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

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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. I. 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).

obtaining non-volatile products which were not further identified.[13]

Similar studies in our laboratories have resulted in preparation of some new B-substituted borazoles from the reaction of B-trichloroborazole with inorganic salts, usually silver or alkali salts. Thus, B-trithiocyanatoborazole, $B_3(SCN)_3N_3H_3$, was best obtained from the reaction of B-trichloroborazole with potassium thiocyanate in 1,2-dimethoxyethane. B-Tricyanoborazole was obtained in a similar fashion from the reaction of B-trichloroborazole with excess silver cyanide in acetonitrile as solvent. A product completely free of silver was not obtained, however.

The reactions between B-trichloroborazole and silver nitrate and silver nitrite were also investigated; however, no stable reaction products could be identified, although indirect evidence suggests the desired substances were formed but could not be isolated without decomposition.

Experimental

Preparation of B-Trichloroborazole.—Technical grade boron trichloride obtained from Matheson Company was purified from chlorine by bubbling through mercury. Granular ammonium chloride from Baker and Adamson was dried at 110° for at least 24 hr. before use.

For the preparation of B-trichloroborazole a reaction column of 38 mm. Pyrex tubing was used. The reaction zone was heated electrically by wrapping nichrome wire around the column and, to avoid plugging at the column end by deposition of solid product, the standard taper and inner tube at the exit were heated to 110° by toluene maintained at reflux temperature by heating with a small coil of nichrome wire sealed in the glass between the inner tube and the standard taper. The column was filled with 6 moles of ammonium chloride mixed with glass beads and swept out with dry nitrogen to expel all air and moisture. After the column had attained the desired temperatures, generally in excess of 200°, boron trichloride was passed through the column. The B-trichloroborazole produced was trapped in a Dry Ice–acetone bath and the hydrogen chloride escaped through the trap. The trichloroborazole was sublimed out of the trap under vacuum. The sublimed material gave a melting point of 83–83.5° in good agreement with the value of 83.9–84.5° reported in the literature.[8] In all runs considerable quantities of low density non-volatile products were obtained.

Preparation of $[(CH_3CO_2)_2NBH_2]_2$.—One hundred ml. of 99.7% glacial acetic acid was added to 20 g. of trichloroborazole and the warm solution was filtered through a coarse fritted disk after the evolution of hydrogen chloride had subsided. Needle shaped crystals were deposited from the solution on cooling to room temperature. Excess glacial acetic acid was decanted and the crystals were washed with anhydrous diethyl ether. The product was then dried in a vacuum desiccator. The yield was 64% based upon the equation

$$2B_3Cl_3N_3H_3 + 12\ CH_3COOH \longrightarrow 3\ [(CH_3CO_2)_2BNH_2]_2 + 6\ HCl$$

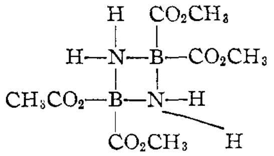
Properties of $[(CH_3CO_2)_2BNH_2]_2$.—The compound melted at 144.5-146° and decomposed in a vacuum above 150° forming acetic acid and an unidentified solid. Solubility tests showed it to be insoluble in most organic solvents being only slightly soluble in glacial acetic acid and acetic anhydride. It is only slightly soluble in water but is readily dissolved by warm dilute acids and bases.

Anal. Calcd: B, 7.48; C, 33.20; H, 5.57; N, 9.67. Found: B, 7.57; C, 33.45, 33.27; H, 5.39, 5.39; N, 9.40, 9.25.

The molecular weight was determined by the freezing point lowering in glacial acetic acid. Calcd. for the dimer, 289.6. Found: 287.8, 295.5.

Single crystal X-ray diffraction studies showed that monoclinic and triclinic crystalline forms were obtained by recrystallizing the material from acetic anhydride and glacial acetic acid, respectively. The lattice constants and angle for the monoclinic form were a_0 = 22.81 Å., b_0 = 10.41 Å., c_0 = 17.6 A., β = 92°45′. The space group determined from systematic extinction is either Ia or I 2/*a*. An observed density of 1.36 g./cm.^{3} obtained by the flotation method in a mixture of bromobenzene and chlorobenzene gave a value of 23.75 monomers per unit cell.[14]

Infrared spectra of the compound showed a splitting of the NH band indicating that two hydrogen atoms are present on each nitrogen. The structure shown appears likely for the dimer



Reaction of Borazole with Anhydrous Acetic Acid.—It appeared of interest to replace the chloroborazole used in the above reaction with borazole itself. The reaction now was found to be highly exothermic and with excess acid there usually was obtained a viscous product containing four to six moles of acid per mole of borazole used. The reaction could be moderated by dissolving the acid in diethyl ether and then adding the borazole into the flask.

In a typical reaction, 19.52 mmoles of acetic acid were dissolved in 50 cc. of ether. The reactants were covered with a blanket of dry nitrogen and 5.8 mmoles of borazole slowly added through a side arm. When about one half the borazole had been added a white precipitate formed. After a reaction period of 8 hr., the mixture was filtered in a dry box and the solid product washed with fresh ether. Titration of the filtrate showed two mmoles of acid to be present indicating almost precisely addition of three molecules of acids to each borazole. No suitable solvent could be found for recrystallization. Analysis of the crude product gave low values for both boron and nitrogen (10.5% observed for boron to 12.5% calculated and 12.5% nitrogen observed to 16.2 calculated). A molecular weight of 236 was observed by freezing point lowering in glacial acetic acid compared to a calculated value of 260.7. Both low analytical results and low molecular weight are consistent with the possible occlusion of solvent in the preparation.

The compound reduced silver nitrate in aqueous solution (indicating retention of the B–H bond) and readily was attacked by water although complete hydrolysis occurred only in strongly acid solution.

Preparation of B-Trithiocyanatoborazole.[15]—Potassium thiocyanate was dehydrated by heating it to its melting point. The solvent, 1,2-dimethoxyethane, from the Ansul Chemical Company was dried by refluxing over sodium.

B-Trichloroborazole and potassium thiocyanate, in a mole ratio of 1:3, were dissolved in separate portions of the solvent. The borazole solution was added slowly to the solution of potassium thiocyanate and warming and immediate precipitation of potassium chloride resulted. The solution was filtered under dry nitrogen and the solvent removed by vacuum distillation. The product was recrystallized from fresh solvent and finally washed with dry hexane.

Properties of B-Trithiocyanatoborazole.—B-Trithiocyanatoborazole is a nearly white, faintly yellow non-sublimable powder melting with decomposition in vacuum at 147–150° and soluble in benzene and acetonitrile but insoluble in hexane and carbon tetrachloride. Like B-Trichloroborazole it reacts rapidly with water. Upon exposure to the atmosphere it turns yellow.

Anal. Calcd: B, 12.8; SCN, 69.2; N (ring), 16.7. Found: B, 12.6; SCN, 68.4; N (ring), 16.6.

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[13] F. B. Hutto, M.S. Thesis, Cornell University, 1950.

[14] The authors wish to thank Mr. Lawrence Dahl for obtaining the X-ray information.

[15] In this as well as in the following preparation the careful exclusion of moisture and air was mandatory in obtaining the desired compounds free from colored decomposition products. Hence, high vacuum techniques were used whenever possible. The general apparatus and methods are described by R. T. Sanderson in "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, Inc., New York, N. Y., 1948.

The molecular weight was determined by the cryoscopic method in benzene. Calcd: 251.7. Found: 253.

Preparation of B-Tricyanoborazole.—Eastman Kodak "white label" acetonitrile was purified carefully according to the procedure reported by Wawzonek and Runner.[16] If the acetonitrile was not treated in this fashion, highly colored by-products usually were formed during the subsequent reaction. A 50% excess of vacuum dried silver cyanide was placed in a round bottom flask with several grams of glass beads. To this was added an acetonitrile solution of B-trichloroborazole. Since silver cyanide is nearly insoluble in acetonitrile (although more soluble than silver chloride), the flask was shaken for approximately one week to bring the reaction to completion. Shorter reaction times resulted in products still containing chlorine. Care was taken to shield the flask from light during the shaking period to prevent decomposition of the silver chloride.

After the shaking period was complete the acetonitrile solution was filtered from silver chloride and excess silver cyanide. The precipitate was extracted several times with acetonitrile. The combined fractions were subjected to a vacuum distillation to remove the solvent. The white solid which was thus obtained was recrystallized four to six times from acetonitrile. In spite of several recrystallizations, the purest reaction product contained nearly 5% of silver by weight, possibly as a silver cyanide complex. The solubility of silver cyanide is much too small to account for the silver present and the high molecular weight of the inorganic salt would result in only slight changes in the cyanide to be expected on analysis.

Properties of B-Tricyanoborazole.—The compound is a white solid and unlike B-trichloroborazole and B-trithiocyanatoborazole it is relatively thermally stable, decomposing in vacuum only at temperatures exceeding 200°. The cyano derivative is insoluble in benzene, toluene, carbon tetrachloride and hexane. Its solubility in acetonitrile at room temperature is 0.6–0.7 g. per 100 cc. solvent. B-Tricyanoborazole is most sensitive toward moist air and in water hydrolyzes immediately to liberate hydrogen cyanide. Attempted reduction with lithium and sodium borohydride lead only to the formation of black unidentified products.

Analytical results on the purest reaction product were: B, 18.4; N(ring), 24.6; CN, 44.9; Ag, 4.8. Calcd: B, 20.8; N(ring), 27; CN, 50.0.

The ratio of boron to ring nitrogen to cyanide thus was 0.99: 1.01:1.00.

Reaction of B-Trichloroborazole with Silver Nitrate and Silver Nitrite.—In a typical experiment 2.9 g. of B-trichloroborazole and 8.5 g. of silver nitrate were dissolved separately in purified acetonitrile and the solutions cooled overnight at −10°. The silver nitrate solution then was added to the B-trichloroborazole solution under a blanket of dry nitrogen maintaining the low temperature. Immediately all three halogens of the B-trichloroborazole were precipitated as silver chloride. After filtration and partial removal of solvent, well formed white crystals were deposited in the flask. Vacuum distillation of the filtrate at 0° produced a white solid that tenaciously retained some acetonitrile. Upon warming to room temperature the solid partly redissolved in the retained solvent and liberated copious quantities of nitrogen dioxide over a period of 12 hr. leaving a pale yellow solid. In one reaction which had been kept slightly above 0° the recovered solvent was subjected to a fractional distillation on the vacuum line. The acetonitrile was trapped in a −63.5° trap whereas a more volatile material was stopped in a liquid nitrogen trap. The vapor pressure, 84 mm. at −112° and the molecular weight, determined by gas density measurement as 44, identified this volatile material as nitrous oxide.

Extractions of the original reaction product with dry diethyl ether below 0° yielded a solid which retained ether but appeared stable toward the evolution of nitrogen dioxide at room temperature. The ether adduct reacted explosively with water with ignition. Although it is apparently not shock sensitive, the ether adduct (and presumably the original product) should be treated most cautiously since it exploded violently on one occasion in contact with toluene below room temperature. Further studies of this reaction would be interesting to determine whether the adduct behaved as a nitrating agent or is itself unstable.

The reaction of B-trichloroborazole with silver nitrite appears to be similar to the reaction with silver nitrate. Solutions were prepared of 12.2 g. of silver nitrite and 5 g. of B-trichloroborazole each dissolved in 50 ml. of purified acetonitrile. The solution of silver nitrite cooled to 0° was added to the cooled B-trichloroborazole solution. An immediate reaction took place as shown by the formation of a white precipitate of silver chloride and evolution of nitrogen dioxide. The solution was filtered and the filtrate vacuum distilled, but the remaining white solid continued to evolve nitrogen dioxide below room temperature and no relatively pure product could be isolated.

Acknowledgments.—Gerald L. Brennan and Gerd H. Dahl gratefully acknowledge the generous financial support of this work by fellowships awarded by the Stauffer Chemical Company. Support of this work at Indiana University by NSF Grant G-6224 is also gratefully acknowledged.

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[16] S. Wawzonek and M. E. Runner, *J. Electrochem. Soc.*, **99**, 457 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN]

The Preparation and Structure of the Diammoniate of Tetraborane[1]

BY G. KODAMA AND R. W. PARRY

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The reaction between ammonia and tetraborane has been examined under a variety of conditions. The pure compound $B_4H_{10}\cdot 2NH_3$ has been isolated and evidence to support the structure $[H_2B(NH_3)_2^+][B_3H_8^-]$ is presented. The "diammoniate of tetraborane" resembles the "diammoniate of diborane" in many of its reactions. Available evidence suggests that the unstable "compounds" $B_4H_{10}\cdot 2.5NH_3$ and $B_4H_{10}\cdot 4NH_3$ reported in an earlier study are complex mixtures.

In their initial study of the reaction between tetraborane and ammonia Stock, *et al.*,[2] reported two unstable compounds, $B_4H_{10}\cdot 4NH_3$ and $B_4H_{10}\cdot 2.5NH_3$. In a careful study of the same system made in this Laboratory neither the formula $B_4H_{10}\cdot 4NH_3$ nor $B_4H_{10}\cdot 2.5NH_3$ could be verified. A modification of the experimental procedures resulted, however, in the isolation of a pure "*diammoniate* of tetraborane," $B_4H_{10}\cdot 2NH_3$, which is stable at room temperature. A preliminary description of this solid has been given.[3] In this

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[2] A. Stock, E. Wiberg and H. Martini, *Ber.*, **63B**, 2927 (1930); A. Stock, E. Wiberg, H. Martini and A. Nicklas, *ibid.*, **65B**, 1711 (1932).

[3] (a) G. Kodama and R. W. Parry, THIS JOURNAL, **79**, 1007 (1957); (b) G. Kodama and R. W. Parry, Paper presented before the Inorganic Section of the Sixteenth International Congress of Pure and Applied Chemistry, Paris, France, 1957, p. 483; (c) G. Kodama, Ph.D. Dissertation, University of Michigan, 1957.