

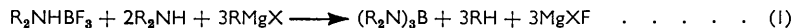
339. Steric Hindrance to Replacement in Boron Trichloride.

By D. W. AUBREY, W. GERRARD, and E. F. MOONEY.

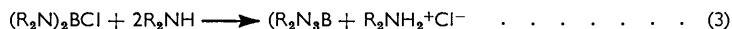
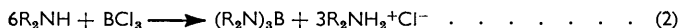
Steric hindrance during the course of replacement of chlorine in boron trichloride to form trisdialkylaminoborons $(R_2N)_3B$ has been demonstrated. If the alkyl group of the secondary amine is branched in the α -position, *e.g.*, if it is di-isopropylamine, di-*s*-butylamine, and dicyclohexylamine, then only the bisdialkylaminoboron chlorides $(R_2N)_2BCl$ are formed; diphenylamine also gave the bisdiphenylaminoboron chloride. Di-isobutylamine, branching in the β -position, afforded the trisdi-isobutylaminoboron, although replacement of the last chlorine was slow.

The steric effect is further demonstrated by the formation of bis(di-isopropylamino)dialkylaminoborons $R_2N \cdot B(NPr^i)_2$ ($R = Me$ and Et) and bis(di-isopropylamino)alkylaminoborons $R \cdot NH \cdot B(NPr^i)_2$ ($R = Me, Et, Pr^a, Pr^i, \text{ or } Bu^a$). The latter compounds are thermally stable, showing no evidence of polycondensation; factors controlling the condensation and hydrolysis of aminoborons are considered.

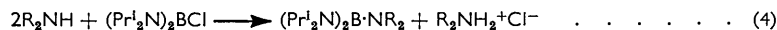
TRISDIALKYLAMINOBORONS $(R_2N)_3B$ have been prepared by the interaction of boron trichloride with an excess of secondary amine ($R = Me, Et, Pr^a, Bu^a, Bu^i, \text{ and } Ph \cdot CH_2$) have now been prepared by reaction (2). The formation of the isobutyl compound $(Bu^i_2N)_3B$ was slow; initially only 2 mol. of di-isobutylammonium chloride were obtained, but during 10 days a



further mol. was formed; reaction (3) is very slow. If there is branching on the α -carbon atom of the alkylamino-group, then reaction (3) does not occur. When $R = Pr^i$, the chloride $(Pr^i_2N)_2BCl$ was recovered from its mixture with di-isopropylamine (2.0 mol.) (0.94 mol. after 13 days at room temperature, 0.89 mol. after 4 hours at 290°). This demonstrates steric hindrance to replacement at a tervalent boron atom, as exemplified by formation of certain mixed dialkylaminobisdi-isopropylaminoborons and alkylamino-bisdi-isopropylaminoborons in high yields by reactions (4) and (5) (see Table).



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The type of condensation (6) of trismonoalkylaminoborons $(R \cdot NH)_3B$ to afford

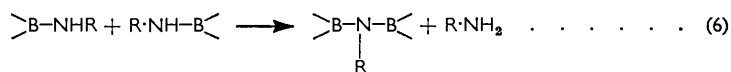
¹ Wiberg and Schuster, *Z. anorg. Chem.*, 1933, **213**, 77.

² Skinner and Smith, *J.*, 1953, 4025.

³ Gerrard, Lappert, and Pearce, *J.*, 1957, 381.

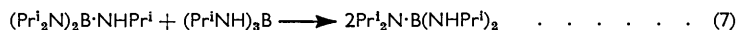
⁴ Dornow and Gehrt, *Z. anorg. Chem.*, 1958, **294**, 81.

borazoles,⁵ and the condensation of tris-*B*-alkylaminoborazoles to give polyborazoles,^{5,6} do not occur when alkylaminobisdi-isopropylaminoborons are heated under reflux. After



4 hours the recovery was 99% for R = Me (300°) or Prⁿ (315°), 91% for Prⁱ (250°), and 85% for Buⁿ (330°). *n*-Propylaminobisdi-*n*-propylaminoboron was not so stable: after 4 hours at 250° there was only a 70% recovery, and trisdi-*n*-propylaminoboron was also formed.

The resistance to condensation just mentioned may be due to steric effects, but electronic factors cannot be neglected. Certainly the electron-releasing propensity of the di-isopropylamine groups would discourage the formation of the quadricovalent transition state, the intermediate suggested for displacement reactions of trivalent boron compounds.⁷ The importance of the electronic factors is further demonstrated in that there was no exchange between the isopropylaminobisdi-isopropylaminoboron and trisisopropylaminoboron which might have been expected to afford the di-isopropylaminobisisopropylaminoboron (reaction 7). It has been shown that the dialkylamino-groups are readily



replaced by monoalkylamino-groups, *e.g.*, in the formation of *B*-monoalkylaminoboroxole⁷ and in the interaction of diethylaminoboron and diphenylaminoboron dichloride with primary amines.⁸

Similar electronic effects can be used to explain the stability of the trisdialkylaminoborons to hydrolysis and alcoholysis. The ready hydrolysis and butanolysis of trisdiethylaminoborons has been demonstrated,³ but the trisdi-isobutylaminoboron is not hydrolysed by water, nor does it undergo alcoholysis with methanol, *n*-, iso-, *s*-, or *t*-butyl alcohol; in comparison, the tris-*N*-methylanilinoboron, in which the nucleophilic function of the nitrogen atoms is reduced by mesomerism with the aromatic nuclei, undergoes alcoholysis with *t*-butyl alcohol.

EXPERIMENTAL

Satisfactory analytical data were obtained for base hydrochlorides and recovered compounds.

Trisdialkylaminoborons.—These compounds (see Table) were generally prepared by addition of boron trichloride to the secondary amine.³ The following are special cases.

Trisdi-isobutylaminoboron. Boron trichloride (25.0 g., 1.0 mol.) and di-isobutylamine (165.0 g., 6.0 mol.) gave the amine hydrochloride (82.5 g., 2.33 mol.), which was filtered off. Solvent was removed at 20°/12 mm., and the residue crystallised during 10 days. The crude product was extracted by pentane, leaving more hydrochloride (14.54 g., 0.42 mol.), and after being washed with water and recrystallised from hexane, white crystalline trisdi-isobutylaminoboron, very soluble in benzene and chloroform, fairly soluble in pentane and hexane, and insoluble in water, methanol, and *t*-butyl alcohol, was obtained.

Trisdibenzylaminoboron. Boron trichloride (5.6 g., 1.0 mol.) in pentane (25 ml.) at -50° was added (5 min.) to dibenzylamine (56.4 g., 6.0 mol.) in the same solvent (200 ml.) at -80°. After 3 weeks at room temperature the insoluble material was filtered off; some dibenzylamine (9.5 g., 1.0 mol.) was recovered from the filtrate. The insoluble residue (13.9 g.) was washed with hot water to afford the insoluble product (6.0 g., 76%) (Found: B, 2.0; N, 6.8%), which on recrystallisation from benzene afforded pure crystals, insoluble in ether and pentane, sparingly soluble in benzene, and soluble in chloroform. Dibenzylamine hydrochloride (7.97 g., 2.6 mol.) was recovered from the aqueous extract.

⁵ Aubrey and Lappert, *J.*, 1959, 2927.

⁶ Gerrard and Mooney, cited by Gerrard, "High-temperature Resistance and Thermal Degradation of Polymers," London, 1960, S.C.I. Monograph, No. 13, p. 328.

⁷ Aubrey and Lappert, *Proc. Chem. Soc.*, 1960, 148.

⁸ Gerrard, Hudson, and Mooney, *J.*, 1962, 113.

Preparation of aminoboron derivatives (R₂N)₂BX.

R	X	Yield (%)	B. p./mm. (or m. p.)	Formula	Found (%)			Required (%)			<i>n</i> _D ²⁰	<i>d</i> ₄ ²⁰
					B	N	M	B	N	M		
Et	Et ₂ N	93	52°/0.2	C ₁₂ H ₃₀ BN ₃	4.8	18.5		4.8	18.5*		1.4460	0.8240
Pr ^a	Pr ^a ₂ N	92	101°/0.15	C ₁₈ H ₄₂ BN ₃	3.4	13.5	305	3.5	13.5	311	1.4576	0.8462
Bu ^a	Bu ^a ₂ N	90	139°/0.2	C ₂₄ H ₅₄ BN ₃	2.8	10.6		2.7	10.6*		1.4584	0.8409
Bu ^l	Bu ^l ₂ N	53	141°/0.2	„	2.7	10.5	375	2.7	10.6	395		
		(129—129.5°)										
Ph·CH ₂	(Ph·CH ₂) ₂ N	76	(266—268°)	C ₄₂ H ₄₂ BN ₃	1.8	6.9	555	1.8	7.0	600		
Pr ^l	Cl	91 ^a	55°/0.08	C ₁₂ H ₂₈ BClN ₂	4.5	11.2 ^d	249	4.4	11.4	247	1.4560	0.9031
Bu ^e	Cl	98 ^b	121°/0.15	C ₁₆ H ₃₆ BClN ₂	3.7	9.2 ^e	302	3.6	9.3	303	1.4556	0.9212
C ₆ H ₁₁	Cl	92 ^c	(116°)	C ₂₄ H ₄₄ BClN ₂	2.7	6.9 ^f	398	2.7	6.9	407		
Ph	Cl	65	192°/0.06	C ₂₄ H ₂₀ BClN ₂	2.9	7.1 ^g	389	2.8	7.3	383		
Pr ^l	Me ₂ N	91	73°/0.7	C ₁₄ H ₃₄ BN ₃	4.3	16.4	269	4.3	16.4	255	1.4589	0.8523
Pr ^l	Et ₂ N	91	110°/4.5	C ₁₆ H ₃₈ BN ₃	3.8	14.8	288	3.8	14.9	283		
		(76—78°)										
Pr ^l	Me·NH	96	83°/2.3	C ₁₃ H ₃₂ BN ₃	4.5	17.1	252	4.5	17.5	241	1.4562 †	0.8494 †
Pr ^l	Et·NH	94	62°/0.05	C ₁₄ H ₃₄ BN ₃	4.3	16.3	256	4.2	16.5	255	1.4566	0.8525
Pr ^l	Pr ^a ·NH	95	92°/0.9	C ₁₅ H ₃₆ BN ₃	3.9	15.4	260	4.0	15.6	269	1.4554 †	0.8456 †
Pr ^l	Pr ^l ·NH	88	62°/0.2	„	4.1	15.6	268	4.0	15.6	269	1.4565	0.8492
Pr ^l	Bu ^a ·NH	99	108°/0.5	C ₁₆ H ₃₈ BN ₃	3.8	14.7	304	3.8	14.8	283	1.4562 †	0.8438 †

* Calc. † Measured at 25°.

^a Di-isopropylammonium chloride (2.04 mol.) (Found: Cl, 25.2; N, 10.5%) obtained. ^b Di-isobutylammonium chloride (2.01 mol.) (Found: Cl, 20.2; N, 8.5%) separated, and di-isobutylamine (11.9 g., 1.01 mol.), b. p. 132°, was obtained on distillation of product. ^c Dicyclohexylammonium chloride (2.04 mol.) (Found: Cl, 16.2; N, 6.4%) separated and unreacted dicyclohexylamine (15.88 g., 1.94 mol.), *n*_D²⁰ 1.4836, recovered on distillation of product. Cl analyses were as follows for (d), (e), (f), and (g), respectively: Found, 14.2, 11.7, 8.8, 9.1. Req'd., 14.4, 11.7, 8.8, 9.3%.

Bisdialkylaminoboron Chlorides.—Boron trichloride (1.0 mol.) was added to the secondary amine (6.0 mol.) as described above. The precipitated amine hydrochloride (only 2.0 mol.) was filtered off. Distillation of the filtrate afforded an excess of amine and the bisdialkylaminoboron chloride (Table).

Bisdi-*n*-propylaminoboron Chloride.—Boron trichloride (20.8 g., 1.0 mol.) in pentane (25 ml.) at -50° was added to di-*n*-propylamine (35.7 g., 2.0 mol.) and triethylamine (35.7 g., 2.0 mol.) in the same solvent (250 ml.) at -80°. After attaining room temperature, the insoluble triethylammonium chloride (48.0 g., 1.97 mol.) was filtered off. The filtrate afforded a pale brown liquid (37.46 g.) at 20°/10 mm., and two distillations gave bisdi-*n*-propylaminoboron chloride (12.3 g., 47.2%) (Found: B, 4.4; Cl, 14.0; N, 11.5%; M, 268. C₁₂H₂₈BClN₂ requires B, 4.4; Cl, 14.4; N, 11.4%; M, 247), b. p. 86°/0.15 mm., *n*_D²⁰ 1.4558, *d*₄²⁰ 0.9051.

Alkylaminobisdi-isopropylaminoborons.—These compounds (see Table) were prepared by addition of the amine (2.0 mol.) to bisdi-isopropylaminoboron chloride (1.0 mol.) in pentane. For the ethylamino-derivative the amine (1.0 mol.) and triethylamine (1.0 mol.) were added to the chloride in the solvent; for the isopropylamino-analogue the chloride in solvent was added to isopropylamine (1.0 mol.) and triethylamine (1.0 mol.). In all cases the insoluble hydrochloride was filtered off and distillation of the filtrate afforded the product.

***n*-Propylaminobisdi-*n*-propylaminoboron.**—*n*-Propylamine (1.7 g., 1.0 mol.) and triethylamine (2.9 g., 1.0 mol.) were added to bisdi-*n*-propylaminoboron chloride (7.1 g., 1.0 mol.) as above. Triethylammonium chloride (3.8 g., 0.95 mol.) was filtered off; the filtrate gave a colourless liquid (7.8 g.). Distillation of part (7.1 g.) of the latter gave bisdi-*n*-propylaminoboron chloride (0.2 g.) and *n*-propylaminobisdi-*n*-propylaminoboron (4.9 g., 64%) (Found: B, 4.1; N, 15.2. C₁₅H₃₆BN₃ requires B, 4.0; N, 15.6%), b. p. 95°/0.2 mm., *d*₄²⁰ 0.8375, *n*_D²⁰ 1.4523, and a third fraction of trisdi-*n*-propylaminoboron (1.1 g.) (Found: B, 3.5; N, 13.3%), b. p. 101—103°/0.15 mm., *n*_D²⁰ 1.4568.

Dialkylaminobisdi-isopropylaminoborons.—These compounds (see Table) were prepared by addition of the secondary amine (2.0 mol.) in pentane to bisdi-isopropylaminoboron chloride (1.0 mol.) in the same solvent. Filtration from the amine hydrochloride (1.0 mol.) and fractional distillation afforded the product.

Stability of Trisdi-isobutylaminoboron to Hydrolysis.—The compound (0.87 g.) was heated in a steam-distillation apparatus for 4 hr. No amine was present in the distillate, but part of the starting material (0.22 g.) was recovered on filtration of the steam-distillate.

Attempted Alcoholysis of Trisdi-isobutylaminoboron.—The compound (1.0 mol.) was boiled with each of the alcohols, n-butyl, isobutyl, s-butyl, and t-butyl (3.0 mol.), for 2 hr. Except in the last, it dissolved, and on distillation was quantitatively recovered as a white crystalline residue, the alcohol being almost quantitatively isolated.

Stability of Diethylaminobisdi-isopropylaminoboron to Hydrolysis.—The compound (0.48 g.) and water (50 ml.) were set aside, with frequent shaking, for 7 days; the compound (0.48 g.) was recovered on filtration; no boric acid was detected in the filtrate. The compound (0.53 g.) was heated in a steam-distillation apparatus for 15 min.; much of it distilled unchanged (0.45 g.). The boric acid in the distillation flask was titrated and corresponded to 0.06 g. of starting material. Hydrolysis was complete on 4 hours' boiling in water.

Pyrolysis of Alkylaminobisdialkylaminoborons.—The compounds are thermally stable up to 300° and were recovered in good yield after 4 hr.

Bisdi-n-propylamino-n-propylaminoboron (3.3 g., 1.0 mol.) was maintained under reflux at 240–250° for 4 hr. Distillation then afforded starting material (2.2 g., 0.7 mol.) and trisdi-n-propylaminoboron (0.7 g., 0.18 mol.) (Found: B, 3.4%), b. p. 100–102°/0.15 mm., n_D^{20} 1.4570.

Attempted Preparation of Di-isopropylaminobisisopropylaminoboron.—Trisisopropylaminoboron⁵ (1.05 g., 1.0 mol.) was added to bisdi-isopropylaminoisopropylaminoboron (A) (1.52 g., 1.0 mol.); fractional distillation afforded trisisopropylaminoboron (0.95 g.) and material (A) (1.40 g.) (Found: B, 4.1%), b. p. 68°/0.09 mm., n_D^{20} 1.4537.

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