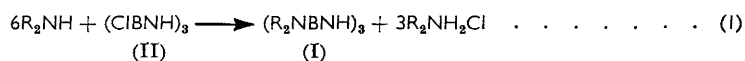


21. Preparation and Reactions of Dialkylaminoborazoles, and Reaction of Diethylaminoboron Dichloride with Primary Amines.

By W. GERRARD, H. R. HUDSON, and E. F. MOONEY.

The preparation of *B*-tris(dialkylaminoborazoles) by direct reaction of *B*-trichloroborazole and the secondary amine, and by base-exchange, is described. *B*-Trisdi-*s*-butylaminoborazole could not be thus prepared, polymerisation occurred spontaneously with the elimination of the amine; thermal polymerisation of other dialkylaminoborazoles involves elimination of the secondary amine. Reaction of diethylaminoboron dichloride and primary amines results in base exchange, with the formation of the *N*-substituted *B*-chloroborazole; the reaction is further complicated by aminolysis of the resultant chloroborazole.

B-TRISDIALKYLAMINOBORAZOLES (I), obtained by the interaction of the appropriate amine and *B*-trichloroborazole (II), have not previously been fully characterised.¹ Modes of formation of aminoborazoles, and the properties of them, are relevant to current researches into the production of borazole-based polymers. Reaction of diethylamine with *B*-trichloroborazole gave a quantitative yield of diethylammonium chloride; the low yield (57.5%) of compound (I; R = Et) in this reaction was a result of unavoidable polycon-



densation by elimination of amine. Reaction (1) afforded the borazoles (I; R = Me and Prⁱ), which were recrystallised from toluene or isopentane, and (I; R = Et, Prⁿ, Buⁿ, and Buⁱ), which were distilled (see Table 1). *B*-Trisdiphenylaminoborazole (I; R = Ph) could not be extracted from the precipitated diphenylammonium chloride, and the latter had to be removed by water. For the compound (I; R₂N = PhMeN) triethylamine was used for dehydrohalogenation.

The liquid products were very viscous; the borazole (I; R = Prⁿ) slowly crystallised and (I; R = Buⁱ) formed a wax. We could not isolate *B*-trisdi-*s*-butylaminoborazole, because of polycondensation.

Attempts to study the exchange of amino-groups attached to boron in the aminoborazoles (I) were complicated by polycondensation. *B*-Trisaminoborazole (I; R = H) was prepared by treating a benzene solution of the diethylamino-analogue (I; R = Et) with ammonia. Trisaminoborazole (I; R = H) could not be prepared from trichloroborazole and gaseous ammonia; only polymeric material was obtained.² Trisaminoborazole

¹ Gould, U.S.P. 2,754,177/1956.

² Gerrard, Mooney, and Rothenbury, unpublished work.

(I; R = H) could be stored for 10 months; but at 200–250° polycondensation occurred by elimination of ammonia. Di-n-butylamine replaced diethylamine from the base (I; R = Et) at 180°, but the yield was low (68%) owing to polycondensation during which di-n-butylamine was liberated. Analysis and infrared spectra showed that the borazole (I; R = Buⁿ) from this preparation was identical with that obtained from *B*-trichloroborazole and di-n-butylamine.

Although it was evident that di-s-butylamine replaced the amino-groups from trisdimethylaminoborazole (I; R = Me) at 140°, the corresponding compound (I; R = Bu^s) could not be isolated because of polycondensation. An indication of the hydrolytic stability of compounds (I) is given in Table 2 (cf. ref. 3).

TABLE 1.
B-Trisdialkylaminoborazoles prepared from *B*-trichloroborazole.

R ₂ N	Yield (%)	Found (%)					Required (%)					M. p. or b. p./mm.
		C	H	B	N	M	C	H	B	N	M	
Me ₂ N ^a ...	50.8	33.7	9.6	15.6	40.0	210	34.4	10.1	15.5	40.1	210	112–115°
Et ₂ N ^a	57.6	48.1	10.2	11.1	28.4	299	49.0	11.3	11.0	28.6	294	120°/0.1
Pr ⁿ ₂ N ...	47.0	56.7	11.8	8.6	22.4	372	57.2	12.0	8.6	22.2	378	32–35°
Pr ⁱ ₂ N ...	51.7	56.5	12.1	8.6	22.4	369	57.2	12.0	8.6	22.2	378	170–172°/0.4
Bu ⁿ ₂ N ...	42	62.3	12.2	7.2	18.2	440	62.4	12.4	7.0	18.2	462	138–143°
Bu ⁱ ₂ N ...	28	63.0	12.4	7.1	18.0	441	62.4	12.4	7.0	18.2	462	200°/0.05
PhMeN ^b ...	64	60.6*	7.2	8.1	21.1	398	63.7	6.9	8.2	21.2	396	47–52°
Ph ₂ N ^c ...	76	69.4*	6.3	5.7	14.2	—	74.3	5.7	5.6	14.4	—	167°/0.3

* With phenyl-substituted borazoles low carbon analyses are usually obtained.

^a Cf. refs. 1 and 9. ^b NEt₃ (3 mol.) used in prepn. ^c Cf. ref. 9. ^d With decomp.

Additional data are: Et₂N, *n*_D²⁰ 1.4728, *d*₄²⁰ 0.9160; Buⁿ₂N, *n*_D²⁰ 1.4720, *d*₄²⁰ 0.8986; Buⁱ₂N, *n*_D²⁰ 1.4690.

TABLE 2.
Stability of *B*-trisdialkylaminoborazoles to hydrolysis.

R ₂ N	Reagent	Found (%)		Hydro-lysis (%)	R ₂ N	Reagent	Found (%)		Hydro-lysis (%)
		B	N				B	N	
Me ₂ N	NaOH (hot) *	15.6	40.0	100	PhMeN	H ₂ O (hot) *	12.4	58.5	
Pr ⁱ ₂ N	H ₂ O (cold) †	5.3	10.4	55	Ph ₂ N	H ₂ O (hot) *	1.0	6.9	
Pr ⁱ ₂ N	H ₂ O (hot) †	8.8	22.2	100	Ph ₂ N	NaOH (hot) *	4.2	29.2	

* Under reflux (30 min.); amine and ammonia absorbed into 0.1N-acid; boric acid determined in residue by titration (phenolphthalein-mannitol).

† Borazole (I) shaken with cold water (30 min.) and filtered; nitrogen and boron determined in filtrate.

The ease of replacement by alkoxy of alkylamino-groups attached to boron has been shown.⁴ Results of the interaction between butan-1-ol and (I; R = Et) indicated the formation of *B*-n-butoxyborazole by presence of the characteristic NH stretching mode at 3546 cm.⁻¹, a strong BN ring vibration at 1504 cm.⁻¹, and a characteristic doublet at 714 and 705 cm.⁻¹ which occurs at higher frequency than in (I; R = Et) but not at such high frequencies as in *n*-butyl metaborate (735 and 720 cm.⁻¹).⁵ The sharp band at 1109 cm.⁻¹ for the diethylamino-compound (I; R = Et), attributed to C–N absorption, is absent, being replaced by a sharp band at 1181 cm.⁻¹ which is attributed to B–O absorption. It may be expected that in *B*-alkoxyborazoles the B–O frequency would be lower than that of alkyl metaborates (1486 cm.⁻¹) and alkyl borates (1346–1316 cm.⁻¹).⁶ Compounds

³ Gerrard, Mooney, and Pratt, cited by Gerrard at Symposium on "High-temperature Resistance and Thermal Degradation of Polymers," London, Sept., 1960, *J. Appl. Chem.*, Monographs, 1961, No. 13, 328.

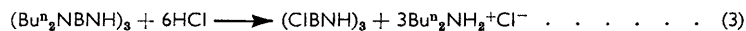
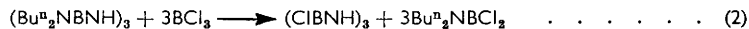
⁴ Gerrard, Lappert, and Pearce, (a) *J.*, 1957, 381; (b) *Chem. and Ind.*, 1958, 292.

⁵ Lappert, *J.*, 1958, 2790.

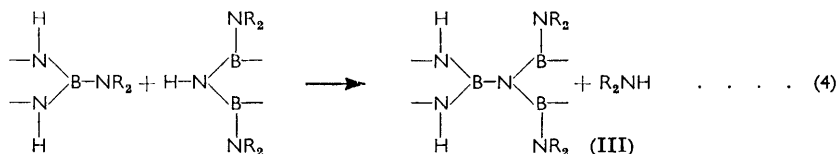
⁶ Werner and O'Brien, *Austral. J. Chem.*, 1955, 8, 355; 1956, 9, 137.

containing diethylamino-groups (very weak bands at 1232 and 1115 cm^{-1}) were also probably present in the product. However, the definite isolation of tri-*n*-butyl borate showed extensive ring rupture, and in addition there was a considerable amount of involatile polymeric material.

With boron trichloride, the aminoborazole (I; $\text{R} = \text{Bu}^n$) reacted as shown in (2), and with hydrogen chloride as in (3). It is postulated that the mechanism is a four-centre (broadside) approach of reactive centres, involving one transition state.

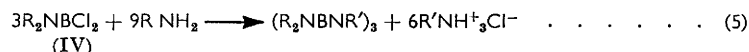


The pyrolysis of alkylaminoboron compounds usually results in the elimination of the primary amine.^{7, 8} We now describe a different type of elimination, which affords the secondary amine, and a new boron-nitrogen bond, thus joining two borazole rings together [scheme (4)]; this process occurs in definite steps, initially giving the polymer (III) which



in turn undergoes further polycondensation; this type of polymerisation also occurs on attempting to prepare the *s*-butyl compound (I; $\text{R} = \text{Bu}^s$) by direct interaction of tri-chloroborazole and di-*s*-butylamine or by base exchange. The polymer (III) still shows the characteristic BN ring deformation doublet 698 and 688 cm^{-1} , but on further elimination the doublet is lost, presumably owing to loss of symmetry of the ring system. The methyl-phenylamino- and diphenylamino-compounds (I) were more thermally stable.

Reaction of Aminoboron Dichlorides with Primary Amines.—It has been reported that *B*-trisdiethylamino-*N*-triethylborazole can be prepared by reaction of diethylaminoboron dichloride and ethylamine, a reaction which was formulated as a general one (5).⁹ A



number of dialkylaminoboron dichlorides have been described¹⁰⁻¹² and this appeared a convenient method of preparing trisdialkylaminoborazoles (I). We have not been able to confirm the generality of reaction (5), and indeed we present evidence of base exchange, resulting in the formation of the *B*-trichloroborazole $(\text{ClBNR}')_3$ which undergoes aminolysis with the added primary amine.¹ Reaction of compound (IV; $\text{R} = \text{Et}$) and ammonia gave ammonium chloride, diethylamine, and *B*-triaminoborazole which underwent polycondensation by elimination of ammonia. The absence of the diethylamino-group from the borazole produced was confirmed by the complete absence of CH_3 and CH_2 stretching and deformation modes. With *n*-butylamine or aniline, the diethylamino-group was found as diethylammonium chloride, and partly aminated *N*-tri-*n*-butyl- and *N*-triphenyl-*B*-trichloroborazoles were obtained. Reaction of ammonia (1.0 mol.) with compound (IV; $\text{R} = \text{Et}$) in methylene dichloride gave a mixture of diethylammonium chloride (1.0 mol.) and *B*-trichloroborazole (0.33 mol.). The reaction in presence of triethylamine gave triethylamine hydrochloride and the impure borazole (I; $\text{R} = \text{Et}$), as indicated from the analysis, although its spectrum was identical with that of the pure compound.

⁷ Aubrey and Lappert, *J.*, 1958, 2927.

⁸ Gerrard and Mooney, cited by Gerrard, see ref. 3.

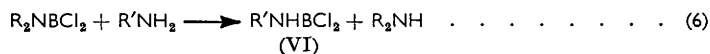
⁹ Niedenzu and Dawson, *J. Amer. Chem. Soc.*, 1959, **81**, 3561.

¹⁰ Gerrard and Lappert, *Chem. Rev.*, 1958, **58**, 1102.

¹¹ Niedenzu and Dawson, *J. Amer. Chem. Soc.*, 1959, **81**, 5553.

¹² Gerrard, Hudson, and Mooney, *J.*, 1960, 5168.

Diphenylaminoboron dichloride with *n*-butylamine gave a precipitate of *n*-butylaminoboron dichloride and *n*-butylammonium chloride, and a mixture of diphenylamine and diphenylammonium chloride was obtained from the ethereal filtrate. It is inferred that base exchange (6) occurs, and that the alkylaminoboron dichloride (V) is dehydrohalogenated by the secondary amine (6) to afford the *N*-trialkyl-*B*-trichloroborazole.



EXPERIMENTAL

The amines were dried and fractionally distilled, and pure *B*-trichloroborazole was prepared by a modification of that reported.¹³ Boron was determined by methanolysis, nitrogen by the Kjeldahl method, and chlorine potentiometrically with a silver-silver chloride electrode. Molecular weights were determined ebullioscopically in benzene solution.

Preparation of *B*-Trisdiethylaminoborazole.—*B*-Trichloroborazole (13.3 g., 1.0 mol.) was added to diethylamine (31.9 g., 6.0 mol.) in benzene (65 ml.), and the precipitated diethylammonium chloride (23.9 g., 3.0 mol.) (Found: Cl, 32.2; N, 12.8. Calc. for $C_4H_{12}ClN$: Cl, 32.4; N, 12.8%) was filtered off. Distillation of the filtrate gave *B*-trisdiethylaminoborazole (12.2 g., 57.5%), b. p. 120–136°/0.4 mm. (twice distilled, see Table I), and a dark polymeric residue (7.0 g.) (Found: B, 11.8; N, 29.2%). Di-*s*-butylamine (85.8 g., 6.4 mol.), added to the crude chloroborazole (19.1 g., 1.0 mol.) in toluene (250 ml.), gave the amine hydrochloride (53.3 g., 3.1 mol.) (Found: Cl, 21.4; N, 8.5. Calc. for $C_8H_{20}ClN$: Cl, 21.4; N, 8.5%) and, from the filtrate, at 0.1 mm., a viscous pasty residue (40.2 g.; loss in mass, 7.8 g.). Attempted distillation of the residue (bath finally at 300°) gave a bulky non-volatile polyaminoborazole (22.0 g.) (Found: B, 14.7; N, 25.9%), showing a loss of 1.86 mol. of amine per mol. of aminoborazole.

Aminolysis of *B*-Trisdialkylaminoborazoles.—(a) *Ammonia*. Ammonia was passed into the borazole (I; R = Et) (9.4 g., 1.0 mol.) in benzene (50 ml.). *B*-Triaminoborazole (3.3 g., 0.83 mol.) (Found: B, 25.8; N, 62.0.* $H_3B_3N_6$ requires B, 25.8; N, 66.9%) was precipitated as a yellow insoluble and infusible solid. The infrared spectrum showed the presence of a strong BN ring vibration at 1508 cm^{-1} and NH stretching bands at 3509, 3401, and 3185 cm^{-1} . On evaporation at 0.1 mm. the filtrate gave polymeric material (1.0 g.) (Found: B, 12.5; N, 23.8%) and a mixture (6.8 g.) (trapped at –80°) of diethylamine and benzene which with hydrogen chloride afforded diethylammonium chloride (4.2 g., 0.4 mol.) (Found: Cl, 32.3%).

(b) *Di-n-butylamine*. The amine (19.8 g., 4.5 mol.) and the borazole (I; R = Et) (10.1 g., 1.0 mol.) were heated at 110–180° for 2.5 hr.; diethylamine (6.7 g., 2.7 mol.), b. p. 56°, n_D^{20} 1.3852, was collected, together with a fraction (2.0 g.) of b. p. 56–158°, n_D^{20} 1.4110. Continued distillation at 0.05 mm. gave a condensate (–80°) of di-*n*-butylamine (5.8 g., 1.3 mol.), n_D^{20} 1.4180, a fore-run (0.5 g.), b. p. 30–200°/0.05 mm., the borazole (I; R = Buⁿ) (10.7 g., 68%) (Found: B, 7.1; N, 17.9%), b. p. 200°/0.05 mm., n_D^{20} 1.4718, and a viscous polymeric residue (3.0 g.) (Found: B, 9.6; N, 20.5. Calc. for loss of 0.96 mol. of di-*n*-butylamine; B, 9.6; N, 20.9%).

(c) *Di-s-butylamine*. Similarly a mixture of the borazole (I; R = Me) (4.9 g., 1.0 mol.) and the amine (9.1 g., 3.0 mol.) when heated under reflux at 140° for 2 hr. gave a condensate (–80°) of dimethylamine (1.06 g., 1.01 mol.) and di-*s*-butylamine (0.37 g., 0.12 mol.), identified by gas chromatography and converted into mixed hydrochlorides (Found: Cl, 37.8%). Distillation of the residue afforded di-*s*-butylamine (5.67 g., 1.87 mol.), b. p. 132–134°, n_D^{20} 1.4088 [converted into the hydrochloride (Found: Cl, 22.0%)], and at 180°/0.1 mm. further di-*s*-butylamine (1.82 g., 0.6 mol.), n_D^{20} 1.4114, was evolved with the formation of a brown polymer (3.3 g.) (Found: B, 19.3; N, 35.8. Calc. for loss of 2.28 mol. of di-*s*-butylamine: B, 19.3; N, 31.0%). There was a sublimate of *B*-trisdimethylaminoborazole (0.7 g.) (Found: B, 15.0%).

Reaction of Butan-1-ol with *B*-Trisdiethylaminoborazole.—The borazole (10.4 g., 1.0 mol.) and butan-1-ol (7.85 g., 3.0 mol.) were mixed at room temperature, the diethylamine [6.2 g., 2.6 mol.; n_D^{20} 1.3848; converted into its hydrochloride (Found: Cl, 32.4%) was removed at 10 mm. and trapped (–80°). The viscous residue gave tri-*n*-butyl borate (2.9 g., 0.36 mol.) (Found: B, 4.8. Calc. for $C_{12}H_{27}BO_3$: B, 4.7%), b. p. 70–80°/0.8 mm., n_D^{20} 1.4095, a liquid

* A low nitrogen value is usually obtained for material of this type.

¹³ Brown and Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 3699.

(0.9 g.) (Found: B, 4.6%), b. p. 80—150°/0.8 mm., n_D^{20} 1.4112, partly alkoxyated aminoborazole (2.5 g.) (Found: B, 9.8; N, 13.6%) (infrared spectrum, p. 114), and a polymeric residue (3.6 g.) (Found: B, 17.0; N, 27.1%).

Reaction of *B-Trisdi-n-butylaminoborazole* with *Boron Trichloride*.—Boron trichloride (5.0 g., 3.7 mol.) in methylene dichloride (10 ml.) at -80° was added dropwise to the aminoborazole (I; R = Buⁿ) (5.3 g., 1.0 mol.) in the same solvent (10 ml.) at -80° . The solvent and excess of boron trichloride were removed at 10 mm., to afford a brown mobile liquid (9.3 g.) which on being heated at 53°/0.8 mm., gave a white crystalline sublimate of trichloroborazole (1.2 g., 57%) (Found: B, 17.4; Cl, 54.7; N, 22.2%) and a colourless liquid distillate (6.2 g.) (Found: Cl, 36.5%), which afforded *di-n-butylaminoboron dichloride* (2.9 g., 40%) (Found: B, 5.2; Cl, 34.0; N, 6.6. C₈H₁₈BCl₂N requires B, 5.2; Cl, 33.8; N, 6.7%), b. p. 41°/0.1 mm., $n_D^{0.2}$ 1.4500.

Reaction of the Borazole (I; R = Buⁿ) with *Hydrogen Chloride*.—Hydrogen chloride was passed into a solution of the borazole (6.7 g., 1.0 mol.) in benzene (35 ml.) at room temperature. The crystalline precipitate (10.6 g.; calc. for 6 HCl, 9.9 g.) (Found: B, 4.5; Cl, 38.0; N, 10.9%) was filtered off, and evaporation of the filtrate at 0.1 mm. gave a solid (0.4 g.). At 80—100°/0.1 mm. the crystals (3.9 g.) gave a sublimate of trichloroborazole (0.62 g., 63%) (Found: B, 16.3; Cl, 55.1; N, 21.4. Calc. for H₃B₃Cl₃N₃: B, 17.4; Cl, 58.0; N, 22.9%), and a residue which afforded di-*n*-butylammonium chloride (1.73 g., 65%) (Found: Cl, 21.7; N, 8.3. Calc. for C₈H₂₀ClN: Cl, 21.4; N, 8.5%) on recrystallisation from methylene dichloride-*n*-pentane.

Pyrolysis of *Trisdialkylaminoborazoles*.—*B-Trisdiethylaminoborazole* (7.3 g., 1.0 mol.) was heated at 160—200°/0.01 mm. for 12 hr. and at 250—280° for 10 hr., affording a brown polymeric residue (A) (5.2 g.) (Found: B, 14.4; N, 30.8. Calc. for loss of 0.94 mol. of diethylamine: B, 14.4; N, 31.5%) and a condensate (-80°) (2.02 g.), n_D^{20} 1.3990, 1.49 g. of which gave the amine hydrochloride (1.77 g.) (Found: Cl, 33.0%); when recrystallised, this gave pure diethylammonium chloride (0.9 g.) (Found: Cl, 32.2%). Further pyrolysis of the residue (A) (4.8 g.) at 400° for 15 min. gave more amine (0.8 g.), n_D^{21} 1.3950, and an infusible polymeric residue (B) (3.9 g.) (Found: B, 18.3; N, 35.5. Calc. for loss of 1.61 mol. of diethylamine: B, 18.3; N, 34.9%), which (infrared) still contained the borazole ring, showing an NH stretching mode at 3570 cm.⁻¹, and a broad BN ring vibration centred on 1460 cm.⁻¹; the characteristic deformation doublet at 700 cm.⁻¹ was, however, absent. When kept at 400°/0.1 mm. for 13 hr. polymer (B) gave diethylamine (0.7 g.), n_D^{20} 1.3982, and a brown brittle polymer (2.0 g.) (Found: B, 22.6; N, 40.6. Calc. for loss of 2.05 mol. of diethylamine: B, 22.6; N, 38.6%), showing an infrared spectrum similar to that of material (B) but more diffuse. The final polymer was readily hydrolysed by distillation with water, the amine and ammonia being collected in 0.1N-acid (Found: N, 39.7%).

Similarly, *B-trisdi-isopropylaminoborazole* (18.0 g., 1.0 mol.) was heated 200—230° (33 hr.), the di-isopropylamine (4.0 g.), n_D^{21} 1.3962 [hydrochloride (Found: Cl, 25.6. Calc. for C₆H₁₆ClN: Cl, 25.8%), being trapped (-80°). The residue (12.7 g.) (Found: B, 11.9; N, 25.0. Calc. for loss of 1.03 mol. of di-isopropylamine: B, 11.9; N, 25.6%) was a brown transparent polyborazole resin, fusible at 200°; the infrared spectrum showed a NH stretching band at 3570 cm.⁻¹, a very strong BN ring mode centred on 1515 cm.⁻¹, and the characteristic ring deformation doublet in the 700 cm.⁻¹ region.

B-Triaminoborazole (I; R = H), prepared from the diethylamino-compound by base exchange, was unchanged on storage in a sealed tube for 10 months (Found: B, 25.6%), but on being heated at 10 mm. the borazole (1.0 g.) eliminated ammonia (Table 3).

Reaction of *Diethylaminoboron Dichloride* (IV; R = Et) with *Ammonia* or *Primary Amines*.—

TABLE 3.

Pyrolysis of *B-triaminoborazole*.

Temp.	Time of heating (hr.)	Total loss of NH ₃ (mol.)	Calc. (%) for loss of NH ₃		Found (%)	
			B	N	B	N
50°	5	0				
100	5	0.9				
200	6	1.1	30.5	64.4	30.2	58.5
250	8	1.6 *	33.1	62.7	31.2	57.3

* Actual loss of ammonia at this temperature was probably less (boron analysis suggests 1.25 mol.), as some solid had sublimed,

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n-Butylamine (3.8 g., 1.0 mol.) was added to compound (IV; R = Et) (8.1 g., 1.0 mol.) in methylene dichloride (50 ml.) at 15°. The crystalline precipitate (6.1 g.) was essentially diethylammonium chloride (Found, for recrystallised material: Cl, 32.3; N, 12.5. Calc. for $C_4H_{12}ClN$: Cl, 32.4; N, 12.8%); it was confirmed as diethylammonium chloride, and not n-butylammonium chloride, by its infrared spectrum. On evaporation the filtrate gave a semisolid residue (5.9 g.) (Found: B, 7.9; Cl, 29.7; N, 11.8%), of which (2.7 g.) gave a viscous liquid (1.8 g.) (extracted by n-pentane) of partly aminated *N*-tri-n-butyl-*B*-trichloroborazole (Found: B, 8.4; Cl, 27.2; N, 11.9. Calc. for $C_{12}H_{27}B_3Cl_3N_3$: B, 9.2; Cl, 30.2; N, 11.9%), showing the NH stretching band at 3530 and BN ring vibration at 1488 cm^{-1} .

When n-butylamine (10.3 g., 1.0 mol.) was added to the compound (IV; R = Et) (21.6 g., 1.0 mol.) (in n-pentane, 80 ml.) at 15°, diethylammonium chloride (15.7 g.) (Found, for material recrystallised from methylene dichloride: Cl, 31.9; N, 12.3%) was precipitated. At 10 mm. the filtrate afforded the partially aminated *N*-tri-n-butyl-*B*-trichloroborazole (Found: B, 8.3; Cl, 28.7; N, 11.9%), which on repeated distillation at 200°/1.0 mm. afforded a wax (1.55 g.) (Found: B, 8.6; Cl, 29.8; N, 11.5%) which was very difficult to handle because of its consistency.

n-Butylamine (7.1 g., 1.0 ml.) was added to a mixture of triethylamine (19.7 g., 2.0 mol.) and compound (IV; R = Et) (14.9 g., 1.0 mol.) in benzene (35 ml.). Triethylammonium chloride (26.2 g., 1.97 mol.) (Found: Cl, 25.8; N, 10.0%) was filtered off. Distillation of the filtrate afforded fractions, (i) (2.61 g.), b. p. 64°/0.3 mm. (Found: B, 5.2; N, 17.8%), (ii) a brown viscous liquid (3.66 g.), b. p. 150—170°/0.5 mm. (Found: B, 6.9; N, 16.9%), (iii) (0.67 g.), b. p. 170—176°/0.5 mm. (Found: B, 6.9; N, 16.8%), and (iv) a hard brown residue (4.87 g.) (Found: B, 9.2; N, 15.9%). Redistillation of fraction (ii) afforded a viscous liquid (0.5 g.), b. p. 120°/0.05 mm. (Found: B, 7.4; N, 16.9%), apparently a borazole derivative; but, from the complexity of the structure in the 1400 cm^{-1} region, some polymerisation had apparently occurred. None of these fractions was the pure *N*-tri-n-butyl-*B*-trisdiethylaminoborazole.

Aniline (2.87 g., 1.0 mol.) was added to compound (IV; R = Et) (4.75 g., 1.0 mol.) in n-pentane (13 ml.) and benzene (10 ml.) at 15°. Diethylammonium chloride (3.12 g., 92%) (Found: Cl, 31.8; N, 12.2%) was filtered off, and the filtrate afforded the off-white crystalline *B*-trichloro-*N*-triphenylborazole (4.26 g.) contaminated with some aminoborazole (Found: B, 7.4; Cl, 23.8; N, 10.1. Calc. for $C_{18}H_{15}B_3Cl_3N_3$: B, 7.9; Cl, 25.8; N, 10.2%); recrystallisation from benzene did not effect purification.

Similarly, aniline (8.7 g., 1.0 mol.) and compound (IV; R = Et) (14.8 g., 1.03 mol.) in benzene (50 ml.) gave a precipitate of diethylammonium chloride (5.4 g., 51%) (Found: Cl, 33.2; N, 12.5%). From the filtrate a crystalline residue (17.3 g.) (Found: B, 5.5; Cl, 24.7; N, 10.9%) was obtained, of which (16.1 g.) on recrystallisation from benzene gave a crystalline mixture (8.3 g.) of diethylammonium chloride (62%) and *B*-trichloro-*N*-triphenylborazole (38%) (Found: B, 3.0; Cl, 30.4; N, 11.9%), the presence of the amine hydrochloride being readily established from the presence of the NH stretching bands of the NH_2^+ group at 2513, 2427, and 1880 cm^{-1} . The filtrate residue (6.1 g.) (Found: B, 7.5; Cl, 21.4; N, 9.8%), of which (4.7 g.), when heated at 100°/0.01 mm. for 10.5 hr., gave a white sublimate of anilinium chloride (0.16 g.) (Found: Cl, 26.5%). At 200°/0.01 mm. (6.5 hr.) there was a sublimate of the slightly fuming, crystalline, partly aminated *B*-trichloro-*N*-triphenylborazole (1.44 g., 16%), m. p. 194—220° (decomp.) (Found: B, 7.7; Cl, 24.1; N, 10.4. Calc. for $C_{18}H_{15}B_3Cl_3N_3$: B, 7.9; Cl, 25.8; N, 10.2. Calc. for 5% replacement of chlorine by $Ph\cdot NHB$, 7.7; Cl, 24.1; N, 10.5%). Further heating at 200°/0.01 mm. for 25 hr. afforded a further sublimate (0.9 g.) (Found: B, 6.8; Cl, 19.8; N, 10.3%), and a pale brown residue of the *B*-anilino-*B*-chloro-*N*-triphenylborazole (Found: B, 9.6; Cl, 5.0; N, 11.0%), which showed NH stretching band at 3676 and BN ring vibration at 1416 cm^{-1} .

Ammonia (1.72 g., 1.0 mol.) in methylene dichloride (85 ml.) was added to the compound (IV; R = Et) (15.5 g., 1.0 mol.) in the same solvent (20 ml.). Removal of the solvent (10 mm.) afforded a white crystalline mixture (16.9 g.) of diethylammonium chloride (1 mol.) and *B*-trichloroborazole (0.33 mol.) (Found: B, 6.0; Cl, 41.2; N, 15.5%). Difficulty was experienced in separating the products; only a small amount of *B*-trichloroborazole (0.05 g.) (Found: Cl, 57.3. Calc. for $H_3B_3Cl_3N_3$: Cl, 57.8%) could be sublimed from the reaction mixture, but recrystallisation of the sublimation residue afforded diethylammonium chloride (5.3 g., 61%) (Found: Cl, 32.2; N, 12.8%), which substantiated the occurrence of the base-exchange reaction.

Ammonia (in excess) was passed into compound (IV; R = Et) (10.6 g., 1.0 mol.) in benzene (50 ml.); filtration afforded a mixture (10.0 g.) of ammonium chloride (3.0 mol.) and *B*-tri-aminoborazole (0.33 mol.) (Found: B, 6.8; Cl, 47.8; N, 37.6%). Infrared examination showed NH stretching bands at 3425, 3125, and 3021 cm^{-1} and a characteristic NH^+ stretching band of ammonium chloride at 1678 cm^{-1} and a BN ring vibration mode at 1408 cm^{-1} . The replacement of all the alkyl groups was shown by complete absence of CH stretching and deformation modes in 2925 and 1458–1380 cm^{-1} regions. Extraction with liquid ammonia effected a partial separation into a soluble (6.0 g.) (Found: Cl, 59.5%) and an insoluble portion (2.0 g.) (Found: Cl, 22.8%); the latter, when heated at 140–220°/0.1 mm. for 78 hr., afforded a sublimate of ammonium chloride (0.5 g.) (Found: Cl, 66.4; N, 26.3. Calc. for H_4ClN : Cl, 66.4; N, 26.3%) and a residue of aminopolyborazole (1.02 g.) (Found: B, 32.0; Cl, 1.3; N, 34.8%).

Preparation of Diphenylaminoboron Dichloride.—Diphenylammonium tetrachloroborate¹² (12.8 g., 1.0 mol.) was kept at 20–25°/0.01 mm. (27 hr.) to afford diphenylaminoboron dichloride (10.3 g., 1.0 mol.) (Found: B, 4.2; Cl, 28.1; N, 5.6. Calc. for $\text{C}_{12}\text{H}_{10}\text{BCl}_2\text{N}$: B, 4.3; Cl, 28.4; N, 5.6%), m. p. 64–67°, as a pale blue residue.

*Reaction of Diphenylaminoboron Dichloride with *n*-Butylamine.*—The amine (1.53 g., 1.0 mol.) was added to compound (IV; R = Ph) (5.22 g., 1.0 mol.) in methylene dichloride (15 ml.), giving a crystalline mixture (1.55 g.) of *n*-butylaminoboron dichloride and *n*-butylammonium chloride [Found: B, 4.2; Cl, 39.9; N, 10.4. Calc. for $\text{C}_4\text{H}_{10}\text{NCl}_2\text{B}$ (60%) plus $\text{C}_4\text{H}_{12}\text{ClN}$ (40%): B, 4.1; Cl, 40.5; N, 10.6%], which was filtered off. Infrared examination confirmed the identity of the components: NH stretching 3205, NH deformation 1565, and NBCl_2 mode 873 of BuNHBCl_2 ,¹⁴ and NH stretching mode of NH_3^+ at 2519 cm^{-1} . The filtrate afforded a pale-green crystalline mixture (5.3 g.) (Found: B, 3.2; Cl, 17.2; N, 7.7%) from which a mixture (2.2 g.) of diphenylamine and diphenylammonium chloride [Found: Cl, 12.8; N, 7.1. Calc. for $\text{C}_{12}\text{H}_{11}\text{N}$ (25%) and $\text{C}_{12}\text{H}_{12}\text{ClN}$ (75%): Cl, 12.9; N, 7.2%] was extracted with ether. Infrared examination confirmed the composition of the mixture, showing NH stretching 3460 and NH deformation 1597 of diphenylamine, and NH stretching modes of NH_2^+ 2688, 2577, 2481, 2049, 1988, and 1957 cm^{-1} of diphenylammonium chloride.

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¹⁴ Gerrard and Mooney, *J.*, 1960, 4028.