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The Reaction of Primary Amines with Boron Halides. Part II.¹ Arylamines. The Effect of *ortho*-substitution: Formation of Di-*B*-halogenoborazoles

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The course of the thermal or base-promoted dehydrohalogenation of the 1:1 adducts of primary arylamines and boron trichloride or boron tribromide is profoundly affected by *ortho*-substitution in the benzene nucleus. On heating in solution the 1:1 adducts of boron trichloride and aniline or *o*-toluidine give excellent yields of the corresponding tri-*B*-chloroborazole, but the evolutoin of hydrogen chloride follows different rate laws in the two cases.

On treatment with a suitable tertiary base aniline-boron trichloride is converted into the tri-*B*-chloroborazole, whereas *o*-toluidine-boron trichloride gives, besides the borazole, a compound $C_{14}H_{14}B_2Cl_2N_2$ which has been identified as 2,4-dichloro-3-*o*-tolyl-8-methyl-2,4-dibora-1,3-diazaronaphthalene.

The 1:1-adducts of 2,6-disubstituted anilines and boron trichloride readily lose one mole of hydrogen chloride on heating, with formation of the borazene, but thereafter reaction is slow, and the tri-*B*-chloroborazole is not formed. When the borazenes are treated with a suitable tertiary base the product is the dichloroborazole, *i.e.*, the product in which one B–CI linkage has been reduced to B–H. The mechanism of this unusual reaction, and the reactions of the diffunctional borazoles to which it gives rise, have been studied.

IN Part I of this Series ¹ we described the effects of steric hindrance upon the dehydrohalogenation of the I:I adducts of primary aliphatic amines and boron trichloride or boron tribromide. In this Paper we describe the effects of *ortho*-substitution upon the

dehydrohalogenation of the 1:1 adducts of primary aromatic amines.

In contrast to the behaviour of primary aliphatic

¹ Part I, H. S. Turner and R. J. Warne, J. Chem. Soc., 1965, 6421.

amines, the direct addition in solution of primary aromatic amines and boron trichloride or boron tribromide normally gives rise mainly to the 1:1 adducts (I; X = Cl or Br). Aniline itself and all the orthosubstituted anilines studied gave excellent yields, but it has been reported 2,3 that certain meta- and parasubstituted anilines give anomalous results. It has been claimed that in several cases impure arylaminoboron dichloride (II; X = Cl) may be recovered in low yield from the liquors from which the 1:1 adduct has been isolated, but the extent of the side reaction leading to the borazene is any in event small compared with that found with many aliphatic primary amines. The dehydrohalogenation of these adducts takes place quite readily when they are heated under suitable conditions, usually in solution. This reaction was first reported, for anilineboron trichloride, by Rideal,⁴ but was first recognised as leading to borazole formation by Jones and Kinney.⁵ In those aromatic amines with at least one unsubstituted ortho-position the reaction proceeds with the elimination of two molecules of hydrogen halide to form substantially pure sym-B-halogeno-N-arylborazole (IV).

A preliminary study of the kinetics of hydrogen chloride evolution from three arylamine-boron trichloride adducts in boiling benzene was made by Gerrard and Mooney.³ The 1:1 adducts studied by these workers are only slightly soluble in benzene, and the system was homogeneous only in the concluding stages; the last 10% of hydrogen chloride evolution was claimed to follow first-order kinetics. We have found that when toluene is used as solvent, the adduct dissolves before any appreciable hydrogen chloride evolution is detected, and the system is homogeneous throughout the reaction, allowing the effect of changes of concentration to be The results for several adducts are set followed. out in Figures 1, 2a and 2b. It is found for anilineboron trichloride, using the well-known relationship between the times taken to complete a definite fraction of the reaction at different initial concentrations,⁶ that hydrogen chloride evolution initially follows firstorder kinetics, but tends progressively towards secondorder kinetics as it proceeds (Table 1).

TABLE 1

Thermal elimination of hydrogen chloride from anilineboron trichloride: variation of order of reaction

Moles of HCl/mole adduct Order of reaction	$0.2 \\ 1.00$	0∙4 1∙16	$0.6 \\ 1.25$	$0.8 \\ 1.42$	${}^{1\cdot 0}_{1\cdot 52}$
Moles of HCl/mole adduct Order of reaction	$1.2 \\ 1.65$	$1.4 \\ 1.80$	1∙6 1∙91	$1.7 \\ 2.02$	

There is no point of inflexion in the reaction curve, and if the reaction is stopped after the elimination of ca. one mole of hydrogen chloride per mole of adduct the product is not anilinoboron dichloride, although the presence of this in small quantity cannot be ex-

- C. R. Kinney and C. L. Mahoney, J. Org. Chem., 1943, 8, 526.
 W. Gerrard and E. F. Mooney, J. Chem. Soc., 1960, 4028.
- 4 S. Rideal, Ber., 1889, 22, 992.
- ⁵ R. G. Jones and C. R. Kinney, J. Amer. Chem. Soc., 1939, **61**, 1378.

cluded, but instead a mixture of unchanged adduct and tri-B-chlorotri-N-phenylborazole.

The observed second-order kinetics cannot be accounted for by the common postulate ^{3,7} that hydrogen chloride is eliminated by two unimolecular steps (Equation 1).

$$\begin{array}{c} \mathsf{RNH}_{2},\mathsf{BX}_{3} \xrightarrow{-\mathsf{HX}} \mathsf{RNH} \cdot \mathsf{BX}_{2} \xrightarrow{-\mathsf{HX}} \mathsf{RNBX} \longrightarrow 1/3 (\mathsf{RNBX})_{3} \quad (1) \\ (\mathrm{II}) \quad (\mathrm{III}) \quad (\mathrm{IV}) \end{array}$$

It is possible that the conversion $(II) \longrightarrow (IV)$ (R = Ph) occurs by a series of bimolecular reactions with the formation of intermediates $H(RN \cdot BCI)_n CI$ (n = 2, 3), followed by a unimolecular ring closure (equation 2).

$$H(RN \cdot BCI)_{3}CI \longrightarrow HCI + (RNBCI)_{3}$$
(2)

FIGURES 1-2b Thermal dehydrochlorination of arylamineboron trichloride adducts, RNH2·BCl3



FIGURE 1 (1) R = Ph, 0.67M in boiling toluene; (2) R = Ph, 1.0M in boiling toluene; (3) R = o-tolyl, 0.67M in boiling toluene; (4) R = 2,6-xylyl, 0.33M in boiling benzene; (5) R = 2,6-xylyl, 1.0M in boiling benzene; (6) R = 2,6-Et₂C₆H₃, melt at $\sim 140^{\circ}$



⁶ See, e.g., Glasstone, "Textbook of Physical Chemistry," London, 2nd edn., 1948, p. 1066.

⁷ E.g., E. K. Mellon, jun. and J. J. Lagowski, Adv. Inorg. Chem. Radiochem., 1963, 5, 259; J. C. Sheldon and B. C. Smith, Quart. Rev., 1960, 14, 200.



The failure to isolate anilinoboron dichloride at an intermediate stage in the reaction is paralleled by the reaction of an excess of boron trichloride with trianilinoboron under mild conditions. Anilinoboron dichloride is not obtained, but aniline-boron trichloride and tri-*B*-chloro-tri-*N*-phenylborazole can be isolated from the product.

Tri-B-chlorotri-N-phenylborazole is also formed when the adduct is dehydrochlorinated by treatment with triethylamine (Equation 3). Attempts to prepare anilinoboron dichloride by using one equivalent of triethylamine merely gave a reduced yield of the borazole.

$$PhNH_{2},BCI_{3} + 2Et_{3}N \longrightarrow I/3(PhNBCI)_{3} + 2Et_{3}NHCI$$
(3)

When o-toluidine-boron trichloride is heated it appears to lose hydrogen chloride in two unimolecular steps (Figure 2a) with formation of the borazole; if the reaction is stopped after one mole of hydrogen chloride is evolved the borazene can be isolated in good yield by evaporation.

When o-toluidine-boron trichloride is dehydrochlorinated by treatment with triethylamine a more complex reaction takes place. Tri-B-chlorotri-N-o-tolylborazole is still formed, but the main identified product is a compound (V), C₁₄H₁₄B₂Cl₂N₂, m. p. 120-122°. We were unable to effect a clear-cut separation of compound (V) from the borazole by crystallisation alone, but by hand sorting of the crystals it was obtained in a pure state. Compound (V) is converted by action of dimethylamine in the presence of triethylamine into a dimethylamino derivative, $C_{14}H_{14}B_2N_2(NMe_2)_2$ (VI). If this reaction is carried out on the mixture of (V) with the borazole, compound (VI) may be separated from its mixture with tris-B-dimethylaminotri-N-o-tolylborazole by vacuum distillation. The most immediate indication that compound (V) is not a borazyne dimer $(C_7H_7NBCl)_2$ lies in the presence in the infrared (i.r.) spectrum of an N-H stretching band at 3445 cm.⁻¹. The chloroborazole reacts with cold water to give a suspension of the insoluble tri-B-hydroxytri-N-o-tolylborazole (see below), but under the same conditions compound (V) gives a clear solution which contains equimolar quantities of o-toluidine hydrochloride, boric acid, and the hydrochloride of an aminophenylboronic acid. When this solution is neutralised a white insoluble solid is precipitated; this may be purified by crystallisation from organic solvents, and is the anhydride of an aminophenylboronic acid, $(C_7H_8BNO)_n$ (VII). The value of n is dependent on solvent and concentration; it is least, ~ 1.8 , in boiling dimethoxyethane and highest, ~ 4.5 , in boiling benzene. The anhydride dissolves readily in aqueous acid and alkali, and from the solution in dilute hydrochloric acid the white crystalline hydrochloride $C_7H_{11}BClNO_2$ (VIII) is deposited; this is quantitatively reconverted by one equivalent of alkali into compound (VII). The anhydride is also regenerated from the solution in alkali upon neutralisation. It is hydrolysed in N-hydrochloric acid at 100° giving equimolar quantities of boric acid and o-toluidine.

Evidence on the structure of compound (V) was provided by experiments with deuterium and by nuclear magnetic resonance (n.m.r.) spectroscopy. Compound (V) was hydrolysed by deuterium oxide, and the o-toluidine recovered from the solution. After replacement of any deuterium in the amino group by exchange with isotopically normal dilute hydrochloric acid, the o-toluidine obtained had an i.r. spectrum identical with that of pure o-toluidine: the molecule contained no C-D bonds. It follows that compound (V) contains an o-CH₃·C₆H₄·N \leq residue, and from the ease of hydrolysis it is probable that the nitrogen atom is attached to two boron atoms. When the anhydride (VII) that had been prepared in water was hydrolysed in n-deuterium chloride-deuterium oxide at 100° the o-toluidine obtained, after removal of N-D bonds as before, was shown on the basis of the i.r. spectrum of the benzoyl derivative to be substituted by deuterium in the ring but not in the methyl group. o-Toluidine that had been treated with deuterium chloride-deuterium oxide under the same conditions was similarly substituted with deuterium: the significant result is the absence of deuterium from the methyl group in both cases. It follows that the second o-tolyl residue in compound (V) has the form (IX). That compound (V) has two methyl groups is borne out by a comparison of the i.r. spectra of (V), tri-B-chlorotri-N-o-tolylborazole, and o-toluidine: the C-H stretching regions are almost identical. The structure [(X); X = Cl] therefore seemed probable for compound (V) with $(X; X = NMe_2)$ for the dimethylamino-compound. The n.m.r. measurements give strong support to this structure.

Thus the proton magnetic resonance spectrum of (X; X = Cl) shows absorption in both the aromatic and methyl regions. There are two peaks, at τ 7.71 and τ 7.92, attributable to two types of methyl group

present in the molecule. The main aromatic absorption is centred about $\tau 2.83$. A smaller peak, with intensity corresponding to absorption by one aromatic proton, occurs at $\tau 2.04$. It is possible that an aromatic proton is deshielded by the anisotropy of a B-Cl bond. The



intensity ratio, aromatic protons : methyl protons, was 6.8:6, close to the theoretical ratio of 7:6 required for structure (X). No peak due to the -NH proton could be observed. However, in the case of borazole derivatives, it has been found 8 that when chlorine is bonded to the boron, the -NH peak is broadened so that it is barely observable.

The proton spectrum of (X; $X = NMe_2$) consists of a band centred about $\tau 2.96$ attributable to the aromatic protons, and four peaks attributable to methyl groups. Two of these peaks (τ 7.70 and 7.78) have intensities half those of each of the other peaks (τ 7.38 and 7.63). They may thus be assigned to the two types of C-methyl and the two types of N-methyl groups, respectively. A broad, weak peak at τ 4.87 may be assigned to the -NH proton. The ratio of intensities, aromatic protons : NH proton: methyl protons is 7:1.1:19.3, close to the theoretical ratio 7:1:18.

The spectrum of tri-B-chlorotri-N-o-tolylborazole consists of two peaks at τ 2.81, 7.79, attributable to the aromatic and methyl protons, respectively. These values of the chemical shift are close to those found for toluene ⁹ $(\tau 2.83, 7.68)$. The intensity ratio of 4.15:3 is close to the expected ratio of 4:3.

The spectrum of tris-B-dimethylaminotri-N-o-tolylborazole consists of an aromatic peak at 7 2.13, a C-methyl peak at τ 7.90 and a N-methyl peak at τ 8.42. The assignment of the methyl peaks is again made on the basis of peak intensities. The N-methyl absorption occurs at an appreciably higher value of the applied field than in compound (X; $X = NMe_2$). The N-methyl groups are shielded by the phenyl groups, which must lie perpendicular to the plane of the borazole ring.¹⁰

The structure (XI) proposed previously¹¹ for compound (V) does not agree with the spectral data. The intensity ratio, aromatic protons: alkyl protons, to be expected for structure (XI) would be 4:2 as against the experimental ratio of 6.8:6. In both (V) and (VI) the chemical shift of the alkyl protons is nearer that

of the methyl protons of toluene $(\tau 7.68^{9})$ than the methylene protons of indene ($\tau 6.67$ ⁹).

The ¹¹B chemical shifts of compound (V), (VI), and some relevant reference compounds are shown in Table 2.

Г	ABLE	2

nВ	Chemical	shifts	of	o-toly	l derivatives
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Compound	Chemical shift $(p.p.m.)$ (BCl ₃ = 0)	Bandwidth (p.p.m.)
(V)	+16.0	~ 20
(VI)	$+22 \cdot 2$	~ 25
Three co-ordinate compounds	;	
(o-C,H,NBCl),	+16.9	~ 12
(o-C,H,NBNMe,),	+16.7	~ 27
(o-C ₇ H ₇ NBOH) ₃	+26.8	~ 20
Four co-ordinate compounds		
(Me, NBCl.),	+38.5	~7
(Bu ^t NHBČl ₂) ₂	+43.3	

It is clear that compounds (V) and (VI) contain 3-coordinate boron. The bandwidth is such that the separation of the two structurally distinct three-co-ordinate boron atoms required by structure (X) would not be expected.



On the basis of these results it is believed that (X; X = Cl) is established as the structure of the compound (V). On this basis the hydrochloride (VIII) has the structure (XII) whereas structure (XI) would require (XIII). The n.m.r. spectrum of compound (VIII), dissolved in heavy water, consists of three peaks, due to the aromatic protons, the "exchangeable" protons, viz. the -NH₂ and hydroxyl protons, and to the methyl The chemical shifts measured relative to protons. sodium 3-(trimethylsilyl)propane-1-sulphonate as internal reference (τ 10.0) are τ 2.53, 5.02, and 7.57, respectively. The intensity ratio, aromatic protons: alkyl protons, is very close to 1:1 in agreement with structure (XII). Structure (XIII) would require this ratio to be 2:1.

Compound (V), structure (X; X = Cl), 2,4-dichloro-3-o-tolyl-8-methyl-2,4-dibora-1,3-diazaronaphthalene,

appears to be the second example of this ring system. 2,4-Diethyl-3-phenyl-2,4-dibora-1,3-diazaronaphthalene has been prepared by Köster and Iwasaki¹² by heating triethylborane, tetraethyldiborane, and phenylaminodiethylborane under pressure. The formation of our compound under the conditions we describe is remarkable. In a preliminary communication we suggested ¹³

⁸ K. Ito, H. Watanabe, and M. Kubo, J. Chem. Phys., 1961,

³⁴, 1043. ""High Resolution NMR Spectra Catalog," Varian Associ-

¹⁰ H. Watanabe and M. Kubo, J. Amer. Chem. Soc., 1960, 82, 2428.

¹¹ Report of the National Chemical Laboratory, HMSO, 1963,

^{25.} ¹² R. Köster and K. Iwasaki, A.C.S. Advances in Chemistry Series, No. 42, 1964, 148. ¹⁸ H. S. Turner, R. J. Warne, and I. J. Lawrenson, Chem.

Comm., 1965, 20.

that the borazene dimer (XIV) might be an intermediate. However, when authentic borazene dimer (obtained by dimerisation of the borazene prepared from o-toluidineboron trichloride by thermal elimination of one mole of hydrogen chloride) is treated with triethylamine, both borazole and compound (V) are formed, and the yield of the latter is less than in the direct preparation from the 1:1 adduct. The mechanism remains obscure.

In contrast to the behaviour of the 1:1 boron trichloride adducts of those arylamines with at least one unsubstituted ortho-position, the thermal dehydrochlorination of the adduct of 2,6-xylidine and other 2,6-disubstituted anilines does not give the corresponding trichloroborazole. One molecule of hydrogen chloride is initially eliminated from these adducts on heating, and the products are the corresponding borazenes (II; X = Cl). Thus the decomposition of 2,6-xylidine-boron trichloride occurs readily in solution and the rate of hydrogen chloride evolution is independent of the initial concentration of adduct (Figure 1). 2,6-Diethylaniline-boron trichloride decomposes only slowly in solution but readily in the molten state, when the reaction also follows first-order kinetics (Figure 2b). The rate of the reaction falls sharply when the equivalent of one molecule of hydrogen chloride per molecule of adduct has been removed. In the later stages boron trichloride is also evolved and in both cases the boronamines (XV) and (XVI) are formed.

RNH•BCI•NR•BCI2	RNH·BCI·NR·BCI·NHR	(RNH)2BCI
(XV)	(XVI)	(XVII)

The action of triethylamine on a (2,6-disubstituted)aniline-boron trichloride adduct in benzene leads to the formation of the corresponding bis(arylamino)boron chloride (XVII). The other products of the reaction (equation 4) are triethylammonium chloride and triethylammonium tetrachloroborate. When an excess of triethylamine is present, the tetrachloroborate ion is converted into the chloride ion and triethylamineboron trichloride: $BCl_4^- + Et_3N \longrightarrow Cl^- + Et_3N, BCl_3$. Bis-(2,6-xylidino)boron chloride is converted by treat-

$$2RNH_2,BCI_3 + 2Et_3N \longrightarrow (RNH)_2BCI + Et_3NHCI + Et_3NHBCI_4$$
(4)

ment with boron trichloride into 2,6-xylidinoboron dichloride and the boronamine (XVI). A similar transformation occurs when the reaction between triethylamine and 2,6-xylidine-boron trichloride is carried out under more drastic conditions, for example when toluene is used as solvent. A reduced yield of tetrachloroborate is obtained and some boronamine (XVI) is formed.

A related reaction is that between diethylaminoboron dichloride and 2,6-xylidine. Niedenzu and Dawson¹⁴ have claimed that *B*-dialkylaminoborazoles are formed by treatment of dialkylaminoboron dichlorides with primary amines. Gerrard, Hudson, and Mooney,¹⁵

14 K. Niedenzu and J. W. Dawson, J. Amer. Chem. Soc., 1959, 81, 3561.

however, found that the initial reaction was a base exchange which was followed by B-chloro- and B-aminoborazole formation; in particular, aniline and diethylaminoboron dichloride gave diethylammonium chloride, B-trichloro-N-triphenylborazole and B-anilino-B-chloro-N-triphenvl borazoles. If such a base exchange were to take place in the case of 2,6-xylidine, the primary product would be xylidinoboron dichloride (II), but instead the product isolated, even in the presence of an excess of diethylaminoboron dichloride, is bis(xylidino)boron chloride (XVII) (Equation 5).

$$2RNH_2 + Et_2NBCI_2 \longrightarrow (RNH)_2BCI + Et_2NH_2CI$$
(5)

The differences in behaviour between aniline and 2,6-dialkylanilines towards boron trichloride are most probably due to the steric effects of the alkyl substituents, since electronic effects would be expected to be small. Thus it could be argued that the formation of trichloroborazole from the corresponding 2,6-dialkylaniline-boron trichloride by the thermal reaction is prevented by the steric hindrance to ring formation exerted by the alkyl groups around the B-N bond. If, however, triethylamine is added to the solution of the borazene (II; X = Cl), triethylammonium chloride is slowly precipitated and the di-B-chlorotri-N-arylborazole (XVIII; R = aryl, X = Cl, Y = H) may be isolated from the solution.¹⁶ The boronamine (XVI) is obtained as a second product.

$$\begin{array}{ll} R & a: R = 2,6-xy|y|, X = CI, Y = H \\ XB & b: R = 2,6-xy|y|, X = OH, Y = H \\ I & c: R = 2,6-xy|y|, X = Y = OH \\ RN & NR & d: R = 2,6-xy|y|, X = Y = CI \\ B & f: R = 2,6-xy|y| \\ Y & f: R = 2,6-xy|y| \\ g: R = 2,6-xy|y| \\ g: R = 2,6-diethylphenyl \\ (XVIII) \end{array}$$

Thus it is clear that ring closure can occur under suitable conditions, and by a mechanism different from that involved in the thermal elimination reaction. The reaction with 2,6-xylidinoboron dichloride, leading to the formation of di-B-chlorotri-N-2,6-xylylborazole (XVIIIa), has been most thoroughly studied.

The formation of a dichloroborazole in this reaction involves the reduction of a B-Cl bond to a B-H bond, a reaction which normally requires strong reducing agents, in a system in which no conventional reducing agent is present. The formulation of this compound as (XVIIIa), therefore, requires convincing evidence, and this is provided by an examination of the chemical and spectral properties of the compound. Elemental analyses and molecular weight determinations are consistent with a molecular formula $C_{24}H_{28}N_3B_3Cl_2$, although these do not determine the number of hydrogen atoms with complete certainty. The borazole structure is indicated by the trimeric nature of the B-N entity and is confirmed by the characteristic absorption at 1390 cm.⁻¹

15 W. Gerrard, H. R. Hudson, and E. F. Mooney, J. Chem. Soc.,

1962, 113.
 ¹⁶ R. K. Bartlett, H. S. Turner, R. J. Warne, M. A. Young, and W. S. McDonald, *Proc. Chem. Soc.*, 1962, 153.

in the i.r. spectrum. There is also an absorption peak at 2535 cm.⁻¹ which is assigned to the stretching frequency of the B-H bond. Proton n.m.r. measurements indicate that the ratio of "aliphatic" hydrogens to "aromatic" hydrogens is 2:1, but the hydrogen attached to boron could not be detected. It is significant that the corresponding absorption due to the B-H protons in tri-N-phenylborazole is weak and diffuse. ¹¹B n.m.r. did not differentiate between the different types of boron atoms in the molecule.

In nucleophilic substitutions, the compound (XVIIIa) shows two or three centres of reactivity depending on the type of reagent involved. Water, alcohols, amines, etc., replace the chlorine atoms but leave the B-H bond intact, forming the disubstituted borazoles (XVIIIe; X = OH, OR, NR'R'', etc.). In general, these reactions are carried out in the presence of a tertiary base (normally triethylamine), which removes hydrogen chloride produced as triethylammonium chloride, although this is not always necessary (e.g., in reactions with amines) and in the case of water can lead to another reaction (see below). Alkyl and aryl lithium reagents, on the other hand, react with compound (XVIIIa) with substitution at all three boron atoms, giving symmetrical borazoles. In addition, phenyl-lithium reacts with the dimethoxy derivative (XVIIIe; X = OMe) giving the tri-B-phenyl derivative (XVIIIf; X = Y =Ph), but in the case of the bis(dimethylamino) derivative only the B-H group is attacked and the product is the unsymmetrical borazole (XVIIIf; X = NMe₂; Y = Ph). Sodium tetrahydroborate reduces the dichloroborazole to the *B*-unsubstituted borazole (XVIII*f*; X = Y = H) with the liberation of two equivalents of chloride ion.

The dihydroxy-borazole (XVIIIb), obtained by aqueous hydrolysis of the dichloroborazole, is remarkably stable. It is decomposed by concentrated sulphuric acid, but only slowly hydrolysed by heating under reflux with dilute acids and not at all by similar treatment with water. It is hydrolysed by heating with water under pressure at 250°, and when heated under reflux with benzyl alcohol gives hydrogen, 2,6-xylidine, and benzyl borate. Benzyl borate is also obtained by refluxing the dimethoxy derivative (XVIIIe; X = OMe) with benzyl alcohol. When the dihydroxyborazole is heated under reflux in toluene-water in the presence of triethylamine, hydrogen is readily evolved and the trihydroxyborazole (XVIIIc) is obtained in good yield.

The hydrolytic stability of the dihydroxyborazole in neutral and weakly acidic aqueous solutions allows it to be isolated with ease from the mixture obtained by the reaction of 2,6-xylidinoboron dichloride with triethylamine. Either the filtrate after the removal of triethylammonium chloride is evaporated to dryness and the residue is heated with water under reflux, or the whole of the reaction mixture is treated with dilute acid and non-basic, volatile components are removed by steam distillation. In either case, the other products of the reaction are hydrolysed to water-soluble compounds and the dihydroxyborazole is obtained as an insoluble precipitate.

When the dihydroxyborazole is heated with thionyl chloride there is no apparent reaction, but addition of a small crystal of pyridinium chloride causes the immediate evolution of hydrogen chloride and the dihydroxyborazole is converted in high yield into the dichloroborazole. This reaction, coupled with the easy isolation of the dihydroxyborazole from the original reaction mixture, affords a convenient route to the dichloro-compound. The trihydroxyborazole (XVIIIc) is also converted into the trichloroborazole by treatment with thionyl chloride in the presence of pyridinium chloride. This trichloroborazole reacts normally with n-butyl-lithium and with ammonia giving tri-B-substituted borazoles.

The di- and tri-hydroxy borazoles are also obtained from the chloro-compounds by treatment with dimethyl sulphoxide. Dimethyl sulphoxide has been reported ¹⁷ to bring about the replacement of active chlorine atoms attached to phosphorus and carbon by hydroxyl groups, while boron oxychloride is produced from boron trichloride.¹⁸ In the case of tri-*B*-chloro-tri-*N*-phenylborazole a gel is produced, presumably due to the formation of a cross-linked network of >B - O - B <links.

B-Aminoborazoles (XVIII*e*; $X = NH_2$; XVIII*f*; $X = Y = NH_2$) react with nitrosyl chloride with the formation of the corresponding hydroxy compound:

 $>B - NH_2 + NOCI \rightarrow >B - OH + N_2 + HCI.$ The hydrogen chloride produced in the reaction tends to react with the starting material, causing the replacement of $B - NH_2$ by B - Cl groups. This side reaction is suppressed when an excess of amyl nitrite, which appears to react preferentially with the hydrogen chloride, is present. Nitrogen evolution begins immediately the reactants are mixed at $0-5^{\circ}$ and there is no evidence for the intermediate formation of a stable diazo-compound.

All of the compounds obtained from (XVIII*a*) by replacement of the chlorine atoms alone show the characteristic absorption at the B-H stretching frequency in the 2550 cm.⁻¹ region of their i.r. spectra, whereas those compounds in which all three boron atoms have been attacked do not show this absorption peak. Furthermore, those compounds which are thought to contain a B-H bond liberate hydrogen when they are hydrolysed by sodium hydroxide in ethane-1,2-diol, while those compounds which are thought to be fully substituted borazoles do not (Table 3).

Attempts to obtain the dibromoborazole (XVIIIe; X = Br) by methods analogous to those used for the chloro-compound were unsuccessful. Hydrogen bromide is eliminated when 2,6-xylidine-boron tribromide is heated in toluene, but the mixture of products obtained by treating the resulting solution with triethylamine

¹⁷ S. K. Ray, R. A. Shaw, and B. C. Smith, *Nature*, 1962, **196**, 372.

1	ABLE 3	
		Hydrolysis moles H ₂ /
Compound	v B-H (cm1)	mole compound
$(XVIIIe; X = Cl) \dots$	2535	0.87
$(XVIIIe; X = OH) \dots$	2550	0.79
$(XVIIIe; X = OMe) \dots$	2500	*
(XVIIIe; $X = OPh$)	2544	0.74
(XVIIIe; $X = OCH_2 \cdot Ph$)	2513	*
$(XVIIIe; X = NH \cdot Et)$	2498	*
$(XVIIIe; X = NMe_2)$	2534	0.79
$(XVIIIe; X = NH \cdot Ph) \dots$	2520	0.66
(XVIIIe; X = H)	2513, 2500, 2481	$2 \cdot 5$
s-N-Triphenylborazole	2607, 2570, 2513	$2 \cdot 3$
* No	ot examined.	

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did not include the dibromoborazole, and hydrolysis of the mixture gave only tris(2,6-xylidino)boron as a water-insoluble product. When the dihydroxyborazole was treated with thionyl bromide, the latter underwent extensive decomposition and no dibromoborazole was isolated. The dibromoborazole was finally obtained by treating the diaminoborazole (XVIIIe; $X = NH_2$) with hydrogen bromide. It had previously been found that hydrogen chloride converted the diaminoborazole to the dichloroborazole, and a similar reaction has been reported by Gerrard.¹⁵

Other di-B-chlorotri-N-arylborazoles have been obtained from the corresponding 2,6-disubstituted anilines by methods analogous to those used in the case of 2,6-xylidine. The substituents are methyl, ethyl, chloro, and bromo, or part of an adjacent ring. The arylamines are 2,4,6-trimethyl-, 2,6-diethyl-, 2-chloro-6-methyl; 2,6-dichloro-, 2,4,6-trichloro-, and 2,6-dibromo-anilines and 1-amino-2-methylnaphthalene (see Table 4). In the general method, a solution of the arylaminoboron dichloride, obtained by heating the arylamine-boron trichloride adduct or by passing boron trichloride into a suspension of the arylammonium chloride in refluxing toluene, was set aside to react with triethylamine for several days. Triethylammonium chloride was removed and the dichloroborazole was obtained by evaporation and crystallisation. Yields varied considerably, and only in the case of 2,6-xylidine have optimum conditions for borazole formation been determined (see below). In general, yields were smaller for the more weakly basic halogen-substituted arylamines, but it is not clear in these cases whether this is a result of smaller actual yields in the reaction, possibly due to the slower rate of reaction, or of a different solubility relationship between the reaction products which increased the difficulties of separation. Nor is it possible in the case of the more weakly basic amines to isolate the dihydroxyborazole by acidifying the reaction mixture and steam distilling out the volatile components. The arylamine liberated by hydrolysis of the nonborazole reaction products is not sufficiently soluble in the dilute acid to allow an easy separation of the dihydroxyborazole, and attempts to remove this arylamine by steam distillation gave the corresponding trihydroxyborazole, presumably because the amine dissolved the dihydroxyborazole and, although only weakly basic, promoted attack on the B-H bond by water. It is possible in some cases, however, to purify

	Prop	perties of tr	i-N-(2,6-disubs	tituted aryl)bora	zoles (XVIII)	
R	х	Y	М. р.	v (BH) (cm. ⁻¹)	v (OH) (cm. ⁻¹)	D.M.S. No.
$2,6-\mathrm{Me_2C_6H_3}$	Cl	н	$255-256^{\circ}$	2535		13,325
,,	ОН	н	252-253	$egin{pmatrix} 2550\2520 \end{cases}$	$\begin{cases} & 3595 \\ & 3550 \\ & 4390 \end{cases}$	12,243
**	н	н	154 - 155	$\left\{egin{array}{c} 2545 \\ 2495 \end{array} ight.$		13,327
,,	\mathbf{Br}	н	258 - 259	2540		13,328
,,	он	ОН	296297		$\begin{cases} 3660 \\ 3550 \\ 3450 \end{cases}$	12,244
$2,6-\text{Et}_2C_6H_3$	C1	\mathbf{H}	243 - 244	2540	(0100	13,336
,,	OH	н	242 - 243	$egin{pmatrix} 2535\2505 \end{bmatrix}$	3550	13,337
$2,4,6-{\rm Me_3C_6H_2}$	Cl	н	262 - 263	2535		13,334
,,	он	н	228-230	2520	$\left\{\begin{array}{cc} 3615\\ 3550\\ 3440\end{array}\right.$	13,335
2-Cl-6-MeC ₆ H ₃	CI	H	232 - 233	2545		13,338
a e ci'e tt	OH	H	287-288	2525	3580	13,339
2,0-Cl ₂ C ₆ H ₃	CI	н	262-264	2560	(9500	13,340
,,	OH	н	287 - 288	2020	3400	13,341
2,4,6-Cl ₂ C ₆ H ₂	Cl	н	286 - 288	2560		13.342
,,	OH	н	194—195	2550	$\left\{\begin{array}{cc} 3630\\ 3410 \end{array}\right.$	13,343
,,	OH	ОН	242 - 243		$\left\{egin{array}{c} 3614 \ 3488 \end{array} ight.$	
$2,6-\mathrm{Br_2C_6H_3}$	Cl	н	298 - 299	2560		13,344
,,	OH	\mathbf{H}	333 - 334	2545	3595	13,345
$2-\mathrm{MeC}_{10}\mathrm{H}_{6}$	C1	н	266 - 267	2540		13,346
**	OH	н	243-245	2535	$\begin{cases} & 3580 \\ & 3540 \\ & 3460 \end{cases}$	13,347

TABLE 4

the crude dichloroborazole, obtained by evaporation and crystallisation, by hydrolysis and reconversion of the dihydroxyborazole to the dichloro-compound. In the case of 1-amino-2-methylnaphthalene, the dichloroborazole was one of the more soluble reaction products and could not easily be isolated by crystallisation. The dihydroxyborazole was necessarily isolated first in this case and was converted into the dichloroborazole by thionyl chloride.

The formation of di-B-chlorotri-N-2,6-xylylborazole has been examined in detail. The stability of the dihydroxyborazole (XVIIIb) is such that the rate of formation of the dichloro-compound (XVIIIa) can be followed by isolating it as the dihydroxy derivative. By varying the conditions, some of the factors involved have been determined; Figure 3 shows how the yield of borazole varies with time. It will be seen that the maximum yield is about 55% based on the aminoboron dichloride (II). The rate of formation of the borazole can be increased by raising the temperature, but this offers little advantage in preparative work. That the initial reactants are the aminoboron dichloride and the tertiary amine is shown by examining the variation in yield of the borazole when different quantities of hydrogen chloride are eliminated from the 1:1 adduct (I; R = 2,6-xylyl; X = Cl). The maximum yield is obtained when one mole of hydrogen chloride has been eliminated from the adduct (Table 5). It must be emphasized that these mixtures were allowed to react for long periods to ensure complete reaction. The production of a low yield of the borazole from the adduct and an excess of triethylamine is interesting. The initial products of this reaction are triethylammonium chloride, bis-(2,6-xylidino)boron chloride and triethylamine-boron trichloride, and it seems likely that the last two react slowly to form 2,6-xylidinoboron dichloride, which then reacts further to form the borazole.

TABLE 5

Variation in the yield of dichloroborazole (XVIIIa) with increasing dehydrochlorination of the adduct

1.06
53

* After 1 mol. has been eliminated from the adduct, boron trichloride is also given off. This is included in the total in terms of HCl.

In addition, it is found that when a solution of the adduct (I) is heated for a long period and trimethylamine is added, the adduct $\text{RNH}\cdot\text{BCl}_2 \leftarrow \text{NMe}_3$ is precipitated and the remaining solution no longer produces the borazole when it is treated with triethylamine. On the other hand, when triethylamine is added to 2,6-xylidinoboron dichloride in the absence of a solvent, the violent reaction which ensues does not lead to the dichloroborazole.

As would be expected, the yield of dichloroborazole is

affected within limits by the quantity of triethylamine used in the reaction (Figure 4). The maximum yield is produced when at least two moles of triethylamine are present for every mole of 2,6-xylidinoboron dichloride. The amount of triethylammonium chloride precipitated is $1\cdot1--1\cdot2$ moles per mole of 2,6-xylidinoboron dichloride. The source of the excess hydrogen ion needed to produce this amine hydrochloride is not



FIGURE 3 Formation of di-B-chlorotri-N-2,6-xylylborazole (XVIIIa) from 2,6-xylidinoboron dichloride (II; R = 2,6-xylyl) and triethylamine. Initial concentrations: (II), 0.67_M; Et₃N, ~1.67_M



FIGURE 4 Reaction of 2,6-xylidinoboron dichloride (II; R = 2,6-xylyl) and triethylamine: variation of yield of borazole (XVIIIa) with mole ratio $Et_3N/(II)$

apparent, but since an excess of triethylamine is necessary to realise the maximum yield of borazole, it is clear that the role of the tertiary base is not solely that of hydrogen chloride acceptor. It seemed possible that it was also the source of the hydrogen of the boron-hydrogen bond. Attempts to detect a possible dehydrogenation product, diethylvinylamine, by means of its colour reaction with 2,5-dichloro-3,6-dimethoxy-p-benzoquinone ¹⁹ were not successful, but the detection of acetaldehyde in the first fraction of the steam distillate from the isolation of the

¹⁹ D. Buckley, S. Dunstan, and H. B. Henbest, J. Chem. Soc., 1957, 4901.

dihydroxyborazole prompted the search for diethylamine. This was isolated as the toluene-*p*-sulphonyl derivative and was found to be present in the same molar quantity as the dichloroborazole. Thus, one molecule of triethylamine is degraded to diethylamine for every boron-hydrogen bond which is formed. Following a mechanism proposed by Henbest ¹⁹ for the oxidation of tertiary amines, a formal degradation scheme, in which hydrogen is abstracted as a hydride ion, may be written:

$$CH_{3}CH_{2} \cdot NEt_{2} \xrightarrow{-H^{-}} [CH_{3}CH \cdot NEt_{2} \xrightarrow{H_{3}O} CH_{3}CHO + H_{2}\dot{N}Et_{2}$$

$$CH_{3}CH = \dot{N}Et_{2}] \xrightarrow{H_{3}O} CH_{3}CHO + H_{2}\dot{N}Et_{2}$$

It is probable, however, that the hydride ion never exists as a free entity, but that the hydrogen and its associated electrons are abstracted by the electrondeficient boron, and the residue of the trialkylamine molecule may exist not as an immonium ion but as some molecule such as $CH_3CH(NEt_2)Z$, where Z could be Cl or RNH. It may be noted that, since the maximum yield of the borazole never exceeds 55%, a ratio of two molecules of triethylamine to one molecule of the aminoboron dichloride is a far greater excess than is required for hydrogen chloride abstraction and boron-hydrogen bond formation.

The nature of the tertiary amine which is used in the reaction has a profound effect on the yield of dichloroborazole. The yields of dichloroborazole produced when 2 mol. of various tertiary amines are allowed to react with 2,6-xylidinoboron dichloride under comparable conditions are shown in Table 6.

TABLE 6

Reaction of 2,6-xylidinoboron dichloride (II; R = 2,6-xylyl; X = Cl) with various tertiary amines

Yield range (%).Amines (yields of XVIIIa) (%).> 30 Et₃N (53), Et·N (CH₂)₅ (52)

- 20-30 Prⁱ· $N_{(24)}$ (CH₂)₅ (27), PrⁱMe₂N (25), Et₂PrN (25), Et₂MeN (24)
- 1-20 MePr₂N (11), $EtPr_2N(3)$
 - 0 Me₃N, EtMe₂N, Me₂PrN, Prⁱ₂MeN, Et₂PrⁱN, Pr₃N, EtPrⁱ₂N, Buⁿ₃N, Et₂PhN, Me·N $\langle | CH_2 \rangle_4, C_5H_5N, N(CH_2CH_2)_3N$

Only a limited number of tertiary bases react with formation of the borazole. In the cases of trimethylamine, ethyldimethylamine, pyridine, and triethylenediamine, 1:1 adducts of the tertiary base and 2,6-xylidinoboron dichloride are formed (Table 9), while tris-(2,6-xylidino)boron is obtained after hydrolysing the products of the reactions with dimethylpropylamine, di-isopropylmethylamine, diethylisopropylamine and trin-propylamine. There is no apparent reaction with trin-butylamine, ethyldi-isopropylamine, and diethylaniline. A small quantity of amine hydrochloride was precipitated with 1,2-dimethylpiperidine but no waterinsoluble hydrolysis product was obtained.

It seems likely that the formation of a loose complex is the first stage in the reaction between 2,6-xylidinoboron dichloride and a tertiary base. Those tertiary amines, e.g., trimethylamine, which form an insoluble complex with the borazene, remove the reactants from the solution, whilst those amines, e.g., ethyldi-isopropylamine, which are too sterically crowded to form such a complex, do not react. It is significant that in the series Et_aN_a Et₂PrN, EtPr₂N, Pr₃N, increased steric crowding around the nitrogen atom is accompanied by a decreased yield of dichloroborazole (53; 25; 3; 0%). Other factors must be involved, however, since on this argument Et₂MeN, which is less sterically hindered than Et₃N but does not form a stable 1:1 adduct with 2,6-xylidinoboron dichloride, would be expected to be more effective than Et₃N; in fact it is only as effective as Et₂PrN.

One of the other factors involved is the availability on the tertiary amine molecule of a hydrogen atom for B-H bond formation. This is probably influenced by steric effects and there may also be competition between hydrogen atoms at different sites in the molecule. Thus in 1-ethylpiperidine, two hydrogen atoms are available at the α -carbon of the ethyl group and at each of the two α -carbons of the ring. By estimating the amount of piperidine produced in the reaction, it is found that 40% of the B-H hydrogen originates in the ethyl group. In the case of 1-isopropylpiperidine, all of the hydrogen of the B-H group appears to originate in the piperidine ring, as no piperidine derivative was isolated from the reaction mixture.

The experiments described indicate that the borazole (XVIIIa) is formed from the aminoboron dichloride and that the tertiary base abstracts hydrogen chloride and supplies the hydrogen of the boron-hydrogen bond. The details of the reaction mechanism are not clear. It is most unlikely that the trichloroborazole (XVIIId) is first produced and then reduced by the tertiary base to the dichloroborazole, since in this case there is no reason why only one B-Cl bond should be reduced, and in fact there is no reaction between the trichloroborazole and triethylamine. When the trichloroborazole is added to a solution of the aminoboron dichloride and triethylamine, the product obtained by hydrolysis is the expected mixture of di- and tri-hydroxyborazoles, and there is no evidence of conversion of the trichloroborazole into dichloroborazole during the course of the reaction. It is probable, therefore, that the reaction takes place in several stages in which successive B-N units are linked together, with ring closure and B-H formation as the final stage or stages. Some evidence for the step-wise nature of the reaction is provided by comparing the rate of disappearance of the aminoboron dichloride with the rate of formation of the dichloroborazole. This may be done by precipitating compound (II; R = 2,6-xylyl, X = Cl) as its trimethylamine adduct at various stages in the reaction and estimating the amount of borazole formed during the

same period by isolating the dihydroxy-compound. It is then found (Figure 5) that the initial rate of disappearance of the aminoboron dichloride is very much greater than the rate of formation of the borazole.

The nature of the intermediates in the step-wise reaction are not known. The boronamine (XVI) is a possibility, since it possesses the -RN-BCI-NR-BCI-NRchain and merely requires the insertion of a B-H unit linking the chain ends to form the borazole. When the boronamine is added to the solution of the borazene (II) and triethylamine, the rate of formation of the dichloroborazole is initially increased, but the overall yield is not significantly affected. A similar affect is observed when triethylamine-boron trichloride is added to the



FIGURE 5 Conversion of aminoboron dichloride (II; R = 2,6-xylyl) into borazole (XVIIIa); ---- line for rate of consumption of (II) = rate of formation of (XVIIIa)



FIGURE 6 Reaction between 2,6-xylidinoboron dichloride and triethylamine; effect upon yield of borazole (XVIII*a*) of adding the boronamine (XVI) (-----) or $Et_3N\cdot BCl_3$ (-----)

reaction mixture (see Figure 6). It appears, therefore, that the boronamine (XVI) and triethylamine-boron trichloride, or compounds related to them, are intermediates in the formation of the dichloroborazole. There is, however, no reaction between the boronamine and triethylamine-boron trichloride under the conditions of borazole formation.

Tris(2,6-xylidino)boron, which is produced in small yields by the action of certain tertiary amines on (II; R = 2,6-xylyl, X = Cl, Br) (see above), has also been obtained by the action of 2,6-xylidine on 2,6-xylidine-

boron trichloride in the presence of triethylamine. In marked contrast to trianilinoboron and trialkylaminoborons, which undergo condensation reactions leading to *B*-aminoborazoles,²⁰ tris(2,6-xylidine)boron can be sublimed unchanged and can withstand prolonged heating at 300°. Its stability relative to the corresponding borazole is indicated by its formation during the pyrolysis of ethyl bis(2,6-xylidino)borinate:

 $3(C_8H_9NH)_2BOEt \longrightarrow 2(C_8H_9NH)_3B + B(OEt)_3$. Aubrey and Lappert²⁰ found that *B*-alkoxyborazoles were obtained by the pyrolysis of alkylaminoborinates. Our failure to obtain *N*-(2,6-xylyl)-borazole derivatives by these routes is undoubtedly due to steric hindrance about the B-N bond.

We were led by our observations on the extraordinary stability of the di- and tri-B-hydroxytri-N-2,6-disubstituted aryl borazoles to investigate less highly substituted compounds. The preparation of tri-B-hydroxytri-N-phenylborazole and the corresponding p-methoxyphenyl compound has been reported ^{5,2} but it seems very likely that the pure substances were not isolated. Our experience has been that the hydrolysis of tri-B-chlorotri-N-phenylborazole by the method used by Jones and Kinney⁵ normally gives products containing little or no hydroxyborazole; exceptionally, however, authentic hydroxyborazole is obtained. A modification of their procedure allows low yields to be obtained fairly consistently. The hydroxyborazole is soluble in benzene and toluene and may be separated from other insoluble contaminants, presumably polymeric borazyl oxides, and isolated by extraction at or below room temperature followed by vacuum evaporation. Thus obtained, the hydroxyborazole is a colourless crystalline solid, indefinitely stable at -20° but rapidly converted into benzene-insoluble products at room temperature. Exceptionally, it is possible to crystallise small quantities from hot benzene, but in most cases the solution decomposes to form a clear gel.

Tri-B-chlorotri-N-o-tolylborazole, by contrast, is hydrolysed by water to give good yields of the much more stable tri-B-hydroxytri-N-o-tolylborazole. This can be crystallised normally from light petroleum or benzene provided heating is brief. Whereas solutions of the hydroxyphenylborazole begin to deposit insoluble matter within a few hours, those of the o-tolyl compound are stable for several days. The solid appears to be indefinitely stable at 0°. With further ortho substitution of the phenyl groups the extremely stable di- and trihydroxyborazoles mentioned above are obtained. Tri-B-hydroxytri-N-2,6-xylylborazole, for example, may be sublimed *in vacuo* at 230° without decomposition.

The preparation of the corresponding N-alkyl compounds ²¹ was then attempted. Wiberg ²² has claimed the preparation of tri-B-hydroxytri-N-methylborazole by heating the adduct of tri-N-methylborazole (1 mole)

D. W. Aubrey and M. F. Lappert, J. Chem. Soc., 1959, 2927.
 R. K. Bartlett, H. S. Turner, R. J. Warne, and M. A. Young, Chem. and Ind., 1964, 1026.

²² E. Wiberg, K. Hertwig, and A. Bolz, Z. anorg. Chem., 1948, 256, 177.

and water (3 moles), but no details were given. When we attempted to prepare the N-methyl and N-cyclohexyl-compounds by the reaction of the calculated amount of water with a solution of the B-chloroborazole in the presence of triethylamine we obtained only illdefined, impure polyborazyl oxides. However, the highly hindered tri-B-chlorotris-N-(1,2-dimethylpropyl)borazole is converted by this method in good yield into the hydroxyborazole. This is soluble in hydrocarbon solvents and separates from light petroleum in colourless needles. Although it decomposes in a few hours at room temperature, whether as solid or in solution, it will survive a few moments' boiling with water, and is stable for several months at -20° .

The B-hydroxy-N-2,6-disubstituted aryl borazoles are converted into the corresponding chloro-compounds by the action of thionyl chloride in the presence of pyridinium chloride, but the less highly substituted hydroxyborazoles do not undergo this reaction. The o-tolyl compound is converted into *o*-tolylsulphinylamine.

The i.r. spectra of solutions of all the hydroxyborazoles show free hydroxyl stretching bands in the

Reactions with Aniline.—Thermal decomposition of anilineboron trichloride. Two samples of aniline-boron trichloride (10.52 g., 0.05 mole) were heated in toluene (75 ml. and 50 ml.) and the rates of evolution of hydrogen chloride (Figures 1 and 2a) were determined in the apparatus described in Part I.¹ When the reactions were finished, the toluene solutions were combined and evaporated, giving crude tri-B-chlorotri-N-phenylborazole (13.86 g., 101%), purified by recrystallisation from toluene.

In another experiment, the adduct (10.50 g., 0.05 mole)was heated in refluxing toluene (75 ml.) for 1 hr. Hydrogen chloride (0.055 mole) was evolved, and on cooling the solution impure aniline-boron trichloride adduct (4.4 g., 42%) was precipitated, identified by its i.r. spectrum and m. p. 166-172° (decomp.), alone and admixed with an authentic specimen (Found: B, 5.3; Cl, 44.6; N, 7.1. Calc. for C₆H₇BCl₃N: B, 5·1; Cl, 50·55; N, 6·7%). Evaporation of the filtrate gave tri-B-chlorotri-N-phenylborazole (3.8 g., 56%) (Found: B, 7.7; Cl, 26.0; N, 10.2. Calc. for $C_{18}H_{15}B_{3}Cl_{3}N_{3}$: B, 7.9; Cl, 25.8; N, 10.2%).

Reaction of boron trichloride with trianilinoboron. A large excess of boron trichloride was condensed on to

1	ABLE	1	

Arylamine-boron trichloride adducts, ArNH2·BCl3

	Vield	Mn	Found %				Calc. %					
Ar	(%)	(decomp.)	ĉ	н	В	Cl	N	c	Н	B	Cl	N
Ph	78	168-172°	$34 \cdot 8$	3.6	5.4	47.7	6.7	$34 \cdot 2$	3.3	$5 \cdot 1$	50.6	6.7
2-C _s H ₄ Me *	85	122 - 125	37.6	4.1	5.0	46.25	6.0	37.5	3.8	4.8	47.5	6.25
2,6-C,H ₃ Me, †	83	113 - 116	40.2	$4 \cdot 9$	4.5	44.5	5.9	40.3	4.6	4.5	44.7	5.9
2,6-C ₆ H ₃ Et ₂	73	63 - 65	44 ·6	5.6	$4 \cdot 0$	$39 \cdot 95$	$5 \cdot 3$	45.0	5.6	4.1	39.4	5.5
	* I.r. s	spectrum: DM	IS card no	5. 13,32 0	. † I.	r. spectru	m: DM	S card no	b. 13,321	•		

3660-3540 cm.⁻¹ range. In the solid substances a very broad band due to the associated hydroxyl group is found between 3500 and 3100 cm.⁻¹, but this is absent in solution. A weak band, believed to be the hydroxyl deformation mode, is found in the 970-950 cm.⁻¹ range. In common with other borazoles these compounds show a very broad and intense absorption envelope at around 1400 cm.⁻¹, and it is believed that the B-O stretching band (which is found in the 1370-1320 cm.⁻¹ region in B-alkoxyborazoles²³) is present but unresolved in this range.

EXPERIMENTAL

Amines which were not available commercially were prepared by standard methods and were dried before use. Solvents were commercial products dried by standard methods. Moisture-sensitive materials were handled in a dry atmosphere. Except where otherwise stated melting points were taken in vacuo 24 and are uncorrected.

The infrared (i.r.) spectra were recorded by Mr. H. M Paisley on a Grubb-Parsons GS-3 spectrometer.

The nuclear magnetic resonance (n.m.r.) spectra were measured on an A.E.I. type RS2 N.M.R. spectrometer.

Microanalyses were carried out by the Microanalytical Section of this Laboratory. Gas analyses were carried out by Mr. P. J. Kipping of the Warren Spring Laboratory, Stevenage, Herts.

Arylamine-boron trichloride adducts were obtained (Table

trianilinoboron 5, 20 (4.74 g.) and the mixture was stored at -20° for several days. Boron trichloride was then allowed to evaporate slowly from the stirred solution and the residue (9 g.) was stirred with toluene (75 ml.) at room temperature for several hours. The insoluble portion was filtered off and was identified as aniline-boron trichloride (4.16 g., 79%) by comparison with an authentic specimen (Found: B, 5.3; Cl, 49.2; N, 6.3%). Evaporation of the filtrate under reduced pressure at room temperature gave a residue (4.8 g.) the i.r. absorption spectrum of which was that expected of a mixture of the borazole and the adduct (Found: B, 7.5; Cl, 32.1; N, 8.1%). These were partly separated by stirring with toluene (40 ml.) at room temperature for several hours, when the insoluble portion (1.38 g.) was the adduct contaminated with the borazole (Found: B, 6.3; Cl, 37.9; N, 8.6%) and the soluble portion (3.16 g.) was the borazole contaminated with the adduct (Found: B, 6.7; Cl, 28.7; N, 8.6%).

Reaction between aniline-boron trichloride and triethyl-Triethylamine (13.8 ml., 0.10 mole) in toluene amine. (50 ml.) was added to a stirred suspension of aniline-boron trichloride (10.5 g., 0.05 mole) in toluene (200 ml.) and the mixture was heated under reflux for 10 min. After cooling overnight, triethylammonium chloride (13.2 g., 0.096 mole) (Found: Cl, 25.9; N, 10.0. Calc. for C₆H₁₆ClN: Cl, 25.8; N. 10.2%) was filtered off, and evaporation of the filtrate

²³ M. J. Bradley, G. E. Ryschkewitsch, and H. H. Sisler, J. Amer. Chem. Soc., 1959, **81**, 2635. ²⁴ H. S. Turner, Chem. and Ind., 1962, 817.

gave impure tri-*B*-chlorotri-*N*-phenylborazole (7.0 g., 102%), purified by recrystallisation and identified by comparison with a specimen prepared by thermal dehydrochlorination of the adduct. When triethylamine (6.9 ml., 0.05 mole) was added to the adduct (10.59 g., 0.05 mole) under the same conditions as the previous experiment, a reduced yield of borazole (3.1 g., 44.5%) was obtained, and the initial precipitate (11.86 g.) approximated to a 2:1 mixture of triethylammonium chloride and aniline-boron trichloride (Found: B, 2.1; Cl, 31.7; N, 8.5. Calc. for $(2C_6H_{16}ClN + C_6H_8BCl_3N)$: B, 2.2; Cl, 36.6; N, 8.6%), although very little soluble material could be extracted from the mixture by hot toluene.

The products of the reaction of aniline with triethylamine-boron trichloride and with a mixture of triethylamine and triethylamine-boron trichloride were exactly the same as those of the reaction of the appropriate amounts of triethylamine with aniline-boron trichloride, but the tri-B-chlorotri-N-phenylborazole obtained was less contaminated with a sticky tar.

Tri-B-hydroxytri-N-phenylborazole. Tri-B-chlorotri-Nphenylborazole (5.00 g.; 0.014 mole) was ground with finely crushed ice (~ 30 g.) and then kept until the ice had melted. The product, which was a thick white paste (in some cases thixotropic), was quickly heated with stirring to $\sim 50^{\circ}$ to effect coagulation, and then filtered. After washing with ice-cold 2n-hydrochloric acid followed by iced water the product (0.21 g.) was dried in vacuo over anhydrous calcium sulphate at 0°. The crude material melted at 161-162°. When this product (0.1 g.) was stirred at room temperature with toluene (2 ml.), most dissolved; the solution was filtered through a sinter and then cooled to -20° . Colourless needles deposited which were collected by centrifugation at -20° ; when placed in a melting point bath at 155° and heated, the product melted at 167° to a colourless liquid (Found: C, 59.7; H, 5.1; B, 8.8; N, 11.7. $C_{18}H_{18}B_3N_3O_3$ requires: C, 60.7; H, 5.1; B, 9.1; N, 11.8%). I.r. spectrum: DMS card no. 12241. Alternatively, a product (0.085 g.) of only slightly lower melting point was obtained by evaporation of the filtrate in vacuo at below -10° . It was stored at -20° .

Reactions with o-Toluidine.—Thermal decomposition of o-toluidine-boron trichloride. The results set out in Figures 1 and 2*a* were obtained as for aniline-boron trichloride (above). Evaporation of the solution gave a quantitative yield of tri-B-chlorotri-N-o-tolylborazole, m. p. 212—213° after crystallisation from light petroleum (b. p. 100— 120°) (Found: C, 55·3; H, 5·1; B, 7·1; Cl, 23·6; N, 9·2%; *M* (cryoscopic), 444. $C_{21}H_{21}B_3Cl_3N_3$ requires: C, 55·5; H, 4·6; B, 7·2; Cl, 23·5; N, 9·25%; *M*, 454). I.r. spectrum: DMS card no. 13313.

In another run the adduct (18.09 g.; 0.0805 mole) in toluene (117 ml.) was heated under reflux until 0.081 g. equiv. of sodium hydroxide solution had been neutralised in the absorber. The reaction mixture was shock-chilled to 0°; the hydrogen chloride evolved totalled 0.0831 g. equiv. (1.035 mol.). The clear, pale yellow solution was evaporated with stirring at or below 0° (oil pump) until a pale yellowish-brown oil remained which was free of toluene. The oil was filtered to remove some suspended colourless crystals (2.30 g.) but the filtrate (10.3 g.) at once deposited more. Over a period of days it was converted into a white solid (Found: C, 45.0; H, 4.4; B, 5.8; Cl, 35.8; N, 7.6. $C_7H_8BCl_2N$ requires C, 44.8; H, 4.3; B, 5.7; Cl, 37.8; N, 7.4%). The solid material had M (cryoscopic

in benzene), 333, corresponding to $(C_7H_3BCl_2N)_{1.77}$. Pure monomer and dimer were not isolated.

Reaction between o-toluidine-boron trichloride and triethylamine: preparation of 2,4-dichloro-3-o-tolyl-8-methyl-2,4-dibora-1,3-diazaronaphthalene (V) (Structure X; X = Cl). A 3-litre 3-neck flask, fitted with a sealed Vibromixer agitator impellor and a double-surface condenser surmounted by a solid carbon dioxide-cooled cold finger condenser, containing toluene (700 ml.) was cooled in an ice-bath and boron trichloride (127.5 g.; 1.09 mole) was distilled in. A solution of freshly redistilled o-toluidine (117 g.; 1.09 mole) in toluene (600 ml.) was then added, followed by triethylamine (233.5 g.; 2.31 moles) in toluene (350 ml.). The mixture was heated gently to the boil and refluxed for 1 hr. After keeping overnight at room temperature, triethylammonium chloride (300 g.; 2.12 moles) was filtered off and the filtrate evaporated under reduced pressure to ~ 280 ml. During three days at 25° this solution deposited impure tri-B-chlorotri-N-o-tolylborazole (30.0 g., containing about 10% of its weight of triethylammonium chloride); evaporation of the liquors gave an orange, resinous material (145.5 g.) which was taken up in hot light petroleum (b. p. 60-80°; 105 ml.). On keeping at room temperature, colourless crystals deposited (47.9 g.), m. p. 109-155°. The liquors, on evaporation, gave an orange, resinous solid (96 g.) (Found: C, 57.9; H, 6.1; B, 6.3; Cl, 19.1; N, 11.3%). The crystalline solid (A) was a mixture of the compound (V) (75-90%) and the borazole (10-25%). The solid (10.0 g.) was crystallised from light petroleum (b. p. 60-80°; 30 ml.): crystals deposited (5-6 g.), which under favourable conditions were of two kinds, fine crystalline powder and large crystalline lumps (up to 5 mm.). The powder was the crude borazole (m. p. $182-204^{\circ}$ contaminated with a little of the compound (V) (Found: C, 55.3; H, 5.0; B, 5.9; Cl, 22.7; N, 8.8. Calc. for $(C_2H_2BCIN)_n$: C, 55.6; H, 4.6; B, 7.2; Cl, 23.5; N, 9.25%). The lumps, if carefully freed from the crystalline powder, were the pure compound (V), m. p. 120-122° (Found: C, 55.7; H, 4.75; B, 7.3; Cl, 22.7; N, 9.40%; M (cryoscopic), 307. $C_{14}H_{14}B_2Cl_2N_2$ requires: C, 55.6; H, 4.6; B, 7.15; Cl, 23.5; N, 9.25%; M, 302.6). I.r. spectrum: DMS card no. 13312. The compound reacts readily with water and must be protected from moist air.

2.4-Bisdimethylamino-3-0-tolyl-8-methyl-2,4-dibora-1,3-diazaronaphthalene. The concentrate (A) (6.235 g.; 0.041 g. equiv. of a sample containing $\sim 20\%$ of borazole) and triethylamine (5.1 g.; 0.05 mole) in benzene (100 ml.) were treated under nitrogen at room temperature with dimethylamine (51 ml. of a 0.88M solution in benzene) and kept for 2 days. Filtration gave triethylammonium chloride (5.32 g.; 0.039 mole) and a filtrate which was evaporated in vacuo to give a colourless syrup (6.45 g.) from which on distillation a fraction, b. p. 177-202°/ \sim 0.01 mm. (4.99 g.), was obtained as a thick oil which solidified on cooling. On crystallisation from light petroleum (b. p. 40—60°; 2.5 ml. per gram) the pure compound was obtained in colourless crystals, m. p. 87-89° (Found: C, 67.2; H, 8.0; B, 6.5; N, 16.8%; M (cryoscopic), 296. C₁₈H₂₈B₂N₄ requires C, 67.5; H, 8.14; B, 6.75; N, 17.5%; M, 320). I.r. spectrum: DMS card no. 13314. The residue from the distillation (1.71 g.) was the crude B-dimethylaminoborazole. Tris-B-dimethylaminotri-N-o-tolylborazole was prepared in the same manner from tri-B-chlorotri-N-o-tolylborazole. It separated from light petroleum (b. p. 60–80°) in colourless crystals, m. p. 122–125° (Found: C, 67.5; H, 8.3; B, 7.0; N, 17.0%; *M* (Mechrolab osmometer), 421. $C_{24}H_{39}B_3N_6$ requires: C, 67.5; H, 8.1; B, 6.75; N, 17.5%; *M*, 480). DMS card no. 13315.

Anhydride of 2-amino-3-methylphenylboronic acid. The concentrate (A) (7.68 g.; 0.051 g. equiv.) was ground in a mortar under nitrogen with pure ice (50 g.) until the mixture had warmed to room temperature ($\sim 2\frac{1}{4}$ hr.). The suspension was filtered to remove tri-B-hydroxytri-N-o-tolylborazole (1.35 g.; 0.0034 mole) and the filtrate and washings titrated with 5N-sodium hydroxide (9.90 ml.) to pH 7.2. After keeping overnight at 0° the white solid was filtered off, washed, and dried in vacuo. The white solid (3.01 g.; 0.023 g. equiv.) was the substantially pure anhydride. It separated in fine needles from benzene (140 ml./g.) or acetonitrile (55 ml./g.), m. p. 184-186° with re-solidification (Found: C, 63.6; H, 6.2; B, 8.1; N, 10.3. $(C_7H_8BNO)_n$ requires: C, 63·3; H, 6·1; B, 8·1; N, 10·5%); DMS card no. 13318. The molecular weight was determined ebullioscopically in benzene (n = 4.5), isobutyronitrile $(n = 2 \cdot 2 - 3 \cdot 0, \text{ increasing with concentration})$ and dimethoxyethane (n = 1.7 - 1.9), increasing with concentration). Under the conditions of this experiment the conversion of tri-B-chlorotri-N-o-tolylborazole into the hydroxy compound is about 94%. The borazole content of the original concentrate was therefore about 21.5%. The anhydride is soluble in dilute acid and alkali. When it is dissolved in the cold in a slight excess of N-hydrochloric acid and the solution evaporated in vacuo without heating, white needles of the hydrochloride of 2-amino-3-methylphenylboronic acid are obtained (Found: C, 40.5; H, 6.5; B, 5.0; Cl, 17.3; N, 6.9. $C_7H_{11}BClNO_2,H_2O$ requires: C, 40.9; H, 6.4; B, 5.3; Cl, 17.3; N, 6.8%); DMS card no. 13317.

In a similar hydrolysis pure compound (V) (7.56 g.; 0.025 mole) reacted with ice (50 g.); titration to pH 7.1 required 0.0495 g. equiv. of sodium hydroxide solution. The anhydride that was precipitated was contaminated with o-toluidine: it was filtered off, washed with a little water, and pumped at 0.001 mm. through a cold trap. The o-toluidine in the trap was collected and combined with that extracted from the liquors by methylene chloride. After drying, the extract gave on evaporation 2.48 g. (0.023 mole) of o-toluidine (pure by i.r. spectrum) which was converted virtually quantitatively into aceto-o-toluidide, m. p. 112—113°. The anhydride, after drying, had m. p. 175-180° (3.12 g.; 0.0235 mole). The aqueous liquors from the hydrolysis contained chloride ion (0.0495 g. equiv.) and boron (0.024 g. atom). In no preparation did the yield of the anhydride exceed 1 mole per mole of compound (V). Solutions of the anhydride in dilute hydrochloric acid were stable during long periods at room temperature: the anhydride is quantitatively recovered on neutralisation.

Hydrolysis of the concentrate in deuterium oxide. The concentrate (A) (0.985 g.; 0.0065 g. equiv.) was ground with deuterium oxide (5.0 ml.; 99.81 mol.-%) at 0° with careful exclusion of water. After $1\frac{1}{2}$ hr., tri-B-[²H]-hydroxy-tri-N-o-tolylborazole (0.125 g.) was filtered off and washed with deuterium oxide (2.0 ml.; 99.81 mol.-%). The combined filtrate was titrated with sodium [²H]hydrox-ide (3.62N: 1.80 ml.) to pH 7.0, filtered, and the anhydride dried in vacuo. The crude product (0.38 g.) was crystallised from dry benzene (55 ml.) to give the [²H]anhydride (0.31 g.), m. p. 182°. The methyl C-H stretching bands of the i.r.

spectrum were identical with those of the compound prepared in water. The filtrate from the neutralisation was made alkaline and distilled through a short column. The *o*-toluidine, which distilled with the first 3 ml. water, was extracted with methylene dichloride, then extracted from the methylene dichloride into excess of N-hydrochloric acid. The solution was made alkaline and the amine extracted with ether, dried over 50% potassium hydroxide solution, then over potassium hydroxide pellets, and finally evaporated and distilled. *o*-Toluidine (~ 0.1 g.) was collected at 112—114°/68 mm. The i.r. spectrum was identical with that of pure *o*-toluidine.

Hydrolysis of the anhydride in deuterium oxide-deuterium chloride. The anhydride (0.272 g.; 0.00205 g. equiv.) in DCl-D₂O (1.04N: 3.60 ml.; 0.00373 g. equiv.), prepared from 99.81 mols-% D₂O, was sealed under nitrogen in a glass tube and heated at 100° for $2\frac{3}{4}$ hr. The product was worked up as above for o-toluidine (yield 0.15 g., b. p. 114—116°/65 mm.) and converted into the benzoyl derivative, which after crystallisation from ethyl acetate had m. p. 144° [mixed m. p. with authentic benzoyl o-toluidide (m. p. 145°), 144.5—145°].

o-Toluidine (0.265 g.; 0.0025 mole) in DCl-D₂O (1.00N; 3.44 ml.) was heated as above, and recovered and converted into benzoyl-o-toluidide, m. p. 144° [mixed m. p. with authentic compound (m. p. 145°) 144.5—145°].

A comparison of the i.r. spectra of the two experimental samples of benzoyl-o-toluidide with the authentic untreated substance showed (a) that the N-H stretching band and the methyl C-H stretching bands were present at the same frequency and intensity in all three samples, (b) that of the aromatic C-H stretching bands at 3070 and 3030 cm.⁻¹, the latter had diminished intensity in the treated samples, and (c) a new band attributable to the aromatic C-D stretching mode, was found at 2270 cm.⁻¹ in both treated samples.

Diacetyl 2-acetamido-3-methylphenylboronate. The anhydride (0.92 g.; 0.0069 g. equiv.) and acetic anhydride (3.5 ml.) were heated under nitrogen at 100° in a closed tube for 2 hr. On cooling, white crystals deposited: these were filtered off, washed with acetic anhydrideacetic acid and dried *in vacuo*; yield 1.32 g., m. p. 248— 249° (Found: C, 56.5; H, 5.7; B, 4.0; N, 5.0. C₁₃H₁₆BNO₅ requires: C, 56.3; H, 5.8; B, 3.9; N, 5.1%). The i.r spectrum (DMS card no. 13319) displays the N-H deformation band characteristic of the C₆H₅·NH group at 1580 cm.⁻¹.

2-Acetamido-3-methylphenylboronic acid. Diacetyl 2-acetamido-3-methylphenylboronate (0.52 g.; 0.00188 mole) was dissolved in oxygen-free water (3.05 ml.) at the boil. On cooling, white plates deposited: the crystals were filtered off, and dried at ~ 0.01 mm. at room temperature. Volatile products from the filtration and the drying were collected in a trap at -80° . This substance appeared to have solvent of crystallisation which was lost on pumping. Yield 0.22 g., m. p. 173-180° (Found: C, 56.5; H, 6.1; B, 6.0; N, 7.4. C₉H₁₂BNO₃ requires: C, 56.1; H, 6.25; B, 5.6; N, 7.25%). The filtrate was pumped to dryness, the volatiles being collected with those above in a cold trap. The solid residue (0.11 g.) was identical (i.r. spectra) with the crystals: the combined volatile fractions contained 0.00335 g. equiv. of acetic acid (neutralisation curve identical with that of authentic acetic acid of the same concentration), i.e., 1.8 equivalents per mole of the triacetate.

Bromination of diacetyl 2-acetamido-3-methylphenylboronate. The anhydride (0.39 g.; 0.00293 g. equiv.) was acetylated as above with acetic anhydride (2.0 ml.), and transferred with acetic acid containing $\sim 10\%$ acetic anhydride (3.0 ml.) to a flask carrying a reflux condenser. Bromine (0.5 ml.; 1.64 g.; 0.010 mole) in glacial acetic acid (1.0 ml.) was added down the condenser; after a brief period of induction the bromine colour was discharged. When all had been added the solution was evaporated to give a crude product (1.42 g.), which was crystallised from acetonitrile: m. p. 218-220° (Found: C, 36.2; H, 3.4; B, 3.0; Br, 35.8; N, 3.2. C₁₃H₁₄BBr₂NO₅ requires: C, 35.8; H, 3.2; B, 2.5; Br, 35.8; N, 3.2%).

Tri-B-hydroxytri-N-o-tolylborazole. The chloroborazole (5.00 g.; 0.011 mole) was hydrolysed by the method used for the preparation of tri-B-hydroxytri-N-phenylborazole. After heating to 60° to effect coagulation the precipitate was filtered off, washed with water, and dried at 0° in vacuo: yield 3.05 g.

This was crystallised quickly from benzene (~ 3.3 ml. per gram) or light petroleum (b. p. 100-120°; 33 ml. per gram) to give colourless crystals of the hydroxyborazole, m. p. 126-127° with subsequent solidification to a colourless glass (Found: C, 63.15; H, 6.20; B, 7.2; N, 10.4; M (Mechrolab Osmometer, in benzene), 437. C₂₁H₂₄B₃N₃O₃ requires: C, 63.4; H, 6.04; B, 8.15; N, 10.55%; M, 399). Solutions of the hydroxyborazole become cloudy after keeping for a few days at room temperature, while the solid becomes partly insoluble in a few weeks. It appears to be stable indefinitely at -20° . I.r. spectrum: DMS card no. 12242.

Reactions with 2,6-Xylidine.—Thermal decomposition of 2.6-xylidine-boron trichloride. The samples of 2,6-xylidineboron trichloride $(12 \cdot 1 \text{ g.}, 0.05 \text{ mole})$ were heated in benzene (50 ml. and 100 ml.) and the rates of evolution of hydrogen chloride were measured as in the case of the aniline compound (Figures 1 and 2b).

In another experiment, the adduct (24.0 g.; 0.1 mole) was heated in refluxing toluene (100 ml.) for 3 min., and after cooling, the solution was evaporated under reduced pressure at room temperature. The residue (21 g.) was impure 2,6-xylidinoboron dichloride (Found: B, 5.0; Cl, 33.8; N, 7.0%) from which a pure specimen was obtained by sublimation (45-50°/0.04 mm.), m. p. 54-55° (Found: C, 47·4; H, 5·0; B, 5·3; Cl, $35\cdot3$; N, $6\cdot9\%$; M, 206. C₈H₁₀BCl₂N requires: C, 47.6; H, 5.0; B, 5.4; Cl, 35.2; N, 6.9%; M, 202). I.r. spectrum: DMS card no. 13322. In another experiment, the adduct (24.0 g.; 0.1 mole) was heated in toluene (100 ml.) for one week. After removing the solvent, xylidinoboron dichloride (8.4 g.; 0.04 mole) was sublimed ($50^{\circ}/0.05$ mm.) from the residue. A small quantity (1.5 g.) of material which sublimed at $160^{\circ}/0.05$ mm. was possibly the boronamine (XV; R = 2,6-xylyl) (Found: B, 5.9; Cl, 27.0; N, 7.5. C₁₆H₁₉B₂Cl₃N₂ requires: B, 5.9; Cl, 29.0; N, 7.6%). The residue (6.1 g.) from the sublimation was recrystallised from toluene and gave the boronamine (XVI; R = 2,6-xylyl) (4.2 g.; 0.0093 mole; 28%), m. p. 191-192° (Found: C, 64.0; H, 6.5; B, 4.9; Cl, 15.7; N, 9.2%; M, 465. C₂₄H₂₉B₂Cl₂N₃ requires: C, 63.8; H, 6.4; B, 4.8; Cl, 15.7; N, 9.3%; M, 452). I.r. spectrum: DMS card no. 13324. When the decomposition of the adduct was carried out in boiling chlorobenzene the yield of boronamine (XVI) was increased to 48%.

Reaction between 2.6-xylidine-boron trichloride and triethyl-

amine. Triethylamine (6.9 ml.; 0.05 mole) in benzene (25 ml.) was added to 2,6-xylidine-boron trichloride (11.95 g.; 0.05 mole) in benzene (200 ml.) at room temperature. Two liquid layers appeared but very little solid precipitate was produced. The solution was heated under reflux for 10 min. and set aside to cool overnight. Solvent was removed under reduced pressure and the residue was extracted several times with light petroleum. The insoluble portion (9.1 g.) was identified as a mixture of triethylammonium chloride and triethylammonium tetrachloroborate by analysis (Found: B, 2.3; Cl, 42.1; N, 6.9. Calc. for $C_6H_{16}ClN + C_6H_{16}BCl_4N$: B, 2.8; Cl, 45.2; N, 7.1%) and by its i.r. spectrum, which showed the characteristic absorption 25 of the BCl₄⁻ ion in the region 800-600 cm.⁻¹. Evaporation of the light petroleum extract gave bis(2,6-xylidino)boron chloride (6.6 g.; 0.023 mole) which was purified by sublimation $(140^{\circ}/0.1 \text{ mm.})$ and recrystallisation from light petroleum, m. p. 154-155° (Found: C, 66.7; H, 7.4; B, 3.9; Cl, 12.2; N, 9.7%; M, 275. C₁₆H₂₀BClN₂ requires: C, 67.0; H, 7.0; B, 3.8; Cl, 12.4; N, 9.8%; M, 256). I.r. spectrum: DMS card no. 13323. When this reaction was carried out using toluene as solvent, the tetrachloroborate content of the light petroleum-insoluble portion was reduced (Found: B, 1.8%) and recrystallisation of the light petroleum extract gave the boronamine (XVI).

Addition of triethylamine (6.9 ml.; 0.05 mole) in benzene (25 ml.) to 2,6-xylidine-boron trichloride (12.0 g.; 0.05 mole) in benzene (200 ml.), as in the previous experiment. gave a solution containing two liquid layers. Addition of more triethylamine (6.9 ml.) in benzene (25 ml.) caused the formation of a solid precipitate and the disappearance of the second liquid layer. The mixture was heated under reflux for 10 min., set aside to cool, and triethylammonium chloride (8.2 g.; 0.06 mole) was filtered off (Found: Cl, 26.4; N, 10.5%). Evaporation of the filtrate at room temperature under reduced pressure gave a residue (12.0 g.)with an i.r. spectrum corresponding to a mixture of bis(2,6xylidino)boron chloride and triethylamine-boron trichloride (Found: B, 4.4; Cl, 26.5; N, 8.1. Calc. for $C_{16}H_{20}BClN_2$ + C₈H₁₅BCl₃N: B, 4.3; Cl, 27.9; N, 8.3%). A portion (1.0 g) of the mixture in acetone was poured on to a mixture of crushed ice and dilute hydrochloric acid. When the ice had melted, the precipitate (0.32 g.) was filtered off, dried, and identified as triethylamine-boron trichloride by comparison with an authentic specimen.²⁶ The recovery of triethylamine-boron trichloride was 75%.

When the mixture (7.5 g.) of triethylammonium chloride and tetrachloroborate, obtained from the first experiment, was stirred with triethylamine (5 ml.) in toluene, a precipitate of triethylammonium chloride (5.7 g.) formed, and triethylamine-boron trichloride (3.4 g.) was obtained from the filtrate.

Bis(2,6-xylidino)boron chloride was also prepared by adding 2,6-xylidine (12 ml.; 0.1 mole) and triethylamine (27.6 ml.; 0.2 mole) in toluene (40 ml.) to 2,6-xylidineboron trichloride (24 g.; 0.1 mole) in toluene (250 ml.) and refluxing for 1 hr. After cooling, triethylammonium chloride (28.3 g.; 102%) was filtered off, and evaporation of the filtrate gave the bis(arylamino) boron chloride $(22 \cdot 3)$ g.; 78%).

²⁵ W. Kynaston, B. E. Larcombe, and H. S. Turner, J. Chem.

Soc., 1960, 1772. ²⁶ W. Gerrard, M. F. Lappert, and C. A. Pearce, J. Chem. Soc., 1957, 381.

Reaction of diethylaminoboron dichloride with 2,6-xylidine. 2,6-Xylidine (20 g.; 0.17 mole) in toluene (50 ml.) was added to diethylaminoboron dichloride ¹⁴ (26 g.; 0.17 mole) in toluene (100 ml.) at -70° and the resulting slurry was heated to the boiling point and refluxed for 2 hr. After cooling, the precipitate of diethylammonium chloride (9.06 g.; 0.08 mole) (Found: B, 0.9; Cl, 33.5; N, 13.0. Calc. for C₄H₁₂ClN: Cl, 32.4; N, 12.8%) was filtered off, and evaporation of the filtrate gave bis(2,6-xylidino)boron chloride (22.0 g.; 0.077 mole).

Reaction of boron trichloride with bis(2,6-xylidino)boron chloride. Boron trichloride (6 g.; 0.05 mole) was added to bis(2,6-xylidino)boron chloride (3.7 g.; 0.013 mole) in toluene (50 ml.) and the mixture was gently heated under reflux under a water-cooled condenser surmounted by a "dry-ice" condenser. The solution was then evaporated, and 2,6-xylidinoboron dichloride (2.07 g.; 0.01 mole) was sublimed (50°/0.01 mm.) from the residue leaving the boronamine (XVI; R = 2,6-xylyl) (1.8 g.; 0.004 mole).

Tris(2,6-xylidino)boron. Triethylamine (8.2 ml.; 0.060 mole) and 2,6-xylidine (4.8 ml.; 0.040 mole) in toluene (25 ml.) were added to 2,6-xylidine-boron trichloride (4.8 g.; 0.020 mole) in toluene (75 ml.) at room temperature, and the mixture was heated under reflux for $\frac{1}{2}$ hr. The precipitate (8 g.) was filtered off, the filtrate evaporated to dryness, and the residue was extracted with water, leaving tris(2,6-xylidino)boron (3.7 g.). A further quantity (1.0 g.) was obtained by aqueous extraction of the precipitate from the preparation, and the combined yield (4.7 g.; 0.013 mole) was purified by sublimation (220°/0.1 mm.) and recrystallisation from ethanol; m. p. 247-248° (Found: C, 77.6; H, 8.2; B, 3.1; N, 11.5. C₂₄H₃₀BN₃ requires: C, 77.7; H, 8.1; B, 2.9; N, 11.3%).

After the compound (1.9 g.) had been heated during 5 hr. at 300° in nitrogen, 1.45 g. was recovered unchanged by sublimation.

Ethyl bis(2,6-xylidino)borinate. Ethanol (2.9 ml.; 0.050 mole) and triethylamine (7 ml.; 0.050 mole) in toluene (20 ml.) were added dropwise to bis(2,6-xylidino)boron chloride (14.3 g.; 0.050 mole) in toluene (250 ml.). After standing overnight, triethylammonium chloride (6.6 g.; 0.048 mole) was filtered off and ethyl bis(2,6-xylidino)borinate (14.6 g.; 0.049 mole), obtained by evaporating the filtrate to dryness, was purified by recrystallisation from light petroleum; m. p. 123-125° (Found: C, 72.7; H, 8.7; B, 3.3; N, 9.7. C₁₈H₂₅BN₂O requires: C, 73.0; H, 8.45; B, 3.65; N, 9.5%).

Ethyl bis(2,6-xylidino)borinate (1.57 g.; 0.0053 mole) was heated at 250° in nitrogen. Triethyl borate distilled off and the residue was sublimed, giving tris(2,6-xylidino)-boron (1.27 g.; 0.0033 mole; 97%), identified by comparison with an authentic specimen.

Di-B-chlorotri-N-(2,6-xylyl)borazole (XVIIIa). 2,6-Xylidine-boron trichloride (119·2 g.; 0·5 mole) in toluene (500 ml.) was heated at reflux temperature till the first vigorous reaction had subsided. After cooling, triethylamine (140 ml.; 1·0 mole) was added and the mixture was set aside for several weeks at 25°. Triethylammonium chloride (81·0 g.; 0·59 mole) (Found: Cl, 25·7; N, 9·8. Calc. for C₆H₁₆ClN: Cl, 25·8; N, 10·2%) was filtered off, and the filtrate was evaporated to *ca*. 150 ml. The precipitate (39·6 g.) which formed was recrystallised from light petroleum giving *di*-B-*chlorotri*-N-(2,6-*xylyl*)*borazole* (32·2 g.; 0·076 mole; 45%), m. p. 248-253°. Sublimation and recrystall-K K isation gave a specimen of m. p. $255-256^{\circ}$ (Found: C, $62\cdot5$; H, $6\cdot1$; B, $7\cdot0$; Cl, $15\cdot6$; N, $9\cdot0\%$; M, 455. C₂₄H₂₈B₃N₃Cl₂ requires: C, $62\cdot5$; H, $6\cdot1$; B, $7\cdot1$; Cl, $15\cdot4$; N, $9\cdot1\%$ M, 461). I.r. spectrum: DMS card no. 13325. Hydrolysis with sodium hydroxide in ethane-1,2-diol gave hydrogen (Table 3).

The filtrate obtained after separating the crude dichloroborazole was evaporated under reduced pressure, and the sticky material obtained was crystallised from light petroleum (100 ml.). The product was identified, after several further recrystallisations, as the boronamine (XVI) by comparison with a specimen obtained by heating 2,6-xylidinoboron dichloride.

Di-B-hydroxytri-N-(2,6-xylyl)borazole (XVIIIb). The dichloroborazole (3.68 g.) in water was heated under reflux for 3 hr., giving di-B-hydroxytri-N-(2,6-xylyl)borazole (3.26 g.; 95%), purified by sublimation and recrystallisation from light petroleum; m. p. 252-253° (Found: C, 67.9; H, 7.4; B, 7.9; N, 9.6. $C_{24}H_{30}B_3N_3O_2$ requires: C, 67.9; H, 7.1; B, 7.6; N, 9.9%). I.r. spectrum: DMS card no. 12243. Hydrolysis with sodium hydroxide in ethane-1,2-diol gave hydrogen (Table 3).

In another experiment, boron trichloride was passed slowly into a suspension of 2,6-xylylammonium chloride (79 g.; 0.5 mole) in refluxing toluene (500 ml.) until a clear solution was obtained (\sim 1 hr.). The excess of boron trichloride was removed by refluxing for a further hour, and, after cooling, triethylamine (140 ml.; 1.0 mole) was added. The mixture was left at room temperature for about two weeks; 2N-hydrochloric acid (500 ml.) was then added and the solvent removed by steam distillation. The dihydroxyborazole (37.5 g.; 53%) was obtained as an off-white precipitate.

Acid-hydrolysis of the dihydroxyborazole (XVIIIb). The dihydroxyborazole (0.6 g.) was dissolved in concentrated sulphuric acid (10 ml.) and after a few minutes the solution was poured on to crushed ice. The unchanged dihydroxy compound (0.15 g.) was filtered off and the filtrate was made alkaline, liberating 2,6-xylidine, identified as its benzoyl derivative.

The dihydroxy compound (8.5 g.; 0.020 mole) in ethanol (300 ml.) and 2N-sulphuric acid (50 ml.) was heated under reflux for six days. Hydrogen (\sim 300 ml.) was given off. The solution was evaporated to \sim 100 ml., water (200 ml.) and benzene (200 ml.) were added, and the mixture was steam distilled. Unchanged dihydroxy compound (2.5 g.; 0.006 mole), m. p. 240—248°, was filtered off. The filtrate was made alkaline and the liberated 2,6-xylidine was identified as its benzoyl derivative.

Alcoholysis of the dihydroxyborazole. The dihydroxyborazole (4.25 g.; 0.010 mole) in benzyl alcohol (40 ml.) was heated under reflux for 4 hr. Hydrogen (~250 ml.) was evolved. The solution was distilled and a fraction (b. p. 175—185°/0.05 mm.) (Found: C, 77.2; H, 6.7; B, 3.0. Calc. for $C_{21}H_{21}BO_3$: C, 75.9; H, 6.3; B, 3.3%) was identified as tribenzyl borate by comparison of its i.r. absorption spectrum with that of an authentic specimen. 2,6-Xylidine was recovered from the low-boiling fraction by extraction with dilute acid.

Alkaline hydrolysis of the dihydroxyborazole: tri-Bhydroxytri-N-(2,6-xylyl)borazole (XVIIIc). The dihydroxyborazole (53 g.; 0.125 mole) in toluene (300 ml.) was heated under reflux with water (20 ml.) and triethylamine (140 ml.). Hydrogen was evolved on warming, and the reaction was complete within 2 hr. More water was added, and organic liquids were removed by steam distillation, giving a precipitate (54g.; 0.123 mole) of tri-*B*-hydroxytri-*N*-(2,6-xylyl)borazole,²¹ m. p. 296—297°. I.r. spectrum: DMS card no. 12244. No hydrogen was liberated when the compound was heated with a solution of sodium hydroxide in ethane-1,2-diol.

Reaction between the dihydroxyborazole (XVIIIb) and thionyl chloride. The dihydroxyborazole (50 g.) was heated in purified thionyl chloride (250 ml.) containing a crystal of pyridinium chloride until hydrogen chloride evolution had ceased. The excess of thionyl chloride was evaporated under reduced pressure and the residual dichloroborazole (XVIIIa) (54 g.) was purified by sublimation and crystallisation. The final yield was 45 g. (82%).

Tri-B-chlorotri-N-(2,6-xylyl)borazole (XVIIId). The trihydroxyborazole (XVIIIc) (52 g.) was treated with thionyl chloride in the same way as the dihydroxyborazole. Tri-B-chlorotri-N-(2,6-xylyl)borazole (42 g.; 72%), m. p. 316— 318°, was obtained by recrystallising the crude material from toluene (Found: C, 58·2; H, 5·6; B, 6·7; Cl, 21·2; N, 8·4. $C_{24}H_{27}B_3Cl_3N_3$ requires: C, 58·1; H, 5·4; B, 6·5; Cl, 21·5; N, 8·5%). I.r. spectrum: DMS card no. 13326.

Reaction of chloroborazoles with dimethyl sulphoxide. The trichloroborazole (XVIIId) (1.9 g.) dissolved in dimethylsulphoxide (15 ml.) with the evolution of heat. After standing overnight, the excess dimethyl sulphoxide was evaporated off ($\sim 100^{\circ}/0.03$ mm.), and the residue sublimed and recrystallised from toluene-light petroleum. The product (1.34 g.; 80%) was identified as tri-*B*-hydroxytri-*N*-(2,6-xylyl)borazole by comparison with an authentic specimen (Found: Cl, < 0.2%; S, 0.2%).

The dichloroborazole (XVIIIa) was similarly converted to the dihydroxyborazole (XVIIIb).

Tri-B-chloro-tri-N-phenylborazole also dissolved in dimethylsulphoxide with the evolution of heat, but the solution set to a gel before any product could be isolated.

Di-B-methoxytri-N-(2,6-xylyl)borazole (XVIIIe; X = OMe). The dichloroborazole (XVIIIa) (46 g.; 0·1 mole) in benzene (600 ml.) was treated at 5° with dry methanol (8·6 ml.; 0·21 mole) and triethylamine (32 ml.; 0·22 mole). After standing for two days at room temperature, triethyl-ammonium chloride was filtered off and the filtrate was evaporated under reduced pressure. The residue was washed with a little water, dried, and recrystallised from light petroleum giving di-B-methoxytri-N-(2,6-xylyl)borazole (40·3 g.; 0·09 mole), m. p. 187–188° (Found: C, 68·7; H, 7·8; B, 7·5; N, 9·3. C₂₆H₃₄B₃N₃O₂ requires: C, 68·9; H, 7·5; B, 7·2; N, 9·3%).

Partial methylation of the dihydroxyborazole (XVIIIb). Methyl iodide (7.5 ml.; 0.120 mole) was added to the dihydroxy compound (3.94 g.; 0.0092 mole) and sodium methoxide (1.035 g.; 0.0192 mole) in methanol (150 ml.) and the solution was heated under reflux for 7 hr. The solid (6.95 g.) obtained by evaporation was well washed with water and the dried residue (4.08 g.), m. p. 160—165°, was recrystallised from light petroleum (25 ml.), giving the di-methoxy derivative (1.82 g.), m. p. 178—181°, which was shown by its i.r. spectrum to contain up to 15% of unchanged dihydroxyborazole. A further crop (1.19 g.) of material, m. p. 162—168°, was obtained by evaporating the mother-liquors.

Di-B-benzyloxytri-N-(2,6-xylyl)borazole (XVIIIe; X = OCH₂Ph). Treatment of the dichloroborazole (3.87 g.; 0.0084 mole) in benzene (100 ml.) with benzyl alcohol (1.95 ml.; 0.0185 mole) and triethylamine (2.8 ml., 0.020

mole) at room temperature gave, after several hours, a precipitate of triethylammonium chloride (0.0169 mole) and, by evaporating the filtrate, *di*-B-*benzyloxytri*-N-(2,6-*xylyl)borazole* (4.85 g.) as a viscous liquid, apparently miscible in all proportions with light petroleum (Found: C, 76.6; H, 7.3; B, 5.3; N, 7.0. $C_{38}H_{42}B_3N_3O_2$ requires: C, 75.6; H, 7.0; B, 5.4; N, 7.0%).

Attempted preparation of (XVIIIe; $X = OCH_2Ph$) by trans-etherification. When the dimethoxyborazole (XVIIIe; X = OMe) (4.5 g.; 0.010 mole) was heated with benzyl alcohol (40 ml.) in a stream of nitrogen, a low boiling (<90°) liquid (0.54 g.; cal. for 0.020 mole MeOH, 0.64 g.) was given off, and fractionation of the residue gave benzyl borate (b. p. 155—156°/0.05 mm.), identified by its i.r. spectrum.

Di-B-phenoxytri-N-(2,6-xylyl)borazole (XVIIIe; X = OPh). Phenol (1.85 g.; 0.0197 mole) in benzene (40 ml.) was added at room temperature to compound (XVIIIa) (4.16 g.; 0.009 mole) and triethylamine (3.0 ml.; 0.020 mole) in benzene (60 ml.). After several hours, triethyl-ammonium chloride (0.018 mole) was removed by filtration. Evaporation of the filtrate under reduced pressure and recrystallisation of the residue from light petroleum gave di-B-phenoxytri-N-(2,6-xylyl)borazole (2.73 g.; 52.4%), m. p. 182—183° (Found: C, 75.1; H, 6.8; B, 5.9; N, 7.0. C₃₈H₃₈B₃N₃O₂ requires: C, 74.9; H, 6.6; B, 5.6; N, 7.3%). Hydrolysis with sodium hydroxide in ethane-1,2-diol gave hydrogen (Table 3).

Di-B-(2-chloroethoxy)tri-N-(2,6-xylyl)borazole (XVIIIe; X = OCH₂CH₂Cl). The dichloroborazole (18·4 g.; 0·040 mole), 2-chloroethanol (5·2 ml.; 0·100 mole) and triethylamine (20 ml.; 0·150 mole) were heated under reflux in toluene (600 ml.) for 3 hr. The precipitated triethylammonium chloride (11·2 g.; 0·082 mole) was filtered off, and evaporation of filtrate gave a brownish residue (24·3 g.). Crystallisation from ethanol gave di-B-(2-chloroethoxy)tri-N-(2,6-xylyl)borazole (16·7 g.) as colourless needles, m. p. 121-122° (Found: C, 60·8; H, 6·5; B, 5·7; Cl, 13·0; N, 7·7. C₂₈H₃₆B₃Cl₂N₃O₂ requires: C, 61·2; H, 6·6; B, 5·9; Cl, 12·9; N, 7·6%). I.r. spectrum: DMS card no. 13333.

Bis-B-(dimethylamino)tri-N-(2,6-xylyl)borazole (XVIIIe; X = NMe₂). The dichloroborazole (18.45 g.; 0.040 mole) in benzene (400 ml.) was added slowly to a cool (5°) stirred solution of dimethylamine (4.5 g.; 0.10 mole) and triethylamine (10.1 g.; 0.100 mole) in benzene (400 ml.). After standing overnight at room temperature, the precipitate was filtered off, and bis-B-(dimethylamino)tri-N-(2,6-xylyl)borazole (20.0 g.; 105%) was obtained by evaporation of the filtrate. Two recrystallisations from light petroleum gave the pure compound, m. p. 197–198° (Found: C, 70.4; H, 8.9; B, 6.4; N, 14.2. C₂₈H₄₀B₃N₅ requires: C, 70.3; H, 8.4; B, 6.8; N, 14.6%). I.r. spectrum: DMS card no. 13331. Hydrolysis with sodium hydroxide in ethane-1,2-diol slowly liberated hydrogen.

Di-B-(ethylamino)tri-N-(2,6-xylyl)borazole (XVIIIe; X = NHEt). Addition of the dichloroborazole (4.83 g.; 0.0105 mole) in benzene (75 ml.) to a cold solution of ethylamine in benzene (12.7 ml.; 1.81N solution) gave, after removal of the precipitate and evaporation of the filtrate, a quantitative yield of di-B-(ethylamino)tri-N-(2,6-xylyl)borazole, m. p. 106-108° (Found: C, 69-2; H, 8.1; B, 6.5; N, 14.3. C₂₈H₄₀B₃N₅ requires: C, 70.3; H, 8.4; B, 6.8; N, 14.6%).

Di-B-anilinotri-N-(2,6-xylyl)borazole (XVIIIe; X = NHPh). A solution of the dichloroborazole (4.61 g.; 0.010

mole), aniline (2·4 g.; 0·025 mole) and ethyldi-isopropylamine ²⁷ (3·9 g.; 0·030 mole) in toluene (175 ml.) was heated under reflux for 20 hr. Ethyldi-isopropylammonium chloride (3·3 g.; 0·020 mole) was filtered off, and evaporation of the filtrate gave *di*-B-*anilinotri*-N-(2,6-*xylyl*)*borazole*, which after recrystallisation from light petroleum had m. p. 149—151° (Found: C, 74·9; H, 7·2; B, 5·6; N, 12·3. $C_{36}H_{40}B_3N_5$ requires: C, 75·3; H, 7·0; B, 5·6; N, 12·2%). Hydrolysis with sodium hydroxide in ethane-1,2-diol slowly liberated hydrogen.

Bis-B-[2(diethylamino)ethylamino]tri-N-(2,6-xylyl)borazole (XVIIIe; $X = NH \cdot CH_2 \cdot CH_2 \cdot NEt_2$). The dichloroborazole (4.6 g.; 0.010 mole), 2-(diethylamino)ethylamine (2.4 g.; 0.020 mole) and triethylamine (2.25 g.; 0.025 mole) were heated under reflux in benzene (50 ml.) for 2 hr. After filtering off the triethylammonium chloride (2.5 g.; 0.018 mole), evaporation of the solution gave a sticky solid (6.2 g)which was very soluble in the common solvents. Crystallisation from a small quantity of light petroleum gave the compound (XVIIIe; $X = NH \cdot CH_2 \cdot CH_2 \cdot NEt_2$), m. p. 85-90° (Found: C, 69.0; H, 9.6; B, 5.5; N, 15.1. C₃₆H₅₈B₃N₇ requires: C, 69.6; H, 9.4; B, 5.2; N, 15.8%). Addition of methyl iodide to an ethereal solution of this compound gave a mixture of mono- and dimethiodides (Found: C, 54.8; H, 8.1; B, 4.0; I, 17.6; N, 11.5. C37H61B3IN7 requires: C, 58.2; H, 8.0; B, 4.2; I, 16.7; N, 12.9%. C₃₈H₆₄B₃I₂N₇ requires: C, 50.4; H, 7.1; B, 3.5; I, 28.2; N, 10.8%). The mixture of methiodides was sparingly soluble in water.

Di-B-aminotri-N-(2,6-xylyl)borazole (XVIIIe; X = NH₂). Moisture-free liquid ammonia was added dropwise to a stirred solution of the dichloroborazole (35.5 g.; 0.076 mole) in toluene (1 l.) at -80° , until an excess was present. After a further hour, the mixture was left to warm up to room temperature and the excess of ammonia evaporated off. The precipitate (11.2 g) was filtered off; evaporation of the filtrate gave di-B-aminotri-N-(2, 6-xylyl) borazole (27.8 g.). The precipitate was washed with hot water to remove ammonium chloride (8.0 g.) leaving a further 3.2 g. of the diamino-compound. Recrystallisation of the combined yield (96%) from light petroleum gave colourless needles (22.5 g.), m. p. 285-287°. Further purification by sublimation $(200^{\circ}/0.05 \text{ mm.})$ and recrystallisation gave a sample, m. p. 286-287° (Found: C, 68.7; H, 7.8; B, 7.7; N, 16.7. C₂₄H₃₂B₃N₅ requires C, 68·2; H, 7·6; B, 7·7; N, 16·7%). I.r. spectrum: DMS card no. 13330.

Tri-B-aminotri-N-(2,6-xylyl)borazole (XVIIIf, $X = Y = NH_2$). The trichloroborazole (9.95 g.; 0.020 mole) was converted into the triaminoborazole (8.85 g.; 0.020 mole) in the way described for the diaminoborazole. Recrystallisation from light petroleum gave the pure compound, m. p. 325–326° (Found: C, 65.4; H, 7.5; B, 7.3; N, 19.3. C₂₄H₃₃B₃N₆ requires: C, 65.9; H, 7.6; B, 7.4; N, 19.2%).

Reactions of aminoborazoles with nitrosyl chloride. The diaminoborazole (XVIIIe; $X = NH_2$) (4.2 g.; 0.010 mole) in toluene (200 ml.) was treated with nitrosyl chloride (~1 ml.) in toluene (25 ml.) at 0°. After standing at room temperature for some time, the precipitate of ammonium chloride (0.37 g.) was filtered off; evaporation of the filtrate gave a mixture (4.55 g.) of the dihydroxy and dichloroborazoles (Found: B, 7.4; Cl, 4.3; N, 9.4%).

The triaminoborazole (XVIIIf, $X = Y = NH_2$) (1.46 g.; 0.0033 mole) in 1,2-dimethoxyethane (275 ml.) at 5° was treated with nitrosyl chloride (2 ml.) and amyl nitrite (10 ml.) in 1,2-dimethoxyethane (25 ml.). Gas evolution began immediately. After some time, the solution was left to warm up to room temperature, and the residue (1.88 g.) after evaporation was recrystallised from light petroleum, giving the trihydroxyborazole only slightly contaminated with the chloro-compound (Found: Cl, 0.6%).

Tri-B-n-butyltri-N-(2,6-xylyl)borazole (XVIIIf; X = Y = Buⁿ). A heptane solution (2.15M) of n-butyl-lithium (14.5)ml.; 0.035 mole) diluted with ether (100 ml.) was added during 30 min. to the dichloroborazole (4.61 g.; 0.010 mole) in ether (100 ml.) and the mixture was heated under reflux for 1 hr. After filtering and evaporating the solution, the residue was extracted with light petroleum and the extracted material was sublimed (200°/0.03 mm.) giving tri-B-n-butyltri-N-(2,6-xylyl)borazole (3.9 g.; 0.007 mole), which after recrystallisation from 1,2-dimethoxyethane had m. p. 175-176° (Found: C, 77.1; H, 9.8; B, 6.1; N, 7.8. C₃₆H₅₄B₃N₃ requires: C, 77.1; H, 9.6; B, 5.8; N, 7.5%). This compound was also obtained when n-butyl-lithium (30 ml.; 2.15m in heptane) find the trichloroborazole (XVIIId) (10 g.) were heated under reflux for 1 hr. in ether (100 ml.). Lithium chloride (2.1 g.; calc. 2.5 g.) was filtered off, and the product was isolated as described in the previous experiment.

Tri-B-phenyltri-N-(2,6-xylyl)borazole (XVIIIf; X = Y = Ph). A solution of the dichloroborazole (6.35 g.; 0.0137 mole) and phenyl-lithium (0.048 mole) in ether (300 ml.) was heated under reflux for 2 hr. The precipitate (9.14 g.) was filtered off and washed with water, and the residue, tri-B-phenyltri-N-(2,6-xylyl)borazole (7.8 g.; 0.0125 mole), was recrystallised from 1,2-dimethoxyethane; m. p. 350-353° [Found: C, 81.6; H, 6.9; B, 5.2; N, 6.7%. M (ebull.), 619. $C_{42}H_{42}B_3N_3$ requires: C, 81.3; H, 6.8; B, 5.2; N, 6.8%. M, 620]. I.r. spectrum: DMS card no. 13329. No hydrogen was evolved when the product was heated with sodium hydroxide in ethane-1,2-diol. This compound was also formed when the dimethoxyborazole (XVIIIe; X = OMe) (4.52 g.; 0.010 mole) and phenyllithium (0.064 mole) were heated under reflux in ether (300 ml.) for 5 hr.; it was isolated (60%) as described in the previous experiment.

Tri-B-(p-bromophenyl)tri-N-(2,6-xylyl)borazole, (XVIIIf; X = Y = p-BrC₆H₄). p-Bromophenyl-lithium was prepared from p-dibromobenzene (16.6 g.; 0.070 mole) in ether (50 ml.) and n-butyl-lithium in heptane (31 ml.; 2.15M soln.); the dichloroborazole (6.8 g.; 0.015 mole) in ether (300 ml.) was added and the mixture was heated under reflux for 4 hr. After filtering off the precipitate, evaporation of the solution to small bulk gave tri-B-(pbromophenyl)tri-N-(2,6-xylyl)borazole (6.93 g.; 0.008 mole), m. p. 332-333° (after recrystallisation from light petroleum) (Found: C, 59.1; H, 5.1; B, 4.0; Br, 26.8; N, 4.5. C₄₂H₃₉B₃Br₃N₃ requires: C, 58.8; H, 4.6; B, 3.8; Br, 28.0; N, 4.9%).

B-Phenylbis-B-(dimethylamino)tri-N-(2,6-xylyl)borazole (XVIII; R = 2,6-xylyl; $X = NMe_2$; Y = Ph). The bis(dimethylamino)-compound (XVIIIe; $X = NMe_2$) (2·4 g.; 0·005 mole) and phenyl-lithium (0·005 mole) were heated under reflux for 2 hr. in ether (160 ml.), and the precipitate (40 mg.) was filtered off. The residue obtained by evaporation of the filtrate was recrystallised twice from 1,2-dimethoxyethane, giving B-phenylbis-B-(dimethylamino)tri-N-(2,6-xylyl)borazole (1·4 g.; 0·0025 mole), m. p. 255-256° (Found: C, 74·6; H. 8·2; B, 5·8; N, 12·5.

²⁷ S. Hünig and M. Kiessel, Chem. Ber., 1958, 91, 380.

 $C_{34}H_{44}B_3N_5$ requires: C, 73.6; H, 8.0; B, 5.8; N, 12.6%). I.r. spectrum: DMS card no. 13332. No hydrogen was liberated when this compound was heated with sodium hydroxide in ethane-1,2-diol.

Tri-N-(2,6-xylyl)borazole (XVIIIe; X = H). The dichloroborazole (1.13 g.; 0.00244 mole) and sodium tetrahydroborate (0.232 g.; 0.0061 mole) were milled together with 1,2-dimethoxyethane (15 ml.) for 3 days. The solid residue (Cl content, 0.0049 mole) was filtered off, and the residue obtained by evaporating the filtrate was recrystallised from light petroleum giving tri-N-(2,6-xylyl)borazole, m. p. 154-155° (Found: C, 73·4; H, 7·8; B, 8·6; N, 10·5. C₂₄H₃₀B₃N₃ requires: C, 73·4; H, 7·7; B, 8·3; N, 10·7%). Infrared spectrum: DMS card no. 13327. Hydrolysis of a specimen with sodium hydroxide in ethane-1,2-diol gave hydrogen (Table 3). The purified compound was stable in moist air for several weeks, but the material obtained initially from the preparation decomposed in moist air to a sticky solid whose i.r. spectrum no longer showed absorption in the 2550 cm.⁻¹ region.

2,6-Xylidine-boron tribromide. The amine (26 g.; 0.215 mole) in light petroleum (20 ml.) was added to boron tribromide (20 ml.; 0.215 mole) in light petroleum (300 ml.) at 0° and the *adduct* (52.5 g.; 0.140 mole) was filtered off (Found: C, 26.4; H, 3.3; B, 2.7; Br, 62.2; N, 3.8. $C_8H_{11}BBr_3N$ requires: C, 25.8; H, 3.0; B, 2.9; Br, 64.6; N, 3.8%).

Dehydrobromination of 2,6-xylidine-boron tribromide. The adduct (46·1 g.; 0·125 mole) was heated in toluene (500 ml.) for 4 hr. and, after cooling, triethylamine (100 ml.) was added. After several days, triethylammonium bromide (27·8 g.; 0·150 mole) was filtered off, and the filtrate was evaporated under reduced pressure. The i.r. spectrum of the residue showed no absorption in the 2550 cm.⁻¹ region, and hydrolysis of a portion (1·1 g.) gave tri(2,6-xylidino)-boron (0·5 g.), identified by comparison with an authentic specimen.

Reaction between the dihydroxyborazole (XVIIIb) and thionyl bromide. When the hydroxyborazole (2.13 g.; 0.005 mole) and a drop of pyridine were heated gently with thionyl bromide ²⁸ (20 ml.) extensive decomposition of the latter occurred, and evaporation of the solution followed by extraction with light petroleum gave sulphurcontaining products which showed no absorption in the 2550 cm.⁻¹ region of their i.r. spectra.

Di-B-bromotri-N-(2,6-xylyl)borazole (XVIIIe; X = Br). An excess of hydrogen bromide was passed into the diaminoborazole (XVIIIe; X = NH₂) (8.4 g.; 0.020 mole) in benzene (400 ml.) and the precipitated ammonium bromide (4.0 g., 0.040 mole) was filtered off. Evaporation of the filtrate gave di-B-bromotri-N-(2,6-xylyl)borazole (10.8 g.; 0.020 mole) which, after sublimation (200°/0.05 mm.) and recrystallisation from light petroleum, had m. p. 258– 259° (Found: C, 52.5; H, 5.2; B, 6.0; Br, 28.3; N, 7.6. C₂₄H₂₈B₃Br₂N₃ requires: C, 52.3; H, 5.1; B, 5.9; Br, 29.1; N, 7.6%). I.r. spectrum: DMS card no. 13328. In an analogous manner, the trichloroborazole (0.72 g.; 100%) and ammonium chloride (0.22 g.; 95%) were obtained by the action of hydrogen chloride on the triaminoborazole (XVIIIf, X = Y = NH₂) (0.63 g.).

Experiments on the Mechanism of Formation of the Borazole (XVIIIa).—Rate of formation. In the general method, a solution containing 2,6-xylidinoboron dichloride (II) was treated with triethylamine in a separating funnel and portions of the stirred mixture were run under nitrogen into weighed flasks. The known weights of solution were allowed to react for the appropriate times and were then treated with dilute hydrochloric acid. Solvent was removed by steam distillation and the dihydroxyborazole was filtered off into weighed, sintered crucibles. A blank experiment showed that there was no significant loss of borazole during the steam distillation. The results are set out in Figure 3.

When another compound, *i.e.*, the boronamine (XVI; R = 2,6-xylyl; X = Cl) or triethylamine-boron trichloride was added to the reaction mixture, it was added as a solution to one half of a solution of (II) and an equal volume of solvent was added to the other half of the solution of (II), which was used as a blank. Each solution was then treated with triethylamine and separated into portions as described. The results are set out in Figure 6.

Effect of heat on the rate of formation of the borazole (XVIIIa). Triethylamine (56 ml.; 0.4 mole) was added to a solution of 2,6-xylidinoboron dichloride (II) (0.2 mole) and the mixture was divided into two equal parts. One part was heated to $\sim 90^{\circ}$ for 6 hr., set aside to cool overnight, and worked up for the dihydroxyborazole, the yield of which was 4.3 g. (0.010 mole; 30%). The other part was kept at room temperature for the same total time; yield of dihydroxyborazole, 2.7 g. (0.0064 mole; 19%).

Variation in the yield of borazole (XVIIIa) with increasing initial dehydrochlorination of 2,6-xylidine-boron trichloride. Portions (12 g., 0.050 mole) of 2,6-xylidine-boron trichloride were heated in toluene (50 ml.) in a stream of nitrogen, and the gases evolved were absorbed in sodium hydroxide solutions equivalent to 0.25, 0.5, 0.75, 1.0, 1.25, 1.5, and 1.75 mole hydrogen chloride per mole of adduct and containing an acid-base indicator. The toluene solutions were rapidly cooled when the appropriate quantity of hydrogen chloride had been adsorbed, and the chloride content of the absorber solutions were determined by titration with silver nitrate solution. The toluene solutions were treated with triethylamine (20 ml.) and allowed to stand for several weeks, when the dihydroxyborazole was isolated. The results are set out in Table 5. In another experiment, 2,6-xylidine-boron trichloride (12.1 g.; 0.050 mole) in refluxing benzene (50 ml.) gave off during 23 hr. hydrogen chloride and boron trichloride equivalent to 0.075 g. atom Cl. Addition of an excess of trimethylamine gave the adduct, C₈H₉NH·BCl₂,NMe₃ (Table 9) (7.25 g.; 0.0278 mole). Triethylamine (20 ml.) was added to the filtrate and, after a month, the mixture was worked up for the dihydroxyborazole, but none was obtained.

Effect on borazole formation of varying the molar ratio of triethylamine. A toluene solution of 2,6-xylidinoboron dichloride was divided into ten 100 ml. portions each containing ~ 0.080 mole, and each was treated with the appropriate quantity of triethylamine (0.020-0.32 mole). After a month, the dihydroxyborazole was isolated in the usual way. A separate experiment showed that there was no significant increase in the yield of borazole after a month at the lowest concentration of triethylamine. The results are shown in Figure 4.

Isolation of acetaldehyde and secondary amine derivatives from the reaction between 2,6-xylidinoboron dichloride and tertiary amines. Triethylamine (140 ml.; 1.0 mole), which had been distilled from acetic anhydride, was added to a

²⁸ R. E. Johnson, T. H. Norris, and J. L. Huston, *J. Amer. Chem. Soc.*, 1951, **73**, 3052; M. J. Frazer and W. Gerrard, *Chem. and Ind.*, 1954, 280.

toluene solution (~500 ml.) containing 2,6-xylidinoboron dichloride (II) (0.5 mole). After a week, 2N-hydrochloric acid (200 ml.) was added, and the mixture was distilled through a reflux condenser at $40-45^{\circ}$. The low-boiling distillate was collected in an ice-cooled receiver and was shown to contain acetaldehyde by the formation of a "dimedone" derivative, m. p. 139-140°, its "anhydride," m. p. 172-174°, and the 2,4-dinitrophenylhydrazone, m. p.

In a second experiment, the precipitate of triethylammonium chloride produced in the reaction between 2,6-xylidinoboron dichloride and triethylamine was filtered off before hydrolysing the reaction mixture. No diethylamine derivatives could be detected in the precipitate, and from the filtrate, NN-diethyl-*p*-toluenesulphonamide and the dihydroxyborazole were obtained in the yield ratio of 0.96:1.

TABLE 8

Treatment of 2,6-xylidinoboron dichloride (II) with various tertiary bases

	Vield	Amine hyd Foun	trochloride d (%)	Calc.	(%)	
Amine	(moles per mole II)	Cl	N	Cl	N	Hydrolysis product
Et_3N	1.15	25.7	10.2	$25 \cdot 8$	10.2	(XVIIIb)
EtN [CH ₂] ₅	1.14	24.0	9.1	23.7	9.4))
^{i}N [CH ₂] ₅	0.65	21.2	7.5	21.7	8.6	,,
PriMe.N	*	*	*	*	*	.,
Et,PrN	0.75	$23 \cdot 6$	9.2	$23 \cdot 45$	9.25))
Et ₂ MeN	1.03	$29 \cdot 2$	11.7	28.75	11.3	* *
MePr ₂ N	0.30	$24 \cdot 8$	9.1	$23 \cdot 45$	9.25	3.3
EtPr ₂ N	0.00					,,
Me ₂ PrN	0.12	$29 \cdot 1$	11.6	28.75	11.3	$(2,6-Me_{2}C_{6}H_{3}NH)_{3}B^{\dagger}$
Pr ⁱ ₂ MeN	0.02	$23 \cdot 1$	9.4	$23 \cdot 45$	9.25	,,
Et ₂ Pr ⁱ N	0.00					,,
Pr ₃ N	0.00			—		,,
$MeN \stackrel{[CH_2]_4}{\underset{CHMe}{\leftarrow}} \dots \dots$	0.16	23.4	9.5	23.7	9.4	None
Bu ₃ N		No re	action			
EtPr ⁱ 2N			,,			
Et ₂ PhN		L				
* See te	xt. † Identified by c	omparison v	with authen	tic specimer	ı.	

TABLE 9

Tertiary amine-2,6-xylidinoboron dichloride adducts

	Vield M n			Found %				Required %				
Amine	(%)	(decomp.)	C	н	В	Cl	N	c	H	В	Cl	N
Me ₂ N	96	140°	50.3	7.4	$4 \cdot 2$	26.9	10.9	50.6	7.3	4.1	27.2	10.7
EtMe,N	65	92	$52 \cdot 4$	7.6	$4 \cdot 2$	$24 \cdot 9$	10.2	52.4	$7 \cdot 6$	$3 \cdot 9$	25.7	10.2
$C_5H_5N^a$					$4 \cdot 0$	$21 \cdot 4$	10.6			3.85	25.3	10.0
N _[CH ₃ ·CH ₃] ₃ N ^b	80	150	53.6	$7 \cdot 2$	$3 \cdot 6$	$22 \cdot 9$	13.5	53.55	7.0	3.4	$22 \cdot 6$	13.4
,, ^c	77	280	51.2	6.7	4 ·7	26.7	10.8	51.2	$6 \cdot 2$	$4 \cdot 2$	27.5	10·9
		^a Crude	material:	^b 1:1 a	dduct:	° 1 : 2-a	dduct.					

162-163°, all of which were identical with authentic specimens. The reflux condenser was replaced by a stillhead, the organic liquids were steam distilled, and the dihydroxyborazole (XVIIIa) (38 g.; 0.089 mole; 53%), m. p. 246-250°, was removed by filtration. The filtrate was made up to 300 ml. with water and 30 ml. of the resulting solution was treated with 50% potassium hydroxide solution (10 ml.). The amines thus liberated were steam distilled, treated with toluene-p-sulphonyl chloride, and the sulphonamides were separated by the Hinsberg procedure. NN-diethyl-p-toluenesulphonamide (2.15 g.; 0.0095 mole), m. p. 51-53°, not depressed by admixture with an authentic specimen, was obtained, and its identity confirmed by its i.r. spectrum. Recrystallisation from methanol-water gave a specimen of m. p. 58-59°. The ratio of the mole yields of diethylamine derivative and dihydroxyborazole was 1.07:1.

In a similar experiment using 1-ethylpiperidine, acetaldehyde was detected, and the molar ratio of 1-toluenep-sulphonylpiperidine to hydroxyborazole was found to be 0.41:1. In the case of 1-isopropylpiperidine, no acetone or piperidine derivative was detected.

Treatment of 2,6-xylidinoboron dichloride with various tertiary amines. A toluene solution of the dichloride was divided into portions (~ 0.1 mole) and each portion was treated with a different tertiary amine (~ 0.2 mole). After two weeks, any precipitate was filtered off, and the filtrate was worked up for dihydroxyborazole. The yields of dihydroxyborazole are given in Table 6, and the yields and analyses of the amine hydrochlorides are given in Table 8. In the case of isopropyldimethylamine, the initial precipitate contains boron (Found: B, 2.2; Cl, 21.2; N, 10.0%) but extraction with hot toluene leaves the amine hydrochloride (Found: Cl, 27.9; N, 11.4. Calc. for

 $C_{5}H_{14}ClN$: Cl, 28.75; N, 11.3%) and evaporation of the extract gave an impure sample of the boronamine (XVI; R = 2,6-xylyl) (Found: B, 5.3; Cl, 16.2; N, 8.6. Calc. for (XVI; R = 2,6-xylyl): B, 4.8; Cl, 15.7; N, 9.3%).

Four amines gave precipitates of 1:1 adducts with 2,6-xylidinoboron dichloride (Table 9). Three of these readily crystallised from toluene, but the pyridine adduct decomposed during recrystallisation, forming pyridine-boron trichloride (Found: B, 5.6; Cl, 54.5; N, 7.5. Calc. for $C_5H_5BCl_3N$: B, 5.55; Cl, 54.2; N, 7.1%). Triethyl-enediamine also formed a 1:2 adduct in the presence of an excess of the dichloride.

Treatment of tri-B-chlorotri-N-(2,6-xylyl)borazole (XVIIId) with triethylamine. When triethylamine (10 ml.) was added to a toluene solution of the trichloroborazole (5 g.), there was no apparent reaction after several days, and evaporation of the solution gave unchanged starting material.

Effect of addition of tri-B-chlorotri-N-(2,6-xylyl)borazole on the reaction between 2,6-xylidinoboron dichloride and triethylamine. A solution of the dichloride $(0\cdot 1 \text{ mole})$ was divided into two equal portions (90 ml.); portion A was treated with triethylamine (20 ml.) and portion B with the trichloroborazole $(1\cdot 1 \text{ g.})$ and triethylamine (20 ml.). After several days, each solution was worked up for hydroxyborazole. Solution A gave the dihydroxyborazole $(4\cdot 26 \text{ g.})$, m. p. $243-250^{\circ}$. Solution B gave a mixture of di- and tri-hydroxyborazoles $(5\cdot 32 \text{ g.})$, m. p. $253-261^{\circ}$. The relative intensities of the absorptions at the OH and BH stretching frequencies in the i.r. spectrum of the mixture from solution B were consistent with the composition: $4\cdot 28$ g. dihydroxyborazole $+ 1\cdot 04$ g. trihydroxyborazole.

Relative rates of consumption of 2,6-xylidinoboron dichloride and formation of the dichloroborazole (XVIIIa). A toluene solution (425 ml.) of the dichloride (0.5 mole) was treated with triethylamine (75 ml.) and divided into weighed portions. After the appropriate reaction times, the precipitated triethylammonium chloride was filtered off, trimethylamine (2 mol.) was added to the filtrate and after several hours the precipitate of the 1:1 adduct of Me₃N and the dichloride was removed. The filtrate was worked up for the dihydroxyborazole in the usual way. Hydrolysis of the adduct confirmed that no trimethylamine-boron trichloride was present. The results are set out in Figure 5.

Action of triethylamine-boron trichloride on the boronamine (XVI; R = 2,6-xylyl). A solution of the boronamine (XVI) (4.5 g.; 0.010 mole), triethylamine-boron trichloride (2.2 g.; 0.010 mole) and triethylamine (1.5 ml.) in toluene (120 ml.) was set aside for several days. There was no apparent reaction, and evaporation of the solution gave a mixture (6.7 g.) of the unchanged starting materials. Hydrolysis of a portion (3.6 g.) with dilute acid gave triethylamine-boron trichloride (0.66 g.; 56% recovery), while recrystallisation of a further portion (2.35 g.) from toluene gave the boronamine (XVI) (1.1 g.; 70%).

Reactions with 2,6-Diethylaniline.—Thermal decomposition of 2,6-diethylaniline-boron trichloride. When the adduct (45 g.; 0.17 mole) was heated in toluene (300 ml.) hydrogen chloride was only slowly evolved (0.035 g. equiv. in 5 hr.).

When the adduct was heated at 140° (bath temp.) without solvent, slightly more than one mol of hydrogen chloride was rapidly evolved, but the reaction then slowed considerably (Figure 1). The adduct (13.3 g.; 0.05 mole) was heated without solvent for 15 min. (bath temp. 150°), when hydrogen chloride (0.055 mole) was evolved. The reaction product was distilled (88°/0.06 mm.) giving 2,6-diethylanilinoboron dichloride (9.2 g.; 0.04 mole) m. p. 7-7.5° (Found: C, 52.4; H, 6.1; B, 4.8; Cl, 30.8; N, 6.2%; M, 233. C₁₀H₁₄BCl₂N requires: C, 52.3; H, 6.1; B, 4.7; Cl, 30.9; N, 6.1%; M, 230) and a residual tar (Found: B, 4.0; Cl, 10.4; N, 7.7%) which was not further examined.

2,6-Diethylaniline (149 g.; 1 mole) in toluene (250 ml.) was added to boron trichloride (85 ml.; 1.1 mole) in toluene (400 ml.) at -70° . After allowing to warm up to room temperature overnight, solvent and excess of boron trichloride were distilled off at atmospheric pressure (bath temperature up to 200°) and the residue was fractionated under reduced pressure giving: (i) 2,6-diethylanilinoboron dichloride (155 g.; 0.675 mole), b. p. 88°/0.06 mm.; (ii) the boronamine (XV; R = 2,6-diethylphenyl) (20.1 g., 0.048 mole) (Found: C, 56.9; H, 6.6; B, 5.4; Cl, 24.8; N, 6.4%; M, 415. $C_{20}H_{27}B_2Cl_3N_2$ requires: C, 56.7; H, 6.4; B, 5.1; Cl, 25.2; N, 6.6%; M, 423); b. p. 168- $172^{\circ}/0.025$ mm.; (iii) the boronamine (XVI; R = 2,6-diethylphenyl) (19.3 g.; 0.036 mole), b. p. 215-220°/0.025 mm., which solidified and was recrystallised from light petroleum; m. p. 82-84° (Found: C, 67.1; H, 7.9; B, 3.8; Cl, 13.2; N, 7.5%; M, 517. C₃₀H₄₁B₃Cl₂N₃ requires: C, 67.2; H, 7.7; B, 4.0; Cl, 13.3; N, 7.8%; M, 536).

Reaction between 2,6-diethylaniline-boron trichloride and triethylamine. The adduct $(13\cdot3 \text{ g}., 0\cdot050 \text{ mole})$ was treated with triethylamine (6·9 ml.) in the manner described for 2,6-xylidine-boron trichloride. Evaporation of the liquid layers and extraction of the residue $(18\cdot2 \text{ g}.)$ with light petroleum gave an insoluble mixture $(10\cdot1 \text{ g}.: \text{ calc. } 9\cdot81 \text{ g}.)$ of triethylammonium chloride and triethylammonium tetra-chloroborate (Found: B, 2·9; Cl, 42·75; N, 6·7. Calc. for C₆H₁₆ClN + C₆H₁₆BCl₄N: B, 2·8; Cl, 45·2; N, 7·1%), while bis(2,6-diethylamilino)boron chloride (XVII) (8·4 g., 98%), m. p. 59-60°, was obtained from the light petroleum extract. (Found: C, 69·4; H, 7·9; B, 3·3; Cl, 10·7; N, 7·8; M, 350. C₂₀H₂₃BClN₂ requires: C, 70·0; H, 8·2; B, 3·2; Cl, 10·4; N, 8·2%; M, 342).

Di-B-chloro- and di-B-hydroxytri-N-(2,6-diethylphenyl) borazole, (XVIIIg; X = Cl or OH, Y = H). Triethylamine (200 ml.) was added to 2,6-diethylanilinoboron dichloride (57.4 g.; 0.25 mole) in toluene (200 ml.), and after standing for a week at room temperature triethylammonium chloride (44.7 g.; 0.325 mole) was filtered off. The filtrate was concentrated to 50 ml. and left to crystallise, giving di-B-chlorotri-N-(2,6-diethylphenyl)borazole (12.4 g.; 0.023 mole). After sublimation (220°/0.05 mm.) and recrystallisation from light petroleum, the compound (6.0 g.) had m. p. 243-244° (Found: C, 65.9; H, 7.5; B, 6.0; Cl, 12.9; N, 7.7. C₃₀H₄₀B₃Cl₂N₃ requires: C, 65.9; H, 7.3; B, 5.9; Cl, 13.0; N, 7.7%). I.r. spectrum: DMS card no. 13336. The filtrate obtained after removing the dichloroborazole was acidified with dilute hydrochloric acid and volatile organic materials were removed by steamdistillation. The precipitated di-B-hydroxytri-N-(2,6-diethylphenyl)borazole (17.6 g.; 0.034 mole) was sublimed (220°/0.05 mm.) and recrystallised from light petroleum, giving the pure compound (16.0 g.) m. p. 242-243° (Found: C, 70.9; H, 8.5; B, 6.4; N, 8.3. $C_{30}H_{42}B_3N_3O_2$ requires: C, 70.8; H, 8.3; B. 6.4; N, 8.3%). I.r. spectrum: DMS card no. 13337.

Treatment of the dihydroxyborazole (15.25 g.; 0.030

mole) with thionyl chloride (75 ml.) containing pyridinium chloride (one crystal) in the way described previously gave the dichloroborazole (14.36 g.; 0.026 mole), identical with that obtained directly.

The dichloroborazole (3.36 g.) was converted into the dihydroxyborazole (2.42 g.; 78%) by treatment with dimethyl sulphoxide in the way described for the N-(2,6-xylyl)borazoles.

Tri-B-hydroxy- and tri-B-chloro-tri-N-(2,6-diethylphenylborazole (XVIIIg; X = Y = OH or Cl). The dihydroxy borazole (9.9 g.; 0.020 mole), toluene (300 ml.), water (9 ml.), and triethylamine (70 ml.) were heated under reflux until hydrogen evolution had ceased. Tri-B-hydroxytri-N-(2,6-diethylphenyl)borazole (9.9 g.; 98%) was obtained by removing the solvent by steam distillation, and after recrystallisation from light petroleum had m. p. 289-290° (Found: C, 69·2; H, 8·3; B, 6·2; N, 7·5. C₃₀H₄₂B₃N₃O₃ requires: C, 68.7; H, 8.0; B, 6.2; N, 8.0%). The trichloroborazole, m. p. 307-309° (Found: C, 62.0; H, 6.9; B, 5.2; N, 6.9. C₃₀H₃₉B₃Cl₃N₃ requires: C, 62.1; H, 6.7; B, 5.6; N, 7.2%), was obtained from the hydroxycompound by treatment with thionyl chloride, and was purified by sublimation and recrystallisation from light petroleum.

The trichloroborazole (0.65 g.) was converted into the trihydroxyborazole (0.36 g.; 60%) by treatment with dimethylsulphoxide in the manner described previously.

Reactions with other 2,6-Disubstituted Anilines .--- Di-Bchloro- and di-B-hydroxytri-N-mesitylborazole, (XVIII; R = 2,4,6-Me₃C₆H₂; X = Cl or OH; Y = H). Boron trichloride was passed into a suspension of mesitylammonium chloride (34.3 g.; 0.200 mole) in refluxing toluene (500 ml.) until an excess was present. The excess was removed by boiling the clear solution for a further hour and, after cooling, triethylamine (140 ml.; 1.00 mole) was added. After standing for several days at room temperature, triethylammonium chloride (22.5 g., 0.160 mole) was filtered off and the filtrate was evaporated under reduced pressure. The residue was recrystallised from light petroleum, giving di-B-chloro-tri-N-mesitylborazole (4.0 g.; 0.008 mole), m. p. 262-263° (Found: C, 64.5; H, 6.9; B, 6.0; Cl, 13.8; N, 8.1. C₂₇H₃₄B₃Cl₂N₃ requires: C, 64.4; H, 6.8; B, 6.4; Cl, 14.1; N, 8.4%). I.r. spectrum: DMS card no. 13334. The mother-liquors from the separation and purification of the dichloroborazole were combined and evaporated to dryness, and the residue was heated under reflux with water, giving di-B-hydroxytri-N-mesitylborazole (6.0 g.; 0.013 mole), which, after recrystallisation from light petroleum, had m. p. 228-230° (Found: C, 69.3; H, 7.8; B, 6.7; N, 9.0. $C_{27}H_{36}B_3N_3O_2$ requires: C, 69.4; H, 7.7; B, 6.9; N, 9.0%). I.r. spectrum: DMS card No. 13335.

Di-B-chloro- and di-B-hydroxytri-N-(2-chloro-6-methylphenyl)borazole (XVIII; R = 2,6-MeClC₆H₂, X = Cl or OH, Y = H). An excess of boron trichloride was passed into 2-chloro-6-methylaniline (28·4 g.; 0·200 mole) in refluxing toluene (500 ml.) and the excess was then allowed to distil off. Triethylamine (70 ml., 0·50 mole) was added to the cooled solution and, after standing overnight, triethylammonium chloride (32·9 g.; 0·024 mole) was filtered off. The residue (46·4 g.) obtained by evaporating the filtrate to dryness was recrystallised from light petroleum and the crude product (7·8 g.; 0·015 mole), m. p. 224—226°, was recrystallised from 1,2-dimethoxyethane, giving di-Bchlorotri-N-(2-chloro-6-methylphenyl)borazole, m. p. 232233° (Found: C, 48.5; H, 3.4; B, 6.0; Cl, 33.7; N, 7.7. $C_{21}H_{19}B_3Cl_5N_3$ requires: C, 48.2; H, 3.6; B, 6.2; Cl, 34.0; N, 8.0%). Infrared spectrum: DMS card no. 13338. The residue obtained by evaporating the light petroleum mother-liquors from the dichloroborazole separation was heated under reflux with water, and the water-insoluble residue was recrystallised from light petroleum giving di-B-hydroxytri-N-(2-chloro-6-methylphenyl)borazole, m. p. 287-288° (Found: C, 51.9; H, 4.2; B, 6.6; Cl, 21.8; N, 8.5. $C_{21}H_{21}B_3Cl_3N_3O_2$ requires: C, 51.8; H, 4.3; B, 6.7; Cl, 21.9; N, 8.6%). I.r. spectrum: DMS card no. 13339. Hydrolysis of the dihydroxyborazole (0.27 g.) with sodium hydroxide in ethane-1,2-diol gave 12.5 ml. hydrogen (calc. 12.3 ml.).

Di-B-hydroxy- and di-B-chlorotri-N-(2,6-dichlorophenyl)borazole (XVIII; R = 2,6-Cl₂C₆H₃, X = OH or Cl, Y = H). Boron trichloride (26.0 g.; 0.220 mole) was passed into 2,6-dichloroaniline (32.4 g.; 0.200 mole) in refluxing toluene (500 ml.), the solution was cooled, triethylamine (70 ml.; 0.500 mole) was added and the mixture was kept overnight. Triethylammonium chloride (31.7 g.; 0.230 mole) was filtered off, and the residue obtained by evaporating the filtrate was triturated with light petroleum and then heated under reflux with water. The solid residue was recrystallised from 1,2-dimethoxyethane (twice), giving di-B-hydroxytri-N-(2,6-dichlorophenyl)borazole (2.3 g.), m. p. 287-288° (Found: C, 39.8; H, 2.5; B, 5.9; Cl, 33.1; N, 7.9. C₁₈H₁₂B₃Cl₆N₃O₂ requires: C, 39.4; H, 2.2; B, 5.9; Cl, 38.9; N, 7.7%). I.r. spectrum: DMS card no. 13341. Hydrolysis of a sample (0.27 g.) with sodium hydroxide in ethane-1,2-diol gave 11.6 ml. hydrogen (calc., 11.3 ml.).

The hydroxyborazole (1.0 g.) was treated with thionyl chloride (5 ml.) containing pyridinium chloride; recrystallisation of the product from light petroleum gave *di*-B-*chlorotri*-N-(2,6-*dichlorophenyl*)borazole (0.65 g.) m. p. 262-264° (Found: C, 36.8; H, 2.0; B, 5.6; Cl, 45.9; N, 7.2. C₁₈H₁₀B₂Cl₈N₃ requires: C, 37.0; H, 1.7; B, 5.6; Cl, 48.6; N, 7.2%). I.r. spectrum: DMS card no. 13340.

Di-B-chloro- and di-B-hydroxytri-N-(2,4,6-trichlorphenyl)borazole (XVIII; R = 2,4,6-Cl₃C₆H₂, X = Cl or OH, Y = H). 2,4,6-Trichloroaniline (34.4 g.; 0.175 mole) in toluene (200 ml.) was added to boron trichloride (20.5 g.; 0.175 mole) in toluene (200 ml.) at -50° and the mixture was warmed gently to the reflux temperature. After refluxing for 2 hr., the solution was cooled, triethylamine (70 ml.; 0.500 mole) was added, and the mixture was set aside at room temperature for several days, when triethylammonium chloride (25 g.; 0.184 mole) was filtered off. The filtrate was evaporated to dryness and the residue was well extracted with isopentane, leaving a residue of di-B-chlorotri-N-(2,4,6-trichlorophenyl)borazole (9.5 g.), m. p. 276-282°, which was recrystallised twice from benzenelight petroleum giving the pure compound, m. p. 286-288° (Found: C, 31.8; H, 1.3; B, 4.5; Cl, 55.9; N, 5.8. C₁₈H₇B₃Cl₁₁N₃ requires: C, 31.4; H, 1.0; B, 4.7; Cl, 56.7; N, 6.1%). I.r. spectrum: DMS card no. 13342.

Di-B-hydroxytri-N-(2,4,6-trichlorophenyl)borazole, m. p. 194—195° (decomp.) was obtained by refluxing the dichloroborazole in water and was crystallised from light petroleum (Found: C, $33\cdot2$; H, $1\cdot5$; B, $5\cdot1$; Cl, $48\cdot0$; N, $6\cdot5$. C₁₈H₉B₃Cl₉N₃O₂ requires: C, $33\cdot15$; H, $1\cdot4$; B, $4\cdot0$; Cl, $49\cdot0$; N, $6\cdot45\%$). I.r. spectrum: DMS card no. 13343.

Tri-B-hydroxyand tri-B-chloro-tri-N-(2,4,6-trichlorophenyl)borazole (XVIII; R = 2,4,6-Cl₃C₆H₂, X = Y = OHor Cl). A solution of the arylaminoboron dichloride was prepared as described previously from 2,4,6-trichloroaniline (49.1 g.; 0.25 mole) and boron trichloride (25 ml.) in toluene (300 ml.) and was treated with triethylamine (75 ml.) for a week. Triethylammonium chloride (41 g.; 0.300 mole) was filtered off, and the sticky residue obtained by evaporating the filtrate under reduced pressure was treated with water and steam distilled. The insoluble residue was sublimed and recrystallised twice from light petroleum, giving tri-B-hydroxytri-N-(2,4,6-trichlorophenyl)borazole (3.6 g.), m. p. 242-243° (Found: C, 32.4; H, 1.6; B, 5.3; Cl, 46.6; N, 6.35. $C_{18}H_9B_3Cl_9N_3O_3$ requires: C, 32·35; H, 1·35; B, 4·9; Cl, 47·9; N, 6·4%). Tri-B-chlorotri-N-(2,4,6-trichlorophenyl)borazole (1.5 g.), m. p. 338-340° was obtained by treating the trihydroxyborazole $(3\cdot 2 g.)$ with thionyl chloride and purifying the crude product by sublimation and recrystallisation from light petroleum (Found: C, 30.3; H, 1.0; B, 4.8; Cl, 56.7; N, 5.9. C₁₈H₆B₃Cl₁₂N₃ requires: C, 29.95; H, 0.8; B, 4.5; Cl, 59.0; N, 5.8%).

Di-B-chloro- and di-B-hydroxytri-N-(2,6-dibromophenyl)borazole (XVIII; R = 2,6-Br₂C₆H₃, X = Cl or OH, Y =H). 2,6-Dibromoaniline (25 g.; 0.10 mole) in toluene (100 ml.) was added to a cold solution of boron trichloride (10 ml.; ~ 0.125 mole) in toluene (150 ml.) and the mixture was heated gently to reflux temperature. After an hour, the solution was cooled, triethylamine (42 ml.; 0.300 mole) was added, and the mixture was kept for a month. Triethylammonium chloride (16.5 g.; 0.120 mole) was filtered off, the filtrate was evaporated to ~ 50 ml., and light petroleum (25 ml.) was added. The precipitate (4.75 g.) obtained was recrystallised twice from light petroleum, giving di-B-chlorotri-N-(2,6-dibromophenyl)borazole (1.1 g.), m. p. 298-299° (Found: C, 25.6; H, 1.5; B, 3.8; Br, 54.7; Cl, 7.8; N, 5.1. $C_{18}H_{10}B_{3}Br_{6}Cl_{2}N_{3}$ requires: C, 25.4; H, 1.2; B, 3.8; Br, 56.4; Cl, 8.3; N, 4.9%). I.r. spectrum: DMS card no. 13344. Hydrolysis of the dichloroborazole gave di-B-hydroxytri-N-(2,6-dibromophenyl)borazole, m. p. 333-334° after recrystallisation from 1,2-dimethoxyethane (Found: C, 26.5; H, 1.5; B, 4.0; Br, 56.5; N, 5.0. C₁₈H₁₂B₃Br₆N₃O₂ requires: C, 26.6; H, 1.5; B, 4.0; Br, 59.0; N, 5.2%). I.r. spectrum: DMS card no. 13345. Hydrolysis of the dihydroxyborazole (0.43 g.) with sodium hydroxide in ethane-1,2-diol gave 11.9 ml. hydrogen (calc. 11.8 ml.).

Di-B-hydroxy- and di-B-chloro-tri-N-(2-methylnaphthyl) borazole (XVIII; R = 2-MeC₁₀H₆, X = OH or Cl, Y = H). A solution of the arylaminoboron dichloride (II; R = 2-MeC₁₀H₆; X = Cl), obtained by passing boron trichloride into 2-methyl-naphthylammonium chloride (30 g.; 0.155 mole) in refluxing toluene (200 ml.), was treated with triethylamine (50 ml.; 0.350 mole) and set aside for several weeks. Triethylammonium chloride (28 g.; 0.200 mole) was filtered off, the filtrate was concentrated to 100 ml., and light petroleum (100 ml.) was added. The low-melting solid (6.0 g.) which separated appeared to be an impure specimen of the boronamine (XVI; R = 2-MeC₁₀H₆; X = Cl) (Found: B, 4.5; Cl, 13.1; N, 7.6. Calc. for $C_{33}H_{29}B_2Cl_2N_3\colon$ B, 3.9; Cl, 12.7; N, 7.5%) and was completely hydrolysed by water. The filtrate from the separation of the boronamine was evaporated to dryness, the residue was heated with light petroleum, cooled, and the clear solution was decanted off. After three such extractions, the combined extracts were steam distilled and the solid residue was purified by recrystallisation from ethanol and by sublimation, giving di-B-hydroxytri-N-(2-methylnaphthyl)borazole (7.0 g.), m. p. 243-245° (Found: C, 74.4; H, 5.8; B, 6.4; N, 7.6. C₃₃H₃₀B₃N₃O₂ requires: C, 74·4; H, 5·6; B, 6·1; N, 7·9%). I.r. spectrum: DMS card no. 13347. The dihydroxyborazole (3.9 g.) was treated with thionyl chloride to give di-B-chlorotri-N-(2methylnaphthyl)borazole (4.0 g.), purified by sublimation and recrystallisation from light petroleum, m. p. 266-267° (Found: C, 70.6; H, 4.9; B, 5.7; Cl, 12.6; N, 7.2. C33H28B3Cl2N3 requires: C, 69.6; H, 4.9; B, 5.7; Cl, 12.5; N, 7.4%). DMS card no. 13346.

Tri-B-hydroxytris-N-(1,2-dimethylpropyl)borazole. A solution of tri-B-chlorotris-N-(1,2-dimethylpropyl)borazole¹ (5.95 g.; 0.0151 mole) and di-isopropylethylamine 21 (8·2 ml.; 6·08 g.; 0·047 mole) in dry ether (50 ml.) was added during $\frac{1}{2}$ hr. to a well-stirred solution of water (0.86 ml.; 0.0477 mole) in dry ether (200 ml.) at below 1°. After stirring for a further 2 hr. at 0° , the mixture was filtered at 0° to give a residue of di-isopropylethylammonium chloride (4.25 g.; 56.5% of theory) and a filtrate that was evaporated in vacuo at below 0° to give a colourless semi-solid mass (~ 5.8 g.) which still contained 5.3%chlorine. This product (1.96 g.) was ground with ice $(\sim 20 \text{ g.})$; as soon as the mixture had warmed to room temperature, the suspended solid was filtered off, washed with water, and dried in vacuo at 0° (yield 1.47 g.), 1.20 g. of this product was dissolved in warm isopentane (5 ml.), the solution filtered, and the filtrate evaporated at room temperature. The *product* (1.07 g.) was a white crystalline solid, m. p. 76.5-80° (Found: C, 52.7; H, 10.5; B, 9.4; N, 11.8%; M (cryoscopic), 333. C₁₅H₃₆B₃N₃O₃ requires C, 53·1; H, 10·65; B, 9·6; N, $12\cdot 4\%$. M, 338). I.r. spectrum: DMS card no. 12240. It is stable for several months at -20° , but decomposes in a few hours at room temperature, both as solid and in solution.

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