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Diboron Tetrachloride, B_2Cl_4, as a Reagent for the Synthesis of Organo-boron Compounds. I. The Reaction of Diboron Tetrachloride with Ethylene[1]

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Diboron tetrachloride reacts with ethylene to form a stable compound to which we assign the formula $Cl_2BC_2H_4BCl_2$ on the basis of evidence given in the text, in which the physical properties of the new compound are described. Its chlorine atoms are readily replaced by methoxy and by methyl radicals. The methyl derivative at room temperature undergoes slow decomposition which may, however, be greatly accelerated by the presence of impurities. The products of decomposition, aside from trimethylboron, though not yet thoroughly investigated, appear to represent new types of organo-boron compounds. Preliminary experiments have shown that acetylene and cyclopropane undergo similar reactions with diboron tetrachloride. It is evident, therefore, that the latter is a valuable reagent for the synthesis of organo-boron compounds.

At temperatures as low as −80°, one mole of diboron tetrachloride[2] reacts with one mole of ethylene to form a liquid compound, stable to moderately high temperatures, to which we have assigned the formula $Cl_2BC_2H_4BCl_2$. The basis for the assumption that the boron-to-boron bond of diboron tetrachloride has been severed in the reaction is the fact that treatment of the new compound with aqueous sodium hydroxide generates no hydrogen even at temperatures approaching 100°. In contrast thereto hydrogen is generated in the hydrolysis of diboron tetrachloride or its derivatives.[2a] Details of preparation and analyses, as well as data on the physical properties of this and the other new compounds described in this paper are given in the Experimental part.

Treatment of $Cl_2BC_2H_4BCl_2$[3] at room temperature with methanol produces a liquid having a vapor density which is in agreement with the formula $(CH_3O)_2BC_2H_4B(OCH_3)_2$. The formula is confirmed by the fact that in the methanol reaction 99.8% of the theoretical amount of hydrogen chloride is generated.

The compound $Cl_2BC_2H_4BCl_2$ does not react with trimethylboron at room temperature; its reaction with dimethylzinc, on the other hand, is too vigorous to be readily controlled in the absence of solvents. Dimethylzinc may, however, be used for replacement of the chlorine atoms by methyl groups if the reaction is carried out in either trimethylboron or *n*-pentane as solvents. By keeping the temperature at −23° or below, and by isolating the main volatile reaction product with minimum exposure of the vapors to higher temperatures, there have been obtained yields of 90% of that required by the equation

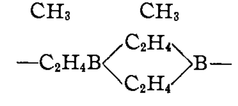
$$Cl_2BC_2H_4BCl_2 + 2Zn(CH_3)_2 \longrightarrow (CH_3)_2BC_2H_4B(CH_3)_2 + 2ZnCl_2 \quad (1)$$

The formula of the methyl derivative is based on (1) the stoichiometry of the reaction, (2) the vapor density and analyses of the product, and (3) determination of the amount of methanol produced by oxidation of the product with perbenzoic acid, as explained more fully in the Experimental part.

The methyl derivative in question is not entirely stable. A carefully purified sample lost 0.03 mmole of trimethylboron per mmole of $(CH_3)_2BC_2H_4B(CH_3)_2$ in 24 hours at room temperature; at 100° about 0.15 mmole was lost per day. Pyrolysis of the compound in a sealed tube at 100° for 5 days produced a non-volatile material, a volatile liquid condensable at −80°, and trimethylboron. In the process of separating these products further quantities of volatile and non-volatile liquids were formed, a white solid was deposited and more trimethylboron was generated. The total amount of trimethylboron obtained corresponded to almost *all* of the methyl groups of the sample which had been pyrolyzed.

The rate of decomposition of the tetramethyl derivative seems to be greatly affected by impurities. Thus, a sample which had stood for a week without appreciable decomposition at room temperature began to generate trimethylboron immediately when brought into contact with the solid pyrolysis product mentioned in the preceding paragraph. Another sample, which had been prepared in a reaction vessel in which some decomposition of a previous preparation had occurred,[4] began to generate trimethylboron as soon as its temperature had risen to between −10 and 0°. In this case the decomposition seemed to cease when only 75% instead of 100% of the methyl groups of the initial $(CH_3)_2BC_2H_4{\cdot}B(CH_3)_2$ was converted to trimethylboron.

Both in the pyrolysis at 100° in which all the methyl groups of the tetramethyl derivative were transformed to trimethylboron and in the "catalyzed" decomposition at −10 to 0° in which only 75% was so transformed, the other decomposition products were of two kinds: (1) a small amount of moderately volatile liquid material having a vapor density corresponding to a molecular weight of between 105 and 110, and (2) considerably larger amounts of glassy material which slowly lost traces of trimethylboron and solidified. Hence the decomposition seems to follow two courses. One of these appears to lead to polymerized material which may consist of chains of units such as



$$\underset{CH_3}{-B}-C_2H_4-\underset{CH_3}{B}- \text{ or}$$

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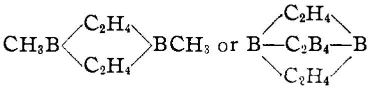
[1] The work herein reported was carried out under Contract N6ori-20, Task Order X (NR 052, 255) between the Office of Naval Research and the University of Chicago.

[2] (a) Grant Urry, Thomas Wartik, R. E. Moore and H. I. Schlesinger, THIS JOURNAL, **76**, 5293 (1954); (b) Thomas Wartik, R. E. Moore and H. I. Schlesinger, *ibid.*, **71**, 3265 (1949).

[3] We are deferring assignment of names to the compound and to its methoxy and methyl derivatives until a committee now considering nomenclature of boron compounds has reached a final decision.

[4] The preparation in which some decomposition had occurred was one carried out in the absence of solvents.

The other course appears to lead to the formation of fairly stable, somewhat volatile liquids. As indicated by their molecular weights, these liquids might be compounds having formulas[5] such as



the former corresponding to a 75%, the latter to a 100% loss of the methyl groups of the $(CH_3)_2BC_2H_4B(CH_3)_2$. Experiments designed to elucidate the structure of the several decomposition products are under way.

Experiments to ascertain whether the chlorine atoms of $Cl_2BC_2H_4BCl_2$ can be replaced by hydrogen atoms should be mentioned. Both diborane and lithium borohydride have been used as hydrogenating agents. Although there is evidence that hydrogenation occurs, the products thus far obtained have been unstable and difficult to purify.

Acetylene and cyclopropane react with diboron tetrachloride much as does ethylene. The reaction with acetylene may be carried out at −80°. In the case of cyclopropane interaction does not occur appreciably at that temperature; it is still very slow at −30° but occurs at a reasonable rate at 0°. At the last named temperature there is sufficient decomposition of diboron tetrachloride itself to prevent a clear cut stoichiometry of the reaction.

Although the products of the reactions with acetylene and with cyclopropane have not yet been fully characterized, preliminary data on the stoichiometry, the molecular weights and analyses of the major products formed leave little doubt that in each case the hydrocarbon in question reacted in a 1:1 molar ratio with diboron tetrachloride. In the acetylene reaction there is some, though as yet not conclusive evidence that a small amount of a product containing more than 1 mole of the diboron tetrachloride per mole of the hydrocarbon was obtained at the temperature used. Details of the hydrogenation reaction and of the reactions of diboron tetrachloride with cyclopropane and with acetylene will be reported in later papers.

In spite of the fact that the study of the reactions of diboron tetrachloride with hydrocarbons other than ethylene is still in its early stages, we have reported some of the results herein to call attention to the probable usefulness of the reagent for the synthesis of organo-boron compounds. We expect to define that usefulness more precisely, as well as to determine its limitations by extending our investigation to include other hydrocarbons and their derivatives.

Experimental

Materials and Apparatus.—Diboron tetrachloride was prepared as described by Urry, Wartik, Moore and Schlesinger.[2] Ethylene was the technical grade (Mathieson), purified by passage through a −160° trap into one at −196°. The product had a vapor tension of 453 mm. at −111.9° (accepted value 455 mm.). Dimethylzinc and trimethylboron were prepared by standard procedures; the former had a 0° vapor tension of 124 mm. (literature values vary from 123.6 to 125 mm.), the latter 31 mm. at −80° (accepted value 32 mm.). Absolute methanol was redistilled from sodium.

All reactions were carried out in the absence of air and moisture, for which purpose we used standard vacuum lines having two manifolds, one equipped with mercury float valves and the other with stopcocks.

Preparation and Properties of $Cl_2BC_2H_4BCl_2$.—In a typical preparation, a mixture of 6.6 mmoles of diboron tetrachloride and 10.36 mmoles of ethylene (both measured as gases) was allowed to react for 4 hours at −80°. To overcome the effect of occlusion of unchanged reactants by the solid product, the mixture was warmed to room temperature and was distilled into another part of the line. The condensate was then returned to the reaction vessel, and allowed to react further at −80° overnight. The product was fractionated in a train of traps at −45, −111.9 and −196°. The amounts of unchanged reactants collected in the latter two traps showed that 6.17 mmoles of the tetrachloride had reacted with 6.22 mmoles of ethylene. The yield was thus about 95%. In other experiments in which the removal of the reaction mixture from the reaction vessel and its return thereto was repeated several times, yields approaching 100% were obtained.

The compound $Cl_2BC_2H_4BCl_2$ is a liquid at ordinary temperature which fumes in air but is not spontaneously inflammable. The solid form melts at −28.5°. The pressure exerted by the vapor of a 0.0996-g. sample at 123.2° in a volume of 245.1 cc. was 54.15 mm., corresponding to a molecular weight of 185.5 (calcd. for $Cl_2BC_2H_4BCl_2$, 191.3). The vapor tensions of the liquid are recorded in Table I.

TABLE I

VAPOR TENSIONS OF $Cl_2BC_2H_4BC_2$

t, °C.	p, mm.		t, °C.	p, mm.	
	Calcd.	Found		Calcd.	Found
26.3	6.6	6.9	59.4	35.9	36.8
35.3	10.9	11.2	69.5	56.5	56.9
41.6	15.1	15.4	74.5	70.0	69.7
48.4	21.0	21.4	82.5	97.4	95.6
54.8	29.0	29.1	91.8	135.2	134.1

As seen from the calculated vapor tensions, the data are reproduced by the equation $\log p = 8.230 - (2220/T)$. The extrapolated boiling point is 142°, the heat of evaporation 10,140 cal./mole, and the Trouton constant 24.4.

For further confirmation of the formula, 1.46 mmoles of the compound was treated with a slight deficiency[6] of

TABLE II[a]

VAPOR TENSIONS OF THE COMPOUND $(CH_3O)_2BC_2H_4B(OCH_3)_2$

t, °C.	p, mm.		t, °C.	p, mm.	
	Calcd.	Found		Calcd.	Found
28.3	1.4	1.4	59.2	9.3	9.7
33.2	2.0	1.9	69.2	15.9	16.5
38.2	2.8	2.6	75.7	22.2	22.5
44.1	4.1	4.0	78.5	26.6	25.8
48.9	5.2	5.3	91.6	48.2	44.5
54.0	6.9	7.1	93.3	51.4	50.2
56.8	8.2	7.9			

[a] Because of the difficulty of removing all traces of methanol or hydrogen chloride, both of which would presumably raise the vapor tensions, measurements made with both rising and falling temperatures and with different gas volumes are included in the data of the table. The values for the heat of evaporation and of the Trouton constant (as calculated from the extrapolated boiling point, 164°), namely, 12,000 cal./mole and 27.6, respectively, are unusually large in spite of the precautions taken to ensure a pure sample.

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(5) It is possible that in the experiments in which only 75% of the methyl groups of the tetramethyl derivative were lost as trimethylboron, a part of the tetramethyl derivative had lost all of its methyl groups to give the volatile liquid and that the remainder had lost less than 75% in the incompleted process of forming the polymeric material. The fact that a 75% loss has occurred in several experiments makes this interpretation unlikely, but the possibility is nevertheless being explored.

(6) A deficiency of methanol was employed to avoid the tedious separation of methanol from the hydrogen chloride, which would have been necessary to determine both the methanol consumed and the hydrogen chloride evolved.

methanol (5.71 moles instead of the 5.84 mmoles required for replacement of all of the chlorine). The amount of hydrogen chloride generated was 99.8% of the theoretical. A 0.1003-g. sample of the liquid product obtained exerted a pressure of 58.0 mm. when volatilized in a 243.5-cc. volume at 108.8°, corresponding to a molecular weight of 169 (calcd. for $(CH_3O)_4B_2C_2H_4$, 173.6). The melting point of the solidified material was $-21.4 \pm 0.6°$, and the vapor tensions are reproduced by the equation $\log p = 8.933 - (2647/T)$, as shown in Table II.

Preparation and Physical Properties of the Compound $(CH_3)_2BC_2H_4B(CH_3)_2$.—Since there were no significant differences in preparations carried out in trimethylboron or in *n*-pentane as solvents, one typical reaction in the latter is described. A mixture of 11.02 mmoles of dimethylzinc and 5.55 mmoles of $Cl_2BC_2H_4BCl_2$ was allowed to warm to −45° and to react for 2 hours at that temperature and for an additional 2 hours at −23°. No trimethylboron was produced. Purification of the product was effected by distillation through a train consisting of −45, −63, −80 and −196° traps. The major portion of the desired product was retained at −63°, but a smaller portion, which had collected in the −80° trap, had the same vapor tension. The yield, 4.91 mmoles, was about 88% of the theoretical.

For analysis, the nitric oxide catalyzed combustion with oxygen[7] was employed. Two analyses, only the second one of which included a hydrogen determination, were carried out with samples weighing 41.6 and 24.5 g., respectively.

Anal. Calcd. for $(CH_3)_2BC_2H_4B(CH_3)_2$: B, 19.70; C, 65.61; H, 14.69. Found: B, 19.98, 19.92; C, 65.9, 66.1; H, 14.25. Vapor tensions are recorded in Table III.

TABLE III

VAPOR TENSIONS OF THE COMPOUND $(CH_3)_2BC_2H_4B(CH_3)_2$

t, °C.	−23	0.0	5.1	15.7	23.7
p (obsd.), mm.	2.8	12	16.0	29.0	41.5
p (calcd.), mm.	2.8	11.9	15.8	27.9	41.7

The calculated values were obtained by the equation: $\log p = 7.916 - (1869/T)$, according to which the extrapolated boiling point is 98°, the heat of evaporation 8540 cal./mole, and the Trouton constant 23.0. Two melting point determinations gave values of −114.8 and −115.0°, respectively. The data for two vapor density determinations were as follows: weight samples, 41.6 and 53.1 mg.; pressures 11.5 and 15.5 mm.; volumes 618.1 and 572.8 cc.; temperatures 27.5 and 25.4°, respectively. The corresponding molecular weights are 109.7 and 110.9 (calculated for $(CH_3)_2BC_2H_4B(CH_3)_2$, 109.6).

At the time these measurements were made it was not certain whether the correct formula of the compound under discussion is $(CH_3)_2BC_2H_4B(CH_3)_2$ or $(CH_3)B(C_2H_4)_2B(CH_3)$. Neither molecular weight determinations nor analysis can distinguish reliably between the two. For this purpose a 0.518 mmole sample of the compound was treated with 3.51 mmoles of perbenzoic acid in ether solution. The resulting methanol and ether were separated by fractionation from the water used to hydrolyze the esters formed in the reaction; remaining traces of moisture were removed from the ether–methanol mixture by calcium oxide. Lithium hydride was then added to the dried solution; the hydrogen evolved was taken as a measure of the methanol content of the mixture.[8] The quantity of methanol so obtained (1.67 mmoles) was only 80% of that required for a compound of the formula $[(CH_3)_2B]_2C_2H_4$, but was over 60% greater than could possibly have been formed from a compound of the formula $(CH_3B)_2(C_2H_4)_2$. In view of the other evidence now available, these facts were considered adequate to exclude the latter formula.[9]

Decomposition of $(CH_3)_2BC_2H_4B(CH_3)_2$.—The statement in the introduction that the unstable sample of $(CH_3)_2BC_2H_4B(CH_3)_2$ readily lost 75% of its methyl groups was based on the following observations. The sample was prepared at −30° from 3.91 mmoles of $Cl_2BC_2H_4BCl_2$ by use of an equivalent amount of dimethylzinc in trimethylboron as diluent. By the fractionation described in the preceding section, all of the trimethylboron was recovered. When the product collected in the −63° trap was warmed to between −10 and 0°, 3.8 mmoles of trimethylboron, or one mole per mole of the tetramethyl derivative, was evolved fairly rapidly. In addition to the trimethylboron, a liquid of vapor tension between 5 and 10 mm. at 0° and a viscous liquid which gradually solidified were obtained.

For the pyrolysis, 3.026 mmoles of the tetramethyl derivative was heated at 100° in a sealed tube for 5 days. The reaction product consisted of 3.44 mmoles of trimethylboron together with volatile and non-volatile liquids. When the volatile liquid, after separation from the non-volatile one and from trimethylboron, was warmed to room temperature it immediately began to decompose and ultimately generated 0.58 mmole of trimethylboron, bringing the total amount of that substance obtained to 4.02 mmoles or almost exactly 4/3 of the number of mmoles of $(CH_3)BC_2H_4B(CH_3)_2$ used. It should be added that in the decomposition of the liquid, which yielded the 0.58 mmole of trimethylboron, additional amounts of slightly volatile and non-volatile liquids, as well as a white solid were obtained. These products are still to be investigated.

For the decomposition initiated by bringing a very pure, stable sample of the tetramethyl derivative into contact with solid just mentioned, 4.24 mmoles of the former was used. The fairly rapid reaction which resulted generated 4.89 moles of trimethylboron, *i.e.*, an amount containing 86.5% of the methyl groups originally present. That this percentage lies between the 75% obtained from the sample which began to decompose at −10° and the 100% obtained by pyrolysis may be due to the fact that the decomposition which led to the 86% loss occurred at an intermediate temperature, *i.e.*, at about 25°.

Reaction of $(CH_3)_2BC_2H_4B(CH_3)_2$ with Trimethylamine.—A 7.01-mmoles sample of the tetramethyl derivative was treated with 16.92 mmoles of trimethylamine for two hours at room temperature. After removal of unchanged amine (3.68 mmoles), only a white, slightly volatile crystalline solid was left. The trimethylamine to tetramethyl derivative ratio is thus 1.89/1.00 instead of the expected 2/1. The crystals reacted with 13.39 mmoles of hydrogen chloride to regenerate 6.37 mmoles of the tetramethyl derivative (a 90% recovery) and to form small quantities of trimethylboron and of an unidentified volatile substance.

Acknowledgment.—We gratefully acknowledge the financial support of the Office of Naval Research which made this investigation possible, as well as the continued interest of that organization in the work.

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[7] Herbert C. Brown, H. I. Schlesinger and Anton B. Burg, THIS JOURNAL, **61**, 673 (1939).

[8] The reliability of the method was checked by applying it to a sample of pure trimethylboron, by which procedure 94% of the expected methanol was obtained.

[9] The low recovery of methanol was probably due to the fact that not enough perbenzoic acid was used to oxidize both the carbon-to-boron and the carbon-to-carbon bonds. It should be mentioned that no ethylene glycol was observed, but that may have been due to its low volatility which makes its isolation difficult by the procedure used.