Anal. Calcd. for $C_{54}H_{56}B_{10}N_2P_4$ (965.1): C, 67.20; H, 5.85; B, 11.21; N, 2.90; P, 12.84. Found: C, 66.70; H, 5.96; B, 11.78; N, 3.08; P, 12.10.

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CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO, CHICAGO, ILLINOIS,
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The Chemistry of the Boron Subhalides. I. Some Properties of Tetraboron Tetrachloride, B_4Cl_4[1]

BY GRANT URRY,[2] ALFRED G. GARRETT, AND H. I. SCHLESINGER

Received August 18, 1962

The characterization of tetraboron tetrachloride is described along with some of the physical properties of this compound. Some of its chemical properties are compared with those of diboron tetrachloride. Like B_2Cl_4, tetraboron tetrachloride reacts violently with dry air, emitting light and forming boron trichloride and white solids in the process. In reactions with methylating agents such as dimethylzinc, $B_4Cl_3CH_3$ is the main product. In reactions with water or methanol, B_4Cl_4 evolves 3 moles of H_2 and 4 moles of hydrogen chloride in the hydrolysis and 4 moles of methyl chloride in the methanolysis. Tetraboron tetrachloride appears to react with dimethylamine in a fashion similar to that of diboron tetrachloride since a product, tentatively identified as $B_4[N(CH_3)_2]_4$, is formed with no evolution of hydrogen. Diethyl ether solutions of B_4Cl_4 slowly evolve ethyl chloride. Tetraboron tetrachloride, unlike B_2Cl_4, does not react with ethylene or phosphorus trichloride.

Introduction

The reduction of boron trichloride in a high voltage a.c. mercury arc results in a series of subchlorides.[3–5] The present paper will describe some of the properties of tetraboron tetrachloride, which is produced in the arc reduction in minute quantities.[6] Tetraboron tetrachloride is a clear pale yellow crystalline solid slightly volatile at room temperature *in vacuo.*

The structure of tetraboron tetrachloride has been determined by Atoji and Lipscomb,[7] using X-ray diffraction techniques. The structure consists of a tetrahedral cage of boron atoms each with a terminal chlorine attached.

The infrared absorption spectrum of B_4Cl_4 in the vapor phase at low pressure is shown in Fig. 1. The intense band centered at 1010 cm.$^{-1}$ is apparently a characteristic absorption of boron cages.[8–10]

Results and Discussion

In spite of the limitations imposed by the small amounts of tetraboron tetrachloride available to us, it has been possible to obtain several analyses, to fix the molecular weight by vapor density, to determine vapor tensions at several temperatures, and to study with a fair degree of thoroughness a number of chemical reactions.

From a study of the chemical properties of tetraboron tetrachloride it is evident that the nature of bonding in this subchloride is quite different from that in diboron tetrachloride. Both of these compounds ignite spontaneously in dry air. The reaction of B_4Cl_4 is more vigorous than that of B_2Cl_4 and the inflammability of the latter may be promoted by small unavoidable traces of the former. Diboron tetrachloride disproportionates slowly even at 0° *in vacuo*, while tetraboron tetrachloride is stable to temperatures as high as 70°. Hydrogen gas reacts rapidly with B_2Cl_4 at temperatures considerably below 0° to give a mixture of boron trichloride and diborane, while B_4Cl_4 is essentially unreactive toward hydrogen at room temperature. Even at temperatures as high as 70° hydrogen gas reacts very slowly with B_4Cl_4 to produce traces of hydrogen chloride. After 18 hr. at this temperature approximately 95% of the B_4Cl_4 is recovered unchanged.

Treatment of diboron tetrachloride with methylating agents such as dimethylzinc results in a vigorous reaction accompanied by the formation of trimethylborane and black solids containing boron. The reactions of B_4Cl_4 with similar reagents are moderate and result in the formation of $B_4Cl_3CH_3$ along with a small

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[1] A portion of the work herein reported partially fulfilled the requirements for the Doctor of Philosophy degree of G. Urry at the University of Chicago, 1953.

[2] To whom inquiries concerning this publication should be addressed at the Department of Chemistry, Purdue University, Lafayette, Indiana.

[3] T. Wartik, R. Moore, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **71**, 3265 (1949).

[4] G. Urry, T. Wartik, and H. I. Schlesinger, *ibid.*, **74**, 5809 (1952).

[5] G. Urry, T. Wartik, R. Moore, and H. I. Schlesinger, *ibid.*, **76**, 5293 (1954).

[6] B_4Cl_4 also is produced in the disproportionation of diboron tetrachloride at 0° and higher temperatures along with BCl_3 and a red subchloride, $B_{12}Cl_{11}$, which will be the subject of a later paper in this series. A yellow subchloride, less volatile than B_4Cl_4 but more volatile than $B_{12}Cl_{11}$, a slightly less volatile dark purple solid, and a non-volatile white subchloride also are produced in this disproportionation.

[7] M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, **21**, 172 (1953); *Acta Cryst.*, **6**, 547 (1953).

[8] M. F. Hawthorne and A. R. Pitochelli, *J. Am. Chem. Soc.*, **82**, 3228 (1960).

[9] E. L. Muetterties, R. E. Merrifield, H. C. Miller, W. H. Knoth, and J. R. Downing, *J. Am. Chem. Soc.*, **84**, 2506 (1962).

[10] G. Urry, E. P. Schram, and S. I. Weissman, *ibid.*, **84**, 2654 (1962).

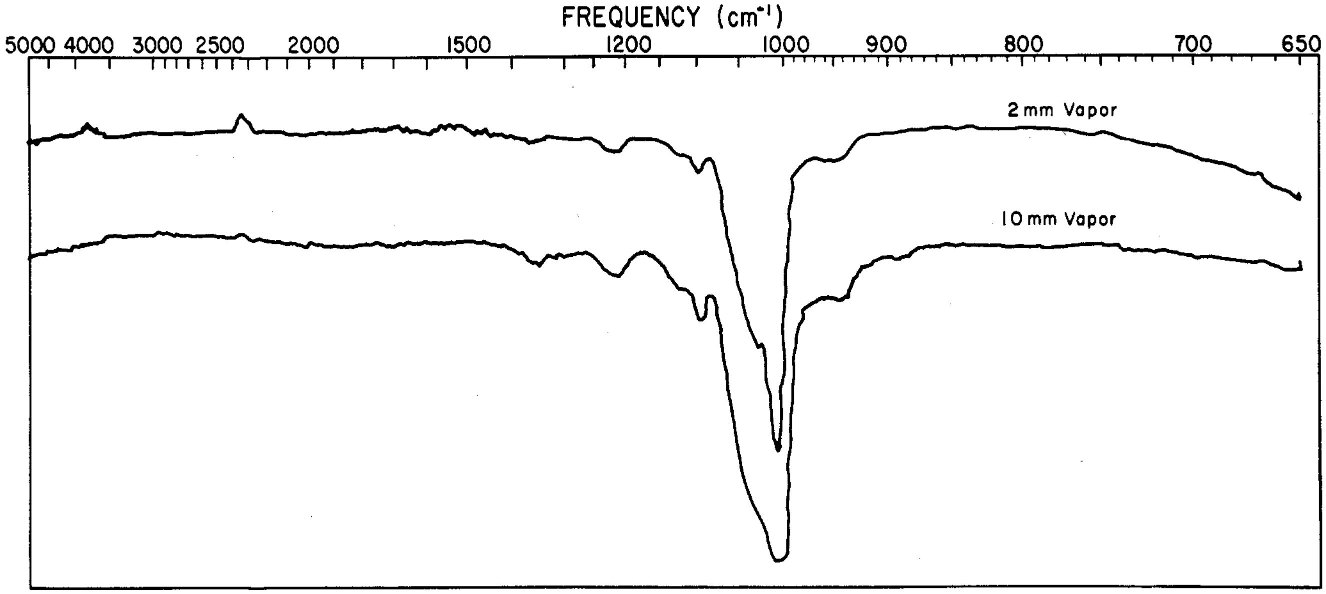


Fig. 1. —Infrared spectrum of B_4Cl_4 vapor.

trace of material more volatile than $B_4Cl_3CH_3$ which is difficult to separate from the excess methylating agent and decomposes slowly to produce red solids and trimethylborane.

Diboron tetrachloride reacts with methanol according to the equation

$$4CH_3OH + B_2Cl_4 \longrightarrow 4HCl + B_2(OCH_3)_4 \qquad (1)$$

The reaction of B_4Cl_4 occurs in a fashion represented by the equation

$$6CH_3OH + B_4Cl_4 \longrightarrow 3H_2 + 4CH_3Cl + \underset{\text{I}}{[B_4O_4(OCH_3)_2]_n} \qquad (2)$$

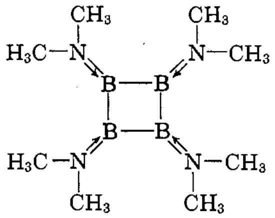
Treatment of I with aqueous alkali generates an additional mole of H_2. There is presently no evidence to indicate the homogeneity of I. It is likely a mixture.

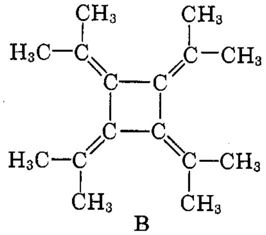
Although the reactions of diboron tetrachloride and tetraboron tetrachloride with water are superficially similar in that both hydrolyses liberate 4 moles of hydrogen chloride per mole of boron chloride, the two reactions are fundamentally different. The reaction of diboron tetrachloride produces no hydrogen, while that of tetraboron tetrachloride produces 3 moles of H_2 per mole of boron chloride. The reactions of methanol and of water with B_4Cl_4 are thus analogous.

There is a similarity in the reactions of these two subchlorides with dimethylamine. The reaction with diboron tetrachloride proceeds according to the equation

$$8(CH_3)_2NH + B_2Cl_4 \longrightarrow 4(CH_3)_2NH_2Cl + B_2[N(CH_3)_2]_4 \qquad (3)$$

A more complicated reaction occurs in the case of B_4Cl_4 but it is similar to the reaction just described in that no measurable amount of hydrogen is evolved. A product of this reaction tentatively identified as $B_4[N(CH_3)_2]_4$ exhibits an infrared absorption spectrum which does not have a typical boron cage absorption. It is possible that in this case the dimethylamine substituent with the enhanced π-bonding capabilities of the "non-bonding" electron pair on the nitrogen reduces the necessity of boron to form the three center bonds typical of cage structures. The structure is possibly a planar four-membered ring (A). Such a ring compound would be an isostere of an unknown carbon compound with unusual conjugation (B).


A


B

With diborane, diboron tetrachloride and tetraboron tetrachloride apparently undergo a similar reaction. Both reactions are complicated and appear to involve an initial addition of 1 mole of diborane per mole of boron subchloride, followed by a decomposition of this addition compound into boron trichloride and higher boron hydrides

The evidence for the addition compound $B_4Cl_4 \cdot B_2H_6$ is discussed in the Experimental part.

Both B_2Cl_4 and B_4Cl_4 form complexes with diethyl ether. In the case of the diboron compound the crystalline complex, $B_2Cl_4 \cdot 2[O(C_2H_5)_2]$, is stable in the presence of excess ether. Removal of ether from this mixture *in vacuo* produces the monoetherate, which decomposes slowly at room temperature producing ethyl chloride and boron suboxide. An ether solution of B_4Cl_4 slowly evolves ethyl chloride at room temperature.

Diboron tetrachloride reacts readily with most olefins at temperatures as low as $-79°$[11,12] but B_4Cl_4 does not

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[11] G. Urry, J. V. Kerrigan, T. D. Parsons, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **76**, 5299 (1954).

[12] P. Ceron, A. Finch, J. Frey, J. Kerrigan, T. Parsons, G. Urry, and H. I. Schlesinger, *ibid.*, **81**, 6368 (1959).

react with ethylene at any temperature below its decomposition temperature, 70°, and above that temperature no organoboranes were found among the products of decomposition.

Diboron tetrachloride forms a complex with phosphorus trichloride, $B_2Cl_4{\cdot}2PCl_3$, the nature of which will be discussed in paper II of this series. Treatment of B_4Cl_4 with a large amount of PCl_3 resulted in a pale golden solution from which both constituents could be recovered quantitatively.

Experimental

Apparatus and Experimental Methods.—Unless otherwise stated all the reactions described in the present series of papers were carried out in the absence of air and moisture inside a standard glass vacuum apparatus similar to that previously described in the literature.[13]

Transfer weighing of materials volatile only at elevated temperatures were effected in apparatus using O-ring joints sealed with Viton A O-rings.

Special techniques will be described as necessary throughout the series.

Analytical Methods.—Except where otherwise noted standard analytical techniques for boron, chlorine, carbon, hydrogen, and nitrogen were employed. Measurements of hydrogen and volatile materials were made in calibrated volumes of the vacuum apparatus and are expressed as volumes corrected to standard conditions.

Reagents.—**Hydrogen** in small amounts was conveniently prepared by the thermal decomposition of lithium aluminum hydride in the vacuum line.[14] This method produces hydrogen of high purity. **Methyl alcohol** was purified by treatment with sodium metal followed by distillation. **Dimethylzinc** was prepared by the reaction between methylmagnesium iodide and zinc chloride in ether. Fractional distillation yields dimethylzinc of good purity (boiling point 46°).[15] **Diborane** was obtained by treatment of lithium borohydride with diethyl ether–boron trifluoride. The material thus obtained had a vapor tension of 225 mm. at −119°.[16] **Dimethylamine**, anhydrous, was obtained from Distillation Products Industries, Rochester, N. Y. It was further purified by repeated distillations through a trap maintained at −79° into one maintained at −95° until the material retained at −95° exhibited a 0° vapor tension of 565 mm. **Diethyl ether** was dried and purified by stirring for several hours in contact with sodium hydride followed by vacuum distillation. **Tetraboron tetrachloride** was prepared and purified as previously described.[4]

Analysis of Tetraboron Tetrachloride.—A tube containing 0.0596 g. of tetraboron tetrachloride was broken beneath the surface of a dilute solution of sodium hydroxide contained in a silver dish. The mixture which resulted was evaporated to dryness and sulfuric acid was added to approximate neutrality. Thirty % hydrogen peroxide then was added, and the mixture was allowed to stand overnight. The excess peroxide was decomposed with platinum black. Boron was determined by titration of boric acid, and chlorine gravimetrically as the silver salt.

Anal. Calcd. for $(BCl)_x$: B, 23.4; Cl, 76.6. Found: B, 23.0; Cl, 75.0.

Physical Properties of Tetraboron Tetrachloride.—The vapor tensions of tetraboron tetrachloride were determined at several temperatures (Table I). The calculated values were obtained from the equation

$$\log p_{\mathrm{mm}} = -2719/T + 9.464 \qquad (4)$$

TABLE I

VAPOR TENSIONS OF B_4Cl_4

t, °C.	23.0	30.0	40.8	45.6	52.4	57.4	67.7
p_{mm}, obsd.	1.60	3.15	7.05	8.95	12.95	17.7	34.3
p_{mm}, calcd.	1.94	3.16	6.42	9.61	13.20	17.8	31.2

At temperatures above 70° the subchloride begins to decompose slowly into boron trichloride and unidentified yellow solids.

Molecular Weight of Tetraboron Tetrachloride.—A sample weighing 0.0683 g. was found to exert a pressure of 30.1 mm. at 70° in a volume of 253.1 cc. The corresponding vapor density at S.T.P. is 8.56 g./l., and the molecular weight is 191. A second sample weighing 0.0516 g. exerted a pressure of 17.9 mm. at 69° in a volume of 268 cc. The corresponding values of the vapor density and the molecular weight are 8.26 g./l. and 185, respectively. The value of the molecular weight obtained at the higher pressure is slightly greater than the one obtained at the lower pressure. This may be an indication of association in the vapor state. The small quantities employed and the low pressures necessitated by instability at higher temperatures did not allow measurement of sufficient precision to justify such a conclusion. The average (188) of the two molecular weight values satisfactorily established the molecular formula B_4Cl_4 (mol. wt. 185.1).

The Inflammability of the Subchlorides of Boron.—When diboron tetrachloride, from which tetraboron tetrachloride had been removed as completely as possible by repeated distillation through a −63° trap, was exposed to air it ignited and burned with a quiet green flame, depositing white solids in the process. When tetraboron tetrachloride was tested in a like manner, it burned with a brilliant incandescence. White solids were produced as in the case of diboron tetrachloride.

The Treatment of Tetraboron Tetrachloride with Hydrogen.—Pure tetraboron tetrachloride when allowed to stand in contact with hydrogen at room temperature or at 70° produces traces of hydrogen chloride, identified by its vapor tension (125 mm. at −111.9°).[17] Removal of the hydrogen chloride from the mixture followed by a repetition of the treatment with hydrogen results in additional traces of hydrogen chloride. A non-volatile white solid also is formed in minute quantities. Treatment of this solid with hydrogen chloride, after removal of all gaseous and volatile materials, failed to produce any hydrogen. The reaction is evidently not reversible. The total amount of the non-volatile solid was too small for identification.

Reaction of Tetraboron Tetrachloride with Dimethylzinc.—Tetraboron tetrachloride, weighing 0.0375 g. (0.2027 mmole), was allowed to stand for 0.5 hr. at room temperature with 9.08 cc. (0.4054 mmole) of dimethylzinc. At the end of this period a small amount of red precipitate, mentioned in the Introduction, was noted. The volatile liquids were distilled through traps maintained at −79, −119, and −196°.

The fraction collected in the −196° trap was identified as trimethylborane (vapor tension 32 mm. at −79°).[18]

The fraction retained by the −119° trap was not entirely pure since its vapor tension, originally almost identical with that of dimethylzinc, slowly increased during several hours at room temperature. Thereafter, refractionation of the material through a −119° trap to a −196° trap indicated that the rise was due to the formation of additional trimethylborane. The phenomenon needs further investigation.

The crystalline fraction retained at −79° had the appearance of tetraboron tetrachloride, but exhibited different vapor tensions, as shown in Table II, in which the second row records the observed values, and the third row values of the vapor tensions calculated from eq. 5 for these crystals. To point out

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(13) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, New York, N. Y., 1949.

(14) A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, *J. Am. Chem. Soc.*, **69**, 1199 (1947).

(15) H. W. Thompson and J. W. Linnett, *Trans. Faraday Soc.*, **32**, 681 (1936).

(16) H. C. Brown, H. I. Schlesinger, and A. B. Burg, *J. Am. Chem. Soc.*, **61**, 673 (1939).

(17) A. Stock, *Z. Elektrochem.*, **29**, 357 (1923).

(18) A. Stock and F. Zeidler, *Ber.*, **54B**, 531 (1921).

TABLE II

COMPARISON OF THE VAPOR TENSIONS OF B_4Cl_4 WITH ITS METHYLATION PRODUCT

t, °C.	45.10	50.10	55.40
p_{mm}, obsd.	5.10	8.05	12.10
p_{mm}, calcd.	5.36	7.71	12.30
p_{mm}, B_4Cl_4, calcd.	7.00	11.25	15.38

the difference between tetraboron tetrachloride and the new crystalline material, the vapor tensions of the former, as calculated from eq. 4, are reproduced in the fourth row of the table.

$$\log p_{mm} = -4176/T + 13.8017 \qquad (5)$$

That the product is probably a monomethyl derivative of tetraboron tetrachloride (*i.e.*, $CH_3B_4Cl_3$) is indicated by its vapor density and chlorine content. A sample weighing 0.0351 g. exerted a pressure of 17.45 mm. at 63.1° in a volume of 262 cc., corresponding to a molecular weight of 162 (theory 165), and contained 62% chlorine (theory 64.6%). Use of a large excess of dimethylzinc in the reaction by which the monomethyl derivative is formed did not appear to lead to further methylation.

The Reaction of Tetraboron Tetrachloride with Methanol.—A 0.0450-g. (0.243-mmole) sample of B_4Cl_4 was treated with 32.60 cc. (1.455 mmoles) of methanol vapor for 12 hr. at room temperature. At the end of this period 16.7 cc. (0.745 mmole) of hydrogen had been generated. A volatile liquid which also was formed was shown to be methyl chloride by its −97.5° melting point (CH_3Cl m.p., −97.7°), and had a gas volume of 21.6 cc. (0.964 mmole). No other volatile material was obtained. The white non-volatile solid remaining in the reaction tube generated 5.25 ml. or 0.234 mmole of hydrogen when treated with aqueous potassium hydroxide. The molar ratios to which these data correspond are recorded in Table III. They have been discussed in the Introduction.

TABLE III

MOLAR QUANTITIES OF REACTANTS AND REACTION PRODUCTS PER MOLE OF B_4Cl_4

	ROH[a]	Initial H_2	H_2 alkaline hyd.	RCl[a]
Methanol reaction	5.99	3.06	0.982	3.96
Water reaction	5.75	2.98	1.01	3.92

[a] For the alcohol reaction R = CH_3, for the water reaction R = H.

When a larger relative amount of methanol was used in the reaction, the same amount of hydrogen was produced per mole of B_4Cl_4. In this case the fractionation of the mixture is complicated by the excess of methanol and only qualitative separation of its components was achieved. Methyl chloride again is obtained, and in addition the presence of methyl borate was demonstrated by isolation of its methanol azeotrope, identified by its apparent vapor density and boron analysis.

Reaction of Tetraboron Tetrachloride with Water.—Tetraboron tetrachloride weighing 0.0233 g. (0.126 mmole) was treated with 16.25 cc. (0.725 mmole) of water vapor.[1] After 12 hr. at room temperature 8.42 cc. (0.375 mmole) of hydrogen had been generated. The only other volatile material was 11.05 cc. (0.494 mmole) of hydrogen chloride, identified by its vapor tension of 125 mm. at −111.9°.[16] The non-volatile, solid residue generated 2.84 cc. (0.127 mmole) of hydrogen on treatment with aqueous potassium hydroxide.

It will be seen from the ratios recorded in Table III for this reaction that the behavior of tetraboron tetrachloride toward water is entirely analogous to its behavior toward methanol.

The Reaction between Tetraboron Tetrachloride and Diborane.—A 0.0371-g. (0.200-mmole) sample of the subchloride and 8.88 cc. (0.397 mmole) of diborane were heated together in a closed tube at 55° for a period of 48 hr. At the end of this time all of the tetraboron tetrachloride had disappeared, and a yellow solid coated the tube. The volatile products of the reaction were distilled twice through a trap maintained at −126° into one at −196°. The material retained at −126° was boron trichloride, identified by its 0° vapor tension of 477 mm., of which 2.32 cc. (0.104 mmole) was obtained. The −196° trap was found to contain 5.03 cc. (0.225 mmole) of diborane, identified by its −119° vapor tension of 225 mm. No other volatile materials were obtained. Hence for 0.172 mmole of diborane consumed in the reaction 0.104 mmole of boron trichloride was produced.

If it is assumed that the yellow non-volatile material contains a substance with a composition corresponding to the formula $(BH)_x$[19] and that it is the only product formed in the reaction by which boron trichloride is produced, it is possible to make an estimate of the composition of the other non-volatile material. The results of such a calculation may be recorded by the equations

$$0.078B_4Cl_4 + 0.052B_2H_6 \longrightarrow (0.212/x)(BH)_x + 0.104BCl_3 \qquad (6)$$

$$0.120B_4Cl_4 + 0.120B_2H_6 \longrightarrow 0.120B_6Cl_4H_6 \qquad (7)$$

$$\overline{0.198B_4Cl_4 + 0.172B_2H_6 \longrightarrow 0.212/x)(BH)_x + 0.104BCl_3 + 0.120B_6Cl_4H_6} \qquad (8)$$

The experimental data correspond to within 1% of the prefixes for the tetrachloride, the trichloride, and the diborane in eq. 8. Equations 6 and 7 may be rewritten as eq. 9 and 10 to express the prefixes as whole numbers.

$$3B_4Cl_4 + 2B_2H_6 \longrightarrow (12/x)(BH)_x + 4BCl_3 \qquad (9)$$

$$B_4Cl_4 + B_2H_6 \longrightarrow B_6Cl_4H_6 \qquad (10)$$

These equations must be considered as only tentative suggestions for the possible course of reaction, both because of the small amounts of reactants employed, and because of the unproved assumption that the solid contains a compound represented by the formula $(BH)_x$. The equations are presented nevertheless because they suggest that the reaction of diborane with tetraboron tetrachloride may possibly lead to the formation of an adduct of B_4Cl_4 with diborane which would be a tetrachloro derivative of the little known hexaborane, B_6H_{10}. Efforts will be made to ascertain if the solid residue of the reaction in question can be hydrogenated and whether hexaborane can thus be obtained.

Reaction of Tetraboron Tetrachloride with Dimethylamine.—In a single experiment a sample of B_4Cl_4 weighing 0.0384 g. (0.207 mmole) was treated with a large excess of dimethylamine (3.34 mmoles) over that required for the reaction

$$B_4Cl_4 + 8N(CH_3)_2H \longrightarrow B_4[N(CH_3)_2]_4 + 4(CH_3)_2NH_2Cl \qquad (11)$$

Upon warming the mixture of reactants from liquid nitrogen temperatures a reaction occurred at a low temperature near the melting point of dimethylamine. The reaction vessel was allowed to stand at room temperature for a period of approximately 2 hr. before being attached to the vacuum system. After this period the material in the reaction vessel volatile *in vacuo* at room temperature was removed and distilled through a series of U-tube traps maintained at −63, −79, and −196°.

The material retained at −196° was shown to be pure dimethylamine, 1.52 mmoles in quantity. Thus the maximum amount of amine consumed in the reaction was 1.82 mmoles, which corresponds to a 9% excess of that required by eq. 11. The material retained in the −79° trap appeared to be a mixture containing dimethylamine and a less volatile material similar to that retained in the −63° trap. This mixture was obtained in quantities too small to study extensively but the dimethylamine contained in the mixture could not be greater than the 0.17 mmole unaccounted for by eq. 11.

The amount of this material obtained was too small to de-

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[19] Yellow solids having this composition very frequently are encountered as decomposition products of boranes.

termine an accurate molecular weight from vapor density data but a rough value of 600 was obtained as an upper limit. The volatility of this material is similar to that reported for $B_2[N(CH_3)_2]_4$,[20] but from the small amount of data available it would appear to have a lower heat of vaporization. The infrared absorption spectrum is fairly complex and different from that of $B_2[N(CH_3)_2]_4$ but consistent with the presence of B–N and C–N bonds. The most interesting feature of the spectrum is the disappearance or major shift in frequency of the band at 1010 cm.$^{-1}$ attributed to the B_4 cage in the spectrum of the parent B_4Cl_4.

Reaction of Tetraboron Tetrachloride with Diethyl Ether.—A sample of B_4Cl_4 weighing 0.0736 g. (0.398 mmole) was dissolved in 3.17 mmoles of anhydrous diethyl ether. When the solution was warmed from −79° to room temperature a reaction occurred, as indicated by the formation of a red solid precipitate. After 1 hr. at room temperature the volatile materials were removed from the reaction mixture and found to be a mixture of unchanged diethyl ether and 0.48 mmole of ethyl chloride. When the red solid remaining in the reaction vessel was again treated with diethyl ether more ethyl chloride was formed. The separation of ethyl chloride and diethyl ether is difficult and estimates of the amount of ethyl chloride formed did not indicate any favored stoichiometry.

Acknowledgment.—We gratefully extend our sincere appreciation to the Office of Naval Research for the generous financial support of that portion of the research, herein reported, carried out at the University of Chicago. The work accomplished at Purdue University enjoyed similar invaluable financial support from the National Cancer Institute of the Public Health Service under Grant Number CY-4382 and for this we are grateful.

Finally, in a more personal vein, G. U. cannot forego the opportunity, here afforded, to express his gratitude and indebtedness to his professor and the senior author of this paper, Dr. Hermann Irving Schlesinger, now deceased, for the patient understanding with which he displayed for this neophyte the elegance and power of chemistry as an experimental science.

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Contribution from the Richard Benbridge Wetherill Laboratory,
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The Chemistry of the Boron Subhalides. II. Reactions of Diboron Tetrachloride with Compounds of Nitrogen and Phosphorus[1]

By ALFRED G. GARRETT and GRANT URRY[2]

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The results of the treatment of diboron tetrachloride with tetrafluorohydrazine, phosphorus trichloride, tetrachlorodiphosphine, and tetramethyldiphosphine are reported. With N_2F_4 a slow reaction occurs, forming nitrogen and a mixture of boron trichloride and boron trifluoride. With PCl_3 a complex, $B_2Cl_4 \cdot 2PCl_3$, is formed. No such complex is formed when diboron tetrachloride is treated with P_2Cl_4. With tetramethyldiphosphine B_2Cl_4 forms a complex, $B_2Cl_4 \cdot P_2(CH_3)_4$. Treatment of $B_2Cl_4 \cdot P_2(CH_3)_4$ with trimethylamine results in a new complex, $B_2Cl_4 \cdot P_2(CH_3)_4 \cdot N(CH_3)_3$. Pyrolysis of $B_2Cl_4 \cdot P_2(CH_3)_4$ produces a new substance which on the basis of its physical and chemical properties is tentatively identified as $[(CH_3)_2P \rightrightarrows B \leftleftarrows P(CH_3)_2]^+BCl_4^-$.

Introduction

Reactions of boron trichloride with various nitrogen compounds have been studied extensively. The formation of donor–acceptor addition compounds is the first result of most such reactions. In cases where protolytic hydrogens are present in the donor molecule, secondary reactions occur which lead either to substitution of amino moieties for chlorine or to more complex structures such as the borazenes.[3,4]

The extensive literature of boron nitrogen chemistry is already very well reviewed.[5–8]

Fewer reactions of boron trichloride with phosphorus compounds have been studied. Notable among these is the work of Gamble and Gilmont,[9] reporting the preparation of a boron trichloride–phosphine complex. A reported boron trichloride–phosphorus trichloride complex[10] was later shown to be a complex of boron trichloride with phosphorus oxychloride, $POCl_3$.[11]

Reactions of boron trichloride with alkylphosphines are reported to give stable adducts.[12] Another type of boron halide phosphorus compound results when the dimethylphosphinoborane trimer, $[(CH_3)_2PBH_2]_3$, is treated with methyl chloride–aluminum chloride mixtures to produce the analogous chlorinated trimer, $[(CH_3)_2PBCl_2]_3$.[13] A general review by Stone[14] of

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