Reactions of Diborane with Organic Isocyanates and Isothiocyanates

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Methyl and phenyl isocyanates react with diborane to yield *N*-methyl- or *N*-phenyl-*N*-borylformamide cyclic trimer and dimethylaminoborane or *N*-methylanilinoborane. The analogous isothiocyanates also react with diborane. Whereas the methylisothiocyanate–diborane reaction forms the thio analogue of the cyclic trimer obtained from the methylisocyanate–diborane reaction, the phenylisothiocyanate–diborane reaction forms the monomer $PhNCS{\cdot}BH_3$ and the dimer $(PhNCS{\cdot}BH_3)_2$. The identification of the compounds in the solid was by precision mass spectroscopy.

REACTIONS of diborane with the electron-donor compounds having $-C{=}O$, $-C{\equiv}N$, $-N{\equiv}C{-}CONR_2$, and $-C{=}C-$ groups have been extensively investigated. Aldehydes,[1] ketones,[1,2] and esters[3] form dialkoxyboranes with diborane. Methyl cyanide[4,5] and ethyl cyanide[5] produce thermally unstable borane adducts which yield

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[1] H. C. Brown, H. I. Schlesinger, and A. B. Burg, *J. Amer. Chem. Soc.*, 1939, **61**, 673.

[2] H. C. Brown and W. Korytnyk, *J. Amer. Chem. Soc.*, 1960, **82**, 3866.

[3] H. Steinberg and R. J. Brotherton, ' Organoboron Chemistry,' John Wiley & Sons, New York, 1966, vol. II, p. 488.

[4] H. I. Schlesinger and A. B. Burg, *Chem. Rev.*, 1942, **31**, 1.

[5] H. J. Emeleus and K. Wade, *J. Chem. Soc.*, 1960, 2614.

NN'N''-trialkylborazoles upon decomposition. With phenyl isocyanide and diborane, dimerization of the borane adduct leads to two different cyclic compounds depending upon reaction conditions.[6,7] Amides react with diborane under mild conditions to form amidoboranes[8] while at higher temperatures reduction to the amine occurs.[9,10] The reaction of dimethyl sulphoxide with diborane in inert solvent at −80° leads to an asymmetric cleavage product.[11] Olefins are known to form alkylboranes.[10]

The reactions of organic isocyanates and isothiocyanates with some boron Lewis acids have been investigated. Substituted boranes (BCl_3, $PhBCl_2$, Ph_2BCl) react with aryl isocyanates to give substituted diamidoboranes.[12] Reactions of isocyanates and isothiocyanates with aminoboranes[13,14] and with amine–boranes[15] have also been studied. However, the reactions with diborane and other boron hydrides has not been reported.

The present investigation of the reactions of phenyl and methyl isocyanate (RNCO) and the corresponding isothiocyanates (RNCS) with diborane was undertaken to determine whether nitrogen or oxygen (sulphur) is the preferred addition site, if varying the *N*-substituent (alkyl or aryl) would significantly change the site preference and if, as expected, the double bonds would enhance rearrangement of the initially formed mono- or di-adduct.

EXPERIMENTAL

Materials.—Toluene and hexane were stored in evacuated glass vessels over calcium hydride. Chloroform was stored in a similar fashion over P_2O_5. *o*-Xylene was distilled from calcium hydride on a vacuum line. Diborane was prepared by treating sodium borohydride with conc. H_2SO_4[16] and was purified by repeated distillations through two −126° traps. Phenyl isocyanate (Matheson Coleman & Bell) was distilled under reduced pressure, the fraction b.p. 50—51° at 15 mm being collected. Phenyl isothiocyanate (Matheson Coleman & Bell) was distilled under reduced pressure, the fraction b.p. 69—70° at 10 mm being collected. Methyl isocyanate (Aldrich Chemical Co.) was further purified by distillation on a vacuum line. All solvents were reagent grade.

Reaction of Diborane with Methyl Isocyanate in Toluene.—Methyl isocyanate was introduced into a reaction vessel by distillation from weighted glass storage ampoules. Approximately 10 ml of dry toluene was distilled into the reaction tube followed by an amount of diborane calculated to be more than the molar equivalent of methyl isocyanate taken. After several hours of stirring at −23°, the reaction mixture was allowed to warm to room temperature. The reaction was carried out for 12 h during which time a solid appeared and diborane uptake ceased. The non-condensable gases were collected with a Toepler pump, the unchanged diborane was collected and measured, and the volatile solvent and reaction products were distilled into a trap on the vacuum line. The remaining solid was further dried by keeping it under high vacuum overnight. The volatile reaction product could be separated from toluene by distillation through traps cooled to −63°.

Reaction of Diborane with Neat Methyl Isocyanate.—The isocyanate was transferred into one arm of an inverted U-tube from a weighed storage ampoule. The isocyanate was kept at −126°, whilst diborane was condensed into the other arm at −196°. The reaction tube was sealed and the isocyanate arm was allowed to warm to room temperature before the diborane was allowed to vaporize. After 2—3 days the tube which contained a solid reaction product was opened to the vacuum line. The non-condensable fraction was collected by Toepler pumping through four liquid-nitrogen traps into a calibrated volume. Excess of diborane was collected in a −196° trap before removal of the other condensable gases by passage of the mixture through two −63·5° traps and a −126° trap.

The Gas-phase Reaction of μ-Dimethylamino-diborane (μ-DMADB) *with Methyl Isocyanate.*—Equimolar amounts of each compound (*ca.* 0·5 mmol) were quantitatively measured by treating the vapours as ideal gases. The reactants were separately distilled into the reaction tube which was then sealed *in vacuo*. After 24 h at room temperature the tube which contained a viscous liquid was opened to the vacuum line and the unchanged gases were collected and identified in order to ascertain reaction stoicheiometry.

Reaction of Diborane with Phenyl Isocyanate in Inert Solvents.—Approximately 0·1—0·4 g quantities of the isocyanate were either weighed by difference in a 1-ml syringe or distilled in from weighed glass storage ampoules into a 50-ml tubular reaction vessel. Approximately 15 ml of the dry solvent (toluene or hexane) was then transferred into the frozen, evacuated reaction tube. After a measured quantity of diborane, always in excess, was distilled into the tube, the temperature was adjusted to −63·5° and the diborane uptake was monitored with a mercury manometer. The reaction stoicheiometry was determined by collecting the unchanged diborane with the reaction tube maintained at −63·5°. In the reaction at room temperature, the diborane uptake and the precipitation of a white solid was complete after 12 h. The white solid was washed with chloroform *in vacuo* in a special inverted U-shaped vessel by condensing chloroform into the arm containing the solid and decanting out to the other arm.

Reaction of Diborane with Methyl Isothiocyanate.—Reactions were carried out in sealed inverted U-tubes with volumes ranging from 300 to 500 ml. Approximately 0·3—0·4 g of the isothiocyanate was weighed in a glass ampoule and transferred *in vacuo* into one arm of the tube. Hexane (*ca.* 10 ml) and a measured excess of diborane were distilled into the vessel. The reactants in the sealed tube were kept at 0° for 8 h and then allowed to warm to room

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[6] J. Tanaka and J. C. Carter, *Tetrahedron Letters*, 1965, 329.

[7] S. Bresadola, F. Rossetto, and G. Puosi, *Tetrahedron Letters*, 1965, 4775.

[8] E. M. Fedneva, V. N. Konoplev, and V. D. Krasnoperova, *Russ. J. Inorg. Chem.*, 1966, **11**, 1094.

[9] H. C. Brown and P. Heim, *J. Amer. Chem. Soc.*, 1964, **86**, 3566.

[10] H. C. Brown, 'Hydroboration,' W. A. Benjamin, Inc., New York, N.Y., 1962, p. 249.

[11] S. G. Shore and G. E. M. Achran, *Inorg. Chem.*, 1965, **4**, 125.

[12] M. F. Lappert and B. Proksi, *J. Chem. Soc.*, 1963, 4223.

[13] H. Beyer, J. W. Dawson, H. Jenne, and K. Niedenzu, *J. Chem. Soc.*, 1964, 2115.

[14] R. H. Cragg, M. F. Lappert, and B. P. Tilley, *J. Chem. Soc.*, 1964, 2108.

[15] R. H. Cragg and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1967, 961.

[16] H. Weiss and I. Shapiro, *J. Amer. Chem. Soc.*, 1959, **81**, 6167.

temperatures for an additional 1—2 days. Hexane along with a volatile reaction product and diborane were distilled into a vacuum line. The volatile compound was isolated in a −126° trap with the diborane being collected in a −196° trap. The solids formed were washed *in vacuo* with dry chloroform.

Reaction of Diborane with Phenyl Isothiocyanate.—An appropriate quantity of the isothiocyanate (0·2—0·4 g) was weighed by difference in a 1-ml syringe and transferred into a 150-mm long reaction tube. Approximately 10 ml of dry toluene or hexane was transferred *in vacuo* and the contents were melted and thoroughly mixed. A measured excess of diborane was then added. The reaction was carried out with stirring at room temperature for 2—3 days. Diborane uptake was monitored with a mercury manometer. Hydrogen was removed with a Toepler pump and the solvent and volatile materials were transferred to a trap on the vacuum line. The pale yellow solid was washed with dry chloroform under an inert atmosphere.

Hydridic Hydrogen Analysis.—A sample, usually from 20 to 100 mg, was carefully transferred into the hydrolysis tube under dry nitrogen. A 1 ml portion of deaerated concentrated HCl was transferred *in vacuo*. The hydrolysis vessel was then sealed and the reaction was allowed to proceed at room temperature until the initial vigorous bubbling ceased. The tube was then placed in a 100° oil-bath for a minimum of 48 h to ensure complete reaction. After this time the tube was cooled to 0° and opened to the vacuum line. Hydrogen was quantitatively collected by Toepler pumping through four −196° traps into a calibrated volume. Its identity was verified by either gas density molecular-weight determination or mass spectrometry. Quinoline was used to remove hydrogen chloride from carbon dioxide, hydrogen sulphide, or carbonyl sulphide generated by hydrolyses.

Determination of Dimethylamine Generated in Acid Hydrolysis.—The solution containing the amine hydrochloride was made basic with NaOH in a vacuum system and the volatile amine generated was purified by distillation through a −63·5° trap to a −196° trap. The gaseous amine was identified by i.r. spectroscopy or mass spectrometry.

Determination of N-*Methylaniline Generated in Acid Hydrolysis.*—After hydrogen and carbon dioxide were collected, an excess of 10% NaOH was added to the *N*-methylaniline hydrochloride remaining in the hydrolysis tube. The free amine was extracted using chloroform and analysed by i.r. analysis between salt plates and by t.l.c. on silica gel.

Identification of Boric Acid.—Boric acid formed in the hydrolysis reaction was separated from amine hydrochlorides by washing the solids on a Büchner funnel with dilute HCl and cold water until only the boric acid crystals remained on the filter paper. These crystals were identified by their i.r. spectrum (run as a KBr pellet) and by their *X*-ray powder pattern.

Thermal Decomposition of Solid Reaction Products.—Approximately 50—100 mg of solid was placed in a reaction tube. After evacuation of the tube, it was heated at *ca.* 300° by means of a heat gun until decomposition was noted. Condensable fractions were collected in four traps cooled at −196°. Noncondensable gases were Toepler pumped into a 50-ml bulb. Volatiles were analysed by i.r. spectroscopy and by mass spectrometry.

Mass Spectra.—For identification of products the AEI MS-12 and -10 mass spectrometers were used. Air-sensitive solids were introduced into the solid probe under an inert atmosphere in a polyethylene glove bag that enclosed the sample inlet system. Liquids and gases were introduced through a standard inlet system.

The high-precision mass spectra were obtained on glass plates using a CEC 21-110 high-resolution mass spectrometer. Perfluorokerosene (PFK) was used as a mass marker. The mass spectral plates were read on a micro-densitometer interfaced with a computer and the computer readout yielded the relative intensity, determined and calculated exact mass, and possible elemental compositions for each mass read. Because of the enormous amount of data, selected regions of each spectrum were read.

RESULTS AND DISCUSSION

Methyl isocyanate reacts with diborane. A very slow reaction takes place at −22° and even at room temperatures the reaction takes *ca.* 12 h for completion. A solid product is formed which consists of some glassy material and a white powder; a volatile reaction product is also formed. The presence of a solvent such as toluene had no effect on the reaction, similar products being obtained in the absence of solvent.

The volatile product, identified as μ-dimethylamino-diborane, was isolated in yields varying from 10 to 30% based on methyl isocyanate. Better yields of μ-dimethylamino-diborane were obtained when higher ratios of diborane to methyl isocyanate were used. This compound, first reported by Burg,[17] was characterized in several ways. The gas density molecular weight was determined to be 69·4 and 70·8 (average 70·1, calc. 70·6). The freezing point as determined by the Stock plunger technique[18] was −56° (reported −54·8 to −54·4°). The inaccuracy here is probably due to the fact that a toluene thermometer was used to measure the temperature of the cold bath. A 0·5 mmol sample of gas was hydrolysed in aqueous hydrochloric acid to yield 2·5 mmol of hydrogen. This agrees with the expected five hydridic hydrogens per mole. The i.r. spectrum was identical to that reported by Mann.[19] The mass spectrum shows a parent peak at 71 and has major peaks indicating loss of fragments of mass 14 ($^{11}BH_3$) and 29 (NCH_3) from the parent with metastable peaks at 45·9 and 24·8 to confirm the loss of these fragments from the molecule ion.

The white powder formed in this reaction could not be dissolved in chloroform, methylene chloride, carbon tetrachloride, diethyl ether, light petroleum, dioxan, *o*-xylene, or tetrahydrofuran. When acetone was condensed into the solid, vigorous bubbling was observed. There was, however, very little hydrogen generated. The solid reacted with ethanol giving off hydrogen. The m.p. range of this solid was 108—115°. The *X*-ray powder pattern indicated an amorphous structure.

The mass spectrum of this solid material indicated that it was a mixture. The major component had a

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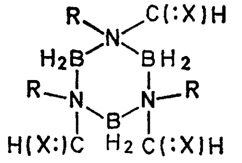
[17] A. B. Burg and C. L. Randolph, jun., *J. Amer. Chem. Soc.*, 1951, **73**, 953.

[18] A. Stock, 'Hydrides of Boron and Silicon,' Cornell University Press, Ithaca, 1957, pp. 183—184.

[19] D. E. Mann, *J. Chem. Phys.*, 1954, **22**, 70.

parent peak corresponding to $(MeNCO{\cdot}BH_3)_3$. Because separations could not be carried out, precision mass determinations for selected peaks were used to assign the elemental composition of these ions. The results are listed in Table 1. The parent ion, at mass 213, was assigned the formula $C_6H_{18}N_3O_3{}^{11}B_3$ and the structure (I) which is that for *N*-methyl-*N*-boryl cyclic trimer. The mass spectrometer did not resolve peaks of the same nominal mass in the parent group mass range. For example, in the spectrum of the *N*-methyl-*N*-boryl cyclic trimer, the line at mass 212 is due to two ions, (1) the molecular ion $C_6H_{18}N_3O_3{}^{11}B_2{}^{10}B^+$ (212·1663) and (2) the fragment ion $C_6H_{17}N_2O_3{}^{11}B_3{}^+$ (212·1549) resulting from the loss of H from the $^{11}B_3$ molecular ion. The relative abundance of these two ions is calculated and the weighted average of the precision masses of the ions at this nominal mass gives a result that is in close agreement with the experimental precision masses. Extending this procedure to masses 211, 210, and 209 the observed intensities of all the ions in the parent mass group can be explained. The results of these calculations are shown in Table 1. The precision mass determined for some of the fragment ions support this trimeric structure. The peak at mass 71·0776 corresponds to the $CH_3N{\cdot}{}^{11}BH_2{\cdot}NCH_3{}^+$ fragment (calc. 71·0781) and the peak at mass 141·1006 corresponds to $CH_3N{\cdot}CO{\cdot}H{\cdot}{}^{11}BH_2{\cdot}CH_3N{\cdot}CO{\cdot}H{\cdot}{}^{11}BH^+$ (calc. 141·1002).



Structure of cyclic trimers

(1) R = Me, X = *O*, *N*-methyl-*N*-borylformamide cyclic trimer.

(2) R = Ph, X = *O*, *N*-phenyl-*N*-borylformamide cyclic trimer

(3) R = Me, X = *S*, *N*-methyl-*N*-borylthioformamide cyclic trimer

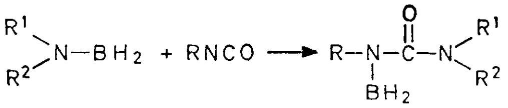
All the characterization data is consistent with the proposal that trimer (1) is a major component of the mixture. The hydridic hydrogen values obtained in acid hydrolyses experiments (conc. HCl) yielded an average value of 5·7 ± 1·1 hydridic hydrogens per mol based on the gram molecular weight of the trimer. Allowing for the known impurities, these values seem to support three BH_2 groups per trimer. The hydrolysis in conc. hydrochloric acid at 100° also yielded dimethylamine hydrochloride, *N*-methylformamide, boric acid, and carbon dioxide. The dimethylamine, carbon dioxide, and *N*-methylformamide were identified by mass spectrometry. Dimethylamine was also identified by gas-phase i.r. spectroscopy. Boric acid was identified by *X*-ray diffraction. Pyrolysis of the *N*-methyl-*N*-boryl cyclic trimer yielded methyl isocyanate. The identification was by gas-phase i.r. spectroscopy. The i.r. spectrum of the solid mixture showed indistinct absorption from 1300 to 700 cm^{-1}. Distinct bands, however, are present at 2950, 2450, 1680, 1475, and 1400 cm^{-1}. The 2450 band indicates a BH stretch and the 1680 band is consistent with an amide C=O. An elemental analysis of the mixture indicated that the B/N ratio was 1 : 1.

TABLE 1

Precision mass data: *N*-methyl-*N*-borylformamide cyclic trimer

Exptl. *m/e*	ΔMass	Relative intensities (observed)	Relative abundance corrected for ^{13}C	Assignment	Relative intensities corrected	Calculated *m/e*
214·1666		6	3	^{13}C isomer		214·1661
	1·0043					
213·1623		48	41	$C_6H_{18}N_3O_3{}^{11}B_3$	41	213·1627
	1·0061					
212·1562		100	95	$C_6H_{18}N_3O_3{}^{11}B_2{}^{10}B$ $C_6H_{17}N_3O_3{}^{11}B_3$	31 64	212·1663 212·1549
	0·9951					
211·1611		73	71	$C_6H_{18}N_3{}^{11}B^{10}B_2$ $C_6H_{17}N_3O_3{}^{11}B_2{}^{10}B$ $C_6H_{16}N_3{}^{11}B_3$	8 48 15	211·1699 211·1584 211·1471
	0·9991					
210·1620		25	25	$C_6H_{18}N_3O_3{}^{10}B_3$ $C_6H_{17}N_3O_3{}^{11}B^{10}B_2$ $C_6H_{16}N_3O_3{}^{11}B_2{}^{10}B$	1 12 11	210·1735 210·1620 210·1507
	0·9949					
209·1671		2	2	$C_6H_{17}N_3O_3{}^{10}B_3$ $C_6H_{16}N_3O_3{}^{11}B^{10}B_2$	1 3	209·1656 209·1543

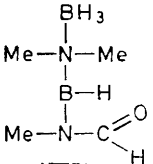
The dimethylamine in the hydrolysis products can be explained by the presence of the aminoborane, $Me_2N{\cdot}BH_2$ in the solid mixture as indicated by the medium intensity peaks with an indicated parent at 58 in the mass spectra. The presence of this compound in the mixture indicates a more extensively reduced product than the cyclic trimer and may well be the precursor of the volatile μ-dimethylamino-diborane. The observation of the fragment ion $CH_3NHCON(CH_3)_2{}^+$ was interpreted to indicate the presence of a ureidoborane as one of the components of the mixture. Ureidoboranes can be formed by the reaction of aminoborane with isocyanates as shown in the equation:



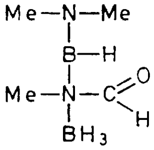
$$R^1R^2N{-}BH_2 + RNCO \longrightarrow R{-}N(BH_2){-}C({=}O){-}NR^1R^2$$

When increased amounts of diborane were used in the methyl isocyanate–diborane reaction, there was a colourless viscous liquid formed together with a larger yield of μ-dimethylamino-diborane. Because this suggested that the glassy solid formed in the usual methyl-isocyanate–diborane reaction might be due to the reaction of methyl isocyanate with μ-dimethylamino-diborane, this latter reaction was investigated. The μ-dimethylamino-diborane–methyl isocyanate reactions were carried out in sealed bulbs at room temperature. Methyl isocyanate was present in large molar excess. A viscous liquid was obtained from this reaction which had an i.r. spectrum similar to the viscous liquid obtained in the methyl isocyanate–diborane reaction. The liquid proved to be very soluble in chloroform.

The reaction of μ-dimethylamino-diborane with methyl isocyanate was also studied in the gas phase. Since both reactants are volatile liquids, this reaction was readily carried out. Equimolar quantities of the two compounds were condensed into a vessel which was then sealed and maintained at room temperature. As the reaction proceeded, a colourless, viscous liquid formed in the reaction vessel. No volatiles were found when the bulb was reopened on a vacuum line. The stoicheiometry of this reaction was, therefore, 1 : 1. Acid hydrolysis (conc. HCl) of the product yielded 5 hydridic hydrogens per mol based on a gram formula weight of 128 (the 1 : 1 adduct CH_3NCO-μ-DMADB). The hydrolysis products were identified as boric acid, dimethylamine, and hydrogen. An i.r. spectrum (salt plates) of the viscous liquid showed strong absorptions assigned as: C–H stretch at 3000 cm^{-1}, B–H terminal stretch at 2450 cm^{-1}, and C=O stretch at 1670 cm^{-1}. Between 1400 and 800 cm^{-1} there is a high background region with a number of peaks extending a short distance from the background. No evidence for methyl isocyanate was found in the i.r. spectrum. A medium resolution mass spectrum was taken of the liquid. No significant peaks were observed in the region above mass 128. The 128, 127, 126 parent grouping showed the characteristic 16 : 8 : 1 peak height ratio expected for a species containing two boron atoms. The 128 peak was assigned as $(CH_3)_3N_2COB_2H_5^+$. Two possible structures for this adduct are (IV) and (V). Although both structures are possible on the basis of the i.r., hydrolysis, stoicheiometric, and parent-ion mass spectral data, structure (IV) is assigned to this adduct on the basis of the unique ion fragment, $CH_3NCO^{11}BH^+$, at mass 69 which is not a reasonable fragmentation product from structure (V). Although there seemed to be a slight viscosity difference between the product formed in the methyl isocyanate–diborane reaction and the methyl isocyanate-μ-dimethylamino-diborane reaction, the similarity of the i.r. spectra leads one to speculate that a compound of structure (IV) exists in the solid mixture formed in the diborane reaction.



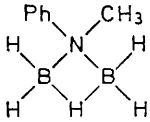
(IV)



(V)

Phenyl isocyanate is less reactive toward diborane than methyl isocyanate. Although diborane adds to phenyl isocyanate in inert solvents at −63° to form a 1 : 1 adduct, at −22° the adduct decomposes to the starting materials. In the presence of an excess of diborane in the temperature range 0—25°, diborane uptake was again noted and was accompanied by the generation of hydrogen, a volatile hydridic material, and the precipitation of a white solid. Kjeldahl nitrogen determinations indicated that approximately half the starting nitrogen ends up as the volatile product.

The volatile reaction product was separated from diborane by distillation through a −126° trap to a liquid-nitrogen trap. The diborane passed through the −126° trap whereas the solvent and the volatile reaction product condensed in the −126° trap. In analogy to the methyl isocyanate–diborane reaction this volatile product was assumed to be μ-*N*-methylanilino-diborane (VI). This compound, however, could not be separated from the solvent. Hexane, toluene, and *o*-xylene were used in an effort to find vapour-pressure differences which would make the separation feasible. When the solution was allowed to warm to room temperature, vigorous bubbling was observed and a white solid was precipitated. The evolved gas was identified as diborane by its i.r. spectrum. Hydrolysis of the solid, postulated to be *N*-methylanilinoborane, Ph(Me)N·BH_2, in conc. hydrochloric acid yielded hydrogen, boric acid, and *N*-methylaniline hydrochloride. Hydrogen was identified by mass spectroscopy, *N*-methylaniline by i.r. spectroscopy, and boric acid by i.r. and *X*-ray spectroscopy. A solution of μ-*N*-methylanilino-diborane yielded 12·9 mmol of hydrogen on hydrolysis. The Kjeldahl determination for nitrogen on the hydrolysate gave 2·14 milliequivalents of nitrogen. This experimental ratio of N : H = 1 : 6 indicates support for a compound calculated to have an N : H = 1 : 5.



(VI)

The conversion of μ-*N*-methylanilino-diborane to *N*-methylanilino-borane has precedence in the equilibrium reactions reported for μ-dimethylamino-diborane by Burg.[20] That the μ-*N*-methylanilino-diborane is less stable than the μ-dimethylamino-diborane is not unreasonable when the basic strength of the corresponding amines, *N*-methylaniline, and dimethylamine, is

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[20] A. B. Burg and J. S. Sandhu, *Inorg. Chem.*, 1965, **4**, 1467.

considered. Dimethylamine is a better base than *N*-methylaniline by six orders of magnitude.[21] The delocalization of the electrons over the benzene ring which causes this lowered base strength also implies a destabilization of the B–N–B bond.

The solid reaction product, like that formed in the methyl isocyanate reaction, was a mixture which could not be separated. Hydridic hydrogen analysis gave an average value of 5·9 ± 0·8 hydridic hydrogens per mol based on the gram molecular weight of the trimer. Its behaviour toward solvents was identical to that described for the methyl isocyanate solid. No way could be found for separating the components of the mixture.

TABLE 2

Precision mass spectral data *N*-phenyl-*N*-borylformamide cyclic trimer

Exptl. *m/e*	ΔMass	Relative intensities (observed)	Relative abundance corrected for ^{13}C	Assignment	Relative intensities (corrected)	Calc. *m/e*
400·2102		22	3	^{13}C isomer		400·2130
	1·0031					
399·2071		80	59	$C_{21}H_{24}N_3O_3{}^{11}B_3$	59	399·2097
	0·9971					
398·2100		100	90	$C_{21}H_{24}N_3O_3{}^{11}B_2{}^{10}B$ $C_{21}H_{23}N_3O_3{}^{11}B_3$	44 46	398·2133 398·2019
	0·9943					
397·2157		49	46	$C_{21}H_{24}N_3O_3{}^{11}B{}^{10}B_2$ $C_{21}H_{23}N_3O_3{}^{11}B_2{}^{10}B$	11 35	397·2169 397·2055
	1·0027					
396·2130		13	10	$C_{21}H_{24}N_3O_3{}^{10}B_3$ $C_{21}H_{23}N_3O_3{}^{11}B{}^{10}B_2$	1 9	396·2205 396·2091

The presence in this mixture of *N*-phenyl-*N*-boryl cyclic trimer was shown by mass spectrometry. A medium resolution mass spectrum taken on the AEI MS-12 indicated that the most intense ions occurred at masses 396, 397, 398, and 399. No significant peaks occurred above this mass group. Masses 396—399 are those which correspond to three PhNCO and three BH_3 groups. The complexity of the fragmentation pattern below this mass group made identification of the fragments impossible. A high-resolution mass spectrum was obtained with a CEC 21-110 so that the elemental analysis of the ions of interest could be determined. The mass spectral data for the parent ions of the solid are presented in Table 2. On the basis of these data the parent ion mass 399 was assigned the formula $C_{21}H_{24}N_3O_3{}^{11}B_3$. The structure assigned to this species was (II). The intensities of the ions in this parent mass group has been correlated with the distribution of the ^{10}B and ^{11}B isotopes. That this compound is analogous to that formed in the methyl isocyanate reaction is indicated by the experimental mass difference of 186·0448 a.m.u. between the two trimers. The calculated difference in mass between three phenyl and three methyl groups is 186·0470 a.m.u. This difference is within the ±3 m.m.u. experimental error acceptable for exact mass determinations with the mass spectrometer.

The characterization of the solid mixture gave no evidence to refute the proposed structure. *X*-Ray powder diffraction data showed this solid mixture to be amorphous. Sealed capillary m.p. data indicated that the solid melted with slow decomposition over the range 165—175°. The hydrolysis of the solid in conc. HCl at 100° was carried out in a sealed tube. The products of this hydrolysis were hydrogen, carbon dioxide, boric acid, and *N*-methylaniline hydrochloride. The i.r. spectrum of the solid run as a KBr wafer showed strong peaks that were assigned to B–H terminal stretch at 2400 cm^{-1} and C=O stretch at 1625 cm^{-1}. The characteristic aromatic absorptions due to the phenyl group(s) were also identified. The characteristic N=C=O absorption at 2250 cm^{-1} was notably absent.

The reaction of methyl isothiocyanate with diborane in inert solvents yielded a white solid and μ-dimethylamino-diborane. The white solid, like the reaction product of the oxygen analogue, was found to contain *N*-methyl-*N*-borylthioformamide cyclic trimer [structure (III)]. The solid was insoluble in common solvents. Its *X*-ray powder diffraction pattern showed it to be amorphous. The solid melted with decomposition over the temperature range 79—81°. The i.r. spectrum (KBr pellet) for the solid showed absorption bands attributable to C–H stretch at 3000 cm^{-1}, B–H terminal stretch at 2430 cm^{-1}, and C=S stretch at 1460 cm^{-1}. The characteristic N=C=S band was not observed. Acid hydrolysis of the solid yielded hydrogen, carbonyl sulphide, dimethylamine, hydrogen sulphide, and boric acid. A medium-resolution mass spectrum of the solid gave a peak at mass 261 identified as $(CH_3NCS{}^{11}BH_3)_3{}^+$. The related isotopic boron peaks were also present. The fragmentation pattern showed the successive loss of $CH_3NCS{}^{11}BH_3$ fragments. Hydridic hydrogen determination by hydrolysis yielded a value of 5·5 hydridic hydrogens per mole assuming the solid to be essentially pure trimer. This assumption was not too bad since the mass spectral and m.p. data indicate that the solid is essentially pure trimer.

The reaction of phenyl isothiocyanate with diborane was studied in the inert solvents toluene and hexane. A pale yellow solid precipitated from the solution. It was not possible to make a positive characterization of this solid. Mass spectral evidence indicated that both a

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[21] L. F. Fieser and M. Fieser, 'Organic Chemistry,' D. C. Heath and Co., Boston, 1944, pp. 227, 602.

monomer $PhNCS,BH_3$ and a dimer $(PhNCS,BH_3)_2$ were present, however, no peaks were found in the high mass region, indicating the absence of a trimer analogous to the *N*-phenyl-*N*-borylformamide trimer. From the solvent of this reaction a volatile boron–nitrogen compound was recovered. This product was identified by acid hydrolysis and Kjeldahl nitrogen determination as μ-*N*-methylanilino-diborane. This is the same compound that was produced in the phenylisocyanate–diborane reaction.

The reaction of organic isocyanates and isothiocyanates with diborane has in each case yielded, as one of the reaction products, μ-amino-diboranes with bridging amino-groups of the type $R-N-CH_3$. The R group is that of the particular RNCO or RNCS compound reacted, while the CH_3 group results from complete reduction of the N=C bond. Such a reduction requires addition of BH_3 to both nitrogen and oxygen in the case of the isocyanate, and nitrogen and sulphur in the case of the isothiocyanate, with resulting C=O or C=S bond cleavage. The product of this reaction is probably the aminoborane $R(Me)N\cdot BH_2$ since this has been identified in the reaction products and is a likely precursor to the μ-amino-diboranes. Although C=O (S) bond cleavage did occur in these reactions, no intermediate products with B–O or B–S bonds have been identified. All the reaction products containing boron which have been identified show boron bonded to nitrogen. Because the major reaction products (cyclic trimers) contain oxygen or sulphur in the unreduced state, the indication is that nitrogen is the preferred addition site for BH_3 in both the RNCO and RNCS compounds.

We thank Mr. M. Bazinet of the Army Natick Laboratories, Dr. Tom Mead of American Cyanamid, and Dr. Graham Cooks of Purdue for their aid with the precision mass spectroscopy. We also acknowledge the support of the NSF Grant which made the use of the computer possible.

[1/2376 *Received, 10th December, 1971*]