586. *Cyclic Organic Boron Compounds. Part IV.*[1] B-*Amino- and* B-*Alkoxy-borazoles and their Precursors the Tris(primary amino)borons and (Primary amino)boron Alkoxides.*

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Interaction of boron trichloride with an excess of primary amine (R in $R{\cdot}NH_2$ = Me, Et, Pr^i, Bu^n, Bu^s, Bu^t, cyclohexyl, $Ph{\cdot}CH_2$, Ph) afforded the triaminoboron $B(NHR)_3$, which on pyrolysis afforded in the first instance the *B*-aminoborazole (I) and eventually the thermally stable (at least up to 600°) polymeric borazole (III). Similarly, the n-butoxyboron chlorides and ethylamine gave the primary aminoboron n-butoxides, which when heated gave the *B*-n-butoxyborazole (IV). The characterising constants and molecular weights of all the non-polymeric compounds have been determined.

THE preparation of trisethylaminoboron, $(Et{\cdot}NH)_3B$, n-butyl bisethylaminoborinate, $Bu^nO{\cdot}B(NHEt)_2$, and di-n-butyl ethylaminoboronate, $(Bu^nO)_2B{\cdot}NHEt$, has been briefly described;[1] pyrolysis of the triaminoboron gave the borazole (I; R = Et) and eventually polyborazoles, whereas the n-butoxy-compounds gave the borazole (IV). These experiments are now described in detail and also reported are extensions to other monoalkylamino-, benzylamino-, and anilino-systems.

Addition of boron trichloride to a primary amine in an inert solvent at −78° afforded the triaminoboron in high yield (Table 1): $BCl_3 + 6R{\cdot}NH_2 \longrightarrow B(NHR)_3 + 3R{\cdot}NH_2,HCl$. The trisethylaminoboron,[1] and the phenyl,[2] *p*-tolyl,[3] and *p*-methoxyphenyl[4] compounds were the only previously described tris(primary amino)borons. The method hitherto used[2,3,4] for obtaining these trisarylaminoborons was more laborious than the present one and involved initial preparation of the amine–boron trichloride complex, and treatment of this with more amine under somewhat forcing conditions. In view of the eliminations which the tris-compounds undergo when heated (see below), mild reaction conditions for their preparation are preferable. Reference has been made to trisethylaminoboron (obtained from boron trifluoride, ethylamine, and lithium), but it was not characterised.[5]

TABLE 1. *Characterisation and yields of the triaminoborons,* $B(NHR)_3$.

R	Yield (%)	B. p./mm. (m. p.)	d_4^{20}	n_D^{20}	Molar refractivity Found	Calc.*
Me	71	59°/33	0·8871	1·4465	30·3	30·2
Et	55	62—63°/10	0·833	1·4380	44·9	44·8
Pr^i	81	37°/1	0·8000	1·4267	59·3	58·8
Bu^n	91	84°/0·005	0·8347	1·4462	72·4	72·6
Bu^s	92	49°/0·1	0·8186	1·4355	72·3	72·1
Bu^t	84	42°/0·05	0·7971	1·4272	72·8	73·4
Cyclohexyl	90	(92—94°)	—	—	—	—
$Ph{\cdot}CH_2$	80	Decomp.	1·0479	1·5805	104·8	103·9
Ph	81	Decomp.	—	—	—	—

* Based on Vogel's values (" A Text-book of Practical Organic Chemistry," Longmans, Green & Co., London, 1948, p. 900) and the value 3·0 for boron.

The characterising constants of the triaminoborons are shown in Table 1, as are the molar refractivities of the liquid members. Assigning a value of 3·0 for the atomic refractivity of boron gives fair agreement between experimental and calculated values for molar refractivities; the value in trialkyl borates is 2·65.[6] The compounds are monomeric (Table 3) and colourless liquids or crystals and are easily hydrolysed by cold water to the

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[1] Lappert, *Proc. Chem. Soc.*, 1959, 59.

[2] Jones and Kinney, *J. Amer. Chem. Soc.*, 1939, **61**, 1378.

[3] Kinney and Kolbezen, *ibid.*, 1942, **64**, 1584.

[4] Kinney and Mahoney, *J. Org. Chem.*, 1943, **8**, 526.

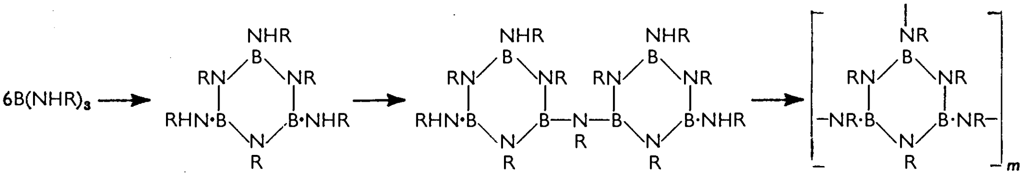
[5] Kraus and Brown, *J. Amer. Chem. Soc.*, 1930, **52**, 4414,

[6] Lappert, *J.*, 1956, 1768.

primary amine and boric acid. The aliphatic compounds are soluble in non-polar solvents, such as pentane and benzene, but the benzyl compound was only sparingly soluble in pentane; the trianilinoboron was insoluble in pentane but soluble in hot benzene and chloroform.

Interaction of ethylamine and the n-butoxyboron chlorides afforded the ethylaminoboron n-butoxides: $(Bu^nO)_xBCl_{3-x} + 2(3 - x)Et{\cdot}NH_2 \longrightarrow (Bu^nO)_xB(NHEt)_{3-x} + (3 - x)Et{\cdot}NH_2,HCl$ ($x = 1$ or 2). These compounds are the first (primary amino)boron alkoxides to be reported, but four (secondary amino)boron alkoxides, $(Bu^nO)_xB(NR_2)_{3-x}$, are known.[7,8]

At 200° trisethylaminoboron was almost quantitatively converted in 3½ hr. into the borazole (I; R = Et). Further heating resulted in elimination of ethylamine, corresponding to formation of the condensation dimer (II), which ultimately at 600° afforded a polymer (III). Spectroscopic evidence (to be detailed later) has been outlined[1] to show that compound (I) is a borazole and that compounds (II) and (III) are polyborazoles. The borazole (I; R = Et) was a viscous, colourless liquid, which during pyrolysis gradually darkened, increased in viscosity, changed to a light brown rubber (mobile liquid when hot), and finally into a dark brown, non-thermoplastic brittle resin, which was insoluble in inert organic solvents and was evidently highly cross-linked. The ultimate polymer was only slowly attacked by cold water, but was hydrolysed in boiling water to boric acid and ethylamine. A polymeric borazole, obtained as a distillation residue by redistilling the borazole (I; R = Et), was elastomeric, insoluble in organic solvents, and unaffected by boiling water, but hydrolysed by concentrated hydrochloric acid.



(I) (II) (III)

Other borazoles (Table 2) were obtained similarly, either as higher-boiling fractions obtained when distilling the triaminoborons, or as pyrolysis products (R = cyclohexyl, $Ph{\cdot}CH_2$, or Ph). Their molecular weights (Table 5) corresponded to formula (I), *i.e.*, $(R{\cdot}NH{\cdot}B{\cdot}NR)_3$. When heated they polymerised further, except for the compound (I; R = Bu^t; this may be due to steric hindrance making elimination of t-butylamine difficult). The borazoles (I) were soluble in many non-polar organic solvents and, except for the phenyl compound, were easily hydrolysed by cold water; the phenylborazole was hydrolysed by hot water.

TABLE 2. *Characterisation of the* B-*aminoborazoles* (I).

R	B. p./mm. (m. p.)	d_4^{20}	n_D^{20}	Molar refractivity Found	Calc.*
Me	110°/0·1	1·016	1·5082	61·7	61·9
Et	145—150°/0·1	0·933	1·4826	89·8	89·8
Pr^i	106°/0·03	0·8220	1·4628	118·0	117·9
Bu^n	158°/0·005	0·900	1·4730	144·3	145·7
Bu^s	135°/0·01	0·892	1·4695	144·2	144·6
Bu^t	103°/0·04	0·883	1·4631	144·0	147·1
Cyclohexyl	(52—55°)	—	—	—	—
$Ph{\cdot}CH_2$	>250°/0·005	1·156	1·642	208·1	209·1
Ph	(152—155°)	—	—	—	—

* See footnote to Table 1.

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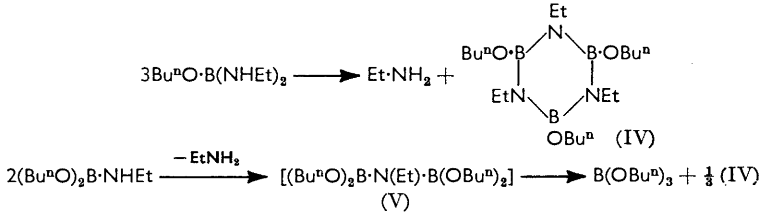
[7] Gerrard, Lappert, and Pearce, *J.*, 1957, 381.

[8] *Idem, Chem. and Ind.*, 1958, 292.

Preparation of *B*-aminoborazoles has previously (except for R = Et[1]) been described in only one other work,[9] the compounds then being obtained from *B*-chloroborazoles and amines. The polynuclear borazoles appear to be novel and are of interest because they are polymers having wholly inorganic skeletons, and because polycyclic inorganic compounds are virtually unknown. The remarkable thermal stability of the polymer (III; R = Et) is attributed to the absence of organic radicals in the main chain.

Pyrolysis of the ethylaminoboron n-butoxides afforded the borazole (IV); with di-n-butyl ethylaminoboronate there was no evidence for the presumed intermediate (V). The molecular weight and the infrared spectrum[1] of the intermediate were consistent with its formulation as a *B*-alkoxyborazole; such compounds were unknown before our earlier[1] communication.



EXPERIMENTAL

General Procedures.—Amines were dried and purified by heating under reflux with, and fractionation from, barium oxide. Analysis for chlorine was by Volhard's method, for boron by Thomas's method,[10] for nitrogen either as amino-group by steam distillation from potassium hydroxide and distillation into standard acid, or by the Kjeldahl procedure (for I; R = Ph). Molecular weights were determined ebullioscopically in benzene. The identity of the amines, obtained as pyrolysis products during formation of borazoles, was established by demonstrating their identity with authentic specimens by gas chromatography and infrared spectroscopy.

Preparation of Triaminoborons.—Boron trichloride (1 mol.; usually 0·1 mole) in n-pentane (25 c.c.) at −78° was added slowly from a cooling-jacketed dropping funnel to the amine (6 mol.) in n-pentane (250 c.c.) at −78°. Reaction was invariably highly exothermal and accompanied by formation of a white precipitate. The mixture was set aside for 2 hr. at 20° and then filtered. The precipitate which was exclusively the amine hydrochloride in all except the benzylamine and aniline experiments (when it was a mixture of the amine hydrochloride and triaminoboron) was washed with more solvent, freed from solvent at 20°/15 mm., weighed, and analysed; from the filtrate, after removal of solvent, there was obtained the crude triaminoboron which was purified by fractional distillation or crystallisation (the yields shown in Table 1 are of purified product). In the benzylamine and aniline experiments the components of the precipitate were separated by extracting the triaminoboron with hot benzene. Attempted distillation of trisbenzylaminoboron resulted in elimination of benzylamine, but the undistilled material was pure as shown by analysis and molecular-weight determination. The yields and characterisation of the triaminoborons are shown in Table 1, whilst in Tables 3 and 4 are shown the analytical data for the triaminoborons and the amine hydrochlorides respectively.

TABLE 3. *Analysis of the triaminoborons,* $B(NHR)_3$.

	Found					Required				
R	C (%)	H (%)	N (%)	B (%)	*M*	C (%)	H (%)	N (%)	B (%)	*M*
Me	35·6	11·5	41·0	11·2	106	35·7	11·9	41·7	10·7	101
Et	50·4	12·4	29·0	7·9	146	50·3	12·7	29·4	7·7	143
Pr^i	58·3	12·5	22·5	5·8	188	58·5	12·9	22·7	5·8	185
Bu^n	62·8	13·2	18·5	4·8	217	63·4	13·2	18·5	4·8	227
Bu^s	64·5	13·5	18·0	4·7	231	63·4	13·2	18·5	4·8	227
Bu^t	63·7	13·2	18·3	4·7	243	63·4	13·2	18·5	4·8	227
Cyclohexyl	71·3	12·2	13·9	3·8	302	70·8	11·8	13·9	3·5	305
$Ph{\cdot}CH_2$	76·5	7·6	12·7	3·0	332	76·6	7·3	12·8	3·3	329
Ph			14·6	3·8				14·7	3·8	

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[9] Gould, U.S.P. 2,754,177/1956.

[10] Thomas, *J.*, 1946, 820.

Preparation of Borazoles (I).—Only for ethylamino- (83%), cyclohexylamino- (100%), benzylamino- (100%), and anilino-borazole (100%) do the stated yields have meaning, because in the remaining experiments no separate effort was made to pyrolyse appropriate triaminoborons, the corresponding borazoles [R in $(R{\cdot}NH{\cdot}B{\cdot}NR)_3$ = Me (4·3%), Pr^i (14·7%), Bu^n (15·8%), Bu^s (16·3%), Bu^t (18·4%)] being obtained merely as higher-boiling fractions during the preparation of the triaminoborons.

TABLE 4. *Yield and analysis of* $R{\cdot}NH_2,HCl$.

R	Yield (mols.)	Found (%): N	Found (%): Cl	Calc. (%): N	Calc. (%): Cl
Me	3·12	20·5	50·0	20·7	52·5
Et	3·02	17·3	43·3	17·2	43·6
Pr^i	2·68	14·5	37·0	14·7	37·1
Bu^n	2·98	12·6	31·9	12·8	32·4
Bu^s	3·03	13·1	32·4	12·8	32·4
Bu^t	2·89	12·6	29·5	12·8	32·4
Cyclohexyl	3·07	10·5	24·3	10·3	26·2
$Ph{\cdot}CH_2$	3·42	9·9	23·5	9·8	24·7
Ph	3·27	11·3	25·5	10·8	27·4

The triaminoborons were pyrolysed under reflux (R = Et at 200° for 3½ hr.; R = cyclohexyl at 200°/0·1 mm. for 5 hr.; R = $Ph{\cdot}CH_2$ at 250°/0·005 mm. for 2 hr.; R = Ph at 250°/10 mm. for 2 hr.), under conditions such that elimination of amine (collected as a condensate at −78°) corresponded to that required for borazole formation. The *B*-ethylaminoborazole was then distilled, but this was not possible for the others. Characterisation of the borazoles (I) is shown in Table 2, and in Table 5 are the analytical data.

TABLE 5. *Analysis of the* B-*aminoborazoles* (I).

	Found					Required				
R	C (%)	H (%)	N (%)	B (%)	*M*	C (%)	H (%)	N (%)	B (%)	*M*
Me	33·4	9·8	40·0	15·7	211	34·3	10·1	40·1	15·5	210
Et	48·5	11·0	28·8	11·1	290	49·0	11·2	28·6	11·3	294
Pr^i	56·1	11·5	22·4	8·9	365	57·2	12·0	22·2	8·6	378
Bu^n	62·0	12·4	18·1	7·3	446	62·3	12·4	18·2	7·0	462
Bu^s	61·8	12·1	18·0	7·2	471	62·3	12·4	18·2	7·0	462
Bu^t	61·5	12·0	18·3	7·2	445	62·3	12·4	18·2	7·0	462
Cyclohexyl *	71·3	10·8	13·4	4·9	564	69·9	11·3	13·8	5·3	618
$Ph{\cdot}CH_2$ *	73·4	6·6	12·4	5·2	579	75·6	6·8	12·6	4·9	666
Ph *	72·1	5·8	13·6	5·8	541	74·2	5·7	14·4	5·6	582

* Undistilled.

Pyrolysis of the Borazole (I; R = Et).—The borazole (11·40 g.) was not appreciably changed at 200° in 3 hr. At 300°, however, ethylamine [0·87 g. Calc., 0·86 g., for formation of (II)] was eliminated during 4 hr. and further heating at 300° had little effect. At 320° evolution of ethylamine continued and after 5 hr. the amount corresponded approximately to the formation of the linear decacyclic borazole. A total of 1·65 g. of ethylamine had been evolved and a further loss in weight of 2·36 g. occurred after 9 hr. at ~600° to leave the polymer, a section of which is formulated as (III).

Interaction of Butyl Dichloroborinate and Ethylamine.—The dichloroborinate [11,12] (10·30 g., 1 mol.) in n-pentane (20 c.c.) was slowly added to the amine (14·03 g., >4 mol.) in n-pentane (30 c.c.) at −78°. The reaction was highly exothermal. The precipitated ethylamine hydrochloride (10·53 g., 97%) (Found: N, 17·0; Cl, 43·5%) was filtered off and the residue obtained from the filtrate by evaporation was fractionated, to give (i) 4·07 g., b. p. 37—38°/0·2 mm., n_D^{20} 1·4223, d_4^{20} 0·826 (Found: N, 12·7; B, 6·9%), (ii) 2·94 g., b. p. 38—39°/0·2 mm., n_D^{20} 1·4200, (iii) crude borazole (IV), 3·13 g., b. p. 128—129°/0·1 mm., n_D^{20} 1·4595, d_4^{20} 0·935 (Found: N, 11·7; B, 9·0%), and a residue (0·84 g.). There was no condensate. Components (i) and (ii) were combined and after three successive fractionations, there was obtained *n-butyl bisethylaminoborinate* (3·13 g., 28%) (Found: C, 55·4; H, 12·2; N, 16·0; B, 6·2%; *M*, 180.

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[11] Gerrard and Lappert, *J.*, 1951, 2545.
[12] *Idem, J*, 1955, 3084.

$C_8H_{21}ON_2B$ requires C, 55·8; H, 12·3; N, 16·3; B, 6·3%; *M*, 172), b. p. 38—39°/0·2 mm., n_D^{20} 1·4280, d_4^{20} 0·839. Examination of the other fractions indicated that some disproportionation, as well as elimination of amine to give the borazole (IV) [2·32 g., obtained from (iii), b. p. 152—154°/0·3 mm., n_D^{20} 1·4540 (Found: N, 10·9; B, 8·5%)], had also taken place.

Interaction of Di-n-butyl Chloroboronate and Ethylamine.—By a similar procedure there was obtained from the chloroboronate [6,11] (27·8 g., 1 mol.) and the amine (16·00 g., >2 mol.) in n-pentane (total 100 c.c.), ethylamine hydrochloride (11·50 g., 98%) (Found: N, 17·1; Cl, 43·5%) as insoluble product. The filtrate, after several redistillations, afforded *di-n-butyl ethylaminoboronate* (8·23 g., 28%), b. p. 49—51°/0·1 mm., n_D^{20} 1·4178, d_4^{20} 0·846 (Found: C, 59·9; H, 12·3; N, 7·4; B, 5·6%; *M*, 211. $C_{10}H_{24}O_2NB$ requires C, 59·7; H, 12·0; N, 7·6; B, 5·4%; *M*, 201). Analyses and physical constants of other fractions indicated that disproportionation of the aminoboronate (to give the triaminoboron, the diaminoborinate, and the borate) also occurred; only a trace of (IV) was isolated.

Pyrolysis of the Ethylaminoboron n-Butoxides.—n-Butyl bisethylaminoborinate (4·17 g.) was heated under reflux. After 1 hr. at 160° no ethylamine had been lost, but at 260° (2½ hr.) the amine (0·84 g., 77%) (characterised by gas chromatography) was collected as a condensate. The residue, after two distillations, afforded the borazole (IV) (2·06 g., 66%), b. p. 153—156°/0·4 mm., n_D^{20} 1·4544, d_4^{20} 0·935 (Found: C, 56·0; H, 12·1; N, 11·0; B, 8·6%; *M*, 394. $C_{18}H_{42}O_3N_3B_3$ requires C, 56·7; H, 11·0; N, 11·0; B, 8·6%; *M*, 381).

Similarly, from di-n-butyl ethylaminoboronate (13·85 g.) there were obtained (after 5½ hr. at 220°) ethylamine (1·24 g., 80%), tri-n-butyl borate (6·92 g., 87%), b. p. 48—52°/0·2 mm., n_D^{20} 1·4100 (authentic infrared spectrum), and the borazole (IV) (2·44 g., 56%), b. p. 153—157°/0·4 mm., n_D^{20} 1·4530 (Found: N, 10·8; B, 8·5%). The pyrolysis mixture before distillation was shown (infrared spectrum) to be a mixture of the borate and borazole.

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