chloramine molecule of the less basic of the two hydrazine nitrogens, followed by the migration of a proton. Since the ^1H nmr spectrum shows only two signals (NH_2, τ 3.28; CH_3, τ 6.47, area ratio 4:6) and the infrared spectrum has no absorption between 2700 and 2200 cm^{-1} (indicating the probable absence of NH^+, NH_2^+, and NH_3^+), it is proposed that dimethyltriazanium chloride has the structure II. Alternative conclusions are highly improbable.

Hydrazine and chloramine (mole ratio 1:1) react in ether to give a mixture of hydrazinium chloride, ammonium chloride, and nitrogen. Reaction at $-50°$ indicates that, in accordance with the previously published assumption,[3] the first step in this reaction is the formation of triazanium chloride

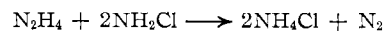$$NH_2-NH_2 + NH_2Cl \longrightarrow [NH_2-NH_2-NH_2]^+Cl^-$$
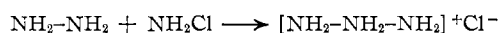
which subsequently on warming to room temperature decomposes. Two stoichiometries for the decomposition suggest themselves

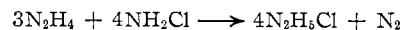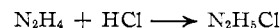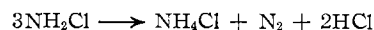$$2N_3H_6Cl \longrightarrow 2NH_4Cl + N_2H_4 + N_2$$

and

$$4N_3H_6Cl \longrightarrow 4N_2H_5Cl + N_2H_4 + N_2$$
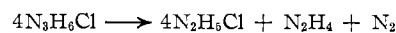
so the over-all reactions for the two decompositions are, respectively

$$N_2H_4 + 2NH_2Cl \longrightarrow 2NH_4Cl + N_2$$

and

$$3N_2H_4 + 4NH_2Cl \longrightarrow 4N_2H_5Cl + N_2$$

The formation of the N_2H_5Cl can be explained also by a decomposition of chloramine on the solid reaction product

$$3NH_2Cl \longrightarrow NH_4Cl + N_2 + 2HCl$$
$$N_2H_4 + HCl \longrightarrow N_2H_5Cl$$

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Possible Intermediates in the Formation of 1,3,5-Trimethylborazine

BY O. T. BEACHLEY, JR.

The 110° pyrolysis of $H_2B(NH_2CH_3)_2^+Cl^-$, $H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3^+Cl^-$, and mixtures of $(H_2BNHCH_3)_3$ and CH_3NH_3Cl give $H_3B_3N_3(CH_3)_3$, CH_3NH_3Cl, and H_2. The intermediates in the formation of the borazine ring have been investigated by studying the conversion of $H_2B(NH_2CH_3)_2^+Cl^-$ to $H_3B_3N_3(CH_3)_3$ in a mass spectrometer and by attempting to prepare possible intermediates. The current experimental evidence suggests that an initial intermediate is a linear, six-membered boron–nitrogen chain. Then, an intramolecular dehydrogenation ring-closure reaction between the ends of the chain leads to a species analogous to cyclohexenes. The more stable borazine ring is then formed from the cyclohexene type of species by the rapid loss of H_2.

The pyrolysis[1] of $H_2B[N(CH_3)_3]_2^+Cl^-$ at 200–250° in a vacuum sublimator provides a good route to $H_2ClBN(CH_3)_3$. We wish to report our results on the pyrolysis of the remaining two members of the series, $H_2B[N(CH_3)_2H]_2^+Cl^-$ and $H_2B[NH_2CH_3]_2^+Cl^-$, the analogous compound, $H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3^+Cl^-$, and, based on these reactions and others, our observations of possible intermediates in the formation of 1,3,5-trimethylborazine.

The compound $H_2B[N(CH_3)_2H]_2^+Cl^-$ readily sublimes unchanged at 125–130° and does not undergo any apparent chemical reaction in a sealed tube at 150°. In contrast, $H_2B[NH_2CH_3]_2^+Cl^-$ decomposes at 110° to form $H_3B_3N_3(CH_3)_3$, CH_3NH_3Cl, and H_2. The compound[2] $H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3^+Cl^-$ also decomposes at 110° to form the identical products, but the rate of formation of $H_3B_3N_3(CH_3)_3$ is signifi-

cantly faster than for $H_2B[NH_2CH_3]_2^+Cl^-$. The following equations summarize these pyrolytic reactions

$$H_2B[N(CH_3)_2H]_2^+Cl^- \xrightarrow{125-150°} \text{sublimation with no decomposition} \quad (1)$$

$$H_2B[NH_2CH_3]_2^+Cl^- \xrightarrow{110-125°} {}^1/_3H_3B_3N_3(CH_3)_3 + CH_3NH_3Cl + H_2 \quad (2)$$

$$H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3^+Cl^- \xrightarrow{110-125°} {}^2/_3H_3B_3N_3(CH_3)_3 + CH_3NH_3Cl + 2H_2 \quad (3)$$
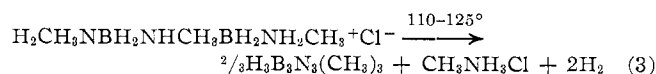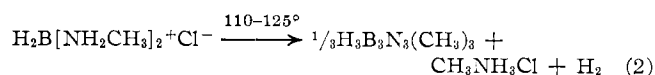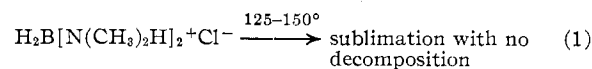
There are two distinctly different routes for the formation of the borazine ring from the pyrolysis of $H_2B(NH_2CH_3)_2^+Cl^-$ or $H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3^+Cl^-$. The simplest mechanism involves the formation of the monomeric borazyne species $HBNCH_3$ which then associates to give the trimer. The other mechanism requires the formation of complex linear species which undergo ring closure, then dehydrogenation to form $H_3B_3N_3(CH_3)_3$. Our experimental data suggest that the compound $H_2CH_3NBH_2NHCH_3BH_2$-

(1) N. E. Miller, B. L. Chamberland, and E. L. Muetterties, *Inorg. Chem.*, **3**, 1064 (1964).

(2) O. T. Beachley, Jr., *ibid.*, **6**, 870 (1967).

TABLE I

PYROLYSES AT 110°

Reactants (mmoles)	Yield of volatile products, mmoles			
	24 hr		11 days	
	H_2	$H_3B_3N_3(CH_3)_3$	H_2	$H_3B_3N_3(CH_3)_3$
$H_2B(NH_2CH_3)_2{}^+Cl^-$ (1.25)	1.02	0.285	1.06	0.335
$H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3{}^+Cl^-$ (1.25)	2.16	0.601	2.36	0.668
eee[a] $(H_2BNHCH_3)_3$ (0.970)	...	...	0.207	0
eea[b] $(H_2BNHCH_3)_3$ (0.966)	...	...	0.636	0.0138
eee $(H_2BNHCH_3)_3$ (0.903), CH_3NH_3Cl (0.903)	1.92	0.570	2.46	0.730
eea $(H_2BNHCH_3)_3$ (0.918), CH_3NH_3Cl (0.918)	2.65	0.742	2.79	0.810
eee $(H_2BNHCH_3)_3$ (0.838), $H_2B(NH_2CH_3)_2{}^+Cl^-$ (0.838)	2.49	0.790	2.82	0.903
eea $(H_2BNHCH_3)_3$ (1.01), $H_2B(NH_2CH_3)_2{}^+Cl^-$ (1.01)	3.73	1.06	4.27	1.19

[a] eee signifies a $(H_2BNHCH_3)_3$ isomer[7] with three equatorial methyl groups. [b] eea signifies a $(H_2BNHCH_3)_3$ isomer[7] with one axial and two equatorial methyl groups.

$NHCH_3BH_2NH_2CH_3{}^+Cl^-$ is a primary intermediate for the formation of the borazine ring from these reactions. If this compound looses a molecule of NH_2CH_3 which in turn acts as a base to remove a proton, species such as $H_2BNHCH_3BH_2NHCH_3BH_2$-$NHCH_3$ or $H_2BNCH_3BH_2NHCH_3BH_2NH_2CH_3$ will be formed. The next reaction, ring closure by an intramolecular dehydrogenation between the two ends of the chain, would lead to derivatives analogous to cyclohexenes, which would then rapidly lose the second and third molecules of H_2 to form the significantly more stable $H_3B_3N_3(CH_3)_3$. The proposed reaction for ring closure is analogous to that proposed for the formation of the N-methylaminoborane trimer[2] $(H_2$-$BNHCH_3)_3$. If the end groups H_3B and NH_2CH_3 are four-coordinate, the N-methylaminoborane trimer will form, whereas, if one of the end groups H_2B or $NHCH_3$ is three-coordinate, the cyclohexene species and eventually the borazine ring will form. This set of intermediates does not require the aminoborane trimer to be an intermediate, as they are generally not observed[3] in the formation of borazines. However, the boron amines,[3,4] $H[NRBCl]_nCl$, observed when borazines are not formed, would be formed if there is steric hindrance to the ring-closure reaction. The rapid dehydrogenation of the cyclohexene type of species is consistent with the observation that failures in the attempted preparation[5] of a cyclohexadiene derivative, $H_4B_3N_3H(CH_3)_3$, were due to rapid dehydrogenation at 0° to form $H_3B_3N_3(CH_3)_3$.

The attempts to distinguish the intermediates in the formation of the borazine ring were initiated by directly studying the pyrolysis of $H_2B(NH_2CH_3)_2{}^+Cl^-$ at 110° in a mass spectrometer.[6] The species initially formed had one and two boron atoms (m/e 115–111, 86–81, 57–51, 43–41) but had more hydrogen than is possible for a borazyne species $(HBNCH_3)_x$. There were also masses (m/e 129–125) corresponding to three boron atoms, $(H_2BNHCH_3)_3$. Therefore, these observations initially suggest that the association of H_2BNHCH_3 species followed by the elimination of H_2 leads to the formation of the borazine.

The masses 129–125 corresponding to $(H_2BNHCH_3)_3$ suggest that a possible route to the borazine ring might be the simple dehydrogenation of the six-membered ring of the N-methylaminoborane trimer. To test this hypothesis, the pyrolyses of the two isomers[7] of $(H_2BNHCH_3)_3$ were investigated under conditions identical with the pyrolysis of $H_2B(NH_2CH_3)_2{}^+Cl^-$, a sealed tube at 110° (Table I). Only 14% of the isomer initially having one axial and two equatorial methyl groups was converted to $H_3B_3N_3(CH_3)_3$ after heating for 11 days. The remainder was converted to the isomer with three equatorial methyl groups. The isomer with three equatorial methyl groups was essentially unchanged after being exposed to identical conditions, 110° for 11 days. In comparison, the 110° pyrolysis of $H_2B(NH_2CH_3)_2{}^+Cl^-$ or $H_2CH_3NBH_2$-$NHCH_3BH_2NH_2CH_3{}^+Cl^-$ leads to the formation of 70% of the possible $H_3B_3N_3(CH_3)_3$ in only 24 hr. Therefore, the simple dehydrogenation of the cyclic molecule $(H_2BNHCH_3)_3$ is probably not the route to $H_3B_3N_3(CH_3)_3$. The $(H_2BNHCH_3)_3$ ring system might not be expected to be formed because the intermediates[2] suggested for its formation are not present. If the ring system of $(H_2BNHCH_3)_3$ could form by a different route, it is apparently still too stable to form $H_3B_3N_3(CH_3)_3$ under the conditions of pyrolysis. However, the species with m/e 129–125 could be a linear rather than cyclic molecule and hence could be significantly more reactive.

Another mode of reaction for the three boron atom species (m/e 129–125) might involve the other component of the reaction mixture, CH_3NH_3Cl, a product and possible catalyst for the dehydrogenation of $(H_2BNHCH_3)_3$. The ammonium ion[8] has been previously observed to be a catalyst for the dehydrogenation of amine boranes, RH_2BNH_3. The pyrolysis of mixtures of $(H_2BNHCH_3)_3$ and CH_3NH_3Cl at 110° for 24 hr led to the formation of 63% of the possible borazine. Similarily, a mixture of $(H_2BNHCH_3)_3$ and $H_2B(NH_2CH_3)_2{}^+Cl^-$ led to 75% of the possible $H_3B_3N_3(CH_3)_3$. The less symmetrical isomer was always observed to be more reactive than the isomer with three equatorial methyl groups.

(3) H. S. Turner and R. J. Warne, *J. Chem. Soc.*, 6421 (1965).
(4) M. F. Lappert and M. K. Majumdar, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 227.
(5) D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 3592 (1963).
(6) R. F. Porter and R. C. Schoonmaker, *J. Phys. Chem.*, **62**, 234 (1958).

(7) D. F. Gaines and R. Schaeffer, *J. Am. Chem. Soc.*, **85**, 395 (1963).
(8) M. F. Hawthorne, *ibid.*, **83**, 833 (1961).

The catalyst, CH_3NH_3Cl, might provide a low-energy path for ring cleavage and lead to the formation of $H_2CH_3NBH_2NHCH_3BH_2NHCH_3BH_2NH_2CH_3{}^+Cl^-$. The initial dissociation of CH_3NH_3Cl would provide the reactive species HCl and CH_3NH_2. The HCl would cleave the ring and the amine would displace the chlorine to form the desired species, a primary intermediate for the formation of the borazine ring. Similarily, the addition of HCl and CH_3NH_2 to the species with three boron atoms (m/e 129–125) observed with the mass spectrometer would give the identical compound. Therefore, both starting materials, H_2B-$(NH_2CH_3)_2{}^+Cl^-$ or a mixture of $(H_2BNHCH_3)_3$ and CH_3NH_3Cl, can give the same intermediate species, $H_2CH_3NBH_2NHCH_3BH_2NHCH_3BH_2NH_2CH_3{}^+$-$Cl^-$, and a consistent route to the borazine is possible. A partial pyrolysis of a mixture of $(H_2BNHCH_3)_3$ and CH_3NH_3Cl at 110° demonstrated that a compound having the properties expected for $H_2CH_3NBH_2$-$NHCH_3BH_2NHCH_3BH_2NH_2CH_3{}^+Cl^-$ is formed along with larger amounts of $H_2CH_3NBH_2NHCH_3BH_2NH_2$-$CH_3{}^+Cl^-$ and $H_2B(NH_2CH_3)_2{}^+Cl^-$. If the ionic species with three boron atoms is a precursor to the borazine ring, one would expected this species to be the most reactive and present in the smallest quantities, compared to the less reactive $H_2CH_3NBH_2NHCH_3BH_2$-$NH_2CH_3{}^+Cl^-$ and $H_2B(NH_2CH_3)_2{}^+Cl^-$. The species with one and two boron atoms require the association of H_2BNHCH_3 species, an apparently reversible step, before ring closure of species of the type H_2BNHCH_3-$BH_2NHCH_3BH_2NHCH_3$ and borazine formation can occur. This conclusion is also consistent with the initial observation that $H_2B(NH_2CH_3)_2{}^+Cl^-$ is converted to $H_3B_3N_3(CH_3)_3$ more slowly than $H_2CH_3NBH_2$-$NHCH_3BH_2NH_2CH_3{}^+Cl^-$. There is further evidence that the amine hydrochloride actually enters into the reaction. The pyrolysis of a mixture of $(H_2BNHCH_3)_3$ and $C_2H_5NH_3Cl$ at 110° gives a mixture of all of the possible unsymmetrical N-methylethylborazines, 1,3,5-trimethylborazine, and 1,3,5-triethylborazine. The unsymmetrical borazines are not formed from the interaction of 1,3,5-trimethylborazine and $C_2H_5NH_3Cl$ at 110°.

On the basis of the currently available experimental evidence, ring closure to form a species analogous to cyclohexenes followed by rapid dehydrogenation is a more likely route to the borazine ring than the association of monomeric borazyne species, if an amine hydrochloride is a component of the reaction mixture. However, there is no specific evidence which can be used unequivocally to eliminate a borazyne species ($HBNCH_3$) as a possible intermediate. Similarly, there is also no evidence to support the presence of monomeric borazyne species.

Experimental Section

All reactions were carried out either under vacuum or in a purified nitrogen atmosphere. The compounds $H_2B[N(CH_3)_2$-$H]_2{}^+Cl^-$, $H_2B(NH_2CH_3)_2{}^+Cl^-$, $H_2CH_3NBH_2NHCH_3BH_2NH_2$-$CH_3{}^+Cl^-$, and $(H_2BNHCH_3)_3$ were prepared according to previously described procedures.[2,5]

Pyrolytic Reactions.—The pyrolytic reactions were carried out in evacuated, sealed tubes. After heating at 110° for the time desired, a side-arm break-seal was used to remove the volatile components. The hydrogen was measured with a Toepler pump-gas buret assembly. If further heating of the same sample was required, the side arm was sealed off and removed. In experiments in which the volatile components were measured twice, the pyrolysis tubes had two break-seal side arms. The results of the pyrolytic reactions are given in Table I. The products, CH_3NH_3Cl and $H_3B_3N_3(CH_3)_3$, were identified by their infrared spectra. The unsymmetrical N-methylethylborazines were identified by their mass spectra.

Partial Pyrolysis of a Mixture of $(H_2BNHCH_3)_3$ and CH_3NH_3-Cl.—A mixture of the $(H_2BNHCH_3)_3$ isomer[7] with one axial and two equatorial methyl groups (0.945 mmole) and CH_3NH_3Cl (0.934 mmole) was heated at 110° for 2 hr in a sealed tube. The reaction was then rapidly quenched by cooling to $-196°$. The tube was opened and 1.1 mmoles of H_2 and 0.35 mmole of $H_3B_3N_3(CH_3)_3$ were removed as the volatile components. The contents of the tube were then initially extracted with diethyl ether to remove the unreacted $(H_2BNHCH_3)_3$ (0.41 mmole), then chloroform to remove $H_2B(NH_2CH_3)_2{}^+Cl^-$, and finally water to remove a mixture of the unreacted CH_3NH_3Cl and $H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3{}^+Cl^-$. These products were all identified by their infrared spectra[2] and physical properties.[2] After these extractions, an insoluble material remained in the tube. This material was soluble in methanol and ethanol but was not hydrolyzed by dilute acids, 3 M HCl. The infrared spectrum was extremely similar to, only broader than the spectrum of $H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3{}^+Cl^-$. All of these properties suggest that the compound comprising the insoluble material might be $H_2CH_3NBH_2NHCH_3BH_2NHCH_3BH_2NH_2CH_3{}^+Cl^-$. However, the sample was too small for further analysis and complete identification.

Attempted Preparation of $H_2CH_3NBH_2NHCH_3BH_2NHCH_3BH_2$-$NH_2CH_3{}^+Cl^-$.—A 2.78-mmole sample of $H_2B(NH_2CH_3)_2{}^+Cl^-$ and 5.51 mmoles of $H_3BNH_2CH_3$ were thoroughly mixed in a sealed tube at 35°. At this temperature the mixture is a liquid. After heating for 19 hr at 85°, 5.90 mmoles of H_2, a trace of $H_3B_3N_3$-$(CH_3)_3$, and a crystalline solid were formed. The nonvolatile crystalline solid in the tube was extracted with diethyl ether and a small amount of $(H_2BNHCH_3)_3$, identified by its infrared spectrum, was isolated. The remaining crystalline material was insoluble in water, soluble in methanol and ethanol, but not hydrolyzed by dilute HCl. The infrared spectrum was identical with but broader than the spectrum of $H_2CH_3NBH_2$-$NHCH_3BH_2NH_2CH_3{}^+Cl^-$. The X-ray powder pattern and the proton nmr spectrum of a very concentrated methanol solution demonstrated that this material was a mixture of $H_2CH_3NBH_2$-$NHCH_3BH_2NH_2CH_3{}^+Cl^-$ and another component, most probably the desired compound $H_2CH_3NBH_2NHCH_3BH_2NHCH_3$-$BH_2NH_2CH_3{}^+Cl^-$. However, it was not possible to prepare a pure sample of the desired compound. *Anal.* Calcd for H_2CH_3-$NBH_2NHCH_3BH_2NHCH_3BH_2NH_2CH_3{}^+Cl^-$: B, 16.5; N, 28.6; Cl, 18.1. Found: B, 16.1; N, 28.0; Cl, 18.5.