cm. gas cell with NaCl windows. This cell could be evacuated independently of the rest of the system. A solution of 3.8 g. of ammonium chloride in 20 cc. of distilled water was placed in the generator, the system swept with tank nitrogen, and with a slow sweep of nitrogen, 100 cc. of sodium hypobromite reagent was added dropwise to the ammonium chloride solution. At the conclusion of the reaction the liquid nitrogen trap was isolated from the rest of the system, the gas cell was evacuated and the condensed sample in the liquid nitrogen trap was allowed to expand by evaporation into the gas cell. The contents were finally brought to atmospheric pressure by the addition of tank nitrogen.

Nitric oxide generated by the addition of 50% sulfuric acid to a 4 M solution of potassium nitrite containing 1 M potassium iodide, was collected and purified as described by Johnston and Giauque.[7]

The redistilled nitric oxide was expanded into the 5-cm. gas cell and diluted with nitrogen for spectroscopic examination. The spectra were obtained with a Baird model B double beam infrared spectrophotometer equipped with a sodium chloride prism. The 5-cm. cell containing the gas to be analyzed was placed in the sample beam and a sodium chloride block was placed in the comparison beam.

Oxidation of Ammonia in the Presence of Hydrazine.—The following example is typical of the procedure used in various experiments: 531 mg. of ammonium sulfate, containing 1.064 at. per cent. excess N^{15}, and 529 mg. of hydrazine sulfate were dissolved in a minimal amount of water, cooled with ice, and sodium hypobromite solution was added with vigorous stirring. The amount of sodium hypobromite employed was roughly one-half that required to completely oxidize the combined ammonia and hydrazine present in the solution, and was determined independently on similar quantities of unlabeled material. After the nitrogen evolution had ceased, 0.5 cc. of benzaldehyde was added, the solution was stirred several hours and allowed to stand for 3 days at room temperature. The benzalazine, which separated as yellow crystalline lumps, was filtered with suction, washed well with water and dried. The total yield of 340 mg. was recrystallized twice from ethanol. The two filtrates from the crystallizations, and the crystals of benzalazine were each refluxed 6 hours with 1.5 g. of zinc dust and 6 cc. of 50% acetic acid in ethanol and finally digested with Kjeldahl acid. The at. per cent. excess N^{15} found in the first filtrate, second filtrate and crystals was 0.005, 0.000 and 0.000, respectively.

A similar procedure was used in oxidations involving NaOCl and in some instances the benzalazine was recrystallized three or four times.

Oxidation of Ammonia in the Presence of Hydroxylamine.—A solution of 100 mg. of ammonium sulfate containing 67 at. per cent. N^{15} and 100 mg. of hydroxylamine hydrochloride in 26 cc. of water was cooled with ice, made alkaline with 1 cc. of 6 M sodium hydroxide and with stirring, 0.75 cc. of 0.95 M sodium hypochlorite in 1 M sodium hydroxide was added. After 3–4 minutes the cold solution was acidified with 0.6 ml. of acetic acid and 25 ml. of a 0.25 M solution of acetic acid saturated with salicylaldehyde was added and the mixture warmed. After 10 minutes, 25 ml. of a 3.3% solution of cupric acetate in 0.12 M acetic acid was added and after 15 minutes the solution was cooled and filtered. The copper salicylaldoxime after washing and drying was dissolved in 5 ml. of dioxane and reprecipitated by adding 20 ml. of 0.1 M ammonium acetate in 0.02 M acetic acid. The reprecipitation was repeated three more times. The copper salicylaldoxime was reduced with stannous chloride in 50% acetic acid in ethanol, prior to Kjeldahl digestion.

The procedure employing NaOBr as oxidant was similar.

Los Angeles, California

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[7] H. L. Johnston and W. F. Giauque, This Journal, **51**, 3194 (1929).

[Contribution from the George Herbert Jones Laboratory of the University of Chicago and from the Naval Research Laboratory]

Preparation of Borazole by the Reduction of Trichloroborazole[1a]

By Riley Schaeffer,[1b,c] Martin Steindler,[1b,d] Leo Hohnstedt,[1b] H. S. Smith, Jr.,[1e] L. B. Eddy[1e] and H. I. Schlesinger[1b]

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Trichloroborazole, prepared by the method of Laubengayer and Brown, may be reduced to borazole by lithium aluminum hydride in ethereal solutions, but the borazole cannot be satisfactorily recovered from the reaction product for reasons which are discussed. The difficulty may be overcome by use of lithium borohydride as the reducing agent. The diborane, formed as a by-product in the latter reaction, may be absorbed by sodium trimethoxyborohydride. A satisfactory procedure for preparing borazole by the reduction reaction is described. Reduction of tribromoborazole, prepared as described in the text, offered no advantages. Attention is called to the fact that borazole undergoes slow decomposition even at room temperatures.

A number of inquiries about sources of supply for borazole, $B_3N_3H_6$, and about satisfactory methods for its preparation recently have been received by us. It seems desirable, therefore, to describe newly developed preparative methods, even though we are not certain that we have as yet discovered the most favorable conditions for carrying out the method to be described. Originally borazole was obtained by pyrolysis of either the compounds $B_2H_6{\cdot}2NH_3$ or $B_4H_{10}{\cdot}4NH_3$,[2a] or of mixtures of ammonia and diborane.[2b] More recently it has been prepared by pyrolysis of mixtures of solid lithium borohydride and solid ammonium chloride.[3] The latter method avoids the use of diborane and is rapid, but the yields are no better than obtained by the older methods, and the procedure is not readily adaptable to the preparation of more than small quantities.

A new approach to the problem was suggested by the discovery by Laubengayer and Brown[4] that B-trichloroborazole may be prepared by the action of boron trichloride on ammonium chloride

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[1] (a) The subject matter of this paper is taken from Final Reports on Contract N6ori-20 during the period 1950–1952 and from NRL Memorandum Report 209 (September 15, 1953). The reason for the joint publication and the contribution of each laboratory are explained in the text. (b) University of Chicago; (c) Iowa State College, Ames, Iowa; (d) Argonne National Laboratory, Lemont, Ill.; (e) Naval Research Laboratory.

[2] (a) A. Stock and E. Poland, *Ber.*, **59**, 2215 (1926); A. Stock, E. Wiberg, H. Martini and A. Nicklas, *ibid.*, **63**, 2927 (1930); (b) H. I. Schlesinger, D. M. Ritter and A. B. Burg, This Journal, **60**, 1296 (1938); E. Wiberg and A. Bolz, *Ber.*, **73**, 209 (1940); E. Wiberg, *Naturwiss.*, **35**, 184 (1948).

[3] G. W. Schaeffer, Riley Schaeffer and H. I. Schlesinger, This Journal, **73**, 1612 (1951). It is not unlikely that lithium borohydride could be replaced by sodium borohydride, which is now commercially available.

[4] A. W. Laubengayer and C. A. Brown, Abstracts of Papers presented at the September Meeting of the American Chemical Society, p. 10, P (1949). A detailed description is found in the thesis, "A Study of the Compound B-Trichloroborazole" by Charles A. Brown, Cornell University, 1948.

suspended in chlorobenzene. These authors also report that the compound reacts with lithium aluminum hydride in di-*n*-butyl ether, but they were unable to isolate borazole from the reaction product.

We, nevertheless, decided to investigate the reaction further on the assumption that the unfavorable results obtained by Laubengayer and Brown might have been due to difficulty in recovering borazole from the reaction mixture, rather than to failure of the reaction to proceed in the desired direction. This supposition received support from our observation that small yields of borazole were obtained by the reaction between lithium aluminum hydride and trichloroborazole at room temperature in the absence of solvent. Raising the temperature decreased the yield still further, apparently by secondary reactions leading to the formation of B-chloroborazoles.[5]

After unsuccessful attempts to carry the reaction out in non-ethereal solvents such as chlorobenzene and methylcyclohexane, attention was again turned to ethers. In a number of instances preliminary experiments showed that separation of borazole from the solvents would be difficult.[6] Mixtures of borazole and di-*n*-butyl ether can, however, be distilled away from lithium aluminum hydride and the two volatile components can be separated from each other by fractionation, as shown in the Experimental part.

Nevertheless, practically no borazole was found in the volatile material resulting from the reaction of trichloroborazole with lithium aluminum hydride in di-*n*-butyl ether. We were, therefore, led to consider the possibility that the difficulty might be due to the presence of aluminum hydride formed according to the equation[7]

$$3LiAlH_4 + B_3N_3H_3Cl_3 \longrightarrow B_3N_3H_6 + 3LiCl + 3AlH_3$$

This explanation has received support from the fact that the addition of aluminum hydride to a mixture of borazole and lithium aluminum hydride in the butyl ether prevents the recovery of the borazole. Furthermore, if the interpretation is correct, the difficulty might be overcome by adding lithium hydride to the reaction mixture in order to convert any aluminum hydride formed into lithium aluminum hydride. Actually in a small scale experiment of this sort, about 84% of the theoretically possible borazole was obtained.[8] Unfortunately experiments on a larger scale were unsuccessful. Further observations bearing on this point are mentioned later.

The difficulty due to aluminum hydride can obviously be avoided by using lithium borohydride to reduce trichloroborazole according to the equation[9]

$$3LiBH_4 + B_3N_3H_3Cl_3 \longrightarrow B_3N_3H_6 + 1.5B_2H_6 + 3LiCl$$

The evolution of gaseous diborane makes it possible to follow the course of the reaction without having to separate the borazole from the less volatile products. Thus measurement of the diborane generated showed that the reaction proceeds nearly quantitatively when carried out in diethyl ether solution, even though the borazole could not be recovered easily.[6] Similarly, measurement of the diborane from a reaction carried out in di-*n*-butyl ether indicated that the reaction had gone 95% to completion. In this experiment at least 91% of the theoretical amount of borazole was produced, as shown by its partial isolation and by hydrolysis of the borazole retained by the butyl ether.

Useful as the generation of diborane is as a criterion of the course of the reaction, it is a decided disadvantage to a preparative procedure unless one has use for diborane, and has the apparatus necessary for collecting and storing it. In attempts to avoid or at least to minimize the difficulty, we first used as the reducing agent a mixture containing a relatively small amount of lithium borohydride and a larger quantity of lithium hydride, with the idea that the borohydride might be regenerated by the interaction of the simple hydride with diborane in the presence of the ether.[10] Under these conditions there was no indication that reduction occurred. When we used a mixture containing enough of the borohydride to reduce the trichloroborazole and more than enough of the simple hydride to absorb all of the diborane formed, the pressure of the system first rose rapidly and then dropped slowly. This observation indicates that the evolution of diborane is more rapid than its absorption by lithium hydride. This difficulty might be overcome if it were not for the more serious one that lithium hydride interferes with the separation of the borazole from the reaction mixture.[11]

The most satisfactory solution of the diborane problem so far found is to carry out the reduction with lithium borohydride in apparatus connected with an absorption tower or column charged with sodium trimethoxyborohydride,[12] which absorbs

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[5] In a separate experiment, a mixture of borazole with trichloroborazole, when heated for 15 minutes at 150°, underwent partial conversion to the mono- and dichloro derivatives, as well as some decomposition to non-volatile products.

[6] For example, diethyl ether seems to form an etherate or an azeotrope with borazole, as shown by the fact that at room temperature a mixture of the two liquids has a vapor tension lower than that of either liquid alone. Separation of borazole from dimethyl cellosolve by fractionation could be achieved only after the addition of aluminum chloride, which, however, slowly attacks the borazole.

[7] J. E. Johnson, R. H. Blizzard and H. W. Carhart, THIS JOURNAL, **70**, 3664 (1948), have presented evidence that aluminum hydride is formed as an intermediate in the reduction of alkyl halides by lithium aluminum hydride.

[8] Of the borazole about 75% was isolated as such; the remaining 25% was not separated from the ether but was estimated by hydrolysis of the solution.

[9] We have not attempted to replace the lithium borohydride by the corresponding sodium salt because of the smaller solubility of the latter in ethers. It is conceivable that a slurry of the sodium salt in the solvent might prove effective.

[10] H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and L. R. Rapp, THIS JOURNAL, **75**, 199 (1953).

[11] Partial recovery of borazole may be achieved if the reaction mixture is first filtered and the borazole is separated from the filtrate; but even under these conditions the yields have been low (*ca.* 30%). Preliminary experiments have indicated that lithium hydride may react with borazole, but we do not have reliable data on which to base an explanation of the difficulties caused by either aluminum hydride or by lithium hydride.

[12] The preparation of this compound and its reaction with diborane are described by H. C. Brown, H. I. Schlesinger, I. Sheft and D. M. Ritter, THIS JOURNAL, **75**, 192 (1953), and by H. I. Schlesinger, H. C. Brown, H. R. Hoekstra and Louis R. Rapp, *ibid.*, 200. Sodium trimethoxyborohydride is now available commercially (Metal Hydrides, Inc., Beverly, Massachusetts).

diborane according to the equation

$$B_2H_6 + 2NaBH(OCH_3)_3 \longrightarrow 2NaBH_4 + 2B(OCH_3)_3$$

Absorption of diborane is sufficiently rapid that the methyl borate generated may be exposed to air without hazard, as is described in the Experimental part.[13]

The yields in both steps of the method, *i.e.*, the preparation of trichloroborazole and its reduction to borazole, are greatly dependent on the techniques and conditions employed. After the method of reduction had been developed at the University of Chicago it was employed by H. S. Smith, Jr., and L. B. Eddy at the Naval Research Laboratory. The procedures developed by them are herein described since they are in general superior to those used at Chicago.

It should be mentioned that a number of experiments were made to ascertain whether tribromoborazole could be more readily reduced than the chloro derivative. Since no significant differences were observed, these experiments are not herein reported but the preparation of the bromo derivative is briefly described.

Attention is called to the fact that borazole is somewhat less stable than seems to be generally recognized. The misapprehension is probably due to statements made long ago and based on experiments with small quantities of gaseous borazole. Thus Stock and Pohland[1] stated that borazole remains unchanged for a number of months and that only after long standing does it produce a very thin white deposit on the walls of the vessel. They did not observe the formation of hydrogen in this decomposition.

In contrast thereto we have found that traces of a non-volatile white solid are formed during periods as short as several days, even though the sample of borazole was maintained at −80°. During periods of several weeks at room temperature considerable quantities of hydrogen, together with smaller amounts of diborane and other volatile products are generated. The decomposition seems to occur chiefly in the liquid phase since only traces of hydrogen were formed when borazole was stored in the gaseous state for several months. A few examples are given in the Experimental part.

Experimental Part[14]

Materials.—Chlorobenzene, boron trichloride and lithium hydride were of commercial grade, and were used without purification. Although lithium aluminum hydride and lithium borohydride were recrystallized from diethyl ether for a few experiments, samples of 80–90% purity seemed equally effective. The ammonium chloride was dried at 110° and ground with powdered glass to 200 mesh in a ball mill.

It is necessary to use di-*n*-butyl ether of high purity. Purification* was effected as follows: To 250 cc. of commercial di-*n*-butyl ether in a glass stoppered bottle, 50 cc. of calcium chloride (25 mesh) was added. The stopper was taped shut, and the bottle rolled for four hours. The mixture was filtered through a plug of glass wool and poured through activated silica gel (25–120 mesh) contained in a column 2.5 cm. in diameter and 30 cm. long. The latter process was repeated several dozen times until the refractive index reached a constant value.

Apparatus.—For small scale experiments standard vacuum lines, equipped with mercury float valves and U-tubes for fractional evaporation and condensation, were used. The apparatus for larger scale experiments is described later.

Separation of Borazole from Di-*n*-butyl Ether and Lithium Aluminum Hydride.—The following experiments were carried out to demonstrate that borazole, if formed, could be removed from mixtures containing di-*n*-butyl ether and lithium aluminum hydride.

(a) Mixtures of borazole and the ether were heated in sealed bulbs, and then transferred to the vacuum line. Traces of hydrogen were pumped off, and the volatile material was distilled into concentrated hydrochloric acid. The amount of hydrogen thereby liberated was taken as a measure of the unchanged borazole. In one experiment, in which a mixture of 10 ml. of butyl ether and 1.25 mmoles of borazole was heated for 30 minutes at 100°, 87% of the latter was recovered; from a more concentrated solution (5 ml. of the ether and 1.42 mmoles of borazole) heated for 2 hours at 50°, 92% of the borazole was recovered. These experiments demonstrate that no etherate, non-volatile at the temperatures used, is formed.

(b) A mixture of 4.79 g. of borazole and 30 ml. of the ether was distilled through a small column packed with glass helices. The fraction passing over between 52–54° was collected and weighed. It consisted of about 3.8 g. of borazole, a recovery of 80%. Use of a more effective column would undoubtedly have improved the result.

(c) From a mixture of lithium aluminum hydride and borazole, 85% of the latter was recovered after the mixture had stood for 10 hours at room temperature.

Small Scale Reduction of Trichloroborazole by a Mixture of Lithium Hydride and Lithium Aluminum Hydride.—Trichloroborazole (2.75 mmoles) was mixed with excess lithium hydride in a dry flask. After evacuation of the system a saturated solution of lithium aluminum hydride in di-*n*-butyl ether was added. The mixture was stirred overnight and then fractionated,[15] giving 1.71 mmoles of pure borazole and a fraction containing an additional 0.6 mmole of borazole in *n*-butyl ether. The total yield was thus 84% of the theoretical. However, in a similar experiment in which 30 mmoles of trichloroborazole was to be reduced, practically no borazole was obtained.

Absorption of Diborane by Sodium Trimethoxyborohydride.—To test the effectiveness of sodium trimethoxyborohydride in absorbing the diborane generated in the reduction of trichloroborazole by lithium borohydride, a reduction involving 0.093 mole of the former and about 0.5 mole (a nearly twofold excess) of the latter was carried out in di-*n*-butyl ether. The evolved gas passed from the reaction vessel through a condenser (cooled by circulating methanol at about −60°) into a −80° trap, and from there through an absorption column into a −196° trap. The condenser returned borazole and any unchanged chloroborazoles to the reaction vessel, thus preventing the loss of borazole and assuring complete reduction of lower chloro derivatives. The −80° trap prevented back diffusion of methyl borate, which is formed in the absorption column and which would have destroyed any borazole with which it might have come into contact. The absorption column was approximately 35 cm. in length and 5.2 cm. in diameter, and was charged with 1.0–1.6 cm. lengths of 5 to 8 mm. glass tubing and an amount of sodium trimethoxyborohydride sufficient for a considerable number of preparations.[16] The −196° trap condensed the methyl borate together with any diborane which might have escaped the column.

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[13] Unfortunately methyl borate reacts with borazole. Otherwise trimethoxyborohydride or a mixture thereof with sodium borohydride might be used both to reduce trichloroborazole and to prevent evolution of diborane. It would be desirable to ascertain whether sodium borohydride can be used as the reducing agent in place of the lithium salt; in that case the borohydride produced in the step of absorbing the diborane could be used for further reductions.

[14] Items marked with an asterisk are taken from the NRL Memorandum Report by Smith and Eddy referred to in footnote 1a.

[15] For the fractionation, the reaction mixture was heated till its vapor tension was approximately 150 mm. in a vessel separated from the vacuum line by a float valve. The valve was then opened, and the mixture was distilled rapidly through a −45° trap into one at −196°. Several repetitions of the procedure accumulated a borazole-rich fraction in the latter trap and a dilute borazole fraction in the −45° trap. The former was distilled through a trap at −80° to obtain pure borazole. The dilute fraction was hydrolyzed to determine its borazole content.

[16] The amount used was usually about 250 g. of material still slightly moist with methyl borate.

The trichloroborazole mixed with di-*n*-butyl ether was added to a suspension of lithium borohydride in the same solvent at such a rate that there was no pressure rise due to evolution of diborane. The reaction was carried out in a nitrogen atmosphere and nitrogen was slowly passed through the system after reaction was complete, in order to sweep all diborane into the absorption tower. Completeness of the absorption of diborane is shown by the fact that although the quantities of reagents used were such as to have produced over 3 liters of diborane, the −196° trap could be safely opened to air. Details of manipulation are omitted in view of the description in the section on "Preparation of Borazole."

Preparation of Trichloroborazole.*—The apparatus for the preparation of trichloroborazole consisted of a 2-l., 3-neck flask fitted with a stirrer, a boron trichloride entry tube in the form of a finger cooled by Dry Ice, and with an exit tube having a water cooled condenser topped with another Dry Ice cold finger. The flask was charged with 400 ml. of chlorobenzene and 50 g. of the mixture of ammonium chloride and ground glass (prepared as previously described) and was warmed by a Glas-col heater maintained at 140–150°. Boron chloride was then admitted at a rate such as to produce a drop of condensed gas at about 3-second intervals; the reflux rate at the exit tube was kept low. It was usually possible to introduce about 15–25 g. of boron chloride per hour, and to complete the reaction in about 5 hours, as judged by cessation of the evolution of hydrogen chloride. Excess boron chloride (*ca.* 5%) was allowed to reflux at the exit cold finger for 1 to 1.5 hours after its addition had been completed. Thereafter this cold finger was allowed to warm, and the excess boron trichloride allowed to distil away.

After the reactor had cooled, the supernatant liquid was drawn off and centrifuged. The residual solids were returned to the reaction flask. The centrifugate was separated by fractional distillation into a liquid, which was also returned to the reaction flask, and a solid consisting of crude trichloroborazole. The latter may be purified by vacuum sublimation at 50–60°.

An initial run gave a yield of about 40% based on the equation: $3BCl_3 + 3NH_4Cl \rightarrow B_3N_3Cl_3H_3 + 9HCl$. When the reaction was repeated by adding to the solid residue and the recovered chlorobenzene left over from the first reaction amounts of the reagents equal to those originally used, the yield rose to about 60%. After 2 or 3 repetitions, yields (based on boron chloride consumed) approached 90%. These observations suggest that there may be a gradual build up of intermediates in a series of stepwise, reversible reactions, and that, once equilibrium is attained, practically all of the boron trichloride emerges from the reaction system as trichloroborazole.

Preparation of Borazole.*—In the experiment herein described for the reduction of trichloroborazole to borazole by lithium borohydride, the diborane generated in the reaction was not absorbed. The apparatus for its collection is not shown. The system can be readily adapted for absorption of diborane by sodium trimethoxyborohydride according to the procedure described above.

For the reduction of trichloroborazole, the apparatus was like that for its preparation. The condenser was not used. In its place, the corresponding opening of the 2-l., 3-neck reaction flask was connected by ground glass joints to a smaller flask (200 ml.) which could be rotated so as to discharge its contents into the reaction vessel. The latter was charged with 18 g. of lithium borohydride, 150 ml. of di-*n*-butyl ether (purified as previously described) and 10 g. of powdered Pyrex glass. The smaller (200 ml.) flask contained a mixture of 100 ml. of the ether with 40 g. of trichloroborazole. After flushing the system with dry nitrogen this mixture was slowly added (without contact with stop-cock grease) to the reaction flask by turning the smaller flask. By adding the trichloroborazole to the lithium borohydride an excess of reducing agent is present at all times. This condition is essential to avoid formation of partially reduced chloroborazoles which are difficult to separate from the borazole. The rate of addition was such that about 2 hours were required for the mixing of the reactants; under these conditions reaction occurred about as fast as the trichloroborazole suspension was added, as indicated by the rate of diborane evolution. The reaction proceeded more rapidly in the presence of ground Pyrex glass than without it.

When the reduction was complete, an initial crude separation of borazole from the butyl ether was made by a vacuum distillation of the borazole past the cold finger kept at 0°. The borazole began to distil at about 20 mm. pressure. The pressure gradually fell to about 5 mm., at which the butyl ether started to reflux. Distillation was then stopped.

For purification of the borazole, the impure sample (about 25 ml.) was condensed into a small vessel connected to a manometer and through a stopcock to the vacuum line. The container was maintained at 0° (or at 25°) until the pressure became constant. Thereupon the stopcock was opened slightly and the vapor bled off and discarded, till the pressure of the remaining liquid was within about a millimeter of the vapor tension of pure borazole. The vapor coming off thereafter was collected until the pressure in the container fell more than about a millimeter below the vapor tension of borazole. The residue in the container was discarded. Several repetitions of the procedure led to 13 g. of borazole with vapor tensions of 85 mm. at 0° and 172 mm. at 15°, as compared with literature values of 85 and 170 mm., respectively. The yield was 65% of the theoretical.

Stability of Borazole.—The following observations indicate the extent to which borazole decomposes at room temperature: (1) A 5-mmole sample of borazole after 3 years standing in a glass ampoule had generated 5 mmoles of hydrogen. (2) A small sample (15 cc. gas at S.T.P.) had generated 1.7, 5.7, 9.15 and 12 cc. of hydrogen after 1.8, 4.3, 6.9 and 12.9 months, respectively. (3) Four bulbs containing 25.1, 18.3, 17.6 and 22.8 cc. (S.T.P.) of borazole entirely in the gaseous state gave in 3.5 months only 0.2, 0.06, 0.03 and 0.06 cc. of hydrogen, respectively. During the same time 32.7 cc. of borazole, confined in a tube so that only a small fraction was present as a gas, produced 7.4 cc. of hydrogen. No significant difference in rate of decomposition was observed between experiments run in Pyrex tubes whether they were stored in the dark or exposed to diffuse light in the laboratory. However, in a quartz cell used to determine the ultraviolet spectrum of gaseous borazole, a pronounced white deposit was observed after a few hours. (4) A larger sample (50 mmoles) contained in a 50-cc. bulb had generated 20 mmoles of hydrogen and 1.5 mmoles of diborane after two months. Also formed was a non-volatile white solid and two additional volatile materials, unstable at room temperature, containing boron, nitrogen and hydrogen but not further characterized.

Although the rate of decomposition of borazole is relatively small, it cannot be neglected in connection with the storage of larger quantities of the liquid in sealed glass vessels, nor in experiments requiring high purity.

Preparation of Tribromoborazole.—Tribromoborazole was prepared by a method analogous with that used for the chloro derivative. A considerable excess of boron bromide, after being shaken with mercury to remove traces of bromine, was distilled onto solid ammonium bromide which had been dried at 110° and placed into the 500-ml. reaction flask. To the mixture, approximately 7 ml. of bromobenzene (dried with sodium hydride) per gram of ammonium bromide was added. The flask was fitted with a reflux condenser, and the reactants were heated for 8–12 hours at 120–130°. After the solid ammonium bromide had disappeared and evolution of hydrogen bromide had ceased, the reaction mixture was filtered through a fritted glass filter funnel. The solid product, left after removal of the bromobenzene from the solution, was purified by vacuum sublimation at 60–70°. The purified material melted from 126–128°, but began to decompose slowly at a temperature as low as 90°; at 220° about 75% decomposition occurred in 5 hours.

Anal. Calcd. for $B_3N_3H_3Br_3$: B, 10.2; Br, 75.5; N, 13.3. Found: 11.3, 74.6, 14.2, resp.

CHICAGO, ILLINOIS