

525. *Reaction of Diborane with Volatile Cyanides.*

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Methyl and ethyl cyanide react with diborane and form borine adducts of the type  $\text{RCN}\cdot\text{BH}_3$ , which dissociate reversibly at low temperatures. They decompose at *ca.*  $20^\circ$  and  $0^\circ$ , respectively, to form  $N'N''N'''$ -triethyl- and  $N'N''N'''$ -tri-n-propyl-borazole. Evidence is presented for the intermediate formation of a compound of the type  $(\text{R}\cdot\text{CH}=\text{N}\cdot\text{BH}_2)_n$ . Preliminary experiments show that similar but less stable borine adducts are formed by vinyl and phenyl cyanide. Diborane also reacts with cyanogen and hydrogen cyanide, but these products were not characterised.

LITTLE information is available on the reaction of diborane with volatile cyanides. Schlesinger and Burg<sup>1</sup> reported the formation of a solid adduct  $\text{MeCN}\cdot\text{BH}_3$  from diborane and methyl cyanide. Its dissociation at room temperature into the gaseous reactants was accompanied by slight decomposition to an involatile liquid, which was not identified. Burg<sup>2</sup> suggests that two hydrogen atoms shift from boron to the carbon of the cyanide group forming an *N*-substituted borazole, but gives no supporting evidence. Preliminary experiments on the reaction of diborane with acrylonitrile have also shown that a mixture of unidentified involatile products is formed.<sup>3</sup> Silyl cyanide also reacts with diborane, forming initially an adduct similar to that with methyl cyanide. When heated, however, monosilane is lost, leaving a polymer  $(\text{BH}_2\text{CN})_x$ .<sup>4</sup>

The experiments described in this paper were made to determine the nature of the decomposition products from the methyl cyanide adduct and also to find if similar adducts are formed by other cyanides. The formation of the compound  $\text{MeCN}\cdot\text{BH}_3$  was confirmed and, from measurements of its dissociation pressure ( $-34^\circ$  to  $4^\circ$ ) a heat of dissociation of the solid complex into methyl cyanide and diborane of  $11\cdot2$  kcal. mole<sup>-1</sup> was deduced. This may be compared with the value of  $31\cdot3$  kcal. mole<sup>-1</sup> for the dissociation of solid trimethylamine-borine,  $\text{Me}_3\text{N}\cdot\text{BH}_3$  into gaseous trimethylamine and diborane.<sup>5</sup> Using Bauer's<sup>6</sup> value of 28 kcal. mole<sup>-1</sup> for the heat of dissociation of diborane into borine radicals, the heat of dissociation of  $\text{MeCN}\cdot\text{BH}_3$  into gaseous  $\text{MeCN}$  and  $\text{BH}_3$  is 25 kcal. mole<sup>-1</sup>. Comparable values for other methyl cyanide adducts are:  $\text{MeCN}\cdot\text{BF}_3$ ,  $26\cdot5$  kcal. mole<sup>-1</sup>;  $\text{MeCN}\cdot\text{BCl}_3$ ,  $33\cdot4$  kcal. mole<sup>-1</sup> (ref. 7).

The infrared spectrum of the adduct showed bands at 3000, 2940, 2280, 1445, 1414, 1366, 1030, and 913  $\text{cm}^{-1}$  which, after allowance for small shifts, are common to methyl cyanide<sup>8</sup> and the adduct. The chief additional bands were at 2400—2340  $\text{cm}^{-1}$  (B-H stretch) and 1160—1140 (asymmetrical  $\text{BH}_3$  deformation). The position of absorption bands due to the B-N stretch vibration is not certain. Bands in the region 1250—980  $\text{cm}^{-1}$  have been assigned to this vibration in boron-nitrogen addition compounds by various authors,<sup>9</sup> although Taylor and Cluff,<sup>10</sup> who studied the spectra of deuterated derivatives of ammonia-borine,  $\text{H}_3\text{N}\cdot\text{BH}_3$ , concluded that the B-N band appears in the region 750—650  $\text{cm}^{-1}$ .

The solid adduct decomposed in a few days at  $20^\circ$  to a colourless liquid from which

<sup>1</sup> Schlesinger and Burg, *Chem. Rev.*, 1942, **31**, 1.

<sup>2</sup> Burg, *Record of Chemical Progress* (Kresge-Hooker Science Library), 1954, **15**, 159.

<sup>3</sup> Stone and Emeléus, *J.*, 1950, 2755.

<sup>4</sup> Evers, Freitag, Keith, Kriner, MacDiarmid, and Sujishi, *J. Amer. Chem. Soc.*, 1959, **81**, 4493.

<sup>5</sup> McCoy and Bauer, *J. Amer. Chem. Soc.*, 1956, **78**, 2061.

<sup>6</sup> Bauer, *J. Amer. Chem. Soc.*, 1956, **78**, 5775.

<sup>7</sup> Laubengayer and Sears, *J. Amer. Chem. Soc.*, 1945, **67**, 164.

<sup>8</sup> Venkateswarlu, *J. Chem. Phys.*, 1951, **19**, 293.

<sup>9</sup> Goubeau and Mitschelen, *Z. phys. Chem. (Frankfurt)*, 1958, **14**, 61; Luther, Mootz, and Radwitz, *J. prakt. Chem.*, 1958, **277**, 242; Goubeau and Becher, *Z. anorg. Chem.*, 1952, **268**, 1; Rice, Galiano, and Lehmann, *J. Phys. Chem.*, 1957, **61**, 1222.

<sup>10</sup> Taylor and Cluff, *Nature*, 1958, **182**, 390.

about a 50% yield of  $N'N''N'''$ -triethylborazole was recovered. This reaction must involve a hydrogen-transfer of the type proposed by Burg:<sup>2</sup>



The infrared spectrum of  $N'N''N'''$ -triethylborazole has not been previously described, but there is a general similarity between it and that of  $N'N''N'''$ -trimethylborazole.<sup>11</sup> The chief features are bands at 2970, 2900 (C-H stretch), 2480 (B-H stretch), and 1500—1300  $cm^{-1}$  (C-H bend). Ring and skeletal vibrations occur at 1500—750  $cm^{-1}$ , but cannot be definitely identified.

One fraction (II) obtained in separating the liquid decomposition product from the adduct also showed infrared bands due to the borazole, together with a number of additional bands. This fraction was very small and was not separated, but the spectrum indicated that it might be the intermediate  $(CH_3\cdot CH=N\cdot BH_2)_n$  postulated above. Thus a strong new band at 1685  $cm^{-1}$  may be due to a C=N vibration. This band is unlikely to be due to N-H deformation in view of the absence of absorption in the N-H stretch region around 3400  $cm^{-1}$ . There was also an additional strong B-H band at 2400  $cm^{-1}$ , in keeping with the observation<sup>11</sup> that  $Me_2N\cdot BH_2$  has two bands, at 2447 and 2396  $cm^{-1}$ . Hydrolysis of fraction II with 10% aqueous sodium hydroxide at 110° gave hydrogen, ethylamine, and ammonia. Hydrogen, ammonia, and acetaldehyde would be expected to be the volatile hydrolysis products of an intermediate  $(CH_3\cdot CH=N\cdot BH_2)_n$ . That no acetaldehyde was detected may have been because it was polymerised under such strongly alkaline conditions. A further fraction (III) had a composition and molecular weight corresponding with the formula  $(CH_3\cdot CH_2-N=BH)_{4-5}$ . It showed C-H stretch absorption at 3000—2850  $cm^{-1}$ , B-H stretch absorption at 2470  $cm^{-1}$ , and a number of peaks at 1500—650  $cm^{-1}$  which were not identified. Strong bands at 1440—1430, 1255—1235, 890—880 and 688—686  $cm^{-1}$  were common to the spectrum of this substance and to that of a similar fraction obtained from the decomposition of the ethyl cyanide-borane adduct (see below).

Diborane and ethyl cyanide gave an adduct  $EtCN, BH_3$ , which was less stable than that from methyl cyanide. It showed infrared bands at 2950, 2880, 2260, 1430, 1302, 1070, and 914  $cm^{-1}$ , identifiable with those of ethyl cyanide.<sup>12</sup> It dissociated reversibly at -30° to 0° and the heat of dissociation of the solid complex into diborane and ethyl cyanide was 9.8 kcal. mole<sup>-1</sup>, or 24 kcal. mole<sup>-1</sup> for dissociation to borane and ethyl cyanide. The compound decomposed violently at 20° to unidentified solids and hydrogen. Decomposition at -10° to 0° was, however, similar to that of the methyl cyanide adduct and gave a 60% yield of  $N'N''N'''$ -tri-*n*-propylborazole. Small quantities of an intermediate [possibly  $Et\cdot CH(CN)\cdot BH_2$ ] were again formed and there was a small fraction of the formula  $(Et\cdot CH_2\cdot BH)_n$ .

Two molecules of vinyl cyanide react at -132° to -40° with one of diborane to form a pale yellow solid, presumably  $CH_2\cdot CH\cdot CN, BH_3$ . This decomposed violently above 0° and it was not found possible in the preliminary experiments described to control the decomposition to yield borazole derivatives. Phenyl cyanide and diborane also reacted in proportions corresponding to the formation of  $Ph\cdot CN, BH_3$  but the decomposition of this adduct has not yet been studied. Hydrogen cyanide and diborane reacted at 20—100°, forming involatile pastes of composition ranging from 2.0 to 2.3 moles of hydrogen cyanide per mole of diborane. This reaction is probably complicated by the polymerisation of hydrogen cyanide and no  $N'N''N'''$ -trimethylborazole was isolated. Cyanogen and diborane reacted at 45—95° in a molar ratio of 1.2—1.4 : 1, the products being hydrogen and polymeric solids.

#### EXPERIMENTAL

Diborane was prepared from boron trifluoride-ether complex and lithium aluminium hydride and purified by vacuum-distillation.<sup>13</sup> Cyanogen was prepared by adding potassium cyanide

<sup>11</sup> Price, Fraser, Robinson, and Longuet-Higgins, *Discuss. Faraday Soc.*, 1950, **9**, 131.

<sup>12</sup> Duncan and Janz, *J. Chem. Phys.*, 1955, **23**, 434.

<sup>13</sup> Shapiro, Weiss, Schmich, Skolnik, and Smith, *J. Amer. Chem. Soc.*, 1952, **74**, 901.

solution to copper sulphate and purified as described by Janz.<sup>14</sup> Methyl, ethyl, vinyl, and phenyl cyanides were purified by vacuum-distillation from phosphorus pentoxide. Iodine cyanide was prepared by adding iodine slowly to concentrated aqueous potassium cyanide at 0°. The precipitate was washed with ice-water, recrystallised from water, and sublimed.<sup>15</sup> Vacuum-techniques were used in preparing reaction mixtures and isolating the products. Infrared spectra were recorded on a Perkin-Elmer Model 21 spectrometer.

*Reaction of Diborane with Methyl Cyanide.*—Diborane (0.028 g., 1.0 mmole) and methyl cyanide (0.082 g., 2.0 mmole) were condensed in a tube at -196° and warmed to 20°. White crystals were formed, with a vapour pressure of *ca.* 40 mm. at 20°. This vapour was shown by fractionation to contain only the reactants in a 1:2 molar ratio. Its infrared spectrum also showed only bands due to the two reactants. The molecular weight was 37. The vapour pressure of the solid (-34° to 4°) was given by  $\log_{10} p_{\text{mm.}} = 7.285 - 1640/T$ . The infrared spectrum of the solid, obtained with mulls of Nujol and hexachlorobutadiene, showed bands at 3000m, 2940m, 2400—2340s, 2280m, sh, 2070w, 1827w, 1445m, 1414m, 1366m, 1152s, 1030m, 973m, 913m, and 806w  $\text{cm.}^{-1}$ .

A sample of the adduct made from diborane (0.268 g.) and methyl cyanide (0.611 g.) changed to a colourless viscous liquid in 6 days at 20°. Hydrogen (0.0002 g.) and diborane (0.053 g.) were recovered. The liquid was separated by fractional condensation in traps cooled to -36° (I; 0.4 g.) and -63° (II; 0.1 g.). A viscous liquid residue (III; 0.3 g.), involatile at room temperature, was also obtained. Fraction I was *N'N''N'''*-triethylborazole [Found: C, 43.8; H, 11.0; N, 25.1%; *M* (cryoscopic in benzene), 169; *M* (from vapour density), 164. Calc. for  $\text{C}_6\text{H}_{18}\text{N}_3\text{B}_3$ : C, 43.8; H, 11.0; N, 25.5%; *M*, 165]. A sample (0.0168 g.) on hydrolysis with 10% aqueous sodium hydroxide at 110° for 4 hr. gave hydrogen (0.0006 g.) and ethylamine (0.0135 mg.) (Calc. for  $\text{Et}_3\text{N}_3\text{B}_3\text{H}_3$ : H, 0.0006 g.;  $\text{Et}\cdot\text{NH}_2$ , 0.0135 mg.). The v. p. at 20° was 2.5 mm. (lit.,<sup>16</sup> 2.6 mm.). The infrared spectrum showed bands at 2970m, 2900w, sh, 2480m, 2400w, 1483m, 1453s, 1382m, 1358w, 1332m, 1133m, 1088w, 884w, and 792w  $\text{cm.}^{-1}$ .

Fraction II had an infrared spectrum which showed the presence of *N'N''N'''*-triethylborazole. There were additional bands at 3010, 2560, 2490, 1720, 1685, 1640, 1460, 1390, 1200, 1070, and 960  $\text{cm.}^{-1}$ . The components could not be separated by fractionation. Hydrolysis with 10% aqueous sodium hydroxide at 110° gave hydrogen, ethylamine, and ammonia.

Fraction III had the composition  $(\text{C}_2\text{H}_6\text{NB})_n$  (Found: C, 43.5; H, 11.2; N, 25.8.  $\text{C}_2\text{H}_6\text{NB}$  requires C, 43.8; H, 11.0; N, 25.5%). Much of it distilled in a high vacuum at 150°. The molecular weight in benzene was 310, corresponding to  $n = 5-6$ . Hydrolysis of III (48.5 mg.) with 10% sodium hydroxide solution at 110° for 4 hr. gave hydrogen (0.50 mmole) and a mixture of ammonia and ethylamine (0.4 mmole). The infrared spectrum showed bands at 2890s, 2900m, sh, 2470s, 2350w, sh, 1658w, 1500s, sh, 1477s, sh, 1438s, 1398s, sh, 1377s, 1350s, 1335s, 1304s, 1256s, 1239m, sh, 1193m, 1133m, 1117m, 1100m, 1078m, 1021w, 972w, 880s, 792w, and 686m  $\text{cm.}^{-1}$ .

*Reaction of Diborane with Ethyl Cyanide.*—Diborane (0.0153 g., 0.55 mmole) and ethyl cyanide (0.060 g., 1.1 mmole) formed a white solid at -78°, the vapour pressure of which (-30° to 0°) was given by  $\log_{10} p_{\text{mm.}} = 6.102 - 1434/T$ . The infrared spectrum of the vapour showed that only diborane and ethyl cyanide were present. The infrared spectrum of the solid obtained with mulls of Nujol and hexachlorobutadiene showed bands at 2950m, 2880m, 2400—2340s, 2260m, sh, 2060w, 1825w, 1430m, 1302w, 1145s, 1070m, 914m, and 774w  $\text{cm.}^{-1}$ . It was immediately decomposed by water to boric acid, hydrogen, and ethyl cyanide.

The above adduct decomposed violently in a vacuum when warmed rapidly to room temperature, leaving a pale brown amorphous solid which contained carbon, hydrogen, nitrogen, and boron and was insoluble in common solvents. Hydrogen, diborane, and ethyl cyanide were also formed. Decomposition of the solid adduct was controlled by mixing diborane (0.270 g.) and ethyl cyanide (0.884 g.) at -132° and allowing the temperature to rise to 20° during 2 days. The product after a further 3 days at 20° was a colourless liquid. Unchanged diborane (1.7 mmole) and hydrogen (0.2 mmole) were recovered. The liquid residue was distilled in a vacuum at 50—100°. The most volatile fraction (I; 0.6 g.) distilled at 20°/0.5 mm., a second (II; 0.3 g.) at 150°/8 mm., and the residue (III; 0.2 g.) was a pale yellow glue.

Fraction I was *N'N''N'''*-tri-*n*-propylborazole [Found: C, 52.2; H, 11.2; N, 20.3%; *M*

<sup>14</sup> Janz, *Inorg. Synth.*, 1957, **5**, 43.

<sup>15</sup> Glusker and Thompson, *J.*, 1955, 471.

<sup>16</sup> Hough, Schaeffer, Dzurus, and Stewart, *J. Amer. Chem. Soc.*, 1955, **77**, 864.

(cryoscopic in benzene),  $230 \pm 10$ . Calc. for  $C_9H_{24}N_3B_3$ : C, 52.3; H, 11.7; N, 20.3%;  $M$ , 207]. Vapour pressures ( $100-210^\circ$ ) were within  $\pm 2$  mm. of the recorded values.<sup>16</sup> Hydrolysis of I (0.111 g.) at  $120^\circ$  (6 hr.) with 40% aqueous sodium hydroxide gave 36.7 ml. of hydrogen and 9.3 mg. of propylamine (Calc. for  $Pr_3N_3B_3H_3$ : 36.2 ml. of  $H_2$ ; 9.4 mg. of  $Pr-NH_2$ ). The infrared spectrum showed bands at 2940s, 2870m, sh, 2480s, 1470s, sh, 1440s, 1382m, 1370m, 1345m, 1325m, 1295m, 1079m, 926w, and 887m  $cm^{-1}$ .

Fraction II had the composition  $(C_3H_8NB)_n$  (Found: C, 52.4; H, 11.1; N, 20.4. Calc. for  $C_3H_8NB$ : C, 52.3; H, 11.7; N, 20.3%). The molecular weight in benzene was 300 and, from vapour-density measurement at  $200^\circ$ , was 450, indicating that  $n$  was 4—6. Hydrolysis with sodium hydroxide solution at  $100^\circ$  gave hydrogen, ammonia, and propylamine. The infrared spectrum, which was similar to that of fraction III from the methyl cyanide reaction described above, showed bands at 2940s, 2880s, sh, 2470s, 2350w, sh, 1500s, 1465s, sh, 1433s, 1400m, sh, 1380m, 1366m, 1344m, 1332m, 1295m, 1270m, 1235s, 1217m, sh, 1186m, 1136m, 1117m, 1098m, 1077m, 1040w, 960w, 888s, 780w, 745w, and 688m  $cm^{-1}$ . Fraction III, which was slightly soluble in benzene, had a molecular weight of about 900 in this solvent.

*Reaction of Diborane with Vinyl Cyanide.*—Diborane (0.021 g., 0.75 mmole) and vinyl cyanide (0.166 g., 3.08 mmoles) were mixed in a sealed tube at  $-132^\circ$  and warmed gradually to  $-40^\circ$  (18 hr.). No hydrogen was formed, but diborane (0.05 mmole) and vinyl cyanide (1.69 mmole) were pumped off at  $-40^\circ$ . The solid residue had therefore been formed from 0.70 and 1.39 mmole respectively of the reactants. The solid decomposed violently at about  $10^\circ$ , forming an amorphous brown solid which contained carbon, hydrogen, nitrogen, and boron.

*Reaction of Diborane with Phenyl Cyanide.*—Diborane (0.0614 g. 2.19 mmole) and phenyl cyanide (0.059 g., 0.57 mmole) were allowed to react at  $-78^\circ$  and formed a white solid, which decomposed partially, forming a colourless liquid. No hydrogen was formed, but diborane (0.0538 g., 1.91 mmoles) was recovered, showing the reaction of 0.28 mmole of diborane with 0.57 mmole of phenyl cyanide.

*Reaction of Diborane with Cyanogen.*—Diborane and cyanogen did not react at  $20^\circ$ . Diborane (0.041 g., 1.48 mmole) and cyanogen (0.0755 g., 1.45 mmole) were heated at  $95^\circ$  for 5 hr. Hydrogen (6.9 ml.), diborane (0.0137 g., 0.49 mmole), and cyanogen (0.010 g., 0.20 mmole) were recovered, showing that 0.99 mmole of diborane and 1.25 mmoles of cyanogen had reacted. The product was a pale brown amorphous solid.

*Reaction of Diborane with Hydrogen Cyanide.*—There was no reaction at  $25^\circ$  for an equimolar mixture of gaseous reactants at 1 atm. With liquid hydrogen cyanide present a slow reaction occurred at  $20^\circ$ . In a typical experiment hydrogen cyanide (0.115 g., 4.3 mmoles) and diborane (0.061 g., 2.2 mmoles) in a sealed tube (80 ml.) at  $20^\circ$  for 16 hr. gave 0.1 mmole of hydrogen, 1.88 mmoles of hydrogen cyanide, and 1.05 mmoles of diborane. Thus 2.4 and 1.15 mmoles respectively had reacted. The product was a colourless involatile paste, insoluble in benzene and carbon tetrachloride. It decomposed at  $200^\circ$  to hydrogen, hydrogen cyanide, and a brown solid. When the initial product was heated to  $100^\circ$  a colourless oil distilled, the infrared spectrum of which shows maxima at 2600—2900, 2500—2200, and 1700—800  $cm^{-1}$ . A maximum at 2430  $cm^{-1}$  may be attributed to the presence of a B—H bond. Hydrolysis of the oil (0.103 g.) with water in a sealed tube gave 3.8 mmoles of hydrogen. The gases reacted at  $50-100^\circ$ , giving similar products, the reactant ratio being  $B_2H_6 : HCN, 1 : 2-2.3$ .

*Reaction of Diborane with Iodine Cyanide.*—Solid iodine cyanide reacted explosively with gaseous diborane at  $20^\circ$  after an induction period of 5—10 min., during which free iodine was formed. After reaction, an amorphous brown solid separated on the walls of the reaction vessel. The volatile products were hydrogen, hydrogen cyanide, iodine, and unchanged diborane. Hydrolysis of the solid product with water gave hydrogen and hydrogen cyanide. A slow non-explosive reaction occurred below  $0^\circ$  and gave the same volatile products.

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