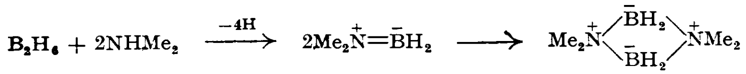
685. *Some Amino-derivatives of Borine.*

By G. E. Coates.

Whereas $Me_2N{\cdot}BX_2$ (X = H or Cl) associates, giving remarkably stable dimers, $(Me_2N)_2BH$ and $(Me_2N)_2BCl$ are monomeric. Attempted preparation of bis(dimethylamino)methylborine gave only the disproportionation products dimethylaminodimethylborine (II) and trisdimethylaminoborine. The former product and methanol give a 1 : 1 addition product (IV), which with hydrogen chloride forms dimethylamine hydrochloride and methyl dimethylboronate. The co-ordination complex (IV) is also formed directly from dimethylamine and methyl dimethylboronate. Lithium aluminium hydride reduction of chlorobisdimethylaminoborine gives the monomeric bisdimethylaminoborine.

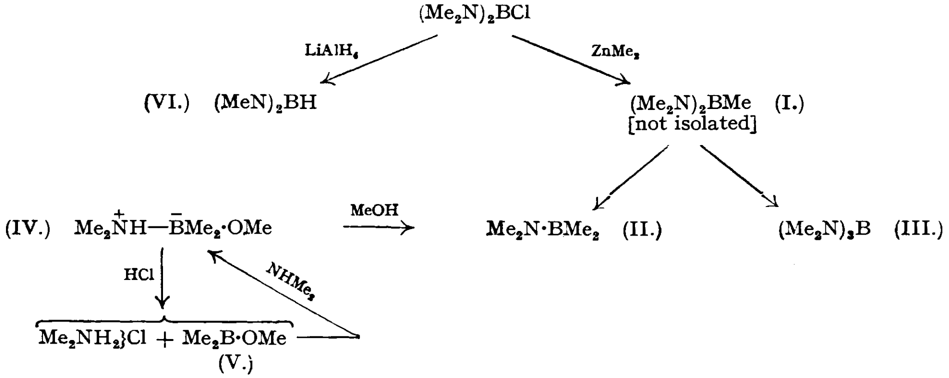
Derivatives of borine, BH_3, in which one or more of the hydrogen atoms are substituted by electron-donor atoms or groups, are of interest on account of the nature of the bond between boron and the substituent atom. For example, dimethylaminoborine may be written $Me_2N{\cdot}BH_2$ or $Me_2\overset{+}{N}{=}\overset{-}{B}H_2$, and the latter formulation indicates that association could occur; thus, the above compound (from diborane and dimethylamine) is very readily hydrolysed, but gives a crystalline dimer stable to, and insoluble in, water (Wiberg and Bolz, "FIAT Review of German Science, 1939—1946," published 1949, p. 129) :



$$B_2H_6 + 2NHMe_2 \xrightarrow{-4H} 2Me_2\overset{+}{N}{=}\overset{-}{B}H_2 \longrightarrow Me_2\overset{+}{N}\langle{}^{\overset{-}{B}H_2}_{\overset{-}{B}H_2}\rangle\overset{+}{N}Me_2$$

Perhaps the most striking example of this is to be found among the dimethylamino-derivatives of boron trichloride (Wiberg and Schuster, *Z. anorg. Chem.*, 1933, **213**, 77, 89). The monosubstitution product $Me_2N{\cdot}BCl_2$ is a colourless fuming liquid, b. p. 112°, and when freshly prepared from boron trichloride and dimethylamine it is monomeric and violently hydrolysed by water. On storage, it slowly forms a crystalline dimer which is inert even to boiling dilute acids and alkalis. Many other similar compounds have been prepared and are reviewed by Wiberg (*op. cit.*, pp. 125—147) and by Goubeau (*ibid.*, pp. 228—234).

The disubstitution product $(Me_2N)_2BCl$, chlorobisdimethylaminoborine, remains monomeric under all conditions (Wiberg and Schuster, *loc. cit.*).



With the object of preparing bis(dimethylamino)methylborine (I), chlorobisdimethylaminoborine was allowed to react with dimethylzinc, but low-temperature fractional distillation of the product gave approximately equimolecular quantities of its disproportionation products, the monomeric dimethylaminodimethylborine (II) and trisdimethylaminoborine (III). The properties of (II) and (III) are identical with those given for these substances prepared by other methods (see Experimental).

The volatile product (II) reacted rapidly with methanol at low temperature forming a beautifully crystalline addition compound (IV), the vapour of which was wholly dissociated at all temperatures from 50° to 100°. This compound was readily transferred within the vacuum-apparatus since its vapour pressure was 24 mm. at 20°; it reacted immediately in the cold with one molar equivalent of dry hydrogen chloride, giving dimethylamine hydrochloride, and a gas which must be methyl dimethylboronate (methoxydimethylborine) (V). The vapour of this compound, which is the oxygen analogue of (II), is also monomeric.

The solid compound (IV) is considered to be the co-ordination complex of methyl dimethylboronate with dimethylamine; it is also obtained by the direct addition of these components, consequently its vapour probably consists of these two substances rather than of (II) and methanol.

Lithium aluminium hydride reduction of chlorobisdimethylaminoborine gave bisdimethylaminoborine (VI) which, in contrast to its methyl derivative (I), is stable and does not disproportionate. The hydride is a colourless liquid, m. p. $-55°$ to $-56°$, and is monomeric in the vapour state. This compound, prepared by another method, has already been reported, and its properties are similar to those given in the FIAT Review.

The vapour pressures of the compounds described above were measured over the following temperature ranges: (II), 0—55°; (IV), 20—45°; (V), $-55°$ to $-10°$; (VI), 20—50° (see table).

Compound.	*A*.*	*B*.*	B. p. (extrap.).	L_v,† kcals./g.-mol.	Trouton const.
$Me_2N\cdot BMe_2$	1600	7·6130	65°	7·32	21·6
$Me_2\overset{+}{N}H-\overset{-}{B}Me_2\cdot OMe$	3285	12·571	51—52 (m. p.)	15·03 ‡	—
$Me_2B\cdot OMe$	1450	7·749	24·6	6·64	22·2
$(Me_2N)_2BH$	1875	7·814	107	8·58	22·6

* $\log_{10}$ (v. p.)$_{mm.}$ $= -(A/T) + B$. † L_v = latent heat of evaporation.
‡ Latent heat of sublimation.

EXPERIMENTAL.

The preparations, reactions, vapour pressures, and molecular-weight measurements were carried out in a vacuum-apparatus of the usual type (see, *e.g.*, Stock, "Hydrides of Boron and Silicon," Cornell, 1933; Sanderson, "Vacuum Manipulation of Volatile Compounds," Wiley, 1948), in which those parts of the apparatus to which reactive compounds have access are connected together by mercury float valves instead of greased stopcocks.

Dichlorodimethylaminoborine and Chlorobisdimethylaminoborine.—These compounds were prepared by Wiberg and Schuster's method (*loc. cit.*) except that carefully dried *n*-pentane was used as diluent. It was necessary to work as quickly as possible in order to separate the mono- and di-chloro-products before the former had time to associate to the dimeric form to any great extent.

Reaction of Chlorobisdimethylaminoborine with Dimethylzinc; Dimethylaminodimethylborine (II) *and Trisdimethylaminoborine* (III).—Dimethylzinc (68·1 normal c.c., *i.e.*, c.c. of gas at N.T.P.; 40% excess) was condensed on chlorobisdimethylaminoborine (0·3011 g., equiv. to 48·4 normal c.c. of gas) in a reaction vessel (120 c.c.) and allowed to warm up to room temperature. During 3 days a white solid slowly separated, and the volatile components of the mixture were then transferred to a fractionation apparatus. Slow fractionation (low temperature) gave unchanged dimethylzinc (v. p. 123 mm. at 0°), and dimethylaminodimethylborine (v. p. 53 mm. at 0°) and trisdimethylaminoborine (v. p. 2·8 mm. at 0°), which were formed in nearly equimolecular amount.

The dimethylaminodimethylborine was analysed by microcombustion, for which the sample was condensed in a capillary containing a weighed crystal of potassium chlorate and sealed (Found: C, 57·0; H, 14·2. Calc. for $C_4H_{12}NB$: C, 56·6; H, 14·2%). The vapour pressure and molecular weight were measured by condensing a weighed sample in the "high-temperature bulb" (Sanderson, *op. cit.*, p. 79) which was then immersed in a thermostatically controlled oil-bath. Measurements of vapour pressure were made at increasing temperatures until all the sample was present as vapour, whereafter further pressure measurements enabled the molecular weight to be calculated, since the volume of the bulb was known (Found: *M*, 86·0. Calc. for monomeric $C_4H_{12}NB$: *M*, 85·0).

Wiberg and Buchheit (FIAT Review, p. 228) have prepared this compound by heating the addition compound of trimethylboron and dimethylamine. They record only one vapour pressure (53 mm. at 0°) and an estimated b. p. of 80—85°.

The trisdimethylaminoborine was analysed by hydrolysis and titration of the liberated dimethylamine, followed by removal of the latter and mannitol titration of the boron now present as boric acid [Found: $B_{1\cdot02}(NMe_2)_{2\cdot99}$]. The vapour pressure and molecular weight were also measured and the identity of the compound was confirmed by comparison with Wiberg and Schuster's results (*loc. cit.*), who prepared it from boron trichloride and excess of dimethylamine.

Methyl Dimethylboronate (V).—Dimethylaminodimethylborine (17·8 normal c.c.) was transferred to a reaction vessel provided with a manometer and forming part of the vacuum-apparatus, and to this was added an equimolar quantity of pure methanol. Reaction occurred as the reactants melted, with the formation of a white crystalline mass which easily sublimed with the warmth of the hand; the m. p. in a sealed tube was 51—52°. The greater part of this addition product (IV) was weighed (90·7 mg.) and transferred to the high-temperature bulb for measurement of vapour pressure and molecular weight. The vapour pressure at 20° was 23·6 mm. The rather high molar heat of sublimation, 15·0 kcals./g.-mol., given in the table, includes the heat of dissociation, since measurement of vapour density between 50° (when the sample was completely gaseous) and 100° gave a constant molecular weight of 59·4 corresponding to 99% dissociation. The sample was then transferred to a weighed tube attached to the vacuum-apparatus by a ground joint, and one molar equivalent (17·2 c.c.) of hydrogen chloride condensed on it. Reaction occurred on warming of the mixture to room temperature, with the formation of a gas (17·4 c.c.) (Found: *M*, 71·1. C_3H_9OB requires *M*, 71·9) and a white non-volatile solid (62·1 mg.; calc. 62·6) which was identified as dimethylamine hydrochloride, being characterised as *NN*-dimethyl-*N'*-α-naphthylurea, m. p. 158—159°. Since no material was lost in these operations the gas could only be $Me_2B{\cdot}OMe$, *methyl dimethylboronate* (*methoxydimethylborine*).

To confirm that the compound (IV) should be regarded as the co-ordination complex of methyl dimethylboronate with dimethylamine, 17·6 normal c.c. (56·5 mg.) of the former were condensed in a tube in the vacuum-apparatus, and 17·6 normal c.c. of dimethylamine were added. Reaction occurred on melting, with the formation of the white crystalline volatile solid (IV), m. p. 51—52° (sealed tube), v. p. 23·5 mm. at 20° (cf. above).

Bisdimethylaminoborine (VI).—Lithium aluminium hydride (218 mg., about 100% excess) was quickly powdered and transferred to a tube, which was then attached by a ground joint to the vacuum-apparatus. Chlorobisdimethylaminoborine (1·406 g.) was condensed *in vacuo* on the lithium aluminium hydride, and the mixture allowed to warm to room temperature; it then slowly bubbled for just over an hour and became just warm. The product was frozen, a trace of permanent gas pumped off, and the volatile material fractionated into two components: 0·24 c.c., v. p. 25 mm. at 20°; and 1·0 c.c., v. p. 3·8 mm. at 20°. The less volatile fraction evolved no gas on hydrolysis, and analysis showed that it consisted of a mixture of starting material with some trisdimethylaminoborine. The latter must have been formed by a disproportionation reaction, although no dimethylaminoborine, was detected. The more volatile fraction was divided into three parts: the first (0·0512 g.) was vaporised at room temperature in a calibrated volume and exerted a pressure corresponding to a molecular weight of 100·7 [Calc. for $(Me_2N)_2BH$: *M*, 100]; the second (0·0600 g.) was analysed by hydrolysis and gave 12·8 c.c. of hydrogen at 27°/769·3 mm., 1·068 millimoles of $NHMe_2$, and 0·532 millimoles of H_3BO_3, corresponding to a formula $B_{1\cdot000}(NMe_2)_{2\cdot007}H_{0\cdot991}$; the remainder was transferred to the high-temperature bulb, and its vapour pressure and vapour density were determined. The vapour pressure is given in the table; the vapour density corresponded to a molecular weight of 100·1. The substance appeared to be quite stable on storage and did not disproportionate into dimethylaminoborine (or the dimer) and trisdimethylaminoborine.

The author thanks Mr. D. G. Blackburn for his assistance in the preparation of the chlorobisdimethylaminoborine. The microcombustion was carried out by Mr. W. M. Eno of this Department.

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