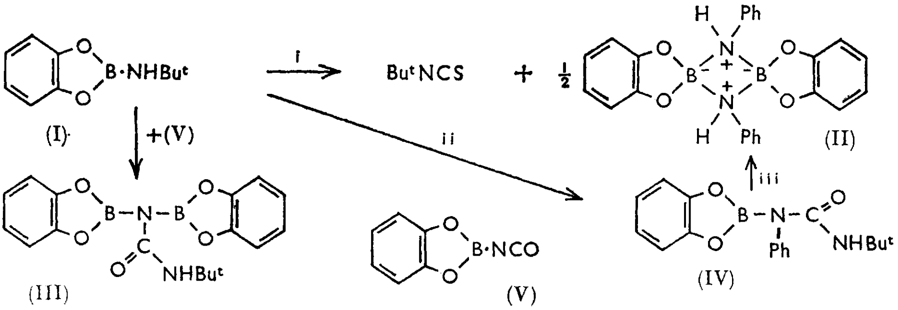
# 394. *Chloroboration and Allied Reactions of Unsaturated Compounds. Part III.*[1] *Aminoboration and Alkoxyboration of Isocyanates and Isothiocyanates.*

By R. H. Cragg, M. F. Lappert, and B. P. Tilley.

Selected monoaminoboranes, $X_2B{\cdot}NR^1R^2$, and bisaminoboranes, $X{\cdot}B(NR^1R^2)_2$, reacted with phenyl isocyanate to afford mono- or bis-ureidoboranes, $>B{\cdot}NPh{\cdot}C{\cdot}NR^1R^2$, characterised by alcoholic degradation and by their infrared spectra. By contrast, the boranes ($R^1 = H$) and phenyl isothiocyanate afforded $R^2{\cdot}NCS$ and either $X_2B{\cdot}NHPh$ or $X{\cdot}B(NHPh)_2$, respectively; borothioureas were possible intermediates, since some corresponding boroureas gave analogous products, but only when heated. An example of aminoboration of an isocyanatoborane to afford an *N*-amido-diborylamine, is reported. From cyclic bisaminoboranes the synthesis of nine-membered cyclic bisureidoboranes has been effected. An example of alkoxyboration, to afford novel urethanoboranes is described. The mechanism of boration is discussed, and the relative migratory aptitudes ($>NHR > NR_2 > Ph > Cl$, generally) of groups attached originally to boron and ultimately to carbon is interpreted thermodynamically, in terms of a transition state approaching more closely to that of the products than of the reactants.

In Part I,[2] chloroboration and organoboration of aryl iso- and isothio-cyanates were described: $2ArNCQ + BX^1X^2X^3 \longrightarrow X^1B[N(Ar){\cdot}C({:}Q)X^2][N(Ar){\cdot}C({:}Q)X^3]$, where $Q = O$ or S, and $X^1$, $X^2$, $X^3 = Cl$ or Ar′. Earlier literature on other reactions ($Z{:}Y + BX^1X^2X^3 \longrightarrow X^1X^2B{-}Z{-}Y{-}X^3$, which fall under the general title for this series, was then reviewed. In Part II,[1] some reactions of acetylenes were reported.

The present Paper is concerned with aminoboration and, to a much lesser extent, alkoxyboration of iso- and isothio-cyanates; *i.e.*, systems in which ZY = PhNCO or PhNCS and $X^3$ is an amino- or alkoxy-group, the products thus being ureido- or urethanoboranes. We have previously reported results[3] for aminoboration of iso- and isothiocyanates, particularly in relation to synthesis of cyclic diureidoboranes, and also have shown[4] that aminometallation of iso- and isothio-cyanates is applicable for a wide range of metals and metalloids. We now discuss aminoborations under two headings; results



i, PhNCS. ii, PhNCO. iii, $-Bu^tNCO$ at 190—200°.

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[1] Part II, Lappert and Prokai, *J. Organometallic Chem.*, 1964, **1**, 384.

[2] Lappert and Prokai, *J.*, 1963, 4223.

[3] Cragg and Lappert, Preprints of Papers, International Symposium on Boron–Nitrogen Chemistry, Durham, N.C., U.S.A., April 1963; *Adv. Chem.*, 1964, Ser. No. 42, 220.

[4] Jones and Lappert, *Proc. Chem. Soc.*, 1962, 358.

are available also on trisaminoboranes,[3,5] aminoborazines,[3,6] and tetrakis(dimethylamino)diboron.[5,6]

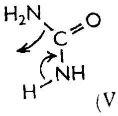
*Reactions of Monoaminoboranes.*—These are summarised above for 2-t-butylamino-1,3,2-benzodioxaborole (I). In a similar way, t-butylaminodiphenylborane and 2-diethylamino-1,3,2-benzodioxaborole each afforded corresponding ureidoboranes with phenyl isocyanate (as did diethylaminodipentylborane[6]), but phenyl isothiocyanate failed to react with the latter reagent.

The substituted 1,3,2-benzodioxaboroles (I) and (II) were prepared independently and the indicated structures were established on the basis of molecular weights and infrared spectra.[7]

The formation of t-butyl isothiocyanate from phenyl isothiocyanate is noteworthy. To determine whether the thioureidoborane might have been an unstable intermediate, the pyrolysis of (IV) was investigated. The products (i) were t-butyl isocyanate and di-t-butylcarbodi-imide, and we regard the latter as a decomposition product of the former, by analogy with other organic isocyanates.

$$\text{(IV)} \xrightarrow{190\text{–}200^\circ} \text{(II)} + \text{Bu}^t\text{NCO} \xrightarrow{190\text{–}200^\circ} \text{CO}_2 + \text{Bu}^t\text{N=C=NBu}^t \qquad \text{(i)}$$

The pyrolysis of the borourea (IV) is evidently following a similar course [see (VI)], to that of urea itself, which upon heating affords ammonia and cyanuric acid.[9] Alternative products of decomposition of (IV), consistent with this mechanism, would have been (ii) $o\text{-C}_6\text{H}_4\text{O}_2\text{B·NCO} + \text{PhNHBu}^t$, or (iii) $o\text{-C}_6\text{H}_4\text{O}_2\text{B·NHBu}^t + \text{PhNCO}$. Path (i) is apparently preferred, both on steric grounds and because the formation of the dimer (II) is thermodynamically advantageous. Scheme (VI) is suggested as a formalism and it is appreciated that the detailed mechanism of urea or thiourea decomposition may be more complex.[10]



(VI)

The reaction (I + V ⟶ III) leading to the *N*-amidodiborylamine shows that aminoboration of isocyanates is not restricted to carbon derivatives. However, the use of an isocyanatoborane[11] may not be of general application, since interaction of certain isothiocyanatoboranes and aminoboranes led[5] instead to functional-group exchange [*e.g.*, $2o\text{-C}_6\text{H}_4\text{O}_2\text{B·NCS} + \text{B(NMe}_2)_3 \longrightarrow 2o\text{-C}_6\text{H}_4\text{O}_2\text{B·NMe}_2 + \text{Me}_2\text{N·B(NCS)}_2$].

The nature of the product of reaction between (I) and (V) depends upon the conditions employed (see Experimental section). In particular, (III) was formed only under forcing conditions, whilst at room temperature a 1 : 1-complex of uncertain structure was obtained. Compound (III) is of interest as a rare[12] example of a diborylamine.

t-Butylaminodiphenylborane reacted exclusively in 1 : 1-stoicheiometry, even with a large excess of phenyl isocyanate, thus showing that phenylboration does not proceed under these conditions.

*Reactions of Bisaminoboranes.*—These are summarised below for di-(t-butylamino)-phenylborane (VII).[13]

$$2\text{Bu}^t\text{NCS} + \text{PhB(NHPh)}_2 \xleftarrow{2\text{PhNCS}} \underset{\text{(VII)}}{\text{Ph·B(NHBu}^t)_2} \xrightarrow{2\text{PhNCO}} \underset{\text{(VIII)}}{\text{Ph·B(NPh·CO·NHBu}^t)_2}$$

A thioureidoborane was not isolated from the reaction between (VII) and phenyl isothiocyanate, although $\text{Ph·B·NMe}_2\text{NPh·CS·NMe}_2$ was obtained[3] from bis(dimethylamino)phenylborane, as was the oxygen analogue, by using a deficiency of the isothio- or

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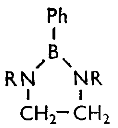
[5] Heying and Smith, *Adv. Chem.*, 1964, Ser. No. 42, 201.
[6] Beyer, Dawson, Jenne, and Niedenzu, following paper.
[7] Lappert and Tilley, unpublished observations.
[8] Cf. Neumann and Fischer, *Angew. Chem., Internat. Edn.*, 1962, **1**, 617.
[9] Bennett, Saunders, and Hardy, *J. Amer. Chem. Soc.*, 1953, **75**, 2101.
[10] Rahman, *Rec. Trav. chim.*, 1956, **75**, 164; Rahman, Medrano, and Mittal, *ibid.*, 1960, **79**, 188.
[11] Lappert and Pyszora, *Proc. Chem. Soc.*, 1960, 350.
[12] Nöth, *Z. Naturforsch.*, 1961, **16**b, 618; Lappert and Majumdar, *Proc. Chem. Soc.*, 1963, 88.
[13] Burch, Gerrard, and Mooney, *J.*, 1962, 2200.

iso-cyanate, respectively. A reaction analogous to (VII) ⟶ (VIII) (which proceeded smoothly under mild conditions and in high yield), but using $PhB{\cdot}(NMe_2)_2$, required forcing conditions and afforded the bisureidoborane in poor yield.[5,6] Thioureidoboranes have readily been obtained by aminoboration of phenyl isothiocyanate, with tris-t-butylamino-[3] and trisdimethylamino-[5] boranes or tetrakisdimethylaminodiboron.

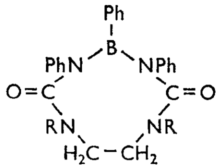
It appears that thioureidoboranes (unlike ureidoboranes) are stable only if (i) the terminal nitrogen atom is doubly substituted, or (ii) it is a trithioureidoborane, the terminal nitrogen atom may then even be singly substituted. Both (i) and (ii) follow reasonably from the assumption that the mechanism of decomposition requires an initial prototropic shift, although the greater stability of ureidoboranes [at least with respect to (i)] remains obscure.

Compound (VIII) was reasonably stable thermally, failing to decompose either in the manner of (IV), or, in the manner[3] of $Pr^i_2N{\cdot}B(NPh{\cdot}CO{\cdot}NHBu^t)(NPh{\cdot}CO{\cdot}NPr^i_2)$, to give a cyclic diureidoborane.

An interesting extension of aminoboration of isocyanates was the synthesis of the cyclic bisureidoboranes (X) from the 2-phenyl-1,3,2-diazaborolidines (IX). Compound (IXa) is known,[14] whilst (IXb) was synthesised by transamination. The nine-membered ring compounds (X) are the largest boron-containing rings described to date; seven-membered rings are known.[15] In the light of experience with other aminometallation reactions,[4] analogous compounds containing different hetero-atoms, for example tin(IV) and phosphorus(III) should become accessible.

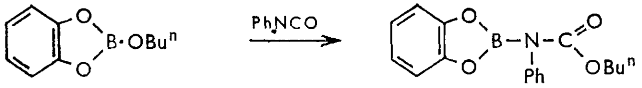


(IXa: R = H)
(IXb: R = Bu$^n$)

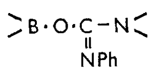


(Xa: R = H)
(Xb: R = Bu$^n$)

*The Alkoxyboration Reaction.*—This has so far only been effected in one instance. n-Butoxy-1,3,2-benzodioxaborole was available,[16] whilst (XI) is of interest as the first example of a urethanoborane. By contrast, tri-n-butoxyborane did not react with phenyl isocyanate, under stated conditions.



(XI)



(XII)

*The Structures of the Ureido- and Urethano-boranes.*—Other ureidoboranes have been unambiguously synthesised from certain isocyanatoboranes and amines.[17] For the products of aminoboration of iso- and isothio-cyanates, apart from the structures now suggested, others based on the unit (XII) are feasible. Against this are: (i) addition reactions to isocyanates normally involve the $-N=C=$ rather than the $=C=O$ bond[2] and (ii) the i.r. spectra.[2] The technique of alcoholic degradation[2] was used in the present investigation for compounds (III), (IV), and (VIII), and for $o$-$C_6H_4O_2BNPh{\cdot}CO{\cdot}NEt_2$; but this does not distinguish between the structural alternatives.

Reaction of (IXa) to give (Xa) provides no indication as to structure, since the presence

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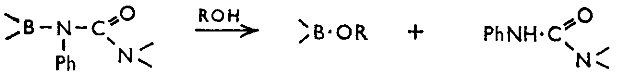
[14] Niedenzu, Beyer, and Dawson, *Inorg. Chem.*, 1962, **1**, 738.

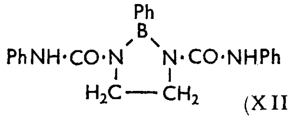
[15] Cf. Lappert, *Chem. Rev.*, 1956, **56**, 959; Gerrard, "The Organic Chemistry of Boron," Academic Press, New York, 1961.

[16] Gerrard, Lappert, and Mountfield, *J.*, 1959, 1529.

[17] Lappert and Pyszora, Abstracts of Papers, International Symposium on Inorganic Polymers, Nottingham, July 1961; *J.*, 1963, 1744.

of hydrogens on the nitrogen atoms permits an alternative formulation (XIII). Therefore (IXb) was used to give (Xb), thereby firmly establishing the nine-membered ring.





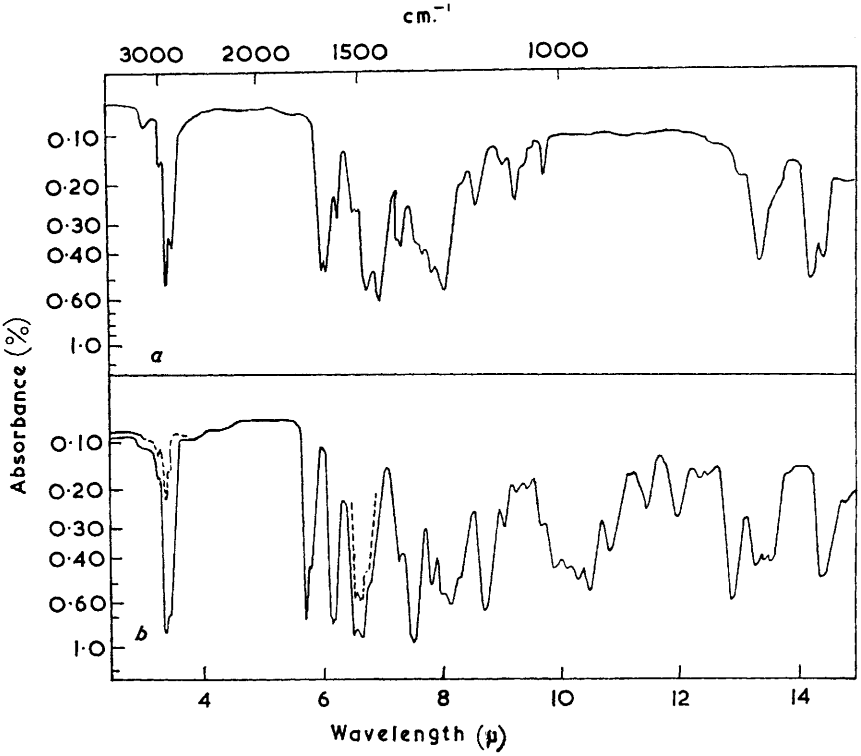
(XIII)

*Infrared Spectra of the Ureido- and Urethano-boranes.*—Correlations are indicated in Table 1, and the spectra of (Xb) and (XI) are reproduced in the Figure.

TABLE 1.

Principal absorption bands (max. in cm.$^{-1}$) in ureidoboranes.

| | (III) | (IV) | (IV; $Et_2$ for $HBu^t$) | $Ph_2B{\cdot}NPh{\cdot}CO{\cdot}NHBu^t$ | (VIII) | (Xa) | (Xb) | (XI) |
|---|---|---|---|---|---|---|---|---|
| N–H Str. | 3497m | 3425w | — | 3333m | 3333m | 3356s | — | — |
| C=O Str. | 1629m | 1613vs | 1724<br>1613 } vs | 1689vs | 1709m sh<br>1661vs | 1701w<br>1639vs | 1656<br>1639 } vs | 1727vs<br>1704s |
| B–N Str. | 1379 | 1325vs | 1320vs | 1429s | 1439vs | 1443vs | 1441vs | 1325vs |



Infrared spectra. Curve *a*, (Xb) as liquid film; 2941, 1656, 1639, 1481, 1441, 1376, 1239, 1166, 1081, 1028, 749, 702, 693 cm.$^{-1}$.

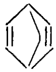
Curve *b*, (XI) in Nujol and hexachlorobutadiene mulls; 2967, 1727, 1592, 1511, 1481, 1325, 1269, 1218, 1135, 946, 941, 866, 830, 771, 749, 693 cm.$^{-1}$.

*The Mechanism of Aminoboration.*—This is discussed in terms of the results already presented, the relative migratory aptitudes of groups originally attached to boron and ultimately to carbon (Table 2), and the observations that aminoboranes do not react with olefins [5] or with acetylenes.[7]

Conclusions to be drawn appear to be that: (i) the relative rates of reaction are not necessarily connected with the relative migratory aptitudes of groups; (ii) the driving force in some of the reactions seems to be a function of the electrophilic character of the borane and in others of a nucleophilic character; (iii) the order of relative migratory aptitude may vary from one substrate to another; (iv) the governing factor which provides rationalisation for the observed relative migratory aptitudes of groups appears to be thermodynamic, in terms of a transition state which is more closely related to the products than to the reactants; and (v) steric factors are important.

TABLE 2.

Data on relative migratory aptitudes (R.M.A.) in borations.

| Unsaturated substrate | Borane | Boration | R.M.A. | Ref. |
|---|---|---|---|---|
|  | $PhBCl_2$ | Phenyl- | Ph>Cl | 18 |
| PhC≡CH | $PhBCl_2$ | Chloro- | Cl>Ph | 1 |
| $Bu^nC≡CH$ | $PhBCl_2$ | Phenyl- | Ph>Cl | 1 |
| PhNCO | $PhBCl_2$ | Phenyl- and chloro- | Ph>Cl | 2 |
| PhNCO | $Ph_2BCl$ | Phenyl- | Ph>Cl | 2 |
| PhNCO | $(Pr_2{}^iN)_2B{\cdot}NHBu^t$ | t-Butylamino- | $NHR>NR_2$ | 3 |
| PhNCO | $Ph_2B{\cdot}NHBu^t$ | Amino- | NHR>Ph | This Paper |
| PhNCO | $PhB(NHBu^t)_2$ | Amino- | NHR>Ph | This Paper |
| PhNCO | $(n\text{-}C_5H_{11})_2B{\cdot}NEt_2$ | Amino- | $NR_2>R^1$ | 6 |
| PhNCO | $PhB(NMe_2)_2$ | Amino- | $NR_2>Ph$ | 5, 6 |
| EtNCO | $PhB(NMe_2)_2$ | Amino- | $NR_2>Ph$ | 6 |
| PhNCS | $PhB(NMe_2)_2$ | Amino- | $NR_2>Ph$ | 6 |

Points (i) and (ii) are related, and may be explained, in part, by results on norbornadiene. The relative acceptor strengths of the boranes are certainly $Ph{\cdot}BCl_2 > Ph_2B{\cdot}Cl > Ph{\cdot}B(NMe_2)_2$;[19] rates of reaction follow the same order, but relative migratory aptitudes show Ph > Cl.

Results on phenyl iso- and isothio-cyanates illustrate reactions in which the opposite type of reactivity (see ii) is required, at any rate in some instances. Thus, in acceptor strengths: $B(NR_2)_3 < Ph{\cdot}B(NR_2)_2 < o\text{-}C_6H_4O_2B{\cdot}NR_2$,[16] but examples have been given of ready reaction of phenyl isothiocyanate with trisaminoboranes, but not (in some cases) with the last two types of reagent. This can scarcely be due to steric effects, since these are likely to be the most significant for trisaminoboranes. Also, with respect to aminoboration, phenyl isocyanate is more reactive than the isothiocyanate; this is the same order of reactivity as that with respect to addition of alcohols and formation of urethanes and thiourethanes,[20] processes which are established as involving the alcohol behaving as a nucleophile.[21] On the other hand, iso- and isothio-cyanates with strong Lewis acids ($BCl_3$, $BPh_3$, etc.) almost certainly do react as nucleophiles (see also ref. 2). An anomalous result seems to be that which shows that 2-n-butoxy-1,3,2-benzodioxaborole, unlike tri-n-butoxyborane, is capable of effecting alkoxyboration of phenyl isocyanate; unless this is to be explained on the same basis, in terms of relative acceptor strengths, which are certainly $o\text{-}C_6H_4O_2B{\cdot}OBu^n > B(OBu^n)_3$.[16]

The suggestion (ii), of duality of mechanism in reactivity of boranes with various unsaturated substrates, is in keeping with the fact that whilst olefins are normally susceptible to electrophilic attack, the opposite is true of isocyanates.

Point (iii) is illustrated by the addition of dichlorophenylborane to phenyl- and n-butylacetylenes. This is explicable in terms of (iv) and has been discussed in Part II.[1]

In order to comment upon (iv), it is necessary to consider the steric course of the

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[18] Joy and Lappert, *Proc. Chem. Soc.*, 1960, 353.
[19] Abel, Gerrard, Lappert, and Shafferman, *J.*, 1958, 2895.
[20] Assony, " Organic Sulfur Compounds," ed. Kharasch, Pergamon Press, Oxford, 1961, Ch. 28.
[21] Baker and Gaunt, *J.*, 1949, 19.

boration. The only data available are on acetylenes,[1] where *cis*-addition is established for substituted derivatives (although the *trans*-product is obtained from acetylene itself). This makes it reasonable to assume a cyclic four-centre transition state. Two extreme situations can be envisaged, as discussed under (ii). For $PhNCO + Ph_2B{\cdot}X \longrightarrow Ph_2B{\cdot}NPh{\cdot}CO{\cdot}X$, the relative migratory aptitudes of X are $X = NHR > NR_2 > Ph > Cl$. If it be recognised that the stabilisation of the developing product depends upon maximum conjugation being effected, then the results fall into place, since structures such as (XIV) will be of decreasing importance in the series $X = NHR > NR_2 > Ph > Cl$. The relative positions of NHR and $NR_2$ are explicable in steric terms, because of the necessity of retaining coplanarity of all atoms (except those attached to aliphatic carbon) for maximum conjugation; this may not be possible in (XV). To establish these arguments rigorously, more thermodynamic data would be required, particularly in order to take into account the *difference in energy* between a system wherein X is attached as shown in (XIV) and one where X is directly bonded to boron.

$$Ph_2\overset{-}{B}{=}\overset{+}{N}Ph{\cdot}C({\cdot}\overset{-}{O}){=}X^+$$

(XIV)

$$Ph_2B{\cdot}NPh{\cdot}C(\dot{:}O)NR_2$$

(XV)

A number of examples of steric effects (v) emerge. The relative migratory order, $NHR > NR_2$, has been commented upon. A second example refers to the same order, but with respect to reactivity; thus, bis-(t-butylamino)phenylborane reacted with greater facility with phenyl isocyanate than did bis-(dimethylamino)phenylborane.

## EXPERIMENTAL

*General Procedures.*—n-Butyl alcohol was dried by distillation from metallic calcium and n-octyl alcohol by direct fractionation. The light petroleum was always of b. p. 40—60°. Analyses, except for boron, were carried out in the microanalytical laboratories of this Department and we thank Mr. B. Manohin and his staff. Boron was estimated by Thomas's method.[22] Molecular weights were determined by Mrs. Vaszko using a Mecrolab vapour-pressure osmometer. The following boranes, used as starting materials, were prepared by known methods; bis-(t-butylamino)phenylborane,[13] 1,3-dihydro-2-phenyl-1,3,2,-diazaborole,[23] 2-isocyanato-1,3,2-benzodioxaborole,[24] 2-butoxy-1,3,2-benzodioxaborole.[16] I.r. spectra were recorded on a Perkin-Elmer model 21 (2—15 μ) instrument equipped with sodium chloride optics. Precautions were taken to avoid contamination by atmospheric moisture. Melting points were taken in sealed capillary tubes.

*Reaction of* 2-*t-Butylamino*-1,3,2-*benzodioxaborole with Phenyl Isothiocyanate.*—Phenyl isothiocyanate (5·95 g., 1 mol.) was refluxed with 2-t-butylamino-1,3,2-benzodioxaborole (8·87 g., 1 mol.) in benzene (20 ml.) for 2 hr. After filtration and washing with light petroleum, the crystalline residue gave 2-phenylamino-1,3,2-dioxaborole dimer (6·05 g., 62·5%), m. p. 268° (Found: C, 67·9; H, 5·1; N, 6·6; B, 5·2%; *M*, 422. Calc. for $(C_{12}H_{10}NBO_2)$: C, 68·3; H, 4·7; N, 6·6; B, 5·2%; *M*, 422). After removal of the solvent, the filtrate afforded t-butyl isothiocyanate (4·22 g., 84%), b. p. 139° (Found: N, 12·2. Calc. for $C_5H_9NS$: N, 12·2%).

*Preparation of* (III).—2-Isocyanato-1,3,2-benzodioxaborole (2·75 g., 1 mol.) was heated with 2-t-butylamino-1,3,2-benzodioxaborole (3·6 g., 1·1 mol.) at 180° for 1 hr. After cooling, the product was refluxed in light petroleum (to facilitate removal of excess of the t-butylamino-compound), cooled, and filtered; the residue gave N′-*t-butyl*-NN-*di*-(1,3,2-*benzodioxaborol*-2-*yl*)*urea* (III) (5·8 g., 96%), m. p. 198° (Found: N, 7·8; B, 6·1. $C_{17}H_{18}N_2O$ requires N, 8·0; B, 6·1%).

Alcoholysis of (III) (3·9 g.) with n-butyl alcohol gave *N*-butylurea (1·0 g., 77%), m. p. 172° (Found: N, 12·0. Calc. for $C_5H_{12}N_2O$: N, 12·1%), tri-n-butyoxyborane (2·3 g., 94%), and catechol (1·3 g., 100%).

*Preparation of the Borourea* (IV).—Phenyl isocyanate (4·04 g., 1 mol.) and 2-t-butylamino-1,3,2-benzodioxaborole (6·77 g., 10·4 mol.) in benzene (10 ml.) were set aside for 12 hr. The

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[22] Thomas, *J.*, 1946, 820.

[23] Nöth, *Z. Naturforsch.*, 1961, **16**b, 470.

[24] Lappert and Pyszora, *Proc. Chem. Soc.*, 1960, 350.

resulting solid was washed with light petroleum, and afforded N-(1,3,2-*benzodioxaborol*-2-*yl*)-N-*phenyl*-N′-*t-butylurea* (IV) (5·95 g., 55·1%), m. p. 181° (Found: C, 65·5; H, 6·5; N, 9·1; B, 3·6%; *M*, 303. $C_{17}H_{19}N_2BO_3$ requires C, 65·9; H, 6·1; N, 9·0; B, 3·5%; *M*, 310). After removal of solvent (20°/12 mm.) and washing with light petroleum, the filtrate afforded more (IV) (4·73 g., 43·8%).

On alcoholysis with octyl alcohol, the urea (IV) (6·35 g.) gave *N*-t-butyl-*N*′-phenylurea (1·7 g., 43%), m. p. 149°, tri-n-octyloxyborane (2·1 g., 45%), catechol (1·1 g., 49%), and unchanged (IV) (3·2 g., 51%).

*Pyrolysis of the Urea* (IV).—The urea (IV) (8·2 g.) was heated at 190°/12 mm. for 2 hr. The volatile materials were collected at −78° and upon fractionation gave t-butyl isocyanate (1·23 g., 47%), b. p. 86° (Found: N, 13·9. Calc. for $C_6H_9NO$: N, 14·1%), and *NN*′-bis-t-butylcarbodi-imide (0·8 g.), b. p. 145° (Found: N, 18·5. Calc. for $C_9H_{18}N_2$: N, 18·7%). The residue afforded the dimer (II) (from benzene) (4·4 g., 79%), m. p. 266° (Found: N, 6·4; B, 5·1. Calc. for $C_{12}H_{10}NBO_2$: N, 6·6; B, 5·2%).

*Preparation of* N-(1,3,2-*Benzodioxaborol*-2-*yl*)-N′N′-*diethyl*-N-*phenylurea*.—Phenyl isocyanate (4·0 g., 1 mol.) was heated with 2-diethylamino-1,3,2-benzodioxaborole (6·44 g., 1 mol.) at 160° for 1 hr. After cooling, the product was refluxed in light petroleum, cooled, and filtered; the residue afforded the *bororurea* (10·54 g., 99·5%), m. p. 204° (Found: C, 65·6; H, 5·8; N, 9·3; B, 3·5%; *M*, 312. $C_{17}H_{19}N_2BO_3$ requires C, 65·9; H, 6·1; N, 9·0; B, 3·5%; *M*, 310).

Alcoholysis with n-butyl alcohol gave *N,N*-diethyl-*N*′-phenylurea (2·5 g., 83%; from 4·9 g.), m. p. 80°, tri-n-butoxyborane (3·2 g., 88%), and catechol (1·8 g., 100%).

*Interaction of* 2-*Diethylamino*-1,3,2-*benzodioxaborole and Phenyl Isothiocyanate*.—The starting materials were recovered when phenyl isothiocyanate was heated at 160° with the diethylamino-compound for 3 hr.

*Preparation of* t-*Butylaminodiphenylborane*.—Diphenylchloroborane (4·4 g., 1 mol.) was added to t-butylamine (1·7 g., 1 mol.) in light petroleum (20 ml.) at −78°. The mixture was allowed to attain room temperature, and excess of triethylamine (∼4 g.) was then added. Triethylammonium chloride (2·95 g., 95%) (Found: Cl, 25·2. Calc. for $C_6H_{16}NCl$: Cl, 25·7%) was filtered off. After removal of the solvent (20°/10 mm.), *diphenyl-t-butylaminoborane* (4·5 g., 87%), b. p. 108°/0·05 mm., $n_D^{20}$ 1·5531 (Found: N, 6·2; B, 4·45%; *M*, 243. $C_{16}H_{20}NB$ requires N, 5·9; B, 4·5%; *M*, 237) was obtained.

*Interaction of Diphenyl t-Butylaminoborane and Phenyl Isocyanate*.—Reaction of 1 : 1 and 1 : 2 proportions gave the same product:

Diphenyl t-butylaminoborane (2·0 g., 1 mol.) and phenyl isocyanate (2·0 g., 2 mol.) were refluxed in light petroleum (20 ml.) for 3 hr. A white solid *diphenyl*-(N-*phenyl*-N′-*t-butylureido*)*borane* (3·4 g., 83%), m. p. 77—79° (Found: C, 76·5; H, 6·8; N, 7·6; B, 3·0%; *M*, 364. $C_{23}H_{25}N_2OB$ requires C, 77·4; H, 7·0; N, 7·8; B, 3·05%; *M*, 359), was filtered off.

*Preparation of the Borane* (VIII).—Phenylbis-t-butylaminoborane* (4·3 g., 1 mol.) and phenyl isocyanate (4·4 g., 2 mol.) were refluxed in benzene (30 ml.) for 6 hr. Removal of solvent at 20°/12 mm. and crystallisation from benzene gave *phenylbis*(N-*phenyl*-N′-*t-butylureido*)*borane* (7·9 g., 90%), m. p. 158—160° (Found: C, 70·6; H, 7·3; N, 12·2; B, 2·45. $C_{28}H_{35}N_4O_2B$ requires C, 71·4; H, 7·45; N, 12·0; B, 2·3%).

Butanolysis of (VIII) (1·45 g.) gave *N*-phenyl-*N*′-t-butylurea (1·0 g., 85%), m. p. 149—151° (Found: N, 14·4. Calc. for $C_{11}H_{16}N_2O$: N, 14·7%), and dibutoxyphenylborane (0·63 g., 87%), $n_D^{20}$ 1·4744 (Found: B, 4·6. Calc. for $C_{14}H_{23}O_2B$: B, 4·7%).

*Pyrolysis of* (VIII).—After being heated for 3 hr. at 140°/0·04 mm., the original compound was recovered.

*Interaction of Bis-*(*t-butylamino*)*phenylborane and Phenyl Isothiocyanate*.—A solution of bis-(t-butylamino)phenylborane (3·3 g., 1 mol.) and phenyl isothiocyanate (3·85 g., 2 mol.) in benzene (30 ml.) was refluxed for 3 hr. After removal of solvent, the residue afforded t-butyl isothiocyanate (2·0 g., 63%), b. p. 140°. Ether (40 ml.) and light petroleum (10 ml.) were added to the distillation residue (3·95 g.), whereupon dianilinophenylborane (0·75 g., 20%), m. p. 79—82° (Found: N, 9·9; B, 3·8. Calc. for $C_{18}H_{17}N_2B$: N, 10·2; B, 3·95%), was precipitated.

*Preparation of the Macrocycle* (Xa).—Phenyl isocyanate (4·3 g., 2 mol.) and the dioxaborolidine (IXa) (2·3 g., 1 mol.) in benzene (30 ml.) were refluxed for 3 hr., cooled to 20°, and freed from solvent; crystallisation of the residue from benzene gave the *tetra-azaboranine* (Xa)

* It has previously been reported[13] that di-t-butylaminoborane is a liquid. In our experiment a solid m. p. 23° was obtained.

(5·7 g., 93%), m. p. 232° (Found: C, 69·0; H, 5·5; N, 14·5; B, 2·7. $C_{22}H_{21}N_4O_2B$ requires C, 69·0; H, 5·7; N, 14·7; B, 2·8%).

*Preparation of Diazoborolidine* (IXb).—Bis(diethylamino)phenylborane (7·5 g., 1 mol.) and *NN'*-di-n-butylethylenediamine (5·4 g., 1 mol.) were refluxed in toluene (50 ml.) for 3 hr. Diethylamine (4·25 g., 90%) was trapped at −78°. On removal of the solvent and distillation of the residue, the *diazaborolidine* (IXb) (7·35 g., 88%), b. p. 100—105°/0·2 mm., $d_4^{20}$ 0·9289, $n_D^{20}$ 1·5047 (Found: C, 74·0; H, 11·2; N, 10·8; B, 4·0. $C_{16}H_{27}N_2B$ requires C, 73·8; H, 10·5; N, 10·8; B, 4·2%), was obtained.

*Preparation of the Macrocycle* (Xb).—Phenyl isocyanate (2·9 g., 2 mol.) was added to diazaborolidine (IXb) (3·10 g., 1 mol.) in toluene (30 ml.). The mixture was refluxed for 3 hr., and freed from solvent, giving the *tetra-azaboranine* (Xb) (5·8 g., 97%), b. p. 156—160°/0·2 mm., $n_D^{20}$ 1·5430 (Found: C, 72·5; H, 9·7; N, 11·5; B, 2·05. $C_{30}H_{37}N_4O_2B$ requires C, 72·5; H, 7·5; N, 11·3; B, 2·2%). A slight amount of decomposition was observed during distillation of (Xb).

*Preparation of the Urethane* (XI).—Phenyl isocyanate (3·42 g., 1 mol.) and 2-n-butoxy-1,3,2-benzodioxaborole (5·5 g., 1 mol.) were set aside for 30 days. Ether was then added. The precipitate was *butyl* N-(1,3,2-*benzodioxaborol*-2-*yl*)*phenylurethane* (2·17 g., 24·3%), m. p. 58° (Found: C, 65·9; H, 5·2; N, 4·5; B, 3·5%; *M*, 270. $C_{17}H_{18}NBO_4$ requires C, 65·6; H, 5·8; N, 4·5; B, 3·5%; *M*, 311). The filtrate gave phenyl isocyanate (2·5 g., 75%) and 2-n-butoxy-1,3,2-benzodioxaborole (4·2 g., 76%).

*Interaction of Phenyl Isocyanate and Tri-n-butoxyborane.*—Tri-n-butoxyborane (2·29 g., 1 mol.) and phenyl isocyanate (2·38 g., 3 mol.) were refluxed for 3 hr. On distillation the starting materials were obtained.

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Chemistry Department, Faculty of Technology,
University of Manchester.

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