(15 ml.) and triphenylethylphosphonium iodide (1.05 g., 0.0025 mole) in acetone (35 ml.) were mixed and refluxed for 0.5 hr., then evaporated to dryness *in vacuo*. The solid residue was thoroughly washed with water and, after drying, recrystallized from a mixture (3:1) of acetone and ethyl acetate to give pure VIII (1.28 g., 86%), m.p. 242°. It was soluble in acetone and acetonitrile.

Anal. Calcd. for $C_{32}H_{43}B_{10}P_2$ (596.8): C, 64.40; H, 7.09; B, 18.13; P, 10.38. Found: C, 64.28; H, 7.51; B, 18.20; P, 10.10.

(b) **From Diphenylchlorophosphoniumdiphenylphosphinodecaborane (XII).**—A solution of XII (1.32 g., 0.0025 mole) and triphenylethylphosphonium iodide (1.05 g., 0.0025 mole) in anhydrous acetone (90 ml.) was refluxed for 0.5 hr., then evaporated to dryness *in vacuo*. The solid residue was extracted with 45 ml. of hot chloroform; the undissolved product (0.91 g., 61%) was pure VIII, m.p. 242°. *Anal.* Found: P, 10.18. The infrared spectrum was identical with that of the above product.

Triethylammoniumbenzyldecaborane (IX).—A solution of ethylamine (0.5 g., 0.005 mole) in ether (10 ml.) was added slowly to a stirred solution of benzyldecaborane[5] (0.53 g., 0.0025 mole) in ether (20 ml.). The reaction product separated as a viscous liquid. Solidification was achieved by replacing the ether with petroleum ether (b.p. 30–40°) and rapid stirring of this mixture; yield of crude IX: 0.71 g. (91%); m.p. 94–95°. A sample was recrystallized from CCl_4, m.p. 95°.

Anal. Calcd. for $C_{13}H_{35}B_{10}N$ (313.6): C, 49.78; H, 11.25; B, 34.50; N, 4.47. Found: C, 49.48; H, 11.94; B, 34.20; N, 4.18.

Triphenylphosphoniumtriphenylphosphine Diphenylphosphinodecaborane (X).—A solution of triphenylphosphine (1.73 g., 0.006 mole) in ether (10 ml.) was added with stirring to a solution of diphenylphosphinodecaborane (IV, 1 g., 0.0033 mole) in ether (40 ml.). The reaction product started precipitating immediately, but the mixture was refluxed for 3 hr. Filtration gave 2.3 g. (92%) of product, m.p. 130–146°. Upon washing with a small amount of acetone, the m.p. was raised to 149–151°.

Anal. Calcd. for $C_{48}H_{53}B_{10}P_3$ (831.0): C, 69.37; H, 6.43; B, 13.02; P, 11.18. Found (washed product): C, 70.46; H, 6.75; B, 13.40; P, 11.10.

Diphenylphosphoniumdiphenylphosphinodecaborane (XI).—A solution of diphenylphosphine (1.23 g., 0.0066 mole) in benzene (10 ml.) was added with stirring to a solution of diphenylphosphinodecaborane (IV, 1 g., 0.0033 mole) in benzene (20 ml.); the system was kept under nitrogen. After 10 min., a precipitate started to form which dissolved upon heating. After refluxing for 3 hr. and standing for 12 hr. at room temperature, some insoluble product (m.p. < 300°) was removed by filtration and the filtrate was evaporated to dryness. The residue was recrystallized from CCl_4 to give 1 g. (61%) of XI, m.p. 114–117°.

Anal. Calcd. for $C_{24}H_{34}B_{10}P_2$ (492.7): C, 58.51; H, 6.96; P, 12.58. Found: C, 60.18; H, 6.99; P, 12.60.

Diphenylchlorophosphoniumdiphenylphosphinodecaborane (XII).—To a solution of diphenylphosphinodecaborane (IV, 1.22 g., 0.004 mole) in ether (45 ml.) was added at 20° a solution of diphenylchlorophosphine (1.76 g., 0.008 mole) in ether (25 ml.). Upon refluxing for 1 hr., a viscous oil separated which solidified after standing for 20 hr. at room temperature; yield of crude XII: 2 g. (95%), m.p. 173–177°; after washing with a small amount of acetone, m.p. 182–184°.

Anal. Calcd. for $C_{24}H_{33}B_{10}ClP_2$ (527.1): C, 54.67; H, 6.31; B, 20.53; Cl, 6.73; P, 11.75. Found: C, 54.54; H, 6.81; B, 19.60; Cl, 6.85; P, 11.60.

Acknowledgment.—This work was supported by the Office of Naval Research. The author is indebted to Dr. C. Naar-Colin for performing the B^{11} n.m.r. spectra and to Drs. T. L. Heying and S. I. Trotz for stimulating discussions.

CONTRIBUTION FROM THE ORGANICS DIVISION,
OLIN MATHIESON CHEMICAL CORPORATION, NEW HAVEN, CONNECTICUT

Chemistry of Decaborane–Phosphorus Compounds. III. Decaborane-14–Phosphine Polymers[1]

BY HANSJUERGEN SCHROEDER, JOSEPH R. REINER, AND THOMAS A. KNOWLES

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Under basic conditions $B_{10}H_{12}((C_6H_5)_2P\cdot Cl)_2$ and $B_{10}H_{12}((C_6H_5)_2P\cdot OH)_2$ were found to enter into a condensation polymerization with elimination of hydrogen chloride to form a P–O–P linked polymer, $(\text{-}OP(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2\text{-})_x$. A study of the pyrolysis of this polymer and monomeric compounds of the type $B_{10}H_{12}((C_6H_5)_2P\cdot R)_2$ was conducted. $B_{10}H_{12}((C_6H_5)_2\text{-}P\cdot N_3)_2$ and diphosphines reacted in refluxing benzene with evolution of nitrogen to give P=N—P linked polymers of high thermal stability, *e.g.*, $(=P(C_6H_5)_2—C_6H_4—P(C_6H_5)_2=N—P(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2N=)_x$, dec. >340°.

In the first paper of this series, the syntheses of bis-(chlorodiphenylphosphine)decaborane-14 (I) and various derivatives were described.[2] Interest in this class of compounds had been stimulated by the possibility that some members of this series might serve as starting materials for the preparation of unusual boron based polymers. The original impetus for the present work arose from an observation made during an attempt to prepare bis-(diethylaminodiphenylphosphine)-decaborane (II) by treating $B_{10}H_{12}((C_6H_5)_2P\cdot Cl)_2$ with triethylamine hoping to split out ethyl chloride and thus obtain $B_{10}H_{12}((C_6H_5)_2PN(C_2H_5)_2)_2$. Several experiments of this type using commercial benzene and technical grade triethylamine gave no indication of proceeding as desired.

$$B_{10}H_{12}((C_6H_5)_2PCl)_2 + 2(C_2H_5)_3N \longrightarrow B_{10}H_{12}((C_6H_5)_2PN(C_2H_5)_2)_2 + 2C_2H_5Cl$$

Instead, the bistriethylammonium salt of bis-(hydroxydiphenylphosphine)-decaborane, $B_{10}H_{12}((C_6H_5)_2P\cdot OH)_2\cdot 2(C_2H_5)_3N$ (III), and a very insoluble and high melting

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[1] Preceding communication: H. Schroeder, *Inorg. Chem.*, **2**, 390 (1963).

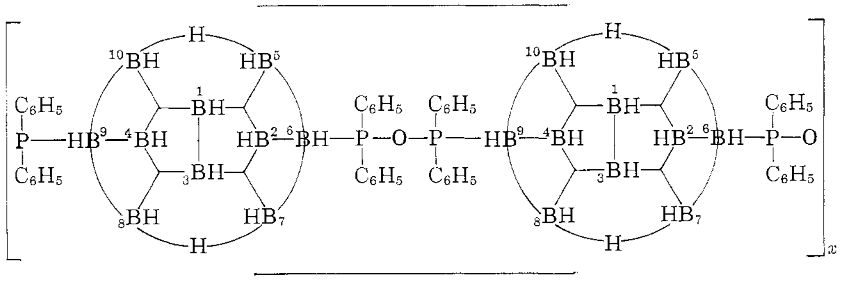
[2] H. Schroeder, J. R. Reiner, and T. L. Heying, *ibid.*, **1**, 618 (1962).

material were isolated in moderate yield. Elemental analysis of the latter product, which was chlorine and nitrogen free, was in agreement with the formula of apolymer, $OH{-}P(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2(-OP(C_6H_5)_2{-}B_{10}H_{12}P(C_6H_5)_2{-})_xOH$, which could be expected from a condensation polymerization between $B_{10}H_{12}((C_6H_5)_2{-}P\cdot Cl)_2$ and bis-(hydroxydiphenylphosphine)-decaborane (IV), a compound easily obtained by hydrolysis of I in organic solvents.[2] Since III was formed in this reaction, partial hydrolysis (probably from traces of water present) of I to IV must have occurred, thus establishing the conditions necessary for the formation of the polymer. This assumption prompted us to undertake a thorough study of the reaction of I with IV.

An initial attempt to react equimolar quantities of $B_{10}H_{12}((C_6H_5)_2P\cdot Cl)_2$ and $B_{10}H_{12}((C_6H_5)_2P\cdot OH)_2$ in refluxing benzene under strictly anhydrous conditions led to the quantitative recovery of the starting materials. Upon addition of two molar equivalents of dry triethylamine to such a mixture, however, the expected reaction occurred according to the following scheme, producing the same polymer obtained previously and in 87% yield.

$$\underset{\text{I}}{n\text{ClP}(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2Cl} + \underset{\text{IV}}{n\text{OHP}(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2OH} + 2n(C_2H_5)_3N \longrightarrow \underset{\text{V}}{(OP(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2)_{2n}} + 2n(C_2H_5)_3N\cdot HCl$$

The condensation polymer V is the first polymer described containing in its linear chain a number of decaborane nuclei which, in this special case, are linked together by P–O–P groups. It also is a fully inorganic polymer based upon the definition that it must not contain carbon atoms in its skeleton.[3]



Molecular weight determination by the light-scattering method in N-methylpyrrolidone gave a value of 27,000; the polymer's distinct infrared spectrum could be interpreted in accord with the above formula. When V was heated to 320°, no apparent change was observed, but when heated in a calibrated system under reduced pressure, hydrogen evolution was found to occur beginning at 270°. Continued heating to 350° resulted in the release of four moles of hydrogen per unit. It was now of interest to determine the source of this hydrogen, *i.e.*, whether it came from the decaborane nuclei or the phenyl rings. To this end, an investigation of the pyrolysis of $B_{10}H_{12}((C_6H_5)_2P\cdot OH)_2$ and similar monomeric compounds at 350° was undertaken. The gaseous decomposition products were identified by mass spectrometer analysis and the results are summarized in Table I.

TABLE I

THERMAL DECOMPOSITION OF SUBSTITUTED BIS-(DIPHENYLPHOSPHINE)-DECABORANE DERIVATIVES AT 350°

	Compounds	H_2, moles	N_2, moles	C_6H_6, moles	C_2H_6, moles
V	$(OP(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2)_x$	4		Trace	
IV	$B_{10}H_{12}((C_6H_5)_2P\cdot OH)_2$	4.9		Trace	
VII	$B_{10}H_{12}((C_6H_5)_2P\cdot OCH_2CH_2OH)_2$	3.9		Trace	Trace
VIII	$B_{10}H_{12}((C_6H_5)_2P\cdot N_3)_2$	4.4	2.1	0.04	
	$B_{10}H_{12}((C_6H_5)_2P\cdot NHNH_2)_2$[2]	4.1		Trace	
VI	$B_{10}H_{12}((C_6H_5)_2P\cdot N(CH_2CH_2))_2$	2.4		Trace	0.2

With the exception of bis-(aziridinodiphenylphosphine)-decaborane (VI),[2] all compounds investigated eliminated an average of four moles of hydrogen with only traces of benzene. Since in this group of compounds the phosphine portion of the molecule is variously substituted while the decaborane nucleus is constant, it is not conclusively proved but highly probable that the hydrogen evolution arises uniquely from the $B_{10}H_{12}$ units. Elemental analyses of the residues of IV, V, and VII support this assumption because they agree with the respective formulas less eight hydrogen atoms. In the event of dehydrogenation of the phenyl rings, a more extensive disruption of the molecule as a whole could be expected.

Whereas the initial approach of this investigation was concerned with the preparation of oxygen bridged bis-(diphenylphosphine)-decaborane polymers, attention subsequently was turned to the synthesis of nitrogen-linked polymers. In light of the recent success in the preparation of a linear polymer with the phosphonitrile bonding system from 1,4-diazidobenzene and a diphosphine,[4] the reaction of bis-(azidodiphenylphosphine)-decaborane (VIII)[2] with diphosphines appeared to be a promising synthetic scheme for the desired type of polymers. The question of whether $B_{10}H_{12}{-}((C_6H_5)_2P\cdot N_3)_2$ would split off two moles of nitrogen at elevated temperatures in the presence of phosphines to form phosphineimino compounds was verified by its reaction with two moles of triphenylphosphine in re-

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(3) J. S. Anderson, Intern. Symp. on Inorg. Polymers, Nottingham, 1961.

(4) D. L. Herring, *J. Org. Chem.*, **26**, 3998 (1961).

fluxing benzene, which resulted in the isolation of the expected bisphosphineimino compound IX.

$$B_{10}H_{12}((C_6H_5)_2P\cdot N_3)_2 + 2(C_6H_5)_3P \longrightarrow$$
$$\underset{\text{IX}}{(C_6H_5)_3P{=}N{-}P(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2{-}N{=}P(C_6H_5)_3}$$

Having established the fundamental reaction, it was extended to the use of diphosphines in the hope of preparing the derived P=N—P polymers.

1,2-Bis-(diphenylphosphino)-ethane[5] (X) and 1,4-bis-(diphenylphosphino)-benzene[4] (XI) were selected for our studies and each was found to react with an equimolar amount of $B_{10}H_{12}((C_6H_5)_2P\cdot N_3)_2$ according to the equation

$$\underset{\text{VIII}}{nN_3P(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2N_3} +$$
$$\underset{\text{X: R = CH}_2\text{CH}_2\text{; XI: R = C}_6\text{H}_4}{P(C_6H_5)_2{-}R{-}P(C_6H_5)_2} \longrightarrow$$
$$({=}P(C_6H_5)_2{-}R{-}P(C_6H_5)_2{=}N{-}P(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2{-}N{=})_n + 2nN_2$$
$$\text{XII: R = CH}_2\text{CH}_2\text{; XIII: R = C}_6\text{H}_4$$

Insolubility in common organic solvents and resistance to thermal decomposition are characteristics of the polymers XII and XIII. Herring[4] recently reported the preparation of the polymer $({=}P(C_6H_5)_2{-}C_6H_4{-}P(C_6H_5)_2{=}N{-}C_6H_4{-}N{=})_x$ (XIV), which softens over the range 150–200°. In comparison the polymer XIII, which can be considered as derived from XIV by substitution of the bis-(diphenylphosphine)-decaborane nucleus for the diimino substituted phenylene ring, starts to soften only above 340°, accompanied by the release of hydrogen.

Extension of this phase of chemistry to the use of differently substituted $\equiv PB_{10}H_{12}P\equiv$ units is hoped to provide polymers with a wider spectrum of physical properties, so that physicochemical investigations of these unique types will be possible.

Experimental[6]

Preparation of $(OP(C_6H_5)_2B_{10}H_{12}P(C_6H_5)_2)_x$ (V).—(a) A solution of 2.1 g. (0.02 mole) of triethylamine (dried over potassium hydroxide) in anhydrous benzene (50 ml.) was added, with stirring, to a suspension of bis-(chlorodiphenylphosphine)-decaborane (I, 5.6 g., 0.01 mole) and bis-(hyroxydiphenylphosphine)-decaborane (IV, 5.2 g., 0.01 mole) in anhydrous benzene (50 ml.) over a period of 20 min. After the addition was complete, the mixture was refluxed for 1 hr. and then filtered. The residue was washed first with acetone, then with water, and finally extracted with hot acetone to remove all by-products; yield of remaining pure V (m.p. > 300°): 4.4 g. (87%).

Anal. Calcd. for $C_{24}H_{32}B_{10}OP_2$ (506.7): C, 56.89; H, 6.37; B, 21.36; P, 12.23. Found: C, 56.64; H, 6.65; B, 20.80; P, 11.90. Major infrared absorption bands: Terminal B–H (st.), 4 μ; phenyl (P-bonded), 7 and 9 μ; P–O–P, 10.3 μ; phenyl absorptions, 13–15 μ.

(b) To a suspension of bis-(chlorodiphenylphosphine)-decaborane (I, 2.8 g., 0.005 mole) in benzene (100 ml.) was added, with stirring, technical grade triethylamine (1 g., 0.01 mole) dissolved in 20 ml. of benzene. The reaction mixture turned dark yellow and, after 15 min., was refluxed for 1 hr., then filtered. The precipitate thus obtained was washed with acetone, water, and finally with hot acetone; yield of V: 0.71 g. (28%).

Anal. Found: C, 56.60; H, 6.71; B, 20.89; P, 11.78.

Bis-(hydroxydiphenylphosphine)-decaborane Bistriethylammonium Salt.—III (0.6 g.) precipitated from the hot acetone extract upon cooling and was recrystallized from acetone; m.p. 202–204°.

Anal. Calcd. for $C_{36}H_{64}B_{10}O_2N_2P_2$ (727.0): C, 59.47; H, 8.87; B, 14.88; N, 4.40; P, 8.52. Found: C, 58.95; H, 9.00; B, 15.90; N, 4.19; P, 8.28.

Pyrolysis Experiments.—Weighed samples (0.001 to 0.003 mole) of the compounds listed in Table I were pyrolyzed under reduced pressure in a calibrated system (265 ml.) which permitted measurement of pressure changes. In a typical experiment, a sample tube containing 1.006 g. (0.002 mole) of V was attached to a vacuum manifold to which a gas sampling bulb also was connected. The entire apparatus was evacuated (10^{-4} mm.) and the temperature was raised at a rate of 2°/min. to 350° and held there for 0.5 hr. After cooling to room temperature, the volume at STP of the gaseous decomposition products was measured (179 ml.) and their identity determined by mass spectrometric analysis (99.9% hydrogen, traces of benzene). The solid residue was reweighed (0.998 g.) to give a 1.9% loss in weight (1.58% corresponds to the loss of eight hydrogens).

Anal. Calcd. for $C_{24}H_{24}B_{10}OP_2$ (formula of compound V less 8 hydrogens): C, 57.81; H, 4.85; B, 21.70; P, 12.43. Found: C, 57.92; H, 5.45; B, 20.20; P, 11.60.

Compound IV showed a weight loss of 1.8%.

Anal. Calcd. for $C_{24}H_{26}B_{10}O_2P_2$ (formula of compound IV less 8 hydrogens): C, 55.80; H, 5.07; B, 20.95; P, 12.00. Found: C, 54.71; H, 5.62; B, 21.56; P, 11.39.

Compound VII showed a weight loss of 1.322%.

Anal. Calcd. for $C_{28}H_{34}B_{10}O_4P_2$ (formula of compound VII less 8 hydrogens): C, 55.61; H, 5.67; B, 17.89; P, 10.25. Found: C, 54.76; H, 6.45; B, 17.87; P, 10.70.

Bis-(triphenylphosphineiminodiphenylphosphine)-decaborane (IX).—Solutions of bis-(azidodiphenylphosphine)-decaborane (VIII, 1.15 g., 0.002 mole) in benzene (20 ml.) and of triphenylphosphine (1.05 g., 0.004 mole) in benzene (10 ml.) were mixed and refluxed for 10 hr. There was no precipitate. After evaporation to dryness, the residue was thoroughly washed with ether to give 1.9 g. (91%) of crude IX, m.p. 121–125°. For purification a sample was dissolved in acetone and carefully reprecipitated with ether; m.p. 124–126°.

Anal. Calcd. for $C_{50}H_{62}B_{10}N_2P_4$ (1043.2): C, 69.07; H, 6.00; B, 10.37; N, 2.69; P, 11.88. Found: C, 70.13; H, 6.78; B, 9.66; N, 2.79; P, 11.53.

Reaction of Bis-(azidodiphenylphosphine)-decaborane (VIII) with 1,2-Bis-(diphenylphosphino)-ethane (X).—Benzene (40 ml.) solutions of VIII (2.87 g., 0.005 mole) and of X (2.0 g., 0.005 mole) were mixed and refluxed for 5 hr. in a nitrogen atmosphere. The hot reaction mixture was filtered and the filter residue was extracted with acetonitrile (30 ml.) under reflux to remove all soluble material. The yield of polymer XII remaining was 3.1 g. (67.5%); it softened slightly at ~255° and was soluble in hot dimethylformamide.

Anal. Calcd. for $C_{50}H_{56}B_{10}N_2P_4$ (917.1): C, 65.48; H, 6.16; B, 11.80; N, 3.06; P, 13.51. Found: C,6 4.94; H, 6.62; B, 10.30; N, 3.31; P, 12.90. Major infrared absorption bands: Terminal B–H (st.), 4 μ; phenyl (P-bonded), 7 and 9 μ; P=N—P, 7.7 μ (broad); phenyl absorptions, 13–15 μ.

Reaction of Bis-(azidodiphenylphosphine)-decaborane (VIII) with 1,4-Bis-(diphenylphosphino)-benzene (XI).—A solution of VIII (5.74 g., 0.01 mole) and XI (4.46 g., 0.01 mole) in benzene (75 ml.) was refluxed for 5 hr. in a nitrogen atmosphere. The hot reaction mixture was filtered to give 5.8 g. of reaction product, m.p. > 300°; extraction with hot acetonitrile did not decrease the yield. Polymer XIII softens slightly at 340–350° with release of hydrogen (2.4 moles per unit) but does not melt at <400°. The *major* infrared absorption bands of XIII were essentially identical with those of XII.

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[5] K. Issleib and D. W. Müller, *Chem. Ber.*, **92**, 3175 (1959).

[6] Melting points are uncorrected; microanalyses were by R. Rittner, R. Culmo, and D. E. Aylwin of the Olin Mathieson Microchemical Section.

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, AND THE RICHARD BENBRIDGE WETHERILL LABORATORY, PURDUE UNIVERSITY, LAFAYETTE, INDIANA

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).

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