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Borazine Polymers. B–N Linked Borazine Rings and Polyborazylene Oxides[1,2]

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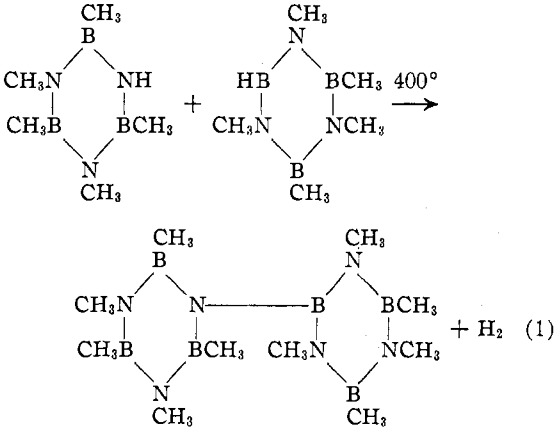
Appreciable disproportionation to tri-, tetra-, and hexamethylborazines with interchange of hydrogen and methyl substituents only between like atoms was observed on attempted pyrolytic dehydrogenation of an equimolar mixture of the isomeric pentamethylborazines. Only traces of decamethyl-N,B′-biborazyl (I) were produced. Condensation polymerization with elimination of lithium chloride from selected N-lithio- and B-chloroborazine derivatives provided the first practical synthesis of (I). By extension of this synthetic method a series of new polycyclic borazine compounds and finally a biborazylene polymer composed of a chain of ten rings were prepared. Another series of condensation polymers was synthesized by controlled hydrolysis of selected B-chloroborazine derivatives. A number of materials containing from 2 to 23 borazine nuclei joined together by oxide (B–O–B) linkages were prepared. Selected physical constants of the new compounds are reported.

Since the original work of Stock[3a] describing the exceptional thermal stability of borazine vapor and the lability of liquid borazine toward dehydrogenation at ambient temperatures, little further effort[3b] appeared to have been made to investigate the nature of the presumably polymeric substances intermediate between $(HNBH)_3$ and $(BNH)_n$. In view of the growing requirements for polymeric materials of high thermal stability, we undertook an investigation of the condensation polymerization of selected borazines by pyrolytic dehydrogenation. This approach was based on the well documented[4] fact that elemental hydrogen is readily eliminated from molecules containing both protonic and hydridic hydrogen, such as amine borines, and on the assumption that the facile dehydrogenation of liquid borazine is a reaction of the same type. To simplify the interpretation of experimental data we chose to limit the functionality of the borazine species to a value of two by blocking the remaining positions with methyl groups. The necessary N–H and B–H functions were most readily obtained in separate molecules and accordingly the reaction set forth in equation 1 was selected for the initial study.



I

During the course of our study Laubengayer and co-workers[5] reinvestigated the pyrolysis of borazine at 340–440° and reported small yields of compounds, $B_6N_6H_{10}$ and $B_5N_5H_8$, which were

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[2] Because of the structural complexity of a number of the borazine derivatives reported in this paper relative to the majority of known borazine compounds a brief summary of the nomenclature used appears warranted. Substitution on compounds containing a single borazine ring will be indicated by the symbol of the element and the appropriate Greek prefix except when a simple name will connote a unique structure (see footnote 2, ref. 6). The one reported (ref. 5) isomer of the three possible biborazyls (or biborazinyls, *i.e.*, analogs of biphenyl) contains the N,B′-biborazyl (or 1,2′-biborazyl) skeleton (I) wherein a nitrogen atom in one ring is bonded directly to a boron atom in the other. The use of a prime (or double prime, etc.) with the symbol of an element is reserved to denote that the element is in another borazine ring; it is not to be confused with the superfluous N,N′,N″,B,B′,B″ system often used with simple borazine derivatives. Compounds containing either three or four borazine rings have been named as borazylborazines using the numerical designation of the Ring Index for location of structural features, *i.e.*, 1,3,5 for nitrogen and 2,4,6 for boron substitution. Difunctional radicals are named as analogs of the corresponding aromatic radicals, *e.g.*, borazylene (phenylene) and biborazylene (biphenylene).

[3] (a) A. Stock and E. Pohland, *Ber.*, **59**, 2215 (1926); (b) R. O. Schaeffer, M. Steindler, L. F. Honstedt, H. S. Smith, Jr., L. B. Eddy, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **76**, 3303 (1954).

[4] H. I. Schlesinger and A. B. Burg, *Chem. Revs.*, **31**, 1 (1942); F. G. A. Stone, *Quart. Revs.* (London), **9**, 174 (1955); F. G. A. Stone, "Advances in Inorganic and Radiochemistry," Vol. 2, Academic Press, Inc., New York, N. Y., 1960, Chemical Reactivity of the Boron Hydrides and Related Compounds.

[5] (a) P. C. Moews, Jr., and A. W. Laubengayer, Abstracts of 136th National Meeting, American Chemical Society, Atlantic City, N. J., Sept. 1959, p. 53-N; (b) A. W. Laubengayer, P. C. Moews, Jr., and R. F. Porter, *J. Am. Chem. Soc.*, **83**, 1337 (1961); (c) after our paper was submitted, J. J. Harris, *J. Org. Chem.*, **26**, 2155 (1961) reported B-pentabutyl-N,B′-biborazyl, which is another derivative of the N,B′-biborazyl skeleton.

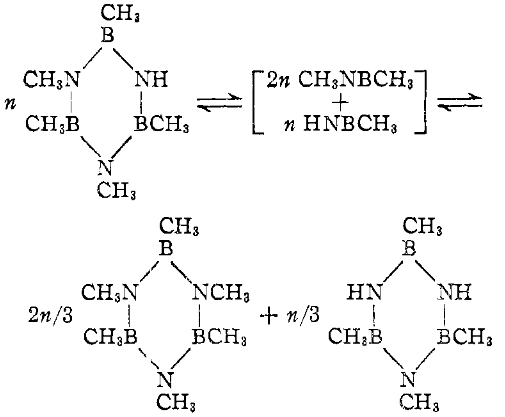
shown to be analogs of biphenyl and naphthalene, as well as B-amino-substituted borazines and evidence for higher molecular weight compounds.

Our pyrolysis of an equimolar mixture of isomeric pentamethylborazines gave only a trace amount of condensation product (I) indicating a remarkable resistance of these substituted derivatives toward elimination of hydrogen. Independent pyrolyses of the pentamethylborazine isomers suggested but did not prove that the principal gaseous product, methane, arose primarily by interaction of N-H and B-CH_3 functions. In each of the independent pyrolyses the major portion (*ca.* 89%) of the starting materials was recovered unchanged and apparent disproportionation products (tri-, tetra-, and hexamethylborazines) accounted for all but a trace of the remainder of the starting pentamethylborazine isomer. The disproportionation products formed in each of the independent pyrolyses of the pentamethylborazine isomers were shown by infrared analysis to have been formed with interchange of substituents only among like skeletal atoms.

$$(CH_3)_2HN_3B_3(CH_3)_3 \longrightarrow (CH_3)_{3-n}H_nN_3B_3(CH_3)_3 \quad (2)$$

$$(CH_3)_3N_3B_3H(CH_3)_2 \longrightarrow (CH_3)_3N_3B_3H_n(CH_3)_{3-n} \quad (3)$$

A possible reaction path might be a complete depolymerization of the borazine ring and random recombination of the monomer fragments, or perhaps a less extreme form of depolymerization, such as a ring opening followed by random polymerization and scission of the chains, and finally recyclization. Another obvious means of accounting for the observed products is a simple exchange of the boron substituents by way of a bridge-bonded transition state for which there is considerable precedent.[4] However, this type of exchange does not appear to explain as well the exchange of substituents on nitrogen. Considering Laubengayer's[5a] data, which clearly show borazine ring opening at temperatures comparable to that used to effect the disproportionation, the depolymerization mechanism appears to be the more likely reaction path. In the absence of additional data, such as might be obtained from pyrolyses using labeled (B^{10}) or doubly labeled (B^{10} and H^2) borazine derivatives, no final conclusion can be drawn with respect to the validity of either of these or other plausible mechanisms.



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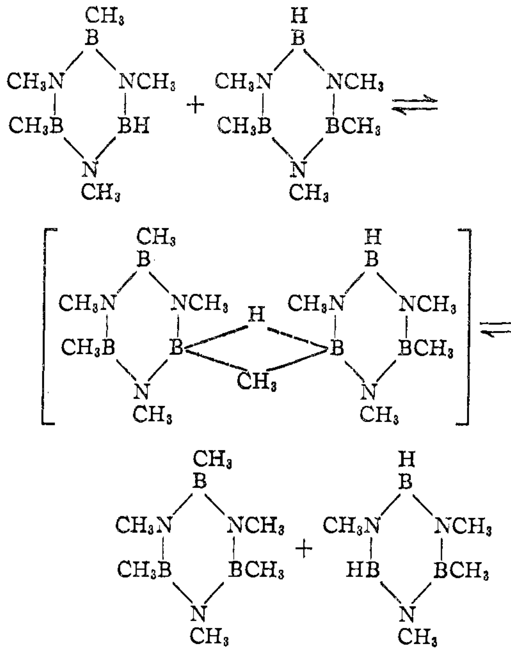

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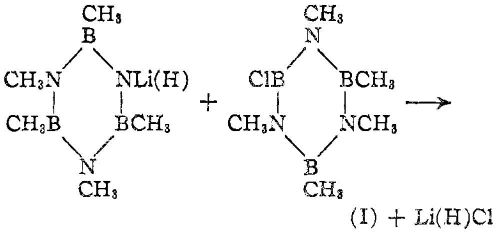
The preparatively insignificant yield of decamethyl-N,B′-biborazyl (I) formed by pyrolytic dehydrogenation prompted us to try two alternate means of effecting condensation polymerization of selected borazine derivatives: (1) lithium chloride elimination, and (2) dehydrohalogenation.

The successful condensation of two borazine nuclei to prepare decamethyl-N,B′-biborazyl (I) was accomplished by elimination of lithium chloride from an equimolar mixture of N-lithiopentamethylborazine[6] and pentamethyl-B-chloroborazine[6] in diethyl ether solution. Extension of this type reaction to polyfunctional borazine derivatives led to the preparation of two isomeric diborazylborazines (II), one of the isomeric tri-



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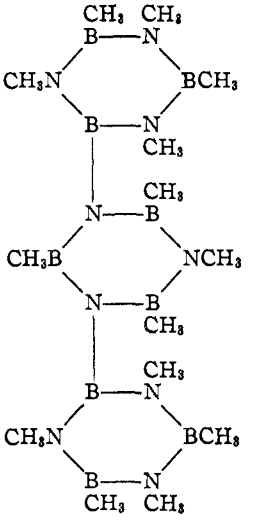
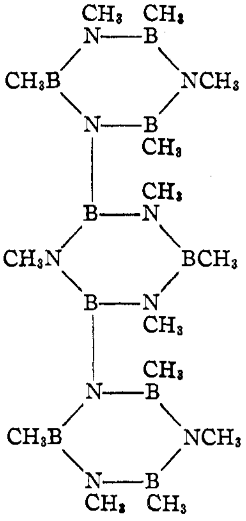
(6) R. I. Wagner and J. L. Bradford, *Inorg. Chem.*, 1, 93 (1962).

borazylborazines (IIIb), and finally a biborazylene polymer (IV).


IIa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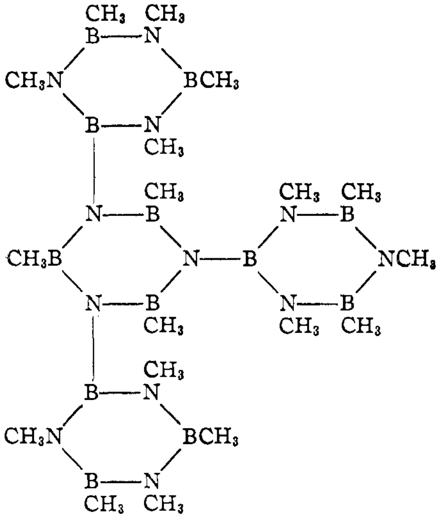
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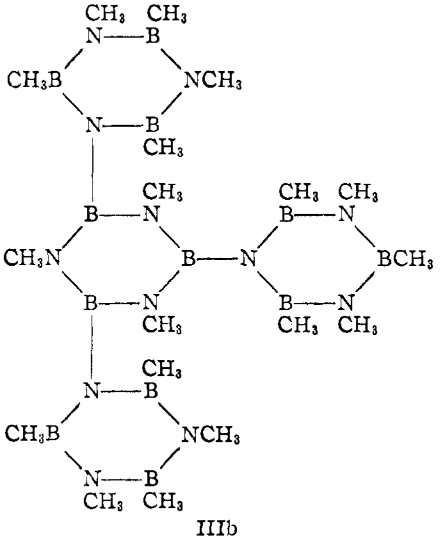
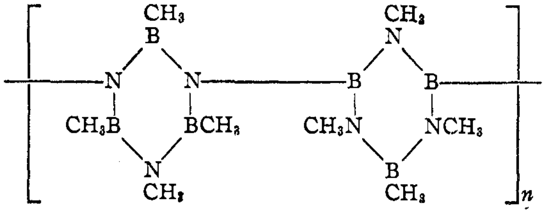

IIIb


IV

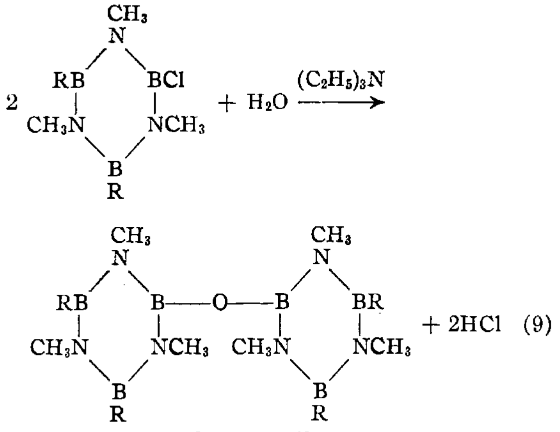
A series of attempts to prepare the N-triborazylborazine derivative (IIIa) in ether solution gave as the principal products decamethyl-B,B′-diborazyl oxide (Va) and N-triethyl-B-trimethylborazine, the latter only tentatively characterized. Other materials isolated from the reaction mixtures in a crude state were not definitively characterized but appeared to be primarily recovered starting materials. In an attempt to approach the synthesis of IIIa in a stepwise manner through the intermediate compounds, 1′,2,3′,4,4′,5,6,6′-octamethyl-1,2′-biborazyl and 1,3-bis(pentamethyl-2′-borazyl)-2,4,6-trimethylborazine, the principal products were the same as observed in the attempted direct preparation. The relative volatilities of two of the minor components observed on vapor phase chromatographic analysis of the mixture of reaction products suggested that they might be the two compounds sought as intermediates. However, the small amounts (0.5 and 9.5% of the isolated mixture) of these materials in the seven-component mixture made their isolation appear impractical. An attempt was made to obviate the problems created by the use of ether as solvent by substituting *n*-hexane, with the result that the intermediate N-trilithio-B-trimethylborazine failed to form.

The source of the oxygen atom (and the ethyl group as well) must have been the ether solvent rather than water since the experimental techniques had been shown to be adequate to prevent significant hydrolysis. The ether was not contaminated with hydroxylic compounds since it subsequently was used in successful preparation of related borazine derivatives. Presumably the course of reaction with the solvent is described by equations 7 and 8. In each of the lithium chloride elimination reactions the moderate yields

$$Li_3N_3B_3(CH_3)_3 + 3(C_2H_5)_2O \longrightarrow 3LiOC_2H_5 + (C_2H_5)_3N_3B_3(CH_3)_3 \quad (7)$$

$$LiOC_2H_5 + 2(CH_3)_3N_3B_3Cl(CH_3)_2 \longrightarrow (Va) + LiCl + C_2H_5Cl \quad (8)$$

(26–50%) are ascribed primarily to large mechanical losses during the extensive purification, although the possibility exists that some ether cleav-



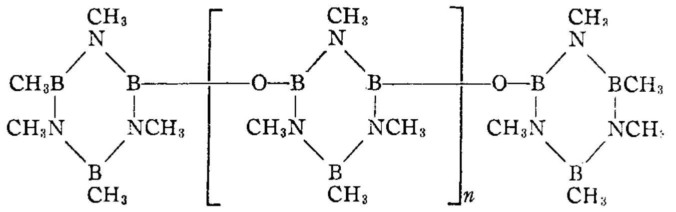
(9)

Va [R = CH_3)]
b [R = $CH_2Si(CH_3)_3$]

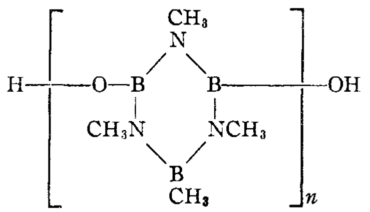
age by the N-lithioborazine reagents did occur. Perhaps such side-reactions leading to some N-ethyl substitution products and borazine oxides rendered purification of the main products difficult.

Another type of condensation polymerization of borazene rings is that wherein the rings are joined together through an oxygen atom in a manner analogous to aromatic ethers. A compound of this class was discovered in an approach to decamethyl-N,B'-biborazyl (I) by way of the dehydrohalogenation of equimolar quantities of N-dimethyl-B-trimethylborazine and pentamethyl-B-chloroborazine with tertiary amines. Repeated attempts to effect the dehydrohalogenation under a variety of conditions failed to produce any isolable product other than a crystalline compound which was identical with decamethyl-B,B'-diborazyl oxide (Va) prepared by hydrolysis of pentamethyl-B-chloroborazine. The yield of this oxide varied from 0-67% and appeared to depend entirely on the rigor exercised in excluding atmospheric moisture from the reaction mixtures. An analogous compound (Vb) was isolated by Seyferth and Kögler[7] as a by-product from the reaction of a B-trihaloborazine derivative with a deficiency of Grignard reagent. Similar materials connected by a primary amino nitrogen bridge also have been reported recently.[8]

Hydrolysis of mixtures of mono- and dihalo-substituted borazine derivatives with the stoichiometric quantity of water gave a homologous series of semi-solid products (VI, where n = 0-3) with an increasing number of borazine rings in the chain, while hydrolysis of the dihaloborazine derivative alone gave a glassy polymeric chain of rings (VII) with a degree of polymerization of approximately 23. Only for the simplest compound (Va) was characterization definitive; each of the higher homologs showed the characteristic B-O-B infrared absorption at 10.5 μ. The more complex materials, indicated by the idealized formula (VI), may be a mixture of three different compounds for each value of n, since one or both of the terminal rings could be derived from the dichloro- rather than the monochloroborazine derivative. Terminal rings of this origin carry a B-hydroxy functional group as indicated in formula VII.



VI



VII

Infrared spectra are listed in Table I so that bands may be compared, although no attempt was made to make assignments other than associating the absorption at 10.52-10.57 μ with the B-O-B bonded compounds.

Experimental

Starting Materials.—The preparation of all monocyclic borazine derivatives used in this work is described in the preceding paper.[6] All melting points are uncorrected and all molecular weights unless otherwise noted were done in benzene solution following the procedure of Neumayer.[9] Infrared spectra were determined using a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics. Vapor phase chromatographic analyses were performed with a Perkin-Elmer 154B vapor fractometer using a 2-m. Silicone oil/Celite column.

Pyrolysis Reactions.—Pyrolysis of N-dimethyl-B-trimethylborazine and N-trimethyl-B-dimethylborazine both separately and together was done with approximately 3 mmoles of material in sealed 5-ml. Pyrex tubes at 400°. No visible evidence of extensive decomposition was observed. Non-condensable gaseous products were handled using conventional high vacuum techniques. Condensable products were analyzed using infrared spectroscopy

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(7) D. Seyferth and H. P. Kögler, *J. Inorg. & Nuclear Chem.*, **15**, 99 (1960).

(8) D. W. Aubrey and M. F. Lappert, *J. Chem. Soc.*, 2927 (1959).

(9) J. J. Neumayer, *Anal. Chim. Acta*, **20**, 519 (1959).

TABLE I

INFRARED SPECTRA OF SOME POLYCYCLIC BORAZINE DERIVATIVES

I KBr	IIa KBr	IIb KBr	IIIb KBr	IV KBr	Va KBr	VI ($n = 1$) KBr	VI ($n = 3$) KBr	VII KBr, CS_2, CCl_4
3.40 (m)	3.42 (m)	3.40 (m)	3.41 (m)	3.41 (m)	3.40 (m)	3.41 (m)	3.41 (m)	3.40 (m)
3.54 (w)	3.54 (w)	3.52 (w)	3.54 (w)	3.53 (w)	3.51 (w)	3.51 (w)	3.51 (w)	3.51 (w)
6.80 (sh)	6.81 (sh)	6.78 (sh)	6.82 (sh)	6.82 (sh)	6.80 (sh)	6.82 (sh)	...	6.80 (sh)
6.92 (vs)	6.92 (vs)	6.94 (vs)	6.93 (vs)	6.92 (vs)	6.91 (vs)	6.92 (vs)	...	6.90 (vs)
					7.15 (sh)			
7.24 (vs)	7.27 (vs)	7.21 (vs)	7.21 (vs)	7.26 (vs)	7.30 (vs)	...	...	7.17 (vs)
7.61 (w)	7.62 (w)	7.62 (w)	7.65 (w)	7.63 (w)	7.55 (w)	7.60 (w)		7.45 (sh)
					7.82 (w)	7.86 (w)	7.90 (w)	7.90 (w)
7.88 (m)	7.90 (m)	7.89 (m)	7.88 (m)	7.92 (m)	7.97 (w)	8.05 (w)	8.10 (w)	
8.20 (w)		8.24 (w)	8.20 (w)			8.34 (w)	8.32 (w)	8.30 (w)
8.38 (w)	8.56 (w)	8.42 (w)	8.38 (w)					
8.81 (w)						8.86 (w)	8.55 (w)	8.81 (w)
9.14 (s)	9.08 (s)	9.16 (s)	9.17 (s)	9.10 (m)	8.94 (s)	9.03 (m)	9.04 (m)	9.03 (m)
						9.55 (w)	9.54 (w)	9.53 (w)
9.73 (w)	9.72 (w)	9.76 (w)	9.74 (w)	9.75 (w)	9.78 (w)	9.80 (w)	9.80 (w)	10.05 (w)
	9.84 (w)				10.57 (w)	10.52 (w)	10.52 (w)	10.52 (w)
11.34 (m)	11.36 (m)	11.32 (s)	11.35 (s)	11.32 (m)	11.35 (m)	11.41 (m)	11.38 (m)	11.40 (w)
13.30 (vw)		13.25 (w)	13.21 (w)					14.15 (m)
14.40 (vw)	14.60 (w)	14.45 (w)	14.20 (w)	14.35 (m)	14.33 (w)	14.45 (m)	14.42 (s)	14.40 (m)
14.80 (w)	15.04 (w)				14.84 (m)	14.81 (m)	14.75 (w)	

TABLE II

PYROLYTIC DISPROPORTIONATION PRODUCTS FROM THE ISOMERIC PENTAMETHYLBORAZINES

Millimoles of starting material	Pyrolysis time at 400°, hr.	Non-condensable gas, cc.	Borazine product	% of total
3.357 $(CH_3)_2HN_3B_3(CH_3)_3$[a]	16	0.09[b]	$H_3N_3B_3(CH_3)_3$	0.40
			$CH_3H_2N_3B_3(CH_3)_3$	5.48
			Unknown	0.17
			$(CH_3)_2HN_3B_3(CH_3)_3$	88.8
			$(CH_3)_3N_3B_3(CH_3)_3$	5.12
2.938 $(CH_3)_3N_3B_3H(CH_3)_2$[c]	16	0.01	$(CH_3)_3N_3B_3H_3$	0.03
			$(CH_3)_3N_3B_3H_2CH_3$	5.18
			$(CH_3)_3N_3B_3H(CH_3)_2$	88.4
			$(CH_3)_3N_3B_3(CH_3)_3$	6.35
1.521 $(CH_3)_2HN_3B_3(CH_3)_3$[a] + 1.473 $(CH_3)_3N_3B_3H(CH_3)_2$[c]	33	13.96 CH_4 + 4.69 H_2	$H_3N_3B_3(CH_3)_3$ + $(CH_3)_3N_3B_3H_3$	0.00
			$CH_3H_2N_3B_3(CH_3)_3$ + $(CH_3)_3N_3B_3H_3CH_3$	15.3
			Unknown[d]	2.46
			$(CH_3)_2HN_3B_3(CH_3)_3$ + $(CH_3)_3N_3B_3H(CH_3)_2$	74.9
			$(CH_3)_3N_3B_3(CH_3)_3$	7.37
			0.0189 g. residue[e]	

[a] Assay 99.3% $(CH_3)_2HN_3B_3(CH_3)_3$ + 0.6% $CH_3H_2N_3B_3(CH_3)_3$. [b] Predominantly methane. [c] Assay 99.9% $(CH_3)_3N_3B_3H(CH_3)_2$ + 0.1% $(CH_3)_3N_3B_3H_2CH_3$. [d] Possibly a mixture of $(CH_3)_2HN_3B_3H(CH_3)_2$ isomers. [e] Non-volatile at 25° containing a trace of decamethyl-N,B′-biborazyl.

and vapor phase chromatography. The data are summarized in Table II.

Lithium Chloride Elimination Reactions.—In each of the syntheses involving elimination of lithium chloride the experimental procedure was essentially the same and therefore will be described in detail only for the preparation of decamethyl-N,B′-biborazyl.

(a) **Preparation of Decamethyl-N,B′-biborazyl** (I).—Into a nitrogen-filled 6-ml. bomb tube was syringed 0.2219 g. (1.473 mmoles) of N-dimethyl-B-trimethylborazine (assay 99.3%). The tube was cooled to −196° under nitrogen, and 1.475 mmoles of ethereal methyllithium was added from a syringe. The tube was sealed under vacuum, allowed to warm to room temperature, and heated briefly at 50° to complete reaction. After cooling to −196° the tube was opened and 32.44 cc. of non-condensable gas (98.5%) was removed. The tube was warmed to room temperature and 0.2745 g. (1.483 mmoles) of pentamethyl-B-chloroborazine dissolved in 1.5 ml. of ether was syringed into the N-lithiopentamethylborazine solution through a rubber septum closure on the tube. Gentle agitation of the mixture produced cloudiness and an evolution of heat. Finally the mixture was shaken vigorously and then centrifuged. The supernatant liquid was withdrawn by a syringe and the solids were washed with 1 ml. of ether and vacuum-dried to yield 0.1300 g. of fine powder analyzing: Li^+, 0.87 meq.; Cl^-, 1.09 meq.; B, 0.15 meq. The residue obtained on evaporation of the ether solution was extracted with 10 ml. of petroleum ether (b.r. 30–60°) leaving 0.0993 g. of fine powder analyzing: Li^+, 0.54 meq.; I^-, 0.49 meq.; B, 0.09 meq. Sublimation of the petroleum ether extract residue yielded 0.0490 g. (0.265 mmole, 17.8%) of unreacted pentamethyl-B-chloroborazine at 50° and 0.2324 g. of sublimate at 100°, leaving 0.1072 g. of residue. Recrystallization of the sublimate from isopropylamine followed by resublimation at 100° yielded 0.1840 g. (0.617 mmole, 42%) of needles, m.p. 172–174°, which were characterized by elemental analyses and molecular weight. *Anal.* Calcd. for $C_{10}H_{30}B_6N_6$: C, 40.13; H, 10.10; mol. wt., 299.3. Found: C, 40.05; H, 10.19; mol. wt., 291.8.

A second experiment on a seven-fold larger scale using the reverse order of addition of the reagents gave decamethyl-N,B′-biborazyl in 50.6% yield. The improved yield is not considered as preparatively significant and probably represents decreased mechanical losses.

An attempt to use standard laboratory glassware and precautions normally employed to exclude moisture from common organometallic reactions resulted in no isolable product other than decamethyl-B,B′-diborazyl oxide (Va), formed by hydrolysis of the pentamethyl-B-chloroborazine and described more fully below.

(b) **Preparation of 1,3-Bis(pentamethyl-2′-borazyl)-2,4,5,6-tetramethylborazine (IIa).**—Using the same technique, 0.6892 g. (5.044 mmoles) of N-methyl-B-trimethylborazine was treated with 10.1 mmoles of methyllithium to prepare N-dilithiotetramethylborazine and 226.3 cc. (100.3%) of by-product methane. Addition of an ethereal solution of 1.8674 g. (10.09 mmoles) of pentamethyl-B-chloroborazine followed by solvent exchange and high vacuum sublimation at a series of ascending temperatures gave the following fractions: at 50°, 0.3313 g., m.p. 85–95°; at 100°, 0.3204 g., m.p. 103–117°; at 140°, 1.2724 g., m.p. 192–206°. The last fraction was resublimed first at 120° to deliver 0.1151 g., m.p. 141–196°; and then at 140° to obtain 1.0190 g., m.p. 196–209°, which was recrystallized from isopropylamine and then resublimed under the same conditions to give 0.6074 g. (1.400 mmoles, 27.8%) of IIa, m.p. 207–210°. *Anal.* Calcd. for $C_{14}H_{42}B_9N_9$: C, 38.75; H, 9.76; mol. wt., 433.9. Found: C, 39.04; H, 9.77; mol. wt., 433.9.

(c) **Preparation of 1,3,5,6-Tetramethyl-2,4-bis(pentamethyl-1′-borazyl)borazine (IIb).**—The same sequence of experimental operations using 1.5122 g. (10.04 mmoles) of N-dimethyl-B-trimethylborazine, 9.79 mmoles of methyllithium, and 1.0045 g. (4.887 mmoles) of tetramethyl-B-dichloroborazine yielded 220.9 cc. (100.8%) of methane and solvent-extracted solids which were fractionally sublimed to obtain (at 100°) 0.2470 g. of solid, m.p. 100–111° and (at 150°) 1.1144 g. of solid. The latter sublimate was recrystallized from isopropylamine and then resublimed at 100° to remove 0.1545 g. of sirupy material and finally at 140° to obtain 0.5550 g. (1.279 mmoles, 26.2%) of IIb, m.p. 135–138°. *Anal.* Calcd. for $C_{14}H_{42}B_9N_9$: C, 38.75; H, 9.76; mol. wt., 433.9. Found: C, 39.13; H, 9.79; mol. wt., 443.0.

(d) **Attempt to Prepare 1,3,5-Tris(pentamethyl-2′-borazyl)-2,4,6-trimethylborazine (IIIa).**—In the same manner as before, combination of 0.4796 g. (3.91 mmoles) of B-trimethylborazine, 11.74 mmoles of methyllithium, and 2.1719 g. (11.73 mmoles) of pentamethyl-B-chloroborazine in ether produced on work-up 0.11 g. of crude pentamethyl-B-chloroborazine, approximately 1 g. of crude decamethyl-B,B′-diborazyl oxide, and approximately 0.5 g. of a viscous oil with molecular weight 211. Vapor phase chromatographic analysis of this oil at 300° showed it to consist of four components, the retention times (min.) of which are indicated in parentheses: 93.1% (2.85), 1.4% (3.75), 4.8% (7.55, shown by comparison with an authentic sample to be decamethyl-B,B′-diborazyl oxide), and 0.6% (9.90). The molecular weight data suggest the major component to be N-triethyl-B-trimethylborazine (mol. wt. 206.78). The retention time of the major component was 33.70 min. when the same sample was chromatographed at 166°. A plot of log (retention volume) *vs.* number of carbons at the latter temperature of B-trimethyl-, N-methyl-B-trimethyl-, N-dimethyl-B-trimethyl- and hexamethylborazines when extrapolated to nine carbon atoms gave a calculated retention time of 39.7 min.

A duplicate experiment served only to confirm the results of the first. The crude decamethyl-B,B′-diborazyl oxide was found to have only slight solubility in liquid ammonia at ambient temperature and accordingly it was recrystallized once from isopropylamine and twice from methylamine in a Schlenk tube to give, depending on the rate of cooling, either fine needles or rhombs, m.p. 133–135°. *Anal.* Calcd. for $C_{15}H_{54}B_{12}N_{12}$: C, 38.03; H, 9.57; mol. wt., 568.5. Calcd. for $C_{10}H_{30}B_6N_6O$: C, 38.09; H, 9.59; mol. wt., 315.3. Found: C, 38.26; H, 9.81; mol. wt., 318.4. The product was proved to be decamethyl-B,B′-diborazyl oxide by melting point, molecular weight, and its infrared spectrum, which was superimposable on that of an authentic sample.

In an effort to avoid the problems caused by cleavage of the solvent ether, another experiment using *n*-hexane as solvent was attempted. The experiment was discontinued when only 26.6 cc. (1.19 mmoles, 33.3%) of ethane was obtained on allowing 0.4373 g. (3.567 mmoles) of B-trimethylborazine to react for 1 hr. with 40 ml. of a 0.37 *N* *n*-hexane solution of ethyllithium (14.8 mmoles).

A final attempt was made to synthesize IIIa using a stepwise approach. In the usual manner, 2.5913 g. (21.13 mmoles) of B-trimethylborazine, 39.0 ml. of 0.82 *N* ethereal methyllithium (32.0 mmoles), and 5.9162 g. (31.96 mmoles) of pentamethyl-B-chloroborazine were combined. From the ratio of the methyllithium to B-trimethylborazine used an equimolar mixture of N-lithio- and N-dilithio-B-trimethylborazines should have been formed. During the exothermic reaction of the mixture of N-lithio-derivatives with pentamethyl-B-chloroborazine a strong odor of trimethylborine was noted in the ether vapor venting from the boiling mixture. After exchanging solvents in the usual manner to remove inorganic lithium salts, the *n*-pentane-soluble products were sublimed in high vacuum at temperatures up to 200°. The sublimate consisted of 4.14 g. of a colorless mass of fine crystals wet with a viscous liquid. A presumably representative sample of this mixture was analyzed vapor phase chromatographically at 300° and compared with standard samples of decamethyl-N,B′-biborazyl (ret. time, 4.85 min.), decamethyl-B,B′-diborazyl oxide (r.t., 7.20 min.), and 1,3-bis(pentamethyl-2′-borazyl)-2,4,5,6-tetramethylborazine (r.t., 24.35 min.) run under identical conditions. The relative amounts and retention times (min.) of the components were 8.1% (1.20), 7.8% (1.45), 40.9% (2.80), *ca.* 0.5% (3.80), 20.6% (7.20), 11.1% (9.45), and 9.5% (18.40). The remaining 1.5% of the mixture was observed as tailing on the first four peaks. The peaks observed at 2.80 and 7.20 min. correspond to those previously observed for N-triethyl-B-trimethylborazine and decamethyl-B,B′-diborazyl oxide, respectively.

(e) **Preparation of 1,3,5-Trimethyl-2,4,6-tris(pentamethyl-1′-borazyl)borazine (IIIb).**—In the same manner, 1.5340 g. (10.18 mmoles) of N-dimethyl-B-trimethylborazine was treated successively with 10.3 mmoles of ethereal methyllithium and 0.7626 g. (3.39 mmoles) of N-trimethyl-B-trichloroborazine, each in 10 ml. of ether. The residue obtained from the solvent extract was sublimed to give, during 3 hr. at 175°, 0.9030 g. (1.59 mmoles, 46.9% yield) of a glassy sublimate, m.p. 189–229°. A single recrystallization from methylamine in a Schlenk tube yielded needles, m.p. 236–245°. *Anal.* Calcd. for $C_{18}H_{54}B_{12}N_{12}$: C, 38.03; H, 9.57; mol. wt., 568.5. Found: C, 38.29; H, 9.72; mol. wt., 593.2.

(f) **Preparation of Poly(1′,2,3′,4,5,5′,6,6′-octamethylbiborazylene) (IV).**—N-Dilithiotetramethylborazine, prepared from 0.6916 g. (5.061 mmoles) of N-methyl-B-trimethylborazine and 10.16 mmoles of methyllithium in 25 ml. of ether, was treated with 1.0417 g. (5.068 mmoles) of tetramethyl-B-dichloroborazine dissolved in 10 ml. of ether. After solvent exchange and washing of the lithium salts, the petroleum ether soluble product was freed of solvent by heating at 150° under high vacuum. The resulting clear yellow resin weighed 1.3128 g. (96.5% yield) and had a wide melting range, 140–160°. The molecular weight was determined microebulliometrically[10] in benzene to be 1356. A large part of the product was reheated under high vacuum to 215°, at which temperature a very small amount of viscous material was removed. The residual material then had a molecular weight of 1382, corresponding to an average degree of polymerization (D.P.) of 5 or a chain of ten rings. The melting range of the material, 163–168° (softens 155°), still was quite broad. *Anal.* Calcd. for $(C_4H_{12}B_3N_3)_n$: C, 35.69; H, 8.98; B, 24.11; N, 31.22; mol. wt., $(134.62)_n$. Calcd. for $C_{40}H_{120}B_{30}N_{30}LiCl$: C, 34.60; H, 8.71; B, 23.38; N, 30.26; Li, 0.50; Cl. 2.55; mol. wt., 1388.6. Found: C, 34.91; H, 8.90; B, 22.3; N, 29.1; Cl, 0.76; mol. wt., 1382.

Attempted Dehydrohalogenation Reactions. (a) **Attempt to Prepare Decamethyl-N,B′-biborazyl (I).**—Eight experiments were performed in which equimolar mixtures of N-dimethyl-B-trimethylborazine and pentamethyl-B-chloroborazine in either benzene or ether solution were heated with an equivalent amount of a tertiary amine (triethylamine, pyridine, or triethylenediamine). In no case was any evidence for formation of decamethyl-N,B′-biborazyl found. The only isolable materials were the amine hydrohalide, starting materials, and decamethyl-B,B′-diborazyl oxide (Va) formed by hydrolysis of the haloborazine compound. The yields of this hydrolysis product varied from 0–67% and were less in those experiments where more rigorous conditions for exclusion of moisture were observed.

In a typical experiment, 2.2386 g. (12.09 mmoles) of N-trimethyl-B-dimethyl-B-chloroborazine (assay, 99.0% by chlorine analysis), 1.8806 g. (12.48 mmoles) of N-dimethyl-B-trimethylborazine (assay, 99.3%), and 200 ml. of anhydrous benzene were placed in a nitrogen-swept 500-ml. flask fitted with a stirrer, a 50-ml. addition funnel, and a condenser. The mixture was stirred to produce a clear solution and then 50 ml. of benzene containing 1.7266 g. (17.06 mmoles) triethylamine (assay, 99.9+%) was added dropwise at room temperature during 30 min. The initially clear solution became cloudy as the insoluble triethylammonium chloride formed. The slurry was refluxed overnight with stirring. An attempt to follow the progress of the reaction by infrared spectroscopic analysis of slurry samples was unsuccessful at the low reactant concentrations. The mixture was filtered under nitrogen. The solids were washed with two 25-ml. portions of benzene and dried first in a stream of nitrogen and finally on the vacuum line to yield 0.9027 g. (54%) of triethylammonium chloride, identified by infrared analysis and low (0.06%) boron content. The solvent was removed from the filtrate leaving 3.6 g. of crude borazine derivatives from which 0.2700 g. (1.79 mmoles, 14.3%) of N-dimethyl-B-trimethylborazine was recovered on the vacuum line. High vacuum sublimation of the residual mixture yielded 0.5556 g. (3.00 mmoles, 24.8%) of recovered pentamethyl-B-chloroborazine at 55° and 1.0318 g. of sublimate at 100°, leaving 0.2030 g. of a dark-brown greasy residue. Recrystallization of the second sublimate from isopropylamine gave 0.7265 g. of vacuum-dried colorless crystals and a mother liquor residue weighing 0.1966 g. The crystals were resublimed at 100° to yield 0.6647 g. (46.3% based on unrecovered B-chloro-derivative) of a crystalline sublimate, m.p. 133–134° and 0.0098 g. of tan fluffy residue. *Anal.* Calcd. for $C_{10}H_{30}B_6N_6$: C, 40.13; H, 10.10; mol. wt., 299.32. Calcd. for $C_{10}H_{30}B_6N_6O$: C, 38.09; H, 9.59; mol. wt., 315.3. Found: C, 37.75; H, 9.61; mol. wt., 313.0. From the density, 1.05 g./cc., determined by flotation at 25°, and the cell dimensions[11] of the orthorhombic crystals (space group P_{na2}, or P_{mna}), $a = 14.27 \pm 0.07$ Å., $b = 11.63 \pm 0.03$ Å., $c = 21.20 \pm 0.03$ Å., $Z = 4$, the molecular weight was calculated to be 320.

(b) **Attempt to Prepare Poly(1′,2,3′,4,5,5′,6,6′-octamethylbiborazylene) (IV).**—In the same manner, an equimolar mixture of tetramethyl-B-dichloroborazine, N-methyl-B-trimethylborazine, and triethylamine was refluxed in benzene for 6 hr., yielding a mixture from which only triethylammonium chloride and a part of the tetramethyl-B-dichloroborazine could be isolated as recognizable compounds.

Hydrolysis Reactions. (a) **Preparation of Deca-**

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[10] M. Dimbat and F. H. Stross, *Anal. Chem.*, **29**, 1517 (1957).

[11] The authors thank Drs. Joseph R. Schwartz, Loyola University of Los Angeles, and Kenneth N. Trueblood, University of California at Los Angeles, for the preliminary X-ray work.

methyl-B,B′-diborazyl Oxide (Va).—Into a nitrogen-filled 15-ml. centrifuge cone fitted with a rubber septum was placed 0.3931 g. (2.12 mmoles) of pentamethyl-B-chloroborazine and 3 ml. of ether. An estimated 0.39–0.44 mmole of distilled water was added by mixing 0.25 ml. of water with 10 ml. of ether and adding 0.77 ml. of this mixture to the agitated borazine solution which deposited a white, milky solid. Addition of 0.2145 g. (2.12 mmoles) of triethylamine resulted in an evolution of heat and precipitation of 0.1826 g. of crude triethylammonium chloride, which was removed by filtration. The ethereal filtrate was evaporated leaving a solid residue which was sublimed at 50° to recover 0.1630 g. (0.881 mmole, 41.5%) of pentamethyl-B-chloroborazine. Further sublimation at 100° yielded 0.0791 g. of solid and left 0.0124 g. of glassy residue. The latter sublimate, recrystallized from isopropylamine and resublimed, had a m.p. 125–129°. However, the infrared spectrum was identical with that of decamethyl-B,B′-diborazyl oxide (m.p. 133–134°) isolated from attempted dehydrohalogenation experiments (*vide supra*). The mixture melting point of these two materials was 126–130°.

(b) **Preparation of Poly(1,3,5,6-tetramethyl-2,4-borazylene Oxide) (VII).**—Into a 100-ml. nitrogen-filled septum bottle equipped with a magnetic stirring bar was placed 2.2805 g. (11.10 mmoles) of tetramethyl-B-dichloroborazine and 50 ml. of ether. A 0.200-ml. (11.11 mmoles) quantity of distilled water was slowly syringed into the stirred borazine solution, producing a voluminous white precipitate. Addition of 2.2774 g. (22.51 mmoles) of triethylamine resulted in considerable evolution of heat. The stirring was continued for 1 hr., after which the solids were filtered, washed with two 10-ml. portions of ether, and vacuum-dried to give 2.6060 g. (18.93 mmoles, 86.7%) of tan, amorphous powder, characterized by infrared and elemental analyses as predominantly triethylammonium chloride. *Anal.* Calcd. for $C_6H_{16}NCl$: N, 10.18; Cl, 25.76. Found: N, 10.58; Cl, 24.37; B, 2.87. Only a trace of material volatilized from the filtrate residue at 150° on attempted vacuum sublimation. The residual light brown glass weighed 1.0790 g. (7.164 mmoles as monomer, 64.7%), melted over the range 180–200°, and showed the characteristic B–O–B infrared absorption (10.52 μ) shown by this class of compounds. *Anal.* Calcd. for $(C_4H_{12}N_3B_3O)_n$: C, 31.89; H, 8.03; mol. wt., $(150.6)_n$. Found: C, 29.17; H, 8.13; mol. wt., 3512 (n = 23.2).

(c) **Preparation of Low Molecular Weight 2,4-Borazylene Oxides (VI).**—Co-hydrolysis of a mixture of 1.1146 g. (6.021 mmoles) of pentamethyl-B-chloroborazine and 0.6186 g. (3.010 mmoles) of tetramethyl-B-dichloroborazine with the stoichiometric quantity of aqueous triethylamine yielded on sublimation the following fractions: (1) 0.2102 g. (0.6667 mmole) or 22.1% of the pentamethyl-B-chloroborazine as decamethyl-B,B′-diborazyl oxide (obtained at 100°), identified by m.p. 126–131° and infrared spectrum; (2) 0.2051 g. of a colorless sticky sublimate (obtained at 140°), m.p. 133–155°, mol. wt. 478.6, tentatively characterized as a "dioxide" (VI where n = 1, mol. wt. 465.9–469.9); and (3) 0.4460 g. of a brittle yellow glassy residue of molecular weight 734.5 or approximately a "tetraoxide" (VI where n = 3, mol. wt. 766.2–771.1).

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B_5H_9–DCl Exchange Catalyzed by $AlCl_3$

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Treatment of pentaborane-9 with deuterium chloride in the presence of aluminum chloride results in the rapid exchange of hydrogen and deuterium in the 1-position. 1-Deuteriopentaborane was identified by the B^{11} and H^1 n.m.r. spectra and confirmed by the stoichiometry of the exchanging species at equilibrium.

Introduction

Perdeuteriopentaborane[1,2] and 1,2,3,4,5-pentadeuteriopentaborane[3] are the only deuterium-substituted pentaborane species (see Table I) reported in the literature. In this work is described a synthesis of 1-deuteriopentaborane by deuterium exchange of pentaborane-9 with deu-

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(3) (a) W. S. Koski, J. J. Kaufman, and P. C. Lauterbur, *J. Am. Chem. Soc.*, **79**, 2382 (1957); (b) exchange of $B_2{}^{10}H_6$ with B_5H_9 indicates that some bridge deuteration also is taking place as indicated by infrared and mass spectral data; J. F. Ditter, unpublished data.