lets at 10 cps (12H, Si–CH_3) and 40 cps (4H, Si–CH_2), a triplet centered at 70 cps (J = 7 cps, 3H, O–CH_2–CH_3), and a quartet centered at 240.5 cps (J = 7 cps, 2H, O–CH_2–CH_3).

Anal. Calcd for $C_9H_{21}NO_3Si_2$: C, 46.70; H, 9.15; N, 6.05; Si, 24.27. Found: C, 46.93; H, 9.25; N, 5.85; Si, 24.06.

N,N′-Dicarbethoxy-3,3,6,6-tetramethyl-1,2-diaza-3,6-disilacyclohexane (VIII).—1,2-Bis(dimethylchlorosilyl)ethane (3.077 g, 0.01429 mole) in dry benzene (28 ml) was added to a stirred suspension of sodium hydride (0.0322 mole) and ethyl hydrazodicarboxylate (2.538 g, 0.01440 mole) in dry benzene (9 ml). No reaction was evident, even after refluxing the mixture for 6.5 hr. Dry dimethylformamide (15 ml) was added to the mixture which was refluxed for 5 hr, at which time glpc indicated the reaction was complete. Filtration of the precipitated solids and fractional distillation of the filtrate afforded 1.646 g (36%) of the desired product as a viscous liquid, bp 97° (0.4 mm); $\nu_{\max}^{CCl_4}$: 1725, 1695, 1255, 845 cm^{-1}. The nmr spectrum showed singlets at 15.5 and 25 cps (nonequivalent Si–CH_3), a poorly resolved multiplet centered at 43 cps (Si–CH_2–CH_2–Si, nonequivalent), a triplet centered at 76 cps (J = 7 cps, $COOCH_2$–CH_3), and a quartet centered at 249 cps (J = 7 cps, $COOCH_2$–CH_3).

Anal. Calcd for $C_{12}H_{26}N_2O_4Si_2$: C, 45.25; H, 8.23; N, 8.79; Si, 17.63; mol wt, 318.5. Found: C, 45.15; H, 8.09; N, 9.07; Si, 17.39; mol wt ($CHCl_3$), 328.

Oxidation of 1,1- and 1,2-Bis(trimethylsilyl)hydrazine. A. With Mercuric Oxide.—An equilibrium mixture of 1,1- and 1,2-bis(trimethylsilyl)hydrazine (4.428 g, 0.02408 mole) was added dropwise to a stirred slurry of yellow mercuric oxide (10.10 g, 0.04663 mole) and anhydrous magnesium sulfate (10.10 g) in dry xylene (30 ml), regulating the temperature of the mixture at 25–30°. After stirring overnight, the mixture was filtered, washing the solids with dry xylene. Glpc of the filtrate showed trimethylsilanol (84%) and hexamethyldisiloxane (16%) to be the only products. The products were isolated by distillation and their structures confirmed by comparison with the infrared spectra of authentic samples; yield, 3.168 g.

When the oxidation was carried out using cyclohexene as the solvent, the same results were obtained. However, because of the similarity in boiling points, the separation of the products from the solvent was impractical.

B. With Ethyl Azodicarboxylate.—Ethyl azodicarboxylate (12.81 g, 0.7354 mole) was added dropwise to a stirred solution of 1,1- and 1,2-bis(trimethylsilyl)hydrazine (7.859 g, 0.04455 mole; 43% of 1,1 isomer, 57% of 1,2 isomer) in dry xylene (50 ml) at room temperature until the color of the oxidant persisted. The reaction mixture was filtered, to give ethyl hydrazodicarboxylate (5.035 g, 0.02857 mole). Glpc of the filtrate showed the presence of two products—diethyl N-trimethylsilylhydrazodicarboxylate (X, 20%) and diethyl N,N′-bis(trimethylsilyl)hydrazodicarboxylate (XI, 80%). No hexamethyldisilane was detected. The filtrate was distilled to afford 11.283 g of a mixture of X and XI, boiling at 82–90° (0.44 mm). Repeated fractional distillation of the mixture afforded analytical samples of the two products.

The nmr spectrum (CCl_4) of X showed a singlet at 15 cps (9H, Si–CH_3), a triplet centered at 75.5 cps (6H, J = 7 cps, O–CH_2–CH_3), two overlapping quartets centered at 243.5 and 245 cps (4H, J = 7 cps, O–CH_2–CH_3), and broad absorption from 410 to 420 cps (1H, NH); $\nu_{\max}^{liq}$: 3305 (broad, NH), 1730 (broad, N–$COOC_2H_5$), 1260 (Si–CH_3), and 855 (Si–N) cm^{-1}; bp 73.5° (0.09 mm).

Anal. Calcd for $C_9H_{20}N_2O_4Si$: C, 43.53; H, 8.12; N, 11.28; Si, 11.31. Found: C, 43.46; H, 7.98; N, 11.39; Si, 11.11.

The nmr spectrum (CCl_4) of XI showed a singlet at 12 cps (18H, Si–CH_3), a triplet centered at 75.5 cps (6H, J = 7.5 cps, O–CH_2–CH_3), and a quartet centered at 238.5 cps (4H, J = 7.5 cps, O–CH_2–CH_3); $\nu_{\max}^{liq}$: 1730, 1700 (N–$COOC_2H_5$), 1260 (Si–CH_3), 855 (Si–N) cm^{-1}; bp 60° (0.1 mm).

Anal. Calcd for $C_{12}H_{28}N_2O_4Si_2$: C, 44.97; H, 8.80; N, 8.74; Si, 17.52. Found: C, 45.09; H, 8.65; N, 8.92; Si, 17.31.

C. With Chloranil.—A solution of chloranil (250 mg, 0.834 mmole) in dry xylene (6 ml) was added in portions to a solution of 1,1- and 1,2-bis(trimethylsilyl)hydrazine (202 mg, 1.15 mmoles; 24% of 1,1- isomer, 76% of 1,2 isomer) in dry xylene (1 ml). No hexamethyldisilane could be detected by glpc and, after half of the chloranil solution had been added, the only product formed in the reaction was shown to have the same retention time as 1,4-bis(trimethylsiloxy)-2,3,5,6-tetrachlorobenzene.

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Intermediates in the Formation of N-Methylaminoborane Trimer and N,N-Dimethylaminoborane Dimer

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Experimental evidence for the intermediates in the formation of N-methylaminoborane trimer, $(H_2BNHCH_3)_3$, and N,N-dimethylaminoborane dimer, $(H_2BN(CH_3)_2)_2$, has been obtained by synthetic methods and trapping procedures. The pyrolysis of methylamine borane, $H_3BNH_2CH_3$, yields the six-membered ring of $(H_2BNHCH_3)_3$ by initially forming $H_2B(NH_2CH_3)_2{}^+BH_4{}^-$, then $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+BH_4{}^-$ through a series of successive dehydrogenation condensation reactions. The final step of the proposed mechanism is ring closure by dehydrogenation. The new compound, $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+Cl^-$, was prepared by heating a mixture of $H_2B(NH_2CH_3)_2{}^+Cl^-$ and $H_3BNH_2CH_3$ and was characterized by elemental analysis, its reactions with $FeCl_3$ and $NaBH_4$, and its pmr spectrum. The experimental evidence for the intermediates during the pyrolysis of dimethylamine borane to form $(H_2BN(CH_3)_2)_2$ is consistent with monomeric $H_2BN(CH_3)_2$ species which then associate to give the dimer.

Introduction

Amine boranes, which have at least one hydrogen bound to the nitrogen, readily undergo elimination reactions,[2] such as dehydrogenation or dehydrohalogenation, to form aminoboranes. The aminoboranes have been observed as monomers or associated species,

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(2) K. Niedenzu and J. W. Dawson, "Boron–Nitrogen Compounds," Academic Press Inc., New York, N. Y., 1965, p 8.

such as dimers, trimers, tetramers, or polymers, depending on the groups bound to the boron and nitrogen atoms. The factors which have been suggested to correlate the different degrees of association with the substituents of the aminoborane are steric effects, thermodynamic effects,[3] valency angle strain,[4] and the intermediates in reaction mechanism.[5] The purpose of this investigation, therefore, was to elucidate the nature of the intermediates in the formation of N-methylaminoborane trimer, $(H_2BNHCH_3)_3$, and N,N-dimethylaminoborane dimer, $(H_2BN(CH_3)_2)_2$, and to determine the significance of the intermediates to the degree of association of the aminoborane.

A determination of the intermediates in a reaction can be attacked by two methods—trapping the reactive species or synthesizing compounds as possible candidates and then converting them to the desired final product. The synthetic method was initially chosen for this investigation because previous research on the preparation of N-methylaminoborane trimer[6,7] did not suggest a possible method for trapping intermediates. Diborane reacts with methylamine to form a mixture[8,9] of $H_2B(NH_2CH_3)_2{}^+BH_4{}^-$ and $H_3BNH_2CH_3$ which slowly decomposes[9] at 25° forming unknown compounds and hydrogen or is converted[6] to $(H_2BNHCH_3)_3$ and hydrogen at 100°. These observations suggested, as one possibility, that $H_3BNH_2CH_3$ might react with $H_2B(NH_2CH_3)_2{}^+$ to form a more polymeric boron–nitrogen compound, which could eventually lead to the trimer. Therefore, the reaction of $H_3BNH_2CH_3$ with $H_2B(NH_2CH_3)_2{}^+Cl^-$ was investigated as a route to a stable compound which could then react with $NaBH_4$ to form $(H_2BNHCH_3)_3$.

Experimental Section

Preparation of $H_3BNH_2CH_3$.—The reagents $NaBH_4$ (0.14 mole) and CH_3NH_3Cl (0.13 mole) were allowed to react in monoglyme at 0° according to a previously described procedure.[10] The yields of $H_3BNH_2CH_3$, based on CH_3NH_3Cl, were 40–60% if 150 ml of monoglyme was used. However, under concentrated conditions, 30–50 ml of solvent, no $H_3BNH_2CH_3$ was isolated. Only an insoluble, nonvolatile white paste was obtained.

Preparation of $H_2B(NH_2CH_3)_2{}^+Cl^-$.—A 250-ml flask, equipped with a side arm for addition of solvent and a condenser, was charged with 7.2 g (0.19 mole) of $NaBH_4$ and 31.0 g (0.44 mole) of CH_3NH_3Cl. The reactants and solvent, 50 ml of monoglyme, were cooled to 0° and then mixed. Aftr the initial vigorous hydrogen evolution had ceased, the reaction mixture was maintained at 0° with stirring for an additional 3 hr. The monoglyme, which contained some $H_3BNH_2CH_3$, was then removed by filtration. The remaining insoluble material was extracted at 0° with diethyl ether to remove any $H_3BNH_2CH_3$ which was not separated with the monoglyme. The $H_3BNH_2CH_3$ was subsequently recrystallized from ether and purified by sublimation at 40° (1.2 g, 14% yield based on $NaBH_4$). The monoglyme- and ether-insoluble material from the initial reaction mixture was finally extracted at 25° with chloroform. The chloroform was removed by vacuum distillation, and 6.8 g (32% yield based on $NaBH_4$) of $H_2B(NH_2CH_3)_2{}^+Cl^-$, which was identified[9] by its melting point, infrared spectrum, and X-ray powder pattern, was obtained.

In an attempt to prepare $H_2B(NH_2CH_3)_2{}^+Cl^-$ directly, 2.23 mmoles of $H_3BNH_2CH_3$ and 2.23 mmoles of CH_3NH_3Cl were combined in 35 ml of refluxing monoglyme (about 85°) for 8 hr. Only the unchanged starting materials were isolated after the monoglyme was removed. Similarly, there was no reaction in refluxing chloroform.

Reaction of $H_2B(NH_2CH_3)_2{}^+Cl^-$ and $H_3BNH_2CH_3$.—As a typical example, 2.94 mmoles of $H_2B(NH_2CH_3)_2{}^+Cl^-$ and 2.96 mmoles of $H_3BNH_2CH_3$ were loaded into a tube which was then evacuated and sealed. The reaction mixture, which was a liquid at 30°, was thoroughly mixed and then heated at 85–90° for 19 hr. The pyrolysis tube was then attached to the vacuum line and the break-seal in the side arm was opened. The H_2 (2.82 mmoles) was removed and measured with a Toepler pump–gas buret assembly. A colorless, crystalline, nonvolatile solid remained after trace amounts of $(H_2BNHCH_3)_3$ and $H_3B_3N_3(CH_3)_3$, identified by their mass spectra, were removed by sublimation or extraction with diethyl ether. The crystalline solid was then further purified by recrystallization from ethanol.

Anal. Calcd for $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+Cl^-$: B, 14.1; N, 27.4; Cl, 23.1. Found: B, 14.0; N, 27.2; Cl, 22.9. The reaction of 1 mole of $H_2B(NH_2CH_3)_2{}^+Cl^-$ with 1 mole of $H_3BNH_2CH_3$ can be represented by the general equation

$$H_2B(NH_2CH_3)_2{}^+Cl^- + H_3BNH_2CH_3 \xrightarrow{85^\circ} [H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+Cl^- + H_2$$

However, if $H_2B(NH_2CH_3)_2{}^+Cl^-$ was allowed to react with $H_3BNH_2CH_3$ in mole ratios greater than 1:2, the stoichiometric quantity of H_2 was obtained but $(H_2BNHCH_3)_3$ and $H_3B_3N_3(CH_3)_3$ were produced in significant amounts, and an impure, glassy, nonvolatile material remained.

Properties of $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+Cl^-$.—The pure compound is soluble in methanol, ethanol, and water, insoluble in chloroform, acetonitrile, acetone, ether, monoglyme, and benzene, and completely stable to hydrolysis in 3 *M* HCl and HNO_3. However, it decomposes readily in aqueous sodium hydroxide and thermally at 136–137°, under conditions of rapid heating.

Characterization of $(H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+Cl^-$ by Reaction with $FeCl_3$.—A 0.626-mmole sample of $(H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+Cl^-$, suspended in diethyl ether, was allowed to react with 0.608 mmole of anhydrous $FeCl_3$ at 25°. A yellow ether-soluble material was formed, and a small amount (2.5 mg) of the insoluble $(H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+Cl^-$ remained unreacted. After the reaction mixture was filtered, the ether was removed and a yellow glassy material remained.

Anal. Calcd for $(H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+FeCl_4{}^-$: B, 6.79; N, 13.2; Cl, 44.6. Found: B, 6.60; N, 13.3; Cl, 44.4. The infrared spectrum of this ether-soluble yellow compound was very similar to that of the initial 1:1 compound. The observed stoichiometry, analysis, and physical changes are consistent with the reaction

$$(H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+Cl^- + FeCl_3 \xrightarrow[25^\circ]{\text{ether}} (H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+FeCl_4{}^-$$

and confirm the formulation of the starting material. A similar experiment[11] confirmed the formulation of $H_2B(t\text{-}C_4H_9NH_2)_2{}^+Cl^-$.

Infrared Spectrum.—The infrared spectrum of $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+Cl^-$ as a Nujol mull was recorded with a Perkin-Elmer 337 grating spectrometer in the range 4000–400 cm^{-1}. The spectra of this compound and $H_2B(NH_2CH_3)_2{}^+Cl^-$ [10] are very similar. This would be consistent with a significant structural analogy between the two compounds. There is some slight shifting of absorption bands and greater splitting of bands

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TABLE I

REACTION OF $H_2B(NH_2CH_3)_2{}^+Cl^-$ AND $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+Cl^-$ WITH $NaBH_4$

Reagents	Products, mmoles		
	$H_3BNH_2CH_3$	$(H_2BNHCH_3)_3$	$H_3B_3N_3(CH_3)_3$
2.00 mmoles of $H_2B(NH_2CH_3)_2{}^+Cl^-$, 2.02 mmoles of $NaBH_4$, 5 ml of monoglyme	2.27	0	0
2.00 mmoles of $(H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+Cl^-$, 2.02 mmoles of $NaBH_4$, 5 ml of monoglyme	1.40	0.570	0
1.68 mmoles of $H_2B(NH_2CH_3)_2{}^+Cl^-$, 1.70 mmoles of $NaBH_4$, 1 ml of monoglyme	0.513	0	0
1.35 mmoles of $(H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+Cl^-$, 1.35 mmoles of $NaBH_4$, 1 ml of monoglyme	0	0.825	0.390

in the low-frequency region in the spectrum of $H_2B(NH_2CH_3)_2{}^+Cl^-$ than in the spectrum of $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+Cl^-$.

Infrared spectrum of $(H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+Cl^-$ (cm^{-1}): 3190 s, 3145–3120 s, 3080 s, 3005 m, 2980 sh, 2945 vs, 2910 sh, 2845 vs, 2710 vs, 2698 vs, 2675 sh, 2410 vs, 2390 sh, 2320 vs, 1610 s, 1470 s, 1435 s, 1380 vs, 1370 m, 1355 s, 1330 s, 1260 s, 1200 sh, 1190 s, 1178 sh, 1170 vs, 1161 sh, 1140 m, 1128 sh, 1115 sh, 1095 w, 1078 m, 1068 sh, 1043 s, 1019 s, 1010 sh, 994 sh, 970 vs, 930 s, 918 sh, 892 m, 870 sh, 860 s, 828 sh, 821 m, 810 m, 752 w, 733 w, 720 w, 698 w.

X-Ray Powder Pattern.—The X-ray powder pattern of $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+Cl^-$ was recorded with a 57.3-mm diameter camera using Cu Kα radiation. The *d* spacings are reported in Ångstrom units: 6.76 m, 6.03 m, 5.37 m, 4.62 vs, 4.06 vs, 3.52 s, 3.36 s, 3.09 s, 2.78 s, 2.66 m, 2.19 m, 1.99 m, 1.91 s, 1.85 w, 1.78 m, 1.73 w, 1.67 w, 1.63 w, 1.60 m, 1.55 w, 1.51 m, 1.42 w, 1.39 w.

Nuclear Magnetic Resonance Spectrum.—The proton nmr spectrum of a D_2O solution of $(H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+Cl^-$ was recorded at 60 Mc using a Varian A-60 spectrometer. The chemical shifts for the resonances of the methyl groups were observed at -2.35 and -2.27 ppm with an integrated intensity ratio of approximately 2:1. These chemical shifts are relative to the sodium salt of 3-(trimethylsilyl)propanesulfonic acid.

Reaction of $H_2B(NH_2CH_3)_2{}^+Cl^-$ and $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+Cl^-$ with $NaBH_4$ in Monoglyme.—A weighed sample of $NaBH_4$ was added, by means of a side-arm addition tube, to an equimolar sample of $H_2B(NH_2CH_3)_2{}^+Cl^-$ or $(H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+Cl^-$ (Table I) suspended in monoglyme. The mixture was then stirred at room temperature for 5 hr and then finally refluxed (85°) for 5 hr. The monoglyme was removed by a fractional vacuum distillation through a $-46°$ trap to isolate any $H_3B_3N_3(CH_3)_3$ formed during the reaction. The solid remaining in the reaction flask was then subjected to a high-vacuum sublimation. If 5 ml of monoglyme was used, $H_3BNH_2CH_3$ was isolated by sublimation at 40–50° from all of the reactions. However, if 1 ml of monoglyme was used, only the reaction of $(H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+Cl^-$ with $NaBH_4$ gave $(H_2BNHCH_3)_3$, which sublimed at 100–110° from the reaction mixture, and $H_3B_3N_3(CH_3)_3$ as the volatile products. There was no formation of $H_3BNH_2CH_3$ under these concentrated conditions. The reactions of small samples of $H_2B(NH_2CH_3)_2{}^+Cl^-$ with $NaBH_4$ under concentrated conditions (1 ml of monoglyme) gave $H_3BNH_2CH_3$ and nonvolatile, insoluble products. There was no $H_3B_3N_3(CH_3)_3$ nor $(H_2BNHCH_3)_3$ observed. If large amounts of $H_2B(NH_2CH_3)_2{}^+Cl^-$ (0.010 mole) were treated with $NaBH_4$ (0.010 mole) in 5 ml of monoglyme, the heat of reaction was sufficient to reflux the solvent, and 0.133 mmole (19.9%) of $(H_2BNHCH_3)_3$ and a nonvolatile, insoluble material were obtained.

Metathetical Reaction of $(H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+Cl^-$ and $NaBH_4$ in Liquid NH_2CH_3.—A 0.503-mmole sample of $(H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+Cl^-$ and 0.503 mmole of $NaBH_4$ were allowed to react at $-30°$ in a small double Shlenk tube using methylamine as the solvent. An insoluble solid, NaCl (0.490 mmole), was formed and removed by filtration. The resulting methylamine solution was evaporated and a glassy solid remained. The stoichiometry of the reaction is consistent with the formation of $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+BH_4^-$.

Pyrolysis of $(H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+BH_4^-$.—A 0.503-mmole sample of $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+BH_4^-$ was pyrolyzed at 100° for 2 hr. The products were 1.54 mmoles of H_2, 0.0587 mmole of $H_3B_3N_3(CH_3)_3$, and 0.416 mmole (82.7%) of $(H_2BNHCH_3)_3$. This stoichiometry is consistent with the results from the reaction of $(H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3)^+Cl^-$ with $NaBH_4$ in 1 ml of monoglyme and the pyrolysis[6] of $H_2B(NH_2CH_3)_2{}^+BH_4^-$.

Partial Pyrolysis of $H_3BNH_2CH_3$.—A pyrolysis tube loaded with 8.28 mmoles of $H_3BNH_2CH_3$ was sealed and then heated at 100° for 1 hr. The tube was then rapidly cooled to $-196°$ and opened, and the H_2 was removed. Ether (15 ml), followed by 15 ml of distilled water, was added to the tube, and then the ether layer was separated. The ether was evaporated and 1.07 mmoles of $(H_2BNHCH_3)_3$, identified by its infrared spectrum, remained. The aqueous solution was then hydrolyzed with 3 *M* HCl and evaporated to dryness by a vacuum distillation. The resulting solid was extracted with chloroform, and 0.550 mmole of $H_2B(NH_2CH_3)_2{}^+Cl^-$, identified by its infrared spectrum,[9] was isolated after the solvent was removed. The infrared spectrum of the chloroform-insoluble solid indicated the presence of H_3BO_3, CH_3NH_3Cl, and a boron hydride species. The absorptions which could not be assigned to either H_3BO_3 or CH_3NH_3Cl were consistent with the spectrum of $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+Cl^-$.

Preparation of $H_2B(N(CH_3)_2H)_2{}^+Cl^-$.—A tube loaded with 3.13 mmoles of $H_3BN(CH_3)_2H$ and 3.15 mmoles of $(CH_3)_2NH_2Cl$ was sealed and then heated at 110° for 20 hr. Hydrogen (3.14 mmoles) and a nonvolatile crystalline solid were formed. The crystalline solid, purified by recrystallization from acetonitrile, melted at 174–175°. The stoichiometry of the reaction is consistent with the formation of $H_2B(N(CH_3)_2H)_2{}^+Cl^-$. This compound has been previously reported,[11] but the melting point was given as 78°.

Anal. Calcd for $H_2B(N(CH_3)_2H)_2{}^+Cl^-$: B, 7.79; N, 20.2; Cl, 25.6. Found: B, 7.65; N, 20.3; Cl, 25.8.

The reaction of 3.36 mmoles of dimethylaminoborane and 3.40 mmoles of $(CH_3)_2NH_2Cl$ in a sealed tube at 110° for 20 hr gave only a nonvolatile, crystalline solid which had a melting point and infrared spectrum identical with those of the sample prepared from $H_3BN(CH_3)_2H$ and $(CH_3)_2NH_2Cl$.

The reaction of $NaBH_4$ with 2 moles of $(CH_3)_2NH_2Cl$ in monoglyme at 0° was also examined as a possible preparative route to $H_2B(N(CH_3)_2H)_2{}^+Cl^-$ because $H_2B(NH_2CH_3)_2{}^+Cl^-$ was prepared by the analogous reaction. However, $H_3BN(CH_3)_2H$ was the only boron-containing product formed. There was no evidence for the formation of $H_2B(N(CH_3)_2H)_2{}^+Cl^-$.

Attempted Preparation of $[H(CH_3)_2NBH_2N(CH_3)_2BH_2N(CH_3)_2H]^+Cl^-$.—A tube, loaded with 1.38 mmoles of $H_2B(N(CH_3)_2H)_2{}^+Cl^-$ and 1.40 mmoles of $H_3BN(CH_3)_2H$, was evacuated, sealed, and heated at 110° for 20 hr. The products of this reaction—1.36 mmoles of H_2, 0.64 mmole of $(H_2BN(CH_3)_2)_2$, and 1.35 mmoles of unreacted $H_2B(N(CH_3)_2H)_2{}^+Cl^-$—indicated that $[H(CH_3)_2NBH_2N(CH_3)_2BH_2N(CH_3)_2H]^+Cl^-$ was not formed. Only the dehydrogenation of $H_3BN(CH_3)_2H$ to form $[H_2BN(CH_3)_2]_2$ was observed. Conditions of 145–150° also initiated only dehydrogenation of $H_3BN(CH_3)_2H$. More moderate conditions of 85° or refluxing the mixture in chloroform, acetonitrile, or monoglyme initiated only incomplete dehydrogenation of $H_3BN(CH_3)_2H$. In all of these experiments, no volatile species other than H_2, $[H_2BN(CH_3)_2]_2$, or unreacted $H_3BN(CH_3)_2H$ were observed, and the only nonvolatile compound was $H_2B(N(CH_3)_2H)_2{}^+Cl^-$.

Partial Pyrolysis of $H_3BN(CH_3)_2H$.—A 3.33-mmole sample of $H_3BN(CH_3)_2H$ was pyrolyzed in a sealed tube at 110° for 1 hr. The tube was then rapidly quenched at −196° and opened, and the hydrogen (1.25 mmole) was removed. The dimethylaminoborane (1.23 mmole) was then separated from a crystalline solid which remained in the tube. The crystalline solid was completely soluble in benzene and identified as only unreacted $H_3BN(CH_3)_2H$ (2.08 mmoles). There was no other boron-nitrogen compound observed.

Attempted Preparation of $[H_2CH_3NBH_2NHCH_3BH_2N(CH_3)_2H]^+Cl^-$.—A mixture of 1.00 mmole of $H_2B(NHCH_3)_2{}^+Cl^-$ and 1.00 mmole of $H_3BN(CH_3)_2H$ was heated in a selaed tube at 85° for 44 hr. The products of the reaction were 1.26 mmoles of H_2 and a clear, colorless glass which could not be purified. The glass reacted with $NaBH_4$ in monoglyme to form a mixture of $H_3BNH_2CH_3$ and $H_3BN(CH_3)_2H$, which were identified by their mass spectra.

Attempted Preparation of $H_2B(NH_2CH_3)(N(CH_3)_2H)^+Cl^-$.—A mixture of 6.15 mmoles of $H_3BN(CH_3)_2H$ and 6.08 mmoles of CH_3NH_3Cl was heated at 110° for 8 hr. The products of the reaction were 5.85 mmoles of H_2 and a clear, colorless glass which could not be purified. A mixture of $H_2B(NH_2CH_3)_2{}^+Cl^-$ and $H_2B(N(CH_3)_2H)_2{}^+Cl^-$ also gave a clear, colorless glass after dissolution in and removal of $CHCl_3$. This observation suggests that the product from the reaction of $H_3BN(CH_3)_2H$ and CH_3NH_3Cl is probably a mixture of $H_2B(NH_2CH_3)_2{}^+Cl^-$ and $H_2B(N(CH_3)_2H)_2{}^+Cl^-$. Similarly, the product from the reaction of $H_2B(NH_2CH_3)_2{}^+Cl^-$ and $H_3BN(CH_3)_2H$ is probably also a mixture of ionic species.

Discussion

A mechanism for the formation of 1,3,5-trimethylcycloborazane might include the following series of steps

$$2H_3BNH_2CH_3 \longrightarrow \underset{\mathrm{I}}{H_2B(NH_2CH_3)_2{}^+BH_4{}^-} \quad (1)$$

$$\mathrm{I} + H_3BNH_2CH_3 \longrightarrow \underset{\mathrm{II}}{[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+BH_4{}^-} + H_2 \quad (2)$$

$$\mathrm{II} \longrightarrow \underset{\mathrm{III}}{H_3BNHCH_3BH_2NHCH_3BH_2NH_2CH_3} + H_2 \quad (3)$$

$$\mathrm{III} \longrightarrow (H_2BNHCH_3)_3 + H_2 \quad (4)$$

The role of $H_2B(NH_2CH_3)_2{}^+BH_4{}^-$ (I) and $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+BH_4{}^-$ (II) as intermediates was suggested, when these compounds were synthesized and then converted to $(H_2BNHCH_3)_3$, and confirmed, when they were separated as the corresponding chloride salts in the partial pyrolysis of $H_3BNH_2CH_3$. The compound $H_3BNHCH_3BH_2NHCH_3BH_2NH_2CH_3$ (III) was not isolated, but its existence as an intermediate is consistent with all of the experimental observations.

The initial step (1) of the proposed mechanism is the formation of the ionic compound $H_2B(NH_2CH_3)_2{}^+BH_4{}^-$. This species was identified by the same series of reactions that provided its initial characterization.[9] The observation that the cation $H_2B(NH_2CH_3)_2{}^+$ is also formed from the reaction of $NaBH_4$ with CH_3NH_3Cl in monoglyme, another method[7] for preparing $(H_2BNHCH_3)_3$, substantiates the significance of this species to the formation of the trimer. This cation is apparently the prerequisite for the more polymeric intermediate II.

The cation of the intermediate, II, was initially prepared by allowing $H_2B(NH_2CH_3)_2{}^+Cl^-$ to react with $H_3BNH_2CH_3$ and was also identified as a species formed during the pyrolysis of $H_3BNH_2CH_3$. The structure of the compound $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+Cl^-$ was elucidated by its elemental analysis, chemistry, and proton nmr spectrum. The ionic nature of the compound was suggested by its solubility in water, its conductivity, and its resistance to acid hydrolysis, a characteristic property[12] of cationic boron hydrides. The chloride anion was identified by its reaction with anhydrous $FeCl_3$ in ether to form $FeCl_4{}^-$ and with $NaBH_4$ in liquid methylamine to form NaCl. The stoichiometry of these reactions further substantiated a composition of one chloride ion per formula unit. The proton nmr spectrum confirmed the proposed cation structure. There are two magnetically nonequivalent types of methyl groups—the two terminal $-NH_2CH_3$ groups and the one $-NHCH_3-$ group. The spectrum has only two methyl resonances—one at −2.35 and the other at −2.27 ppm. The first one is twice as intense as the second. Similarily, the infrared spectrum is consistent with the proposed structure.

There are two possible routes to the formation of $H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3{}^+$—an intermolecular dehydrogenation reaction or a type of insertion process. An intermolecular dehydrogenation reaction between $H_2B(NH_2CH_3)_2{}^+$ and $H_3BNH_2CH_3$ would give the desired product. However, it has been observed that $H_3BN(CH_3)_3$ does not react with $H_2B(NH_2CH_3)_2{}^+Cl^-$ at 100°, and this suggests that the intermolecular process probably does not occur. It is doubtful that the hydrogen atoms bound to boron in $H_3BN(CH_3)_3$ are significantly different enough from those in $H_3BNH_2CH_3$ to prevent reaction. The insertion type of process might involve the reaction of monomeric H_2BNHCH_3 species with either the B–N or N–H bonds of $H_2B(NH_2CH_3)_2{}^+$. The monomeric species would be formed by the dissociation of $H_2B(NH_2CH_3)_2{}^+$ or $H_3BNHCH_3BH_2NH_2CH_3$ (IV)

$$H_2B(NH_2CH_3)_2{}^+ \longrightarrow H_2BNHCH_3 + CH_3NH_3{}^+ \quad (5)$$

$$\underset{\mathrm{IV}}{H_3BNHCH_3BH_2NH_2CH_3} \longrightarrow H_3BNH_2CH_3 + H_2BNHCH_3 \quad (6)$$

The latter compound (IV) could be formed by the reaction of $H_2B(NH_2CH_3)_2{}^+$ with $BH_4{}^-$, observed intermediates. Compounds similar to IV are known to dissociate[13] in this manner.

The third step of the proposed mechanism is the interionic dehydrogenation of intermediate II to form

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III, $H_3BNHCH_3BH_2NHCH_3BH_2NH_2CH_3$, the only postulated intermediate which was not isolated. It is apparently unstable with respect to the trimer under the conditions of the pyrolysis. Some experimental evidence which might be consistent with the presence of III is the formation of $H_3BNH_2CH_3$ from the reaction of $[H_2CH_3NBH_2NHCH_3BH_2NH_2CH_3]^+Cl^-$ with $NaBH_4$ in a dilute monoglyme solution. Compound III should be soluble in monoglyme and could dissociate[13] to form, under dilute conditions, $H_3BNH_2CH_3$ and $(H_2BNHCH_3)_x$ polymer, the observed products. However, under very concentrated conditions, monoglyme solution or pyrolysis of II, the six-membered ring is formed by an intramolecular dehydrogenation reaction (eq 4) and disproportionation is averted.

In contrast to the ionic and polymeric type of intermediates, which characterized the formation of $(H_2BNHCH_3)_3$, the mechanism for the pyrolysis of $H_3BN(CH_3)_2H$ probably involves only neutral species. There was no experimental evidence for the cation $H_2B(N(CH_3)_2H)_2{}^+$ during the pyrolysis of $H_3BN(CH_3)_2H$ or the reaction of $NaBH_4$ and $(CH_3)_2NH_2Cl$ in etherated solvents. Similarily, the cation $[H(CH_3)_2NBH_2N(CH_3)_2BH_2N(CH_3)_2H]^+$ could not be prepared. Even though no intermediates could be isolated during the partial pyrolysis of $H_3BN(CH_3)_2H$, the experimental evidence is consistent with neutral monomeric species, $H_2BN(CH_3)_2$, which associate to give the dimer. The dimer is also in equilibrium with the proposed monomeric species. The association of monomers[14] was originally suggested to account for the formation of all aminoboranes.

The most likely route to the monomer $H_2BN(CH_3)_2$ is an intramolecular dehydrogenation of $H_3BN(CH_3)_2H$. Another possible route might be related to the initial formation of $H_3BN(CH_3)_2BH_2N(CH_3)_2H$ by the intermolecular dehydrogenation of two $H_3BN(CH_3)_2H$ molecules followed by either dissociation to give $H_3BN(CH_3)_2H$ and the monomer $H_2BN(CH_3)_2$ or an intramolecular ring-closure reaction by dehydrogenation. However, the observation that 2 moles of H_2 is formed for every mole of $(H_2BN(CH_3)_2)_2$ in the quenching experiment suggests that $H_3BN(CH_3)_2BH_2N(CH_3)_2H$ either is not a primary intermediate or is too unstable for a measurable quantity to be present under the pyrolytic conditions. It should be noted that the dimer has been prepared from $H_3BN(CH_3)_2BH_2N(CH_3)_2H$, but pyrolytic conditions[15] of 200° were used.

In conclusion, the most significant factor for the determination of the degree of association of aminoboranes appears to be the intermediates in their formation. All aminoboranes cannot be considered to be formed by the association of monomeric species. Therefore, steric effects should not be used as the only factor to explain the change in the degree of association with the substituents on the boron and nitrogen atoms. The differences in the intermediates might be related to steric effects, but the basicity of the amine and the strengths of the N–H bonds should also be considered.

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Molecular and Crystal Structure of *m*-$B_{10}Br_2H_8C_2H_2$

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The product of dibromination of *m*-$B_{10}H_{10}C_2H_2$ in the presence of $AlBr_3$ is shown to be a derivative with Br atoms substituted on B atoms 9 and 10, those farthest from the C atoms and the most negative B atoms in nonempirical molecular orbital studies of *m*-$B_{10}H_{10}C_2H_2$. There are four molecules in a unit cell having parameters $a = 13.14$, $b = 7.08$, and $c = 12.64$ A. The space group is Pnam. A tentative assignment of the ^{11}B nuclear magnetic resonance spectrum is proposed.

The charge distribution[1] in *o*-$B_{10}C_2H_{12}$, as computed by molecular orbital theory, gives a reasonable account of some simple electrophilic free radical and electrophilic reactions which occur at various B atoms. Thus the icosahedral $B_{10}C_2$ framework is strongly polarized by the C atoms to give ground-state charges of -0.16 at B(8) and B(10), of -0.16 at B(9) and B(12), of -0.03 at B(4), B(5), B(7), and B(11), and of $+0.08$ at B(3) and B(6). Hitherto unpublished studies by less empirical procedures,[2] in which parameters were taken from B_4H_4[3] for B atoms and in which one- and two-center zero overlap matrix elements have been included, yield -0.29, -0.27, -0.02, and $+0.22$, in the order listed above. Where the charges are similar, for B(8)

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