N, 23.0; C, 59.0; H, 12.1; mol wt, 183.1. Found: B, 5.8; N, 22.8; C, 58.7; H, 12.2; mol wt (by mass spectroscopy and cryoscopy in benzene), 155.

1,3,5-Trimethyl-2-dimethylamino-1,3,2-diazaboracyclohexane, bp 81° (14 mm), was obtained in an analogous procedure using hexane as solvent in 77% yield. In a second experiment under identical conditions the yield was only 18%. *Anal.* Calcd for $BN_3C_8H_{20}$: B, 6.4; N, 24.9; C, 56.8; H, 11.9; mol wt, 169.1. Found: B, 6.3; N, 25.0; C, 56.4; H, 11.8; mol wt (by mass spectroscopy and cryoscopy in benzene), 169.

The yields cited above represent only one or two experiments in each case. No attempt has been made to obtain maximum yields or to improve on them.

Dodecahydrotris((1,3,2)-diazaborino[1,2-*a*:1′,2′-*c*:1″,2″-*e*])-*s*-triazatriborine (IV).—A mixture of 9.8 g (0.1 mol) of tris(dimethylamino)borane and 7.4 g (0.1 mol) of 1,3-diaminopropane was heated in an oil bath of 175° for 2 hr. The reaction product was distilled *in vacuo* and 5.7 g (70%) of IV was obtained; bp 178–182° (0.1 mm), mp 155°, mol wt 203 (by mass spectroscopy); calcd for $B_3N_3C_9H_{21}$: mol wt 203.8, lit.[4] bp 190–195° (1 mm), lit.[4] mp 154–155°.

Discussion

The great potential of the transamination reaction in preparative boron–nitrogen chemistry[7] is again demonstrated by the preparation of 2-amino-1,3,2-diazaboracycloalkanes. The failure to isolate pure products in which the annular nitrogen atoms are not substituted with organic groups can be related to the fact that in the intermediate product, III, all three boron–nitrogen bonds are likely to be coplanar.[8] This latter situation provides for a ready opportunity for intermolecular elimination of dimethylamine and formation of the thermally stable and planar borazine ring system, IV.

When ethylenediamine was allowed to react with tris(dimethylamino)borane, a polymeric material was obtained as primary product. This event seems to indicate that formation of the 1,3,2-diazaboracyclopentane system competes with the formation of the linear product $(-BNR_2-NH-CH_2-CH_2NH-)_n$. It appears possible that ring strain in the five-membered B–N–C heterocycle may be causing the competing reaction to occur. On the other hand, N,N′-disubstituted ethylenediamines readily form the cyclic system in reasonable yield[9] and there may be additional factors which play an important role in directing the course of the reaction.

The infrared spectra of the 2-amino-1,3,2-diazaboracycloalkanes are very similar to the spectrum of tris(dimethylamino)borane. This observation is not surprising since their structures are related. The major difference is the observation of ring pulsation modes in the B–N–C heterocycles. The frequencies of these modes were reported for 2-organo-substituted 1,3,2-diazaboracycloalkanes[2,10] with a tentative assignment near 850 cm^{-1} for the five-membered rings and near 740 cm^{-1} for the six-membered B–N–C heterocycles. This observation corresponds with our present data.

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The N-Methyl Derivatives of Borazine

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Schlesinger, Ritter, and Burg[1] first prepared the N-methyl derivatives of borazine in 1938 by heating mixtures of CH_3NH_2, NH_3, and B_2H_6. Because they were difficult to obtain, very little was known about these compounds until recently when Beachley[2] reported new synthetic methods for the four unsymmetrically substituted N-methyl and B-methyl borazines along with their boron-11 and proton nmr, infrared, and mass spectra. As part of a general study of the mechanism of cleavage of B_5H_9 we have found that $H_3B_3N_3H_3$, $H_3B_3N_3H_2CH_3$, $H_3B_3N_3H(CH_3)_2$, $H_3B_3N_3(CH_3)_3$, and μ-$CH_3NHB_2H_5$ can be prepared in a series of reactions involving B_5H_9, NH_3, and CH_3NH_2.

Experimental Section

Materials.—B_5H_9 (Callery), NH_3 (Matheson), and CH_3NH_2 (Matheson) were purified by repeated fractionation through low temperature traps: B_5H_9 (−63 and −95°), NH_3 (−63 and −95°), and CH_3NH_2 (−23 and −95°). The fraction condensing at the lower temperature was retained. Purity was monitored by gas chromatography and infrared spectroscopy.

Apparatus and Procedures.—All compounds used in this study were handled in a standard vacuum system. Reactions were carried out in sealed Pyrex flasks equipped with break-off tips. Volatile products were detected and separated in an air-free gas chromatographic system using either a 9.8 ft × 0.25 in. column of Kel-F on Chromosorb W or a 9.8 ft × 0.25 in. column of Apiezon-L on Chromosorb W.

Infrared spectra were recorded in the range 4000–600 cm^{-1} on a Perkin-Elmer 337 spectrophotometer using a 9-cm gas cell equipped with NaCl windows. Mass spectra were obtained on a CEC-104 spectrometer.

Proton nmr spectra were recorded on a Varian HA-100 spectrometer.

Reactions of Pentaborane(9) with Monomethylamine.—Measured quantities (Table I) of B_5H_9 and CH_3NH_2 were condensed into a 120-ml flask which had been evacuated and cooled in liquid nitrogen. The reactor was then sealed and the liquid nitrogen removed. After warming to room temperature the reaction was allowed to proceed at the desired temperature. In all reactions a small amount of viscous liquid appeared at the bottom of the flask shortly after the reaction began. Although the liquid appeared to form throughout most of the reaction time, the total amount was never very large. At the end of each experiment the reactor was cooled in liquid nitrogen and opened into the vacuum line. Noncondensables were pumped out of the system, after which the volatile materials were transferred into the vacuum line and separated by gas chromatography. The viscous liquid which formed in the reaction turned out to be nonvolatile and did not transfer out of the reactor.

Reactions of Pentaborane(9) with Monomethylamine and Ammonia.—The experimental procedure was essentially the same as that followed in the reactions of B_5H_9 with CH_3NH_2 (Table I). Approximately the same amount of nonvolatile liquid formed.

Pyrolysis of μ-Methylaminodiborane.—A measured quantity

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Table I

Reactions of B_5H_9 with NH_3 and CH_3NH_2

Reactants, mmol					Products, mmol				
B_5H_9	NH_3	CH_3NH_2	Temp, °C	Time, hr	μ-$CH_3NHB_2H_5$	$H_3B_3N_3H_3$	$H_3B_3N_3H_2CH_3$	$H_3B_3N_3H(CH_3)_2$	$H_3B_3N_3(CH_3)_3$
1.20	1.20	1.20	25	23	0.25	...	0.01	0.01	*a*
1.20	1.20	1.20	100	1	0.83	0.45	0.21	0.01	*a*
1.20		1.20	25	23	0.24	...	*a*	*a*	0.06
1.20		1.20	100	1	0.85	...	*a*	*a*	0.33

[a] Very small, but easily detectable, amounts.

of μ-$CH_3NHB_2H_5$ (1.40 mmol) was condensed into a previously evacuated 20-ml reactor cooled in liquid nitrogen, after which the flask was sealed, the liquid nitrogen removed, and the reactor and its contents, allowed to warm to room temperature. After heating in an oven at 110° for 1 hr, the reactor was again cooled in liquid nitrogen and opened into the vacuum line. The volatile materials were transferred into the vacuum line and separated by gas chromatography. The resulting products, with yields, were: B_5H_9 (0.06 mmol), B_2H_6 (0.02 mmol), $H_3B_3N_3(CH_3)_3$ (0.4 mmol), recovered μ-$CH_3NHB_2H_5$ (0.33 mmol), and trace amounts of $H_3B_3N_3H_3$, $H_3B_3N_3H_2CH_3$, and $H_3B_3N_3H(CH_3)_2$.

Results and Discussion

As shown in Table I, $H_3B_3N_3H_3$, $H_3B_3N_3H_2CH_3$, $H_3B_3N_3H(CH_3)_2$, $H_3B_3N_3(CH_3)_3$, and μ-$CH_3NHB_2H_5$ were prepared by allowing B_5H_9 to react with NH_3 and CH_3NH_2 in the gas phase at 100°. With the exception of unsubstituted borazine the same products were formed in the reaction between B_5H_9 and CH_3NH_2; however, the yields of unsymmetrical derivatives were lower than in the reactions which included NH_3, while the yield of the trimethyl derivative was higher. In addition to the volatile products a small amount of nonvolatile, highly viscous liquid formed in every reaction. Others have reported some work on the characterization of this liquid.[3]

Borazine and $H_3B_3N_3(CH_3)_3$ were identified by comparison of the infrared spectra with that of the published spectra.[4] $H_3B_3N_3H_2CH_3$ and $H_3B_3N_3H(CH_3)_2$ were identified by infrared, proton nmr, and mass spectra. The data corresponded very closely to those reported by Beachley.[2] μ-Methylaminodiborane was identified by comparing the infrared and mass spectra with that of an authentic sample made by the method of Burg and Randolph.[5]

The presence of μ-methylaminodiborane also suggested a possible mechanism for the formation of the borazine ring in which B_5H_9 and the amine(s) react to form μ-methylaminodiborane followed by conversion to the borazine ring system. This would be consistent with the work of Schlesinger, Ritter, and Burg,[6] who reported obtaining high yields of borazine by heating μ-aminodiborane. When 1.40 mmol of μ-methylaminodiborane was heated at 110° for 1 hr good yields of $H_3B_3N_3(CH_3)_3$ were obtained along with trace amounts of $H_3B_3N_3H_3$, $H_3B_3N_3H_2CH_3$, and $H_3B_3N_3H(CH_3)_2$. This result strongly supports the above mechanism for the formation of the trimethyl derivatives but the formation of unsymmetrical derivatives probably involves some additional interaction between μ-$CH_3NHB_2H_5$ and one or more of the original reactants. This aspect is currently being investigated.

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Metal-Metal Stretching Frequencies in Polymetallic Carbonyls

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In recent years, Raman and far-infrared spectroscopies have been shown to be effective tools for studying metal-metal stretching vibrations.[1-3] Having recently prepared several novel linear polymetallic carbonyls,[4-6] we report the results of an investigation of the Raman and far-infrared spectra of these and other similar compounds.

Table I summarizes the metal-metal stretching frequencies which have been observed in the present work along with earlier published data. In most cases, there is little uncertainty about the assignments of these bands to metal-metal stretching vibrations since in metal carbonyls ν_{M-CO} and δ_{MCO} lie above 300 cm^{-1} and δ_{CMC} modes are found below 120 cm^{-1}.[3] One can further distinguish between ν_{M-M} and δ_{CMC} by means of intensity, the metal-metal stretching modes being more intense, especially in the Raman spectrum.

For the bimetallic homonuclear carbonyls ν_{M-M} appears as an intense polarized line in the Raman spectra.[1] This vibration is not allowed in the infrared spectrum. However, when the molecule is heteronuclear, $\nu_{M'-M}$ is both Raman and ir active but is generally weak in the far-infrared region.[3] For $ReMn(CO)_{10}$ our assignment differs from that of Gager, Lewis, and Ware.[1] They assigned a band at 182 cm^{-1}

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