

at 1150 and 1140  $\text{cm.}^{-1}$  with a strong peak at 1390  $\text{cm.}^{-1}$ . Accordingly, it is not unusual then to note a similar absence for a substance presumed to be related structurally. Regarding the presence of a  $\text{P}=\text{N}$  group, again caution must be exercised since assignments on analogous compounds are lacking.

In phosphoric triamide,  $\text{PO}(\text{NH}_2)_3$ , Steger<sup>12</sup> assigned an observed 1200  $\text{cm.}^{-1}$  peak to the  $\text{P}=\text{O}$  group, which is close to the 1170  $\text{cm.}^{-1}$  peak observed (Table I) for the related phosphoric tri-N-

methylamide,  $\text{PO}(\text{NHCH}_3)_3$  (chloroform solution).

The above discussion is given as an insight into the structural features that may be encountered and it is hoped that it will prove useful as a guide to future research.

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## Preparation of Some Unsymmetrically Substituted Borazines<sup>1,2</sup>

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N-Lithio-substituted borazine compounds, N-lithio-B-trimethylborazine, N-dilithio-B-trimethylborazine, N-lithiopentamethylborazine, and N-dilithiotetramethylborazine, have been prepared as a new class of derivatives which enable a ready preparation of unsymmetrically substituted N-alkylborazines by reaction with alkyl halides. Reaction of partially B-alkylated borazines with a stoichiometric quantity of hydrogen halide yields the corresponding B-alkyl-B-haloborazine derivatives in high purity and yield. Physical constants for a number of new borazine derivatives are given together with newly determined physical constants for several known borazine derivatives.

Since the discovery of borazine by Stock<sup>3</sup> a considerable volume of literature on the chemistry of borazine and its derivatives has been published and reviewed extensively.<sup>4</sup> Synthetic approaches to borazine derivatives fall into two principal classifications: (1) those in which the substituents are attached either to the nitrogen or boron pre-

cursors or both, and (2) those in which one substituent is replaced by another on a borazine nucleus. Both of these synthetic approaches lead generally to derivatives in which substitution is symmetrical with respect to the nitrogen and boron atoms.

Only a few borazine derivatives which are unsymmetrically substituted with respect to one or both of the skeletal atoms have been reported. Schlesinger, Burg, and co-workers report the only use of a mixture of precursors to prepare B-methyl- and B-dimethylborazines<sup>5</sup> and also N-methyl- and N-dimethylborazines.<sup>6</sup> A greater but limited number of examples of replacement reactions are to be found wherein unsymmetrically substituted borazines have been prepared. In each of these references replacement has been limited to boron substituents only. Trimethylborine,<sup>6</sup> elemental chlorine and bromine,<sup>7</sup> trichloro- and tribromo-

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(2) Throughout this paper the use of N defines a mono-substitution product on nitrogen. Di- and tri-substitution products on nitrogen (or similarly on boron) are indicated by the symbol of the element and the appropriate Greek numerical prefix eliminating the superfluous N', and N'' symbols of the often used N,N',N'' nomenclature, e.g., N-methylborazine, N-dilithio-B-trimethylborazine, N-trimethyl-B-methylborazine, etc. For the sake of brevity simple names which connote a unique structure are used rather than the more generally definitive nomenclature just described, i.e., pentamethyl-B-chloroborazine rather than N-trimethyl-B-dimethyl-B-chloroborazine or 1,3,4,5,6-pentamethyl-2-chloroborazine, N-dilithio-tetramethylborazine rather than N-methyl-N-dilithio-B-trimethylborazine or 1,3-dilithio-2,4,5,6-tetramethylborazine, etc.

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

(4) (a) F. G. A. Stone, *Quart. Revs.* (London), **9**, 174 (1955); (b) E. M. Smolin and L. Rapoport, "s-Triazine and Derivatives," Interscience Publishers, New York, N. Y., 1959, Chapter XI; (c) J. C. Sheldon and B. C. Smith, *Quart. Revs.* (London), **14**, 200 (1960).

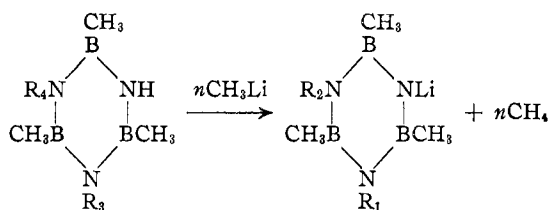
(5) H. I. Schlesinger, L. Horvitz, and A. B. Burg, *J. Am. Chem. Soc.*, **58**, 409 (1936).

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

(7) E. Wilberg and A. Bolz, *Ber.*, **73**, 209 (1940).

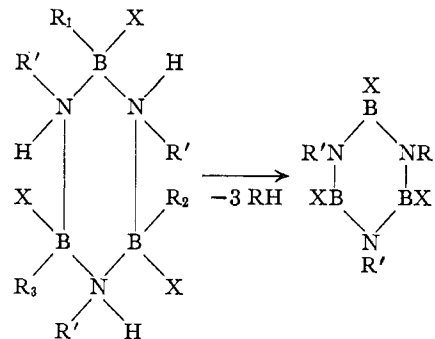
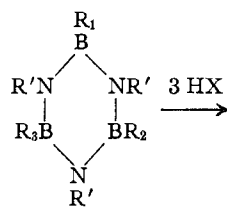
borine<sup>8</sup> and Grignard reagents<sup>9,10</sup> have been used to effect partial replacement of either hydrogen or halogen atoms by alkyl groups or hydrogen by halogen atoms.

During the course of an investigation of linked-ring borazine polymers<sup>11</sup> a new type of borazine derivative was prepared which is the first type of compound that can be used to effect unsymmetrical substitution on the nitrogen atoms of the borazine ring. In this paper we report the preparation of N-lithio-B-trimethylborazine (Ia) by treatment of B-trimethylborazine with an equimolar quantity of methyllithium. A lesser amount of N-dilithio-B-trimethylborazine (Ib) is formed as a by-product. The N-lithio-B-trimethylborazine was characterized by treating it with methyl iodide to prepare the known N-methyl-B-trimethylborazine<sup>6</sup> which was identified by infrared and vapor phase chromatographic analyses. Also prepared were N-lithio-pentamethylborazine (Ic) and N-dilithiotetramethylborazine (Id) by reaction of the corresponding methylborazine derivatives with stoichiometric quantities of methyllithium. Derivatives of some of these lithioborazine compounds formed by reaction with active halogen compounds other than alkyl compounds are discussed in the following paper.<sup>11</sup>



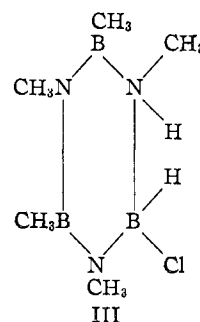
- Ia (R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub> = H; n = 1)  
 b (R<sub>1</sub> = Li; R<sub>2</sub>R<sub>3</sub>R<sub>4</sub> = H; n = 2)  
 c (R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub> = CH<sub>3</sub>; n = 1)  
 d (R<sub>1</sub> = Li; R<sub>2</sub>R<sub>4</sub> = CH<sub>3</sub>; R<sub>3</sub> = H; n = 2)

The reaction of borazine compounds with hydrogen halides yields trimeric aminoborane (borazane) derivatives which on heating lose either hydrogen<sup>7</sup> (from IIa) at 100° or methane<sup>12</sup> (from IIb) at 450° to regenerate a borazine nucleus with halogen substitution. Application of this reaction to the unsymmetrically substituted compound, N-trimethyl-B-dimethylborazine, ad-



- IIa (R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R' = H)  
 b (R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R' = CH<sub>3</sub>)  
 c (R<sub>1</sub>R<sub>2</sub>R' = CH<sub>3</sub>; R<sub>3</sub> = H; X = Cl)  
 d (R<sub>1</sub>R' = CH<sub>3</sub>; R<sub>2</sub>R<sub>3</sub> = H; X = Cl)

mixed with one-third molar quantity of hydrogen halide yields pentamethyl-B-chloroborazine in high purity and yield. Although the nature of the intermediate was not clearly defined in this synthetic procedure, the reaction mixture was observed to consist of a solid (presumably the aminoborane IIc) admixed with a liquid which solidified on standing (presumably N-trimethyl-B-dimethylborazine, m.p. 32.8°). These observations suggest that three hydrogen halide molecules add to one-third of the N-trimethyl-B-dimethylborazine molecules rather than forming a 1:1 adduct, III, which would appear to be a less likely intermediate from consideration of its probably higher chemical potential relative to the initial borazine compound.<sup>4b</sup> Pyrolysis of IIc would release two of the three hydrogen halide molecules which react with more of the initial N-trimethyl-B-dimethylborazine. Confirmatory evidence for this hypothesis was obtained by pyrolyzing one mole of IIc with two moles of N-trimethyl-B-dimethylborazine to obtain pentamethyl-B-chloroborazine in 96.7% yield.



(8) G. W. Schaeffer, R. Schaeffer, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **73**, 1612 (1951).

(9) J. H. Smalley and S. F. Stafiej, *ibid.*, **81**, 582 (1959).

(10) G. E. Ryschkewitsch, J. J. Harris, and H. H. Sisler, *ibid.*, **80**, 4515 (1958).

(11) R. I. Wagner and J. L. Bradford, *Inorg. Chem.*, **1**, 99 (1962).

(12) E. Wiberg, K. Hertwig, and A. Bolz, *Z. anorg. Chem.*, **256**, 177 (1948).

TABLE I  
PHYSICAL CONSTANTS OF SOME BORAZINE DERIVATIVES

Compound	M.p., °C.	B.p., °C.	V.p.c. assay	$d_{25}^{25}$
B-Trimethylborazine	...	129-131 <sup>a</sup>	100	0.84 <sup>b</sup>
N-Methyl-B-trimethylborazine	...	157-159 <sup>c</sup>	99.4	0.86
N-Dimethyl-B-trimethylborazine	...	187-188	99.3	0.88
N-Trimethyl-B-methylborazine	-14.5	76.2(38 <sup>d</sup> )	99.7	0.85
N-Trimethyl-B-dimethylborazine	32.8	101.2(38 <sup>d</sup> )	99.9	0.87 <sup>b</sup>
Tetramethyl-B-dichloroborazine	145-146	...	98.4 <sup>f</sup>	...
Pentamethyl-B-chloroborazine	127-128.5	...	99.0 <sup>f</sup>	...
Tetramethyl-B-dibromoborazine	140-142	...	95.8 <sup>f</sup>	...
Pentamethyl-B-bromoborazine	127-129	...	98.0 <sup>f</sup>	...

<sup>a</sup> Ref. 5 gives calcd. value 129°. <sup>b</sup> Density at 35°. <sup>c</sup> Ref. 6 gives calcd. value 158°. <sup>d</sup> Ref. 9 gives 161.5-162.5° at atm. pressure. <sup>e</sup> Ref. 9 gives 186-187° at atm. pressure. <sup>f</sup> Assay by halogen analysis assuming the only impurity to be a borazine having one more halogen atom and one less methyl group per molecule.

Halogenation with hydrogen halides proved to be more convenient for preparation of B-mono- and B-dihalogen-substituted borazines than partial alkylation of B-trihalo-derivatives with organolithium compounds, which produces a mixture of products. We observed that the separation of pentamethyl-B-chloroborazine and tetramethyl-B-dichloroborazine from each other and from hexamethyl- and N-trimethyl-B-trichloroborazines by high vacuum fractional sublimation is extremely tedious due to similar volatilities of adjacent members of the series. Although it has been implied<sup>10,13</sup> that disproportionation prevents isolation of pure partially B-alkylated-B-chloroborazines, we have found that pure materials are readily isolated from the reaction products of the hydrogen halide synthesis under conditions identical to those used to obtain only partially purified materials prepared by the organometallic route. No evidence was found to substantiate the hypothesis that lower B-alkyl-B-chloroborazines undergo facile disproportionation. The halogenation with hydrogen halide works equally well for both chloro- and bromo-derivatives with yields of 86-98%.

Physical constants for the borazine derivatives are summarized in Table I. In Table II infrared spectra are listed so that bands may be compared although no attempt was undertaken to make assignments.

### Experimental

All of the N-lithioborazine derivatives were prepared in containers sealed with a rubber septum closure through which materials could be added or removed by means of a hypodermic syringe to minimize contact with atmospheric moisture. The B-haloborazine derivatives were handled using either conventional high vacuum techniques or in a

dry-box, or in the laboratory atmosphere during many rapid transfer operations.

All infrared spectra were determined using a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. Vapor phase chromatographic analyses were done using a Perkin-Elmer 154B vapor fractometer with a 2-m. Silicone oil/Celite column.

**Starting Materials.**—(a) **B-Trimethylborazine** came as a by-product of the preparation of **N-methyl-** and **N-dimethyl-B-trimethylborazines** by the coprolysis of a mixture of ammonia trimethylborine and methylamine trimethylborine scaled-up 500-fold over the reported analogous reaction of mixed borine adducts of ammonia and methylamine.<sup>6</sup> The pyrolysis reaction, carried out in an 1100-ml. stainless steel vessel at 380° for 6 hr., was observed to proceed vigorously and exothermically at 220° raising the temperature rapidly to 260° and the pressure to 3000 p.s.i.g. in 10 min. Mechanical losses due to a faulty gasket seat in each of three runs using a combined total of 4.32 moles of ammonia trimethylborine and 5.43 moles of methylamine trimethylborine limited the yield of crude products to 299 g. (63.0%). Fractionation of the crude product through a 2.5 × 61 cm. column filled with 0.4 × 0.4 cm. stainless steel protruded packing yielded (1) 20 g. (0.16 mole, 5.0%) B-trimethylborazine, b.p. 129-131°,  $d_{25}^{25}$  0.84; (2) 75.5 g. (0.55 mole, 17.0%) N-methyl-B-trimethylborazine, b.p. 157-159°,  $d_{25}^{25}$  0.86; (3) 66 g. (0.44 mole, 13.5%) N-dimethyl-B-trimethylborazine, b.p. 187-188°,  $d_{25}^{25}$  0.88; and (4) 15 g. (0.09 mole, 2.8%) hexamethylborazine (identified by infrared spectrum).

(b) **N-Trimethylborazine** was prepared by pyrolysis of trimeric methylaminoborine by the method of Bissot and Parry.<sup>14</sup> The reaction was scaled up over 11,000-fold, which enabled observation of the previously unreported exothermic nature of each stage of the stepwise dehydrogenation. A 936-g. (20.8 moles) quantity of methylamine borine in a 4-l. resin flask was heated slowly to 100°, at which temperature an extremely vigorous exothermic evolution of hydrogen was observed. Some loss of product occurred leaving 702 g. (5.46 moles, 78.5%) of methylaminoborine trimer. Pyrolysis of methylaminoborine trimer in two runs was accomplished in an 1100-ml.

(13) *Chem. & Eng. News*, **45**, 67 (Sept. 16, 1957).

(14) T. C. Bissot and R. W. Parry, *J. Am. Chem. Soc.*, **77**, 3481 (1955).

TABLE II  
INFRARED SPECTRA OF SOME BORAZINE DERIVATIVES

$\text{Na}_2\text{H}_2\text{CH}_2$ $\text{B}_2(\text{CH}_3)_2$ film	$\text{NaH}(\text{CH}_3)_2$ $\text{B}_2(\text{CH}_3)_2$ film	$\text{Na}(\text{CH}_3)_2$ $\text{B}_2\text{H}(\text{CH}_3)_2$ film	$\text{N}_2(\text{CH}_3)_2$ $\text{B}_2\text{H}_2\text{CH}_3$ film	$\text{N}_2(\text{CH}_3)_2$ $\text{B}_2\text{Cl}(\text{CH}_3)_2$ film	$\text{N}_2(\text{CH}_3)_2$ $\text{B}_2\text{Cl}(\text{CH}_3)_2$ $\text{CS}_2$ $\text{C}_6\text{H}_6$ $\text{CCl}_4$	$\text{N}_2(\text{CH}_3)_2$ $\text{B}_2\text{Cl}_2$ $\text{CCl}_4$ $\text{C}_6\text{H}_6$	$\text{N}_2(\text{CH}_3)_2$ $\text{B}_2\text{Br}(\text{CH}_3)_2$ $\text{C}_6\text{H}_6$ $\text{CCl}_4$	$\text{N}_2(\text{CH}_3)_2$ $\text{B}_2\text{Br}(\text{CH}_3)_2$ $\text{C}_6\text{H}_6$ $\text{CCl}_4$
2.93 (m)	2.92 (m)	3.38 (s)	3.40 (s)	3.41 (s)	3.38 (m)	3.39 (w)		
3.40 (m)	3.38 (s)	3.52 (w)	3.52 (w)	3.52 (w)	3.52 (w)			
	3.51 (w)	4.03 (m)	4.03 (m)	4.04 (m)				
6.77 (vs)	6.77 (vs)	6.77 (vs)	6.72 (vs)	6.73 (vs)	6.74 (sh)			6.74 (sh)
	7.00 (vs)	6.88 (vs)	6.85 (vs)	6.86 (vs)	6.84 (vs)	6.87 (vs)		6.84 (vs)
		7.11 (vs)	7.10 (vs)	7.11 (vs)	7.08 (vs)	7.18 (vs)		7.10 (vs)
					7.26 (vs)			7.30 (vs)
7.51 (s)	7.46 (s)	7.47 (w)	7.45 (w)	7.50 (w)	7.55 (w)	7.78 (w)		7.82 (w)
7.71 (w)	7.69 (m)	7.67 (m)	7.74 (m)	7.64 (w)	7.82 (w)			
	7.99 (w)	7.87 (w)	7.93 (w)		7.74 (w)			
	8.33 (w)		8.26 (w)		7.52 (w)			
	8.45 (w)		8.77 (w)		7.96 (w)			
9.24 (m)	9.22 (m)	9.09 (s)	8.93 (w)	9.03 (m)	8.86 (w)			9.29 (w)
	9.49 (w)		9.10 (m)	9.24 (m)	9.24 (s)	9.21 (m)		
			9.30 (w)	9.40 (w)				
			9.84 (m)	10.19 (m)	10.03 (s)			
				10.65 (w)	10.25 (s)			
				10.77 (m)				
11.23 (s)	11.29 (s)	11.31 (s)	11.12 (w)	10.93 (s)				
12.24 (w)	12.30 (w)	12.35 (w)	11.41 (s)	11.11 (w)				
	12.84 (w)	12.73 (w)	12.18 (w)	11.46 (vs)	11.36 (m)	11.40 (w)		11.35 (w)
								12.05 (w)
13.98 (s)	14.18 (vs)	14.47 (m)	13.40 (w)	14.93 (w)	14.55 (w)	14.73 (m)		
						14.89 (m)		
						15.06 (m)		15.20 (w)

stainless steel pressure vessel at 225° during 5 hr. In each run a rapid exotherm was observed at 180° which raised the temperature to 245° and the pressure to 5500 p.s.i.g. in about 10 min. Distillation of the pyrolyzate gave 568 g. (4.63 moles, 85%) of pure N-trimethylborazine, b.p. 130.5–131.5°.

(c) **N-Trimethyl-B-methyl- and N-trimethyl-B-dimethylborazines** were prepared by the method of Smalley and Stafiej,<sup>9</sup> although a series of experiments were required to define experimental conditions needed to duplicate their results. Our best results for the preparation of N-trimethyl-B-dimethylborazine were obtained using a 0.5 M hexane solution of N-trimethylborazine to which was added 2 M methylmagnesium iodide. The reaction mixture obtained from 125 g. (1.02 moles) of N-trimethylborazine and 2.06 moles of Grignard reagent was decomposed using saturated aqueous ammonium chloride (125 ml./g.-atom, Mg). The organic layer was separated, filtered through anhydrous sodium sulfate, and fractionated to deliver 39.5 g. (0.298 mole, 28.3%) of N-trimethyl-B-methylborazine, b.p. 76.2° (38 mm.), m.p. -14.5°,  $d_{25}^{25}$  0.85; 72.9 g. (0.484 mole, 47.4%) N-trimethyl-B-dimethylborazine, b.p. 101.2° (38 mm.), m.p. 32.8°,  $d_{25}^{25}$  0.87; and ca. 18 g. (0.11 mole, 11%) hexamethylborazine.

(d) **N-Trimethyl-B-trichloroborazine** was prepared by dehydrochlorination of methylamine trichloroborane with triethylamine by the method of Turner and Warne.<sup>15</sup>

**Preparation and Alkylation of N-Lithio-borazine Compounds.** (a) **N-Lithiopentamethylborazine** was treated with methyl iodide to prepare hexamethylborazine as a convenient means of characterization. Into a 6-ml. nitrogen-filled bomb tube was placed 0.2704 g. (1.795 mmoles) of N-dimethyl-B-trimethylborazine (assay 99.3%). The borazine was cooled to -196°, a layer of degassed ether was added and frozen above it, and then 1.90 ml. of 0.95 M ethereal methyllithium (1.805 mmoles) was added from a syringe and the tube sealed under vacuum at -196°. Upon warming to room temperature, considerable effervescence of the mixture was noted. The tube then was warmed briefly to 50° and allowed to stand overnight. From the opened tube, 40.14 cc. (99.8% of theoretical) of non-condensable gas (CH<sub>4</sub>) was removed. To further characterize the product, 0.2598 g. (1.830 mmoles) of methyl iodide was added to the degassed N-lithiopentamethylborazine solution at -196° and the tube was resealed. After heating briefly to 50° with shaking, the tube was cooled to -196° and opened. A trace of non-condensable gas and ether was removed through a -30° trap which retained the major volatile product. After purification by high vacuum sublimation<sup>16</sup> at 100°, the product was identified by infrared analysis as hexamethylborazine. Analysis of the 0.5016 g. sublimation residue for both lithium and iodine indicated it was predominantly lithium iodide with a trace of boron-containing impurity.

(b) **N-Dilithiotetramethylborazine** was prepared from 0.6892 g. (5.044 mmoles) of N-methyl-B-trimethylborazine and 10.1 mmoles of ethereal methyllithium using the same experimental procedure outlined for N-lithio-

pentamethylborazine. By-product methane was formed in 100.3% yield (226.3 cc.). The N-dilithiotetramethylborazine was not characterized directly by reaction with an alkyl halide but was used in the synthesis of borazine polymers.<sup>11</sup>

(c) **N-Methyl-B-trimethylborazine** was prepared by treating N-lithio-B-trimethylborazine with methyl iodide. The N-lithio-compound was prepared by reaction of 1.3511 g. (11.02 mmoles) of B-trimethylborazine with 11.60 ml. of ethereal 0.95 M methyllithium in a 30-ml. glass bomb tube closed with a rubber septum. After cessation of methane evolution a 3.40-ml. aliquot of a 10-ml. ethereal solution containing 4.5893 g. of methyl iodide (11.02 mmoles) was added from a syringe. The sealed tube was heated at 80° for 3.5 hr., cooled, and opened. The ether, which was shown in a preliminary experiment to contain less than 5% of the methyl iodide, was removed on the vacuum line through a -45 ± 5° trap. The residual solid (predominantly LiI) was extracted with eight 2-ml. portions of *n*-pentane. Most of the pentane was removed on the vacuum line through a -45 ± 5° trap which retained 1.2716 g. of crude product. Vapor phase chromatographic and infrared (no B-H stretch at 4.03  $\mu$ ) analyses indicated pentane, 9.8%; B-trimethylborazine, 34.9% (32.8% recovered); N-methyl-B-trimethylborazine, 40.6%; N-dimethyl-B-trimethylborazine, 13.5%; and hexamethylborazine, 1.1%; corresponding to yields of 51.1% tetra-, 15.4% penta-, and 1.1% hexamethylborazines based on unrecovered B-trimethylborazine.

**Preparation of B-Mono- and Dihalo-substituted Borazines.** (a) **Pentamethyl-B-chloroborazine** was prepared by dissolving 13.5333 g. (89.82 mmoles) of N-trimethyl-B-dimethylborazine in 125 ml. of carbon tetrachloride. The pressure over the solution cooled in an ice-bath was lowered to its vapor pressure before addition from a 10-ml. cylinder of 3.3560 g. (94.62 mmoles) of anhydrous hydrogen chloride, which was introduced at a rate sufficient to raise the pressure to atmospheric. On completion of the addition the pressure returned to that of the solution, which now contained a precipitate. Solvent was removed at reduced pressure on a rotary evaporator leaving 16.3390 g. (96.7%) of a slurry which solidified on standing overnight. The mixture was transferred to a glass liner of a 43-ml. stainless steel pressure vessel in which it was heated for 4 hr. at 160°. The by-product hydrogen, vented from the cooled bomb through a wet test meter, was measured as 1900 ± 28 cc. (98%). The colorless crystalline product was sublimed at 75° to give 14.9522 g. of material, m.p. 120–128°, analyzing 19.1% chlorine. The broad melting range suggested the presence of unreacted starting material and accordingly the sublimate was reheated for 4 hr. at 130° in an 80-ml. glass bomb tube with 167.3 cc. (7.46 mmoles) of hydrogen chloride. An additional 43.4 cc. (2.2%) of hydrogen was produced. Resublimation of the product at 70° yielded 14.3302 g. (77.41 mmoles, 86.2%) of pentamethyl-B-chloroborazine, m.p. 127–128.5°. *Anal.* Calcd. for C<sub>5</sub>H<sub>15</sub>B<sub>3</sub>N<sub>3</sub>Cl: Cl, 19.15. Found: Cl, 19.4.

In another experiment 3.0544 g. (20.27 mmoles) of N-trimethyl-B-dimethylborazine was allowed to react with 1508 cc. (67.32 mmoles) of hydrogen chloride in a sealed 200-ml. bomb tube at 30–40° for 1 hr. in the absence of a solvent. The tube was opened and 86.0 cc. (3.84 mmoles) of non-condensable gas (subsequently shown to be hydro-

(15) H. S. Turner and R. J. Warne, *Chem. & Ind.* (London), 526 (1958).

(16) Throughout this work all sublimations were done under high vacuum.

gen) and 385.8 cc. (17.22 mmoles) of hydrogen chloride were removed, suggesting that the replacement of hydridic hydrogen by chlorine had proceeded to the extent of 18.9%. The hydrogen chloride retained as an adduct thus was  $67.32 - 17.22 - 3.84 = 46.26$  mmoles, or a ratio of 2.28 HCl/substituted-borazine, somewhat less than the theoretical 3.00. Since the reaction mixture appeared at all times to be a solid mass, the low value is not surprising. The tube was filled with dry nitrogen and 4.2959 g. (28.51 mmoles) of N-trimethyl-B-dimethylborazine was added to the tube to lower the molar ratio of HCl/substituted-borazine to 1.03. The sealed evacuated tube was heated for 2 hr. at 130°. The non-condensable gas produced was combined with the 86.0 cc. of gas previously isolated to obtain a total of 1146.8 cc. (51.20 mmoles) of hydrogen (by combustion over copper oxide). The residual solid was sublimed at 70° to obtain 8.7337 g. (47.18 mmoles, 96.7% yield) of pentamethyl-B-chloroborazine, m.p. 125–127°. *Anal.* Calcd. for  $C_5H_{15}B_3N_3Cl$ : Cl, 19.15. Found: Cl, 18.9.

Unsuccessful attempts were made to chlorinate N-trimethyl-B-dimethylborazine using either carbon tetrachloride, N-chlorosuccinimide, or cupric chloride as halogenating agents.

An alternate preparation of pentamethyl-B-chloroborazine, namely, partial methylation of N-trimethyl-B-trichloroborazine, appeared attractive because it used more readily available starting materials. A typical experiment is described for comparison with the hydrogen halide method.

Into a nitrogen-swept 2000-ml. flask fitted with a Hershberg stirrer, Friederichs condenser, and 250-ml. addition funnel was placed 11.3550 g. (50.2 mmoles) N-trimethyl-B-trichloroborazine in 750 ml. of anhydrous ether. A 110-ml. quantity of 0.906 M ethereal methyllithium (99.7 mmoles) was diluted to 250 ml. in the addition funnel and added dropwise during 3 hr. to the vigorously stirred borazine solution at 0°. The resultant light yellow slurry was filtered in an enclosed fritted glass filter of medium porosity under nitrogen pressure, and the precipitate was washed with two 50-ml. portions of ether. Solvent was removed from the filtrate on a rotary film evaporator, leaving a yellow solid residue which was slurried in 500 ml. of petroleum ether (b.r. 20–40°). The insoluble lithium salts were filtered and washed with two 70-ml. portions of petroleum ether. The filtrate again was evaporated to dryness yielding 9.5 g. of crude yellow product, which was sublimed at 80–90° from residual lithium salts. The sublimate was fractionally resublimed at 60° to yield 4.9557 g. of crystalline product, m.p. 120–129°. *Anal.* Calcd. for  $C_5H_{15}B_3N_3Cl$ : Cl, 19.15. Found: Cl, 21.3. From the chlorine analysis an assay of 85.9% pentamethyl-B-chloroborazine (45.8% yield) and 14.1% tetramethyl-B-dichloroborazine was calculated.

(b) **Tetramethyl-B-dichloroborazine** was prepared in a manner similar to that described for pentamethyl-B-chloroborazine by condensing the hydrogen chloride derived from 2.9605 g. (55.34 mmoles) of ammonium chloride and excess sulfuric acid into a 120-ml. glass bomb tube containing 3.4368 g. (25.15 mmoles) of N-trimethyl-B-methylborazine. The sealed tube was heated for 3 hr. at 150° to yield 1139.4 cc. (101%) of hydrogen (identified by combustion over CuO) and a colorless solid. Sublimation of the solid at 70° delivered 5.0613 g. (24.62

mmoles, 97.9%) of tetramethyl-B-dichloroborazine, m.p. 145–146°. *Anal.* Calcd. for  $C_4H_{12}B_3N_3Cl_2$ : Cl, 34.50. Found: Cl, 34.7.

Partial methylation of N-trimethyl-B-trichloroborazine proved to be less successful in preparing the B-dichloro-derivative than the monochloro-derivative. Using the same apparatus previously described for the alkylation of N-trimethyl-B-trichloroborazine, 11.3568 g. (50.26 mmoles) of N-trimethyl-B-trichloroborazine dissolved in 750 ml. of anhydrous ether was cooled to 0° and 155 ml. of 0.341 M ethereal methyllithium (50.3 mmoles) was added dropwise during 1 hr. After standing overnight the mixture was filtered under nitrogen and the solids washed with two 50-ml. portions of ether. The filtrate was evaporated to dryness at reduced pressure and the residue was slurried in 500 ml. of petroleum ether (b.r. 20–40°) and filtered, and the solids were washed with two 50-ml. portions of petroleum ether. The filtrate was evaporated to dryness leaving 9.2 g. of crude product, which was sublimed at 170° to remove an additional 2.1 g. of lithium salts. Resublimation of the crude product gave 3.0927 g. of crystalline material at 60° and an additional 2.4750 g. of crystalline material at 80°, leaving 0.8493 g. of brown, tarry residue. *Anal.* Calcd. for  $C_4H_{12}B_3N_3Cl_2$ : C, 23.37; H, 5.89; Cl, 34.50. Found for 60° fraction: m.p. 146–148°; C, 20.68; H, 5.60; Cl, 37.8; for 80° fraction: m.p. 148–150°; C, 20.48; H, 5.40; Cl, 38.8. From the chlorine analyses the two fractions assay 74.0% and 66.9% tetramethyl-B-dichloroborazine, respectively, contaminated with N-trimethyl-B-trichloroborazine.

(c) **Pentamethyl-B-bromoborazine** was prepared by heating 0.3313 g. (2.20 mmoles) of N-trimethyl-B-dimethylborazine and 51.6 cc. (2.30 mmoles) of hydrogen bromide in a sealed tube at 180° for 2 hr. The solid product after removal of 49.6 cc. (100.6%) of hydrogen was sublimed at 70° to yield 0.4585 g. (2.00 mmoles, 90.9%) of colorless pentamethyl-B-bromoborazine, m.p. 127–129°. A mixture melting point with the chlorine analog, 110–115°, was determined because of their similar melting points and infrared spectra. *Anal.* Calcd. for  $C_5H_{15}B_3N_3Br$ : Br, 34.81. Found: Br, 35.2.

(d) **Tetramethyl-B-dibromoborazine** was prepared in the same manner as the B-monobromo compound from 0.8040 g. (5.88 mmoles) of N-trimethyl-B-methylborazine and 270.0 cc. (12.05 mmoles) of hydrogen bromide. Vacuum sublimation at 70° of the material obtained after heating the reactants for 2 hr. at 220° gave 1.6163 g. (5.49 mmoles, 93.4%) of colorless tetramethyl-B-dibromoborazine, m.p. 140–142°. A mixture melting point with the chlorine analog, 136–140°, was determined because of their similar melting points and infrared spectra. *Anal.* Calcd. for  $C_4H_{12}B_3N_3Br_2$ : Br, 54.28. Found: Br, 54.8.

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