

hydric hydrogen analyses were obtained. A conventional vacuum line equipped with a gas measuring apparatus was used. Approximately 2.0 mmoles of sample was accurately weighed and introduced into a dry flask attached to the vacuum line. About 10 ml. of approximately 1 *N* aqueous trifluoroacetic acid was added through a side arm and the evolved hydrogen collected. Table I records the results obtained.

General Procedure for the Preparation of 2-Alkylborobenzimidazolines.—The 2-alkylborobenzimidazolines reported in Table I were prepared by the method of Nyilas and

Soloway.⁹ These same materials were prepared by the reaction of 0.02 mole each of trimethylamine alkylborane and *o*-phenylenediamine in 10 ml. of dry benzene at the reflux temperature. After the cessation of hydrogen and trimethylamine evolution, the reaction mixture was cooled, the solvent reduced in volume to about 3–4 ml. and 10 ml. of dry pentane was added. The crystalline product was separated by filtration and recrystallized to constant melting point from benzene–pentane. Table I reports the analytical data and melting points obtained. Yields reported in Table I are yields of crude, although essentially pure, product.

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Amine Boranes. VI. The Preparation of B,B,B-Trialkylborazines from Trimethylamine Alkylboranes and Ammonia¹

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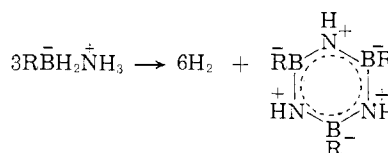
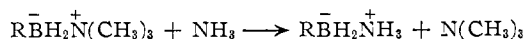
The reaction of trimethylamine alkylboranes with excess ammonia in diglyme solution at 100–150° yields the corresponding B,B,B-trialkylborazines, hydrogen and trimethylamine. The reaction apparently is catalyzed by ammonium chloride. Yields of borazine ranged from 65 to 91%.

The previous paper of this series² described a convenient synthesis of a variety of trimethylamine alkylboranes. In addition, the conversion of these materials to the corresponding 2-alkyl borobenzimidazolines was demonstrated. The latter series of reactions consisted of the elimination of a hydrogen molecule from a hydric B–H group and an acidic hydrogen of a primary amino function. The similar reaction of a series of trimethylamine alkylboranes and ammonia was subsequently employed as a general route to the relatively rare B,B,B-trialkylborazines. That study is reported here.

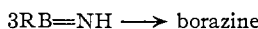
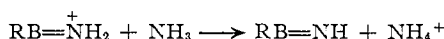
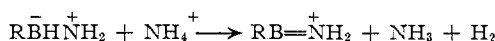
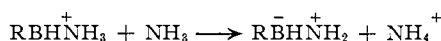
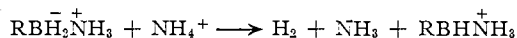
Although borazine has been known for some years and many varieties of substituted borazines have been prepared by convenient procedures, relatively few B,B,B-trialkylborazines have been reported. Procedures employed in the past for the preparation of these compounds have been of three general types: treatment of trimethylborane with borazine³ at high temperature, the condensation of methylboranes with ammonia,⁴ and more recently the direct reaction of alkylchloroboranes with ammonia.⁵ In view of the fact that no convenient method existed for the preparation of borazines of this type, it was desirable to develop a simple and reliable synthetic method.

Trimethylamine alkylboranes were logical starting materials since they could be prepared conveniently in good yield.^{2,3} Furthermore, the ease with which these materials could be handled in the laboratory would allow the use of conventional laboratory equipment and avoid tedious vacuum line manipulations. Formally, the displacement

of trimethylamine from a trimethylamine alkylborane with ammonia would produce an intermediate which is capable of conversion to the corresponding B,B,B-trialkylborazine by the elimination of hydrogen.



Accordingly, trimethylamine alkylboranes were found to react rapidly with excess ammonia at atmospheric pressure and in the presence of ammonium chloride catalyst. Diglyme was employed as the reaction medium and a reaction temperature of 100–150° was required. In each case studied, hydrogen was eliminated smoothly along with trimethylamine. The precise role of the ammonium chloride catalyst is presently unknown. However, it is apparent that the ammonium ion may function as proton source under the reaction conditions and thus catalyze the removal of hydric hydrogen from an intermediate amine borane.⁶ An example of such a reaction sequence is



The B,B,B-trialkylborazine products were isolated from the reaction mixtures by fractional distil-

(6) It is recognized that the reaction of trialkylamine alkylborane with ammonium ion could initiate the reaction sequence which leads to the borazine. Trimethylamine must then be displaced from an intermediate. Such a wide variety of possible mechanisms exist as to make further discussion unprofitable.

(1) Presented in preliminary form as a Communication to the Editor, *J. Am. Chem. Soc.*, **81**, 5836 (1959).

(2) M. F. Hawthorne, *ibid.*, **83**, 831 (1961).

(3) H. I. Schlesinger, D. M. Ritter and A. B. Burg, *ibid.*, **60**, 1296 (1938).

(4) H. I. Schlesinger, L. Horvitz and A. B. Burg, *ibid.*, **58**, 409 (1936).

(5) W. Ruigh, 16th International Congress of Pure and Applied Chemistry, Paris, 1957; "Papers Presented to the Section on Mineral Chemistry," Butterworth's Scientific Publications, London, 1958, p. 545.

TABLE I
 CHARACTERIZATION OF B,B,B-TRIALKYLBORAZINES

B-Alkyl group	Yield, %	B.p.		Analyses, %				Found			
		°C.	mm.	Calcd.		C		H		B	
1-Propyl	88	108	9	52.28	11.70	15.70	20.32	52.36	11.84	15.74	20.25
2-Propyl	79	70	0.5	52.28	11.70	15.70	20.32	51.95	11.62	15.60	20.51
1-Butyl	91	110	.6	57.92	12.16	13.04	16.88	57.97	12.00	12.94	16.68
2-Butyl	85	94	.7	57.92	12.16	13.04	16.88	57.90	11.91	12.90	16.72
<i>i</i> -Butyl	70	72	.03	57.92	12.16	13.04	16.88	57.84	11.87	12.75	17.10
<i>t</i> -Butyl	65	60	.10	57.92	12.16	13.04	16.88	58.21	12.20	12.93	16.60
1-Pentyl	88	125	.07	61.92	12.47	11.16	14.45	61.70	12.35	11.08	14.35
1-Hexyl	86	140	.05	64.92	12.71	12.62	9.75	64.75	12.67	12.52	9.52
Benzyl	70	^a		71.88	6.89	9.25	11.98	72.18	7.73	9.51	11.70

^a Purified by molecular distillation.

lation at reduced pressure. Yields were of the order of 65 to 91%. Table I reports the preparative and characterization data obtained.

Ultraviolet, Infrared and N.m.r. Spectra.—The ultraviolet absorption spectra of several B,B,B-trialkylborazines were examined in *n*-hexane solution. In each case, only weak end absorption was observed. These results are in agreement with those of Rector, Schaeffer and Platt⁷ who found B,B,B-trimethylborazine to be transparent above 210 m μ in *n*-heptane solution.

Examination of the infrared spectrum of each substituted borazine reported in Table I resulted in only three groups of absorptions which were truly characteristic of these compounds: NH stretching at 2.95 μ and strong absorptions near 7.10 and 14.0 μ . The latter two absorptions have been assigned as in-plane ring deformation and NH in-plane bending, respectively.⁸

The H¹ nuclear magnetic resonance spectrum of each of the borazines of Table I was obtained. In every case NH resonance was apparent as a broad, low field singlet. The resonance lines due to the C-H of the various B-alkyl substituents were in good agreement with their assigned structure. Therefore, alkyl group isomerization does not occur under the experimental conditions employed in the preparation and purification of these borazines.⁹

The B¹¹ nuclear magnetic resonance spectrum of each B,B,B-trialkylborazine prepared in this study was observed as a singlet with δ between -16.8 and -18.0 $\times 10^{-6}$ relative to trimethyl borate. Phillips, Miller and Muetterties¹⁰ report δ values of -12.3 $\times 10^{-6}$ and -14.3 $\times 10^{-6}$ for borazine and N,N,N-trimethylborazine, respectively. The

(7) C. W. Rector, G. W. Schaeffer and J. R. Platt, *J. Chem. Phys.*, **17**, 400 (1949).

(8) For a summary of borazine chemistry and spectra see J. C. Sheldon and B. C. Smith, *Quart. Revs.*, **14**, 200 (1960).

(9) In view of the facile isomerization of alkylboranes observed at elevated temperatures this point is significant. See G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutowski, Abstracts of Papers, 130th Meeting of the American Chemical Society, Sept., 1956, p. 53-O, and *J. Am. Chem. Soc.*, **79**, 5190 (1957). See also H. C. Brown and B. C. Subba Rao, *J. Org. Chem.*, **22**, 1136 (1957); and *J. Am. Chem. Soc.*, **81**, 6434 (1959).

(10) W. D. Phillips, H. C. Miller and E. L. Muetterties, *ibid.*, **81**, 4496 (1959).

agreement is satisfactory since all samples were examined as neat liquids.

Chemical Stability of B,B,B-Trialkylborazines.—The B,B,B-trialkylborazines prepared in this study were not vigorously attacked by water. However, upon standing a few hours in contact with water, ammonia and the corresponding alkylboronic acid were formed.

B,B,B-Trialkylborazines which had been stored in the absence of air and water vapor often developed a yellow coloration after a few months and deposited small amounts of unidentified solids.

Experimental

Materials.—Trialkylamine alkylboranes were prepared as previously described.^{2,3} These materials were used without purification.

Diglyme was purified by distillation from lithium aluminum hydride at reduced pressure and stored in tightly sealed bottles; b.p. 62° at 17 mm.

General Procedure for the Preparation of B,B,B-Trialkylborazines.—In a three-necked 100-ml. flask was placed 0.5 g. of dry ammonium chloride, 15 ml. of purified diglyme and 0.10 mole of crude trimethylamine alkylborane. The reaction flask was equipped with an efficient stirrer, gas inlet tube and a water-cooled reflux condenser. The system was thoroughly flushed with dry ammonia and a slow stream (*ca.* 50 ml. per minute) passed beneath the surface of the reaction mixture. An oil-bath at 100° was placed around the reaction flask and the temperature slowly raised to 140–150° during the course of 2 hours. Vigorous stirring was maintained during the reaction period. When hydrogen evolution was no longer observed, the solution was cooled to room temperature and the reaction mixture transferred to a distillation flask. Diglyme was removed at 17 mm. and 62° with an efficient fractionating column of the spinning-band type. The pressure then was lowered and the borazine product slowly distilled. In the case of B,B,B-tribenzyl the product was distilled with a small molecular still of the Washburn type. Table I records yields, boiling points and analytical data. Due to the sensitivity of the products to moisture, refractive indices were not obtained.

Nuclear Magnetic Resonance Measurements.—A Varian high resolution nuclear magnetic resonance spectrometer was employed with 40 mc. and 12.8 mc. probes for H¹ and B¹¹ spectra, respectively. Spectra were obtained with pure liquids. The B¹¹ spectra were measured with reference to methyl borate.¹⁰

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