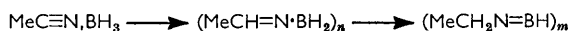


325. *Reactions between Dialkylboranes and Methyl Cyanide. Ethylideneaminodimethylborane and Diethylethylideneaminoborane.*

By J. E. LLOYD and K. WADE.

The dialkylethylideneaminoboranes, $(\text{MeCH}=\text{NBMe}_2)_2$ and $(\text{MeCH}=\text{NBEt}_2)_2$ have been prepared from the appropriate tetra-alkyldiborane and methylcyanide. The same compounds were also obtained, with $N'N''N'''$ -triethylborazine, from the 1,1-dialkyldiborane, R_2BHBH_3 , and methyl cyanide. Two isomers of $(\text{MeCH}=\text{NBMe}_2)_2$ have been isolated, and evidence is presented supporting *cis*- and *trans*-structures for these.

In an earlier communication,¹ methyl cyanide was shown to react with diborane to form a crystalline solid adduct, $\text{MeCN}\cdot\text{BH}_3$, which decomposed at 20° to form $N'N''N'''$ -triethylborazine, $(\text{EtNBH})_3$, together with more highly polymeric materials. The reaction apparently proceeded by step-wise transfer of two hydrogen atoms from the boron atom to the carbon atom of the cyanide group, as originally suggested by Burg:²



The only evidence obtained for the ethylidene intermediate, $(\text{MeCH}=\text{N}\cdot\text{BH}_2)_n$, was spectroscopic. A small quantity of material, detected by its infrared spectrum, showed a strong absorption band at 1685 cm^{-1} which might have been due to a $\text{C}=\text{N}$ vibration.

The experiments described below were carried out to determine whether a stable ethylideneaminoborane compound could be prepared. The method chosen was to select as acceptor molecule a compound in which only one hydrogen atom was attached to boron, the remaining two valencies being occupied by unreactive groups, thus allowing only one hydrogen transfer stage:



Alkyl groups were used as the unreactive groups after it was found that trimethylborane and triethylborane did not react with methyl cyanide at temperatures up to 100° . Since this work was started, Hawthorne³ has shown that it is unnecessary to start with a dialkylborane, BHR_2 , in order to prepare stable alkylideneaminoboranes; reaction of trimethylamine-*t*-butylborane, $\text{Me}_3\text{N}\cdot\text{BH}_2\text{Bu}^t$, with various nitriles RCN afforded stable alkylidene-amino-*t*-butylboranes $(\text{RCH}=\text{NBHBU}^t)_2$.

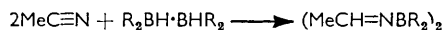
The dialkylboranes, BHR_2 , investigated here were the tetra-alkyldiboranes, $\text{Me}_2\text{BHBHMe}_2$ and $\text{Et}_2\text{BHBHEt}_2$, and the unsymmetrical dialkyldiboranes, Me_2BHBH_3 and Et_2BHBH_3 . The tetra-alkyldiboranes reacted slowly at room temperature with

¹ Emel us and Wade, *J.*, 1960, 2614.

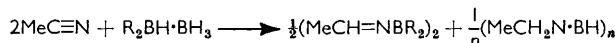
² Burg, "Record of Chemical Progress" (Kresge-Hooker Science Library), 1954, **15**, 159.

³ Hawthorne, *Tetrahedron*, 1962, **17**, 117.

methyl cyanide to form materials identified on the evidence discussed below as the dialkylethylideneaminoboranes $(\text{MeCH}=\text{NBMe}_2)_2$ and $(\text{MeCH}=\text{NBEt}_2)_2$, respectively. These same products were isolated after reaction of the dialkylboranes with methyl cyanide, together with $N'N''N'''$ -triethylborazine and some involatile viscous liquids, similar to those formed by reaction of diborane with methyl cyanide. Clearly, the reactions which had occurred were:

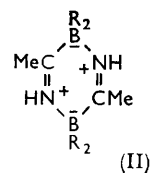
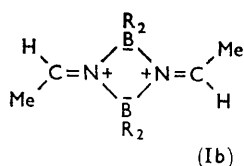
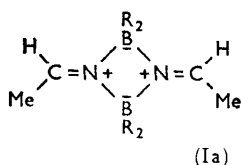


and



No evidence was obtained of an adduct $\text{MeC}\equiv\text{N}\cdot\text{BHR}_2$, in which hydrogen transfer had not occurred, although such a material may have been formed transiently during the reaction.

The dialkylethylideneaminoborane dimers were characterised as follows. Full elemental analysis and molecular weights determined cryoscopically in benzene solution confirmed the formulæ $(\text{C}_4\text{H}_{10}\text{BN})_2$ and $(\text{C}_6\text{H}_{14}\text{BN})_2$ for the products derived, respectively, from tetramethyldiborane and tetraethyldiborane. A strong band in their infrared spectra at about 1695 cm^{-1} was good evidence for the presence of a $\text{C}=\text{N}$ group in the molecule. This conclusion was supported by the formation of ammonia, not ethylamine, on reaction of the compounds with strong alkali at above 100° , and by the isolation of acetaldehyde 2,4-dinitrophenylhydrazone when samples were boiled with dilute acid and the vapours were passed into a solution of 2,4-dinitrophenylhydrazine. Reaction with water at elevated temperatures, or with hydrogen chloride at 150° followed by hydrolysis, yielded the appropriate dialkylborinic acid. All this evidence was consistent with a dialkylethylideneaminoborane formula, $(\text{MeCH}=\text{NBR}_2)_2$, where $\text{R} = \text{Me}$ or Et , and the structure (Ia or Ib), *cis*- and *trans*-isomers differing in the relative orientation of their ethylidene groups.



An alternative explanation in terms of structure (II) was ruled out by further infrared spectroscopic evidence. The spectra showed only very weak bands at about 3400 cm^{-1} , which were better explained as overtones of the very strong bands at 1695 cm^{-1} , rather than as $\text{N}-\text{H}$ stretching bands, while a band at 3000 cm^{-1} could be assigned to the $\text{C}-\text{H}$ stretching vibration of a group $=\text{CMe}-\text{H}$.

Both *cis*- and *trans*-isomers of structure (I) might be expected to be formed in the reactions studied, and in the case of ethylideneaminodimethylborane dimer, $(\text{MeCH}=\text{NBMe}_2)_2$, two isomers were obtained and separated by vacuum distillation. These were a crystalline solid, v. p. $0.6\text{ mm./}20^\circ$, m. p. 76° , and a liquid, v. p. $1.8\text{ mm./}20^\circ$, m. p. *ca.* -5° . Both of these isomers were dimeric in the gas phase at $100-150^\circ$ or in benzene solution, and their infrared spectra were very similar. Each isomer could be recovered after vacuum distillation at room temperature, and was essentially unchanged being heated to 150° , although both decomposed when heated to 155° for 18 hours. No evidence was obtained for the conversion of one isomer into the other *via* thermal dissociation into a monomeric form, $\text{MeCH}=\text{N}=\text{BMe}_2$: the products of thermal decomposition included involatile yellow viscous liquids, small quantities of trimethylborane, and traces of unidentified materials which yielded more trimethylborane on treatment with concentrated sulphuric acid.

It is suggested that the isomer having the lower melting point and higher volatility has

the *cis*-structure (Ia), and that the crystalline solid has the *trans*-structure (Ib). Dr. H. M. M. Shearer and Miss J. Willis of these laboratories are carrying out an X-ray crystallographic study of the crystalline solid isomer. Preliminary observations have shown the crystals to be monoclinic, of space group $P2_1/a$, $a = 6.55$, $b = 11.92$, $c = 7.89$ Å, $\beta = 105^\circ 23'$, and with four $\text{MeCH}=\text{NBMe}_2$ units in the unit cell. These observations are consistent with a dimeric form, $(\text{MeCH}=\text{NBMe}_2)_2$, if the dimer is centrosymmetric, and therefore in the *trans*-configuration.

The nuclear magnetic resonance spectra of solutions in carbon tetrachloride of both the liquid and the solid isomer were recorded on an A.E.I. R.S.2 spectrometer operating at 60 Mc./sec. The spectrum of the solid isomer is consistent with structure (Ib) in that it shows four peaks whose positions relative to an internal reference of tetramethylsilane, and relative intensities (shown in parentheses) are -442.0 (2), -121.1 (3), -115.8 (3), and $+8.65$ (12) c./sec. Positive values are to higher applied magnetic fields than the reference signal. The two sharply defined peaks each of intensity 3 can be attributed to the methyl groups attached to carbon atoms, which are spin-spin coupling to a single hydrogen nucleus. The separation between the two peaks gives $J(\text{Me}-\text{H}) = 5.3$ c./sec., which may be compared with the values of 5.30 – 6.30 c./sec. found in the oximes and various substituted hydrazones of acetaldehyde.⁴ The peak at lowest field is a broad single peak (width at half-height ~ 20 c./sec.) which from its intensity can be assigned to two hydrogen nuclei. The width of this peak is evidence for structure (I) rather than (II) since the CH peaks in (I) would give a 1:3:3:1 quartet from spin-spin coupling with the methyl hydrogen nuclei on the same carbon atom, and each component of the quartet would be broadened by the effect of the nitrogen-14 nuclear quadrupole moment, so that the peak would be an unresolved broad peak of width ~ 20 c./sec. The N-H peaks in structure (II) would also show a quartet structure, but the effect of quadrupolar broadening by the nitrogen-14 nucleus in this case would most probably broaden the peaks beyond the limits of detection. The peak at highest applied field is broad and single, and arises from the four methyl groups attached to boron atoms. A single peak for these methyl groups supports the structure (Ib) for the solid compound since in this structure the *B*-methyl groups have an identical environment and are magnetically equivalent, whereas structure (Ia) should give rise to two *B*-methyl peaks in the nuclear magnetic resonance spectrum.

The spectrum of the liquid isomer as a dilute solution in carbon tetrachloride was identical with that of the solid isomer, except that there are two high-field peaks arising from the *B*-methyl hydrogen nuclei; these are of equal intensity and are at 0.0 and $+12.8$ c./sec. from tetramethylsilane. The presence of two *B*-methyl peaks is consistent with structure (Ia) for the liquid isomer, as in this structure two *B*-methyl groups have only *C*-methyl neighbours through space and the other two have only *C*-H neighbours; hence a chemical shift is expected between the *B*-methyl resonances.

It was not found possible to separate the dimeric diethylethylideneaminoborane, $(\text{MeCH}=\text{NBEt}_2)_2$, melting from -18 to -10° , into isomers by vacuum distillation at room temperature, nor by vapour-phase chromatography using nitrogen as carrier gas over silicone elastomer. The isomers which were presumably present, judging by the melting range of the compound, apparently differed less in their vapour pressures than did their methyl analogues. The nuclear magnetic resonance spectrum of $(\text{MeCH}=\text{N}\cdot\text{BEt}_2)_2$ was recorded, but proved too complicated to allow unambiguous interpretation in terms of the presence of *cis*- and *trans*-isomers. Hawthorne,³ in describing the dimeric alkylidene-amino-*t*-butylboranes $(\text{RCH}=\text{NBHBU}^t)_2$, commented on the possibilities of *cis-trans* isomerism in such systems but was unable to separate his products into geometrical isomers, presumably because his choice of reactants, with only one alkyl group per boron, led to too many opportunities for isomerism. Lappert and Majumdar⁵ have obtained

⁴ Karabatsos, Taller, and Vane, *J. Amer. Chem. Soc.*, 1963, **85**, 2327.

⁵ Lappert and Majumdar, *Proc. Chem. Soc.*, 1963, 88.

spectroscopic evidence for a similar type of isomerism involving a four-membered boron-nitrogen ring with exocyclic double bonds to the boron atoms in the compound 1,3-di-*t*-butyl-2,4-di-*t*-butylamino-1,3-diaza-2,4-boretane but again no isomers were separated.

Attempts to prepare monomeric diethylethylideneaminoborane, $\text{MeCH}=\overset{+}{\text{N}}=\overset{-}{\text{B}}\text{Et}_2$, by thermal dissociation of the dimer were unsuccessful. Prolonged pyrolysis of $(\text{MeCH}=\text{NBEt})_2$ led to products similar to those obtained from $(\text{MeCH}=\text{NBMe}_2)_2$, *i.e.*, some triethylborane, an involatile yellow viscous liquid, and an unidentified fraction which may have been an amine adduct of triethylborane.

EXPERIMENTAL

Trimethylborane and triethylborane were prepared from the appropriate alkylmagnesium bromide and boron trifluoride-ether complex in dibutyl ether or trimethyl borate in diethyl ether. Diborane was prepared from boron trifluoride-ether complex and sodium borohydride in diethylene glycol dimethyl ether.⁶ All three compounds were purified by distillation in the vacuum line. Methyl cyanide was purified by vacuum-distillation from phosphorus pentoxide.

Tetramethyldiborane was prepared by mixing diborane (1 vol.) with trimethylborane (5 vol., *i.e.*, a slight excess over the amount required theoretically) at room temperature in the gas phase. The equilibrium mixture contained some trimethyldiborane and unchanged trimethylborane⁷ which could be detected by bands in the infrared spectrum⁸ at 2510, 1300, and 1150 cm^{-1} . 1,1-Dimethyldiborane was prepared by allowing equimolar quantities of diborane and trimethylborane to interact for a few days in the gas phase at room temperature.⁷ Gas-density measurement showed the average molecular weight to be 56, and the infrared spectrum showed bands corresponding to those found for 1,1-dimethyldiborane by Shapiro and his co-workers.⁹ Extra bands showed the presence of some mono- and tri-methyldiboranes, but these compounds were not separated as their equilibrium concentration would have been regenerated in the 1,1-dimethyldiborane under the conditions by which it was to be treated with methyl cyanide. Tetraethyldiborane was prepared from diborane (1 vol.) and triethylborane (5 vol.). 1,1-Diethyldiborane was prepared by the reaction between sodium borohydride and vinyl bromide in Tetraglyme;¹⁰ its identity was confirmed by its infrared spectrum.⁹

Infrared spectra were recorded on a Grubb-Parsons GS2A grating spectrometer. Samples were studied in potassium bromide discs, as liquid films, or as vapours as appropriate, with cell windows of sodium chloride or potassium bromide.

Reaction of Methyl Cyanide with Trimethylborane or Triethylborane.—Methyl cyanide and trimethylborane were recovered unchanged from mixtures in which gaseous trimethylborane and gaseous or liquid methyl cyanide had been left for 2 weeks at room temperature. No sign of interaction was observed in the infrared spectrum of the gaseous mixture or in the vapour density, or in vapour-pressure measurements at low temperatures. Similar experiments on mixtures of methyl cyanide and triethylborane showed no interaction.

Reaction of Methyl Cyanide with Tetramethyldiborane.—Trimethylborane (0.956 g.; 17.1 mmole) and diborane (0.0945 g.; 3.4 mmole) were left at 20° for 2 days; methyl cyanide (0.789 g.; 19.3 mmole) was then distilled in. At 20° most of the methyl cyanide and tetramethyldiborane remained in the liquid phase. Crystals grew on the vessel walls during 6 days at room temperature. The mixture was separated in the vacuum line into unchanged trimethylborane (0.195 g.; 3.5 mmole), tetramethyldiborane (0.301 g.; 3.6 mmole), methyl cyanide (0.040 g., 0.97 mmole), and a fraction (1.25 g.) which condensed at -25°. Repeated distillation of this last fraction from traps held at between -20 and -15° separated it into two components, a crystalline solid (I; 0.9 g.), *v. p.* 20°/0.6 mm., and a liquid (II; 0.35 g.), *v. p.* 20°/1.8 mm.

Characterisation and Reactions of Fraction (I).—Fraction (I) was identified as dimeric ethylideneaminodimethylborane, $(\text{MeCH}=\text{N}\cdot\text{BMe})_2$, *m. p.* 76° [Found: C, 58.1; H, 12.0; B, 13.0; N, 17.0%; *M* (cryoscopic in benzene), 166; *M* (from vapour density), 158. $\text{C}_8\text{H}_{20}\text{B}_2\text{N}_2$

⁶ Brown and Subba Rao, *J. Org. Chem.*, 1957, **22**, 1135.

⁷ Schlesinger and Walker, *J. Amer. Chem. Soc.*, 1935, **57**, 621.

⁸ Lehmann, Wilson, and Shapiro, *J. Chem. Phys.*, 1961, **34**, 783.

⁹ Lehmann, Wilson, and Shapiro, *J. Chem. Phys.*, 1961, **34**, 476.

¹⁰ Wartik and Pearson, *J. Inorg. Nuclear Chem.*, 1958, **5**, 250.

requires C, 57.8; H, 12.1; B, 13.1; N, 16.9%; *M*, 166]. The infrared spectrum of the gas at 53 and 72° over the range 4000—525 cm.⁻¹ contained bands at 3420vw, 3060vw, 3010vw, 2925vs, 2905m(sh), 2840w(sh), 1700s, 1524vw, 1443w, 1393w, 1366w, 1299s, 1147m, 1120w-m, 1096m, 1042s, 932w, 848w, 715w, 610w, and 574w cm.⁻¹. The vapour pressure (20—80°) was given by $\log_{10}P(\text{mm.}) = 8.775 - 2636/T$. Above about 150°, pressures were not reproducible, increasing slowly, showing that the compound was decomposing. A sample of fraction (I) (0.134 g.), heated in a sealed bulb at 155° for 18 hr., was converted into an involatile yellow glue (0.09 g.) together with some trimethylborane (0.020 g.), and an unidentified solid (III; 0.016 g.), v. p. ca. 20°/13 mm.; ν_{max} 3660vw, 3520vw, 3450vw, 3425vw, 2970m, 2940m, 2860wsh, 1618m, 1608m, 1400s, 1310s, 1202w-m, 1189w-m, 1160m, 1130s, 1100wsh, 943m, 735—730w, and 672w-m cm.⁻¹. In an attempt to identify (III), the whole fraction (0.016 g.) was condensed on to cold concentrated sulphuric acid, and the mixture was shaken at 20° for a few minutes. All the material still volatile (0.006 g.) was then removed and identified by its infrared spectrum as trimethylborane. The sulphuric acid solution was then treated with an excess of concentrated sodium hydroxide solution, but no volatile material other than water was detected in the vapour pumped from the residue.

Fraction (I) slowly volatilised without decomposition on exposure to air, and at 20° was unaffected by water, dilute acids, dilute alkalis, or gaseous hydrogen chloride. Heating with concentrated sulphuric acid decomposed fraction (I), and this reaction was used in analysing for nitrogen (by the Kjeldahl method) and boron (by the methoxide-mannitol method). Heating with dilute sulphuric acid and passage of the vapours through 2,4-dinitrophenylhydrazine solution yielded acetaldehyde 2,4-dinitrophenylhydrazone.

Reaction of fraction (I) with an excess of hydrogen chloride at 105° for 2 days gave dimethylchloroborane, some trimethylborane, and methylchloroborane, and an involatile amorphous brown solid. Reaction of fraction (I) with an excess of water vapour at 105° for 1 day gave an involatile yellow solid, dimethylborinic acid,¹¹ and a trace of methane. Reactions with strong sulphuric acid or sodium hydroxide solutions at 100—150° in sealed tubes generated varying quantities of methane and ammonia; no ethylamine was detected among the products.

Characterisation of Fraction (II).—Fraction (II) from the reaction of tetramethyldiborane with methyl cyanide proved to be an isomer of (I), m. p. -5° [Found: C, 56.8; H, 12.3; B, 12.7; N, 16.9%]; *M* (cryoscopic in benzene), 170; *M* (from vapour density), 159. C₈H₂₀B₂N₂ requires C, 57.8; H, 12.1; B, 13.1; N, 16.9%; *M* 166]; ν_{max} 3410vw, 3000vw, 2920s, 2900m(sh), 2825w(sh), 1740vw(sh), 1698vs, 1615vw, 1433m, 1401m, 1362m, 1289vs, 1145ms, 1114m, 1091s, 1034vs, 923w-m, 844w, and 824vw(sh) cm.⁻¹. The vapour pressure (20—90°) was given by $\log_{10}P(\text{mm.}) = 7.230 - 2044/T$. Above about 150°, pressures increased irreversibly as the compound decomposed, forming an involatile yellow glue, trimethylborane, and traces of unidentified volatile materials similar to those (fraction III) found after pyrolysis of (I).

Heating fraction (II) with water vapour at 100° gave dimethylborinic acid and an involatile residue. Heating with dilute sulphuric acid gave acetaldehyde, identified as its 2,4-dinitrophenylhydrazone. Reaction with strong sodium hydroxide solution in sealed tubes at 100—150° gave ammonia and traces of methane.

Reaction of Methyl Cyanide with 1,1-Dimethyldiborane.—1,1-Dimethyldiborane (0.168 g.; 3.0 mmole) and methyl cyanide (0.200 g., 4.9 mmole) were sealed together; at 20° some methyl cyanide remained as liquid. During several days at room temperature the liquid became more viscous, the gas pressure decreased, and crystals appeared on the bulb walls. After 1 week the volatile contents of the bulb were transferred to the vacuum line and separated into unchanged 1,1-dimethyldiborane (0.090 g.; 1.6 mmole), unchanged methyl cyanide (0.082 g.; 2.0 mmole), a colourless liquid (IV; 0.05 g.), v. p. 20°/2.4 mm., and a crystalline solid (V; 0.06 g.) v. p. 20°/0.6 mm. Left in the vessel was a viscous liquid (VI; 0.09 g.), which was involatile at room temperature.

Fraction (IV) was identified by its infrared spectrum as *N'N''N'''*-triethylborazine, extra bands indicating the presence of some of the liquid dimeric ethylideneaminodimethylborane, (MeCH=N·BMe₂)₂, described as fraction (II) above.

Fraction (V) was identified by its infrared spectrum as the solid isomer of dimeric ethylideneaminodimethylborane, (MeCH=N·BMe₂)₂, described as fraction (I) above.

¹¹ Ulmschneider and Goubeau, *Chem. Ber.*, 1957, **90**, 2733; *Z. phys. Chem. (Frankfurt)*, 1958, **14**, 56.

1654 *Reactions between Dialkylboranes and Methyl Cyanide.*

Fraction (VI), the involatile viscous liquid showing ν_{\max} . 3080m, 2900m, 2470m, 2325m, 1701m, 1686w(sh), 1473m(sh), 1433s, 1374m, 1350m(sh), 1292m, 1253m, 1186w(sh), 1145m, 1101m(sh), 1076m, 1044w(sh), 962w, 897w(sh), 883m, 793w, 688w, and 667w cm^{-1} . This spectrum was very similar to that of the involatile liquid product of the reaction between methyl cyanide and diborane, with extra bands which may indicate the presence of methyl groups attached to boron.

Reaction of Methyl Cyanide with Tetraethyldiborane.—Diborane (0.178 g.; 6.3 mmole) and triethylborane (3.081 g.; 31.5 mmole) were mixed, left for 2 weeks and then mixed with methyl cyanide (1.686 g.; 40.6 mmole). The mixture was mainly liquid at room temperature. After 2 weeks, the volatile materials were distilled into the vacuum line and separated into ethane (0.015 g.; 0.5 mmole) and a mixture of methyl cyanide and triethylborane (1.047 g.). Left was a liquid (VII; 3.8 g.), virtually all of which proved just volatile enough at 20° to distil slowly in a good vacuum on to a cold finger at -78°, where it collected as a crystalline solid, melting over the range -18 to -10°.

Fraction (VII) proved to be dimeric diethylethylideneaminoborane, $(\text{MeCH}=\text{N}\cdot\text{BEt}_2)_2$ [Found: C, 65.1; H, 12.7; B, 9.7; N, 12.8%; M (cryoscopic in benzene), 221. $\text{C}_{12}\text{H}_{28}\text{B}_2\text{N}_2$ requires C, 64.9; H, 12.7; B, 9.7; N, 12.6%; M , 222]; ν_{\max} . 3400vw, 3000w(sh), 2940vs, 2900vs, 2865vs, 2820m, 2715vw, 1692vs, 1457m, 1431m, 1397w-m, 1370w(sh), 1361w-m, 1272m, 1256w(sh), 1227w(sh), 1144s, 1098m, 1082m(sh), 1056vs, 1031w(sh), 1012vw(sh), 973vw, 919s, 903m(sh), 818s, 743vw, and 631vw cm^{-1} . The vapour pressure (110–180°) was given by $\log_{10}P(\text{mm.}) = 7.097 - 2.465/T$, which corresponds to a figure of 10 mm. at 131°, and may be extrapolated to 0.05 mm. at 20°. Above about 150°, pressures increased irreversibly as the compound decomposed, forming an involatile viscous liquid, traces of triethylborane, and a trace of a colourless liquid; ν_{\max} . 3580vw, 3520w, 3435w, 2965vs, 2925ms, 2890s, 1616ms, 1608ms, 1468m, 1403w, 1330ms, 1242vw, 1130m, 1121m, 1100m, 1031w, 966w, 948w, 928w, 835vw, and 770w cm^{-1} .

The diethyl derivative (VII) was unchanged after short exposure to air or moisture, but gave diethylborinic acid when heated with water vapour at 100°. Heating with dilute sulphuric acid gave acetaldehyde, identified as its 2,4-dinitrophenylhydrazone. Attempts to separate (VII) into isomers by vapour-phase chromatography, using nitrogen as carrier gas over a silicone elastomer at temperatures up to 200°, were unsuccessful.

Reaction of Methyl Cyanide with 1,1-Diethyldiborane.—1,1-Diethyldiborane (0.297 g.; 3.5 mmole) and methyl cyanide (0.142 g.; 3.5 mmole) were kept for 6 days. Easily volatile materials were then pumped into the vacuum line, leaving a colourless liquid. Prolonged pumping on this residual liquid showed some (0.2 g.) to be just volatile enough at 20° to be transferred to the line. Its infrared spectrum showed this to be dimeric diethylethylideneaminoborane, identical with the material (VII) [M (cryoscopic in benzene), 230. Calc. for $(\text{MeCH}=\text{N}\cdot\text{BEt}_2)_2$: M , 222].

We are grateful to Mr. N. Dodd, Imperial Chemical Industries Limited (Heavy Organic Chemicals Division) for recording some of the n.m.r. spectra, to Dr. J. W. Emsley of these laboratories for recording the remainder and interpreting them, and to Dr. H. M. M. Shearer and Miss J. Willis for the X-ray crystallographic data. We also thank the D.S.I.R. for a maintenance grant (to J. E. L.) and help towards the cost of spectrometers, and Professor G. E. Coates for comments.

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