422. *Cyclic (Borazole) and Non-cyclic Condensation of Di(alkylamino)phenylborons.*

By J. E. Burch, W. Gerrard, and E. F. Mooney.

Controlled pyrolysis of di(alkylamino)phenylborons $(R{\cdot}NH)_2BPh$, prepared from phenylboron dichloride and the amine (4 mol.), gave the cyclic borazole (R = Me or Et), or a mixture of the cyclic borazole and non-cyclic polyboronamine ($R = Pr^n$ or Bu^n), or only the latter ($R = Pr^i$, Bu^i, Bu^s, or Bu^t); the non-cyclic nature of the boronamines is indicated by infrared spectra. Steric hindrance to ring formation is invoked in explanation.

Di(alkylamino)phenylborons give dialkyl phenylboronates by alcoholysis and undergo transamination with different amines.

Certain *N*-trialkyl-*B*-triphenylborazoles have been prepared[1,2] by interaction of phenylboron dichloride and a primary amine in an inert solvent: $3Ph{\cdot}BCl_2 + 9R{\cdot}NH_2 \longrightarrow (PhBNR)_3 + 6R{\cdot}NH_3^+Cl^-$. A small amount of the di(ethylamino)phenylboron was obtained in addition to the borazole.[2a] We have now prepared a number of di(alkylamino)phenylborons in good yields (Table 1), by using reagents in the proportions $Ph{\cdot}BCl_2 + 4R{\cdot}NH_2 \longrightarrow Ph{\cdot}B(NHR)_2 + 2R{\cdot}NH_3^+Cl^-$, and in ethereal solution.

Distillation of di(alkylamino)phenylborons may lead to two reactions. When R = Me or Et, the cyclic borazole was obtained; when $R = Pr^n$ or Bu^n, both the cyclic borazole and a non-cyclic polyboronamine were formed; but when $R = Bu^i$, Bu^s, or Bu^t, and Pr^i only the non-cyclic polycondensate was obtained.

Pyrolysis under reflux gave similar results (Table 2). Elimination of the amine from the t-butyl compound was very slow.

The compounds mentioned were characterised by infrared spectroscopy; only the

---

[1] Ruigh *et al.*, W.A.D.C. Technical Report 55—26, " Research on Boron Polymers," Parts II—IV.

[2] (*a*) Mikhailov and Aronovich, *Bull. Acad. Sci. U.S.S.R., Div. Chem. Sci.*, 1957, 1146; (*b*) Mikhailov and Kostroma, *ibid.*, 1957, 1149.

relevant bands are dealt with in this paper as a means of assigning structures to the non-cyclic condensates; detailed interpretation of the spectra will be considered elsewhere.[3]

TABLE 1.

Preparation of di(alkylamino)phenylborons, $(R{\cdot}NH)_2BPh$.

	Alkylammonium chloride			Di(alkylamino)phenylboron							
		Found (%)				Found (%)					
R	Yield (mol.)	Cl	N	Yield (%)	B. p./mm.	C	H	B	N	n_D^{20}	d_4^{20}
Me	2·0	52·5	20·7	43 [1]	106—107°/16	64·8	9·1	7·3	17·6 [7]	1·5275	0·9645
Et	1·9	43·2	17·0	70 [2]	106—108°/10	68·3	9·8	6·1	15·7 [8]	1·5055	0·9248
Pr^n	2·0	36·7	14·5	73 [3]	134—135°/11	70·8	10·2	5·3	13·6 [9]	1·5007	0·9097
Pr^i	2·0	37·0	14·4	68 *	109—110°/10	70·7	10·3	5·2	13·6 [9]	1·4901	0·8870
Bu^n	2·0	32·4	12·6	41 [4]	118—119°/0·5	72·7	10·9	4·7	12·1 [10]	1·4954	0·8997
Bu^i	2·0	32·2	12·8	60 [5] *	80—81°/0·1	72·7	10·7	4·6	12·2 [10]	1·4930	0·8949
Bu^s	2·0	32·3	12·7	90 *	80—81°/0·3	72·8	10·8	4·6	12·1 [10]	1·4868	0·8862
Bu^t	1·9	32·3	12·5	72 [6] *	71—72°/0·1	72·8	10·7	4·7	12·2 [10]	1·4837	0·8795

* Distillation residue of non-cyclic polyboronamine.

[1] *N*-Trimethyl-*B*-triphenylborazole (0·45 mol.) (Found: B, 9·3; N, 11·9%), m. p. 276—277°, was filtered from distillation residue and washed with isopentane. [2] *N*-Triethyl-*B*-triphenylborazole (0·2 mol.) (Found: B, 8·2; N, 10·5%), m. p. 208—210°, obtained as in (1). [3] *B*-Triphenyl-*N*-tri-n-propylborazole (1·1 g.) (Found: B, 7·5; N, 9·7%), m. p. 170—171°, was separated by filtration of the distillation residue and washed with isopentane. The filtrate afforded a viscous non-cyclic boronamine (5·3 g.). n-Propylamine (0·7 g.) was trapped at −80° during the distillation. [4] *N*-Tri-n-butyl-*B*-triphenylborazole (1·1 g.) (Found: B, 6·7; N, 8·7%), m. p. 131·5—132·5°, was separated as in (3), and there was a viscous non-cyclic polyboronamine (16·1 g.). During the distillation n-butylamine (1·1 g.) was trapped. [5] Isobutylamine (2·4 g.), b. p. 69°, n_D^{20} 1·3968, was trapped at −80° during distillation. [6] Cold-trap condensate (−80°) of t-butylamine (0·77 g.). [7] $C_8H_{13}BN_2$ requires C, 64·9; H, 8·9; B, 7·3; N, 18·9%. [8] Calc. for $C_{10}H_{17}BN_2$: C, 68·3; H, 9·7; B, 6·1; N, 15·9%. [9] $C_{12}H_{21}BN_2$ requires C, 70·6; H, 10·4; B, 5·3; N, 13·7%. [10] $C_{14}H_{25}BN_2$ requires C, 72·4; H, 10·9; B, 4·7; N, 12·1%.

TABLE 2.

Pyrolysis of di(alkylamino)phenylborons, giving (*a*) *N*-trialkyl-*B*-triphenylborazole and (*b*) polyboronamine.

Alkyl	Temp.	Amine eliminated (mol.*)	Recovery † (mol.)	Distillation residue
Me	250° (½ hr.)	2·85	0·0	(*a*) 12·9 g., 0·97 mol. (Found: C, 72·0; H, 7·1; B, 9·2; N, 11·9. Calc. for $C_{21}H_{24}B_3N_3$: C, 71·9; H, 6·9; B, 9·3; N, 12·0%), m. p. 275—276°.
Et	260° (8 hr.)	2·9	0·0	(*a*) 13·79 g., 0·99 mol. (Found: C, 73·3; H, 7·7; B, 8·2; N, 10·7. Calc. for $C_{24}H_{30}B_3N_3$: C, 73·4; H, 7·7; B, 8·2; N, 10·7%), m. p. 209·5—211°.
Pr^n	275° (30 hr.)	1·4	0·0	(*a*) 2·5 g., 0·25 mol. (Found: C, 74·7; H, 8·4; B, 7·5; N, 9·7. $C_{27}H_{36}B_3N_3$ requires C, 74·5; H, 8·3; B, 7·5; N, 9·7%), m. p. 170—171°; (*b*) 9·7 g., 70% (Found: B, 5·6; N, 13·0%).
Pr^i	265° (50 hr.)	0·65	0·59	(*b*) 3·8 g., 30% (Found: B, 6·3; N, 11·1%).
Bu^n	310° (50 hr.)	2·24	0·0	(*a*) 2·7 g., 0·19 mol. (Found: C, 74·4; H, 8·8; B, 6·8; N, 9·0. $C_{30}H_{42}B_3N_3$ requires C, 75·5; H, 8·9; B, 6·8; N, 8·8%), m. p. 131—132°; (*b*) 10·3 g., 50·5% (Found: B, 6·5; N, 12·4%).
Bu^i	280° (50 hr.)	2·40	0·12	(*b*) 8·5 g., 63% (Found: B, 6·6; N, 12·0%).
Bu^s	290° (50 hr.)	0·89	0·54	(*b*) 10·28 g., 35·8% (Found: B, 6·1; N, 11·9%).
Bu^t	280° (50 hr.)	0·12	0·77	(*b*) 4·94 g., 23·5% (Found: B, 5·2; N, 11·5%).

* Based on $3Ph{\cdot}B(NHR)_2 \longrightarrow 3R{\cdot}NH_2 + (PhBNR)_3$. Amine identified by conversion into hydrochloride or by gas chromatography.

† Dialkylaminophenylborons identified by elementary analysis, physical constants, and infrared spectra.

Viscosities of the condensates showed chain lengths of only 20—40 units; the condensates were thermally stable up to 350°, but were fairly easily hydrolysed.

---

[3] Burch, Gerrard, Goldstein, Mooney, and Willis, unpublished work.

The non-cyclic polycondensation is attributed to steric hindrance. There is evidence [4] that the borazole ring is planar; ultraviolet spectra of *B*-trimethyl-*N*-triphenylborazole and *N*-triphenylborazole suggest that the plane of the *N*-phenyl group is perpendicular to that of the ring,[5] and the limited space between the *N*-phenyl groups would account for the decreased yields of the *B*-alkyl-*N*-triphenylborazoles from *B*-trichloro-*N*-triphenylborazole caused by increased branching of the alkyl group.[6] In the present cases the phenyl groups are on boron, but it is plausible that branching on the alkyl group of the amine will introduce a critical steric factor. The ease of condensation for branched alkylamine groups is in the order $Bu^i > Bu^s \approx Pr^i > Bu^t$ (Table 2), where the effect of the branching is evident.

Di(alkylamino)phenylborons undergo transamination and this was found to be a suitable procedure for the preparation of dicyclohexylaminophenylboron: $Ph{\cdot}B(NHR)_2 + 2R'{\cdot}NH_2 \longrightarrow Ph{\cdot}B(NHR')_2 + 2R{\cdot}NH_2$.

Similarly they undergo alcoholysis, $Ph{\cdot}B(NHR)_2 + 2R'OH \longrightarrow Ph{\cdot}B(OR')_2 + R{\cdot}NH_2$, and this is a useful method for the preparation of dialkylphenylboronates (Table 3), especially di-t-butyl phenylboronate (previously prepared by interaction of t-butyl alcohol with phenylboron dichloride in the presence of pyridine [7]).

Infrared examination of di(alkylamino)phenylborons [3] has revealed characteristic NH stretching, BN stretching, and BN deformation bands; the last two vibrational modes occur in a frequency range different from that for the same modes of cyclic borazoles (Table 4). Comparison of the spectra of di(ethylamino)phenylboron and *N*-triethyl-*B*-triphenylborazole shows the differences in the NH and BN modes. Comparison of the spectra of di(isopropylamino)phenylboron and the condensation product from the same material show the presence of an NH stretching band, the normal BN stretching of non-cyclic boronamines, and the BN chain deformation modes (Table 4).

TABLE 3.

Alcoholysis of di(alkylamino)phenylborons, $(R{\cdot}NH)_2BPh$.

				Dialkyl phenylboronate $Ph{\cdot}B(OR')_2$			
R	R′ in R′OH	Amine collected (mol.)	Identity of amine	Yield (mol.)	B. p./mm.	Found B (%)	n_D^{20}
Bu^n	Bu^n	1·9	B. p. 78°, n_D^{20}, 1·402	0·94	118°/0·1	4·6 *	1·4750
Pr^i	Bu^i	1·9	R.R.T. 0·205 †	0·89	140—141°/21	4·6 *	1·4709
Pr^i	Bu^s	2·0	R.R.T. 0·20 †	0·90	114—116°/12	4·7 *	1·4658
Me	Bu^t	1·8	Hydrochloride	0·79	119—120°/17	4·7 *	1·4628
Me	Pr^i	1·9	Hydrochloride	0·64	108—109°/20	5·2 §	1·4636

* Calc. for $C_{14}H_{23}BO_2$: B, 4·6%. † Relative retention time (C_6H_6 1·00) on a 30% Nujol–Celite column at 43° with N_2 flow 2·0 l./hr. § Calc. for $C_{12}H_{19}BO_2$: B, 5·3%.

TABLE 4.

NH stretching and BN stretching and deformational frequencies (cm.$^{-1}$) of dialkylaminophenylborons and the linear and cyclic condensates.

	NH stretch.	BN stretch.	BN deform.
$(Et{\cdot}NH)_2BPh$	3441, 3421	1511, 1495	657, 643
Borazole	—	1427, 1416	746, 736
$Pr^i{\cdot}NH)_2BPh$	3428, 3405	1497, 1490	662, 645
Linear condensate	3429, 3409sh, 3389sh	1527, 1490	673, 646

---

[4] Coffin and Bauer, *J. Phys. Chem.*, 1955, **59**, 193; Coursen and Hoard, *J. Amer. Chem. Soc.*, 1952, **74**, 1742; Price, Frazer, Robinson, and Longuet-Higgins, *Discuss. Faraday Soc.*, 1950, **9**, 131; Rector, Schaeffer, and Platt, *J. Chem. Phys.*, 1949, **17**, 460.

[5] Becker and Frick, *Angew. Chem.*, 1955, **67**, 711; *Z. phys. Chem.* (*Frankfurt*), 1957, **12**, 241.

[6] Groszos and Stafiej, *J. Amer. Chem. Soc.*, 1958, **80**, 1357.

[7] Brindley, Gerrard, and Lappert, *J.*, 1955, 2956.

EXPERIMENTAL

Preparation of Di(alkylamino)phenylborons.—The amine (4·0 mol.) was added dropwise to phenylboron dichloride[8] (50 g., 1·0 mol.) in ether (~250 ml.). The alkylammonium chloride was filtered off, and the filtrate gave the di(alkylamino)phenylboron (Table 1). Methylamine and ethylamine were distilled and condensed (−80°) into the ethereal solution of phenylboron dichloride.

Pyrolysis of Di(alkylamino)phenylborons.—The aminoborons were heated under reflux (Table 2), and, after cooling, the amines eliminated were removed at 0·5 mm. and trapped at −80°. The pyrolysed liquid was distilled to remove unchanged material and leave the non-cyclic polyboronamine. When the alkyl group was Me, Et, Pr^n, or Bu^n, the cyclic borazole was removed by filtration and washed with isopentane; the polyboronamine was then obtained on removal of the solvent.

Alcoholysis of Di(alkylamino)phenylborons.—The alcohol (7—10 g., 2·0 mol.) and di(alkylamino)phenylboron (1·0 mol.) were refluxed for 1—3 hr. (7 hr. for the t-butyl compound), and the amine removed at 15 mm. and condensed at −80°. Distillation of the residue gave the dialkyl phenylboronate (Table 4).

Interaction of Cyclohexylamine with Di(isobutylamino)phenylboron.—Cyclohexylamine (22·8 g., 3·0 mol.) was added to the boron compound (17·8 g., 1·0 mol.), and the mixture heated under reflux for 15 min. Fractionation then afforded isobutylamine (11·1 g., 1·98 mol.), b. p. 69°, n_D^{20}, 1·3970, whose identity was confirmed by the gas-chromatographic retention time 0·53 (n-butylamine 1·00) on 30% diethanolamine–Celite at 70° with a nitrogen flow of 2·1 l./hr. The residue from distillation at 0·1 mm. gave cyclohexylamine (8·4 g., 1·1 mol.), n_D^{20} 1·459, trapped at −80°, and fractionation afford *di(cyclohexylamino)phenylboron* (18·8 g., 0·86 mol.), b. p. 144—145°/0·05 mm., n_D^{20} 1·5291 (Found: C, 76·1; H, 10·3; B, 3·9; N, 9·8. $C_{18}H_{29}BN_2$ requires C, 76·0; H, 10·3; B, 3·8; N, 9·9%).

This work was presented in part at the Symposium on Inorganic Polymers, Nottingham, July, 1961.

NORTHERN POLYTECHNIC, HOLLOWAY ROAD, LONDON, N.7. [*Received, November 7th*, 1961.]

---

[8] Burch, Gerrard, Howarth, and Mooney, *J.*, 1960, 4916.