152	7,873	2123	9,880	22.8
B <sub>2</sub> F <sub>4</sub> ·C <sub>2</sub> H <sub>4</sub>	-31.5	35	8,259	1656	7,550	24.4
B <sub>2</sub> F <sub>4</sub> ·(CH <sub>2</sub> CH) <sub>2</sub>	.....	68	7,770	1667	7,600	22.3
B <sub>2</sub> Cl <sub>4</sub> ·C <sub>2</sub> H <sub>2</sub>	-129 to -130	144	7,666	1995	9,100	21.8
B <sub>2</sub> F <sub>4</sub> ·C <sub>2</sub> H <sub>2</sub>	-81.7 to -82.6	15	8,565	1635	7,450	25
B <sub>2</sub> (CH <sub>3</sub> ) <sub>4</sub> ·C <sub>2</sub> H <sub>4</sub> <sup>a,c</sup>	-114.9	98	7,916	1869	8,540	23
B <sub>2</sub> (CH <sub>3</sub> ) <sub>4</sub> ·(CH <sub>3</sub> CH) <sub>2</sub> <sup>c</sup>	.....	127	7,928	2017	9,200	23
B <sub>2</sub> (CH <sub>3</sub> ) <sub>4</sub> ·(CH <sub>2</sub> ) <sub>3</sub> <sup>b,c</sup>	-104.7	..	8,514	2121	.....	..

<sup>a</sup> For the source of these data see ref. 2. <sup>b</sup> The vapor tension data cover too short a range to warrant extrapolation to the boiling point or calculation of *H*. <sup>c</sup> The formula B<sub>2</sub>(CH<sub>3</sub>)<sub>4</sub> is used here merely to indicate the composition and not the source of the compound.

boron tetrachloride occurred, as shown by the development of a red color. The extent of decomposition, though small, was large enough to require correction of the reaction ratio for the amount of diboron tetrachloride lost thereby. The correction was based on the amount of boron trichloride generated, and on the fact that, in this type of decomposition, one mole of boron trichloride is formed per mole of the tetrachloride decomposed.<sup>11</sup> The ratio stated in the table is the corrected value.

The formula of the adduct was confirmed by the fact that treatment of a sample with methanol generated 92% of the hydrogen chloride expected for a material of the composition Cl<sub>2</sub>B(CH<sub>2</sub>)<sub>3</sub>BCl<sub>2</sub>.

**Experiment 4.**—Even after several hours at -23° the reaction was incomplete. The corresponding reaction of the tetrachloride was practically complete in about 4 hours at -80°. But, whereas the tetrachloro adduct undergoes extensive decomposition at 100°, the fluoro adduct had to be heated to 270° for 5 days to undergo appreciable change. The decomposition product contained boron trifluoride, diboron tetrafluoride and ethyldifluoroborane (C<sub>2</sub>H<sub>5</sub>)BF<sub>2</sub>.<sup>12</sup>

To confirm the formula of the compound, bisdichloroborylethane (Cl<sub>2</sub>BC<sub>2</sub>H<sub>4</sub>BCl<sub>2</sub>)<sup>2</sup> was treated with an excess of freshly sublimed antimony trifluoride at room temperature (the procedure is that described in ref. 5). The identity of the product so obtained with that prepared by direct interaction of diboron tetrafluoride with ethylene was demonstrated (a) by the molecular weights (127.3 for each sample) and (b) by the vapor tensions of the two samples at 0 and

-25°, respectively (156 and 40 mm. for the former, 160 and 39.2 mm. for the latter).

A 0.561 mmole sample of the material obtained by fluorination of the chloro derivative was hydrolyzed with dilute sodium hydroxide. In the resulting solution fluoride ion was determined by titration with thorium nitrate using alizarin red as the indicator. The fluorine content was 2.23 mmoles (calcd. for (BF<sub>2</sub>)<sub>2</sub>C<sub>2</sub>H<sub>4</sub>, 2.24 mmoles).

**Experiment 5.**—The reaction was incomplete in 36 hours at room temperature; even after 3 hr. at 90° only about 50% of the reactants had undergone change. Due to the small amount of product obtained, only a 0.0734-g. sample was available for a vapor density determination. The value found was 154.4 (theoretical for (F<sub>2</sub>B)<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, 153.4). The fluorine content by the thorium nitrate titration was 47.5% (theoretical 49.4%).

**Experiment 6.**—The mixture of reactants was first stirred at -45° and then at -23° for 2 days. Because of the instability of the reaction product the resulting mixture was then recooled to -45° and the reactor was opened to a -196° trap. In this manner unchanged allyl chloride was removed without warming the product. The molar reaction ratio C<sub>3</sub>H<sub>5</sub>Cl/B<sub>2</sub>Cl<sub>4</sub> was 1.87/1.90.

The reaction product, *i.e.*, the presumable 1:1 adduct, decomposed slowly at -45° to give boron trichloride and a non-volatile residue. The latter was hydrolyzed with methanol to determine its chlorine content. The total chlorine in the boron trichloride plus that in the residue was 7.6 mmoles or exactly the amount of chlorine in the diboron tetrachloride that had reacted. It follows that the carbon-chlorine link of the allyl chloride had not been affected.

Because of the instability of the adduct it was not further examined.

**Experiment 7.**—In this case also the reaction product was too unstable for determination of more than the molar ratio C<sub>3</sub>H<sub>5</sub>Cl/B<sub>2</sub>F<sub>4</sub>. The fact that this ratio was 1.25 instead of the expected 1.0 is probably due to polymerization of the allyl chloride catalyzed by the boron fluorides.

**Experiment 8.**—A mixture of 2.07 mmoles of diboron tetrachloride and 8.36 mmoles of allyl fluoride (a large excess) underwent vigorous reaction at -80°. The reaction vessel, kept at that temperature, was opened to a train of traps at -96, -112, -126 and -196°. The -126° trap collected 0.84 mmole of diboron tetrafluoride or 40% of that theoretically obtained by complete conversion of the tetrachloride to the tetrafluoride according to equation 1. The course of the reaction was confirmed by the isolation of allyl chloride (0.4 mmole) in the -96° trap. The reaction is, however, more complex than represented by the equation, as shown not only by the deficiency in the amount of allyl chloride obtained, but also by the presence of considerable quantities of boron trifluoride (1 mmole) and of boron trichloride (0.3 mmole) in the product.

**Experiment 9.**—Of a mixture of 6.27 mmoles of diboron tetrafluoride and 1.81 mmoles of allyl fluoride, maintained at

(12) B. Bartocha, W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nuclear Chem.*, **6**, 125 (1958).

$-80^{\circ}$  for 2 days, all but 0.65 mmole of the tetrafluoride was recovered but no allyl fluoride was left. The walls of the reactor were coated with a film resembling the products of polymerization of allyl fluoride. If any adduct was formed, its formation was obscured by the polymerization. The experiment is cited as an example of the catalytic properties of diboron tetrafluoride.

**Experiment 10.**—The reaction mixture was kept at  $-80^{\circ}$  overnight and then was maintained for 2 hr. at  $-45^{\circ}$ , 2 hr. at  $-22^{\circ}$  and finally at room temperature for 3 hr. The volatile reaction product consisted practically entirely of diboron tetrachloride. The reaction ratio of 4-chlorobutene-1 to diboron tetrachloride was 0.91 in one experiment, 1.13 in another experiment, average 1.02.

The reaction product left in the reactor by the fractionation procedure was a liquid of so low a vapor tension that days were required to transfer it from the reactor to other parts of the vacuum system. Consequently a sample free from mercury could not be obtained. For this reason and because of the sensitivity of the adduct to moisture an analysis could not be achieved readily, nor could vapor tensions or vapor densities be obtained. In view of the possibility that the fluoro derivative would be sufficiently more volatile, experiment 11 was carried out.

**Experiment 11.**—The reaction of 4-chlorobutene-1 with diboron tetrafluoride was incomplete even after the reaction mixture had been heated for 24 hr. at  $100^{\circ}$ . The same end product, *i.e.*,  $F_2BC_4H_7ClBF_2$ , was obtained by treatment of the corresponding  $BCl_2$  derivative with antimony trifluoride.

A 0.0468-g. sample of the fluorine compound prepared by the antimony trifluoride procedure was analyzed by first hydrolyzing it and then titrating the resulting solution with thorium nitrate; result, 40.1% fluorine found. Two additional analyses gave 40.4 and 38.9%, respectively, an average of 39.8% (*calcd.* for  $B_2F_4C_4H_7Cl$ , 40.4). The melting point was  $-107^{\circ}$  (3 values). Vapor density determinations on samples of only about 0.05 g. gave the values 222, 201 and 220 (average 214). The result is about 14% higher than the calculated value—a not unreasonable deviation in view of the fact that the vapor density was almost that of the saturated vapor.

**Experiment 12.**—The formula of the  $B_2Cl_4C_2H_2$  adduct was confirmed by the vapor density at  $98.8^{\circ}$  (210, *calcd.*, 190) and its chlorine content of 4.07 mmoles of chlorine per mmole of the compound. A sample of the adduct was bled into an absorption cell with rock salt windows. The pressure in the cell was 2 mm. and the path length 10 mm. The infrared spectrum was taken on a Perkin-Elmer Model 21, double beam spectrograph. A definite band at wave number  $1609\text{ cm.}^{-1}$  indicated the presence of the double bond assumed in the formulation  $Cl_2BC_2H_2BCl_2$ .

To show that the adduct does not take up a second mole of diboron tetrachloride, a 1.26-mmole sample of the  $Cl_2BC_2H_2BCl_2$  was added to 4.27 moles of the tetrachloride. The mixture was stirred first at  $-45^{\circ}$  and then at  $-23^{\circ}$  for a total of 21 hr. Material volatile at  $-45^{\circ}$  contained all of the tetrachloride that had been added to the 1:1 acetylene adduct.

**Experiment 13.**—Attention is called to the extraordinary slowness of the reaction of acetylene with diboron tetrafluoride. Even at  $100^{\circ}$  no change was observed in the reaction mixture. To obtain the "adduct" a mixture of the two reactants was heated at  $120-140^{\circ}$  for 24 hr. in a sealed tube of such dimensions that the estimated initial pressure was about 7 atm. Fractionation of the reaction product in a train of  $-96$ ,  $-119$ ,  $-145$  and  $-196^{\circ}$  traps indicated a reaction ratio  $B_2F_4/C_2H_2 = 1.25$ . The high value of this ratio may have been due to partial decomposition of the tetrafluoride at the high temperature and long reaction time. (Note: the ratio given in Table I is the reciprocal of that used here.)

For confirmation of the formula  $F_2BC_2H_2BF_2$ , another sample was prepared by fluorination of the corresponding  $BCl_2$  derivative with antimony trifluoride. The vapor density of the sample thus obtained gave the expected value (see Table I). Heating the "adduct" with concentrated nitric acid in a sealed tube for 2 hr. at  $300^{\circ}$  yielded 2.17 moles (average of 2 determinations) of carbon dioxide per mole of sample. The boric acid in the residue amounted to 1.93

mmoles per mole of compound. (The theoretical value for both products is 2 mmoles.)

That the samples obtained by direct interaction of acetylene with the tetrafluoride and that obtained by fluorination of the  $BCl_2$  derivative are the same compound was shown by the identity of the melting points ( $-81.7$  and  $-82.6^{\circ}$ ) and by the fact that the vapor tensions of both samples could be reproduced satisfactorily by the equation  $\log P_{\text{mm.}} = 8.565 - 1633/T$ .

**Experiments 14 and 15.**—These experiments demonstrate that butadiene may take up one or two moles of diboron tetrachloride.

In experiment 14, 13.7 mmoles of butadiene was stirred with 5.12 mmoles of the tetrachloride at  $-80^{\circ}$ . A white solid melting slightly above this temperature was formed. After 16 hr. material volatile at  $-45^{\circ}$  was removed. It consisted of 9.02 mmoles of butadiene, showing that 4.68 mmoles of it had reacted with the 5.12 mmoles of the tetrachloride. The molar ratio  $B_2Cl_4/(C_4H_6)$  was thus 1.09.

In experiment 15 a mixture of 4.52 mmoles of the tetrachloride and 1.79 mmoles of the butadiene was stirred for 20 hr. at  $-80^{\circ}$  and then at  $-45^{\circ}$ . The reactor, still at  $-45^{\circ}$ , was opened to a series of traps at  $-80$  and  $-196^{\circ}$ . The volatile material consisted of a trace of boron trichloride together with 0.71 mmole of the tetrachloride. The molar ratio was thus 2.12.

**Catalytic Decomposition of Bisdimethylborylethane.**—That zinc compounds catalyze the decomposition of bisdimethylborylethane was demonstrated readily by these two experiments. In one of them the methylation of bisdichloroborylethane was carried out with an excess of dimethylzinc. The sample obtained decomposed rapidly at  $0^{\circ}$ . To a portion of the unstable material excess boron trichloride was added to convert any contaminating volatile zinc compounds to practically non-volatile zinc chloride. After the excess of boron trichloride and trimethylboron had been removed, the remaining bis-dimethylborylethane underwent no change at  $0^{\circ}$  in 90 minutes.

In the second experiment dimethylzinc was treated with a small amount of boron trichloride on the supposition that some methylzinc chloride would be formed thereby. A portion of the mixture then was distilled into a sample of the previously stabilized tetramethyl derivative. The latter then again underwent rapid decomposition at  $0^{\circ}$ . Boron trichloride again inhibited the decomposition. (Boron trichloride does not react appreciably with the methyl derivative.)

If, in the preparation of the bis-dialkylboryl derivatives, even a slight excess of dimethylzinc were inadvertently used, part of the zinc might be transferred to a somewhat volatile zinc compound (*e.g.*,  $CH_3ZnCl$ ) which would not be separated from the desired product. Variation in stability of the latter may thus be accounted for.

**Behavior of Haloethylenes toward Diboron Tetrahalides.**—None of the ethylene derivatives listed gave any indication of "adduct" formation at room or somewhat higher temperatures: vinyl chloride or fluoride, 1,1-difluoroethylene, 1,2-dichloroethylene or tetrafluoroethylene. Insofar as investigated these compounds were equally inert toward the tetrafluoride.

One additional observation deserves mention. Ordinarily diboron tetrachloride decomposes partially at  $0^{\circ}$  with the formation, among other substances, of the red sub-chloride to which the formula  $(BCl_{0.9})_x$  has been tentatively assigned.<sup>11</sup> To bring about this decomposition in mixtures of the tetrachloride with haloethylenes, temperatures well above  $0^{\circ}$  and in some cases as high as  $100^{\circ}$  were required. That this effect is not due to a secondary reaction of the colored sub-chloride with the haloethylene was demonstrated by the fact that the latter does not decolorize the red material once it is formed.

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