798. *Trisaminoboranes.*

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Representative trisaminoboranes have been prepared by 4 methods and characterised. Some " anomalous " features are noted which are readily interpreted in terms of steric effects, including the high stability of (i) hindered bisaminochloroboranes, $(R_2N)_2BCl$ (R = Ph or Pr^i) with respect to attack by the corresponding secondary amine, (ii) a hindered unsymmetrical aminoborane, $(Pr^i_2N)_2B{\cdot}NHBu^t$, with respect to redistribution, and (iii) trismethylphenylaminoborane, $B(NMePh)_3$, with respect to attack by nucleophilic, but not electrophilic, reagents. Transamination appears to be significantly controlled by steric factors. Relevant reaction mechanisms are discussed.

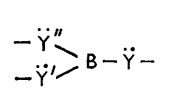
Trisalkylaminoboranes (borazens), $B(NRR')_3$, are generally prepared by addition of boron trichloride to an excess of the amine in an inert solvent at low temperature [$6RR'NH + BCl_3 \longrightarrow B(NRR')_3 + 3RR'NH,HCl$], but have also been obtained from

boron trifluoride, the amine, and a Grignard reagent [1] or lithium; [2] a further method involves transamination, *e.g.*, $(Me_2N)_3B + Me{\cdot}NH_2 \longrightarrow (MeNH)_3B$.[3,4] Our original aim was to investigate systematically the dialkylamino-,[5] monoalkylamino-,[6,7] arylamino-,[7] alkylarylamino-, diarylamino-, and heterocyclic compounds.

Trismethylphenylaminoborane, $B(NMePh)_3$, and tris-*N*-piperidylborane, $B(NC_5H_{10})_3$, were obtained in good yield by the conventional boron trichloride procedure, but the trichloride proved remarkably resistant to diphenylamine; the monosubstituted derivative, $Ph_2N{\cdot}BCl_2$, had previously been obtained.[8] In more forcing conditions (use of triethylamine as carrier for eliminated hydrogen chloride [9]) at a higher temperature, displacement proceeded only to the monochloride, $(Ph_2N)_2BCl$. Difficulty in effecting complete replacement is undoubtedly due to steric hindrance, although trisdiphenylaminoborane has been prepared (with difficulty) by transamination.[4] Steric hindrance to displacement has been observed (see below, and refs. 1 and 3) for the *N*-methylanilino-analogue, $B(NMePh)_3$.

Of the trisdialkylaminoboranes, only the lower n-alkyl (Me, Et, Bu^n) homologues were previously known. Difficulty was experienced in the synthesis of trisdi-isopropylaminoborane; the preparation of di-t-alkyl derivatives was not pursued since di-t-alkylamines are not known with certainty, probably again because of steric hindrance.[10] Boron trichloride and an excess of di-isopropylamine gave the monochloride, $(Pr^i_2N)_2BCl$, and this did not react significantly with more di-isopropylamine, even under reflux in several hours. By analogy with tin(IV) chemistry [aminolysis of tin(IV) chloride with ethylamine failed, but $Sn(NEt_2)_4$ was obtained by using lithiodiethylamine [11]] it was hoped to prepare the tris-compound $(Pr^i_2N)_3B$ by using lithio-amine; this was unsuccessful. These difficulties probably have a steric origin and in line with this the chlorine atom in $(Pr^i_2N)_2BCl$ was replaced without difficulty by t-butylamine, affording the compound $(Pr^i_2N)_2B{\cdot}NHBu^t$, which is the first stable unsymmetrically substituted derivative of triaminoborane.*

Among 3-co-ordinate boron compounds of type (I), which are characterised by atoms with electron pairs in non-bonding orbitals adjacent to the boron atom, unsymmetrical derivatives tend to be unstable. With the alkoxyhalogenoboranes, $(RO)_nBHal_{3-n}$, only the primary alkoxyboron chlorides (the t-alkyl compounds do not exist and the s-alkyl compounds readily decompose [12]) and the alkoxyboron difluorides are reasonably stable [13] (the latter owe their stability to chelation; [14] they are trimeric). The acyclic bromides are exceedingly unstable [15] but infrared spectroscopic evidence for the existence of highly hindered primary alkyl derivatives has been obtained.[16] Among the alkoxyboron and



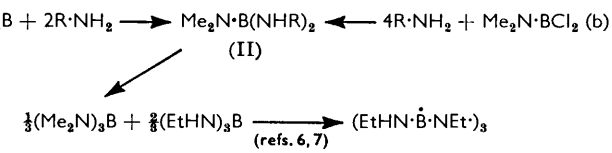
(I)

* [*Added in Proof*]: Aubrey, Gerrard, and Mooney (*J.*, 1962, 1786) recently reported the preparation of other boranes of type $(Pr^i_2N)B{\cdot}NHR$ and also commented on the lack of reaction between $(Pr^i_2N)_2BCl$ and Pr^i_2NH and between $(Ph_2N)_2BCl$ and Ph_2NH.

[1] Dornow and Gehrt, *Angew. Chem.*, 1956, **68**, 619; *Z. anorg. Chem.*, 1958, **294**, 81.
[2] Kraus and Brown, *J. Amer. Chem. Soc.*, 1930, **52**, 4414.
[3] Aubrey and Lappert, *Proc. Chem. Soc.*, 1960, 148.
[4] English, McCloskey, and Steinberg, *J. Amer. Chem. Soc.*, 1961, **83**, 2122; Nöth, *Z. Naturforsch.*, 1961, **16**b, 470.
[5] Gerrard, Lappert, and Pearce, (*a*) *J.*, 1957, 381; (*b*) *Chem. and Ind.*, 1958, 292.
[6] Lappert, *Proc. Chem. Soc.*, 1959, 59.
[7] Aubrey and Lappert, *J.*, 1959, 2927.
[8] Becher, *Z. anorg. Chem.*, 1957, **289**, 262.
[9] Cf. J. F. Brown, *J. Amer. Chem. Soc.*, 1952, **74**, 1219; Musgrave, *J.*, 1956, 4305; Skinner and Smith, *J.*, 1954, 2324.
[10] H. C. Brown, Barbaras, Berneis, Bonner, Johannesen, Grayson, and LeRoi, *J. Amer. Chem. Soc.*, 1953, **75**, 1; see also Klages, Nober, Kircher, and Bock, *Annalen*, 1941, **547**, 1.
[11] Thomas, *Canad. J. Chem.*, 1961, **39**, 1386.
[12] Gerrard and Lappert, *J.*, 1955, 3084; Lappert, *J.*, 1956, 1768.
[13] Lappert, *J.*, 1955, 784; Goubeau and Lücke, *Annalen*, 1952, **575**, 37; Cook, Ilett, Saunders, and Stacey, *J.*, 1950, 3125.
[14] Landesman and Williams, *J. Amer. Chem. Soc.*, 1961, **83**, 2663.
[15] Bujwid, Gerrard, and Lappert, *Chem. and Ind.*, 1957, 1386.
[16] Bujwid, Gerrard, and Lappert, unpublished work; Bujwid, Ph.D. thesis, London, 1959,

aryloxyboron chlorides and bromides, considerable stability has been achieved only in those cases where chelation is possible [*e.g.*, $(o\text{-}C_6H_4O)_2BBr$ or $o\text{-}NO_2\cdot C_6H_4\cdot O\cdot BCl_2$].[17] Alkoxyaminoboranes, $(RO)_nB(NR_2')_{3-n}$,[5] and n-butoxychlorodiethylaminoborane, $Bu^nO\cdot B(Cl)\cdot NEt_2$,[5] disproportionate fairly readily. Indeed, the main cause of instability in all these examples lies in the great facility of the redistribution reactions leading to symmetrical products (or, in the case of the alkoxyboron chlorides and bromides, in reactions forming alkyl halide). Ease of redistribution is most marked in the cases where Y, Y', and Y'' are closest in electronegativity. Thus, the aminohalogenoboranes, $(R_2N)_nB\cdot Hal_{3-n}$, are more stable than the alkoxyhalogenoboranes, and the mixed boron halides are exceedingly unstable.[19] When Y, Y', and Y'' represent the same atom, only the mixed alkoxides $RO\cdot B(OR')_2$ have previously been investigated and these are apparently stable only when chelation is possible, with boron either in a 3- (*e.g.*, R' = CH_2) or a 4-co-ordinate condition (*e.g.*, R = $o\text{-}NO_2\cdot C_6H_4$).[17] The present experiments on the unsymmetrical aminoboranes throw light on the mechanism of redistribution.

The synthesis of dimethylaminobisethylaminoborane (II; R = Et) was attempted by methods (a) and (b). It is possible that this is formed as an intermediate in these reactions, as may be a more hindered compound (II; R = Bu^t) in similar experiments



[route (b) only]. Infrared spectra of undistilled materials, however, were identical with those of mixtures of the disproportionation products.[18] Route (a) to the compound (II; R = Bu^t) proved unfruitful, again illustrating a steric effect in transamination.[3] It had previously been suggested [3] that, in general, primary amines displace secondary amines from dialkylaminoboranes, *i.e.*, $R'NH > R_2N$ in the displacement series, but this requires modification as there is dependence also on the nature of branching in R and R'.[4] Route (b) is interesting because it shows that replacement of chlorine is easier than that of the dimethylamino-group. The reactions of primary amines with dialkylaminodichloroboranes have been discussed before,[20] but this observation is new and the reverse (*i.e.*, $Me_2N > Cl$) was formerly accepted. Evidence rested on identification of the products of 1 : 1 interaction; the borazen (III) was the major product. In the light of our result (b), the mechanism for its formation is likely to involve reaction (1) rather than (2).

$$R_2N\cdot BCl_2 + R'\cdot NH_2 \longrightarrow R_2N\cdot BCl\cdot NHR' \longrightarrow \tfrac{1}{3}(ClB\cdot NR'\cdot)_3\ (III) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

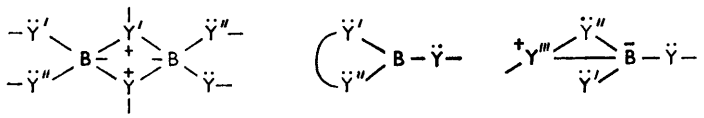
$$R_2N\cdot BCl_2 + R'\cdot NH_2 \longrightarrow R'NH\cdot BCl_2 \longrightarrow \tfrac{1}{3}(III) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The compound $(Pr^i_2N)_2B\cdot NHBu^t$, in contrast to (II), was extremely stable; it withstood several hours' heating under reflux.

The redistribution probably involves a cyclic transition state of type (IV). The stability of any compound of type (I) may therefore by rationalised in terms of a high activation energy for formation of (IV). This would be the case, if chelation were possible as in (V) and (VI), or if for steric reasons the boron atom were inaccessible, as in (II), and if Y and Y' differ widely in electronegativity.

[17] Colclough, Gerrard, and Lappert, *J.*, 1956, 3006; Blau, Gerrard, and Lappert, *J.*, **1957**, **4116**; Gerrard, Lappert, and Mountfield, *J.*, 1959, 1529.
[18] Aubrey, Lappert, and Pyszora, *J.*, 1960, 5239.
[19] Long and Dollimore, *J.*, 1954, 4457; Keller and Bills, Abs. Papers, 126th Meeting Amer. Chem. Soc., September 1954, p. 11R; Higgins, Liesegand, Raw, and Rossouw, *J. Chem. Phys.*, 1955, **23**, 1544; Goubeau, Richter, and Becher, *Z. anorg. Chem.*, 1955, **278**, 12.
[20] Niedenzu and Dawson, *J. Amer. Chem. Soc.*, 1959, **81**, 3561; Gerrard, Hudson, and Mooney, *J.*, 1962, 113.

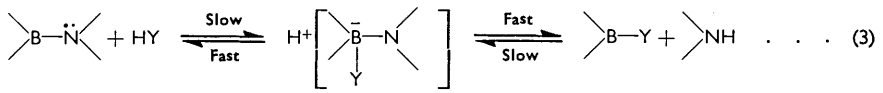
Some of the physical properties of the trisalkylaminoboranes and of three new aminochloroboranes are listed in Table 2. The infrared spectra of all the compounds, except $(Pr^i_2N)_2BCl$ and $(Pr^i_2N)_2B{\cdot}NHBu^t$ (see Experimental) have been discussed before.[18]



(IV) (V) (VI)

Chemical Properties of the Trisalkylaminoboranes.—Trisalkylaminoboranes might be expected to respond to both electrophilic and nucleophilic attack, since they appear to possess both a donor (nitrogen atoms with electron pairs in non-bonding orbitals) and an acceptor site (the boron atom). This picture overlooks delocalisation of the nitrogen non-bonding electrons with formation of a π-type BN molecular orbital (see, *e.g.*, refs, 18, 21).

We found no evidence for the existence of co-ordination compounds. Pyridine did not react with any of the compounds shown in Table 2. The other nucleophilic reagents investigated (ammonia, primary and secondary amines, alcohols, and water) either afforded substitution products or failed to react. The electrophilic reagents used were boron trichloride [$B(NMePh)_3 + 2BCl_3 \longrightarrow 3Cl_2B{\cdot}NMePh$] and hydrogen chloride; B–N cleavage invariably resulted. It is possible that, with both classes of reagent, co-ordination compounds are formed as transient intermediates, although it is perhaps more probable that bond-making and bond-breaking are concerted, as in (3) for nucleophilic processes, or as in (IV) or (4) for electrophilic processes.



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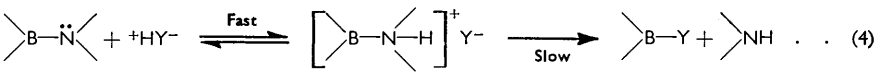

(4)

Trismethylphenylaminoborane (see also refs. 1 and 3) and bisdi-isopropylamino-t-butylaminoborane were resistant to hydrolysis. The former was unaffected even by boiling concentrated sodium hydroxide. Both these compounds were hydrolysed by hot hydrochloric acid. These results, and the others described below, are consistent with the proposed mechanisms. Ammonia did not react with trismethylphenylaminoborane, but with trianilinoborane afforded an impure sample of the very unstable compound $(PhHN)_2B{\cdot}NH_2$. It has been shown [5] that transamination is affected by volatility factors [*e.g.*, $B(NEt_2)_3 + 3Bu^n_2NH \longrightarrow B(NBu^n_2)_3 + 3Et_2NH$]. It is now further shown (see also refs. 3 and 4), as expected from reaction (3), that, in general, primary amines displace secondary amines, independently of volatility considerations. Dimethylamine was displaced from trisdimethylaminoborane by reaction, not only with n-butylamine, but also with methylamine. Similarly, alcoholysis of trisalkylaminoboranes may be carried out by other than high-boiling alcohols; [5] for example, $B(NHPh)_3 + 3MeOH \longrightarrow B(OMe)_3 + 3NH_2Ph$, as was shown analytically.

An interesting reaction was (5). Trisalkylaminoboranes and trialkyl borates do not react with one another,[5] but boron trichloride reacts individually with both species.[5,12] n-Butoxychlorodimethylaminoborane is an example of the rare unsymmetrically substituted boranes.

$$BCl_3 + B(NMe_2)_3 + B(OBu^n)_3 \longrightarrow 3ClB(NMe_2){\cdot}OBu^n \quad . . . . . (5)$$

[21] Barfield, Lappert, and Lee, *Proc. Chem. Soc.*, 1961, 421.

Experimental

In experiments (not detailed here) where absence of reaction has been reported, the reactants were recovered almost quantitatively and were characterised.

Preparation of Trisalkylaminoboranes from Boron Trichloride.—The general procedure was to add the trichloride (0·1 mole) in n-pentane (25 ml.) to the amine (0·6 mole) in n-pentane (250 ml.), with stirring during about ½ hr. at −78°. The white amine hydrochloride was filtered off, weighed, and analysed (Table 1). Solvent was removed from the filtrate and the residual *trisalkylaminoborane* was distilled or sublimed (Table 2).

Table 1.

Compound	Yield (%)	Found (%) Cl	Found (%) N	Calc. (%) Cl	Calc. (%) N
Me_2NH_2Cl	94	43·4	—	43·6	—
Piperidinium chloride	100	28·4	11·4	29·3	11·6

Table 2.

No.	Compound	Method **	Yield (%)	M. p.	B. p./mm.	n_D^{20}	d_4^{20}	$[R_L]_D$ ¶ Found	$[R_L]_D$ ¶ Calc.	Mol. Wt. ‖ Found	Mol. Wt. ‖ Calc.
1	$B(NMe_2)_3$ *	1	68·5		39°/10	1·4462	0·8380	45·3	45·1		
2	$B(NMePh)_3$ †	1	96·8	214—216°	—	—	—	—	—	335	329
3	$B(NC_5H_{10})_3$ ‡	1	94·3	70·5	—	—	—	—	—	250	263
4	$B(NHMe)_3$ §	2	93·0		41°/12	1·4465	0·8871	30·3	30·2	106	101
5	$B(NHBu^n)_3$ §	2	85·0		84°/0·005	1·4460	0·8347	72·4	72·6	217	227
6	$Bu^tNH{\cdot}B(NPr^i_2)_2$	3	83·0		88—91°/1	1·4616	0·8620	90·2	91·8	285	283
7	$Cl{\cdot}B(NPr^i_2)_2$	1	83·0		55—58°/0·1	1·4537	0·8997	74·3	74·2	228	247
8	$Cl{\cdot}B(NPh_2)_2$	4	68·0	50—55	192°/0·03	—	—	—	—	389	383
9	$Cl_2B{\cdot}NMePh$	5	45·6		100°/20	1·5288	1·1976	48·3	48·4		
10	$Cl{\cdot}B(NMe_2){\cdot}OBu^n$	6	67·8		53°/14	1·4242	0·9485	44·0	44·1		

No.	Found (%) C	Found (%) H	Found (%) N	Found (%) B	Found (%) Cl	Formula	Required (%) C	Required (%) H	Required (%) N	Required (%) B	Required (%) Cl
1			29·3	7·5	—	$C_6H_{18}BN_3$			29·4	7·6	—
2	77·0	7·6	12·7	3·3	—	$C_{21}H_{24}BN_3$	76·7	7·4	12·9	3·3	—
3	68·0	10·7	15·7	3·9	—	$C_{15}H_{30}BN_3$	68·6	11·4	15·9	4·0	—
4				10·7	—	$C_3H_{12}BN_3$				10·7	—
5			18·3	4·8	—	$C_{12}H_{30}BN_3$			18·5	4·7	—
6	67·8	13·4	15·2	3·8	—	$C_{16}H_{38}BN_3$	67·9	13·4	14·9	3·8	—
7	58·9	11·3	11·4	4·5	14·3	$C_{12}H_{28}BClN_2$	58·5	11·3	11·3	4·4	14·4
8			7·1	2·9	9·1	$C_{24}H_{20}BClN_2$			7·3	2·8	9·3
9			7·6	6·0	37·8	$C_7H_3BCl_2N$			7·5	5·8	37·5
10	44·7	9·7	8·5	6·4	22·4	$C_6H_{15}BClNO$	44·2	9·2	8·6	6·6	21·8

¶ Calculated values obtained by using Vogel's values ("A Textbook of Practical Organic Chemistry," Longmans, Green and Co., London, 1948, p. 900) and the value 3·0 for boron.

‖ Ebullioscopic in benzene.

** Methods: (1) $BCl_3 + 6NHR_2$; (2) $B(NMe_2)_3 + 3NH_2R$; (3) $(Pr^i_2N)_2BCl + 2NH_2Bu^t$; (4) $BCl_3 + 3R_2NH + 3R_3'N$; (5) $B(NRR')_3 + 2BCl_3$; (6) $BCl_3 + B(NR_2)_3 + B(OR')_3$.

* Previously obtained by several workers (see, *e.g.*, Lappert, *Chem. Rev.*, 1956, **56**, 959), but these physical constants were not recorded.

† Also made from $PhMeNH + BF_3{\cdot}OEt_2 + 3RMgX$ (Dornow and Gehrt, *Angew. Chem.*, 1956, **68**, 619; *Z. anorg. Chem.*, 1958, **294**, 81).

‡ Also made from $B(NHPr^i)_3 + 3C_5H_{10}NH$ (England, McCloskey, and Steinberg, *J. Amer. Chem. Soc.*, 1961, **83**, 2122.

§ Also made from $BCl_3 + 6NH_2R$ (Aubrey and Lappert, *J.*, 1959, 2927).

When the amine was *N*-methylaniline, filtration did not separate the borane from the ammonium salt; separation was achieved by extraction with water (not C_6H_6, CH_2Cl_2, and Et_2O). The insoluble *trisanilinoborane* was dried and recrystallised from benzene (see Table 2). The soluble portion was methylanilinium chloride (100%) (Found: Cl, 24·2; N, 10·2. Calc. for $C_7H_{10}ClN$: Cl, 24·7; N, 9·8%).

Preparation of Trisalkylaminoboranes from Trisdimethylaminoborane.—The primary amine (20 ml.) was condensed (−78°; $MeNH_2$) into or added (20°; Bu^nNH_2) to trisdimethylaminoborane to (2·0—4·0 g.). The mixtures were set aside at 20° for several hours, under reflux

($MeNH_2$) where appropriate. Matter volatile at 20°/30 mm. was removed and the residual *trisalkylaminoborane* was distilled (Table 2).

Preparation of Chlorobisdiphenylaminoborane.—Attempts to prepare this compound without the use of a tertiary base proved unsuccessful. Boron trichloride (9·40 g., 1 mol.) at −50° was added to diphenylamine (40·7 g., 3 mol.) in benzene (100 ml.) at 5° during 5 min. The solution remained clear for 2 min., then a white precipitate began to be formed. After 30 min., when precipitation appeared complete, triethylamine (24·3 g., 3 mol.) was added and the mixture was heated under reflux for 30 min. Filtration at 70—80° and evaporation at 20°/12 mm. afforded triethylammonium chloride (23·3 g., 2·1 mol.) (Found: Cl, 25·2. Calc. for $C_6H_{16}ClN$: Cl, 25·8%). Fractional distillation of the filtrate afforded diphenylamine (4·0 g., 1 mol.), b. p. 106—110°/0·06 mm., m. p. 50—52° (Found: N, 8·3. Calc. for $C_{12}H_{11}N$: N, 8·3%), and *dianilinochloroborane* (see Table 2) as a higher-boiling fraction.

Preparation of Chlorodi-isopropylaminoborane.—Boron trichloride (17·0 g., 1 mol.) at −78°, in light petroleum (40—60°) (25 ml.), was added dropwise to di-isopropylamine (59·0 g., 4 mol.) in the same solvent (300 ml.) at −78°. The white precipitate of di-isopropylammonium chloride (40·0 g. Calc.: 40·0 g.) (Found: Cl, 25·4; N, 10·0. Calc. for $C_6H_{16}ClN$: Cl, 25·8; N, 10·2%) was filtered off and washed with more solvent, and the combined filtrate and washings were evaporated at low pressure. Distillation of the residue afforded *chlorobisdi-isopropylaminoborane*, $\nu_{max.}$ 1475 (B–N stretching) and 772 cm.$^{-1}$ (B–Cl stretching) (see Table 2).

Preparation of Bisdi-isopropylamino-t-butylaminoborane.—Chlorobisdi-isopropylaminoborane (16·0 g., 1 mol.) in dry benzene (25 ml.) was added to t-butylamine (10·5 g., 2·3 mol.). The solution was refluxed for 2 hr. and was set aside for 12 hr. The white precipitate (7·2 g. Calc.: 7·1 g.) of t-butylammonium chloride (Found: Cl, 32·0; N, 12·8. Calc. for $C_4H_{12}ClN$: Cl, 32·5; N, 12·8%) was filtered off. The filtrate was evaporated and distillation of the residue afforded colourless *bisdi-isopropylamino-t-butylaminoborane*, $\nu_{max.}$ 3460 (N–H stretching), 1447 (antisymmetric B–N stretching), 1185 cm.$^{-1}$ (antisymmetric C–N stretching) (see Table 2). These assignments are based on our earlier studies; [19] there is, however, some ambiguity since there are several strong absorption bands in the 1450—1500 cm.$^{-1}$ region (1499, 1481, 1473, and 1447 cm.$^{-1}$), which arise from CH_3 deformation as well as B–N antisymmetric stretching.

Attempted Preparation of Bisethylaminodimethylaminoborane.—(*a*) Ethylamine (3·8 g., 2 mol.) at −78° was added to trisdimethylaminoborane (6·0 g., 1 mol.) at −78°. The mixture was allowed to reflux at 20° for 2½ hr. Dimethylamine (3·80 g., 100%; authentic spectrum) was trapped at −78°. The residue afforded: (i) trisdimethylaminoborane (1·20 g.), b. p. 40—45°/10 mm., n_D^{20} 1·4425 (Found: B, 7·8; N, 28·7%); (ii) trisethylaminoborane (2·33 g.), b. p. 61—64°/10 mm., n_D^{20} 1·4398 (Found: B, 7·5; N, 29·0%); and (iii) a residue (0·5 g.), n_D^{20} 1·4804.

(*b*) Ethylamine (11·2 g., 4 mol.) at −78° was added to dichlorodimethylaminoborane (7·7 g., 1 mol.) in light petroleum (b. p. 60—80°) (150 ml.). The precipitated ethylammonium chloride (10·0 g., 100%), m. p. 109—110° (Found: Cl, 43·0; N, 16·9. Calc. for C_2H_8ClN: Cl, 43·6; N, 17·2%), was filtered off. The filtrate afforded: (i) trisdimethylaminoborane (1·61 g.), b. p. 42—44°/10 mm., n_D^{20} 1·4440 (Found: B, 7·6; N, 28·1%); (ii) trisethylaminoborane (0·80 g.), b. p. 55—60°/10 mm., n_D^{20} 1·4392 (Found: B, 7·7; N, 27·9. Calc. for $C_6H_{18}N_3B$: B, 7·7; N, 29·4%); and (iii) *N*-ethyl-*B*-ethylaminoborazole (2·20 g.), b. p. 110—112°/0·1 mm , n_D^{20} 1·4819 (Found: B, 10·8; N, 28·1. Calc. for $C_{12}H_{33}B_3N_6$: B, 11·3; N, 28·6%).

Attempted Preparation of Bis-t-butylaminodimethylaminoborane.—Methods (*a'*) and (*b'*), similar respectively to (*a*) and (*b*) of the preceding experiments, were carried out, but with t-butylamine in place of ethylamine. By procedure (*b'*) with dichlorodimethylaminoborane (8·29 g.), there were obtained t-butylammonium chloride (94%) (Found: Cl, 32·1. Calc. for $C_4H_{12}ClN$: Cl, 32·5%), trisdimethylaminoborane (1·5 g.) (fully characterised), and tris-t-butylaminoborane (5·6 g.), b. p. 84—86°/10 mm., n_D^{20} 1·4284 (Found: B, 5·0; N, 18·4%). By procedure (*a'*) with trisdimethylaminoborane (3·57 g.), there was no reaction.

Reaction of Trisanilinoborane with Ammonia.—The borane (2·17 g.) and ammonia (excess) were sealed in an ampoule, which was then set aside for 7 days at 20°. Ammonia was removed from the clear solution; the remaining pale yellow solid appeared to be crude aminobisanilinoborane (1·50 g. Calc.: 1·59 g.) (Found: N, 18·5; B, 3·6. Calc. for $C_{12}H_{24}BN_3$: N, 19·8; B, 5·1%). This compound was insoluble in several solvents and appeared to be unaffected by cold water.

Preparation of Dichloromethylphenylaminoborane.—Boron trichloride (15·2 g., 2 mol.) at

−50° was added to trismethylphenylaminoborane (11·3 g., 1 mol.) in n-pentane at −78° during 15 min. The mixture was set aside for several days, whereafter it had become deep green, and a solid was formed. This was filtered off and distillation of the residue afforded the *product* (see Table 2). In other experiments, by Mr. H. Pyszora and Mr. M. Rieber, it was found that this reaction did not occur if the reagents were extremely pure; it was catalysed by ferric chloride and was preferably carried out by heating the reagents under reflux.

Preparation of n-Butoxychlorodimethylaminoborane.—Boron trichloride (5·7 g., 1 mol.) in n-pentane (25 ml.) at −50° was added to trisdimethylaminoborane (7·0 g., 1 mol.) and tri-n-butoxyborane (11·2 g., 1 mol.) in n-pentane (100 ml.) at −78°, during 15 min. Reaction was exothermal and a white precipitate was formed, which melted when the mixture was allowed to attain room temperature. Distillation afforded the pure *borane* (see Table 2).

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