## Reactions of Trimethylamine–lodoborane (1/1) and Related Complexes in Liquid Ammonia

By Peter J. Bratt and Michael P. Brown,\* Donnan Laboratories, University of Liverpool, Liverpool L69 3BX Kenneth R. Seddon, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR

The only trimethylamine-halogenoborane (1/1) in the series NMe<sub>3</sub>·BH<sub>y</sub>X<sub>z</sub> (y + z = 3; X = Cl, Br, or I) to react with liquid ammonia is NMe<sub>3</sub>·BH<sub>2</sub>I which slowly gives diamminedihydroboron iodide [BH<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]. The reaction rate is greatly increased in the presence of a range of halide salts. On reaction with Na[CN], NMe<sub>3</sub>·BH<sub>2</sub>I gives mainly NH<sub>3</sub>·B(CN)H<sub>2</sub> and with Na[NH<sub>2</sub>] mainly polymeric [BH<sub>2</sub>(NH<sub>2</sub>)]<sub>n</sub>. The complexes NMe<sub>3</sub>·BBr<sub>2</sub>H, NMe<sub>3</sub>·BH<sub>1</sub>, and NMe<sub>3</sub>·BBr<sub>3</sub>, as well as NMe<sub>3</sub>·BH<sub>2</sub>I, react with sodium in liquid ammonia; the products include [BH<sub>2</sub>(NH<sub>2</sub>)]<sub>n</sub> and (for NMe<sub>3</sub>·BH<sub>2</sub>I) the borane complex NMe<sub>3</sub>·BH<sub>3</sub>.

AMINE complexes of the boron halides, in contrast to the co-ordinatively unsaturated boron halides themselves, show considerable resistance to hydrolysis. In view of this it seemed possible that these complexes might be sufficiently stable to ammonolysis for their reactions to be studied in liquid ammonia. We report here treatment of the trimethylamine complexes NMe<sub>3</sub>·BH<sub>y</sub>X<sub>z</sub><sup>1</sup> (y + z = 3; X = Cl, Br, or I) (with the exception of NMe<sub>3</sub>·BI<sub>3</sub> which was not studied) with liquid ammonia, with ammoniacal solutions of halide and of other salts, and with ammoniacal solutions of sodium metal.

## RESULTS AND DISCUSSION

The only complex found to react with liquid ammonia at -44 °C was NMe<sub>3</sub>·BH<sub>2</sub>I. The other complexes of the series NMe<sub>3</sub>·BH<sub>y</sub>X<sub>z</sub> were recovered unchanged after being treated with ammonia for many hours. The reaction with NMe<sub>3</sub>·BH<sub>2</sub>I, which was very slow and took 40 h to proceed to completion, was an ammoniation rather than an ammonolysis and gave diamminedihydroboron iodide quantitatively. We have previously published  $^2$  a vibrational spectral analysis of this

$$\mathrm{NMe}_{3} \cdot \mathrm{BH}_{2} \mathrm{I} \xrightarrow{\mathrm{NH}_{3}} [\mathrm{BH}_{2}(\mathrm{NH}_{3})_{2}] \mathrm{I}$$
 (1)

compound and the corresponding chloride and bromide are known.<sup>3</sup>

The complexes  $NMe_3 \cdot BH_y X_z$  were treated with ammoniacal solutions of various metal and ammonium halide salts in order to investigate whether halide exchange, such as that demonstrated by us and other workers for  $NMe_3 \cdot BH_2I$  in organic solvents,<sup>1,4</sup> occurred. Once more,  $NMe_3 \cdot BH_2I$  was the only complex to react and the only products were the diamminedihydroboron salts,  $[BH_2(NH_3)_2]X$ . However, reaction of  $NMe_3 \cdot BH_2I$ in the presence of halide salts was much faster than in

P. J. Bratt, M. P. Brown, and K. R. Seddon, J.C.S. Dalton, 1974, 2161.
P. J. Bratt, M. P. Brown, and K. R. Seddon, J. Inorg.

<sup>&</sup>lt;sup>2</sup> P. J. Bratt, M. P. Brown, and K. R. Seddon, *J. Inorg* Nuclear Chem., 1975, **37**, 887.

<sup>&</sup>lt;sup>3</sup> G. Kodama, J. E. Dunning, and R. W. Parry, J. Amer. Chem. Soc., 1971, **93**, 3372; D. R. Schultz and R. W. Parry, *ibid.*, 1958, **80**, 4; C. E. Nordman and C. R. Peters, *ibid.*, 1959, **81**, 3551.

<sup>3551.</sup> <sup>4</sup> O. T. Beachley, jun., and B. Washburn, *Inorg. Chem.*, 1975, **14**, 120.

## J.C.S. Dalton

pure ammonia solution. For a mole ratio NMe<sub>3</sub>·BH<sub>2</sub>I: MX (MX = NaCl or NaBr, for example) of 1:1, the time for complete reaction was 35-40 min. By varying the mole ratios from 1:0.1 to 1:5, the time for complete reaction varied between 60 and 20 min. A greater mole ratio than 1:5 produced no apparent further increase in reaction rate.

It seems clear that this effect of MX on the reaction rate is an example of the primary salt effect,<sup>5</sup> the increase in the ionic strength of the medium accelerating, in this case, the dissociation of the boron-iodine bond. Thus it seems likely that [NMe<sub>3</sub>·BH<sub>2</sub>]I is an intermediate and that the reaction scheme is as in (2). The

$$NMe_{3} \cdot BH_{2}I \xrightarrow{slow} [NMe_{3} \cdot BH_{2}]I \xrightarrow{fast} [BH_{2}(NMe_{3})(NH_{3})]I \xrightarrow{fast} [BH_{2}(NH_{3})_{2}]I \quad (2)$$

product [BH<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]I did not react when heated under reflux with excess of trimethylamine and this gives credence to the irreversibility of the final step.

B(CN)H<sub>2</sub> did not react with refluxing NMe<sub>3</sub>. A probable intermediate in the formation of NH3.B(CN)H2 is the boron(1+) ion  $[BH_2(NH_3)_2]^+$  since when  $[BH_2(NH_3)_2]I$ was prepared in situ from NMe<sub>3</sub>·BH<sub>2</sub>I and NaI, and then treated with Na[CN], the only product was  $NH_3 \cdot B(CN)H_3$ . It is interesting that cyanide but not halide ion is able to displace ammonia from  $[BH_2(NH_3)_2]^+$  even in the presence of a large excess of NH<sub>3</sub>. We conclude that with Na[CN], two competing reactions, (3) and (4) occur.

When the series of halogenoborane complexes were treated with sodium in liquid ammonia at -44 °C, the following complexes reacted: NMe<sub>3</sub>·BH<sub>2</sub>I; NMe<sub>3</sub>·BHI<sub>2</sub>; NMe<sub>3</sub>·BBr<sub>2</sub>H; and NMe<sub>3</sub>·BBr<sub>3</sub>. When an excess of sodium was used, z moles reacted for one of  $NMe_3 \cdot BH_y X_z$ . In all these reactions new B-H bonds were formed. The complex NMe<sub>3</sub>·BH<sub>2</sub>I was the only one to give a volatile boron-containing product, viz. NMe3·BH3, although some boron was in the form of an involatile residue (mixed with the sodium iodide formed in the reaction). The active H: B ratio of this residue was less than that required for  $[BH_2(NH_2)]_n$  and possibly it

A number of mechanisms involving preionization of boron-halogen bonds in preference to breaking of boron-nitrogen-donor bonds for various reactions of amine-halogenoboranes have been postulated recently, for example the reaction <sup>6</sup> between BCl<sub>3</sub> and NMe<sub>3</sub>·BBr<sub>3</sub> and the hydrolysis 7 of trimethylamine-halogenoboranes. The lack of reactivity of NMe<sub>3</sub>·BHI<sub>2</sub> may be explained by an analogy with similar organic di-iodo-compounds.<sup>8</sup> In the case of NMe<sub>3</sub>·BH<sub>2</sub>I, the single iodine atom will obtain a large partial negative charge by the  $\sigma$ -inductive effect, thus creating a polar B-I bond, favouring ionization. However, in NMe3·BHI2, both of the iodine atoms will be competing for the available electron density, thus effectively reducing the polarity of each B-I bond. The lower reactivity of NMe<sub>3</sub>·BHI<sub>2</sub>, as compared with NMe<sub>3</sub>·BH<sub>2</sub>I, has also been observed in their hydrolysis reactions <sup>7</sup> which also go through a boron(1+) intermediate.

The monoiodo-derivative NMe<sub>3</sub>·BH<sub>2</sub>I was also the only complex of those examined (see Experimental section) to react with sodium cyanide. In this case a different reaction product, the cyano-derivative  $NH_3 \cdot B(CN)H_2$ , was obtained together with a trace amount of  $NMe_3 \cdot B(CN)H_2$ .<sup>1,9</sup> However, the latter complex was not an intermediate in the formation of NH<sub>3</sub>·B(CN)H<sub>2</sub> since treatment of a sample of NMe<sub>3</sub>·  $B(CN)H_2$  with liquid ammonia, with or without the addition of Na[CN], had no effect. Conversely, NH<sub>3</sub>.

<sup>5</sup> C. W. Davies, 'Ion Association,' Butterworths, London, 1962; V. K. La Mer, Chem. Rev., 1932, 10, 185. <sup>6</sup> S. S. Krishnamurthy and M. F. Lappert, Inorg. Nuclear

Chem. Letters, 1971, 7, 919. 7 J. R. Lowe, S. S. Uppal, C. Weidig, and H. C. Kelly, Inorg.

Chem., 1970, 9, 1423.

was a mixture of  $[BH_2(NH_2)]_n$  and  $BH(NH_2)_2$ . The other complexes which reacted gave only polymeric

NT. .....

$$\begin{aligned} \mathrm{NMe_3} \cdot \mathrm{BH_2I} \xrightarrow{\mathrm{Nde_NH_3}} \mathrm{NMe_3} \cdot \mathrm{BH_3} & (64\%) + [\mathrm{BH_2(NH_2)}]_n + \\ & [\mathrm{BH(NH_2)_2]} & (?) & (5) \end{aligned} \\ \mathrm{NMe_3} \cdot \mathrm{BHX_2} & (\mathrm{X} = \mathrm{Br \ or \ I}) \ \mathrm{and} \ \mathrm{NMe_3} \cdot \mathrm{BBr_3} \xrightarrow{\mathrm{Na-NH_3}} \\ & [\mathrm{BH_2(NH_2)}]_n & (6) \end{aligned}$$

aminoborane  $[BH_2(NH_2)]_n$ . Diamminedihydroboron iodide, the product of ammoniation of NMe<sub>3</sub>·BH<sub>2</sub>I, also reacted with sodium in a 1:1 mole ratio. Hydrogen was evolved and  $[BH_2(NH_2)]_n$  was the only product. This reaction resembles that of related boron(1+)salts.<sup>3,10</sup>

$$[BH_2(NH_3)_2]I + Na \longrightarrow$$
  
NaI + NH<sub>3</sub> +  $\frac{1}{n}[BH_2(NH_2)]_n + \frac{1}{2}H_2$  (7)

That the chloro-complexes  $NMe_3 \cdot BCl_z H_y$  (z = 1-3) and the bromo-complex NMe<sub>3</sub>·BBrH<sub>2</sub> did not react in homogeneous solution with sodium was surprising and shows how stable some of these four-co-ordinate boron complexes are. The stability towards ammonolysis of the four complexes which reacted with sodium was further tested by treating them with Na[NH<sub>2</sub>] solution. Only  $NMe_3 \cdot BH_2I$  reacted and gave mainly  $[BH_2(NH_2)]_n$ 

<sup>&</sup>lt;sup>8</sup> W. L. Budde and M. F. Hawthorne, J. Amer. Chem. Soc., 1970, 98, 3147; D. E. Walmsley, W. L. Budde, and M. F. Hawthorne, *ibid.*, p. 3150.

 <sup>&</sup>lt;sup>9</sup> S. S. Uppal and H. C. Kelly, Chem. Comm., 1970, 1619;
<sup>c</sup> C. Weidig, S. S. Uppal, and H. C. Kelly, Inorg. Chem., 1974, 13, 1763.

<sup>&</sup>lt;sup>10</sup> G. W. Schaeffer, M. D. Adams, and F. J. Koenig, J. Amer. Chem. Soc., 1955, 78, 725.

together with a trace amount of NMe<sub>3</sub>·BH<sub>3</sub>. The complexes NMe<sub>3</sub>·BHI<sub>2</sub>, NMe<sub>3</sub>·BBr<sub>2</sub>H, and NMe<sub>3</sub>·BBr<sub>3</sub> were recovered in quantitative yield.

Finally, pyrolysis of [BH2(NH3)2]I proceeded in a different manner to that of [BH<sub>2</sub>(NMe<sub>3</sub>)<sub>2</sub>]X <sup>11</sup> and gave a mixture of aminoborane  $[BH_2(NH_2)]_n$  and borazine  $[BH(NH)]_3$ . The aminoborane was probably formed as

$$[BH2(NH3)2]I \longrightarrow [NH4]I + BH2(NH2) (8)$$

$$3BH_2(NH_2) \longrightarrow [BH(NH)]_3 + 3H_2$$
 (9)

a monomer<sup>12</sup> since it was apparently produced as a vapour and was collected in a trap at -196 °C. On warming, the  $[BH_2(NH_2)]_n$  content of the trap was, however, completely involatile and was presumably polymeric.

EXPERIMENTAL

Starting Materials.—Trimethylamine-borane, m.p. 94 °C, was recrystallized. The complexes NMe<sub>3</sub>·BH<sub>2</sub>X and  $NMe_3 \cdot BHX_2$  (X = Cl, Br, or I) were prepared as described previously 13 and were freshly sublimed before use. Dihydrobis(trimethylamine)boron iodide 14 was prepared by the action of NMe<sub>3</sub> on NMe<sub>3</sub>·BH<sub>2</sub>I in benzene and recrystallized from EtOH-OEt2, m.p. 213 °C. The adducts  $NMe_3 \cdot BX_3$  (X = F, Cl, or Br) were prepared by standard literature methods and had m.p.s in good agreement with the literature values.<sup>15</sup> Liquid ammonia was dried over sodium and distilled prior to use. Organic solvents were dried by conventional methods. All manipulations with liquid ammonia were in vacuo. All other manipulations were made under a dry-nitrogen atmosphere unless otherwise stated.

Instrumental and Analytical Methods .--- I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer. Analyses for C, H, and N were by the Department of Organic Chemistry, University of Liverpool. Boron was estimated by titration as the boric acid-mannitol complex, and halogens were determined gravimetrically as silver(I) halide.

Reaction of Trimethylamine-Monoiodoborane (1/1) with Liquid Ammonia.—Trimethylamine-monoiodoborane (1/1) (4.96 g) was added to liquid ammonia (35 cm<sup>3</sup>) at -44 °C and was stirred at this temperature for 40 h. The ammonia was then removed in vacuo, leaving a white solid which was heated to 120 °C in vacuo to remove any trace of unchanged  $\mathrm{NMe}_3{\cdot}\mathrm{BH}_2\mathrm{I}$  from the involatile diamminedihydroboron iodide, m.p. 175 °C (decomp.) {Found: C, 0.0; H, 4.75; B, 6.35; I, 72.5; N, 15.4. [BH<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]I requires C, 0.0; H, 4.65; B, 6.20; I, 73.0; N, 16.1%]. The i.r. spectrum has been reported elsewhere.<sup>2</sup> On alkaline hydrolysis, the compound evolved only ammonia.

Attempted Reaction of [BH2(NH3)2]I with NMe3.-Trimethylamine (20 cm<sup>3</sup>) was added to [BH<sub>2</sub>(NH<sub>3</sub>)<sub>2</sub>]I (ca. 1 g) and was stirred at room temperature for 8 h. On evaporation of NMe<sub>3</sub>, the starting material was recovered unchanged.

Reaction of NMe<sub>3</sub>·BH<sub>2</sub>I with Liquid Ammonia in the <sup>11</sup> N. E. Miller, B. L. Chamberland, and E. L. Muetterties, *Inorg. Chem.*, 1964, 3, 1064.
<sup>12</sup> C. T. Kwon and H. A. McGee, jun., *Inorg. Chem.*, 1970, 9,

2458.

<sup>13</sup> M. P. Brown, R. W. Heseltine, P. A. Smith, and P. J. Walker, J. Chem. Soc. (A), 1970, 410.

Presence of Halide Salts.-In a typical reaction, NMe<sub>3</sub>·BH<sub>2</sub>I (1.25 g, 6.3 mmol) and NaBr (0.88 g, 8.6 mmol) were mixed with liquid ammonia (25 cm<sup>3</sup>) at -44 °C, and stirred at this temperature for 1 h. Ammonia was then removed in vacuo and the residue was heated to 80 °C in vacuo for 2 h. There was no sublimation from the residue, showing the absence of NMe<sub>3</sub>·BH<sub>2</sub>I and NMe<sub>3</sub>·BBrH<sub>2</sub>. The i.r. spectrum of the residue showed only bands attributable to  $[BH_2(NH_3)_2]^+$ . The same reaction occurred in the presence of NaX (X =F, Cl, Br, or I), AgX (X = Cl, Br, or I),  $[NH_4]X$  (X = F, Cl, Br, or I), KX (X = Cl or Br), and  $[BH_2(NH_3)_2]I$ . In all cases, the reaction resulted in formation of only the  $[BH_2(NH_3)_2]^+$  cation and in all cases the reaction was complete in 1 h or less.

Treatment of Other Trimethylamine-Borane Complexes with Liquid Ammonia and with Ammoniacal Solutions of Halide Salts.—The complexes NMe<sub>3</sub>·BH<sub>3</sub>, NMe<sub>3</sub>·BH<sub>y</sub>X<sub>z</sub> (X = Cl or Br), and  $NMe_3 \cdot BHI_2$  were recovered in virtually quantitative yield by sublimation after treatment for several hours with either liquid NH3 or ammoniacal solutions of varied sodium, potassium, ammonium, and silver(1) halides.

Reaction of NMe<sub>3</sub>·BH<sub>2</sub>I with Sodium Cyanide.-Trimethylamine-monoiodoborane (1/1) (5.1 g, 25.6 mmol) and Na[CN] (1.27 g, 25.9 mmol) were mixed with liquid NH<sub>3</sub>  $(30 \text{ cm}^3)$  at  $-44 \text{ }^\circ\text{C}$  and stirred at this temperature for 4 h. Ammonia was removed in vacuo to leave an oily residue. To this, benzene (25 cm<sup>3</sup>) was added, and after 20 min the benzene solution was filtered and the filtrate was evaporated to dryness. The solid obtained was purified by sublimation in vacuo at 50 °C to yield  $\rm NMe_3 \cdot B(\rm CN)H_2$  (0.02 g, 0.2 mmol) which was identified by comparison of its m.p. (64 °C), mass spectrum (molecular ion at m/e 98), and i.r. spectrum with the literature.<sup>1,9</sup> The fraction which was not soluble in benzene was extracted with OEt2, and n-hexane was added. The resulting white precipitate (0.48 g) was collected by filtration and dried in vacuo to give ammonia-cyanoborane, m.p. 89 °C (Found: C, 21.1; H, 9.10; B, 19.5; N, 48.9. NH<sub>3</sub>·B(CN)H<sub>2</sub> requires C, 21.5; H, 9.00; B, 19.35; N, 50.1%). The i.r. spectrum showed  $\nu(\mathrm{BH}_2)_{asym}$  at 2 430 and 2 410,  $\nu(\mathrm{BH}_2)_{sym}$  at 2 360,  $\nu$ (CN) at 2 202, and  $\nu$ (BN) at 714 cm<sup>-1</sup>. Attempts to sublime NH3.B(CN)H2 at 65 °C in vacuo led to considerable decomposition into hydrogen, ammonia, and hydrogen cyanide.

The compounds NMe3·BH3, NMe3·BHI2, and NMe3·  $BBr_zH_y$  (z = 1-3) did not react with Na[CN] under similar conditions.

Reaction of NMe<sub>3</sub>·BH<sub>2</sub>I with Sodium.-Trimethylaminemonoiodoborane (1/1) (3.1 g, 15.6 mmol) was dissolved in liquid NH<sub>3</sub> (30 cm<sup>3</sup>) at -78 °C and sodium (0.368 g, 16.0 mmol) was added. The blue colour quickly faded (1-2 The liquid  $NH_3$  was then removed in vacuo via a min). U trap held at -44 °C, leaving a white involatile residue in the reaction vessel. The contents of the trap were allowed to warm to room temperature and were purified by fractional distillation in vacuo. A white solid was formed and was identified as NMe<sub>3</sub>·BH<sub>3</sub> (0.723 g, 9.91 mmol) by comparison of its m.p. (94 °C) and i.r. spectrum with those in the literature.<sup>13,16</sup> The involatile residue was heated to 160 °C

<sup>14</sup> N. E. Millar and E. L. Muetterties, J. Amer. Chem. Soc., 1964, 86, 1033.

<sup>16</sup> E. Wiberg and W. Sutterlin, Z. anorg. Chem., 1931, 202, 31;
<sup>16</sup> B. Wiberg and H. Beyer, Chem. Ber., 1960, 93, 2251.
<sup>16</sup> B. Rice, R. J. Galiano, and W. J. Lehmann, J. Phys. Chem., 1977 41, 1979.

1957, 61, 1222.

*in vacuo* but no sublimate was obtained. The mole ratio of active H: B of this residue was 1.403:1 suggesting that it was possibly a mixture of  $\frac{1}{n}[BH_2(NH_2)]_n$  and  $BH(NH_2)_2$  in the mole ratio of 1.0:1.5.

Reaction of Other Trimethylamine-Halogenoboranes with Sodium.-Sodium reacted with NMe<sub>3</sub>·BBr<sub>3</sub>, NMe<sub>3</sub>·BBr<sub>2</sub>H, and  $NMe_3 \cdot BHI_2$  in mole ratios 3:1, 2:1, and 2:1 respectively. In the case of the bromo-complexes, 5-10 min were required for complete reaction. When less sodium than that specified above was used unchanged starting materials were recovered, and when more sodium was used the solution remained permanently blue. The only volatile materials from these reactions were NH<sub>3</sub> and NMe<sub>a</sub> (only partially separated by vacuum fractionation). The only identifiable boron compound formed was  $[BH_2(NH_2)]_n$  isolated by extraction with OEt<sub>2</sub> and evaporation of the filtrate in vacuo. Only in the case of  $NMe_3 \cdot BBr_2H$  was the yield of  $[BH_2(NH_2)]_n$  determined. Thus NMe<sub>3</sub>·BBr<sub>2</sub>H (1.049 g, 4.6 mmol) and sodium (0.215 g, 9.3 mmol) gave  $[BH_2(NH_2)]_n$  (0.130 g, 4.5 mmol) [Found: H, 13.6; B, 37.9; N, 47.9. Calc. for BH<sub>2</sub>(NH<sub>2</sub>): H, 13.8; B, 37.95; N, 48.3%]. Products from the other reactions had similar analyses.

The fact that the bromo-complex  $NMe_3 \cdot BBrH_2$  and the chloro-complexes  $NMe_3 \cdot BCl_zH_y$  (z = 1--3) did not react with sodium under similar conditions was evident from the observation that the solutions remained permanently blue.

Reaction of  $\text{NMe}_3 \cdot \text{BH}_2 \text{I}$  with Sodium Amide.—A solution of  $\text{Na}[\text{NH}_2]$  was produced in situ by adding sodium (0.258 g, 11.2 mmol) to liquid  $\text{NH}_3$  (25 cm<sup>3</sup>) in the presence of an iron catalyst (removed by filtration). Trimethylaminemonoiodoborane (1/1) (2.237 g, 11.3 mmol) was added to the solution at -44 °C and was stirred at this temperature for 4 h. Ammonia was then removed *in vacuo*. The residue was heated to 80 °C and a small amount of NMe<sub>3</sub>·BH<sub>3</sub> (0.036 g, 0.5 mmol), identified by its m.p. (93 °C) and i.r. spectrum, was obtained in a trap at -196 °C. The white involatile material was extracted with OEt<sub>2</sub> and the solution evaporated to dryness leaving  $[BH_2(NH_2)]_n$  (Found: H, 13.6; B, 37.8; N, 48.0%) as a white solid.

Reaction of  $[BH_2(NH_3)_2]I$  with Sodium.—Diamminedihydroboron iodide (1.48 g, 8.5 mmol) and sodium (0.194 g, 8.4 mmol) were added to liquid NH<sub>3</sub> (20 cm<sup>3</sup>) at -78 °C. The blue colour was dissipated within 1 min and a permanent gas was evolved. After 10 min, ammonia was removed *in vacuo* and the residue was heated to 100 °C *in vacuo*. No sublimate was observed. Extraction of the solid residue with OEt<sub>2</sub> gave  $[BH_2(NH_2)]_n$  (Found: H, 13.7; B, 37.7; N, 47.9%) as a white solid.

*Pyrolysis of*  $[BH_2(NH_3)_2]I$ .—The compound (0.327 g, 1.9 mmol) was heated at 170 °C *in vacuo* for 3 h. A sublimate of ammonium iodide (0.26 g, 1.8 mmol) was formed on the cool part of the apparatus. A distillate was collected at -196 °C and was later allowed to warm to room temperature when it gave a gas and a solid. The gas was identified by its i.r. and mass spectrum as borazine  $[BH(NH)]_3$ . The solid, which was no longer volatile even at 180 °C *in vacuo*, was identified by elemental analysis and its i.r. spectrum as  $[BH_2(NH_2)]_n$  (Found: H, 13.7; B, 37.8; N, 47.8%).

We thank the S.R.C. for a maintenance grant (to P. J. B.) and the C.E.G.B. for the award of a research fellowship at St. Catherine's College, Oxford (to K. R. S.).

[5/1060 Received, 2nd June, 1975]