Tetra-(*n*-hexylamino)-diboron.—Tetra-(dimethylamino)-diboron (4.00 g., 20.21 mmoles) and *n*-hexylamine (8.17 g., 80.8 mmoles) which had been distilled from calcium hydride were heated from 24 to 115° for 3.2 hr. The displaced dimethylamine (101.8% of theor.) was entrained in a stream of dry nitrogen and trapped in aqueous hydrochloric acid. The residual material was dried under vacuum to give 7.78 g. (91% yield) of tetra-(*n*-hexylamino)-diboron as a colorless, non-volatile liquid, $n^{25}D$ 1.4606.

Anal. Calcd. for $C_{24}H_{56}N_4B_2$: C, 68.30; H, 13.38; N; 13.23; B, 5.11. Found: C, 67.44; H, 14.00; N, 13.15, B, 5.28.

Tetra-(di-*n*-butylamino)-diboron.—A solution of 5.0 g. (0.025 mole) of tetra-(dimethylamino)-diboron and 13.04 g. (0.101 mole) of di-*n*-butylamine (previously distilled from calcium hydride) in 25 ml. of hexane was heated from 76 to 174° for 21.6 hr. The resulting dimethylamine (96% yield) was swept into standard hydrochloric acid in a stream of dry nitrogen. Solvent and unreacted starting material were removed by distillation at 0.1–0.5 mm., and the residue was distilled to give 12.6 g. (93.4% yield) of tetra-(di-*n*-butylamino)-diboron, b.p. 170–183° (0.55 mm.), $n^{25}D$ 1.4667.

Anal. Calcd. for $C_{32}H_{72}N_4B_2$: C, 71.77; H, 13.57; N, 10.48; B, 4.05; mol. wt., 535. Found: C, 71.14; H, 13.10; N, 10.35; B, 4.37; mol. wt., 557 (cryoscopic in benzene).

Tetra-(anilino)-diboron.—A solution of 18.8 g. (202 mmoles) of aniline which previously had been distilled from calcium hydride and 10.0 g. (50.5 mmoles) of tetra-(dimethylamino)-diboron in 300 ml. of benzene was heated for 130 hr. at 81–82°. The theoretical amount of dimethylamine was removed continuously in a stream of dry nitrogen and trapped in standard hydrochloric acid. The reaction mixture was filtered and the solid product dried under vacuum to give 15.0 g. (76.0% yield) of tetra-(anilino)-diboron.

Anal. Calcd. for $C_{24}H_{24}N_4B_2$: C, 73.89; H, 6.20; N, 14.36; B, 5.57. Found: C, 73.84; H, 6.30; N, 14.50; B, 5.51.

Tetra-(anilino)-diboron melted over the range 181–200° with apparent decomposition. It was soluble in aniline, acetonitrile, dioxane and dimethylformamide and insoluble in benzene and diethyl ether.

[CONTRIBUTION FROM U. S. BORAX RESEARCH CORPORATION, ANAHEIM, CALIFORNIA]

The Preparation and Properties of Some Tetraalkoxydiborons[1]

BY R. J. BROTHERTON, A. L. MCCLOSKEY, J. L. BOONE AND H. M. MANASEVIT

RECEIVED JULY 12, 1960

Several tetraalkoxydiborons and tetraphenoxydiboron have been prepared by the reactions of tetra-(dimethylamino)-diboron with alcohols or phenol in the presence of hydrogen chloride. Tetramethoxy and tetraethoxydiboron were found to be significantly more stable than reported previously.

Introduction

Two examples of tetraalkoxydiboron compounds have been described previously. Wiberg and Ruschmann[2] reportedly prepared tetramethoxy- and tetraethoxydiborons by the reactions of the corresponding chlorodialkoxyboranes with sodium amalgam. Schlesinger, *et al.*,[3] prepared the same diboron compounds by the reactions of diboron tetrachloride with methanol and ethanol. However, Wiberg and Schlesinger fail to agree on the physical properties and stabilities of tetramethoxy- and tetraethoxydiborons. In addition, Wiberg claimed that these materials decomposed to give elemental boron at low temperatures, an observation which was not confirmed by Schlesinger. In a related reaction chlorodi-(isoamyloxy)-borane was added to sodium,[4] but tri-(isoamyloxy)-borane was the only product isolated.

Several tetraalkoxydiborons have now been prepared from tetra-(dimethylamino)-diboron[5] and found to be significantly more stable than anticipated from the results of previous workers, and no elemental boron was isolated among the decomposition products as suggested by Wiberg.[2]

Discussion of Results

Tetraethoxydiboron could not be isolated from the reactions of chlorodiethoxyborane either with sodium amalgam in petroleum ether or with highly dispersed sodium in various solvents. The chloroborane appeared to react with sodium in some cases, but tetraethoxydiboron was not isolated, perhaps because of its instability under conditions necessary for reaction. There is no apparent explanation for the failure to obtain tetraethoxydiboron from chlorodiethoxyborane and sodium amalgam, a result which is in direct contrast with Wiberg's[2] preparations of materials reported to be tetramethoxy- and tetraethoxydiboron by this reaction using chlorodimethoxy- and chlorodiethoxyboranes with sodium amalgam. No reaction was observed between chlorodiethoxyborane and highly dispersed sodium in refluxing diethyl ether, but chlorodiethoxyborane reacted with tetrahydrofuran when it was used as a solvent for the sodium reaction.

This reaction, which is analogous to that of boron trichloride with tetrahydrofuran,[6] is surprising, since Brown and Tierney[7] found that chlorodimethoxyborane did not react with diglyme under similar conditions. The results of this cleavage reaction are summarized in Table I.

Since the related tetra-(amino)-diboron compounds recently have become readily available,[5] their conversion to tetraalkoxydiborons was investigated. The displacement of dimethylamine

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[1] A portion of the research reported in this document was supported by Wright Air Development Division of the U. S. Air Force under Contract AF 33(616)-5931. It was presented in part at the 138th Meeting of the American Chemical Society, New York, N. Y., September, 1960.

[2] E. Wiberg and W. Ruschmann, *Ber.*, **70b**, 1393 (1937).

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

[4] C. R. Kinney, H. T. Thompson and L. C. Cheney, *ibid.*, **57**, 2396 (1935).

[5] R. J. Brotherton, A. L. McCloskey, L. L. Petterson and H. Steinberg, *ibid.*, **82**, 6242 (1960).

[6] J. D. Edwards, W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 1470 (1955).

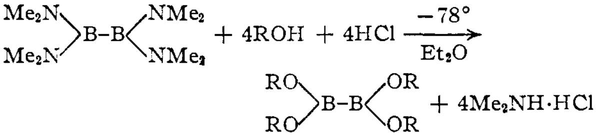
[7] H. C. Brown and P. A. Tierney, THIS JOURNAL, **80**, 1552 (1958).

TABLE I

THE REACTION OF CHLORODIETHOXYBORANE WITH THF AND DIGLYME

$(EtO)_2$-BCl, mole	Solvent	Solvent, mole	Temp., °C.	Time, hr.	$(EtO)_2$-BCl reacted, wt. %
0.071	THF	0.126	25	2	26
.079	THF	.126	25	24	58
.036	THF	.570	25	2	38
.036	THF	.570	25	24	68
.036	THF	.570	25	48	76
.071	THF	.126	55–65	2	51
.072	Diglyme	.126	25	2	0
.072	Diglyme	.126	55–65	2	12
.036	Diglyme	.570	25	24	19
.036	Diglyme	.570	25	48	36

from tetra-(dimethylamino)-diboron by various alcohols proved to be unsatisfactory. The reactions were slow, and complete removal of amine groups was difficult. Various methods which were designed to assist the removal of dimethylamine were investigated. The most convenient procedure developed involves the low-temperature addition of a solution of four equivalents of hydrogen chloride in diethyl ether. This reaction, which is somewhat related to the well known acid hydrolysis of boron–nitrogen derivatives, has been used to prepare tetramethoxy (I), tetraethoxy (II), tetraisopropoxy (III) and tetraphenoxydiborons (IV).



I R = CH_3 III R = $CH(CH_3)_2$
II R = CH_2CH_3 IV R = C_6H_5

Tetramethoxydiboron, which has been obtained in yields approaching 90%, has a vapor pressure of 5.9 mm. at 21° and an extrapolated boiling point of 130° at 760 mm. It is thermally stable up to about 110° in a vacuum-line system. The identity of tetramethoxydiboron (and also tetraethoxydiboron) has been established by elemental analyses, a molecular weight determination and the quantitative evolution of one mole of hydrogen when either alkoxy derivative was hydrolyzed in 10% aqueous sodium hydroxide solution. The evolution of one mole of hydrogen per mole of tetraalkoxydiboron can be represented by the following equation which is analogous to those postulated earlier for the basic hydrolyses of diboron tetrachloride[3,8] and tetra-(dimethylamino)-diboron.[5] Tetramethoxydiboron prepared by Wiberg[2] from chlorodimethoxyborane and sodium amalgam had a vapor pressure of 44 mm. at 21° and decomposed slowly at room temperature. Schlesinger[3] reported that tetramethoxydiboron obtained from the reaction of diboron tetrachloride with methanol was too unstable for physical measurements.

$$B_2(OR)_4 + 2NaOH + 2H_2O \longrightarrow 2NaBO_2 + 4ROH + H_2$$

Tetraethoxydiboron has been obtained from tetra-(dimethylamino)-diboron in over 50% yields. In this case the diboron compound is difficult to separate from small amounts of ethyl borate which are produced simultaneously. Tetraethoxydiboron has a vapor pressure of 1.4 mm. at 35° and an extrapolated boiling point of 170° at 760 mm. It is slightly less stable than the tetramethoxy derivative, since thermal decomposition commenced at about 90° in a vacuum line. Wiberg reported tetraethoxydiboron to be unstable at room temperature with a vapor pressure of <4 mm. at 18°, and Schlesinger described it as a reasonably stable compound with a vapor pressure of 1 mm. at 25.9°.

The decomposition of tetramethoxy and tetraethoxydiborons at temperatures above 110° did not give elemental boron as indicated by Wiberg, but the corresponding orthoborates were obtained as described previously.[2]

It has been observed that the Trouton constants in cal./deg. mole of tetra-(dimethylamino)-diboron (26.3),[5] tetramethoxydiboron (26.0) and tetraethoxydiboron (28.4) are significantly higher than those reported for the simple compounds, tris-(dimethylamino)-borane (20.6),[9] methyl borate (22.6)[10] and ethyl borate (22.7).[10] The higher values imply a greater degree of intermolecular association in the liquid state for the diboron compounds than for the simple boranes.

Tetraethoxydiboron did not react with oxygen at −78° but reaction at 25° gave ethyl borate and a material with the empirical formula EtOBO. This reaction probably proceeds through a type of B–O–B intermediate (V) which also could be proposed for the comparable reaction[11] of oxygen with diboron tetrachloride at −78°. It is not known whether the EtOBO isolated was polymeric or trimeric (boroxine). Tetra-(dimethylamino)-diboron did not react with pure oxygen at 100° or with atmospheric oxygen at 200°.[5]

$$6B_2(OEt)_4 + 3O_2 \longrightarrow \underset{\text{V}}{6[(EtO)_2BOB(OEt)_2]} \longrightarrow 6(EtO)_3B + 2(EtOBO)_3$$

Tetraisopropoxydiboron (III) and tetraphenoxydiboron (IV) have been isolated as residual products from the reactions of tetra-(dimethylamino)-diboron with isopropyl alcohol and phenol in the presence of hydrogen chloride. Tetraisopropoxydiboron is a liquid which decomposed when distillation was attempted, and tetraphenoxydiboron is a solid which could not be recrystallized. The tetraphenoxy derivative appeared to hydrolyze very rapidly, and, like the related compound, phenyl borate, was difficult to purify.

Experimental

Standard vacuum-line apparatus and techniques were used wherever high-vacuum operations are indicated. All experiments which were done outside of the vacuum line were conducted in an atmosphere of dry, oxygen-free nitrogen. Microanalyses were done by Dr. Adelbert Elek, Los Angeles, California, and by Schwarzkopf Laboratories, Woodside, New York. Boron was analyzed by the Parr-Bomb fusion method described by Hunter, *et al.*[12]

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[8] T. Wartik and E. F. Apple, THIS JOURNAL, **80**, 6155 (1958).

[9] A. B. Burg and C. L. Randolph, *ibid.*, **73**, 953 (1951).

[10] E. Wiberg and W. Sutterlin, *Z. anorg. Chem.*, **202**, 1 (1931).

[11] E. F. Apple and T. Wartik, THIS JOURNAL, **80**, 6153 (1958).

[12] D. L. Hunter, L. L. Petterson and H. Steinberg, *Anal. Chem. Acta*, **21**, 523 (1958).

Reactions of Chlorodiethoxyborane with Sodium.—Chlorodiethoxyborane was prepared from ethyl borate and boron trichloride as described previously.[13] Chlorodiethoxyborane was added to sodium amalgam (containing 0.5% sodium) in petroleum ether at −20 to 0° in an attempt to repeat Wiberg's reported[2] synthesis of tetraethoxydiboron. Most of the starting material was recovered unchanged after stirring for 5 hr. Some ethyl borate also was recovered, but no materials containing boron-boron bonds could be isolated. When chlorodiethoxyborane was added to highly dispersed sodium in either toluene or mineral oil, an exothermic reaction occurred at about 50°. The chlorine was converted to sodium chloride quantitatively in these cases, but tetraethoxydiboron could not be isolated. Chlorodiethoxyborane did not react with sodium in refluxing diethyl ether but did react with tetrahydrofuran[14] when this material was used as a solvent for this sodium dispersion reaction.

Reactions of Chlorodiethoxyborane with Tetrahydrofuran (THF) and Diglyme.[14]—Solutions of chlorodiethoxyborane in tetrahydrofuran and diglyme were placed in stoppered flasks. These flasks were held at the given temperatures for the desired time intervals, aliquots were withdrawn, and the reaction mixture was quenched in a large excess of water. Water-hydrolyzable chlorine in unreacted chlorodiethoxyborane was determined by titrating the aqueous solutions with silver nitrate solution to the dichlorofluorescein end-point. In Table I, the per cent. chlorodiethoxyborane reacted is based on the assumption that the chlorine in chlorodiethoxyborane is converted quantitatively to nonhydrolyzable organic chlorine when reaction with the ether solvent occurs.

Tetramethoxydiboron. (a) Preparation and Characterization.—Methanol (41.2 g., 1.285 moles) was added to a solution of tetra-(dimethylamino)-diboron[5] (63.7 g., 0.321 mole) in 200 ml. of anhydrous diethyl ether. The mixture was cooled to − 78° and stirred continuously while 205 ml. of a diethyl ether solution of hydrogen chloride (1.284 moles) was added dropwise (1.5 hr.). The resulting mixture was stirred for an additional 2 hr. at −78°. Most of the solvent was removed by rapid distillation at −60°(0.15 mm.), and 40.9 g. (87.7% yield) of tetramethoxydiboron was separated from small amounts of methyl borate by fractional condensation at −45° under high vacuum.

Anal. Calcd. for $C_4H_{12}O_4B_2$: C, 32.95; H, 8.29; B, 14.86. Found: C, 33.07; H, 8.37; B, 14.44.

The melting point of tetramethoxydiboron was −26.0 ± 0.5°, and its molecular weight was determined in the vapor phase in a 234-ml. high-temperature bulb as

Sample	Sample wt., mg.	T., °C.	P., mm.	Mol. wt.
1	70.8	60.0	42.30	148.2
2	54.8	59.5	33.10	147
Calculated for $B_2(OMe)_4$				145.7

When 0.1410 g. (0.97 mmole) of tetramethoxydiboron was hydrolyzed with 5 ml. of 10% aqueous sodium hydroxide in a sealed ampoule at 110–115° for 20 hr., 22.0 cc. (0.98 mmole) of hydrogen was released.

(b) **Vapor Pressures.**—Vapor pressure data indicated that tetramethoxydiboron is significantly more stable than suggested earlier by Wiberg[2] and Schlesinger,[3] and its vapor pressure can be represented between 0° and 75°, by the expression

$$\log P_{\text{mm}} = \frac{-2298}{T} + 8.5815$$

The extrapolated boiling point of tetramethoxydiboron is 130° at 760 mm., its heat of vaporization over the observed temperature range is 10.5 kcal./mole and its Trouton constant is 26.0. The vapor pressure data are given in Table II.

Tetraethoxydiboron. (a) Preparation and Characterization.—A solution of 21.0 g. (106 mmoles) of tetra-(dimethylamino)-diboron and 19.2 g. (429 mmoles) of ethanol in 50 ml. of anhydrous diethyl ether was cooled to −80° with constant stirring. To this solution was added 75 ml. (450 mmoles) of 6*N* hydrogen chloride in diethyl ether. The addition was completed in 30 minutes, and the solvent was removed at reduced pressure after an additional 30 minutes at −80°. A slow distillation of the residue from room temperature at 10^{-3} mm. into a trap at 0° gave a fraction containing tetraethoxydiboron which was 95% pure. A series of distillations from 0° gave 11.8 g. (55% yield) of tetraethoxydiboron, m.p. −59 ± 1.0°, n^{24}_{D} 1.3960.

TABLE II

VAPOR PRESSURES OF $(MeO)_4B_2$

Temp., °C.	0	30	40	50	60	70	75
Press., mm., obsd.	1.40	10.10	17.6	30.3	49.4	78.4	96.6
calcd.	1.48	10.0	17.8	30.3	48.7	78.4	96.9

Anal. Calcd. for $C_8H_{20}O_4B_2$: B, 10.70; C, 47.60; H, 9.99. Found: B, 10.48; C, 47.56; H, 9.91.

Tetraethoxydiboron (0.0393 g., 0.0195 mmole) exerted a pressure of 18.55 mm. at 90° in a 234-ml. high-temperature bulb which indicates a molecular weight of 205 (calculated for tetraethoxydiboron, 201.6). When this same sample was hydrolyzed in 5 ml. of 10% aqueous sodium hydroxide at 120° for 16 hr. in a sealed ampoule, 4.1 cc. (0.0188 mmole) of hydrogen was recovered. In a subsequent experiment 3.009 mmoles of hydrogen were obtained from the hydrolysis of 3.014 mmoles of tetraethoxydiboron.

(b) **Vapor Pressures.**—The vapor pressures of tetraethoxydiboron were measured in a high-temperature bulb, and the data may be expressed by the equation

$$\log P_{\text{mm.}} = \frac{-2762.8}{T} + 9.1167$$

over the temperature range 0–85°. At 95° a pressure increase of 2.5 mm. over a 1 hr. period indicated that tetraethoxydiboron was decomposing slowly to a more volatile component. The vapor pressures are indicated in Table III. These values imply a heat of vaporization for tetraethoxydiboron of 12.6 kcal./mole over the temperature range 0–85°, an extrapolated boiling point of 170° at 760 mm. and a Trouton constant of 28.4.

TABLE III

VAPOR PRESSURES OF TETRAETHOXYDIBORON

Temp., °C.	0	35	45	55	65	75	85
Press., mm., obsvd.	0.05	1.35	2.65	4.90	8.90	15.4	24.9
calcd.	0.10	1.46	2.76	4.90	8.68	15.4	25.6

The Reaction of Tetraethoxydiboron with Oxygen.—An excess of molecular oxygen (150 mm.) was added to 112.9 mg. (0.561 mmole) of tetraethoxydiboron in a small flask attached to a high-vacuum line. Reaction was slow at −78 to 0°, but addition was complete in 10 minutes at 25°. After removal of the excess oxygen at −78°, the increased weight was equivalent to 9.3 mg. of oxygen (0.290 mmole). The more volatile reaction product, which was removed at −18° under high vacuum, amounted to 81.6 mg. and corresponded to 0.559 mmole of ethyl borate (v.p. = 14.0 mm.(25°); literature, 13.9 mm.). The remaining 40.6 mg. was equal to 0.566 mmole of EtOBO (probably polymeric) and contained 15.27% B (calculated for EtOBO, 15.04%).

Tetraisopropoxydiboron.—A solution containing 4.00 g. (20.21 mmoles) of tetra-(dimethylamino)-diboron and 4.85 g. (80.84 mmoles) of isopropyl alcohol in 50 ml. of diethyl ether was cooled to −85°. Hydrogen chloride (80.84 mmoles) dissolved in 37.6 ml. of diethyl ether was added with stirring over a 15-minute period; white solids formed immediately. The thick slurry was stirred for 0.75 hr. warmed to 0° and stirred for an additional hour. The theoretical dimethylamine hydrochloride, contaminated with tetraisopropoxydiboron, was separated by filtration. The ether solvent was rapidly distilled from the filtrate at −20 to 30° and 2 mm. to give 3.62 g. (71.6% yield) of residual tetraisopropoxydiboron, n^{25}_{D} 1.3970.

Anal. Calcd. for $C_{12}H_{28}O_4B_2$: C, 55.88; H, 10.95; B, 8.39; mol. wt., 258. Found: C, 55.55; H, 11.23; B, 8.22; mol. wt. (cryoscopic in benzene), 262.

Tetraisopropoxydiboron decomposed at 65–76° when distillation was attempted at 2 mm.

Tetraphenoxydiboron.—A solution of 4.19 g. (21.17 mmoles) of tetra-(dimethylamino)-diboron and 7.97 g. (84.68

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[13] E. W. Abel, J. D. Edwards, W. Gerrard and M. F. Lappert, *J. Chem. Soc.*, 501 (1957).

[14] Diglyme (the dimethyl ether of diethylene glycol) and tetrahydrofuran were dried over potassium hydroxide and distilled twice from sodium hydride.

mmoles) of phenol in 30 ml. of anhydrous diethyl ether was cooled to −80°. A solution of 86.4 mmoles of hydrogen chloride in 27 ml. of diethyl ether was added slowly with stirring at −80 to −25°. After one additional hour at −25°, the solid dimethylamine hydrochloride was filtered, and the solvent was removed from the filtrate by low-temperature distillation at 0.5 mm. to give 7.73 g. of tetraphenoxydiboron, m.p. 74–75°, with some preliminary softening at 65–74°.

Anal. Calcd. for $C_{24}H_{20}O_4B_2$: B, 5.50; phenoxy, 94.42; mol. wt., 394. Found: B, 5.11; phenoxy,[15] 93.67; mol. wt. (cryoscopic in benzene), 382.

All attempts to recrystallize tetraphenoxydiboron from a number of solvents were unsuccessful. Insoluble fractions which reduced silver nitrate and contained as high as 15% boron were isolated when recrystallization of crude tetraphenoxydiboron was attempted from petroleum ether.

Acknowledgments.—The authors are indebted to Dr. H. Steinberg, Dr. R. Schaeffer and to Mr. L. L. Petterson for their helpful comments and discussions.

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[15] Repeated analyses by normal combustion methods gave consistently high hydrogen and low carbon values. However, the compound was analyzed by hydrolysis and conversion to tribromophenol, see F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 633.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE UNIVERSITY, AMES, IOWA, AND THE DEPARTMENT OF CHEMISTRY, INDIANA UNIVERSITY, BLOOMINGTON, INDIANA]

Studies of Boron–Nitrogen Compounds. II. Preparation and Reactions of B-Trichloroborazole[1]

BY GERALD L. BRENNAN, GERD H. DAHL AND RILEY SCHAEFFER

RECEIVED JUNE 8, 1960

Suitable conditions have been established for the convenient large laboratory scale preparation of B-trichloroborazole from ammonium chloride and boron trichloride at elevated temperatures. Trichloroborazole was used for studies of the substitution of the halogen by various inorganic groups. Thus, B-tricyanoborazole containing a few mole per cent. of silver and B-trithiocyanatoborazole were prepared and identified. Evidence for the preparation of the apparently unstable B-trinitratoborazole and B-trinitroborazole was obtained. In the course of these investigations it also was observed that B-trichloroborazole reacts with anhydrous acetic acid to form the compound $[(CH_3CO_2)BNH_2]_2$. In contrast, borazole itself reacts with anhydrous acetic acid to form a 1:3 adduct presumably similar to the better known hydrogen chloride adduct.

The reduction of B-trichloroborazole is at present the most convenient way to obtain larger quantities of borazole itself.[2–4] Trichloroborazole has also been used as a starting material for some substitution reactions on the borazole ring.[5,6] It appeared desirable to find a procedure by which B-trichloroborazole can be prepared conveniently on a large scale.

Early reported methods for the preparation of B-trichloroborazole involve the use of borazole itself and hence are not desirable.[7,8] More recently, B-trichloroborazole has been prepared from ammonium chloride and boron trichloride at elevated temperatures either in the presence or absence of a solvent, but the methods described by Brown and Laubengayer are not suitable for relatively large preparations.[9] It appeared that the recovery of the halogenated borazole was achieved most easily by the "dry method." Hence, a further investigation of this procedure to determine optimum conditions seemed to be desirable. Using temperatures above 200°, the authors found that more than 100 g. of trichloroborazole could be prepared in 3.5 hr. Best yields, based upon the amount of the ammonium chloride used, were approximately 40%. Subsequent to the completion of this phase of the present work in 1957, other improved procedures of comparable efficiency for preparation of the desired substance have appeared[10] and consequently in this paper only a brief description of our procedure is given including a novel apparatus to simplify the preparation. The reader is referred to a thesis by G. L. B. for additional details.[11]

While attempting to find a suitable solvent for substitution reactions to be discussed shortly, it was found that B-trichloroborazole vigorously reacts with glacial acetic acid to form HCl and a crystalline material. This compound was found to be a dimer of formula $[(CH_3CO_2)_2BNH_2]_2$. In contrast, borazole itself was found to form a 1:3 adduct with acetic acid.

Whereas a number of substitution reactions on N-substituted trichloroborazoles have been investigated,[12] only a few such reactions have been attempted with trichloroborazole itself. Thus, B-trimethylborazole has been isolated from the reaction between B-trichloroborazole and methylmagnesium iodide.[5] Also, Hutto treated trichloroborazole with mercuric fluoride in various solvents

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[1] Contribution No. 964 from the Department of Chemistry, Indiana University. Reprint requests should be directed to R. S. at that address. For Paper I of this series see reference 4. This work was presented at the 133rd meeting of the American Chemical Society at San Francisco in April, 1958.

[2] R. Schaeffer, M. Steindler and L. Hohnstedt, THIS JOURNAL, **76**, 3303 (1954).

[3] L. Hohnstedt and R. F. Leifield, Abstract presented at the April meeting of the American Chemical Society 1959, p. 35-M.

[4] G. Dahl and R. Schaeffer, *J. Inorg. Nuclear Chem.*, **12**, 380 (1960).

[5] H. I. Schlesinger, R. Schaeffer, L. Hohnstedt, *et al.*, final report. Contract No. N60 ori-20, TOX, August 1, 1950–June 30, 1951, University of Chicago.

[6] H. S. Turner, *Chem. and Ind.* (*London*), **43**, 1405 (1958).

[7] E. Wiberg and A. Bolz, *Ber.*, **73**, 209 (1940).

[8] E. Wiberg, *Naturwissenschaften*, **35**, 182 (1948).

[9] C. A. Brown and A. W. Laubengayer, THIS JOURNAL, **77**, 3699 (1955).

[10] Recently Emeleus reported a yield of 50–60% of trichloroborazole by adding Fe, Ni or Co on pumice to the ammonium chloride as a catalyst; H. I. Emeleus and G. 1. Videla, *J. Chem. Soc.*, 1306 (1959). A hot tube synthesis of trichloroborazole NH_3 and BCl_3 was also recently described by Hohnstedt and Leifield, see ref. 3.

[11] G. L. Brennan, M.S. Thesis, Iowa State University, 1957.

[12] See for example I. Groszos and S. Stafiej, THIS JOURNAL, **80**, 1357 (1958).