

teristic borazine ring absorptions are found near 1400  $\text{cm}^{-1}$  in the N-phenyl derivatives and between 1460 and 1450  $\text{cm}^{-1}$  in the N-methylborazines. Absorption at 1492 and 1497  $\text{cm}^{-1}$  in  $(\text{CH}_3\text{HN})_3[\text{BN}]_3(\text{CH}_3)_3$  and  $[(\text{CH}_3)_2\text{N}]_3[\text{BN}]_3(\text{CH}_3)_3$  may be due to an antisymmetrical deformation mode of the aminomethyl group, since no corresponding band is found in the spectrum of  $(\text{H}_2\text{N})_3[\text{BN}]_3(\text{CH}_3)_3$ . These bands are at higher frequency than normally expected for  $\text{CH}_3$  deformation modes but analogous shifts of the methyl deformation bands in the borate esters have been noted.<sup>16</sup> The B-tris-(methylamino)- and B-tris-(dimethylamino)-N-triphenylborazines absorb at 1450 and 1460  $\text{cm}^{-1}$  and no corresponding band is found for B-triamino-N-triphenylborazine. Accordingly, this band could be assigned to an aminomethyl deformation mode. If reliable assignments of the methyl deformation bands could be made, correlation with the electronic environment of the nitrogen atoms might be possible.<sup>17</sup>

Niendenzu and Dawson<sup>2</sup> have suggested that the side chain B-N vibrational mode absorbs at 1350  $\text{cm}^{-1}$ . No distinct bands were observed at that frequency, for compounds reported here, although weak bands near

(16) W. J. Lehmann, T. P. Onak, and I. Shapiro, *J. Chem. Phys.*, **30**, 1215 (1959).

(17) L. J. Bellamy and R. L. Williams, *J. Chem. Soc.*, 2753 (1956).

1350  $\text{cm}^{-1}$  generally appeared as shoulders on the stronger bands in the 1400  $\text{cm}^{-1}$  region. Medium intensity bands near 700  $\text{cm}^{-1}$  were found for all the B-aminoborazines and these bands may be due to a skeletal  $\text{N}_3\text{B}_3\text{N}_3$  vibration as suggested by Aubrey and Lappert.<sup>3</sup> However, it should be noted that the 697  $\text{cm}^{-1}$  band is characteristic of monosubstituted aromatics and N-trimethylborazine and its B-trichloro derivative absorb near 670  $\text{cm}^{-1}$ .

The spectra of the pyrolysis products, obtained from the solids in KBr matrix, were similar to those of the parent compounds. In general, however, all the bands were broadened and this was particularly true for the bands due to borazine ring vibrations and methyl deformation modes. This effect probably reflects the great multitude of structural features present in the polymeric residues.

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CONTRIBUTION FROM U. S. BORAX RESEARCH CORPORATION,  
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## Borazole Exchange Reactions<sup>1</sup>

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Hexamethylborazole was found to exchange boron substituents with B-trichloro-N-trimethylborazole at 250–350°. An apparent equilibrium is established between starting materials and the unsymmetrical species, B-chloro-B-dimethyl-N-trimethylborazole and B-dichloro-B-methyl-N-trimethylborazole. The equilibrium concentrations do not correspond to a random distribution and indicate the operation of electronic effects in the exchange process. Hexamethylborazole and N-trimethylborazole were observed to exchange boron substituents slowly at 175°.

### Introduction

Substituted borazoles have been reported to undergo exchange with trimethylborane,<sup>2</sup> trihaloboranes,<sup>3</sup> and with amino-(dimethyl)-borane.<sup>4</sup> Evidence for exchange of B-chloro and B-ethyl groups during attempted distillation of a B-chloro-(ethyl)-N-trimethylborazole mixture was observed by Sisler, *et al.*<sup>5</sup> Schaeffer<sup>3</sup> has reported hydrogen-chlorine exchange between borazole and B-trichloroborazole. Substituent exchange

is well known in other boron systems, such as alkylvinylboranes,<sup>6</sup> alkylhaloboranes,<sup>7,8</sup> trialkylboranes,<sup>9</sup> and haloboranes.<sup>10</sup> In the present study, exchange reactions of hexamethylborazole with B-trichloro-N-trimethylborazole and with N-trimethylborazole have been observed.

### Results and Discussion

The exchange reactions were carried out by heating the borazole mixtures in sealed Pyrex tubes. In the B-trichloro-N-trimethylborazole-hexamethylborazole

(1) This research was sponsored by Wright Air Development Division, Air Research and Development Command, United States Air Force, under Contract AF 33(616)-7303.

(2) H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *J. Am. Chem. Soc.*, **60**, 1296 (1938).

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system, the products were reduced with sodium borohydride and the resulting B-hydrido-(methyl)-N-trimethylborazole mixture analyzed by vapor phase chromatography. In the N-trimethylborazole-hexamethylborazole reaction, the products were analyzed directly by vapor phase chromatography.

The changing composition of an initially 2:1 mixture of B-trichloro-N-trimethylborazole and hexamethylborazole at 250 and 350° is shown as a function of time in Fig. 1 and 2. The unsymmetrical species are produced at the expense of starting materials until an apparent equilibrium situation is achieved. The process is shown in eq. 1. Equilibria 2 and 3 also are



A = (ClBNC<sub>3</sub>)<sub>3</sub>; B = (CH<sub>3</sub>BNCH<sub>3</sub>)<sub>3</sub>;  
C = Cl<sub>2</sub>CH<sub>3</sub>B<sub>3</sub>N<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>; D = Cl(CH<sub>3</sub>)<sub>2</sub>B<sub>3</sub>N<sub>3</sub>(CH<sub>3</sub>)<sub>3</sub>

involved, but the over-all exchange can be described by eq. 1. The data at 250° for an initial A:B ratio of 2:1 give an apparent equilibrium constant of 55.

$$K_1 = (C)(D)/(A)(B) = 55$$

In order to verify that equilibrium had been achieved, reaction mixtures with initial A:B molar ratios of 1:1 and 1:2 were prepared and heated for comparison of  $K_1$  values with those obtained for the 2:1 mixture.<sup>11</sup> These runs were carried out at 250° for 153 hr. to correspond with the final values of Table I. The results, listed in Table II, support the contention that equilibrium is achieved under these conditions. The agreement among the  $K_1$  values is within the limits of the vapor phase chromatographic data which lacked quadri-component calibration.

If the exchange processes occurred strictly at random, with no chemical influences being exerted on the product distribution (*i.e.*,  $\Delta H = 0$ ), the equilibrium composition which would obtain is calculable by the method of Calingaert.<sup>12</sup> The random composition is shown in Table I and is indicated by the points in

TABLE I  
EXCHANGE REACTION OF B-TRICHLORO-N-TRIMETHYLBORAZOLE  
AND HEXAMETHYLBORAZOLE AT 250°

Reaction time, hr.	Product mixture, mole %			
	A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	D <sup>d</sup>
0	66.7	33.3	0	0
4	62.4	23.8	6.1	7.7
10	53.8	13.1	14.7	18.3
72	26.4	0.7	56.2	16.7
120	24.7	0.7	57.4	17.2
153	23.5	0.8	57.7	17.9
Random <sup>e</sup>	29.7	3.3	44.5	22.2

<sup>a</sup> B-Trichloro-N-trimethylborazole. <sup>b</sup> Hexamethylborazole.  
<sup>c</sup> B-Dichloro-B-methyl-N-trimethylborazole. <sup>d</sup> B-Chloro-B-dimethyl-N-trimethylborazole. <sup>e</sup> Calculated by the method of Calingaert, ref. 12.

(11) A mixture with an initial molar ratio of 5:1 was treated similarly (250° for 153 hr.). A value of 31 for  $K_1$  was obtained, but the reliability was questionable because two of the components gave peaks on the vapor phase chromatogram which were too small for accurate measurement.

(12) G. Calingaert and H. A. Beatty, *J. Am. Chem. Soc.*, **61**, 2748 (1939).

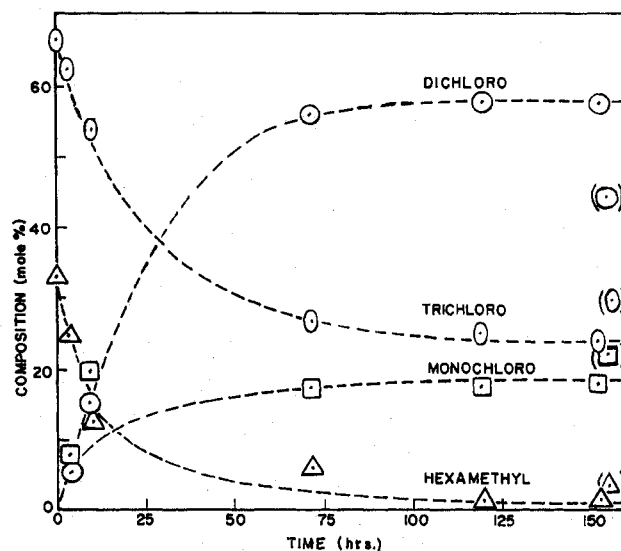


Fig. 1.—B-Trichloro-N-trimethylborazole-hexamethylborazole redistribution at 250°: dichloro = B-dichloro-B-methyl-N-trimethylborazole; trichloro = B-trichloro-N-trimethylborazole; monochloro = B-chloro-B-dimethyl-N-trimethylborazole; hexamethyl = hexamethylborazole.

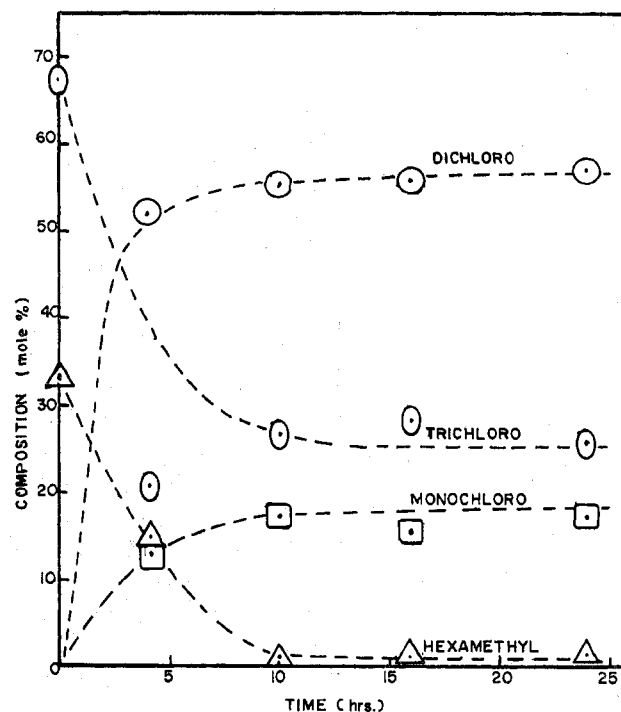


Fig. 2.—B-Trichloro-N-trimethylborazole-hexamethylborazole redistribution at 350°: dichloro = B-dichloro-B-methyl-N-trimethylborazole; trichloro = B-trichloro-N-trimethylborazole; monochloro = B-chloro-B-dimethyl-N-trimethylborazole; hexamethyl = hexamethylborazole.

parentheses in Fig. 1. These theoretical concentrations give a value of 9.0 for  $K_1$ . The lack of correspondence of the constant for random redistribution with that experimentally obtained suggests the operation of substituent effects in the exchange of chloro and methyl groups on boron in these borazoles.

The equilibrium constant at 350° (Fig. 2 and Table III) may be compared with that at 250°. Substitution

TABLE II  
EXCHANGE REACTIONS OF B-TRICHLORO-N-TRIMETHYLBORAZOLE  
AND HEXAMETHYLBORAZOLE MIXTURES AT 250° FOR 153 HOURS

Run	Composition, mole %				K <sub>1</sub> <sup>e</sup>
	A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	D <sup>d</sup>	
1. Initial	50.0	50.0	0	0	
1. Final	6.08	5.31	46.28	42.40	61
2. Initial	33.3	66.7	0	0	
2. Final	1.0	21.7	19.75	57.6	52
3. Initial	66.7	33.3	0	0	
3. Final	23.5	0.8	57.7	17.9	55
					Av. 56 ± 3

<sup>a</sup> B-Trichloro-N-trimethylborazole. <sup>b</sup> Hexamethylborazole.  
<sup>c</sup> B-Dichloro-B-methyl-N-trimethylborazole. <sup>d</sup> B-Chloro-B-dimethyl-N-trimethylborazole. <sup>e</sup> Equilibrium constant for eq. 1.  
<sup>f</sup> See Table I.

TABLE III  
EXCHANGE REACTION OF B-TRICHLORO-N-TRIMETHYLBORAZOLE  
AND HEXAMETHYLBORAZOLE AT 350°

Reaction time, hr.	Product mixture, mole %				K <sub>1</sub> <sup>e</sup>
	A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	D <sup>d</sup>	
0	66.7	33.3	0	0	
4	20.8	13.7	52.3	13.2	
10	26.6	0.7	55.4	17.2	
16	28.0	0.7	55.8	15.5	
24	25.1	1.1	56.8	17.0	35

<sup>a</sup> B-Trichloro-N-trimethylborazole. <sup>b</sup> Hexamethylborazole.  
<sup>c</sup> B-Dichloro-B-methyl-N-trimethylborazole. <sup>d</sup> B-Chloro-B-dimethyl-N-trimethylborazole. <sup>e</sup> Equilibrium constant for eq. 1.

of these values in the Arrhenius equation shows an enthalpy change of  $-3.5$  kcal./mole for the process in eq. 1.

Boron substituent exchange is generally considered<sup>5,6,13,14</sup> to proceed through a four-centered species; whether this represents a transition state or a short-lived intermediate is not resolved. Prior exchange data have been difficult to rationalize completely, probably due to the simultaneous application of steric, inductive, and mesomeric effects. From this standpoint, substituted borazoles provide a convenient system for investigation: the reaction center is flanked by N-methyl groups throughout the reaction series, thus removing any complications due to differences in steric requirements. Therefore, the observed product distributions can be rationalized in terms of electronic effects; differences are due solely to the influence exerted at the reaction center by the substituents on the other two boron atoms. The observation of a greater than random concentration of unsymmetrical species in the equilibrium mixture, therefore, indicates a transfer of electronic effects from boron substituents through the borazole ring.

Previously reported data relating to the question of the ability of the borazole ring to transmit electronic effects are inconclusive. Smalley and Stafiej<sup>15</sup> obtained good selectivity in the partial alkylation of N-triphenylborazole with alkylmagnesium bromide. However, N-trimethylborazole alkylation gave nearly ran-

dom products. Similarly, Sisler<sup>5</sup> found the successive rate constants for the Grignard butylation of B-trichloro-N-trimethylborazole to be essentially equal.

Exchange of hydrogen and methyl groups between N-trimethylborazole and hexamethylborazole also was demonstrated (Table IV). Exchange was found to occur in the same temperature region as for the B-chloro-B-methyl system, but equilibrium was not demonstrated.

TABLE IV  
EXCHANGE REACTION OF N-TRIMETHYLBORAZOLE  
AND HEXAMETHYLBORAZOLE AT 175°

Reaction time, hr.	Product mixture, mole %			
	A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	D <sup>d</sup>
0	71.5	28.5	0	0
28.5	64.6	24.9	5.7	4.8
52.5	62.1	20.2	10.4	7.3
77.3	55.8	18.7	14.5	11.1
100.5	53.5	15.4	18.4	12.8
124.5	51.2	14.5	20.3	13.9
196.5	45.4	9.5	29.1	16.0
Random <sup>e</sup>	36.5	2.3	43.7	17.4

<sup>a</sup> N-Trimethylborazole. <sup>b</sup> Hexamethylborazole. <sup>c</sup> B-Methyl-N-trimethylborazole. <sup>d</sup> B-Dimethyl-N-trimethylborazole. <sup>e</sup> Calculated by the method of Calingaert, ref. 12.

While this paper was in preparation, Wagner and Bradford<sup>16</sup> reported interchange of hydrogen and methyl substituents on boron and also on nitrogen, using unsymmetrical methylborazoles. Their observation of nitrogen substituent exchange under conditions more vigorous than ours (16–33 hr. at 400°) tends to support a ring cleavage mechanism.

## Experimental

**Materials.**—All of the borazoles were prepared by standard methods: B-trichloro-N-trimethylborazole, m.p. 157–159°, lit.<sup>17</sup> m.p. 162–164°, from trichloroborane and methylamine hydrochloride; hexamethylborazole, m.p. 97–99°, lit.<sup>18</sup> m.p. 97°, from the Grignard reaction with B-trichloro-N-trimethylborazole; and N-trimethylborazole, b.p. 128–130°, lit.<sup>2</sup> b.p. 134°, by sodium borohydride reduction of the chloro compound.

B-Trichloro-N-trimethylborazole was purified by recrystallization from hexane, hexamethylborazole was sublimed at 100° (1 mm.), and N-trimethylborazole was purified by fractional distillation. The infrared spectra matched those reported for the respective compounds.<sup>19,20</sup>

**B-Trichloro-N-trimethylborazole-Hexamethylborazole Exchange.**—In a typical experiment, B-trichloro-N-trimethylborazole (5.554 g., 24.59 mmoles) was intimately mixed with hexamethylborazole (2.026 g., 12.33 mmoles) in a drybox. Pyrex ampoules (ca. 7 ml.) were dried, flushed with nitrogen, charged with 2 g. of the mixture, and sealed under vacuum. The ampoules were heated for specific times at 250 or 350° in a fused salt bath, then cooled and opened under nitrogen.

The chloro-(methyl)-borazole mixtures then were reduced with sodium borohydride (1.6 g., 42.3 mmoles) in tetraethyleneglycol dimethyl ether<sup>17</sup> and the borazole products transferred under vacuum to a  $-80^{\circ}$  trap. Analyses of the reduced mixtures

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were effected by gas chromatography on a silicone-firebrick column at 190° using helium carrier gas. The chromatograph consisted of four completely resolved peaks. Retention times for the first and last peaks were identical with known samples of N-trimethylborazole and hexamethylborazole, respectively; intermediate peaks were assumed to represent the two unsymmetrical species. Relative peak areas were equated to weight %, a method which gave less than 5% error on known mixtures of N-trimethylborazole and hexamethylborazole. The reduction step produced >95% of theory on known mixtures of B-trichloro-N-trimethylborazole and hexamethylborazole. Reaction times were increased until duplicate values were obtained, indicating equilibrium (see Fig. 1 and 2). The results are listed in Tables I-III.

**N-Trimethylborazole-Hexamethylborazole Exchange.**—N-Trimethylborazole (2.668 g., 21.8 mmoles) and hexamethylborazole (1.429 g., 8.68 mmoles) were mixed in a drybox. Approximately 0.2-ml. samples of this mixture were placed in Pyrex ampoules, flushed with nitrogen, sealed under vacuum, and placed in an oil bath at 175°. The samples were withdrawn periodically, cooled, and opened under nitrogen. The liquid product mixtures were analyzed by gas chromatography as above. The results are listed in Table IV.

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CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY,  
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## Tris-(ethanolamineborane) Borate and Ethanolamineborane<sup>1</sup>

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Tris-(ethanolamineborane) borate, prepared by the reaction of ethanolamine with diborane in tetrahydrofuran, is a crystalline, hygroscopic solid which decomposes with loss of hydridic hydrogen at room temperature. In the presence of hydroxylic materials, it is converted to ethanolamineborane, a colorless and viscous liquid which has a higher kinetic stability than the parent borate. Identification and structure determination of these products were based on analyses, properties, and B<sup>11</sup> nuclear magnetic resonance spectra.

### Introduction

This investigation of the ethanolamine-diborane system was undertaken as part of a study of the reactions of diborane with difunctional reagents. Results obtained in the ethylenediamine-diborane reaction have been described.<sup>1,2</sup> In connection with the synthesis and characterization of boron-hydrogen compounds, we were interested in the effect of a second functional group on the stability and properties of an amineborane function in the same molecule.

Under the conditions described here, the reaction of diborane with ethanolamine gives tris-(ethanolamineborane) borate. No dialkoxyborane, as obtained in the reaction of diborane with methanol,<sup>3</sup> or heterocyclic compounds were isolated. Recently, comparable results were reported by Miller<sup>4,5</sup> in the synthesis of borane addition compounds of two other aminoalkyl borates. Tris-(ethanolamineborane) borate is easily hydrolyzed to ethanolamineborane. The preparation and properties of this hydroxyalkylamineborane and its parent borate are described herein.

### Experimental

**Materials.**—Ethanolamine (Eastman) was dried by azeotropic distillation with dry benzene and then distilled, b.p. 169–170°.

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Boron trifluoride ethyl ether complex (Eastman) was distilled *in vacuo*, b.p. 54° (25.5 mm.). Lithium aluminum hydride (95+ % purity) was obtained from Metal Hydrides, Inc. Diethyl ether (Mallinckrodt, anhydrous) was used without treatment. Tetrahydrofuran (Matheson Co.) and 1,2-dimethoxyethane (Eastman) were boiled under reflux for several hours with lithium aluminum hydride and distilled using a Widmer column; tetrahydrofuran, b.p. 65.5°; 1,2-dimethoxyethane, b.p. 85°. Other organic compounds were purified by conventional techniques.

**Apparatus.**—Many manipulations were carried out using a "Stock type" vacuum apparatus.<sup>6,7</sup>

**Preparation and Properties of Tris-(ethanolamineborane) Borate.**—A total of 14.3 g. of 95% lithium aluminum hydride (13.6 g., 0.36 mole of pure LiAlH<sub>4</sub>) was suspended in 500 ml. of diethyl ether and stirred under streaming nitrogen. To this suspension was added, dropwise, a solution of 115 g. (0.81 mole) of boron trifluoride etherate in 100 ml. of diethyl ether. The evolved diborane was passed through a condenser (–80°) and into a second vessel, cooled in ice water and containing 125 ml. of freshly distilled tetrahydrofuran. Exit gases were passed through a second condenser (–80°) and through moist acetone to destroy excess diborane. To the tetrahydrofuran-borane solution was added, dropwise, a solution consisting of 6.1 g. (0.10 mole) of ethanolamine diluted to 37 ml. with tetrahydrofuran concurrent with addition of the last two-thirds of the boron trifluoride etherate to the diborane generator. After completion of the addition of ethanolamine, the system was purged with dry nitrogen and maintained at 0° for 4.5 hr. During this time, some of the diethyl ether from the diborane generator was passed by entrainment in the stream of nitrogen into the tetrahydrofuran solution.

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