equations 4 and 5 hold between 110 and 1000°K.

Acknowledgments.—It is a pleasure to acknowledge the help of Prof. J. O. Lord, who examined the single-crystal copper sample, and of L. E. Cox, Cryogenic Laboratory Shop Foreman, who made helpful suggestions in the design of the vacuum-tight glass window.

COLUMBUS, OHIO

The Preparation and Some of the Properties of Diboron Tetrachloride, B₂Cl₄[1]

BY GRANT URRY, THOMAS WARTIK,[1] R. E. MOORE[1] AND H. I. SCHLESINGER

The latest procedure for preparing diboron tetrachloride, B_2Cl_4, is described as are the physical properties and the chemical behavior of the compound. It absorbs hydrogen rapidly at room temperature, forming diborane and boron trichloride. The chlorine atoms of the compound may be replaced by bromine, by alkoxy and dimethylamino groups, but not by methyl radicals. It forms a dietherate stable in excess ether, and a monoetherate which loses ethyl chloride at room temperature. At low temperatures in ether solution it adds one mole of diborane to form an unstable compound the behavior of which is described. With trimethylamine it forms a stable compound having the molecular formula $[B_2Cl_4 \cdot N(CH_3)_3]_4$. Hydrogenation of diboron tetrachloride by treatment with lithium borohydride or with aluminum borohydride results in the formation of diborane and tetraborane together with smaller amounts of pentaborane (B_5H_9), and decaborane. The relative amounts of the boranes obtained depend on the temperature and other conditions under which the reaction is carried out.

In spite of numerous efforts to find more efficient procedures for the preparation of diboron tetrachloride[2] (B_2Cl_4), e.g., by the reduction of boron trichloride by metals, metal borides and other reducing agents we have not yet found a method more satisfactory than the electrical discharge procedure described by Wartik, Moore and Schlesinger.[1] We have, however, improved that procedure by making it almost automatic, with the result that 5–10 g. of the desired compound may be produced per week with very little attention, as is described in the Experimental part.

Diboron tetrachloride is a colorless liquid which ignites in air,[3] and which, at temperatures of 0° and above, undergoes partial decomposition into the moderately volatile, crystalline, pale yellow tetraboron tetrachloride, B_4Cl_4,[3] a much less volatile, viscous red material, and a white, non-volatile solid. The composition of the red material may be represented by the formula $(BCl_{0.9})_x$, whereas that of the white solid corresponds to the formula $(BCl_{0.8})_y$. In spite of the reproducibility of the analytical data obtained from different samples, it is not certain that the red and the white products were homogeneous. The methods of analysis, as well as the analytical data for and physical properties of diboron

tetrachloride itself are recorded in the Experimental section.

The chemical properties of diboron tetrachloride are best discussed under the following headings, although the classification is somewhat arbitrary: reaction with hydrogen, replacement of chlorine by other atoms or groups, hydrogenation and addition reactions. In most cases description of experimental details, yields, analyses and physical properties of the compounds involved are deferred to the Experimental part.

Reaction with Hydrogen.—Hydrogen is taken up rapidly at room temperature and below by diboron tetrachloride in the absence of catalysts. If the reaction is carried out with the liquid tetrachloride, a variety of products is obtained, among them boron trichloride, diborane and mixtures of solid materials with viscous liquids. Results are difficult to reproduce under these conditions. It was soon recognized that the difficulty is due to secondary reactions of diborane with unchanged diboron tetrachloride, as described in the section devoted to "addition reactions." If hydrogen and diboron tetrachloride vapor are mixed at room temperature, the reaction proceeds about 80–90% according to the equation

$$3B_2Cl_4 + 3H_2 \longrightarrow 4BCl_3 + B_2H_6 \qquad (1)$$
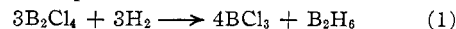
Traces of hydrogen chloride as well as the presence of small quantities of solid material indicate that secondary reactions of diborane with diboron tetrachloride were not completely prevented by the procedure. Some monochlorodiborane was also present, as must be the case in mixtures of diborane and boron trichloride, but a correction for its presence was applied in calculating the yield.

The reaction might have been considered as an addition reaction since the first step is probably that represented by the equation

$$B_2Cl_4 + H_2 \longrightarrow B_2Cl_4H_2 \qquad (2)$$

Since chlorodiboranes disproportionate almost completely into diborane and boron trichloride unless a considerable excess of boron trichloride is present, the postulated intermediate would be almost com-
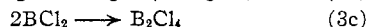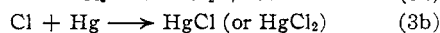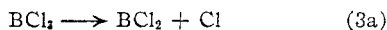
(1) In view of the name, tetraboron tetrachloride, which we have assigned to the compound B₄Cl₄ (see footnote 3), the name diboron tetrachloride for B₂Cl₄ is considered more appropriate than tetrachlorodiborine, as originally suggested by T. Wartik, R. E. Moore and H. I. Schlesinger, THIS JOURNAL, 71, 3265 (1949). Since a committee is now considering boron nomenclature, the new compounds herein described are referred to only by formula. Some of the subject matter of this paper is taken from the thesis presented to the Department of Chemistry of the University of Chicago in 1950 by R. E. Moore, in part fulfillment of the requirements for the degree of Doctor of Philosophy. Most of the subject matter is taken from reports submitted to the Office of Naval Research on Contract No. N6ori-20, Task Order 10, Project NR 356-255, during the period July 1, 1948, to January 31, 1954.

(2) First prepared by A. Stock, A. Brandt and H. Fischer, Ber., 58, 855 (1925).

(3) Although the sample used for the reaction with air had been carefully purified, it is nevertheless possible that its inflammability may have been due to the presence of traces of tetraboron tetrachloride, which seems to react more vigorously with air than does the diboron compound (Grant Urry, Thomas Wartik and H. I. Schlesinger, THIS JOURNAL, 74, 5809 (1952)).

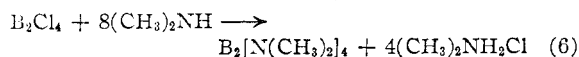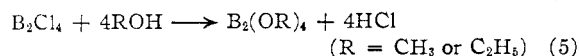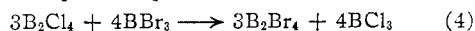pletely transformed to the end-products of equation 1.

These observations suggest that the electrical discharge method of Schlesinger and Burg[4] for the preparation of diborane may be of similar character. One may postulate that the following steps occur in the discharge procedure for preparing diboron tetrachloride.

$$BCl_3 \longrightarrow BCl_2 + Cl \qquad (3a)$$
$$Cl + Hg \longrightarrow HgCl \text{ (or } HgCl_2) \qquad (3b)$$
$$2BCl_2 \longrightarrow B_2Cl_4 \qquad (3c)$$

In the procedure for preparing diborane, the diboron tetrachloride might react with hydrogen as suggested by equation 2, or the hydrogen might react with the BCl_2 fragment to form $HBCl_2$, which would dimerize and disproportionate to give the end-products monochlorodiborane, diborane and boron trichloride.

In the actual preparation of diborane by the discharge procedure, a large excess of hydrogen was used. Under these conditions the presence of diboron tetrachloride as an intermediate could probably not have been detected. The interpretation given for the reaction has, however, received support from our recent observation that when a relatively large proportion of boron trichloride is passed through the arc in the presence of hydrogen, diboron tetrachloride is produced.

Replacement Reactions.—The chlorine of diboron tetrachloride may be replaced by bromine, by alkoxy groups and by dimethylamino groups as represented by the equations

$$3B_2Cl_4 + 4BBr_3 \longrightarrow 3B_2Br_4 + 4BCl_3 \qquad (4)$$
$$B_2Cl_4 + 4ROH \longrightarrow B_2(OR)_4 + 4HCl$$
$$(R = CH_3 \text{ or } C_2H_5) \qquad (5)$$
$$B_2Cl_4 + 8(CH_3)_2NH \longrightarrow$$
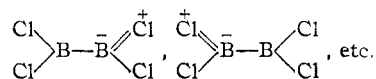$$B_2[N(CH_3)_2]_4 + 4(CH_3)_2NH_2Cl \qquad (6)$$

The reactions, which are not quantitative in all cases, and the analyses and physical properties of the new compounds are described in the Experimental part. Closely related to the replacement reactions just mentioned is the behavior of ammonia toward diboron tetrachloride. The products obtained are all solid and have not yet been completely identified. The fact that 6 moles of ammonia are taken up and 4 moles of ammonium chloride are produced per mole of diboron tetrachloride may be represented by the tentative equation[5]

$$xB_2Cl_4 + 6xNH_3 \longrightarrow 4xNH_4Cl + 2(BNH)_x \qquad (7)$$
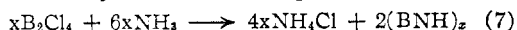
All of the substituents by which we have thus far been able to replace the chlorine of diboron tetrachloride are or contain atoms having unshared electron pairs. Attempts to replace the chlorine by methyl groups (e.g., by treatment with dimethylzinc) have led to what appears to be complete decomposition, i.e., to the formation of trimethylboron, black solids probably containing elementary boron, and other unidentified substances. This observation suggests that molecules containing boron-

(4) H. I. Schlesinger and A. B. Burg, This Journal, **53**, 4321 (1931).

(5) By analogy with the reaction of diboron tetrachloride with trimethylamine (see below), the first step in the ammonia reaction may be the formation of $B_2Cl_4 \cdot 2NH_3$. Attention is called to the fact that A. Stock and E. Pohland, *Ber.*, **59B**, 2210 (1926), report a compound of the composition BNH.

to-boron bonds may not be capable of existence unless they are stabilized by some type of resonance or by some other stabilizing factor. In the boranes the resonance associated with hydrogen bridges may be the factor; in diboron tetrachloride and its stable derivatives it may be resonance of the type represented by structures such as

$$\overset{Cl}{\underset{Cl}{>}}B-\overset{-}{B}\overset{+}{\overset{Cl}{<}}_{Cl} , \quad \overset{+}{\overset{Cl}{\underset{Cl}{>}}}B-\overset{-}{B}\overset{Cl}{<}_{Cl} , \text{ etc.}$$

There is, of course, another possibility, namely, that the methylating agents we have used are acting as reducing agents also. For this reason we are planning to investigate other methods for the preparation of diboron tetraalkyls.

Hydrogenation of Diboron Tetrachloride.—Diboron tetrachloride does not react with lithium aluminum hydride at room temperature either in the absence of solvents or in the presence of diethyl or dimethyl ethers. Calcium aluminum hydride in the presence of tetrahydrofuran also fails to react.

Lithium borohydride as well as aluminum borohydride, on the other hand, react rapidly, even in the absence of solvents and at temperatures as low as $-45°$. The reaction is complex, since diborane, tetraborane, pentaborane (B_5H_9) and traces of decaborane are formed. If an equivalent amount or an excess of reducing agent is used, all of the chlorine is retained in the non-volatile products of the reaction. When the reaction with lithium borohydride was carried out at room temperature over a period of 16 hours, about 13 times more of diborane than of the combined higher hydrides was obtained. As is shown in more detail in the Experimental part, the lower the temperature and the shorter the length of time the reactants and products remain in contact with each other, the smaller is the ratio of the diborane to higher hydrides. Thus when a mixture of aluminum borohydride[6] and diboron tetrachloride was allowed to stand for 45 minutes at $-45°$, the ratio of diborane to higher hydrides was only 3, and very little of hydrides other than diborane and tetraborane was found. These facts are in accord with the hypothesis that tetraborane and diborane are produced initially according to the equation

$$B_2Cl_4 + LiBH_4 \longrightarrow B_4H_{10} + B_2H_6 + 4LiCl \qquad (8)$$

The higher boranes and the excess of diborane formed in the actual experiments, especially at the higher temperatures and longer reaction times, would on this hypothesis be due to secondary decomposition and reactions of the unstable tetraborane.

At the time these experiments were carried out only very small quantities of diboron tetrachloride were available, and the data obtained are not accurate enough to subject the preceding hypothesis to accurate test. We anticipate doing further work on the problem, now that larger amounts of the tetrachloride can be easily prepared.

Addition Reactions. (a) **Reaction with Diethyl Ether.**—Diboron tetrachloride and diethyl ether form a white crystalline dietherate which is stable

(6) Aluminum borohydride was used for the low temperature experiments because it may be cooled to nearly $-65°$ before solidifying.

up to 45° and which may be kept without noticeable change for several weeks at room temperature if dissolved in an excess of the ether. In the absence of excess ether, the crystals decompose at a temperature as low as $-23°$ to form a liquid monoetherate. The latter at room temperature undergoes further decomposition, in the course of which all of its ethyl groups are lost as ethyl chloride. The yellow glassy solid which is simultaneously formed has not been investigated.[7]

(b) **Reaction with Diborane.**—Treatment of either liquid or gaseous diboron tetrachloride with diborane in the absence of solvents leads to a complex reaction among the products of which are hydrogen, boron trichloride, viscous liquids and a very unstable gaseous product. If, however, the reaction is carried out at $-23°$ in the presence of diethyl ether, one mole of diborane takes up one of the tetrachloride. Removal of the ether, as described in the Experimental part, leads to partial decomposition, one of whose products is a white crystalline product melting slightly above $-80°$. Analysis of this material indicated an atomic (and molecular) ratio of $B:Cl:H:Et_2O = 3:4:4:2$. The hydrogen was obtained by hydrolysis with methanol. Hence, if the compound still contained a boron–boron bond, one mole of hydrogen could have been produced by severance of this bond.[8] In that event the formula would be $(B_2Cl_4BH_3)\cdot2Et_2O$. Further work is needed to establish the correct formula.

(c) **Reaction with Trimethylamine.**—When a mixture of diboron tetrachloride and an excess of trimethylamine is warmed slowly, a vigorous reaction sets in at temperatures well below room temperature. Removal of unchanged trimethylamine demonstrates that the reactants had combined in the ratio $N(CH_3)_3/B_2Cl_4 = 1.92$. The reaction does not result in a rupture of the boron–boron bond of the diboron tetrachloride, since treatment of the reaction product with aqueous sodium hydroxide liberates approximately one mole of hydrogen per mole of diboron tetrachloride used in the formation of the compound. The product is not a simple adduct since its molecular weight, determined by the lowering of the freezing point of benzene, is 1170 ± 4, or approximately four times the value (281.5) calculated for the formula $B_2Cl_4\cdot2N(CH_3)_3$. There is as yet no information on which to base hypotheses about the structure of the tetramer.

The tetramer is a very stable substance. Although it begins to soften at 195°, it melts without appreciable decomposition at 228°, and may be sublimed *in vacuo* without dissociation. It is chemically rather inactive. Unlike diboron tetrachloride itself, the trimethylamine tetramer does not react with hydrogen, even at 90°, or with diborane.

(7) Diboron tetrachloride appears also to form a solid dietherate and a liquid monoetherate with dimethyl ether. These compounds have not yet been studied in detail; they seem to be more volatile and more stable than the diethyl etherates.

(8) Attention should, however, be called to the fact that treatment of diboron tetrachloride itself by methanol does not liberate hydrogen and that complete rupture of its boron–boron bond requires the use of alkali. It is of course not impossible that the boron–boron bond of the new compound is more readily broken. Furthermore the presence of hydrogen chloride may have accelerated the hydrolysis in this case.

Treatment with ethanol does not generate hydrogen chloride, but two moles of the reagent is taken up per mole of tetramer. From it neither boron trichloride nor the trifluoride liberate diboron tetrachloride. Methylating agents (*e.g.*, dimethylcadmium[9]) do not bring about replacement of chlorine by methyl groups but give rise to black solids as with diboron tetrachloride itself. The tetramer does react with lithium aluminum hydride and with lithium borohydride, but the reactions are complex and the products difficult to isolate. In the case of the borohydride, diborane and trimethylamine borine, $(CH_3)_3NBH_3$ were identified; in the case of the aluminum compound a material resembling $(CH_3)_3\text{-}NAlH_3$[10] seems to have been formed. Additional data are found in the Experimental part.

Probably the most important chemical property of diboron tetrachloride is its reaction with unsaturated hydrocarbons. Because of the possible significance of the reaction for the synthesis of organo-boron compounds, discussion of this aspect of the behavior of diboron tetrachloride is presented in the paper which follows.

Experimental

Apparatus and Reagents.—Except for the apparatus used for the preparation of diboron tetrachloride, most of the reactions and purification of reaction products were carried out in standard type vacuum lines equipped with mercury float valves.

The **boron trichloride** (Harshaw Chemical Co., highest purity) was repeatedly distilled through a $-80°$ trap into one at $-111.9°$ until its 0° vapor tension was 477 mm. **Boron tribromide**, prepared by the action of bromine on calcium boride, was allowed to stand over mercury to remove bromide, and was then distilled into a $-80°$ trap, which does not retain hydrogen bromide. **Methanol, ethanol** and **ammonia** were freed from moisture by treatment with sodium in the usual way. Traces of moisture were removed from "anhydrous" peroxide-free **diethyl ether** by distillation from lithium aluminum hydride. Eastman **dimethylamine** was used without further treatment. **Trimethylamine** was purified by heating it with phosphorus pentoxide for 15 hours at 100° in a sealed tube (the 0° tension of the product used was 683 mm., accepted value 681 mm.). **Lithium borohydride** was recrystallized from diethyl ether and then heated *in vacuo* to 70° before it was used. **Diborane** was obtained by the interaction of boron fluoride diethyl etherate on either lithium hydride or lithium borohydride, and was freed from ether (when necessary) by passing it through a $-140°$ trap into one at $-196°$. **Aluminum borohydride** which had been prepared by the method of Schlesinger, Brown and Hyde[11] was used.

Preparation of Diboron Tetrachloride.—For carrying out the preparation of diboron tetrachloride by passing boron trichloride through a discharge between mercury electrodes,[1] we used a mercury piston and cylinder in the arrangement shown in Fig. 1.

The piston and cylinder consist of two chambers. At the beginning of the cycle the lower one is filled with mercury to the level A, establishing electrical connections between the tungsten leads 1 and 2. A relay is thereby actuated to turn on the transformer, which establishes a high voltage discharge between the mercury electrodes of the cell (c). At the same time the relay opens the air leak (L). The air thus admitted pushes the mercury through the dip tube into the upper chamber, which is at reduced pressure. Although the connection between leads 1 and 2 is broken as the level of the mercury in the lower chamber falls, the position of the relay remains unchanged (see Fig. 2). But when the mercury level has risen to B in the upper chamber,

(9) Dimethylcadmium was used because we had available a very pure sample of the compound.

(10) O. Stecher and E. Wiberg, *Ber.*, **75**, 2003 (1942).

(11) H. I. Schlesinger, H. C. Brown and E. K. Hyde, THIS JOURNAL, **75**, 209 (1953).
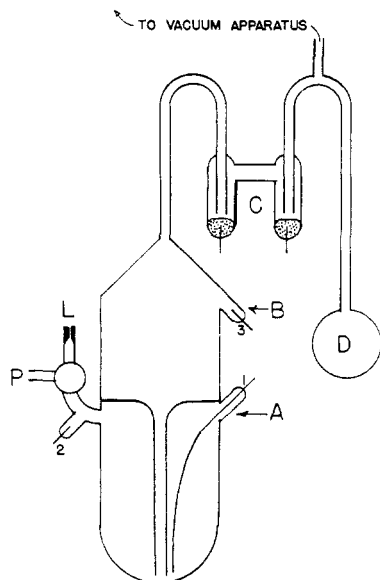
Fig. 1.

electrical connection is established between leads 1 and 3, and the position of the relay changes in such a way that the transformer is turned off, the air leak solenoid valve is closed, and the lower chamber is connected to an oil pump through (P) by means of a second solenoid. The mercury then falls until the original position is re-established, and the cycle automatically repeats itself.
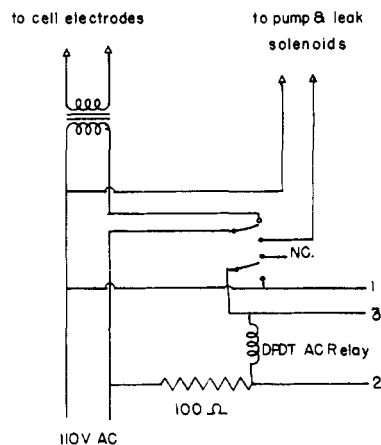

Fig. 2.

Liquid boron trichloride is present in bulb D maintained at −80° at which its vapor tension is 4 mm. During the downstroke of the piston the boron trichloride evaporates from the bulb and passes through the cell (C) into the upper chamber of the circulating pump. During this stage the electrical discharge is not operating. On the upstroke of the piston most of the boron trichloride in the upper chamber is forced back through the cell in which the discharge has now been established. The diboron tetrachloride formed during this stage, together with traces of other subchlorides and with unchanged boron trichloride, is condensed in bulb D. On the succeeding stroke of the piston, only the boron trichloride evaporates from the bulb, since the subchlorides are essentially non-volatile at −80°.

The present apparatus uses eight such assemblies operating simultaneously. The total yield of this group on the average is 8 g. of diboron tetrachloride (together with about 25 mg. of tetraboron tetrachloride) per week. The optimum voltage appears to be about 1000 v. for a 4 cm. path. After a few weeks of operation, the vapor tension of the liquid in D falls so low, as the result of accumulation of the subchlorides, that the arc becomes difficult to establish.

Until that occurs the apparatus requires practically no attention except for daily replenishment of the cooling baths around D.

After the discharge has ceased to operate satisfactorily for the reason just mentioned, the liquid in D is removed to the vacuum line and is there distilled through traps at −63, −80 and −196°. The tetraboron tetrachloride is retained in the −63° trap, and the diboron tetrachloride in the −80° trap; unchanged boron trichloride is collected at −196°, and may be returned to the apparatus.

Analysis of the Subchlorides of Boron.—Diboron tetrachloride, as well as its red and white decomposition products were analyzed by first hydrolyzing the samples by heating them for about 3 hours at 70° with 10% sodium hydroxide solution, and then determining chlorine as silver chloride and boron by the usual titration. In the case of the red and the non-volatile white subchlorides, hydrolysis had to be completed after the treatment with the sodium hydroxide solution by nearly neutralizing the solution, and then adding 90% hydrogen peroxide. The excess of the latter was decomposed by platinum black.

In most instances when alkaline solutions were used for analysis, the sodium hydroxide treatment was carried out in a silver dish. In the few cases in which Pyrex glass apparatus was used a correction for boron dissolved from the glass, based on a blank, was applied. The reliability of the procedure is shown by the following results of an analysis of diboron tetrachloride carried out in glass vessels.[12]

Anal. Calcd. for sample 0.0995 g.: Cl, 0.0863 g.; B, 0.0131 g.; H₂, 13.65 cc. Found: Cl, 0.0878 g.; B, 0.0131 g.; H₂, 13.26 cc.

The agreement between the sample weight and the sum of the weights of chlorine and boron is excellent, as is the agreement of the ratio B:Cl:H₂ = 2:4.08:0.98 with the requirement of the equation

$$B_2Cl_4 + 10NaOH \longrightarrow$$
$$2Na_3BO_3 + 4NaCl + H_2 + 4H_2O \quad (10)$$
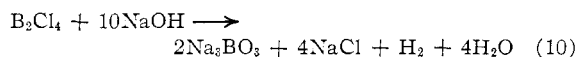
To purify the viscous red substance for analysis, it was solved in benzene and reprecipitated from the filtered solution by evaporation of the solvent.[13] The analytical results obtained may be represented by B:Cl ratios of 1:0.90 and 1:0.92. The ratios for the white product were 1:0.6 and 1:0.61.

Physical Properties of Diboron Tetrachloride.—A 0.0810-g. sample of diboron tetrachloride exerted a pressure of 48.9 mm. at 26.5° in a volume of 191.6 cc., corresponding to a molecular weight of 161.3 (calcd., 163.5). The melting point was −92.6 ± 0.1°. Table I records its vapor tensions.

TABLE I

VAPOR TENSIONS OF B_2Cl_4

t, °C.	−63.5	−45.2	−30.6	−22.6	0.0	6.0	21.2
p (obsd.)	1.0	2.3	6.8	10.7	44.5	61.5	121.7
p (calcd.)	0.5	2.3	6.7	11.5	43.9	60.0	125.9

The calculated values were obtained from the equation: $\log p = 8.057 - (1753/T)$, according to which the normal boiling point would be 65.5°, the heat of evaporation 8029 cal./mole and the Trouton constant 23.7.

Chemical Reactions of Diboron Tetrachloride. (a) Reaction with Hydrogen.—The experiment herein described is one carried out with small quantities of reactants, all of which were in the gas phase. Under these conditions secondary reactions of diborane with unchanged diboron tetrachloride are minimized.

A mixture of 0.496 mmole of diboron tetrachloride with 1.218 mmoles of hydrogen was allowed to stand for one hour at room temperature in a 500-cc. bulb. At the end of that time 0.799 mmole of hydrogen, 0.638 mmole of boron trichloride and 0.167 mmole of a product with a vapor tension of 245 mm. at −111.9° were obtained. Al-

(12) The abbreviation cc. is used for gases at N.T.P., whereas ml. refers to liquids.

(13) Irrespective of the number of repeated purifications, treatment of the red material with benzene left a white residue. The red product evidently decomposes into the white one. It is because of this difficulty that molecular weight determinations by the lowering of the benzene freezing point were considered unreliable, and are not reported.

though the vapor tension of the last named material was considerably higher than that of diborane (225 mm.), the product seemed to consist almost entirely of diborane, monochlorodiborane and hydrogen chloride, as shown by the following data. Hydrolysis of the sample generated 0.732 mmole of hydrogen and the hydrolysate contained 0.251 mmole of boron. These figures correspond to a mixture of 0.107 mmole of diborane and 0.018 mmole of monochlorodiborane. In addition to the hydrogen, hydrolysis also produced 0.049 mmole of hydrogen chloride; on the assumption that 0.018 of this amount came from the hydrolysis of the monochlorodiborane, the sample had originally contained 0.031 mmole of hydrogen chloride. The sum of the diborane, the monochlorodiborane and the hydrogen chloride is thus 0.156 mmole, as compared with the 0.167 mmole of the sample. Although this difference (amounting to only about 0.2 gaseous cc.) could be due to experimental error, it may also be an indication of the presence of a very small amount of an unknown impurity responsible for the high vapor tension of diborane fraction.

The amount of hydrogen consumed ($1.218 - 0.799 = 0.419$ mmole) is about 85% of that which should have reacted with the 0.496 mmole of diboron tetrachloride according to equation 1. The facts that the amount of boron present in the fraction considered to contain a mixture of diborane and its monochloro derivative is only 76% of the expected value, whereas the amount of boron trichloride generated is about 94%, suggests that the reaction had proceeded about 80-90% according to the equations, and that secondary reactions between diboron tetrachloride and diborane produced hydrogen chloride and additional boron trichloride, while reducing the yield of diborane.

(b) Preparation of Diboron Tetrabromide from the Chlorine Derivative.—A mixture of 1.4 mmoles of diboron tetrachloride with an excess of boron tribromide (approximately 3.7 mmoles) was allowed to stand for half an hour at room temperature. The diboron tetrabromide thus formed was distilled away from non-volatile by-products, and was purified by repeatedly passing it through a $-30°$ trap, which retained the desired compound, but did not condense excess boron tribromide or trichloride. The final product having a vapor tension of 5.5 mm. at 22.5° weighed 0.3661 g. (1.073 mmoles), a yield of 77%.

In weighing a sample for analysis, special precautions were taken to prevent reaction with stopcock greases which are rapidly attacked by the compound. Boron and hydrogen (generated by hydrolysis) were determined as described for the corresponding chloro derivative. To the hydrolysate, after acidification with nitric acid, a known amount of silver nitrate solution was added. The excess of silver ion in the filtered solution was then determined as the chloride. The weight of the original silver halide precipitate and its silver content were thus determined, and were found to correspond within experimental error to the ratio for silver bromide. Hence the sample could have contained no more than a negligible amount of chloride ion.

Anal. Calcd. for B_2Br_4 (wt. sample 0.3663 g.): H_2, 1.073; B, 2.146; Br, 4.292 mmoles. Found: H_2, 1.12; B, 2.33; Br, 4.46 mmoles.

The atomic ratios: $H_2:B:Br = 1.00:2.08:3.98$ are in close agreement with the formula B_2Br_4. The amounts of the constituents are slightly above the theoretical, due undoubtedly to the difficulty of determining the weight of the sample.

(c) The Reaction with Ethanol.—A mixture containing 1.553 mmoles (34.4 cc.) of diboron tetrachloride and 6.093 mmoles (0.2807 g.) of ethanol, was allowed to warm to $-80°$, and was maintained at that temperature till evolution of hydrogen chloride ceased. The latter was separated from the other volatile reaction products by passage through a trap at $-111.9°$ to one at $-196°$. The latter then contained 5.81 mmoles (132.0 cc.) of hydrogen chloride (identified by its $-111.9°$ vapor tension of 125 mm. and its molecular weight of 34.5). The amount of hydrogen chloride corresponds to 93.5% of that expected from the equation

$$B_2Cl_4 + 4C_2H_5OH \longrightarrow B_2(OCH_3)_4 + 4HCl \quad (11)$$
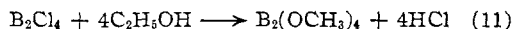
The amounts of the diboron tetraethoxide, however, corresponded to a yield of only 55% in the experiment cited and to 67% in another one. The compound was isolated by distilling the $-111.9°$ fraction of the reaction product through U-tubes maintained at 0 and $-45°$ into one at
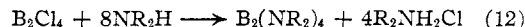
$-196°$. The major portion of the reaction product, retained at 0°, consisted of 0.1710 g. (0.85 mmole) of diboron tetraethoxide, identified by analysis. An unidentified greenish, non-volatile residue was formed as a by-product of the reaction.

For analysis the compound was hydrolyzed with 10% sodium hydroxide solution for 3 hours at about 100°. Carbon was determined by combustion of the volatile portion of the hydrolysate with cupric oxide. Boron was determined in the residue in the usual way after removal of the volatile portion. Only the hydrogen generated during hydrolysis is included in the following data. Chlorine was shown to be absent.

Anal. Calcd. for $B_2(OC_2H_5)_4$ (wt. samples 0.1710 and 0.1814 g.): H_2, 19.0, 20.1 cc.; B, 10.71%; C, 47.61%. Found: H_2, 18.0, 20.0 cc.; B, 10.63 and 11.16%; C, 44.63%.

In the reaction of diboron tetrachloride with methanol, 4 moles of hydrogen chloride was generated per mole of the tetrachloride, but the methoxy derivative was relatively unstable. For this reason satisfactory analyses were not obtained, and no further details are here recorded.[14]

(d) The Reaction with Dimethylamine.—A mixture of 0.893 mmole (20.1 cc.) of diboron tetrachloride with 9.4 mmoles (210.5 cc.) of dimethylamine was allowed to stand for several hours at $-80°$ although the reaction seemed to occur immediately. Excess of dimethylamine was removed by distilling the volatile reaction products through a trap at $-80°$ into one at $-196°$. Judging from the amount recovered, 7.59 moles of dimethylamine had reacted with 1 mole of diboron tetrachloride, instead of the 8 moles required by the equation

$$B_2Cl_4 + 8NR_2H \longrightarrow B_2(NR_2)_4 + 4R_2NH_2Cl \quad (12)$$

The discrepancy is undoubtedly due to the formation of small amounts of the compound $B(NR_2)_3$ and of a very slightly volatile decomposition product.

The material retained at $-80°$ was distilled through a 0° trap. The major portion condensed in this trap and was then analyzed by hydrolysis with 10% sodium hydroxide solution for 4 hours at steam-bath temperature. Dimethylamine was determined by titration of the distillate from the solution; in the latter boron was determined as usual. Hydrogen liberated was measured. Found were 0.553 mmole H_2, 1.147 mmoles B and 2.268 NR_2H, a ratio of $B:NR_2:H_2 = 1.00:1.98:0.48$, in good agreement with the theoretical ratios $1.00:2:0.5$. From the amount of boron recovered, the yield is calculated as about 64%.

(e) Reaction with Ammonia.—From a mixture of 13.3 cc. (0.59 mmole) of diboron tetrachloride with 122.5 cc. of ammonia, which stood for 12 hours at $-80°$, 42.6 cc. of unchanged ammonia was removed, first at $-80°$ and a small remainder at 150°. Hence the molar ratio $NH_3/B_2Cl_4 = 6$. The residual solid was then flamed to drive off ammonium chloride, of which 2.26 mmoles was obtained. In addition, 0.06 mmole of hydrogen chloride was generated, presumably by dissociation of ammonium chloride. Hence the total amount of ammonium chloride was 2.32 mmoles and the ratio NH_4Cl/B_2Cl_4 was 3.93. The data are in satisfactory agreement with equation 7.

(f) Reaction with Borohydrides.—Since the volatile products of the reaction contained no chlorine and very little elementary hydrogen, they must have consisted essentially of boranes. The reactions included herein were carried out in the absence of solvent. Lithium borohydride was used in excess, aluminum borohydride in equivalent amounts. Fractionation was not completely effective because of the small quantities involved and the instability of

(14) E. Wiberg and W. Ruschmann, *Ber.*, **70**, 1393 (1937), have prepared the tetramethoxy and tetraethoxy derivatives by the reaction of sodium amalgam on appropriate compounds of the type $B(OR)_2Cl$. They mention the instability of the tetramethoxy derivative, but were nevertheless able to obtain vapor tension and other data for the sample they prepared. Their observation on the tetraethoxy derivative, however, differs markedly from ours. Thus they report for it a vapor tension of <4 mm. at 18° whereas our sample had a vapor tension of only about 1 mm. at 25.9°. Furthermore our sample seemed reasonably stable at room temperature, whereas theirs is described as decomposing into boron and ethyl borate. Wiberg and Ruschmann mention, however, that traces of moisture catalyze the decomposition. Possibly the differences observed may be due to traces of either moisture or alcohol.

tetraborane. The fractions listed in Table II as diborane had vapor tensions of 223–224 mm. at −111.9° (accepted value 225 mm.); those listed as tetraborane had vapor tensions of 386–394 mm. at 0° (accepted value 388 mm.) or 12.8 to 13.2 mm. at −63° (accepted value 10.8 mm.) and those listed as pentaborane, vapor tensions of 74–83 mm. at 0° (accepted value 66 mm.).[15] Blanks in the B_5H_9 column indicate that either none or quantities too small for isolation were obtained. Only in the first two experiments were traces of decaborane (recognized by the presence of a characteristic crystal or two) observed. Judging from the small amounts of boranes obtained at the two lower temperatures the reactions were far from complete in the time allowed.

TABLE II

REACTIONS OF DIBORON TETRACHLORIDE WITH BOROHYDRIDES

Borohydride used	B_2Cl_4, mmoles	Condition	B_5H_9, mmoles	B_4H_{10}, mmoles	B_5H_9, mmoles	$\dfrac{B_2H_4}{B_4H_{10}}$
LiBH₄	1.158	Room t. 16 hr.	2.451	0.067	0.116	36.6
LiBH₄	0.760	−22.9° 2 hr.	1.201	.168	0.129	7.1
Al(BH₄)₃	1.314	0° 30 min.	1.478	.377	...	4.0
Al(BH₄)₃	0.887	−45° 45 min.	0.615	.202	...	3.0

(g) **Reaction with Diethyl Ether.**—A sample of the dietherate was made by allowing a mixture of 2.09 mmoles of diboron tetrachloride with 8.63 mmoles of diethyl ether to warm slowly from −80° to room temperature. Excess of the ether was removed by pumping at temperatures not exceeding −45°. At −23° loss of additional ether changed the composition from $Et_2O/B_2Cl_4 = 1.93$ to 0.93, and caused the crystalline solid to go over into a yellow, viscous liquid. The latter decomposed at room temperature into 2.18 mmoles of ethyl chloride (molecular weight 64.9, calcd. 64.5; −30° vapor tension, 102 mm., accepted value 100.8 mm.). The excess over the total ethyl groups of the monomer may be due to experimental error (*ca.* 4%) or to retention of excess ether by the etherate.

Reaction with Diborane.—Only the reaction carried out in the presence of diethyl ether at −23° is described because of the complexity of the reaction under other conditions. At the temperature mentioned 2.98 mmoles of diboron tetrachloride combined with 2.8 mmoles of the borane. Removal of the solvent at −80° left behind a straw-colored liquid. Evaporation at room temperature and condensation at −80° and −196° caused the evolution of some diborane and separated residual ether from a product which was retained as white crystals at −80°, but which melted to a colorless liquid at a slightly higher temperature. Analysis gave the following results: B, 5.72; Cl, 7.53; H (by hydrolysis) 7.63; Et_2O, 4.01 mmoles, which are within experimental error of the rounded values given in the introductory section.

(h) **Reaction with Trimethylamine.**—In a typical preparation of the compound $[B_2Cl_4 \cdot 2N(CH_3)_2]_4$, 54.5 cc. of tri-

methylamine was added to 9.13 cc. of diboron tetrachloride. After the mixture had warmed to room temperature and been there maintained for 24 hours, 37.0 cc. of the amine was recovered unchanged. Diboron tetrachloride had therefore reacted with the amine in the molar ratio 1:1.92.

Although the compound fumes in air (undoubtedly due to the liberation of hydrogen chloride by atmospheric moisture) complete hydrolysis by water is slow. To avoid the difficulties introduced in the analysis by these phenomena, a sample of the material was sealed (on the vacuum line) into a weighing tube, which was then broken under a concentrated solution of sodium hydroxide in a silver dish. Boron and chlorine were then determined in the solution. To determine the amount of hydrogen liberated by breaking of the boron-to-boron bond a separate sample was hydrolyzed by sodium hydroxide solution in the vacuum system.

Anal. Calcd. for $[B_2Cl_4 \cdot 2NH_3]_x$ (wt. sample 0.1503 g.): B, 7.69; Cl, 50.4. Found: B, 8.02; Cl, 49.8. In the hydrogen determination a sample prepared from 0.91 mmole of B_2Cl_4 gave 0.86 mmole of hydrogen.

TABLE III

VAPOR TENSIONS OF SOLID $[B_2Cl_4 \cdot 2N(CH_3)_2]_4$

t, °C.	143.8	154.2	182.0	187.0	192.5	201.0	207.0
p (obsd.), mm.	2.5	3.1	12.5	15.5	19.8	30.6	40.8
p (calcd.), mm.	1.6	3.0	12.3	15.7	20.4	30.0	39.1

The calculated values were obtained from the equation $\log p = 10{,}739 - (4390/T)$, according to which the heat of sublimation is approximately 20,000 cal./mole.

The molecular weight was determined by the lowering of the freezing point of benzene.[16] For reliable results the benzene must be carefully purified and transfer of materials, as well as the freezing point measurements, must be carried out with the exclusion of moisture. The thiophene-free benzene, previously fractionally distilled, was treated with lithium aluminum hydride from which it was distilled *in vacuo* to a weighed portion of the trimethylamine "adduct." The latter had been purified by recrystallization from benzene and subsequent fractional sublimation. The solution was weighed, and a portion introduced into the freezing point apparatus. The residual solution was again weighed to determine how much of it had been used. The freezing point lowering apparatus was designed to permit adequate magnetic stirring and removal of portions of the solvent after each freezing point measurement. In this way the freezing point lowering at several concentrations was observed with a single sample of the compound. The results of one of two closely agreeing experiments are as follows: wt. sample, 1.562 g.; wt. C_6H_6, 45.58, 40.85 and 35.12; f.p. lowerings, 0.148, 0.166, 0.192°, resp.; mol. wt. obsd., 1172, 1166, 1174, av., 1171; calcd. for the tetramer 1126.

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(15) The "accepted" values are taken from A. Stock and E. Kuss, *Ber.*, **56**, 789 (1923). It is noteworthy that although these authors give 10.8 mm. for the vapor tension of tetraborane at −63°, the values for 3 of our tetraborane fractions were 13.2, 12.8 and 13.0, respectively.

(16) The compound is also slightly soluble in isopentane and somewhat more soluble in diethyl ether.