and $J_{F_{eq}-CH_n-}$, the spectra of CH_3PF_3H and $C_2H_5PF_3H$ observed correspond closely to those reported for other R_2PF_3 compounds (R = alkyl, aryl).[6] This lends further support to our assumed geometry for the RPF_3H systems.

At higher temperatures one could early see the effect of an intermolecular exchange process which at high enough temperatures leads to nmr equivalence of the axial and equatorial fluorines. In the ^{19}F nmr spectra of both CH_3PF_3H and $C_2H_5PF_3H$, this led to a gradual broadening of the resonances and loss of resolution. However, even at room temperature two broad doublets ($J_{P-F_{av}}$) corresponding to equatorial and axial fluorines were still observable, which suggests that equilibration is occurring at an intermediate rate with respect to the nmr time scale. The proton spectra for these two compounds proved much more interesting, however. The change observed for the upfield half of the hydrogen doublet in CH_3PF_3H as the temperature is raised from −60° to +39° is reproduced in Figure 1. At the higher temperature the proton resonance is a 1:3:3:1 quartet, due to coupling with the three equivalent fluorines. The methyl group proton is also considerably simplified at the higher temperature (Figure 2). The simple six-line pattern (1:3:4:4:3:1) evolves as two overlapping quartets ($J_{F_{av}-CH_3} = 9$ cps; $J_{P-CH_3} = 18$ cps). All of the lines are somewhat broad at this temperature so that the smaller CH_3–H coupling of 1.8 cps, observable at lower temperatures, is not resolved.

Professor Cornwell of this department is continuing the study of the nmr spectra of these compounds.

Acknowledgment.—We wish to thank Dr. Stephen G. Pierce and Miss M. Petrie for assistance in obtaining the nmr and mass spectral data. We are pleased to acknowledge partial support of the Wisconsin Alumni Research Foundation for this work. The nmr and mass spectrographic facilities in the department were obtained on an NSF department equipment grant.

Contribution from the Department of Chemistry,
University of Florida, Gainesville, Florida 32601

The Reaction of 1,1-Dimethylhydrazine with Gaseous Chloramine

By K. Utvary and H. H. Sisler

Received September 7, 1967

The reaction of 1,1-dimethylhydrazine with chloramine or a mixture of chloramine and ammonia yields 2,2-dimethyltriazanium chloride, $[(CH_3)_2N(NH_2)_2]^+Cl^-$. The sole solid by-product in this reaction is ammonium chloride, apparently formed by the decomposition of chloramine on the solid reaction product and possibly also by catalytic decomposition of chloramine by dimethylhydrazine. The dependence of the formation of 2,2-dimethyltriazanium chloride upon temperature, concentration, and reaction time has been investigated. Hydrogen-1 nmr and infrared spectroscopic evidence for the structure is given.

The recently discovered reactions of 2-dialkylamino-1,3,2-dioxophospholanes with a gaseous mixture of chloramine and excess ammonia[1] produced by the gas-phase chlorination of ammonia,[2] yielding 2,2-dialkytriazanium chlorides, led us to consider the reaction of 1,1-dialkylhydrazines with chloramine. Chloramination should yield the dialkyltriazanium chlorides in accordance with the equation

$$R_2N\text{-}NH_2 + NH_2Cl \longrightarrow [R_2N(NH_2)_2]^+Cl^-$$

It had previously been shown[3] that triazanium ion or triazane is a probable intermediate in the decomposition of hydrazine by chloramine in liquid ammonia and that the initial step in this process is probably represented by the equation

$$NH_2NH_2 + NH_2Cl \longrightarrow NH_2NH_2NH_2^+ + Cl^-$$

Triazanium salts with one or two unsubstituted amino groups, produced by amination of the corresponding hydrazines with hydroxylamine-O-sulfonic acid[4] or with 2-acyloxazirides,[5] were reported recently.

Since it has been shown that trialkylamines, ammonia, and chloramine combine to form trialkylhydrazinium chlorides,[6] it might be expected that the reaction of a dialkylhydrazine, chloramine, and ammonia would yield dialkyltriazanium chloride in an analogous manner. This communication reports the results of the study of the chloramination of 1,1-dimethylhydrazine. An account is also given of an attempt to isolate the postulated[3] triazanium chloride from the chloramine–hydrazine reaction mixture.

Experimental Section

Materials.—1,1-Dimethylhydrazine was obtained from Eastman Organic Chemicals, refluxed over potassium hydroxide, and distilled. Diethyl ether (anhydrous, Baker Analyzed reagent) was used as obtained. Anhydrous hydrazine was obtained from Matheson Coleman and Bell and used as obtained.

---

(1) K. Utvary and H. H. Sisler, *Inorg. Chem.*, **5**, 1835 (1966).

(2) H. H. Sisler, F. Neth, R. Drago, and D. Yaney, *J. Amer. Chem. Soc.*, **76**, 3906 (1954).

(3) F. Collier, Jr., H. H. Sisler, J. Calvert, and F. Hurley, *ibid.*, **83**, 6177 (1959).

(4) R. Gösl, *Angew. Chem.*, **74**, 470, (1962); *Angew. Chem. Intern. Ed. Engl.*, **1**, 268 (1962).

(5) E. Schmitz, S. Schramm, and H. Simon, *Angew. Chem.*, **78**, 587 (1966).

(6) H. H. Sisler, R. A. Bafford, G. M. Omietanski, B. Rudner, and R. J. Drago, *J. Org. Chem.*, **24**, 859 (1959).

The gaseous mixture of chloramine and ammonia was produced by the gas-phase reaction of chlorine with an excess of ammonia in a generator of the type described by Sisler and Omietanski.[7] Elemental analyses reported in this paper were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. All decomposition points are uncorrected.

Preparation of Anhydrous Ammonia-Free Chloramine Solution.—A gaseous mixture of chloramine and ammonia was introduced into the solvent, cooled in an ice-salt bath. The solution was warmed to room temperature to decrease the ammonia content and then poured through a column of anhydrous copper sulfate to remove the remaining ammonia.[8] The chloramine solution was stored in a refrigerator, and, prior to any experiment, the chloramine content was determined by shaking a measured sample with potassium iodide in acidic solution and back-titrating the liberated iodine with standard thiosulfate solution.

Infrared Spectra.—The infrared spectra of the products were observed by means of a Beckman IR-10 grating spectrometer. The samples were prepared by pelleting with potassium bromide. The following bands were observed for the purified sample of dimethyltriazanium chloride (in cm^{-1}): 3230 (vs), 3130 (vs), 3030 (s), 2950 (m), 2890 (m), 1620 (s), 1455 (m), 1415 (w), 1395 (w), 1285 (s), 1230 (m), 1155 (m), 1095 (vs), 1075 (s, sh), 955 (s), 930 (s), 885 (m), 860 (s), 740 (w), 525 (m), 485 (m), 435 (m), 390 (w), where s = strong, m = medium, w = weak, v = very, and sh = shoulder.

Nuclear Magnetic Resonance Spectra.—The ^1H nuclear magnetic resonance spectra of the products were determined at 40° in a Varian A-60A spectrometer, in dimethyl-d_6 sulfoxide solution using the sodium salt of 3-(trimethylsilyl)propanesulfonic acid (Uvasol) as an internal standard. The spectrum for a purified sample of dimethyltriazanium chloride is given in Figure 1. Peak A refers to NH_2, peak B to CH_3, peak C to undeuterated impurity in the dimethyl sulfoxide, and peak D to the internal standard. The peak A corresponds to a δ value of 6.72 (τ 3.28) and peak B to a δ value of 3.53 (τ 6.47). The ratio of the areas under peaks A and B is 4:6.

Determination of the Triazanium Content in the Reaction Product.—A 50–200-mg sample of dimethyltriazanium chloride (hereafter abbreviated T^+Cl^-) was dissolved in 100 ml of a solution containing 3 g of potassium iodide and 5 ml of 2 *N* sulfuric acid. After standing for 2 min the liberated iodine was titrated with 0.1 *N* potassium thiosulfate solution.

Reaction of 1,1-Dimethylhydrazine with Ammonia-Free Chloramine.—The following is a description of a typical experiment. Dimethylhydrazine (1 g, 16.66 mmoles) was dissolved in 100 ml of dry ether and the solution was placed in a three-necked flask fitted with a dropping funnel, a stirrer, and a condenser. With stirring, 139 ml of chloramine solution (16.66 mmoles) was added to the hydrazine solution. The mixture was stirred at room temperature for 60 min and filtered. The filtrate was titrated for the amount of unreacted chloramine which was found to be 3.60 mmoles. The solid residue was washed with ether and dried. It weighed 0.85 g and analysis showed it to contain 0.33 g of T^+Cl^- corresponding to 17.8% yield based upon the dimethylhydrazine.

The results of a series of these experiments using varying concentrations of dimethylhydrazine and chloramine are summarized in Table I.

The Reaction of 1,1-Dimethylhydrazine with Ammonia and Chloramine.—The effluent gas from the chloramine generator was bubbled for 30 min through a solution of 2 g (33.33 mmoles) of dimethylhydrazine in 100 ml of dry ether. The solid reaction product was filtered, washed with ether, and dried. It was found to weigh 1.09 g. Analysis showed this product to contain 0.79 g of T^+Cl^- corresponding to 44.2% yield based on the reacted chloramine. Chloride content was 44.7%.

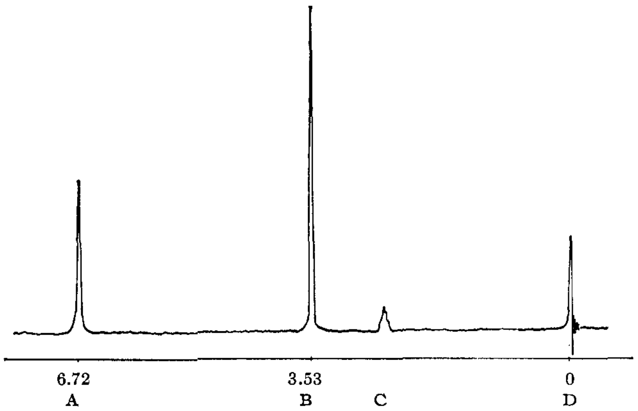

Figure 1.—The ^1H nmr spectrum of purified dimethyltriazanium chloride.

TABLE I

REACTIONS OF 1,1-DIMETHYLHYDRAZINE WITH AMMONIA-FREE CHLORAMINE

$(CH_3)_2$-NNH_2, mmoles	NH_2Cl, mmoles Initial	NH_2Cl, mmoles Re-acted[a]	NH_2Cl, mmoles Re-covered	T^+Cl^-, mmoles	NH_4Cl, mmoles	Yield[d] of T^+Cl^-, %
8.33	16.66	7.97	8.60	3.86	4.11	46.30
16.66	16.66	12.78	3.72	2.96	9.82	17.75
16.66	16.66	14.65	2.00	3.05	11.60	18.30
16.66	16.66	16.14	0.37	4.93	11.21	29.60[b]
50.00	23.70	23.70	0.00	4.48	19.22	...[e]
50.00	23.70	23.70	0.00	4.13[c]	19.57	...[e]

[a] Based on the assumption that the chloride in the solid product comes from only chloramine. [b] Allowed to react for 60 hr. [c] Dimethylhydrazine added to chloramine solution. [d] Based on the dimethylhydrazine. [e] Dimethylhydrazine was in excess.

The results of a series of reactions using various concentrations of dimethylhydrazine, reaction times, and temperatures are summarized in Table II.

TABLE II

REACTIONS OF 1,1-DIMETHYLHYDRAZINE WITH MIXTURES OF AMMONIA AND CHLORAMINE

Expt no.	$(CH_3)_2$-NNH_2, mmoles	NH_2Cl, mmoles	T^+Cl^-, mmoles	NH_4Cl, mmoles	Reaction time, min	Temp, °C	Yield[a] of T^+Cl^-, %
1	16.66	1.90	1.82	0.08	15	15	95.8
2	50.00	9.04	6.54	2.50	15	15	72.4
3	100.00	12.16	8.25	3.91	15	15	67.8
4	16.66	7.40	3.10	4.30	30	15	41.9
5	33.33	13.81	6.11	7.70	30	15	44.2
6	50.00	21.25	9.40	11.85	30	15	44.2
7	83.33	14.77	8.97	5.80	30	15	60.7
8	133.33	17.42	15.92	1.50	30	15	91.2
9	16.66	12.58	7.00	5.58	60	15	55.6
10	33.33	22.30	13.30	9.00	60	15	59.6
11	50.00	32.51	19.50	13.01	60	15	60.0
12	16.66	13.17	7.52	5.65	120	15	57.1
13[b]	16.66	13.08	6.97	6.11	60	15	53.3
14	33.33	35.10	19.00	16.10	60	−40	...
15[c]	33.33	60.25	16.75	43.50	240	15	...
16[d]	33.33	30.57	12.10	18.47	60	15	39.6

[a] Based on chloramine reacted. [b] Allowed to react in the generator for 60 min and to stand for 17 hr. [c] Dimethylhydrazine dropped very slowly into the NH_2Cl solution. [d] Allowed to react in the presence of 85 mmoles of NH_4Cl.

Reaction of 2,2-Dimethyltriazanium Chloride with a Mixture of Chloramine and Ammonia.—T^+Cl^- (1.03 g) was suspended in 100 ml of ether and the effluent gases of the chloramine generator were bubbled through the suspension for 60 min. After filtering and washing with ether, the solid was dried. The product was found to weigh 1.09 g and to contain 91.7% T^+Cl^-. This amounts to 97.3% recovery of T^+Cl^-.

The ^1H nmr spectrum corresponds to the two peaks for T^+Cl^- and only one peak for NH_4Cl.

---

[7] H. H. Sisler and G. Omietanski, *Inorg. Syn.*, **5**, 91 (1957).

[8] I. T. Gilson and H. H. Sisler, *Inorg. Chem.*, **4**, 273 (1965).

Reaction of 2,2-Dimethyltriazanium Chloride with 1,1-Dimethylhydrazine.—T^+Cl^- (0.436 g) was suspended in 21.1 g of dimethylhydrazine and stirred at room temperature for 4 hr. Part of the T^+Cl^- goes into solution. After 4 hr 300 ml of dry ether was added and the mixture was filtered. The product weighed 0.428 g, corresponding to 98.2% of the original T^+Cl^-. The purity of this sample as shown by analysis is 99.7%. Thus, the T^+Cl^- does not react with the excess dimethylhydrazine.

Reaction of 2,2-Dimethyltriazanium Chloride with Ammonia.—T^+Cl^- (0.50 g) was suspended in 100 ml of ether, and for a period of 60 min gaseous NH_3 was bubbled through the suspension. After filtering, the solid residue was dried and weighed 0.49 g. The T^+Cl^- content was shown by analysis to be 99.5%.

Liquid ammonia (50 ml) was condensed onto 0.5 g of T^+Cl^- and the mixture was allowed to warm to 140°. The T^+Cl^- dissolved completely in the liquid ammonia. After stirring the solution for 60 min, the ammonia was allowed to evaporate. The remaining solid was freed from the last traces of NH_3 by applying a low pressure of 1 mm for 20 min. The product weighed 0.50 g, corresponding to a T^+Cl^- content of 99.8%.

These experiments show that T^+Cl^- is unaffected by liquid ammonia or ammonia in ethereal solution.

Purification of 2,2-Dimethyltriazanium Chloride.—The reaction product of the chloramination reaction was boiled 10 min with 30 ml of absolute ethanol, 90 ml of acetone was added, and the mixture was boiled for another 15 min. After filtering, the filtrate was treated with 300 ml of ether and cooled overnight. White crystals were obtained. The weight of the crystalline product generally corresponded to 60–80% of the T^+Cl^- content of the original sample. Its decomposition point (135.5–134°) and the analysis below indicated a high degree of purity. If the recrystallized product was contaminated with NH_4Cl, the decomposition point rose.

Anal. Calcd for $C_2H_{10}N_3Cl$: C, 21.53; H, 9.03; N, 37.66; Cl, 31.77; mol wt, 111.58. Found: C, 21.41; H, 9.10; N, 37.74; Cl, 31.74; mol wt, 115, 120.

The Reaction of Hydrazine with Ammonia-Free Chloramine.—Hydrazine (0.8 g, 25 mmoles) was dissolved in 50 ml of absolute methanol and this solution was added slowly to a cooled solution (−45°) of 1.29 g of NH_2Cl (25 mmoles) in 135 ml of dry ether and 115 ml of absolute methanol. After all the hydrazine was added, stirring was continued for 60 min, and then the solution was allowed to warm to room temperature. Gas evolution occurred. To the clear solution 300 ml of ether was added and the white precipitate was filtered off. A 0.96-g amount of solid which gave a negative test for triazanium ion was obtained (mp 83–85°).

Anal. Calcd for 26.4% of N_2H_5Cl + 73.6% of NH_4Cl: Cl, 62.47; N, 29.63; N_2H_5Cl, 26.40. Found: Cl, 61.70; N, 30.01; N_2H_5Cl, 26.40.

Hydrazine (0.1 g, 3.1 mmoles) was placed in a vacuum line and 0.16 g of chloramine (3.1 mmoles) in 50 ml of dry ether condensed on the hydrazine. The mixture was warmed to −50° and stirred for 60 min. Then most of the ether solution was filtered off, fresh ether was condensed on the residue, and the mixture was stirred again. A sample of the ether gave a negative reaction on testing for excess chloramine. A sample of the white solid was removed as quickly as possible from the vacuum line and tested for triazanium chloride giving a positive reaction. Warming the reaction mixture to room temperature resulted in the decomposition of the sample with the evolution of gas. No triazanium remained in the residue.

Discussion

The experiments described above allow the following conclusions to be drawn.

(1) 2,2-Dimethyltriazanium chloride can be prepared by reaction of 1,1-dimethylhydrazine with chloramine in ethereal solution. From the available experimental data no firm conclusion can be drawn as to whether the presence or absence of ammonia in this reaction is of major importance in the formation of T^+Cl^-. Though the yields of T^+Cl^- in the ammonia–chloramine experiments are generally higher than in the case of the ammonia-free reaction, in the latter experiments the chloramine concentrations are much smaller than in the generator experiments.

(2) The chloramine consumed plus the T^+Cl^- formed in the various reactions is in accord with the assumption that the reaction of 1,1-dimethylhydrazine with chloramine proceeds as indicated by the equation: $(CH_3)_2NNH_2 + NH_2Cl \rightarrow [(CH_3)_2N(NH_2)_2]^+Cl^-$.

(3) Dimethyltriazanium chloride is stable under the experimental conditions for the reactions described. Neither ammonia nor dimethylhydrazine nor chloramine reacts at room temperature with T^+Cl^- in ethereal solution. In dimethylhydrazine T^+Cl^- is moderately soluble but can be almost quantitatively recovered (98%) with a purity of 99.7%. If T^+Cl^- suspended in ether is exposed to the effluent gases of the chloramine generator for 60 min, pure T^+Cl^- can be recovered. Liquid ammonia or ammonia dissolved in ether does not react with T^+Cl^-. In liquid ammonia T^+Cl^- is very soluble.

(4) The ammonium chloride always found in the reaction mixture of dimethylhydrazine with chloramine is formed by decomposition of chloramine on the solid reaction product: $3NH_2Cl + 2NH_3 \rightarrow 3NH_4Cl + N_2$. Experiments 10 and 16 in Table II show that increasing the solid surface in solution by adding finely divided NH_4Cl to the initial solution yields nearly the same amount of T^+Cl^-, whereas the yield of NH_4Cl increases approximately 100%. As long as the "concentration" of solid reaction product in the solution is low (experiment 1, Table II), nearly all of the available chloramine reacts with dimethylhydrazine. Prolonged chloraminations or chloraminations involving high initial dimethylhydrazine concentrations increase the yield of T^+Cl^- and at the same time increase the amount of solid reaction product. This produces by the surface-catalyzed decomposition of chloramine a major increase in the NH_4Cl content of the solid reaction product. Consequently, if dimethylhydrazine is added very slowly to an excess of chloramine, the yields of NH_4Cl are increased, for the concentration of unreacted dimethylhydrazine in solution is not only very low, but remains so over the whole reaction time, whereas the amount of the solid steadily increases and thus favors the formation of NH_4Cl.

(5) Four possible structures may be drawn for dimethyltriazanium chloride

$$[(CH_3)_2N\text{–}\overset{+}{N}H_2\text{–}NH_2]Cl^- \qquad [H_2N\text{–}\overset{+}{N}(CH_3)_2\text{–}NH_2]Cl^-$$

I II

$$[(CH_3)_2N\text{–}NH\text{–}\overset{+}{N}H_3]Cl^- \qquad [(CH_3)_2\overset{+}{N}H\text{–}NH\text{–}NH_2]Cl^-$$

III IV

Of these structures III and IV are improbable because their formation would involve the attack by the chloramine molecule of the less basic of the two hydrazine nitrogens, followed by the migration of a proton. Since the ^{1}H 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

$$NH_2\text{-}NH_2 + NH_2Cl \longrightarrow [NH_2\text{-}NH_2\text{-}NH_2]^+Cl^-$$

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

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

$$N_2H_4 + HCl \longrightarrow N_2H_5Cl$$

Acknowledgment.—We wish to thank the National Institutes of Health for support of this research through Project No. CA-08263 with the University of Florida.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
STATE UNIVERSITY OF NEW YORK AT BUFFALO, BUFFALO, NEW YORK 14214

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

BY O. T. BEACHLEY, JR.

Received August 17, 1967

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

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

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

$$H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3^+Cl^- \xrightarrow{110-125°} {}^2/_3H_3B_3N_3(CH_3)_3 + CH_3NH_3Cl + 2H_2 \tag{3}$$

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).