895. *Transamination of Tetrakisdimethylaminodiboron with Aliphatic Diamines.*

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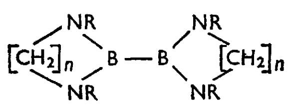
Reactions of tetrakisdimethylaminodiboron with four secondary aliphatic diamines and with trimethylenediamine give monomeric diboron compounds, whereas reactions with ethylenediamine and with propylenediamine appear to give indefinite products. An alternative, and unambiguous, synthesis for the monomeric compounds, by reductive coupling analogous to the Wurtz reaction, shows that their structures are based on diazaborolidine or hexahydrodiazaborine ring systems.

Recent reports[1,2] show that tetrakisdialkylaminodiboron compounds are formed by reductive coupling of bisdialkylaminohalogenoboranes with alkali metals, and that these diboron compounds, which are thermally stable to at least 200°, undergo transamination when heated with amines, giving other diboron compounds of the same type.[1] These transaminations, like those which take place in other boron–nitrogen systems,[3] are reversible and are made to proceed in the required direction by continuous removal of the liberated amine, by using an excess of the entering amine, or by both methods. Tetrakisdimethylaminodiboron is particularly suitable for study of preparative transamination because the liberated dimethylamine is readily volatile.

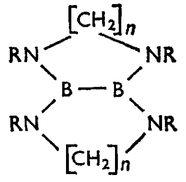
$$(R_2N)_2B\cdot B(NR_2)_2 + 4R'R''NH \rightleftharpoons (R'R''N)_2B\cdot B(NR'R'')_2 + 4R_2NH$$

$R = \text{alkyl}$; $R' = \text{H, alkyl, or aryl}$; $R'' = \text{alkyl or aryl}$.

From the standpoint of these reactions, the tetrakisdialkylaminodiborons, $(R_2N)_2B\cdot B(NR_2)_2$, are tetrafunctional. We have studied the products of reaction between tetrakisdimethylaminodiboron and representative difunctional aliphatic diamines, namely, ethylenediamine and its *NN'*-dimethyl, -diethyl, and -di-isopropyl derivatives, trimethylenediamine and its *NN'*-dimethyl derivative, and propylenediamine ($NH_2\cdot CHMe\cdot CH_2\cdot NH_2$).



(I)



(II)

$n = 2$; $R = \text{Me, Et, or Pr}^i$.
$n = 3$; $R = \text{H, or Me}$.

We find that each diamine liberates dimethylamine almost quantitatively from the diboron compound, and that, whereas ethylene- and propylene-diamine give indefinite,

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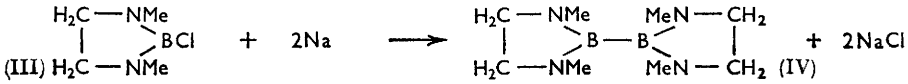
[1] Brotherton, McCloskey, Petterson, and Steinberg, *J. Amer. Chem. Soc.*, 1960, **82**, 6242.

[2] Nöth and Meister, *Chem. Ber.*, 1961, **94**, 509.

[3] Gerrard, Lappert, and Pearce, *Chem. and Ind.*, 1958, 292; English, McCloskey, and Steinberg, *J. Amer. Chem. Soc.*, 1961, **83**, 2122; Nöth, *Z. Naturforsch.*, 1961, **16b**, 470.

possibly polymeric, products, the four secondary diamines and trimethylenediamine give monomeric diboron compounds of the general formula X_2B_2. Although two types of structures (I and II) appear to be possible for these compounds, an alternative synthesis described below provided strong evidence in favour of structures (I).



Thus, 2-chloro-1,3-dimethyl-1,3,2-diazaborolidine (III) has been shown to give the corresponding diboron compound, bi-(1,3-dimethyl-1,3,2-diazaborolidin-2-yl) (IV), on reductive coupling with a sodium dispersion in xylene.[4] This diboron compound must almost certainly have the structure (IV), *i.e.*, type (I). We have carried out similar coupling reactions, using the more reactive sodium–potassium alloy, which reacts with the chloro-derivatives at ambient temperatures and minimises the risk of rearrangement, and we have thus synthesised three further diboron compounds, the corresponding derivatives of *NN'*-diethyl- and *NN'*-di-isopropyl-ethylenediamine and *NN'*-dimethyltrimethylenediamine. By a comparison of infrared spectra (650—3800 cm.$^{-1}$), and of melting points or of boiling points and refractive indexes, each of these three compounds has been shown to be identical with its analogue prepared by transamination.

We therefore conclude that the transamination products have structures (I) and contain the previously reported diazaborolidine and hexahydrodiazaborine ring systems.[5] The simultaneous formation of compounds of type (II), which would contain novel fused ring systems, is not, of course, precluded by the fact that only compounds of type (I) were isolated; however, we were unable to isolate any isomers in these reactions.

It is interesting that, with one exception, these diboron compounds, like tetrakisdimethylaminodiboron, are hydrolysed in moist air or water. The *NN'*-di-isopropylethylenediamine derivative is unique in that it may be left in contact with water for several days without hydrolysis, although it is hydrolysed by hot dilute acid. The enhanced stability is attributed to shielding of the boron atoms by the relatively bulky isopropyl groups; ring formation *per se* does not confer stability to water on these boron–nitrogen compounds.

More complex reactions, from which no definite compounds were isolated, occurred with ethylenediamine and with propylenediamine. With the former, tetrakisdimethylaminodiboron at 100° formed in several hours a material which was involatile *in vacuo* at this temperature, and was a glass when cool. This material had a slightly higher boron content and lower nitrogen content than is calculated for the expected composition $(NH{\cdot}CH_2{\cdot}CH_2{\cdot}NH)_2B_2$. This suggested that condensation-polymerisation of the initial product, with elimination of diamine, had occurred to a limited extent. On further heating to 200° *in vacuo* more diamine was eliminated and it is inferred that further condensation took place. Hydrogen was also evolved and the boron–boron bonds in the final white intractable solid were partially destroyed. The reaction of ethylenediamine with diboron tetrachloride has been reported [6] and it appears that polymers were formed also in this reaction.

The reaction between propylenediamine and tetrakisdimethylaminodiboron followed a similar course during the initial stages. At 90° the product, a viscous liquid, had substantially the composition $(HN{\cdot}CH_2{\cdot}CHMe{\cdot}NH)_2B_2$, but with slightly too high a boron and too low a nitrogen content. On further heating, *in vacuo*, propylenediamine was eliminated, and from about 140° hydrogen was evolved. From about 190—230°, however,

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[4] Personal communication from Dr. R. J. Brotherton, U.S. Borax Research Corporation, Anaheim, California.

[5] Goubeau and Zappel, *Z. anorg. Chem.*, 1955, **279**, 38; Mikhailov, Kozminskaya, Fedotov, and Dorokhov, *Doklady Akad. Nauk S.S.S.R.*, 1959, **127**, 1023.

[6] Holliday, Marsden, and Massey, *J.*, 1961, 3348.

in contrast to the ethylenediamine–tetrakisdimethylaminodiboron system, the bulk of the product distilled *in vacuo* as a viscous liquid, which had a B : N ratio of ~2 : 3 and still largely or completely retained its boron–boron bonds. It appears, therefore, that the initial transamination product had undergone condensation and that approximately one diamino-group in four had been eliminated. The actual boron and nitrogen values, as well as the ratio, are in good agreement with this postulate. Attempts to measure the molecular weight of the moisture-sensitive, viscous product gave inconsistent results, ranging from 200 to 400.

EXPERIMENTAL

Experiments were carried out under dry nitrogen. Molecular weights were determined cryoscopically in benzene, 4—6 measurements, at different concentrations, being made for each compound.

Materials.—*NN'*-Diethylethylenediamine, b. p. 150—152°, was prepared by the reduction of *NN'*-diacetylethylenediamine with lithium aluminium hydride.[7] *NN'*-Di-isopropylethylenediamine, b. p. 68°/16 mm., was prepared by reaction of isopropylamine with 1,2-dichloroethane.[8] Ethylenediamine, trimethylenediamine, propylenediamine, *NN'*-dimethylethylenediamine, and *NN'*-dimethyltrimethylenediamine were obtained commercially, dried (Na or BaO), and fractionated before use. The purity of these amines was checked by acid–base titration. Samples of *NN'*-dimethylethylenediamine obtained from three different suppliers were thus shown to be impure and vapour-phase chromatograms showed the presence of two major components that could not be separated by fractional distillation; the pure compound was, however, obtained from these samples by preparative vapour-phase chromatography. Tetrakisdimethylaminodiboron was supplied by the United States Borax Research Corporation.

Transamination of Tetrakisdimethylaminodiboron.—(*a*) *With diamines which give monomeric products*. A mixture of the diamine and tetrakisdimethylaminodiboron was heated under a reflux condenser and the dimethylamine evolved was collected in a trap at −78° and weighed. When evolution of amine virtually ceased, the residue was worked up by fractional distillation or by low-temperature crystallisation from light petroleum (b. p. 40—60°; dried with $LiAlH_4$).

Thus, *NN'*-dimethylethylenediamine (0·168 mole) and tetrakisdimethylaminodiboron (0·080 mole) at 120° in 5 hr., gave dimethylamine (0·293 mole, 91%) and *bi*-(1,3-*dimethyl*-1,3,2-*diazaborolidin*-2-*yl* (0·069 mole, 86%), m. p. 43—44°, b. p. 85°/5 mm. (Found: C, 49·2; H, 10·5; B, 11·6; N, 28·4%; *M*, 195. $C_8H_{20}B_2N_4$ requires C, 49·5; H, 10·4; B, 11·2; N, 28·9%; *M*, 194).

NN'-Diethylethylenediamine (0·078 mole) and tetrakisdimethylaminodiboron (0·040 mole) at 120° (2·5 hr.) and at 135° (10 hr.) gave dimethylamine (0·140 mole, 87%) and 2-(1,3-*diethyl*-1,3,2-*diazaborolidin*-2-*yl*) (0·036 mole, 92%), b. p. 80°/0·01 mm., n_D^{25} 1·4800 (Found: C, 56·8; H, 11·2; B, 8·7; N, 21·9%; *M*, 242. $C_{12}H_{28}B_2N_4$ requires C, 57·6; H, 11·3; B, 8·7; N, 22·4%; *M*, 250).

NN'-Di-isopropylethylenediamine (0·468 mole) and tetrakisdimethylaminodiboron (0·202 mole) at 160—170° (40 hr.) gave dimethylamine (0·83 mole, 103%) and *bi*-(1,3-*di*-iso*propyl*-1,3,2-*diazaborolidin*-2-*yl* (0·116 mole, 57%), m. p. 130—134° (Found: C, 63·1; H, 11·9; B, 7·1; N, 18·1%; *M*, 307. $C_{16}H_{36}B_2N_4$ requires C, 62·8; H, 11·9; B, 7·1; N, 18·3%; *M*, 306).

Trimethylenediamine (0·159 mole) and tetrakisdimethylaminodiboron (0·080 mole) at 70—125° (6 hr.) and 125° (7 hr.) gave dimethylamine (0·304 mole, 96%) and *bi*(*hexahydro*-1,3,2-*diazaborin*-2-*yl*) (0·043 mole, 54%), m. p. 60—60·5° (Found: C, 42·9; H, 9·9; B, 13·1; N, 33·3%; *M*, 170. $C_6H_{16}B_2N_4$ requires C, 43·4; H, 9·7; B, 13·1; N, 33·8%; *M*, 166).

NN'-Dimethyltrimethylenediamine (0·077 mole) and tetrakisdimethylaminodiboron (0·038 mole) at 120° (4 hr.) and 140° (6 hr.) gave dimethylamine (0·131 mole, 86%) and *bi*(*hexahydro*-(1,3-*dimethyl*-1,3,2-*diazaborin*-2-*yl*) (0·030 mole, 81%), b. p. 74—75°/0·6 mm., n_D^{25} 1·4939 (Found: C, 54·0; H, 11·3; B, 9·8; N, 24·6%; *M*, 224. $C_{10}H_{24}B_2N_4$ requires C, 54·1; H, 10·9; B, 9·8; N, 25·2%; *M*, 222).

(*b*) *With ethylenediamine*. Ethylenediamine (6·79 g., 0·113 mole) and tetrakisdimethylaminodiboron (11·10 g., 0·056 mole) were heated under a reflux condenser leading to a trap at −78°, for 10 hr. at 85—100°. The upper layer of the mixture gradually disappeared. The

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[7] Rice, Armbrecht, Grogan, and Reid, *J. Amer. Chem. Soc.*, 1953, **75**, 1750.

[8] Donia, Shotton, Benz, and Smith, *J. Org. Chem.*, 1949, **14**, 946.

volatile materials (9·74 g.) in the trap were fractionated in a high vacuum and found to consist of dimethylamine (9·60 g., 0·213 mole, 96%) and ethylenediamine (0·10 g.). The viscous residue (8·26 g.) was treated with more ethylenediamine (1·08 g.) and heated for 3 hr. at 95° and then further *in vacuo* from 40° to 75° to remove volatile material. In this way, further amounts of dimethylamine (0·10 g.) and ethylenediamine (2·13 g.), the latter identified by its infrared spectrum, were obtained. The residue was a brittle glass (Found: B, 18·4; N, 38·8. Calc. for $C_4H_{12}B_2N_4$: B, 15·7; N, 40·7%). The boron and nitrogen values were consistent with the total amount of dimethylamine evolved (9·70 g., 0·215 mole, 97%) and ethylenediamine consumed (5·64 g., 0·094 mole, 84%). By forced hydrolysis, a sample of the product gave 0·41 mole of hydrogen per g.-atom of boron, showing that the boron–boron bonds are at least 82% preserved.

A portion of this glass (4·20 g.) was further heated *in vacuo* at 150° for 1 hr.; it first melted and then largely resolidified. It was then heated at 185—200° for 8 hr., giving a white solid (3·75 g.) of somewhat indefinite composition (Found: B, 19·6; N, 38·3%), ethylenediamine (0·34 g.), and hydrogen (which was continuously pumped away). No volatile boron compounds were formed. Hydrolysis of the white solid gave only 0·19 mole of hydrogen per g.-atom of boron, so partial destruction of the boron–boron bond had occurred.

Similar experiments gave similar, although not identical, results; for example, when the temperature was raised to 120° before the product was isolated a white crumbly solid was obtained, the analytical data for which were, within the limits of experimental error, identical with that for the glass from the first experiment.

(*c*) *With propylenediamine.* A mixture of tetrakisdimethylaminodiboron (8·49 g., 0·043 mole) and propylenediamine (6·25 g., 0·084 mole) was heated, in the usual apparatus, at 90° for 5 hr., dimethylamine (7·26 g.) being evolved. The viscous liquid residue was then further heated at 90° *in vacuo* for 40 min., to remove trapped dimethylamine (0·26 g.) and a less volatile liquid (0·92 g.) identified as mainly propylenediamine by its infrared spectrum. The total dimethylamine (7·52 g.) amounted to 97%. The residual product, substantially $(NH\cdot CHMe\cdot CH_2\cdot NH)_2B_2$, was a colourless, highly viscous liquid (Found: B, 14·7; N, 32 2. Calc. for $C_6H_{16}B_2N_4$: B, 13·0; N, 33·8%).

This material (3·76 g.) was then further heated *in vacuo*, the temperature being gradually raised from 100° to 230° during ~1 hr. From about 110° hydrogen was evolved and was continuously removed by pumping. A volatile liquid (0·93 g.), mainly propylenediamine, collected in a trap at −196°. From 190° to 230°, a viscous liquid distilled and was collected at room temperature. Heating was continued at 230° until distillation ceased. The liquid distillate (1·91 g.) (Found: B, 16·9, 17·2; N, 32·2, 32·3%) had an approximate b. p. 116—119°/10^{-3} mm. A brittle, indefinite residue (0·91 g.) (Found: B, 19·1; N, 30·3%) remained.

The distillate, largely or completely, retained its boron–boron bonds since a sample gave, on hydrolysis, 0·43 mole of hydrogen per g.-atom of boron. From the low B : N ratio (2·0 : 2·9) of this material and the recovery of propylenediamine during its formation, it was inferred that approximately one molecule of diamine was eliminated from two units of the initial product.

Preparation of the Chloro-derivatives.—Boron trichloride (14·8 g., 0·169 mole) was added with stirring to *NN'*-di-isopropylethylenediamine (24·6 g., 0·170 mole) in light petroleum (200 ml.; b. p. 40—60°) during 1·5 hr., followed by triethylamine (34·5 g., 0·342 mole). The mixture was warmed to room temperature, left for 15 hr., then refluxed for 1 hr. The product was distilled, after filtration and removal of the solvent, to yield 2-*chloro*-1,3-*di-isopropyl*-1,3,2-*diazaborolidine* (19·7 g., 61·7%), b. p. 64°/3·5 mm. (Found: B, 5·8; Cl, 18·9; N, 14·8%; *M*, 193. $C_8H_{18}BClN_2$ requires B, 5·7; Cl, 18·8; N, 14·9%; *M*, 189).

2-*Chloro*-1,3-*diethyl*-1,3,2-*diazaborolidine*, b. p. 65—66°/10 mm. (Found: B, 6·1; Cl, 20·0; N, 16·6%; *M*, 170. $C_6H_{14}BClN_2$ requires B, 6·7; Cl, 22·1; N, 17·4%; *M*, 161), and *hexahydro*-2-*chloro*-1,3-*dimethyl*-1,3,2-*diazaborine*, b. p. 64°/10 mm. (Found: B, 7·3; Cl, 23·0%; *M*, 155. $C_5H_{12}BClN_2$ requires B, 7·4; Cl, 24·2%; *M*, 146), were prepared similarly except that the diamine was added to the trichloride. This resulted in much lower yields of 11 and 15%, respectively.

Reductive Coupling of the Chloro-derivatives.—An all-glass apparatus was connected to a high-vacuum line and a supply of pure, dry nitrogen by means of a two-way stopcock. A mixture of sodium (2·18 g.) and potassium (8·35 g.) was placed in a side-arm, melted under a vacuum, and filtered through a sintered-glass disc into the reaction bulb. The side-arm containing solid impurities was then sealed off. Light petroleum (10 ml.; b. p. 40—60°; dried with $LiAlH_4$) was condensed into the bulb and then 2-chloro-1,3-di-isopropyl-1,3,2-diazaborolidine (10·0 g., 0·053 mole) was added from a dropping funnel. The mixture was agitated, but reaction was sluggish as indicated by the slow formation of a blue solid. However, overnight the mixture solidified. More light petroleum (about 20 ml.) was added and the mixture was filtered through a side-arm, containing a sintered-glass disc, into a receiver. The dark blue solid was washed by condensing some of the light petroleum *in vacuo* back into the reaction bulb. Removal of the petroleum from the filtrate by pumping left colourless crystals of the fairly pure product (7·4 g., 92%), m. p. 121—128°. Crystallisation from light petroleum gave pure bi-(1,3-di-isopropyl-1,3,2-diazaborolidin-2-yl) (5·72 g.), m. p. 131—134°, identical in infrared spectrum with the compound isolated as above.

The other reductive couplings were carried out similarly. 2-Chloro-1,3-diethyl-1,3,2-diazaborolidine (3·47 g., 0·022 mole) in light petroleum (5 ml.) with sodium (1·0 g.) and potassium (4·0 g.) gave bi-(1,3-diethyl-1,3,2-diazaborolidin-2-yl) (1·43 g., 53%), n_D^{25} 1·4805 (Found: *M*, 255), which was purified by vacuum-condensation. 2-Chlorohexahydro-1,3-dimethyl-1,3,2-diazaborine (5·24 g., 0·036 mole) in light petroleum (10 ml.) with sodium (0·8 g.) and potassium (3·0 g.) gave unchanged starting material (1·12 g.), b. p. 30—32°/0·6 mm. (Found: *M*, 155), and bi(hexahydro-1,3-dimethyl-1,3,2-diazaborin-2-yl) (1·35 g., 44·0%), b. p. 75°/0·6 mm., n_D^{25} 1·4948 (Found: *M*, 222). These two products had infrared spectra identical with those of the corresponding products obtained by transamination.

Analysis.—Compounds were completely hydrolysed by refluxing dilute hydrochloric acid containing hydrogen peroxide; nitrogen was then determined by back-titration with sodium hydroxide. After addition of more sodium hydroxide, the solution was heated to dryness to remove the diamine, and boron was determined, by using mannitol, in the usual way.

Analysis for the boron–boron bonding in the ethylenediamine and propylenediamine products was carried out by heating samples with 15% potassium hydroxide solution at 140° for 24 hr. in sealed tubes; the hydrogen evolved was measured by vacuum-line technique. A check determination with tetrakisdimethylaminodiboron gave 92% of the theoretical hydrogen, in good agreement with the result previously reported.[1]

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