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^{11}B NMR Studies of the Thermal Decomposition of Ammonia–Borane in Solution

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Abstract

Heating solutions of NH_3BH_3 in aprotic solvents above approximately 80 °C resulted in three types of chemical reactions. In etheral solvents NH_3BH_3 underwent stepwise hydrogen-loss decomposition leading to cyclotriborazane and borazine along with other minor products. In pyridine solution base displacement led to pyridine–borane. In acetonitrile both products of hydrogen-loss decomposition and either hydrogenation or hydroboration were identified. ^{11}B NMR spectra peak areas showed that the maximum yields of cyclotriborazane formed in 0.15 M NH_3BH_3 in diglyme at 130 °C.

Introduction

Seeking new synthetic approaches to aminoborane, NH_2BH_2, we have investigated thermal decomposition of ammonia–borane, NH_3BH_3, as a source of the desired compound. In earlier work, gas phase thermal decomposition of NH_3BH_3 was reported to give poly(aminoborane), $(NH_2BH_2)_x$, after condensation of the product at low temperature [1], which is in concert with mass spectrometric observation of NH_2BH_2 in vapors above $NH_3BH_3(s)$ at room temperature [2]. Heating NH_3BH_3 in a closed glass vessel effected stepwise hydrogen-loss reactions resulting finally in boron nitride [3]. A method for preparation of poly(aminoborane), $(NH_2BH_2)_x$, involved heating ammonia–borane above its melting point in an evacuated, cold-finger apparatus [4].

The results of these and other studies show that NH_2BH_2 is formed in the first hydrogen-loss step in the thermal decomposition of NH_3BH_3, but monomeric aminoborane is difficult to study under these conditions owing to its rapid association to poly(aminoborane). Therefore, we elected to examine the thermal decomposition in solution anticipating that the monomer, if formed, might be stabilized by solvent interactions and that reactions of the monomer might be treated advantageously in solution. We wish to report here the results of those studies.

Experimental

All solvents were dried and distilled before use according to literature methods [5] then stored in Schlenk vessels. Ammonia–borane (Callery Chemical) was repeatedly vacuum sublimed at 65 °C to a cold finger at 0 °C until the melting range of the sublimate held in a clay-sealed capillary reached 115–116 °C (Melt-Temp block at 40 V). The melting temperature slowly decreases upon standing so the compound was frequently resublimed before use. The polyether 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) (Aldrich) was used without further purification.

NMR spectra were obtained using a Varian T-60 spectrometer for CW ^1H and an IBM/Brüker AF-80 instrument for FT ^{11}B (25.7 MHz). In the latter case, samples were held in 10 mm tubes with a 5 mm coaxial tube containing D_2O for maintaining a frequency lock. The chemical shift scale was calibrated before each run with $BF_3{\cdot}O(C_2H_5)_2$ set to δ 0.0. Negative δ values indicate shifts towards higher magnetic field. The WALTZ pulse sequence was used to obtain ^1H decoupled spectra. A Hewlett-Packard Model 5890 gas chromatograph with a Model 5970 mass-selective detector was used for identification of some volatile reaction products. A Perkin-Elmer Model 1330 infrared spectrophotometer was used to produce spectra in the range of 4000–650 cm^{-1}; both KBr disks and solution cells were used depending on the characteristics of the sample.

Solutions were prepared of 0.15 M NH_3BH_3 in each of the solvents (acetonitrile, diglyme, glyme, 2-methyl tetrahydrofuran, pyridine and tetrahydrofuran) under a dry nitrogen atmosphere using conventional methods [6]. Attempts to prepare similar solutions in toluene and in isobutyl ether were unsuccessful due to the low solubility of NH_3BH_3. All the solutions were initially homogeneous but precipitates appeared in most instances during heating. Each solution was placed in a Schlenk reaction flask fitted with a reflux condenser and a septum sidearm through which samples of solution were periodically withdrawn for NMR analysis; samples were not returned to the reaction mixture. Several runs were made for each solvent over a range of

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TABLE I. Reaction Conditions for Solvents other than Diglyme

Solvent	Temperature	Time (h)	Comments
Acetonitrile	reflux	15	solvent reaction[a] and NH_3BH_3 decomposition
1,2-Dimethoxyethane	reflux	25	NH_3BH_3 decomposition
2-Methyl tetrahydrofuran	reflux	7	NH_3BH_3 decomposition
Pyridine	reflux	1	solvent reaction[b]
Tetrahydrofuran	reflux	14	NH_3BH_3 decomposition

[a] Apparent hydroboration of CH_3CN observed. [b] Base displacement reaction by solvent suggested by products observed.

TABLE II. Mass Spectrum of Cyclotriborazane, $(NH_2BH_2)_3$

m/z	*RA* (%)	Ions
86.2	10.6	${}^{11}B_3{}^{14}N_3N_{11}^+$ $(p - 1)^+$
85.2	8.2	${}^{11}B_2{}^{10}BN_3H_{11}^+$, ${}^{11}B_3N_3H_{10}^+$
72.1	19.8	${}^{11}B_2N_3H_8^+$
71.2	14.1	${}^{11}B{}^{10}BN_3H_8^+$
57.1	10.3	${}^{11}B_2N_2H_7^+$
56.2	7.7	${}^{11}B{}^{10}BN_2H_7^+$
55.1	6.1	${}^{11}B_2N_2H_5^+$
54.1	4.1	${}^{11}B_3NH_5^+$, ${}^{11}B_2{}^{10}BNH_6^+$
45.1	14.6	${}^{11}BN_2H_5^+$
44.0	5.1	${}^{11}BN_2H_5^+$
43.1	30.4	${}^{11}BN_2H_4^+$
42.1	9.0	${}^{10}BN_2H_4^+$
38.1	4.4	${}^{11}B_2NH_2^+$
36.9	3.7	${}^{11}B{}^{10}BNH_2^+$
32.0	7.2	O_2^+
30.0	5.0	${}^{11}BNH_5^+$
28.9	9.4	${}^{11}BNH_4^+$
28.1	54.0	N_2^+, ${}^{11}BNH_3^+$, ${}^{10}BNH_4^+$
27.2	14.3	${}^{11}BNH_2^+$, ${}^{10}BNH_3^+$
26.0	8.6	${}^{11}BNH^+$, ${}^{10}BNH_2^+$
18.9	7.1	H_3O^+
18.1	100	H_2O^+, NH_4^+
17.1	33.3	HO^+, NH_3^+

temperatures up to the boiling point. A typical reaction is described below for bis(2-methoxy-ethyl)ether (diglyme). Table I lists the conditions employed during investigations of ammonia–borane decompositions in the other solvents included in the study. In all cases 0.15 M NH_3BH_3 solutions were employed.

Although the purpose of the study was to monitor product formation and decomposition with time and temperature and not to isolate products, in a few cases the reaction mixture was filtered by Schlenk methods and the filtrate used to help identify a product.

Ammonia–Borane in Bis(2-methoxyethyl)ether

A 45 ml volume of 0.15 M solution of NH_3BH_3 in diglyme was divided into three approximately equal segments and placed in separate reaction assemblies which were heated under a nitrogen stream to 85, 100 and 115 °C, respectively, and maintained there for 9 h in each case. Samples were withdrawn at convenient time intervals using a nitrogen-flushed syringe and their ${}^{11}B$ NMR spectra, both ${}^{1}H$ coupled and decoupled, were obtained without delay. The relative areas were determined for resonances representing NH_3BH_3, cycloborazanes and borazine*. Three additional 0.15 M solutions were prepared and studied at 120, 130 and 140 °C for 3.5 h.

Complexation with 18-Crown-6

A 30 ml quantity of 0.15 M NH_3BH_3 solution was divided into two equal segments and placed in Schlenk reaction flasks as described earlier. Enough 18-crown-6 polyether was added to one of the solutions to make it 0.15 M in that component as well. Both vessels were placed in the same heated oil bath and maintained, first for 3 h at 87 °C and then for 3 h at 135 °C. Another set of solutions were prepared and studied at 118 °C for 6 h.

Product Isolation

The presence of cyclotriborazane in diglyme reaction mixtures was confirmed by the following procedure. After 9 h, all the starting material having been consumed, the solution was filtered and the volatile components removed by vapor transfer. Vacuum sublimation of the solid residue to a cold finger at −78 °C afforded small amounts of cyclotriborazane, identified by its ${}^{11}B$ resonance, a triplet at δ −11.2, $J = 103$ Hz (lit. [7, 8] δ −11.3, −11.1), and its mass spectrum which exhibited a p-1 ion accompanied by appropriate fragment ions (Table II). In the case of acetonitrile reactions, similar workup gave a white solid product, m.p. 26.5–28 °C, which was identified as ethylamine–borane by its NMR and mass spectra.

Results and Discussion

The thermal decomposition of ammonia–borane in selected solvents was studied by ${}^{11}B$ NMR at temperatures up to and including reflux. Solvents studied

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*Individual resonances were integrated separately for each run. Due to partial overlap, the precision of the measurements is estimated to be ±5%.

TABLE III. ^{11}B NMR Parameters of NH_3BH_3 Thermal Decomposition Reaction Solutions

Solvent	Temperature (°C)[a]	Time[b]	Shift (δ)[c]	Comment
Acetonitrile	reflux	720	30.2 (49%)	br
			26.1 (4%)	
			–11.4 (39%)	t, *J* = 97 Hz
			–19.9 (%)	q, *J* = 95 Hz
			–28.9 (1%)	
Bis(2-methoxyethyl)ether	130	210	30.5 (93%)	d, *J* = 130 Hz
			–11.2 (7%)	t, *J* = 103 Hz
1,2-Dimethoxyethane	reflux	1500	30.5 (61%)	d, *J* = 131
			–3.6 (3%)	
			–5.6 (5%)	
			–11.2 (17%)	t, *J* = 104 Hz
			–24.4 (7%)	
			–27.1 (7%)	
2-Methyl tetrahydrofuran	reflux	840	–10.5 (11%)	t, *J* = 108 Hz
			–22.3 (90%)	q, *J* = 95 Hz
			–27.2 (6%)	
Pyridine	reflux	60	–11.6	q, *J* = 95 Hz
Tetrahydrofuran	reflux	840	–11.3 (11%)	t, *J* = 101 Hz
			–22.2 (83%)	q, *J* = 96 Hz

[a] Oil bath temperature for reactions below reflux. [b] Duration of reaction (min) at measurement. [c] Relative areas (± ~5%) of resonances in parenthesis.

included acetonitrile, diglyme, glyme, 2-methyl tetrahydrofuran, pyridine and tetrahydrofuran, chosen because they dissolve NH_3BH_3 to a reasonable concentration and have a boiling temperature of at least 80 °C, the lowest temperature at which ammonia–borane decomposes at an acceptable rate. Solvents such as alcohols which undergo solvolytic reactions with ammonia–borane were not included in the study. (Table I summarizes reaction conditions and times.)

The purpose of the work was to identify solvents and conditions best suited for preparing and carrying out reactions of NH_2BH_2 generated thermally from ammonia–borane. It was hoped that NH_2BH_2, which is subject to facile association in the solid phase [1, 4], would be stabilized sufficiently by solvation to be at least detectable in solution. If not, amounts of its oligomers detected in the reaction mixtures would indicate the extent of its formation.

Three types of reactions were observed: (1) hydrogen-loss decomposition of NH_3BH_3 leading to cycloborazane(s) and eventually to borazine, (2) base displacement by solvent on NH_3BH_3 giving a solvent·BH_3 adduct, and (3) reaction with the solvent leading to products consistent with an hydroboration pathway. The etheral solvents glyme, diglyme, tetrahydrofuran and 2-methyl tetrahydrofuran gave mainly products suggesting hydrogen-loss decomposition of NH_3BH_3. Table III gives ^{11}B NMR parameters of products from each reaction type under selected conditions.

Since the thermal decomposition of NH_3BH_3 is known to begin with a hydrogen elimination step forming transient NH_2BH_2 [3], detection of the latter was a goal of this study. The ^{11}B chemical shifts of the known di-N-substituted aminoboranes, R_2NBH_2, fall in the range of δ +37 to 38 [9] suggesting that the resonance of NH_2BH_2 might exhibit a similar shift. Unfortunately, no significant resonance resembling that expected for NH_2BH_2 was detected in this region of the spectra of any of the solutions in the study.

Even though NH_2BH_2 itself was not detected, its formation was confirmed by the observation of its oligomer(s) in reactions carried out in etheral solvents. The ^{11}B NMR spectrum of the decomposition reaction in glyme solution is shown in Fig. 1. The triplet ^{11}B resonance seen near δ –11 was assigned in those reactions to cyclotriborazane, $(NH_2BH_2)_3$; the trimer was isolated in small quantities and identified from diglyme reactions. It is recognized, however, that the ^{11}B resonances of $(NH_2BH_2)_3$ and $(NH_2BH_2)_2$ were reported to be indistinguishable [8], so that oligomers other than the trimer may also be present. Table IV shows oligomer chemical shifts calculated from a $\delta^{13}C$–$\delta^{11}B$ correlation reported by Spielvogel and Purser [10]. There is close agreement between the calculated and experimental shifts for the trimer and it is notable that the entire (predicted) range of shifts from the dimer to the pentamer is only about 2.7 ppm. Thus our NMR results show the presence of oligomers

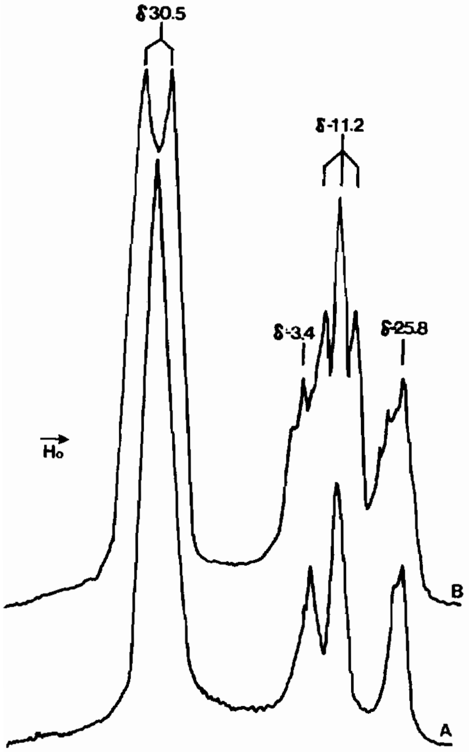

Fig. 1. NMR spectra of glyme solution of NH_3BH_3 after 25 h at reflux (A = ^{11}B, B = $^{11}B\{^1H\}$).

TABLE IV. Calculated ^{11}B Chemical Shifts for $(NH_2BH_2)_n$, $n = 2–5$

Oligomer	$\delta\,^{13}C(C_6H_6)$[a]	$\delta\,^{11}B$ (calc.)[b]	$\delta\,^{11}B$ (exp.)
$(NH_2BH_2)_5$	103.4	−12.1	
$(NH_2BH_2)_4$	101.8	−10.9	
$(NH_2BH_2)_3$	101.4	−10.7	−11.1[c], −11.3[d]
$(NH_2BH_2)_2$	105.4	−13.4	−11.1[d]

[a] Shifts calculated referenced to benzene according to: $\delta\,^{13}C(C_6H_6) = 128.7 - \delta\,^{13}C(TMS)$. [b] Correlation equation: $\delta\,^{11}B = -0.694\,\delta\,^{13}C(C_6H_6) + 59.7$ adapted from ref. 10. Negative δ values correspond to upfield shifts. [c] Ref. 8. [d] Ref. 7.

but do not distinguish among the cycloborazanes. For convenience we refer to the δ − 11 resonance hereafter as representing trimer.

Borazine (δ 30.2) and μ-aminodiborane(6) (δ − 28.9) were also identified among the reaction products. A comparison of the relative areas of ^{11}B resonances representing NH_3BH_3, trimer and borazine in a diglyme solution maintained for 9 h at 85 °C is plotted in Fig. 2. The time dependence of the concentrations of ammonia–borane, trimer and borazine during reaction in diglyme is qualitatively consistent with hydrogen-loss decomposition steps, eqns. (1) and (2).

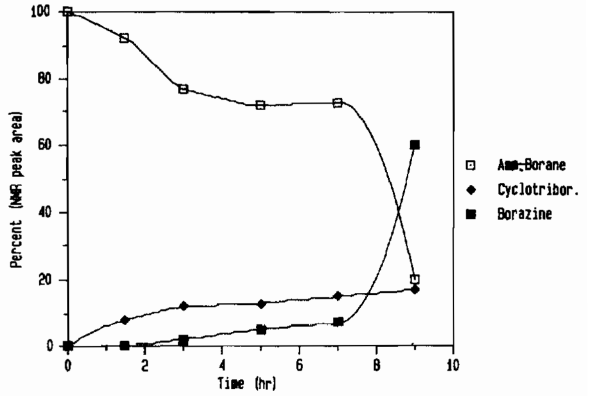

Fig. 2. Relative amounts of ammonia–borane (□), cyclotriborazane (◆) and borazine (■) during reaction in diglyme at 85 °C.

$$NH_3BH_{3(sol)} = \frac{1}{x}(NH_2BH_2)_x + H_2 \qquad (1)$$

$$\frac{3}{x}(NH_2BH_2)_x = (NHBH)_3 + 3H_2 \qquad (2)$$

In this solvent under the conditions used, trimer begins to appear soon after initiation of the reaction and its buildup is accompanied by a reduction in the amount of NH_3BH_3 of approximately equal magnitude during the first few hours of the reaction. Borazine first appears after about 3 h, its concentration slowly increases until about 7 h have passed at which time it increases dramatically becoming the major solution component. Meanwhile, the relative amount of trimer increases slowly to just less than 20%. A reasonable interpretation of the concentration changes of the components up to that time is that the reactions indicated by eqns. (1) and (2) occur sequentially resulting in the gradual conversion of ammonia–borane to trimer, which approaches something like a steady state concentration being formed from NH_3BH_3 and consumed in forming borazine [11]. The temperature ranges where these reactions take place are believed to overlap [3]. We do not have an explanation of the abrupt changes after 7 h. The formation of some minor products such as μ-aminodiborane(6) accompanies the main reaction pathway.

Figure 3 shows higher temperature diglyme reactions; the concentration of trimer goes through a maximum which is more pronounced as the temperature increases (Fig. 3b) and this appears to be reflected in the enhancement of borazine formation with temperature (Fig. 3c). Although we did not attempt to exploit it, heating a diglyme solution of ammonia–borane appears to have potential as an effective preparation of borazine. After 3.5 h at 130 °C in diglyme, the ^{11}B spectrum showed borazine as the only boron-containing product in solution.

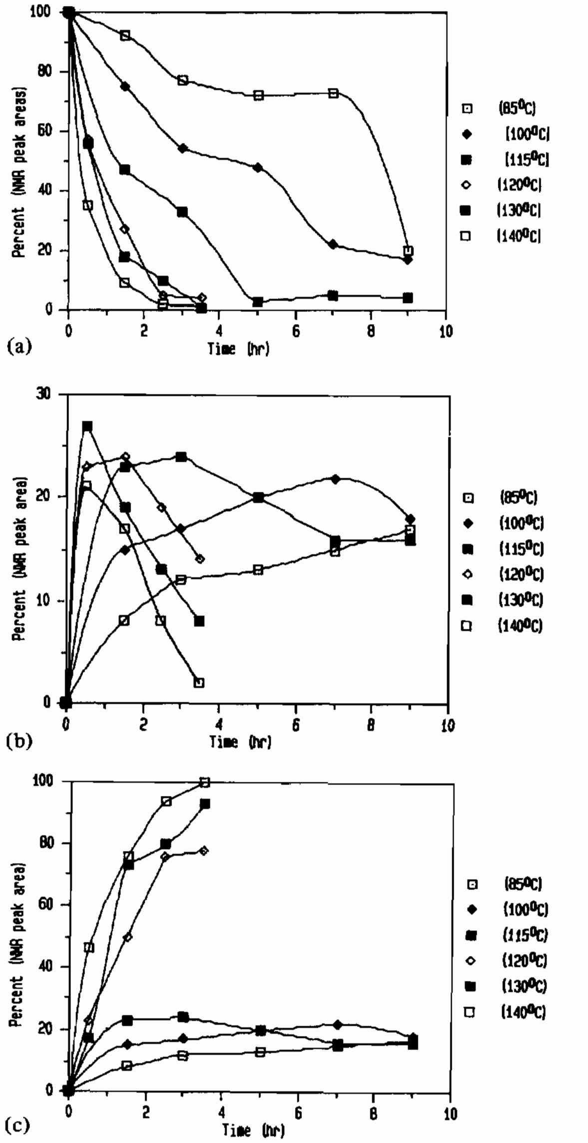

Fig. 3. Relative concentration profiles in diglyme reactions at 85–140 °C: (a) ammonia–borane, (b) cyclotriborazane, (c) borazine.

An effort was made to determine how complexation of ammonia–borane would affect its thermal decomposition in solution. Since 18-crown-6 polyether is known to form a complex with NH_3BH_3 [12], reactions were prepared with equimolar quantities of the two compounds in diglyme solution. The thermal behavior of these differed markedly from other reactions identical except for the absence of the crown ether; the complexed NH_3BH_3 was stable towards decomposition for 2.5 h at 87 °C; temperatures near 120 °C were required for the immediate initiation of hydrogen-loss decomposition (Fig. 4). Unfortunately for our purposes, the reaction at the higher temperature exhibited a more rapid formation of borazine and the disappearance of the trimer after 3 h. Evidently the 18-crown-6 complexation inhibits the normal decomposition process but when the temperature is high enough to initiate it, any trimer formed suffers rapid decomposition.

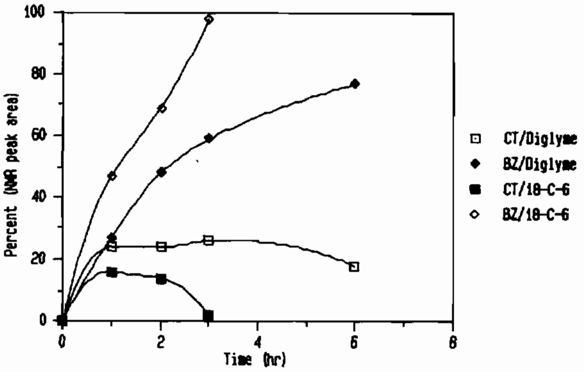

Fig. 4. Relative amounts of cyclotriborazane and borazine at 118 °C in diglyme and in diglyme plus 18-crown-6.

This result suggested another experiment aimed at determining the effect of solvent polarity and donor behavior among those solvents in which hydrogen-loss decomposition occurred. Solutions, 0.15 M in NH_3BH_3, prepared in diglyme and in 2-methyl tetrahydrofuran were held at 82 °C in the same oil bath and monitored over 24 h. The results showed that no trimer formed in the diglyme reaction during that period while in 2-MeTHF the trimer reached a maximum of about 20% after about 5 h at which point borazine formation commenced and the concentration of trimer slowly declined. We believe that a weaker interaction of 2-MeTHF with ammonia–borane permits decomposition at a lower temperature. In this regard it is notable that hydrogen-loss decomposition also takes place in refluxing THF (66 °C), the lowest boiling solvent where it was observed*, but only about 11% of trimer formed after 7 h at which point about 83% of the starting material remained. In refluxing glyme (83 °C) the maximum yield of trimer was 18% found after 7.5 h. Evidently both solvent characteristics and temperature influence the decomposition reaction.

The highest yield of trimer found in any of the solvents which did not react with NH_3BH_3 was *ca.* 27% after 30 min at 130 °C in diglyme. This information will be used in subsequent studies aimed at combining NH_2BH_2 with selected reactants before it associates forming oligomers.

Acetonitrile Reactions

The ^{11}B NMR spectra of 0.15 M NH_3BH_3 solutions in acetonitrile after 6 h at reflux exhibited five

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*Diethyl ether was not studied because its ammonia–borane solutions slowly deposit a white precipitate, possibly $BH_2(NH_3)_2BH_4$, even at room temperature.

resonances (Table III). The major resonances at δ 30.2, −11.4 and −19.9 were attributed to borazine (lit. [13, 14] δ 29.1 to 30.5, J = 133 to 139 Hz), cyclotriborazane and an initially unidentified reaction product. After 12 h at reflux, no starting material remained in the reaction mixture. Removal of volatiles by vapor transfer yielded a solution containing borazine (δ 30.2) and μ-$NH_2B_2H_5$ (δ − 28.9) [15]. The solid residue was sublimed *in vacuo* from ambient to a cold finger at −78 °C. The sublimate (m.p. 26.5–28 °C) was redissolved in $CHCl_3$ or CD_3CN for ^1H and ^{11}B NMR and mass spectra which identified the product as ethylamine–borane, $C_2H_5NH_2 \cdot BH_3$*. The infrared spectrum of the product is consistent with the proposed structure and its mass spectrum exhibited a parent ion mass along with expected fragments.

The observation of ethylamine–borane in the product mixture indicates that either an hydroboration or hydrogenation of solvent accompanies the hydrogen-loss decomposition of NH_3BH_3. Amine–boranes have been reported to produce hydroboration of alkenes [17] but are generally considered to be slow and ineffective hydroboration agents. We are not aware of any other reports of the use of ammonia–borane as a hydroborating agent.

Pyridine Reactions

After reflux of a 0.15 M solution of NH_3BH_3 in pyridine for 1 h, no starting material remained; ^{11}B NMR showed only one resonance (q, δ − 11.6, J(BH) = 95 Hz) assigned to pyridine–borane (lit. [18–21] δ − 11.5 to −13.0, J = 90.4 to 104 Hz). The essentially quantitative conversion of NH_3BH_3 to $C_5H_5NBH_3$, unexpected from the relative pK_b values of ammonia (pK_b = 48) and pyridine (pK_b = 8–9), is probably owing to the presence of a bubbler on the reaction apparatus permitting escape of NH_3 and establishing transamination conditions in the system.

Acknowledgements

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*$^1H(CD_3CN)$ δ − 0.03 (d, J = 93 Hz, BH_3). (The observed doublet is a segment of the expected 1:1:1:1 quartet due to proton coupling to ^{11}B, I = 3/2), 1.05 (t, J = 6.5 Hz, CH_3-CH_2) (lit. [16] 1.20), 2.55 (q, J = 6.3 Hz, CH_3-CH_2) (lit. [16] 2.80) and 3.55 (s, br, NH_2). $^{11}B(CHCl_3)$ δ −19.6, J(BH) = 92 Hz (lit. [19] δ −19.6, J = 92 Hz.)