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The Preparation of Borazole and its Reactions with Boron Halides[1]

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Borazole has been prepared by the interaction of lithium borohydride and ammonium chloride in the absence of solvents at moderately high temperatures. Although the yields (30–35%) are of the same order of magnitude as those obtained in earlier procedures, the new method is more convenient in that it avoids the use of high pressures and high vacuum apparatus, and does not require the use of diborane. The course of the reaction is briefly discussed. The behavior of borazole toward lithium borohydride, toward diborane, toward ammonium chloride, and toward boron trichloride and tribromide has been studied. The first two do not react appreciably. Ammonium chloride causes extensive decomposition of borazole at temperatures of 275° and above. The boron halides react to give the compounds B-mono and dichloro, and mono and dibromoborazoles, some of the physical properties of which are described.

Borazole ($B_3N_3H_6$) was first prepared in 1926 by the action of heat on the "diammoniate of diborane."[4] Since the original method of preparation cannot be adapted to large scale and is quite time consuming, work on the chemical properties of borazole has been hampered by the small amounts available, and a more convenient method of preparation was desired before extensive investigation of its chemical properties was begun.

Recently Schaeffer and Anderson succeeded in preparing N-trimethylborazole in relatively large amounts by the reaction of lithium borohydride with methylammonium chloride in diethyl ether solution.[5] In the present paper the analogous reaction between lithium borohydride and ammonium chloride in the absence of solvents at high temperature is described. Borazole is obtained according to the equation $3LiBH_4 + 3NH_4Cl \longrightarrow B_3N_3H_6 + 9H_2 + 3LiCl$. The yields were only 30–35% of that demanded by the equation, and, as is seen from the next to the last experiment of Table I, yields of this magnitude were obtained only when powdered or crushed Pyrex glass was added to the reacting solids to prevent caking of the mixtures. It is conceivable that the yields could be increased by more elaborate devices to overcome the caking difficulty. However, the fact that ammonium chloride reacts with borazole, as described in the experimental part of this paper, probably imposes another limiting factor on the yield.

Be that as it may, the actual yields have not been much smaller than those obtained by reaction of diborane with ammonia.[6] The new procedure, on the other hand, has great advantages in avoiding the preparation and handling of diborane, as well as in making it possible to carry out the reaction under nitrogen at atmospheric pressure, instead of requiring sealed vessels and the use of high vacuum apparatus and techniques.

In addition to the volatile borazole, the receiving vessels in which the borazole was condensed contained a second product. Since the latter was non-volatile it must have been formed in the receiving vessels, that is, it could not have been a direct product of the high temperature reaction. Its properties suggest that it might be the "diammoniate of diborane," $B_2H_6 \cdot 2NH_3$.[7]

The by-products of the reaction suggest two possible mechanisms. The first may be expressed by the series of equations

$$6NH_4Cl \longrightarrow 6NH_3 + 6HCl$$
$$6HCl + 6LiBH_4 \longrightarrow 3B_2H_6 + 6LiCl + 6H_2$$
$$3B_2H_6 + 6NH_3 \longrightarrow 2B_3N_3H_6 + 12H_2$$

The presence of the "diammoniate of diborane" in the receiving vessels would then be explained by the assumption that a part of the mixture of diborane and ammonia had escaped unchanged from the high temperature zone and had reacted in the cooler portions where conditions were favorable for the formation of the "diammoniate." A second hypothesis is that the first product of the reaction is ammonium borohydride, NH_4BH_4, which subsequently decomposes to hydrogen and the intermediate, BH_3NH_3. The latter might then by further loss of hydrogen form the trimer $(HBNH)_3$, *i.e.*, borazole. The formation of the "diammoniate" would have to be considered as the product of a side reaction occurring in the cooler portions of the apparatus.

With an adequate supply of borazole assured the reaction of borazole with boron halides was investigated as a means of preparing halogen substituted borazoles. Previously Wiberg had obtained B-trichloro-, B-tribromo- and B-dibromoborazoles, but did not describe their physical and chemical properties.[8] Both boron bromide and boron chloride react with borazole to give the respective mono- and dihalogenoborazoles, hydrogen, non-volatile white solids and one-half mole of diborane per mole of boron halide taken. About 35% of the borazole used in the reactions may be recovered as halogen derivatives; the remainder consists of non-volatile products. The halogeno compounds are moderately stable, volatile com-

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(4) A. Stock and E. Pohland, *Ber.*, **59B**, 2215 (1926).

(5) G. W. Schaeffer and Elaine R. Anderson, THIS JOURNAL, **71**, 2143 (1949).

(6) The best yields by the older method, as described by E. Wiberg and A. Bolz (reference 8) and by H. I. Schlesinger, D. M. Ritter and A. B. Burg (THIS JOURNAL, **60**, 1296 (1938)) are from 35–40%. In a report privately circulated in 1946, and in *Naturwissenschaften*, **35**, 184 (1948), Wiberg refers to unpublished work in which yields of about 50% are said to have been obtained by heating diborane and ammonia rapidly to 250–300°, but since no details are given it is impossible to say how reproducible these results are.

(7) Thus, this material reacted with water to evolve hydrogen, gave borazole when heated, and reduced silver ion to silver in slightly acid aqueous solution. These are all reactions exhibited by the so-called "diammoniate of diborane" prepared by the reaction of B_2H_6 with two moles of NH_3.

(8) E. Wiberg and A. Bolz, *Ber.*, **73**, 209 (1940).

pounds that are hydrolyzed by moist air and attacked by grease. At higher temperatures these compounds undergo simultaneous decomposition to hydrogen and non-volatile white solids, and disproportionation to borazoles containing larger and smaller amounts of halogen. Thus both borazole and B-dichloroborazole are products of the thermal decomposition of B-monochloroborazole.

Experimental

A. Apparatus and Techniques.—The methods and apparatus employed in the purification and identification of borazole, in the study of the reactions of borazole, and in experiments where high pressures were desired, were similar to those of Stock and to those described in the publications of Schlesinger and Burg and their co-workers.[9,10,11] For the preparation of borazole the apparatus shown in Fig. 1 was found to be most convenient.

B. Analytical Methods.—The analytical methods used were those employed by Schlesinger, Ritter and Burg in the study of methyl substituted borazoles.

Gas Volumes.—All volumes, unless otherwise stated, are given in cubic centimeters of gas at 0° and 760 mm. pressure.

Measurement of Vapor Tensions.—The pressures of saturated vapors at different temperatures were determined in static systems. Due to the low volatility of these compounds at room temperature, measurements were carried out at elevated temperatures in the apparatus described by Brown, Taylor and Gerstein.[12] The data for each substance were used to calculate the constants in the equation log $P_{\text{mm.}} = (-A/T) + B$ by the method of least squares. Normal boiling points, heats of vaporization and the Trouton constant were calculated from the resulting equations.

Measurement of Molecular Weights.—Molecular weights for the mono substituted borazoles were calculated from their vapor densities. The agreement between observed and calculated molecular weights is quite satisfactory in view of the small sizes of samples available.

C. Preparation of Borazole.—In a typical preparation 0.133 mole of lithium borohydride was mixed with 0.266 mole of ammonium chloride and 11 g. of crushed Pyrex in a long-necked reaction flask. In other experiments, crushed Pyrex or Pyrex beads were used. The flask was attached to the apparatus in Fig. 1, the apparatus evacuated, and the two U-tubes surrounded by baths of liquid nitrogen. The neck of the flask was heated to 300° and the bulb of the flask was surrounded by a furnace at 290°. The reaction started as indicated by the escape of hydrogen through the mercury bubbler, and the temperature fell to 230°, at which it was maintained during the heating period. Since the evolution of hydrogen had ceased at the end of 20 minutes, the heating was discontinued and the apparatus was again slowly evacuated; all condensable products were retained in the two traps. All volatile condensable materials were transferred to a take-off bulb and introduced into the vacuum line for purification. Fractionation of the material through a −95° bath permitted 37.3 cc. of diborane to pass through while borazole was condensed. The material retained at −95° was essentially pure borazole, but was distilled through a −78° bath to remove traces of less volatile impurities. The borazole which passed through had a zero vapor tension of 85.0 mm. (the vapor tension of pure borazole is 85.3 mm.) and weighed 0.6790 g., a 20% yield based on the lithium borohydride taken.[13] Additional experiments are summarized in Table I. Except where noted, the neck of the reaction flask was heated to 300°. Reactions carried out at elevated pressures are summarized in Table II. Pressures were calculated from the total quantity of gas present, the temperature, and the size of the bomb tube, and thus represent the pressure only at the end of the heating period. Best yields were obtained in experiments at atmospheric pressure at reaction temperatures close to 300°. Yields were relatively independent of the length of the heating period, so long as it was continued until hydrogen evolution had ceased, except in sealed tube experiments were yields decreased as the tubes were heated for longer periods. Investigation of the reaction of borazole with the other materials present in the tube (lithium borohydride, diborane and ammonium chloride) showed that appreciable reaction occurred only with the ammonium chloride. Hydrogen, unchanged borazole, and B-monochloroborazole (identified by a zero vapor tension of 7.5 mm., chloride analysis and infrared spectrum) were the only volatile compounds present in the products of the high temperature reaction of borazole with ammonium chloride. The results of several experiments are given in Table III. Both the lower yields and the decrease of yield with increased heating period in the high pressure preparations of

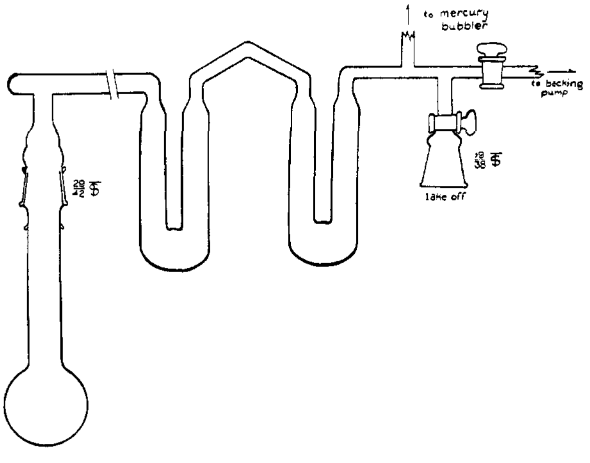

Fig. 1.—Apparatus for the preparation of borazole.

TABLE I

REACTIONS AT ATMOSPHERIC PRESSURE

$LiBH_4$, mole	NH_4Cl, mole	T, °C. init.	T, °C. equil.	Time, min.	Yield, %
0.243	0.485	285	220	30	25.7[a]
.188	.374	275	220	30	32.1[a]
.071	.21	290	220	15	25.7
.105	.13	300	220	15	22.7
.133	.266	290	230	20	28.8
.055	.10	290	230	20	18.2
.076	.15	310	240	20	28.6
.080	.11	300	240	20	35.0
.112	.13	300	290	20	31.5
.118	.13	300	290	30	34.3
.147	.096	300	250	30	9.0[b]
.046	.047	300	220	20	25.0[c]

[a] Neck unheated. [b] No glass beads used in this experiment. [c] Solids allowed to react in ether solution 2.5 hours, solvent removed and solids heated as in other experiments.

TABLE II

REACTIONS AT ELEVATED PRESSURES

$LiBH_4$, mole	NH_4Cl, mole	T, °C. of bomb	Time, min.	P. (app.) atm.	Yield, %
0.229	0.125	100	420	Above 1	3.0[a]
.006	.172	275	35	6.5	17.2
.008	.010	276	30	9.0	19.3
.011	.120	280	30	10.5	24.2
.005	.1	270	20	Above 1	27.9

[a] Reaction mixture ground continuously with six $^1/_8$ inch steel balls.

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[9] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.

[10] H. I. Schlesinger and A. B. Burg, *Chem. Revs.*, **31**, 17 (1942).

[11] H. I. Schlesinger, D. M. Ritter and A. B. Burg, THIS JOURNAL, **60**, 1296 (1938).

[12] H. C. Brown, M. D. Taylor and M. Gerstein, *ibid.*, **66**, 432 (1944).

[13] Borazole may be stored indefinitely with essentially no decomposition as a gas. In the liquid phase at room temperature about 10% of the borazole decomposes per month, evolving hydrogen and diborane in addition to forming non-volatile products.

borazole are probably the result of this secondary reaction with ammonium chloride.

TABLE III

REACTION OF BORAZOLE WITH AMMONIUM CHLORIDE

NH_4Cl, g.	$B_3N_3H_6$, cc.	Temp., °C.	Time, min.	H_2, cc.	$B_3N_3H_6$ recovered, %	$B_3N_3H_5Cl$, cc.
0.5	26.8	100	20	0.0	100	0.0
.1	37.5	275	20	15.5	78	5.2
.58	57.9	290	30	60.9	38	
.5	47.3	270	90	45.8	40	1.9
.5	48.3	310	10	84.6	13	2.0

D. **Reaction of Borazole with Boron Halides.**—The reaction of borazole with boron halides was carried out at room temperature using about four millimoles of borazole per millimole of boron trihalide. Hydrogen and non-volatile solids were produced in all reactions. Volatile, condensable products were transferred to the vacuum line and separated by fractionation through a series of traps at −45°, −80°, −112°, and −196°. On warming, the traps were found to contain the B-dihalogenoborazole, the B-monohalogenoborazole, excess borazole, and diborane, respectively. No evidence was found for the formation of trihalogenoborazoles under the conditions employed.

In a typical experiment, 82.3 cc. of borazole and 23.8 cc. of boron trichloride were allowed to react in a sealed tube for 116 hours at room temperature. The tube was opened and 17.1 cc. of hydrogen removed. The volatile mixture was separated by the fractionation outlined above into 12.2 cc. of diborane (V. T. at −112°, 225 mm.), 9.1 cc. of borazole (zero vapor tension of 85 mm.), 19.6 cc. of monochloroborazole and unmeasured dichloroborazole. Identical procedures using boron bromide in place of boron chloride gave quite similar results.

Analysis of the four compounds gave the following results: Calcd. for $B_3N_3H_5Cl$: hydrogen on hydrolysis, 1.74; B, 28.2; N, 36.5; Cl, 30.8. Found: hydrogen, 1.74; B, 27.8; N, 36.0; Cl, 30.8.

Calcd. for $B_3N_3H_5Br$: hydrogen on hydrolysis, 1.25; B, 20.3; N, 26.3; Br, 50.2. Found: hydrogen, 1.25; B, 20.9; N, 26.0; Br, 53.3.

Calcd. for $B_3N_3H_4Cl_2$: hydrogen on hydrolysis, 0.67; B, 21.7; N, 28.1; Cl, 47.5. Found: hydrogen, 0.67; B, 21.7; N, 28.4; Cl, 47.5.

Calcd. for $B_3N_3H_4Br_2$: hydrogen on hydrolysis, 0.42; B, 13.6; N, 17.6; Br, 67.2. Found: hydrogen, 0.42; B, 14.3; N, 17.5; Br, 61.8.

Only 9 mg. of the dibromo compound was available for analysis and the results are as good as may be expected. The other analyses reported are in general the average of two or more determinations. Characterization as B-derivatives is definitely established by the hydrogen analysis in each case.

The melting points together with the observed and calculated molecular weights are given in Table IV. Both dihalogenoborazoles are unstable toward heat, thus making molecular weight determination at elevated temperatures impossible.

Vapor tensions of the four compounds were determined at several temperatures. The constants of the equation $\log P = (-A/T) + B$ are recorded in Table V for each of the compounds together with physical constants derived from these equations. The equation for B-dibromoborazole is for temperatures above the melting point.

TABLE IV

PHYSICAL PROPERTIES OF THE MONO- AND DIHALOGENOBORAZOLES

Compound	Mol. wt. Obsd.	Mol. wt. Calcd.	M.p., °C.
$B_3N_3H_5Cl$	117.5	114.9	−34.6
$B_3N_3H_5Br$	156.0	159.4	−34.8
$B_3N_3H_4Cl_2$	x	149.4	33.0–33.5
$B_3N_3H_4Br_2$	x	238.3	49.5–50.0

TABLE V

VAPOR TENSIONS OF MONO- AND DIHALOGENOBORAZOLES

Compound	*A* of equation	*B* of equation	B.p.,[a] °C.	Heat of vap., calcd.	Trouton[a] constant
$B_3N_3H_5Cl$	1846	7.703	109.5	8445	22.1
$B_2N_3H_5Br$	2172	8.373	122.3	9939	25.1
$B_3N_3H_4Cl_2$	1994	7.572	151.9	9125	21.5
$B_3N_3H_4Br_2$	2849	9.352	167.1	13037	29.6

[a] Due to the large extrapolation involved, these values must be considered approximate only.

The agreement between the observed pressures and those calculated by use of the constants reported in Table V is quite satisfactory, as can be seen from Table VI.

TABLE VI

COMPARISON OF OBSERVED AND CALCULATED VAPOR TENSIONS

$B_3N_3H_5Cl$							
T, °A., (obsd.)		273.2	282.7	298.7	311.7	315.5	320.2
V.T., mm.	obsd.	8.4	14.9	33.1	62.3	72.2	86.3
	calcd.	8.8	14.9	33.3	60.4	72.2	86.7
$B_3N_3H_5Br$							
T, °A., (obsd.)		299.6	310.0	315.2	327.5	337.1	343.2
V.T., mm.	obsd.	13.3	23.3	30.1	55.1	85.9	110.1
	calcd.	13.3	23.3	30.4	55.1	85.3	111.8
$B_3N_3H_4Cl_2$							
T, °A., (obsd.)		310.8	322.8	331.3	337.2	351.5	361.6
V.T., mm.	obsd.	13.7	24.6	35.2	46.5	81.1	115.8
	calcd.	14.3	24.8	35.7	45.6	79.5	114.5
$B_3N_3H_4Br_2$							
T, °A., (obsd.)		303.8	326.3	340.9	353.4	362.3	390.3
V.T., mm.	obsd.	0.9	4.3	9.3	18.2	31.5	122.4
	calcd.	1.0	4.2	9.9	19.5	30.8	113.0

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