829. *The Preparation of Some Dimeric* sec.-*Aminoboron Dihalides.*

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A number of new *sec.*-aminoboron dihalides has been prepared. The formation of cyclic dimers by these compounds is limited to the products obtained from pyrrolidine, piperidine, and morpholine. In the other cases the steric effects of the substituents on the nitrogen atoms appear to prevent dimerisation.

THE rapid, spontaneous dimerisation of dimethylaminoboron dichloride, $Me_2\overset{+}{N}=\overset{-}{B}Cl_2$, was first observed in 1933 by Wiberg and Schuster.[1] Because of its low reactivity compared with that of the monomer, the crystalline dimer was assigned the cyclic structure (I) which has since received strong support from the small dipole moment found[2] for the compound. Later, dimethylaminoboron dibromide was found to undergo a similar, but much slower, dimerisation.[3,4] The corresponding ethyl compounds, diethylaminoboron dichloride and dibromide however failed to show any signs of dimerisation even after prolonged keeping;[3,4,5] no explanation has been put forward to account for this marked difference.

A number of aminoboron dihalides related to the above compounds has now been prepared from a variety of aliphatic secondary amines by J. F. Brown's method[6] in order to determine the factor controlling the dimerisation. The reaction of the amines with boron trihalides gave the addition compounds (II) which lost hydrogen halide on treatment with triethylamine. After removal of the precipitated triethylammonium halide, vacuum-distillation readily gave the *sec.*-aminoboron dihalides (III) as colourless fuming liquids. In this way the aminoboron dichlorides {III; $X = Cl$, $R_2 = –[CH_2]_4–, –[CH_2]_5–, O(CH_2{\cdot}CH_2–)_2$} were obtained from pyrrolidine, piperidine, and morpholine respectively, while the aminoboron dibromides (III; $X = Br$, $R_2 = –[CH_2]_4–, –[CH_2]_5–$) resulted from pyrrolidine and piperidine. The isolation of morpholinoboron dibromide from the reaction between morpholine, boron tribromide, and triethylamine did not prove to be possible. The product decomposed on attempted distillation owing, probably, to the fission of the morpholine ring by a reaction between the ether linkage and the boron dibromide group.[7]

Of the above compounds, 1-pyrrolidinyl-, piperidino-, and morpholino-boron dichloride quickly dimerised at room temperature, giving highly crystalline, sharp-melting solids. These are considered by analogy with Wiberg and Schuster's compound to have the bis-*spiro*cyclic structures (IV; $X = Cl$), (V; $X = Cl$), and (VI) respectively.

The dimerisation of 1-pyrrolidinylboron dibromide was markedly slower than that of

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[1] Wiberg and Schuster, *Z. anorg. Chem.*, 1933, **213**, 89.

[2] C. A. Brown and Osthoff, *J. Amer. Chem. Soc.*, 1952, **74**, 2340.

[3] Wiberg, FIAT Review of German Science (1939—1946), Inorganic Chemistry, Vol. I (1948), p. 125.

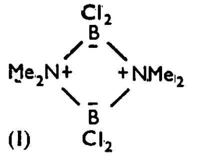
[4] Goubeau, *op. cit.*, p. 215.

[5] Osthoff and C. A. Brown, *J. Amer. Chem. Soc.*, 1952, **74**, 2378.

[6] J. F. Brown, *ibid.*, p. 1219.

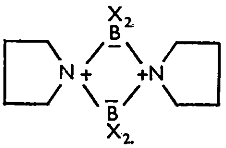
[7] Cf. Benton and Dillon, *ibid.*, 1942, **64**, 1128.

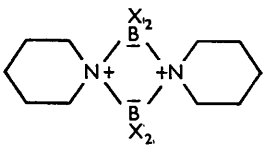
the corresponding dichloride, while piperidinoboron dibromide had not dimerised completely after nine months at room temperature. These dimers are considered to have the structures (IV; X = Br) and (V; X = Br) respectively. All the above dimeric compounds, like the dimethylaminoboron dihalide dimers, are stable indefinitely in moist air and appear to be unaffected by water at 20°. Attempted crystallisation from benzene or chloroform however leads to partial decomposition on prolonged boiling of the solutions in contact with moist air. The molecular weights (determined ebullioscopically in benzene) of the morpholinoboron dichloride and piperidinoboron dibromide dimers show that some dissociation or decomposition of these compounds occurs in solution at 80°. The products from the reactions between boron trichloride and triethylamine with di-*n*-propylamine, di-*n*-butylamine, or 2-methylpiperidine showed no signs of dimerisation after six months at 20° and five days at 100°, and remained highly reactive liquids.

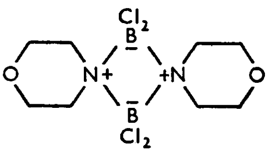

(I)


$\overset{+}{R_2NH}-\overset{-}{B}X_3 \rightarrow R_2\overset{+}{N}=\overset{-}{B}X_2$

(II) (III)


(IV)


(V)


(VI)

The dimerisation of the aminoboron dihalides requires the formation of two N->B co-ordinate bonds, the strength of which is known to be highly dependent on the steric effects of the substituents on the nitrogen atom. Thus dimethylamine–trimethylboron [dissociation constant at 100° (K_{100}), 0·0214 atm.] is more stable than diethylamine–trimethylboron (K_{100}, 1·22 atm.), the lower stability of the latter being attributed to the greater steric effect of the ethyl groups. The replacement of the diethylamino-group by small heterocyclic rings which have much smaller steric requirements, as in pyrrolidine–trimethylboron (K_{100}, 0·0035 atm.) and piperidine–trimethylboron (K_{100}, 0·021 atm.), leads to a considerable increase in stability.[8] The co-ordinate bonds formed by tertiary amines are similar, triethylamine–trimethylboron (completely dissociated above 25°) being much less stable than trimethylamine–trimethylboron (K_{100}, 0·472 atm.) while quinuclidine–trimethylboron (K_{100}, 0·0196 atm.) is more stable.[9]

It appears likely that similar steric effects control the dimerisation and thus provide an explanation for the striking difference in behaviour of the two groups of *sec.*-aminoboron dihalides. The small steric requirements of the substituents on the nitrogen atoms in dimethylamino-, 1-pyrrolidinyl-, piperidino-, and morpholino-boron dichloride permit intermolecular co-ordinate bond formation and, consequently, cyclisation. The rather larger steric requirements of the substituents in the products obtained from diethyl-, di-*n*-propyl-, and di-*n*-butyl-amine, and 2-methylpiperidine do not allow cyclisation to take place.

The dimerisation of the *sec.*-aminoboron dibromides appears to be subject to the same steric restrictions. The much slower dimerisation observed for these compounds as compared with their chlorine analogues may be attributed to the increased steric requirements of the boron dibromide group. The much more rapid formation and greater stability of the dimer from 1-pyrrolidinylboron dibromide as compared with the dimer from the piperidino-compound are no doubt due to the lower steric effects of the α-methylene groups in the five-membered pyrrolidine ring.[8]

[8] H. C. Brown and Gerstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2926.

[9] H. C. Brown and Sujishi, *ibid.*, 1948, **70**, 2878.

EXPERIMENTAL

Analyses were by the Microanalytical Section of this Department.

Monomeric sec.-*Aminoboron Dihalides.*—A solution of the secondary amine (0·2 mol.) in dry benzene (50 ml.) was added during ¼ hr. to a stirred solution of the boron trihalide (0·2 mol.) in the same solvent (50 ml.) at 0°. Moisture was carefully excluded. To the resulting crystalline suspension or solution of the amine–boron trihalide addition compound was added, in a similar manner, a solution of triethylamine (0·2 mol.) in dry benzene (75 ml.). The mixture was stirred at room temperature for ½ hr., kept overnight to ensure complete separation of the triethylammonium halide, and filtered. The filtrate frequently separated into two layers. After removal of the benzene, distillation of the residue under reduced pressure gave the monomeric *aminoboron dihalide* (Table 1) in 35—50% yield, as a colourless mobile liquid which fumed vigorously in moist air and decomposed violently on contact with water.

TABLE 1. *Monomeric* sec.-*aminoboron dihalides,* $R_2\overset{+}{N}=\overset{-}{B}X_2$.

R_2	$-[CH_2]_4-$	$-[CH_2]_5-$	$O(CH_2{\cdot}CH_2-)_2$	$-[CH_2]_4-$	$-[CH_2]_5-$
X	Cl	Cl	Cl	Br	Br
B. p./mm.	70—74°/17	82—83°/20	88—90°/25	97—100°/15	105—106°/14

Dimeric sec.-*Aminoboron Dihalides.*—1-Pyrrolidinyl-, piperidino-, and morpholino-boron dichloride began to deposit crystals within a few hours of their isolation and after 1—2 weeks had almost completely solidified. After the solids had been washed with benzene to remove small amounts of dark oils and any monomeric material, the *dimers* were obtained as colourless, highly crystalline solids which did not require further purification. The dimerisation of piperidinoboron dichloride also occurred when a solution of the monomer in benzene was kept for one month at room temperature; the dimer crystallised from the solution in large colourless prisms. The dimerisation of 1-pyrrolidinyl- and piperidino-boron dibromide was effected by heating the compounds at 80° for 7 days and then keeping them at room temperature. After 9 days the 1-pyrrolidinyl compound had completely solidified; the piperidino-compound had not dimerised completely after 9 months. In both cases the *dimers* were obtained as colourless crystalline solids after washing with benzene. The m. p.s and analyses are recorded in Table 2.

TABLE 2. *Dimeric* sec.-*aminoboron dihalides,* $(R_2\overset{+}{N}{\cdot}\overset{-}{B}X_2)_2$.

R_2		$-[CH_2]_4-$	$-[CH_2]_5-$	$O(CH_2{\cdot}CH_2-)_2$	$-[CH_2]_4-$	$-[CH_2]_5-$
X		Cl	Cl	Cl	Br	Br
M. p.		131—132°	105°	103°	157—158°	130·5—131·5°
Formula		$C_8H_{16}N_2B_2Cl_4$	$C_{10}H_{20}N_2B_2Cl_4$	$C_8H_{16}O_2N_2B_2Cl_4$	$C_8H_{16}N_2B_2Br_4$	$C_{10}H_{20}N_2B_2Br_4$
Found (%)	C	32·15	36·6	28·55	19·85	24·05
	H	5·4	6·2	4·75	3·3	4·0
	N	9·3	8·55	8·15	5·6	4·35 ‡
	Br	—	—	—	66·25	62·65
	Cl	46·45	42·95	42·0	—	—
Found	*M* *	313	336	288	475	315 †
Required (%)	C	31·65	36·2	28·65	19·95	23·55
	H	5·3	6·1	4·8	3·35	3·95
	N	9·2	8·45	8·35	5·8	5·5
	Br	—	—	—	66·4	62·75
	Cl	46·7	42·75	42·25	—	—
Required	*M* *	303·7	331·8	335·7	481·5	509·55

* Determined ebullioscopically in benzene (concn. 10—20 mg./20 ml.).

† Initial value *ca.* 490. ‡ The reason for this low value is unknown.

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