798. *Chloroboration and Allied Reactions of Unsaturated Compounds. Part I. Chloroboration and Organoboration of Isocyanates and Isothiocyanates.*

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Substituted boranes, BXYZ (BCl$_3$, Ph·BCl$_2$, Ph$_2$BCl, and Ar$_3$B), reacted with isocyanates, ArNCO, to give substituted amidoboranes (I), X·B(NAr·CO·Y)·NAr·CO·Z; phenyl isothiocyanate behaved similarly, and 4-methyl-1,3-phenylene di-isocyanate gave polymeric products. The structures of the amidoboranes (I) were established by their infrared spectra, by alcoholic degradation, by the addition reaction with pyridine, and by alternative methods of synthesis. There was spectroscopic evidence that, in one amidoborane (Id), the amide acts as a bidentate ligand. The mechanisms of the reactions are discussed, and of interest are the relative migratory aptitudes (Ph > Cl) of the groups attached originally to boron and ultimately to carbon.

THIS paper is to be the first in a series dealing with the addition of substituted boranes to multiply bonded compounds, Z=Y + BX^{1}X^{2}X^3 ⟶ X^{2}X^{1}B·Z–YX^3, etc. Reactions, in which X^3 = Cl, we describe as chloroborations, and analogous designations are made for reactions involving other values of X^3. The case of X^3 = H is not considered, since hydroboration reactions have received much attention.[1]

Some of the problems are (i) the nature of the substrate ZY, (ii) the mechanism of the reactions, (iii) the relative migratory aptitudes of various groups X^3 attached to boron, and (iv) the structure of the adducts and their subsequent reactions.

We have previously briefly described the chloroboration and phenylboration of certain olefins, such as norbornadiene;[2] acetylene also underwent chloroboration with boron trichloride.[3] In reactions of aldehydes with boron trichloride, chloroboration was the primary step.[4] Reactions with boron trichloride and either dimethyl sulphoxide[5] or acetone[6] did not give rise to chloroborated products; hydrogen chloride was eliminated in both systems and the S=O (and probably also the C=O) bond was cleaved. Other examples of organoboration are found in the autoxidation of organoboranes,[7] the pyrolysis of azidodiphenylborane,[8] and the reaction of organoboranes with nitric oxide.[9]

The present paper is concerned with the behaviour of isocyanates and isothiocyanates towards boron trichloride, triarylboranes, and arylchloroboranes, and with related reactions.

Y·CO·NAr·BX·NAr·CO·Z   Ph·CS·NPh·BCl·NPh·CS·Cl

(I)	X	Y	Z	Ar	(II)
a	Cl	Cl	Cl	Ph	
b	Cl	Cl	Cl	α-C$_{10}$H$_7$	
c	Cl	Cl	Ph	Ph	
d	Cl	Ph	Ph	Ph	
e	Ph	Ph	Ph	Ph	
f	p-Me·C$_6$H$_4$	p-Me·C$_6$H$_4$	p-Me·C$_6$H$_4$	Ph	

[1] Cf. Brown, " Hydroboration," Benjamin, New York, 1962.
[2] Lappert, *Angew. Chem.*, 1960, **72**, 36; Joy and Lappert, *Proc. Chem. Soc.*, 1960, 353.
[3] Arnold, U.S.P. 2,402,589/1946.
[4] Frazer, Gerrard, and Lappert, *J.*, 1957, 739.
[5] Lappert and Smith, *J.*, 1961, 3224.
[6] Massey, *J.*, 1961, 1103.
[7] Cf. Davies, " Organic Peroxides," Butterworths, London, 1962, p. 124.
[8] Opitz, Kleemann, Zimmermann, and Schempp, *Angew. Chem.*, 1962, **74**, 506.
[9] Abraham, Garland, Hill, and Larkworthy, *Chem. and Ind.*, 1962, 1615; Kuhn and Inatome, *J. Amer. Chem. Soc.*, 1963, **85**, 1206.

Diamidoboranes (I) and dithioamidoborane (II) were obtained instantly in practically quantitative yields by the addition of an aryl isocyanate or isothiocyanate, in an inert solvent, to the appropriate borane at 0—25°. Changes in relative molar concentrations or in the order of addition gave identical products. These results are summarised in Table 1.
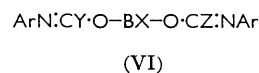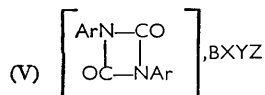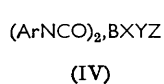
TABLE 1.

Diamidoboranes and dithioamidoborane.

Reactants	Product	Yield (%)	M. p.	Reactants	Product	Yield (%)	M. p.
PhNCO–BCl₃	(Ia)	96·5	140°	PhNCO–Ph₃B	(Ie)	96	118—120°
α-C₁₀H₇·NCO–BCl₃	(Ib)	98	164	PhNCO–(p-Me·C₆H₄)₃B	(If)	97	96
PhNCO–PhBCl₂...	(Ic)	98	197	PhNCS–PhBCl₂	(II)	94	120—123
PhNCO–Ph₂BCl...	(Id)	93	190				

As an extension of this reaction, 4-methyl-1,3-phenylene di-isocyanate with boron trichloride gave a white, microcrystalline polymer having the repeating unit (III). The interesting feature here is the preparation of a polymer having a largely inorganic backbone by a process of polyaddition instead of the more common polycondensation.[10]

Amidoboranes and thioamidoboranes have not hitherto been reported and they are of interest also as rare examples of boron compounds having strongly electron-attracting substituents.

The Structures of the Diamido- and Dithioamido-borane.—In order to establish structures (I) and (II) account has to be taken of alternative possibilities. These are (IV), (V), and (VI) for the oxygen derivatives. Evidence against structure (IV), which involves the isocyanate acting as a monodentate ligand by virtue of either of the two possible (N and O)

$$(ArNCO)_2,BXYZ$$

(IV)

$$\left[\begin{array}{c} ArN\!-\!CO \\ | \quad | \\ OC\!-\!NAr \end{array} \right],BXYZ$$

(V)

$$ArN\!:\!CY\cdot O\!-\!BX\!-\!O\cdot CZ\!:\!NAr$$

(VI)

donor sites, is as follows. Infrared spectra show no absorption at 2300—2200 cm.⁻¹, which is the region characteristic of the asymmetric NCO stretching frequency.[11] Other strong acceptors, such as tin(IV) chloride, boron trifluoride, and trialkylboranes, did not react with phenyl isocyanate under the conditions used to prepare compounds (I) (boron trifluoride formed an unstable complex which dissociated readily); this is evidence against structure (V) also. The 2 : 1 stoicheiometry, L₂BXYZ (L = ligand), required for structure (V) is contrary to the behaviour (1 : 1) of these boranes with donors such as pyridine.[12] Compound (Ia) formed a 1 : 1 adduct, m. p. 132°, with pyridine, whereas on the basis of structures (IV) and (V) ligand exchange would have been expected, as with sulphide–borane complexes.[13]

Structure (V) requires consideration because it is known that aryl isocyanates form cyclic dimers. Typical catalysts for the dimerisation are nucleophiles such as phosphines and amines,[14] but an example of a reagent (NaCl–AlCl₃) which could function as an electrophile has been reported.[15] However, the dimer would be expected to behave as a bidentate ligand and structure (V) is excluded also on the basis of evidence cited above.

Structure (VI) shows boration of the C=O rather than the C=N bond and products

[10] "Developments in Inorganic Polymer Chemistry," ed. Lappert and Leigh, Elsevier, Amsterdam, 1962.

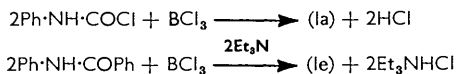[11] Cf. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd ed., 1958, p. 267.

[12] Gerrard and Lappert, *J.*, 1951, 1020; Brindley, Gerrard, and Lappert, *J.*, 1956, 1540; Mikhailov and Fedotov, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1956, 1511; Krause, *Ber.*, 1924, **57**, 813.
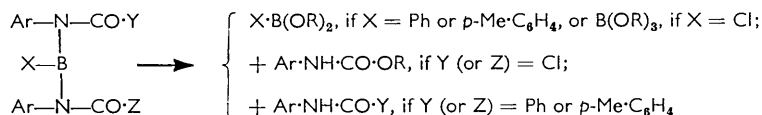
[13] Lappert, *J.*, 1953, 2784.

[14] Cf. Lyon and Thompson, *J.*, 1950, 1971.

[15] Dokunikhin and Gaeva, *Zhur. obshchei Khim.*, 1953, **23**, 606, 798; 1959, **29**, 297.

would thus be derivatives of amides in their imidol forms.   Against this are the following data.   Compounds (I) have an infrared absorption at ∼1750 cm.[-1], which is most probably the amide I band.[16]   It is not impossible, however, that the N=C stretching vibration in (VI) would give rise to absorption in the same region.   On the other hand, compound (II) is transparent in the 1700 cm.[-1] region.   Compound (Ia) was synthesised also from phenyl-carbamoyl chloride, but the possibility of initial dehydrochlorination of the carbamoyl chloride cannot be excluded.   A further synthesis was of compound (Ie), from benzanilide, but again this is ambiguous since tautomerisation is possible.

$$2\text{Ph·NH·COCl} + \text{BCl}_3 \longrightarrow \text{(Ia)} + 2\text{HCl}$$

$$2\text{Ph·NH·COPh} + \text{BCl}_3 \xrightarrow{\text{2Et}_3\text{N}} \text{(Ie)} + 2\text{Et}_3\text{NHCl}$$

The structures of compounds (Ia—f), as far as the mode of attachment of X, Y, and Z is concerned, was established by alcoholysis.

$$
\begin{array}{l}
\text{Ar—N—CO·Y} \\
\qquad | \\
\text{X—B} \\
\qquad | \\
\text{Ar—N—CO·Z}
\end{array}
\longrightarrow
\left\{
\begin{array}{l}
\text{X·B(OR)}_2\text{, if X = Ph or } p\text{-Me·C}_6\text{H}_4\text{, or B(OR)}_3\text{, if X = Cl;} \\
+ \text{Ar·NH·CO·OR, if Y (or Z) = Cl;} \\
+ \text{Ar·NH·CO·Y, if Y (or Z) = Ph or } p\text{-Me·C}_6\text{H}_4
\end{array}
\right.
$$

Structures (I) are also preferred to (VI) because addition to isocyanates generally involves the N=C bond,[17] although rare exceptions are known where addition is made to all three atoms, as in the formation of diphenyl-1,3,4-oxadiazole from phenyl isocyanate and phenylnitrilimine.[18]

Phenyl isocyanate has previously been treated with arylmagnesium halides,[19] to produce anilides on hydrolysis.   It was suggested [20] that this involves initial addition to the C=O bond, but in the light of the present work we favour addition to N=C.

Compounds (I) are characterised by having in the same molecule a strong σ-donor, the carbonyl-oxygen atom, as well as a 3-co-ordinate boron atom as an acceptor.   The possibility of either inter- (VII) or intra-molecular (VIII) interaction is therefore present. It had previously been shown that acetates can behave as bidentate chelating ligands in acetoxyboranes,[21] and similar behaviour in compounds such as basic beryllium acetate is well known.[22]   Examples of amides as bidentate chelating ligands are, as far as we are aware, unknown.

$$
\begin{array}{cc}
\text{Ar·N——CY} & \text{Ar·N—CY=O}^+\text{—B}^- \\
\quad | \bar{\ } \ ^+ || & \quad | \qquad\qquad /|\backslash \\
\text{(VII) Z·CO·NAr·BX—O} & \text{Z·CO·NAr·BX} \qquad\qquad \text{(VIII)}
\end{array}
$$

The infrared spectra of all the compounds have been investigated.   These show that of the six diamidoboranes, only one, (Id), is chelated.   The clearest evidence is that only in compounds (Ic) and (Id) are there two amide I bands.   This is best understood for compound (Id) in terms of structure (VII), which shows one free and the other a chelating type of amide linkage.   It is to be expected that chelation will lower the frequency of the amide I band: this was noted for tertiary amide complexes, such as H·CONMe$_2$,BCl$_3$.[23] Structures (VII) and (VIII) cannot at present be differentiated, since it was not possible to obtain dilute solutions of this substance without some hydrolysis.   Two spectra are

[16] Ref. 11, p. 205.
[17] Cf. Arnold, Nelson, and Verblanc, *Chem. Rev.*, 1957, **57**, 47.
[18] Huisgen, Sturm, and Seidel, *Chem. Ber.*, 1961, **94**, 1555.
[19] Blaise, *Compt. rend.*, 1901, **132**, 38.
[20] Gilman and Kinney, *J. Amer. Chem. Soc.*, 1924, **46**, 493; Gilman, Kirby, and Kinney, *ibid.*, 1929, **51**, 2252.
[21] Duncanson, Gerrard, Lappert, Pyszora, and Shafferman, *J.*, 1958, 3652.
[22] Cf. Wells, " Structural Inorganic Chemistry," Clarendon Press, Oxford, 3rd edn., 1962, p. 403.
[23] Gerrard, Lappert, Pyszora, and Wallis, *J.*, 1960, 2144.

reproduced in the Figure and the amide I frequencies of compounds (Ia—If) are listed in Table 2.

TABLE 2.

Amide I frequencies (cm.$^{-1}$) in diamidoboranes.

| Compound	Ia	Ib	Ic	Id	Ie	If
Frequency	1754	1770	1795—1745	1739—1709	1721	1721

Although the spectrum of compound (Ic) shows an amide I doublet, this is not regarded as evidence for chelation, but is interpreted as due to there being two types of amide groups attached to boron (Y = Ph, Z = Cl). Factors in favour of chelation are that the boron be a good acceptor and the oxygen a good donor. Attachment of chlorine rather than an
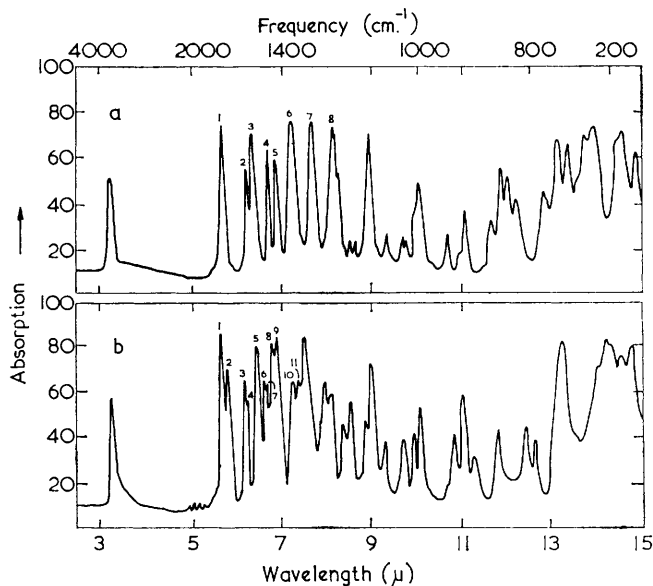
Infrared spectra of (a) compound (Ia) and (b) compound (Id) (see Table 4).

aryl group to boron provides the former, and attachment of phenyl rather than chlorine to carbon provides the latter. We interpret the unique position of compound (Id) among these six compounds to these features.

The Mechanism of Diamidoborane Formation.—As the boranes are strong electron-pair acceptors it is probable that the initial step (a) is the rapid formation of a four-co-ordinate boron complex. This is followed by a rate-determining B–Y cleavage (b) and
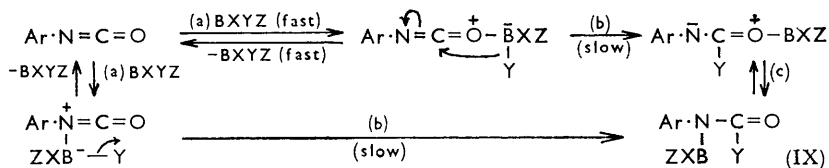
migration of Y from boron to carbon (pictured as a 1,3-nucleophilic rearrangement), and, if the oxygen is the donor site, by a cationotropic 1,3-shift (c) of boron from oxygen to nitrogen. The sequence (a)—(c) is then repeated with a further molecule of ligand.

There is no evidence at present to decide whether the oxygen or the nitrogen is the donor

atom in (a), but the former is the more likely, for steric reasons and because the non-bonding electrons on nitrogen are probably delocalised by π-conjugation with the aromatic ring. That complex formation (a) is the primary step is supported also by the observation that boron trifluoride formed a weak 1 : 1 adduct with phenyl isocyanate.

In (b), Y–C bond-making does not precede B–Y bond-breaking, since with Y = p-Me·C_6H_4 the product (If) was p- and not m-tolylamidoborane.

Reactions leading to compounds (Ic) and (Id), with dichlorophenylborane and chloro-diphenylborane, respectively, show that Ph > Cl in migratory aptitude. This is parallel to the phenylboration of norbornadiene by dichlorophenylborane,[2] but both results are unexpected. With the isocyanates, the explanation may be that phenylboration is preferred over chloroboration because of the thermodynamic advantage of providing extended conjugation in the products; this would not, on the other hand, apply to the dichloro-borylphenylnortricyclene obtained from norbornadiene. The behaviour of the chloro-phenylboranes is in this respect, however, similar to that of organometallic halides such as Grignard reagents or mercurials. The lack of amidoborane formation with boron tri-fluoride is attributed to the difficulty of B–F cleavage required for (b), and with tripentyl-borane to its weak acceptor properties in (a). The latter explanation also accounts for the unreactivity of tetraphenyltin, tin(IV) chloride, and pyridine–boron trichloride with phenyl isocyanate.

It is noteworthy that neither the monoamidoboranes, (IX), nor the triamidoboranes, (X), were isolated in borations but only the diamidoboranes, (I). This is not because compounds (IX) and triamidoboranes are themselves unstable, for they have been obtained independently from amides and either monochloroboranes or boron trichloride, in the presence of triethylamine.[24] We interpret the observation, in part, on the basis of relative acceptor strengths of the boranes required for successive steps (a), which we regard as decreasing in the series (i) Q = Cl > Ph > R > NAr·CO·Cl > NAr·CO·Ar for compounds >B–Q, and (ii) BXYZ > (IX) > (I) > (X). Whereas a compound (IX) is a strong enough Lewis acid to react with phenyl isocyanate, compounds (I) are not. In order to account for the exclusive formation of compounds (I) from BXYZ and phenyl isocyanate, it is necessary to postulate further that, in the double sequence of reactions leading to them, the rate-determining step is the first of the two migrations (b) (*i.e.*, that heterolysis of B–Z is easier than of B–Y). This appears reasonable, since heterolysis is likely to be favoured by there being a relatively high electron density on boron.

EXPERIMENTAL

General Procedures.—Hydrocarbon and ether solvents were dried over sodium wire. n-Butyl alcohol was purified by distillation. Substituted boranes were prepared by standard methods.[25] Boron was estimated by Thomas's method [26] or by aqueous hydrolysis and alkali titration of liberated boric acid in the presence of mannitol. Microanalyses (C, H, and N) were carried out in this department and we thank Mr. V. Manohin and his staff. Pyridine was estimated by steam-distillation from alkaline solution and titration of the distillate with sulphuric acid to the Bromophenol Blue end-point.

Infrared spectroscopic measurements were carried out on a Perkin-Elmer model 21 spectro-photometer, with sodium chloride or with calcium fluoride optics.

M. p.s were taken in sealed capillary tubes.

Boration of Aryl Isocyanates.—The general procedure for the preparation of the diamido-boranes (Ia—If) is illustrated below; other details are to be found in Tables 1 and 3. Phenyl iso-cyanate (10·0 g., 2 mol.) in light petroleum (b. p. 30—40°) (25 ml.) was added dropwise to boron

[24] Lappert and Tilley, unpublished observations.
[25] (PhBCl$_2$) Niedenzu and Dawson, *J. Amer. Chem. Soc.*, 1960, **82**, 4223; Burch, Gerrard, Howarth, and Mooney, *J.*, 1960, 4916; [(Ph$_2$B)$_2$O] Povlock and Lippincott, *J. Amer. Chem. Soc.*, 1958, **80**, 5409; (Ph$_2$BCl) Abel, Dandegaonker, Gerrard, and Lappert, *J.*, 1956, 4697; (Ar$_3$B) Krause and Nitsche, *Ber.*, 1922, **55**, 1261.
[26] Thomas, *J.*, 1946, 820.

trichloride (4·9 g., 1 mol.) in the same solvent (40 ml.) at 5°. The mixture was manually agitated during the addition, which was complete within 30 min. The reaction was exo-thermal. The white microcrystalline substituted *amidoborane* (Ia) (14·2 g., 96·5%), m. p. 140° (Found: C, 47·4; H, 2·2; B, 3·0; Cl, 29·9; N, 7·7. $C_{14}H_{10}BCl_3N_2O_2$ requires C, 47·6; H, 2·3; B, 3·1; Cl, 30·0; N, 7·9%) was filtered off, washed with light petroleum (b. p. 30—40°) (2 × 5 ml.), and freed from solvent at 20°/0·1 mm.

Preparation of Compound (Ia) *from Carbamoyl Chloride.*—Carbamoyl chloride (11·7 g., 2 mol.) in dry chloroform (25 ml.) was added rapidly to boron trichloride (4·4 g., 1 mol.) in the same solvent (20 ml.) at −5° to 0°. The apparatus comprised a two-necked flask, fitted with a dropping funnel, a cold-finger (−78°) condenser, and drying tubes. No visible change occurred below 0°, but vigorous reaction took place at 30—40° with evolution of hydrogen chloride. At the end of the reaction (1·5 hr.) volatile matter was removed at 20°/15 mm. The residue comprised the white, microcrystalline substituted amidoborane (Ia) (12·8 g., 95%). m. p. 138—141° (Found: C, 47·2; H, 2·1; B, 3·1; Cl, 29·7; N, 7·6%), identical (mixed m. p., infra-red measurement) with the compound prepared as above.

Preparation of Compound (Id) *from Benzanilide.*—Benzanilide (12·4 g., 2 mol.) in benzene (150 ml.) was added to boron trichloride (3·7 g., 1 mol.) in benzene (25 ml.) at 0°. Rapid addition of triethylamine (6·35 g., 2 mol.) then caused an exothermal reaction. Triethylammonium chloride (7·8 g., 90%), m. p. 252°, was filtered off. The solvent was removed from the filtrate. The crude solid (Id) was purified by repeated extraction with benzene and reprecipitations with light petroleum. The *product* (11·9 g., 86%) had m. p. 190° (Found: C, 71·5; H, 4·1; B, 2·5; Cl, 7·9; N, 6·4%).

Preparation of a Polymeric Substituted Amidoborane (III).—4-Methyl-1,3-phenylene di-isocyanate (9·5 g., 1 mol.) in light petroleum (b. p. 30—40°) (30 ml.) was added dropwise, with shaking, to boron trichloride (6·4 g., 1 mol.) in the same solvent (50 ml.) in 30 min. The white *polymer* (III) (17·2 g., 93%), which softened at 130° [Found: C, 38·0; H, 2·6; B, 3·1; Cl, 37·0; N, 10·0. $(C_9H_6BCl_3N_2O_2)_n$ requires C, 37·0; H, 2·1; B, 3·7; Cl, 36·5; N, 9·6%], was filtered off.

In a similar experiment with chloroform as solvent, the yield was 95% and the product softened at 132°.

TABLE 3.

Diamidoboranes (I).

Cpd.	Formula	Found (%)					Required (%)				
		C	H	B	Cl	N	C	H	B	Cl	N
Ia	$C_{14}H_{10}BCl_3N_2O_2$	47·4	2·2	3·0	29·9	7·7	47·6	2·3	3·1	30·0	7·9
Ib	$C_{22}H_{14}BCl_3N_2O_2$	55·2	2·9	2·4	23·0	6·3	54·0	3·1	2·4	23·4	6·15
Ic	$C_{20}H_{15}BCl_2N_2O_2$	59·0	3·7	2·6	17·9	6·7	59·2	3·7	2·7	17·5	6·9
Id	$C_{26}H_{20}BClN_2O_2$	71·4	3·8	2·4	8·0	6·3	71·3	4·5	2·5	8·1	6·4
Ie	$C_{32}H_{25}BN_2O_2$	81·1	5·1	2·1	—	5·8	81·2	5·2	2·3	—	5·85
If	$C_{35}H_{28}BN_2O_2$	.82·0	5·6	2·0	—	5·5	82·2	5·5	2·1	—	5·5

Preparation of the Thioamidoborane (II).—Phenyl isothiocyanate (10·66 g., 2 mol.) in light petroleum (b. p. 30—40°) (20 ml.) was added dropwise to phenyldichloroborane (6·72 g., 1 mol.) in the same solvent (40 ml.) at 25°. The reaction was exothermal. The yellow crystalline *thioamidoborane* (II) (16·3 g., 94%), m. p. 120—123° (Found: C, 55·2; H, 3·8; B, 2·5; Cl, 16·3; N, 6·4. $C_{20}H_{15}BCl_2N_2S_2$ requires C, 56·1; H, 3·5; B, 2·6; Cl, 16·5; N, 6·55%), was obtained by filtration.

Interaction of Pyridine and the Diamidoborane (Ia).—Pyridine (1·8 g., 1 mol.) in hexane (10 ml.) was added slowly to compound (Ia) (8·0 g., 1 mol.), suspended in hexane (50 ml.), at 20°. The reaction was exothermal. Matter volatile at 20°/0·1 mm. was removed and the white *pyridine complex* (9·5 g., 97·0%), m. p. 132° (Found: C, 53·0; H, 3·3; B, 2·4; Cl, 24·6; N, 9·5. $C_{19}H_{15}BCl_3N_3O_2$ requires, C, 52·6; H, 3·5; B, 2·5; Cl, 24·6; N, 9·7%), was obtained by filtration.

Alcoholysis of Diamidoboranes (I) *and the Dithioamidoborane* (II).—(a) Butan-1-ol (7·5 g., 5 mol.) in hexane (10 ml.) was added slowly to compound (Ia) (7·2 g., 1 mol.) suspended in hexane (10 ml.) at 25°. Hydrogen chloride was evolved. The vigorous reaction was allowed to proceed at b. p. of hexane (60°) for 1 hr. Matter volatile at 20°/0·1 mm. was removed and trapped at −78° and butyl *N*-phenylcarbamate (7·4 g., 94%), m. p. 61—62° (Found: N, 7·4.

Calc. for $C_{11}H_{15}NO_2$: N, 7·25%), was thus obtained. The liquid (trapped at $-78°$) was fractionally distilled. The second fraction afforded tributyl borate (4·1 g., 92%), b. p. 116—119°/15 mm., n_D^{20} 1·4079 (Found: B, 4·9. Calc. for $C_{12}H_{27}BO_3$: B, 4·9%).

(b) Butan-1-ol (4·41 g., 5 mol.) in n-hexane (10 ml.) was added to compound (Ib) (5·4 g., 1 mol.) suspended in hexane (10 ml.) at 25°. The previous procedure gave butyl N-α-naphthyl-carbamate (5·2 g., 90%) (Found: N, 7·6. Calc. for $C_{15}H_{17}NO_2$: N, 7·75%) and tributyl borate (2·4 g., 89%), b. p. 118°/15 mm., n_D^{20} 1·4080 (Found: B, 4·87%).

(c) Butan-1-ol (5·6 g., 4 mol.) in light petroleum (b. p. 30—40°) (4 ml.) was added to compound (Ic) (7·5 g., 1 mol.) suspended in the same solvent (25 ml.) at 25°. Reaction was allowed to proceed for 2 hr. at 30—40°. The mixture was then cooled and filtered. The precipitate gave benzanilide (3·7 g., 99·9%), m. p. 161—162° (Found: N, 6·9. Calc. for $C_{13}H_{11}NO$: N, 7·1%). The filtrate afforded butyl N-phenylcarbamate (3·2 g., 88%) (Found: N, 7·3%) and tributyl borate (3·5 g., 85%), b. p. 68°/1·8 mm., n_D^{20} 1·4080 (Found: B, 4·9%).

(d) Butan-1-ol (4·1 g., 3 mol.) in light petroleum (b. p. 100—120°) (6 ml.) was added to compound (Id) (8·1 g., 1 mol.) suspended in the same solvent (20 ml.) at 25°. The reaction was slightly exothermal, and was allowed to proceed at the b. p. for 3 hr. A precipitate was identified as benzanilide (7·0 g., 96%), m. p. 161—162° (Found: N, 7·0%). The filtrate afforded tributyl borate (3·6 g., 89%), b. p. 67—68°/1·8 mm., n_D^{20} 1·4081 (Found: B, 4·93%).

(e) Butan-1-ol (3·06 g., 2 mol.) and compound (I) (9·9 g., 1 mol.) in light petroleum (b. p. 100—120°) (35 ml.) at the b. p. (8 hr.) gave benzanilide (7·91 g., 97%), m. p. 162° (Found: N,

TABLE 4.

Principal absorption bands (cm.$^{-1}$) of diamidoboranes (I) (mulls in liquid paraffin and hexachlorobutadiene; CaF$_2$ optics).

Ia	Ib	Ic	Id	Ie	If
1754vvs (1)	1770vvs	1795vvs	1739vvs (1)	1721vvs	1712vvs
1608s (2)	1592vvs	1745s	1709s (2)	1597s	1605m
1580vvs (3)	1575vvs	1608vs	1592s (3)	1582w	1595m
1493vvs (4)	1508vvs	1592vs	1580m (4)	1567w	1570m
1453s (5)	1471vs	1575w	1534vvs (5)	1543vvs	1527vs
1370vvs (6)	1444s	1531vs	1499m (6)	1595s	1488s
1307vs (7)	1389vvs	1497s	1486m (7)	1490s	1456vvs
1235vs (8)	1311vs	1490s	1460vs (8)	1458m	1431vvs
	1276s	1449s	1441vvs (9)	1445m	1377vs
	1250s	1383s	1366m (10)	1433s	1316vvs
	1232m	1285vs	1348m (11)	1319vs	1307vvs
			1323vvs (12)	1289w	1253s
				1252m	

7·2%), and dibutoxyphenylborane (4·4 g., 92%), b. p. 141°/13 mm., n_D^{20} 1·4751 (Found: B, 4·6. Calc. for $C_{14}H_{23}BO_2$: B, 4·63%).

(f) Butan-1-ol (1·98 g., 2 mol.) and compound (If) (6·8 g., 1 mol.) in light petroleum (b. p. 100—120°) (20 ml.) at the b. p. (10 hr.) gave p-toluanilide (5·2 g., 93%), m. p. 146—148° (Found: N, 6·7. Calc. for $C_{14}H_{13}NO$: N, 6·6%), and dibutoxy-p-tolylborane (3·05 g., 90%), b. p. 162—165°/15 mm., n_D^{20} 1·4757 (Found: B, 4·3. Calc. for $C_{15}H_{25}BO_2$: B, 4·37%).

(g) Butan-1-ol (4·2 g., 4 mol.) and compound (II) (6·2 g., 1 mol.) in hexane (26 ml.) at the b. p. (2 hr.) gave thiobenzanilide (2·8 g., 95%), m. p. 98—101° (Found: N, 6·7. Calc. for $C_{13}H_{11}NS$: N, 6·6%), butyl N-phenylcarbamate (2·9 g., 98%), m. p. 55° (Found: N, 6·4. Calc. for $C_{11}H_{15}NOS$: N, 6·7%), and tributyl borate (3·2 g., 98%), b. p. 67—68°/1·8 mm., n_D^{20} 1·4080 (Found: B, 4·9%).

Infrared Spectra of the Diamidoboranes (I).—Table 4 shows results to supplement Table 2.

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