[Contribution from the Department of Chemistry of the University of Michigan]

The Preparation and Properties of Ammonia–Triborane, $H_3NB_3H_7$[1]

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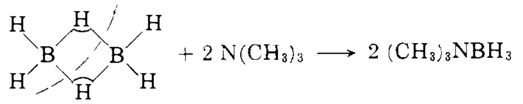
Ammonia–triborane, $H_3NB_3H_7$, can be made from tetraborane by a series of reactions analogous to those used in preparing ammonia–borane, H_3NBH_3, from diborane. Ammonia–triborane is a relatively stable white crystalline solid when pure. Some of its chemical and physical properties are described. A method for synthesizing and purifying the compound in 10 to 20 gram lots also is given.

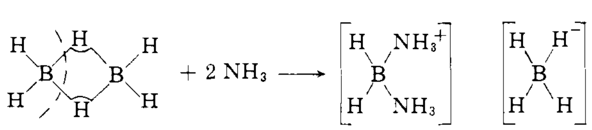
In his pioneer studies on tetraborane, Stock and his co-workers[2] reported that B_4H_{10} reacts with ammonia to form an unstable tetrammoniate of tetraborane, $B_4H_{10} \cdot 4NH_3$. Although Kodama and Parry[3] were unable to verify the existence of the tetrammoniate, they did isolate a stable *di*ammoniate of tetraborane, $B_4H_{10} \cdot 2NH_3$.

The initial study of the reaction between tetraborane and *trimethylamine* by Burg and Stone[4] indicated that the tetraborane molecule can give $3BH_3$ groups which appear as 3 molecules of $H_3BN(CH_3)_3$. A polymeric residue remained in the reaction vessel. The careful and definitive study by Edwards, Hough and Ford[5] on the system $(CH_3)_3N$–B_4H_{10} indicated that under properly controlled reaction conditions $N(CH_3)_3$ and B_4H_{10} will combine to give the new compound $(CH_3)_3NB_3H_7$. Though parts of the foregoing studies are not mutually compatible, all four investigations show clearly that the reaction between ammonia and tetraborane differs markedly from the reaction between trimethylamine and tetraborane.

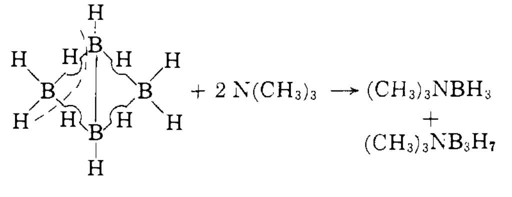
On the other hand, one may note a striking parallel between the reactions of tetraborane and diborane with $N(CH_3)_3$ and the reactions of tetraborane and diborane with NH_3. It is known that trimethylamine brings about symmetrical cleavage of the double bridge bonds in diborane to give $(CH_3)_3NBH_3$



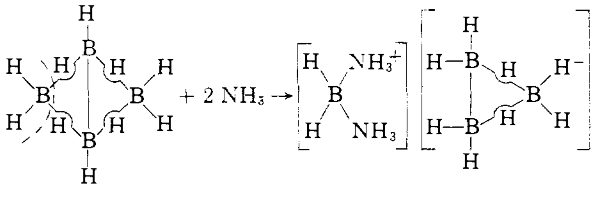
whereas ammonia brings about a non-symmetrical cleavage of the double bridge bonds to give the diammoniate of diborane[6]



Similarly the direct reaction of tetraborane and trimethylamine to produce $(CH_3)_3NB_3H_7$ can be interpreted as a *symmetrical* cleavage of the double bridge bonds in tetraborane[7]



and the direct reaction of ammonia with tetraborane can be interpreted as a *non-symmetrical* cleavage of the double bridge bonds to give the diammoniate of tetraborane[8]



Because the direct reaction of ammonia with diborane gives *non*-symmetrical cleavage of the double bridge bonds, the synthesis of ammonia–borane, H_3NBH_3, was delayed for a number of years and was achieved only by indirect methods.[9] Similarly the triborane analog of H_3NBH_3, namely, $H_3NB_3H_7$, cannot be synthesized by direct reaction of NH_3 and B_4H_{10} but can be prepared by indirect routes. Fortunately, the analogy with diborane chemistry is close and comparable reactions are applicable; however, such an analogy was not established at the beginning of this research.

Methods for Synthesizing $H_3NB_3H_7$.—Shore and Parry[9] showed that the interaction of $LiBH_4$ with an ammonium halide salt proceeded as indicated below

$$LiBH_4 + NH_4Cl \xrightarrow[25°]{Et_2O} H_2\uparrow + H_3NBH_3 + LiCl\downarrow$$

An extension of Shore's reaction to the new compound, NaB_3H_8, described by Hough, Edwards and McElroy[10] gave a process which can be repre-

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(1) This research was supported by the United States Air Force under Contracts No. AF 33(616)-3343 and AF 33(616)-5874 monitored by the Aeronautical Research Laboratory, Wright Air Development Center, Ohio.

(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) G. Kodama and R. W. Parry, This Journal, **79**, 1007 (1957).

(4) A. B. Burg and F. G. A. Stone, *ibid.*, **75**, 228 (1953).

(5) L. J. Edwards. W. V. Hough and M. D. Ford, to be published.

(6) D. R. Schultz, S. G. Shore, R. W. Parry, G. Kodama, P. R. Girardot, R. C. Taylor and A. R. Emery, This Journal, **80**, 1 (1958).

(7) L. J. Edwards, W. V. Hough and M. D. Ford, XVIth International Congress of Pure and Applied Chemistry, Section of Inorg. Chem., Paris, France, July 1957, p. 475; L. J. Edwards, *et al.*, to be published.

(8) (a) G. Kodama, Ph.D. Dissertation, Dept. of Chemistry, University of Michigan, 1957; (b) G. Kodama and R. W. Parry, Proceedings XVIth International Congress of Pure and Applied Chemistry, Section of Inorg. Chem., Paris, France, July 1957, p. 483; (c) G. Kodama and R. W. Parry, to be published.

(9) S. G. Shore and R. W. Parry, This Journal, **80**, 8 (1958).

(10) W. V. Hough, L. J. Edwards and D. McElroy, *ibid.*, **78**, 689 (1956).

sented by the equation

$$NaB_3H_8 + NH_4Cl \xrightarrow[25^\circ]{Et_2O} H_2 + H_3NB_3H_7 + \mathit{NaCl}\downarrow$$

The new compound ammonia–triborane, $H_3NB_3H_7$, was sublimed *in vacuo* at 40 to 50° from the solid residues which remained after removal of the solvent ether. The reaction was not as clean cut as that involving $LiBH_4$. Rather complex side reactions appeared to be taking place. Yields of recovered $H_3NB_3H_7$ ranged from a trace to 38% on the basis of the NaB_3H_8 used. Most yields were in the range 20 to 30%.

A second extrapolation of diborane chemistry provided a direct synthesis of $H_3NB_3H_7$ from the diammoniate of tetraborane, $B_4H_{10}\cdot 2NH_3$; this process provided important information in establishing the structure of $B_4H_{10}\cdot 2NH_3$[8] and will be described in more detail elsewhere.[8c]

The most effective method for the synthesis of 10-g. quantities of $H_3NB_3H_7$ is somewhat analogous to the procedure recommended by Shore and Parry[9] for the synthesis of H_3NBH_3 from the dimethyl etherate of borane

$$B_2H_6 + 2(CH_3)_2O \longrightarrow 2(CH_3)_2OBH_3$$
$$(CH_3)_2OBH_3 + NH_3 \longrightarrow H_3NBH_3$$

Edwards, Hough and Ford[7] reported that a number of ethers will react directly with tetraborane at room temperature to give diborane and the etherates of the B_3H_7 group. Yields were reported as quantitative when tetrahydrofuran was used. The reaction of such etherates with ammonia might then give $H_3NB_3H_7$. The over-all process can be represented as

$$B_4H_{10} + R_2O \xrightarrow[R_2O]{25^\circ} {}^1/_2B_2H_6 + R_2OB_3H_7$$

$$R_2OB_3H_7 + NH_3 \xrightarrow[-78^\circ]{\text{Diethyl ether}} H_3NB_3H_7 + R_2O$$

By proper selection of the ether, good yields of $H_3NB_3H_7$ have been obtained.

Certain characteristics of the ether appear to be of major importance. First, it should be a strong enough base to react smoothly with B_4H_{10} to give a relatively stable B_3H_7 etherate at room temperature. Diethyl and dimethyl ethers were ***not*** suitable because they are too weak as a base and the B_3H_7 group decomposes so rapidly at room temperature that the subsequent low temperature ammonia addition reaction cannot be effected. On the other hand, the triborane etherate, $R_2OB_3H_7$, should not be extremely stable or difficulty might be encountered in displacing the ether by ammonia at −78°. It was found that the tetrahydrofuran adduct of B_3H_7, $C_4H_8OB_3H_7$, reacted with ammonia in a solution of diethyl ether at −78°, but the yields of recovered $H_3NB_3H_7$ were only about 70% and a fair amount of unidentified liquid always contaminated the sublimed product.

It was assumed, though not established with certainty, that the high stability of the tetrahydrofuran adduct contributed to the low yield. According to McLaughlin, Tamres and Searles,[11] tetrahydropyran is intermediate in base strength between diethyl ether and tetrahydrofuran toward BF_3 as a reference acid; it should thus be suitable for $H_3NB_3H_7$ synthesis. When tetrahydropyran was used as the original ether in small scale runs, yields of $H_3NB_3H_7$ were as high as 94% on the basis of the original B_4H_{10} used. Yields of 70 to 80% were obtained in larger scale (20-g. lots) operation.

The product obtained directly from the ether displacement procedure appeared to contain small amounts of impurities which rendered the compound somewhat less stable than the $H_3NB_3H_7$ obtained directly from the reaction between NH_4X and NaB_3H_8. When the ether displacement procedure was utilized in the preparation of 20-g. lots of $H_3NB_3H_7$, the product was crystallized from benzene and then from toluene in order to obtain a solid of high purity.

The Properties of $H_3NB_3H_7$.—Pure ammonia triborane is a white crystalline solid which can be sublimed very slowly under high vacuum. It melts at 73–75° with slow evolution of hydrogen. It can be handled in air without obvious decomposition and is surprisingly resistant to complete hydrolysis; periods of several days at 120° in 6 *N* HCl were used to hydrolyze the product for analysis. It is extremely soluble in diethyl ether; in fact, it picks up ether vapor avidly to give an ether solution. The original compound can be recovered unchanged on vaporization of the ether. It can be dissolved in and recovered unchanged from liquid ammonia at −75° and from benzene. It is soluble in acetone and alcohol and very slightly soluble in petroleum ether. X-Ray powder data for identification of the solid are presented in Table I.

TABLE I

INTERPLANAR SPACINGS AND RELATIVE INTENSITY DATA FOR $H_3NB_3H_7$ HIGH TEMPERATURE FORM (TETRAGONAL)

Intensity[a]	d(Å.)	hkl[b]
s	4.48	101
s	4.33	110
m	3.29	002
m	3.06	200
m	2.62	112
m	2.52	211
w	2.24	202
w	2.07	103
w	1.95	301

[a] s = strong, m = medium, w = weak. [b] These indices were assigned and verified on the basis of intensity data from the single crystal work by Nordman and Reimann.[13]

Westrum and Levitin[12] have shown that it undergoes an apparent first order transition involving an enthalpy increment of 1233 cal./mole and an entropy increment of 4.15 cal./mole × deg. at 297.10°K. The crystal structures of both the low and high temperature forms have been worked out by Nordman and Reimann.[13] Details of compound characterization are in the Experimental section.

At −78°, $H_3NB_3H_7$ was not attacked by trimethylamine, but at room temperature it reacted with an equimolar quantity of the base to give trimethylamine–borane [$(CH_3)_3NBH_3$], and an uni-

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[11] M. Tamres and D. E. McLaughlin, private communication, 1957; D. E. McLaughlin, M. Tamres and S. Searles, presented at the 133rd meeting of the American Chemical Soc., April, 1958.

[12] E. F. Westrum, Jr., and N. E. Levitin, THIS JOURNAL, **81**, 3544 (1959).

[13] C. E. Nordman and C. Reimann, *ibid.*, **81**, 3538 (1959).

dentified solid which decomposed slowly through evolution of hydrogen gas. It was not possible to recover any trimethylamine–triborane, $(CH_3)_3NB_3H_7$, from the products.

Ammonia–triborane in liquid ammonia solution at −78° reacted with dissolved sodium metal (present in excess) to give one *equivalent* of hydrogen per mole of $H_3NB_3H_7$ in 20 minutes. Slow hydrogen evolution continued until a total of 1 mole of H_2 per mole of $H_3NB_3H_7$ was obtained. The residue from removal of the solvent contained $NaBH_4$ on the basis of the X-ray powder pattern. No ether soluble component was detectable in the residue, and no other components were recognized in the mixture. Additional work on the chemistry of $H_3NB_3H_7$ is in progress.

Experimental

Conventional vacuum lines were used for handling volatile and/or air sensitive reactants and products. Moisture-sensitive solids and non-volatile liquids were handled in a dry box.

Materials Used. 1. B_2H_6.—Diborane was prepared from BF_3 and $LiAlH_4$ by conventional techniques.[14]

2. B_4H_{10}.—Most of the tetraborane used in this investigation was donated by Professor Thomas Wartik of the Pennsylvania State University and by the Research Department of Callery Chemical Co. The authors wish to express their sincere appreciation. Some additional supplies of B_4H_{10} were prepared by converting B_2H_6 to B_5H_{11} by the method of Burg and Stone.[4] B_5H_{11} then was converted to B_4H_{10} by heating it in the presence of H_2.[15] Tetraborane also was prepared by high pressure storage of B_2H_6 at room temperature.[16]

B_4H_{10} used in small scale runs was fractionated at −85 or −95° and was stored at −196° until used. It was fractionated at −100° just before use. The vapor pressure of the purified compound was 386 ± 1 mm. at 0°. Tetraborane used in the larger scale preparations was distilled from a −95° bath after initial removal of B_2H_6 at −126°.

3. **$LiAlH_4$, CaH_2 and NaH**: commercial products from Metal Hydrides, Inc.

4. **BF_3**: commercial diethyl etherate from Baker and Adamson. Solution was distilled immediately before use.

5. **NH_3**: commercial, dried in a vacuum line over sodium before use or stored with dissolved sodium in steel tank and distilled directly into vacuum system.

6. **Ethers.** (a) $(C_2H_5)_2O$: reagent grade, stored in a vacuum line over $LiAlH_4$ for several days before use. For larger scale operation anhydrous grade ether was used directly from a fresh can. (b) Tetrahydrofuran: product of E. I. du Pont de Nemours Co., distilled once and stored in a vacuum line over $LiAlH_4$. (c) Tetrahydropyran: product of Eastman Kodak Co. and a research sample from the E. I. du Pont de Nemours Co., distilled once and dried over $LiAlH_4$. For larger scale operation tetrahydropyran was refluxed for 2 hr. over CaH_2 and stored above CaH_2 until used.

7. **Benzene**: reagent grade benzene was dried and stored over CaH_2.

8. **Toluene**: reagent grade toluene was dried and stored over CaH_2.

9. **Methylcyclohexane**: technical grade methylcyclohexane was refluxed over CaH_2, distilled and stored over CaH_2.

10. **NaB_3H_8**: sodium triborohydride first described by Hough, Edwards and McElroy,[10] was prepared in this Laboratory by a new and easier procedure suggested from the work of Hough, Edwards and McElroy.[17]

11. **All other reagents**: these were the best available commercial product and were always dried by appropriate methods prior to use.

The Preparation of $H_3NB_3H_7$ by the Reaction between NaB_3H_8 and Ammonium Halides.—In a typical run, 1 to 3 mmoles of NaB_3H_8 and an amount of ammonium chloride or bromide salt about 10% larger than the NaB_3H_8 sample (on an equivalent basis) were loaded in a dry box into a special reactor tube. The tube was equipped with an electromagnetically activated hopper type stirrer and consisted of a 25-mm. Pyrex tube, about 200 mm. long and fitted on the top end with a ₸ 24/40 inner joint. This joint was sealed into an outer joint with de Khotinsky Cement. The outer joint was fastened through a U-bend to a stopcock which was equipped with a standard type mercury protection plug in order to eliminate attack of ether on the stopcock grease.[18] The stopcock assembly then was fastened through a second U-bend to the vacuum system by a greased ₸ 24/40 joint. Dry diethyl ether (about 5 ml.) was distilled into the reactor. The contents of the system were frozen with liquid nitrogen and the reactor was removed from the line at the greased joint. The mercury was put into place by inverting the unit. Then the system was warmed to room temperature. The ether slurry was magnetically stirred at room temperature for periods ranging from 20 to 40 hr. At intervals the mercury plug was removed from the stopcock by a reversal of the above procedure, the system was replaced on the vacuum system and hydrogen was pumped into a gas buret with a Toepler pump. The reaction was continued until the ratio between evolved H_2 and NaB_3H_8 used approached one. In general NH_4Cl seemed to react more rapidly than NH_4Br.

The white precipitate which formed in the ether was removed by filtration in the vacuum line filter assembly and was identified by its X-ray powder pattern as a sodium halide and a small amount of unreacted ammonium halide. When the solvent was distilled under vacuum from the filtrate, either a white solid or a viscous liquid was left in the tube. The tube then was transferred to a cold finger type vacuum sublimation apparatus. When the outer tube was immersed in a 40 to 50° water-bath, $H_3NB_3H_7$ was sublimed from the residue to the cold finger condenser wall (10°). $H_3NB_3H_7$ could be scraped off the cold finger in open air. Yields ranged from a trace to 38%. The microcrystals of $H_3NB_3H_7$ were first characterized on the basis of an elemental analysis and by a molecular weight determination. The observed values were: B = 57.2%, N = 24.4%, H_2 on acid hydrolysis = 141 mmoles/g. Values calculated for $H_3NB_3H_7$ are: B = 57.4%, N = 24.8%, H_2 = 141.5 mmoles/g. based on the hydrolysis equation

$$H_3NB_3H_7 + 9H_2O + H^+ \longrightarrow NH_4^+ + 3B(OH)_3 + 8H_2$$

The molecular weight as determined by a vapor pressure depression in diethyl ether at 21° was 55 in the concentration range of 0.35 to 0.65 molal; the theoretical value for $H_3NB_3H_7$ is 56.5. The molecular weight procedure is the same as that described earlier[19] except for changes necessitated by the change in solvent. Analytical procedures have been described elsewhere.[20]

The Preparation of $H_3NB_3H_7$ by Displacement of an Ether by Ammonia in an Etherate of Triborane. 1. Large Scale Laboratory Synthesis Involving Displacement of Tetrahydropyran.—The process described below is that which was used in preparing approximately 25-g. samples of ammonia–triborane for calorimetric studies[12] and other investigations. At the present time, it represents a relatively large scale synthesis for compounds of this type. It is proper to note that the rapid evolution of diborane during the formation of the etherate may be dangerous if uncontrolled and that localized heating, which may arise in large scale operation, is a major factor in reducing yields of $H_3NB_3H_7$.

The reactor consisted of a 500-ml. three necked flask. One side neck was fitted with a glass plug and the other neck with a low temperature reflux condenser, the outlet of which was connected to a manometer and then through a stopcock

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(14) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, THIS JOURNAL, **74**, 901 (1952).

(15) A. B. Burg and H. I. Schlesinger, *ibid.*, **55**, 4009 (1933).

(16) W. H. Schechter, C. B. Jackson and R. M. Adams, "Boron Hydrides and Related Compounds," 2nd Ed., Callery Chemical Co., Callery, Pa., 1954, p. 17.

(17) W. V. Hough, L. J. Edwards and A. D. McElroy, to be published.

(18) G. Kodama, Ph.D. Dissertation, University of Michigan (1957), p. 82; see also for related structure R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," Type II, Fig. 19, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 69.

(19) R. W. Parry, G. Kodama and D. R. Schultz, THIS JOURNAL, **80**, 24 (1958).

(20) T. C. Bissot, D. H. Campbell and R. W. Parry, *ibid.*, **80**, 1868 (1958).

to the vacuum system. The center neck was equipped with a commercial "Lew" magnetic stirrer (Sci. Glass Apparatus Co., Bloomfield, N. J.). The reactor was evacuated to remove moisture; dry nitrogen then was admitted to the system and the glass plug was removed. A steady stream of dry nitrogen through the system minimized moisture entry while the plug was out. A 100-ml. quantity of dry tetrahydropyran was added through the opening, the plug was replaced, the tetrahydropyran was cooled to −196° and the system evacuated. A 55-ml. sample of liquid tetraborane, measured at 0°, was condensed into the reactor. The temperature was allowed to rise slowly from −196° until evolution of gaseous diborane was noted. At this point it was necessary to again immerse the flask in liquid N_2 until the reaction was moderated. CAUTION. B_2H_6 evolution may be sudden and vigorous.

As diborane evolution proceeded, B_2H_6 was removed to the vacuum line where it was purified and stored. After most of the diborane had been evolved, the reaction flask was cooled to −78° and allowed to stand overnight. The remainder of the diborane, the excess tetrahydropyran and traces of hydrogen gas were then removed from the reactor over the temperature range −78 to 25°.

The tetrahydropyran–triborane which remained in the reactor melted just below room temperature and was unstable in contact with air. The reactor flask was flooded with dry nitrogen under slight pressure, the glass plug was removed from the side neck, and 200 ml. of dry diethyl ether was added. The ethyl ether solution was cooled to −78°, and the system was evacuated. A 15-ml. quantity of anhydrous *liquid* ammonia (measured at −45°) then was cooled to −78° and opened to the reactor. Ammonia, maintained at a constant pressure near 46 mm. in the reactor, was thus absorbed slowly by the constantly stirred ether solution. Approximately 12 hr. elapsed between the beginning of NH_3 absorption and the beginning of the subsequent step. The flask next was warmed to room temperature and the excess ammonia, displaced tetrahydropyran and ethyl ether solvent were distilled from the system and discarded.

The white solid remaining in the flask was primarily ammonia–triborane. It was extracted with three 50-ml. portions of benzene. Each portion of solution was removed through a fritted filter stick inserted through the neck of the reactor flask. An excess of methylcyclohexane (about 300 ml.) was added to the benzene solution, and ammonia–triborane separated as a precipitate. The product was filtered out under a stream of dry nitrogen (not in vacuum system) and was dried under vacuum.

Further purification was effected using the special apparatus shown in Fig. 1. After drying the apparatus shown in Fig. 1 by passing dry nitrogen through it, a six to eight gram aliquot of the crude $H_3NB_3H_7$ from the process above was dissolved in about 60 ml. of dry benzene and placed in funnel I. Methylcyclohexane from funnel II was introduced into the precipitation vessel and the benzene solution of $H_3NB_3H_7$ was filtered through the frit in the stem of funnel I and allowed to drip into the methylcyclohexane in the precipitation vessel. By adjusting flow rates, methylcyclohexane was maintained in a six to one excess during precipitate formation. After precipitation and filtration the solid was washed with a small aliquot of methylcyclohexane and dried with dry nitrogen.

While the dry nitrogen stream passed through the system, the flask used to collect the liquids from the filter was replaced by the recrystallization tube. Funnel I was removed and a 35-ml. portion of toluene was added to the precipitate in the precipitation vessel. About 30 minutes was allowed for the toluene to become saturated with $H_3NB_3H_7$; then the toluene solution was pulled through the frit into the recrystallization tube. The tube was removed under an N_2 stream and capped. This clear solution was cooled to −95° in a toluene slush and the $H_3NB_3H_7$ which crystallized was filtered at −78° under a dry N_2 atmosphere. All retained toluene was removed from the product under vacuum at 25°.

The toluene solution which was recovered contained a considerable amount of ammonia–triborane and was used to further extract the precipitate.

The yield of crude ammonia-triborane was 70 to 80% based on the tetraborane used. Final purification reduced the over-all yield to about 50%. The high purity of the product obtained from the above process was indicated by its stability and by the analysis. Values found were: N = 24.9%; B, 57.2%; H_2 on acid hydrolysis = 141 mmoles/g. Theory: N = 24.8%, B = 57.4%, H_2 = 141.5 mmoles/g.

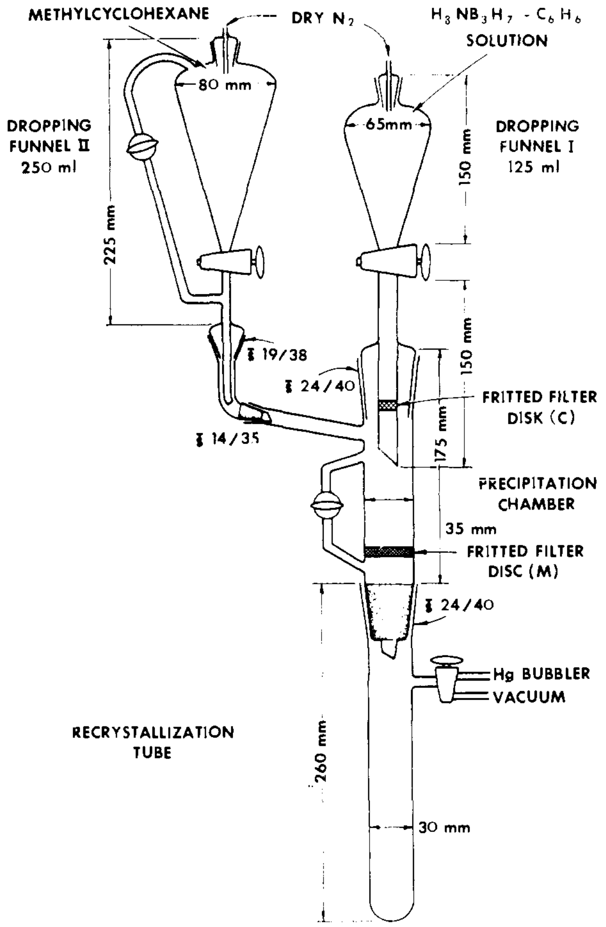

Fig. 1.

2. Small Scale Laboratory Synthesis Involving Displacement of Tetrahydrofuran.—About 5 ml. of tetrahydrofuran and 0.97 mmole of B_4H_{10} were condensed together into a reaction tube; then the temperature was allowed to rise slowly. No reaction was observed up to −23° but at room temperature 0.46 mmole of B_2H_6 was evolved in 0.5 hr. A trace of H_2 gas (0.027 mmole) was collected. Crystalline tetrahydrofuran–triborane remained in the tube when excess tetrahydrofuran was removed. The solid was dissolved in excess tetrahydrofuran again and 0.96 mmole of NH_3 was frozen above the etherate (−196° bath). The system was allowed to warm to room temperature and stirred for 0.5 hr. The solvent was removed at 0°. From the white solid residue a 42.5-mg. sample of $H_3NB_3H_7$ was sublimed (X-ray identification). The yield of still impure product was 79%. Diethyl ether also was used as a solvent for the displacement reaction but neither the yield nor product quality was improved (69%).

3. Attempted Small Scale Laboratory Synthesis using Diethyl Ether.—A sample of B_4H_{10} (1.40 mmoles) was dissolved in about 3 ml. of diethyl ether and the solution was allowed to warm to ice temperature. A very slow and small vapor pressure rise due to B_2H_6 evolution was observed. The system was maintained at ice temperature for 4 hr. Then to permit continuous B_2H_6 removal the stopcock was opened very slightly to the fractionation train while the reaction mixture was maintained at room temperature. B_2H_6 which entered the train was carefully fractionated by vacuum distillation (−78 and −126° traps) until 0.632 mmole of B_2H_6 was obtained. BH_3/B_4H_{10} ratio = 0.975. During the foregoing process less than 0.04 mmole of H_2 was liberated.

Then 1.25 mmoles of NH_3 was introduced slowly to the stirred solution at −78°. A small amount of solid B_4H_{10}·

$2NH_3$ remained in the tube (identified by its X-ray powder pattern) along with a viscous liquid. Only a trace of $H_3NB_3H_7$ could be sublimed from the reaction mixture.

4. **Small Scale Laboratory Synthesis Using Tetrahydropyran.**—A sample of tetraborane (1.69 mmoles) was condensed into 2 ml. of tetrahydropyran and the system was warmed to room temperature. At room temperature the reaction was much slower than that with tetrahydrofuran. In order to minimize attack of the tetrahydropyran on the stopcock grease in the system, the temperature of the reactor was reduced to 0° and maintained for 15 hr. The B_2H_6 evolved (0.817 mmole) was separated by fractionation. The excess tetrahydropyran was removed at 0°; 3 ml. of diethyl ether was condensed into the system; then a sample of ammonia (3.4 mmoles) was added to the reactor and a temperature of −78° was maintained for 10 hr. On removal of the ethers a dry solid was left in the system. $H_3NB_3H_7$ was sublimed at 52° to give an 81% yield (77.8 mg.).

In a second run using 4.75 mmoles of B_4H_{10} and 1.5 ml. of tetrahydropyran conditions were the same as above except the system was allowed to stand for 24 hr. at −78° after addition of 9.80 mmoles (2-fold excess) of ammonia. A 94% yield (0.253 g.) of $H_3NB_3H_7$ could be sublimed from the solid residue.

The Reactions of $H_3NB_3H_7$. 1. **The Reaction of $H_3NB_3H_7$ with Sodium Dissolved in Liquid Ammonia.**—A sample of $H_3NB_3H_7$ (0.189 mmole) was dissolved in about 1.5 ml. of liquid ammonia; sodium metal (0.1 g.) in a small glass tube was added in two portions by breaking the tube immediately before addition. After introducing the first portion, the solution was warmed to −78°. The blue color of Na faded rapidly and 0.10 mmole of H_2 was evolved. No more H_2 was evolved at −78° over 12 hr. The second portion of Na then was added as above. In 20 minutes 0.012 mmole of H_2 was given off. After 5 hr. an additional 0.057 mmole appeared. Total H_2 = 0.169 mmole; $H_2/H_3NB_3H_7 = 0.895$. Further gas evolution was very slow and the solution remained blue. The excess of Na was removed from solution by amalgamation at −35°. Additional H_2 (0.007 mmole) was given off during the amalgamation. The sodium-free clear solution was filtered from the amalgam, and the solvent ammonia was distilled from the filtrate. In the white solid residue $NaBH_4$ was detected by its X-ray powder pattern, but no component soluble in diethyl ether could be extracted from the residue.

2. **The Reaction of $H_3NB_3H_7$ with Trimethylamine.**—A sample of $H_3NB_3H_7$ (0.55 mmole) was placed in a tube and trimethylamine (0.565 mmole) was condensed above it. The system was allowed to warm slowly. At −78° no visible reaction was observed, but as the temperature rose and solid $H_3NB_3H_7$ began to dissolve in liquid trimethylamine, fairly rapid reaction was noted. Without waiting for the completion of the reaction, the non-condensable gas and the volatile components were removed from the system. They were: H_2 = 0.102 mmole, $(CH_3)_3N$ = 0.24 mmole and $(CH_3)_3NBH_3$ about 0.35 mmole. From the solid polymeric residue 0.20 mmole of $H_3NB_3H_7$ was sublimed on warming to 40 to 50°. No $(CH_3)_3NB_3H_7$ could be detected as a product.

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

The Molecular and Crystal Structures of Ammonia-Triborane[1]

BY C. E. NORDMAN AND CURT REIMANN[2]

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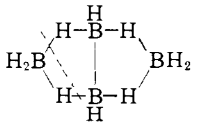
Ammonia-triborane, $H_3NB_3H_7$, forms two crystalline modifications, a disordered, tetragonal form stable at about 25°, and an ordered, monoclinic form stable at lower temperature. Single crystal X-ray diffraction studies of both modifications show that the molecule contains a triangle of boron atoms with a non-coplanar NH_3 group attached to one corner. The arrangement of hydrogen atoms suggests that the B_3H_7 group is a rather strongly distorted fragment of the B_4H_{10} molecule, but the alternative description of $H_3NB_3H_7$ as a bridge substituted diborane, $(H_3NBH_2)B_2H_5$, cannot be entirely ruled out.

Introduction

Ammonia-triborane, $H_3NB_3H_7$, was first prepared by Dr. G. Kodama[3] of this Department. The synthesis was accomplished in low yield by allowing the recently described compound NaB_3H_8[4] to react with NH_4Cl in the presence of diethyl ether.

The structure analysis of the high temperature, disordered modification, to be described below, was begun shortly after the chemical composition and molecular weight had been determined. The main objective of this phase of the structure determination was to establish the gross configuration of the boron-nitrogen skeleton of the molecule.

Ammonia-triborane has subsequently been obtained in good yield through the reaction of NH_3 with several etherates of B_3H_7 such as $Et_2OB_3H_7$, tetrahydropyran-B_3H_7, and others.[3,5] These reactions proceed according to the equation $NH_3 + R_2OB_3H_7 \rightarrow R_2O + H_3NB_3H_7$. It has been shown that such etherates of B_3H_7 are formed, along with B_2H_6, when B_4H_{10} is allowed to react with the appropriate ether.[6] The initial step in the latter reaction presumably involves a cleavage of the tetraborane molecule into BH_3 and B_3H_7 as



This process has been called "symmetrical cleavage" by analogy with a similar cleavage of diborane into two BH_3 groups.

Since the structure of B_4H_{10} is accurately known,[7] an accurate determination of the structure of $H_3NB_3H_7$, including the possible identification of

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[1] Presented, in part, at the Fourth International Congress of the International Union of Crystallography, Montreal, July, 1957, and, in part, at the 133rd Meeting of the American Chemical Society, San Francisco, April, 1958.

[2] Corning Fellow, 1957-1958.

[3] G. Kodama, Doctoral Dissertation, University of Michigan, 1957.

[4] W. V. Hough, L. J. Edwards and A. D. McElroy, THIS JOURNAL, **78**, 689 (1956).

[5] G. Kodama and R. W. Parry, Abstracts, XVI International Congress of Pure and Applied Chemistry, Paris, 1957.

[6] L. J. Edwards, W. V. Hough and M. D. Ford, ref. 5.

[7] M. E. Jones, K. Hedberg and V. Schomaker, THIS JOURNAL, **75**, 4116 (1953); C. E. Nordman and W. N. Lipscomb, *ibid.*, **75**, 4116 (1953); *J. Chem. Phys.*, **21**, 1856 (1953); E. B. Moore, R. E. Dickerson and W. N. Lipscomb, *ibid.*, **27**, 209 (1957).