In order to substantiate structure I, a quantity of 1,1,1,3,3,3-hexafluoro-2-chloroisopropylaminodichloroborane was hydrolyzed (eq 2). The resultant amine II

$$(CF_3)_2CClNHBCl_2 + 3H_2O \longrightarrow \underset{II}{(CF_3)_2CClNH_2} + 2HCl + H_3BO_3 \quad (2)$$

is a solid at room temperature which is quite unstable and readily decomposes to hexafluoroisopropylideneimine and HCl. The structure of II was ascertained by the presence of two NH stretching modes in the infrared spectrum of the compound which were observed at 3140 and 3020 cm^{-1}, respectively. These frequencies are substantially lower than those observed in the spectrum of $(CF_3)_2C(NH_2)_2$.[4]

Compounds of type I fume strongly on contact with air, react violently with water, and are extremely corrosive. However, in inert atmosphere, they can be stored for prolonged periods of time, and they seem to be thermally stable since they can be distilled without decomposition.

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Boron–Nitrogen Compounds. XXXII.[1] 2-Amino-1,3,2-diazaboracycloalkanes

BY KURT NIEDENZU, PAUL J. BUSSE, AND CLIFFORD D. MILLER

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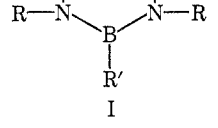
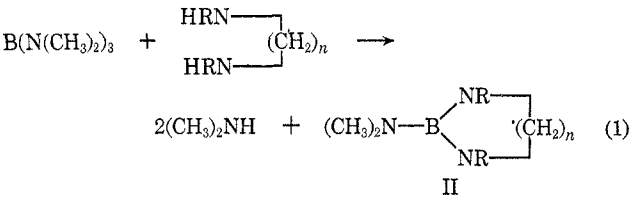
The first synthesis of a σ-bonded boron–nitrogen–carbon heterocycle was reported by Goubeau and Zappel in 1955.[2] Since that date several preparative routes have been explored to provide access to the 1,3,2-diazaboracycloalkane system, I.[3] However, with the exception of a few compounds, only those derivatives of I in which R′ = alkyl or aryl have been described



I

In particular, 1,3,2-diazaboracycloalkanes with an exocyclic boron–nitrogen bond are unknown. Since B–N groups are very reactive, 2-amino-1,3,2-diazaboracycloalkanes may be potential precursors for the synthesis of a variety of boron-substituted 1,3,2-diazaboracycloalkanes.

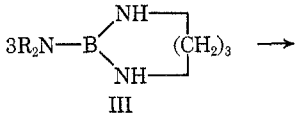
The present study reports on the synthesis of 2-amino-1,3,2-diazaboracycloalkanes. These compounds are readily produced through a transamination reaction between tris(dialkylamino)boranes such as $B[N(CH_3)_2]_3$ and aliphatic N,N′-disubstituted α,ω-diamines in inert organic solvents (eq 1). In order



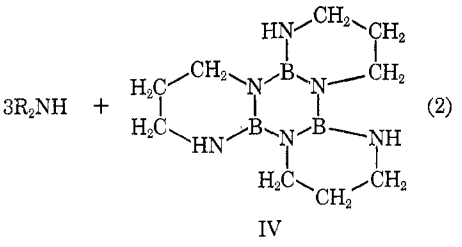
II

to obtain reasonable yields it is necessary to reflux the reaction mixture for several hours.

The utilization of ethylenediamine in an analogous reaction with tris(dimethylamino)borane did not yield the desired product II, R = H, n = 2. Rather, a polymeric material was obtained which could not be purified. Impure 2-dimethylamino-1,3,2-diazaboracyclohexane (III) was obtained on refluxing tris(dimethylamino)borane with 1,3-diaminopropane in ether.[4] On attempts to purify the product by distillation additional elimination of dimethylamine and trimerization occur yielding the borazine derivative IV (eq 2).



III



IV

Experimental Section[5]

Tris(dimethylamino)borane was prepared by a literature procedure.[6] All diamines were obtained from the Ames Laboratories, Milford, Conn.; they were dried over potassium hydroxide and were used without additional purification. Solvents were dried over metallic sodium.

1,3-Dimethyl-2-dimethylaminodiazaboracyclohexane (I, R = CH_3, R′ = $N(CH_3)_2$, n = 3) (Typical Experiment).—A solution of 51 g (0.5 mol) of N,N′-dimethyl-1,3-diaminopropane in 600 ml of pentane was added with stirring to a solution of 48.9 g (0.5 mol) of tris(dimethylamino)borane in 600 ml of pentane. The mixture was refluxed for about 5 hr. Pentane was stripped off at normal pressure and the residue was distilled under reduced pressure to yield 56.5 g (73%) of 1,3-dimethyl-2-dimethylaminodiazaboracyclohexane, bp 50° (2 mm). *Anal.* Calcd for $BN_3C_7H_{18}$: B, 7.0; N, 27.1; C, 54.2; H, 11.7; mol wt, 155.0. Found: B, 6.9; N, 27.3; C, 53.9; H, 11.6; mol wt (by mass spectroscopy and cryscopy in benzene), 155.

1,3-Dimethyl-2-dimethylaminodiazaboracyclopentane, bp 33–34° (2 mm), was obtained in an analogous procedure in 52% yield. Pentane was used as a solvent. *Anal.* Calcd for $BN_3C_6H_{16}$: B, 7.7; N, 29.8; C, 51.1; H, 11.4; mol wt, 141.0. Found: B, 7.5; N, 29.9; C, 50.8; H, 11.3; mol wt (by mass spectroscopy and cryoscopy in benzene), 141.

1,3-Diethyl-2-dimethylaminodiazaboracyclohexane, bp 68° (6 mm), was obtained in an analogous procedure using n-hexane as solvent in 37% yield. *Anal.* Calcd for $BN_3C_9H_{22}$: B, 5.9;

(1) Part XXXI: K. Niedenzu, K. E. Blick, and C. D. Miller, *Inorg. Chem.*, **9**, 975 (1970),

(2) J. Goubeau and A. Zappel, *Z. Anorg. Allgem. Chem.*, **279**, 38 (1955).

(3) K. Niedenzu, *Allgem. Prakt. Chem.*, **17**, 596 (1966).

(4) K. Niedenzu and P. Fritz, *Z. Anorg. Allgem. Chem.*, **340**, 329 (1965).

(5) Infrared spectra of the materials were recorded on a Perkin-Elmer Model 621 spectrophotometer using cesium iodide windows. The instrument was purchased with funds made available by the University of Kentucky Major Research Equipment Committee. Analyses were furnished by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(6) K. Niedenzu and J. W. Dawson, *Inorg. Syn.*, **10**, 135 (1967).

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.

(7) K. Niedenzu and J. W. Dawson, "Boron-Nitrogen Compounds," Springer-Verlag, Berlin, 1965.

(8) K. Niedenzu, C. D. Miller, and S. L. Smith, *Z. Anorg. Allgem. Chem.*, in press.

(9) W. Weber, J. W. Dawson, and K. Niedenzu, *Inorg. Chem.*, **5**, 726 (1966).

(10) K. Niedenzu and P. Fritz, *Z. Anorg. Allgem. Chem.*, **344**, 329 (1966).

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The N-Methyl Derivatives of Borazine

BY C. L. BRAMLETT AND A. T. TABEREAUX, JR.

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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

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

(2) O. T. Beachley, Jr., *Inorg. Chem.*, **8**, 981 (1969).