785. *Pseudohalides. Part II.*[1] *Preparation, Characterisation, and Reactions of 3-Co-ordinate Mononuclear Iso- and Isothio-cyanatoboranes*

By M. F. LAPPERT, H. PYSZORA, and M. RIEBER

Interaction of halogenoboranes and metal salts of cyanic or thiocyanic acid afforded iso- and isothio-cyanatoboranes. These compounds have been characterised. A " displacement series " for reactions $\gt BX \longrightarrow \gt BZ$ has been suggested. The behaviour of selected examples with amines and alcohols has been investigated. Substitution reactions only were observed, either of pseudohalide groups or of other ligands. The results are discussed.

THE preparation of di-n-butoxyisothiocyanatoborane, $(Bu^nO)_2BNCS$, bisdimethylamino-isothiocyanatoborane, $(Me_2N)_2BNCS$, and 2-isothiocyanato-1,3,2-benzodioxaborole, o-$C_6H_4O_2{\cdot}BNCS$, has been briefly described.[2] In addition to these compounds, the only reported mononuclear 3-co-ordinate iso- or isothio-cyanatoboranes are the tris-compounds

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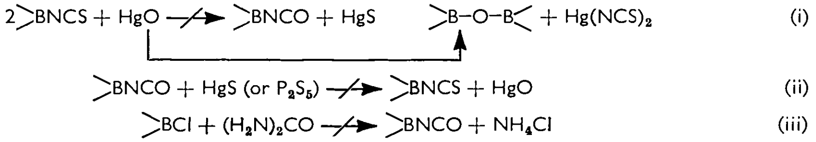
[1] Part I, M. F. Lappert and H. Pyszora, *J.*, 1963, 1744.

[2] M. F. Lappert and H. Pyszora, *Proc. Chem. Soc.*, 1960, 350.

$B(NCO)_3$ [3] and $B(NCS)$,[4,5] dimethylisocyanatoborane Me_2BNCO,[6] 2-isothiocyanato-1,3,2-dioxaborolane $(CH_2)_2O_2BNCS$,[7] 2-isothiocyanato-1,3,2-dioxaborinane $(CH_2)_3O_2BNCS$,[8] 2-isocyanato-1,3,2-dioxaborinane $(CH_2)_3O_2BNCO$,[9] and n-butoxyisothiocyanatophenylborane $PhB(OBu^n)NCS$.[10]

The compounds in Table 2 and the first 10 listed in Table 1 were prepared from the corresponding chlorides or bromides by metathesis with silver, sodium, or lead cyanate or thiocyanate in solvents such as benzene, methylene dichloride, and acetonitrile. Only with silver salts was benzene effective, and sodium or lead salts reacted very slowly, if at all, either when no solvent, or when benzene, was used. Similar behaviour was observed in the preparation of iso- and isothio-cyanatoborazines.[1] All the conversions of 3-co-ordinate halogenoboranes proceeded very readily, the reactions being exothermal, and giving high yields (56·6—95%) after reflux times ranging from 10 min. to 2 hr.

Other potential preparative routes (i—iii), suitable for organic iso- and isothio-cyanates, and for isocyanatosilanes,[11] did not give the desired products.



A mixed halide pseudohalide, $BrB(NCS)_2$, stable to distillation (b. p. 80°/0·15 mm.), was obtained from the interaction of tribromoborane and silver thiocyanate. Its stability may be contrasted with those of the mixed halides of boron, whose existence in equilibrium mixtures has been established spectroscopically [12] without its being possible (but see refs. 12*e* and 13) to isolate them pure. The instability of the mixed halides of boron is probably a kinetic effect, associated with a low activation energy for formation of a halogen-bridged transition state. The stability of $BrB(NCS)_2$ may therefore be a reflection of the poor bridging capacity of bromine and isothiocyanate.

Another interesting compound is $(Pr^i_2N)B(NHBu^t)NCO$, which represents a rare example [14] of a mixed bisaminoborane, no doubt due to steric hindrance to formation of a 4-co-ordinate transition state.

The characterising constants of the iso- and isothio-cyanatoboranes are shown in Tables 1 and 2. The differences in boiling points between the isothiocyanatoboranes and corresponding chloroboranes (~100° at 760 mm., per group) is far greater than between the isothiocyanates and chlorides of phosphorus and silicon (~65° at 760 mm., per group [15]). This must be due to enhanced intermolecular association for the boron compounds, probably due to increased polarisation of the $-N{=}C{=}S$ group, as a result of conjugation with boron. However, all the compounds were monomeric in benzene when freshly prepared, but gradually (over a period of weeks) they solidified at room temperature, and from this it is

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[3] G. S. Forbes and H. H. Anderson, *J. Amer. Chem. Soc.*, 1940, **62**, 761.

[4] H. E. Cocksedge, *J.*, 1908, **93**, 2177; not confirmed by E. Pohland, *Z. anorg. Chem.*, 1931, **201**, 282.

[5] D. B. Sowerby, *J. Amer. Chem. Soc.*, 1962, **84**, 1831.

[6] J. Goubeau and H. Gräbner, *Chem. Ber.*, 1960, **93**, 1379.

[7] A. Finch, P. J. Hendra, and E. J. Pearn, *Spectrochim. Acta*, 1962, **18**, 51.

[8] A. Finch, P. J. Gardner, J. C. Lockhart, and E. J. Pearn, *J.*, 1962, 1428.

[9] A. Finch and E. J. Pearn, *Spectrochim. Acta*, 1963, **19**, 1621.

[10] J. C. Lockhart, *J.*, 1962, 1197.

[11] J. Goubeau and D. Paulin, *Chem. Ber.*, 1960, **93**, 1111.

[12] (*a*) L. H. Long and D. Dollimore, *J.*, 1954, 4457; (*b*) T. H. S. Higgins, E. C. Leisegang, C. J. G. Raw, and A. J. Rossouw, *J. Chem. Phys.*, 1955, **23**, 1544; (*c*) J. Goubeau, D. E. Richter, and H. J. Becher, *Z. anorg. Chem.*, 1955, **278**, 12; (*d*) R. N. Keller and C. W. Bills, Abs. Papers, 126th Meeting, Amer. Chem. Soc., September 1954, p. 11R; (*e*) A. Finch and J. C. Lockhart, *Chem. and Ind.*, 1964, 497.

[13] (*a*) A. Besson, *Compt. rend.*, 1891, **112**, 1001; (*b*) W. Gerrard, M. Howarth, E. F. Mooney, and D. E. Pratt, *J.*, 1963, 1582.

[14] D. W. Aubrey, M. F. Lappert, and M. K. Majumdar, *J.*, 1962, 4088.

[15] H. H. Anderson, *J. Amer. Chem. Soc.*, 1942, **64**, 1757.

TABLE 1

Isocyanatoboranes

Compound	B. p./mm.	n_D^{20}	d_4^{20}	Yield (%)	Found (%)				M	Formula	Required (%)				M
					C	H	N	B			C	H	N	B	
$(MeO)_2BNCO$	48°/88	1·3856	*	61·0	31·5	5·1	12·2	9·5	*	$C_3H_6BNO_3$	31·25	5·26	12·2	9·4	115
$(Bu^nO)_2BNCO$	65—66/2·5	1·4155	0·9613	94·0	54·6	9·0	7·1	5·4	192	$C_9H_{18}BNO_3$	54·3	9·1	7·0	5·4	199
$(Me_2N)_2BNCO$	30/0·3	1·4499	*	82·0	42·9	8·4	29·6	7·7	*	$C_5H_{12}BN_3O$	42·6	8·6	29·8	7·67	141
$(Et_2N)_2BNCO$	61/0·1	1·4475	0·8678	65·3	54·8	10·3	21·6	5·5	190	$C_9H_{20}BN_3O$	54·84	10·2	21·3	5·5	197
$(Pr^i_2N)_2BNCO$	73—75/0·005	1·4502	0·8933	81·0	61·8	10·9	16·4	4·3	242	$C_{13}H_{28}BN_3O$	61·66	11·14	16·6	4·27	253
$Pr^i_2NB(NCO)_2$	74/2·0	1·4529	0·9713	60·2	49·3	7·1	21·4	5·5	*	$C_8H_{14}BN_3O_2$	49·2	7·1	21·5	5·5	195
$(CH_2NPr^n)_2BNCO$	61/0·9	1·4575	0·9264	56·6	54·8	8·9	21·4	5·3	*	$C_9H_{18}BN_3O$	55·4	9·2	21·5	5·5	195
o-$C_6H_4O_2BNCO$	54/0·2	1·5277	*	95·3	52·4	2·3	8·6	6·8	165	$C_7H_4BNO_3$	52·26	2·5	8·6	6·7	162
Ph_2BNCO	89/0·01	1·6092	1·105	95·0	76·0	4·6	6·9	5·3	210	$C_{13}H_{10}BNO$	75·4	4·87	6·8	5·2	207
$PhB(NCO)_2$	60/0·2	1·5527	1·187	74·2	55·9	2·9	16·3	6·3	*	$C_8H_5BN_2O_2$	55·88	2·9	16·3	6·3	172
$(Pr^i_2N)Bu^tNHBNCO$ †	41—43/0·01	1·4453	*	69·1	60·4	10·4	18·9	4·9	230	$C_{11}H_{24}BN_3O$	58·66	10·7	18·7	4·8	225
$(Bu^tNH)_2BNCO$ †	72/0·1	1·4376	*	59·6	54·7	10·2	20·9	5·5	190	$C_9H_{20}BN_3O$	54·84	10·2	21·3	5·5	197
$(Bu^nO)(Pr^i_2N)BNCO$ †	64/0·1	1·4265	0·9190	67·0	58·7	9·9	12·2	4·7	*	$C_{11}H_{23}BN_2O_2$	58·5	10·1	12·3	4·7	226
$(C_6H_{11}O)(Pr^i_2N)BNCO$ †	90/0·25	1·4529	0·9694	55·2	62·0	10·3	11·3	4·3	*	$C_{13}H_{25}BN_2O_2$	61·9	9·9	11·1	4·3	252
$(Bu^tO)(Pr^i_2N)BNCO$ †	32/0·05	1·4213	0·8722	53·0	58·5	10·1	12·2	4·7	*	$C_{11}H_{23}BN_2O_2$	58·5	10·1	12·3	4·7	226
$(Pr^i_2N)(PhNMe)BNCO$ †	80/0·1	1·5051	1·081	82·4	64·5	8·7	17·1	4·3	*	$C_{14}H_{22}BN_3O$	64·9	8·5	16·3	4·1	259

* Not determined. † Obtained from reactions of isocyanatoboranes with amines or alcohols.

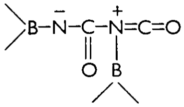
TABLE 2

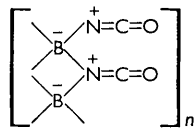
Isothiocyanatoboranes

Compound	B. p./mm.	n_D^{20}	d_4^{20}	Yield (%)	Found (%)					M	Formula	Required (%)					M
					C	H	N	S	B			C	H	N	S	B	
$(Bu^nO)_2BNCS$	64·5—65°/0·25	1·4479	0·9488	85·7	50·0	8·25	6·5	14·6	4·9	205	$C_9H_{18}BNO_2S$	50·3	8·4	6·5	14·9	5·0	215
o-$C_6H_4O_2BNCS$	84/0·7	1·6048	1·2814	84·5	47·9	2·2	7·9	18·5	6·0	181	$C_7H_4BNO_2S$	47·5	2·3	7·9	18·1	6·1	177
$(Me_2N)_2BNCS$	50/0·4	1·5231	0·9941	79·2	38·1	7·7	26·4	21·7	6·9	155	$C_5H_{12}BN_3S$	38·3	7·7	26·8	20·4	6·9	157
$(Et_2N)_2BNCS$	65/0·1	1·5032	0·943	64·9	50·4	9·3	19·9	15·1	5·1	*	$C_9H_{20}BN_3S$	50·7	9·45	19·7	15·1	5·1	213
Ph_2BNCS	114—116/0·02	1·6714	1·119	62·6	69·9	4·4	6·3	14·5	4·8	237	$C_{13}H_{10}BNS$	66·97	4·5	6·3	14·7	4·85	223
$BrB(NCS)_2$	80/0·15	*	1·3721	70·8	*	—	13·1	31·5	5·4	*	$C_2BBrN_2S_2$	11·56	—	13·54	31·0	5·2	207

* Not determined.

to be inferred that they dimerised or polymerised. The tendency for the liquids to solidify seems to be governed by the nature of the other substituents (which determine the electrophilic nature of boron) and also by steric considerations. Dimethylisocyanatoborane was said to be very unstable even at −80°,[6] whereas the compounds here reported ranged from those which slowly polymerised at room temperature to others which were completely stable; susceptibility to polymerisation decreased in the series (i) $R_2B- > Ar_2B- > (R_2N)_2B- > (RO)_2B$; (ii) NCO $\gg$ NCS; and (iii) $B(NCY)_3 > XB(NCY)_2 > X_2B(NCY)$. Detailed information on the structure of the polymeric products is not available, but the infrared spectra recorded on the " solids " showed both NCO and C=O stretching vibrations. Cyclic and linear structures are possible, but only the latter are indicated in (I) and (II). Evidence in favour of polymers not directly involving boron (except in the side-chains), as in (I), is (*a*) that isocyanates of carbon, silicon, and phosphorus polymerise also (though less readily), (*b*) that each of (i)—(iii) is explained, and (*c*) that the spectral characteristics are appropriate. On the other hand, a point of contrast between boron and many other isocyanates is that the isocyanatoboranes do not depolymerise on heating.


(I)


(II)

From the infrared spectra (to be published separately) of the boron pseudohalides, it was concluded that these have the iso-structures (>B–N=C=X, where X = O or S). For isothiocyanates, the structures are further supported by calculations of molar refractivities (Table 3).

TABLE 3

Molar refractivities of some boron isothiocyanates *

Compound	$(Me_2N)_2BNCS$	$(Et_2N)_2BNCS$	$(Bu^nO)_2BNCS$	o-$C_6H_4O_2BNCS$	Ph_2BNCS
$[R_L]_D$ (Found)	46·9	65·9	60·3	46·0	71·3
$[R_L]_D$ (Calc. for BNCS)...	46·1	65·3	61·0	45·7	71·6
$[R_L]_D$ (Calc. for BSCN)...	43·5	63·1	58·7	43·4	69·4

* Based on boron atomic refractivities of 2·65 (M. F. Lappert, *J.*, 1956, 1768), 3·00 (D. W. Aubrey and M. F. Lappert, *J.*, 1959, 2927), and 5·27 (K. Torssell, *Acta Chem. Scand.*, 1954, **8**, 1779) for alkoxy-, amino-, and aryl-derivatives, respectively, and data of A. I. Vogel, " Practical Organic Chemistry," Longmans, Green and Co., London, 2nd edn., 1951, p. 900.

The Boron " Conversion Series."—In the general displacement reaction >B–X ⟶ >B–Z (in a solvent in which both are soluble), the direction of conversion is likely to be governed by the relative affinities of boron for X and Z, and the relative solubilities of the metal salts MX and MZ.

From a limited number of experiments, the following " conversion series " for boron compounds is suggested: >BBr ⟶ >BS– ⟶ >BCN ⟶ >BCl ⟶ >BNCS ⟶ >BNCO ⟶ >BO–. In general, it is possible to convert any compound on the left into one further to the right by the use of either a silver or a mercury(II) salt. Thus, it has been shown that bromoboranes (BBr_3 and $PhBBr_2$),[16] unlike pseudohalogenoboranes,[10] react readily with mercury(II) sulphide to give $(XBS)_3$, and that halogenoboranes and silver cyanide give cyanoboranes;[17] the other experiments to support the series are indicated in this Paper.

The " conversion series " appears to be governed by thermodynamic criteria (*i.e.*, the series runs parallel to increases in BX bond strengths).

Reactions with Alcohols and Amines.—In contrast to the addition reactions observed between amines and isocyanatoborazines,[1] the mononuclear 3-co-ordinate isocyanatoboranes generally underwent transamination. The starting materials were deliberately so

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[16] R. H. Cragg and M. F. Lappert, unpublished observations.

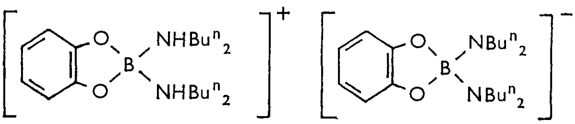
[17] M. F. Lappert, B. Prokai, and H. Pyszora, unpublished observations, cited in " Developments in Inorganic Polymer Chemistry," ed. M. F. Lappert and G. J. Leigh, Elsevier, Amsterdam, 1962, ch. 2.

chosen as sterically to shield the boron atom,[14] and thus encourage attack by the nucleophil (a hindered amine) at the carbon atom of the isocyanate group (cf. ref. 1); this expectation was not realised. Bisdi-isopropylaminoisocyanatoborane failed to react with di-isopropylamine.

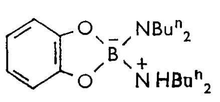
$$(R_2N)_2BNCO + R'R''NH \longrightarrow (R_2N)(R'R''N)BNCO + R_2NH$$
$$(R = Pr^i \text{ and } R'R'' = PhMe \text{ or } Bu^tH)$$
$$(Pr^i{}_2N)_2BNCO + 2Bu^tNH_2 \longrightarrow (Bu^tNH)_2BNCO + 2Pr^i{}_2NH$$

It is interesting that, in contrast to the $(Pr^i{}_2N)_2BNCO$–Bu^tNH_2 experiment, $(Pr^i{}_2N)_2BCl$ and Bu^tNH_2 gave $(Pr^i{}_2N)_2B(NHBu^t)$.[14] These results may be interpreted in terms of decreasing bond strengths in the series $B–NCO > B–NHBu^t > B–NPr^i{}_2 > B–Cl$.

2-Isocyanato-1,3,2-benzodioxaborole reacted with di-n-butylamine in a complex manner. The isolated and identified products were 2-di-n-butylamino-1,3,2-benzodioxaborole, o-$C_6H_4O_2BNBu^n{}_2$, and a crystalline solid having the composition $C_{22}H_{41}O_2N_2B$. The solid was only sparingly soluble in organic solvents, and was very stable towards pyrolysis (195°/0·01 mm., 2 hr.) and alcoholysis. On the basis also of its infrared spectrum, it is tentatively formulated as (III). Structure (IV) would not be consistent with the chemical behaviour. Synthesis of the compound from 2-di-n-butylamino-1,3,2-benzodioxaborole and di-n-butylamine failed.



(III)



(IV)

Bisdiethylaminoisothiocyanatoborane reacted with diethylamine by a displacement path; in this it resembles isothiocyanatoborazines.[1]

$$(Et_2N)_2BNCS + 2Et_2NH \longrightarrow B(NEt_2)_3 + (Et_2NH_2)^+(N\overline{C}S)$$

Likewise, in their reactions with alcohols, the mononuclear pseudohalogenoboranes resembled the borazine analogues in giving pseudohalide group replacement,[1] except for bisdi-isopropylaminoisocyanatoborane, in which preferential displacement of a di-iso-propylamino-group took place [the explanation is doubtless similar to that which accounts for the $(Pr^i{}_2N)_2BNCO$–R_2NH system].

$$(Et_2N)_2BNCX + 2Bu^nOH \longrightarrow (Et_2N)(Bu^nO)_2B + Et_2NH_2,NCX$$
$$(X = O \text{ or } S)$$
$$o\text{-}C_6H_4O_2BNCO + 2ROH \longrightarrow o\text{-}C_6H_4O_2BOR + RCO_2NH_2$$
$$(R = Et \text{ or } Bu^n)$$
$$(Pr^i{}_2N)_2BNCO + ROH \longrightarrow (Pr^i{}_2N)(RO)BNCO + Pr^i{}_2NH$$
$$(R = Bu^n, Bu^t, \text{ or } C_6H_{11})$$

EXPERIMENTAL

General Procedures.—Amines were dried and purified by heating under reflux with, and fractionation from, barium oxide. n-Butyl alcohol was dried by distillation from metallic calcium. Analyses, except for boron, were carried out in the microanalytical laboratories of this Department and we thank Mr. V. Manohin and his staff. Boron was estimated by Thomas's method.[18] Molecular weights were determined cryoscopically in benzene. Halogenoboranes used as starting materials [except for 2-chloro-1,3,2-diaza(*NN'*-n-propyl)borolane] were prepared by known methods.[19]

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[18] L. H. Thomas, *J.*, 1946, 820.

[19] (*a*) M. F. Lappert, *Chem. Rev.*, 1956, **56**, 959; (*b*) D. W. Aubrey, M. F. Lappert, and M. K. Majumdar, *J.*, 1962, 4088; (*c*) H. A. Skinner and N. B. Smith, *J.*, 1954, 2324; (*d*) W. Gerrard, M. F. Lappert, and B. A. Mountfield, *J.*, 1959, 1529; (*e*) E. W. Abel, W. Gerrard, and M. F. Lappert, *J.*, 1959, 3833.

Infrared spectra were recorded on Perkin-Elmer 21 (2—15 μ) and Infracord K14 (15—25 μ) instruments, equipped with sodium chloride and potassium chloride optics, respectively.

Precautions were taken to avoid contamination by atmospheric moisture. M. p.s were taken in sealed capillary tubes.

2-Chloro-1,3,2-diaza(NN'-n-propyl)borolane.—Trichloroborane (12·2 g., 1 mol.) was added dropwise to *NN'*-di-n-propylethylenediamine (15·3 g., 1 mol.) in light petroleum (b. p. 60—80°) (150 ml.) at −80°. The mixture was brought to room temperature and, after addition of triethylamine (21·4 g., 2 mol.) in light petroleum (b. p. 60—80°) (50 ml.), was set aside for 12 hr. Triethylammonium chloride (26·9 g., 97%) (Found: Cl, 25·1. Calc. for $C_6H_{16}ClN$: Cl, 25·8%) was filtered off. The solvent was removed from the filtrate at 20°/15 mm., to leave a crude product, which upon fractional distillation yielded *2-chloro-1,3,2-diaza(NN'-n-propyl)borolane* (5·9 g., 30·1%), b. p. 72°/4 mm., n_D^{20} 1·4582, d_4^{20} 0·9456 (Found: C, 51·4; H, 9·9; N, 14·6; B, 5·7; Cl, 18·3. $C_8H_{18}BClN_2$ requires C, 50·9; H, 9·6; N, 14·8; B, 5·7; Cl, 18·8%).

Preparation of Iso- and Isothio-cyanatoboranes.—The general procedure is illustrated by the preparation of isocyanatobisdi-isopropylaminoborane. Silver cyanate (7·81 g., 1·5 mol.), previously dried for 2 hr. at 140°, was added in a dry-box to a solution of chlorobisdi-isopropylaminoborane (8·57 g., 1 mol.) in benzene (50 ml.). The mixture was refluxed for 1½ hr., and was then set aside overnight. The silver chloride and excess of silver cyanate were filtered off, the precipitate washed with benzene (2 × 15 ml.), and solvent was removed from the combined filtrate and washings first at 20°/15 mm., and then at 20°/0·1 mm., leaving a brown liquid (8·83 g., 100%), which on fractional distillation yielded *isocyanatobisdi-isopropylaminoborane* (7·15 g., 81%) (see Table 1) and an undistilled residue (0·9 g.).

Interaction of Tribromoborane and Silver Thiocyanate.—Tribromoborane (6·7 g., 1 mol.) in methylene dichloride (10 ml.) was added dropwise (10 min.) to a suspension of silver thiocyanate (14·97 g., 3·35 mol.) (previously dried for 2 hr. at 120°) in the same solvent (30 ml.) at ~10°. An exothermal reaction took place. The mixture was shaken for ½ hr., and then left at 20° for an additional 1 hr. The silver bromide and excess of silver thiocyanate were filtered off. The precipitate was washed with methylene dichloride (2 × 20 ml.), and solvent removed from the combined filtrate and washings at 20°/15 mm., leaving a liquid (4·1 g., 74%), which on distillation yielded *bromodi-isothiocyanatoborane* (3·92 g., 70·8%) (see Table 2), and an undistilled residue (0·1 g.).

An infrared spectrum, recorded on the compound as a capillary film, showed the following absorption bands (cm.$^{-1}$): 2890vw, 2740vw, 2577w, 2336m, 2000vvs, 1825m, 1564w, 1342sh, 1300vs, 1064w, 968m, 800sh, and 770vsb.

Interaction of 2-Isocyanato-1,3,2-benzodioxaborole (1 mol.) and n-Butyl Alcohol (2 mol.).—n-Butyl alcohol (2·52 g., 2 mol.) in light petroleum (b. p. 40—60°) (20 ml.) was added dropwise (10 min.) to a solution of 2-isocyanato-1,3,2-benzodioxaborole (2·73 g., 1 mol.) in the same solvent (25 ml.). An exothermal reaction ensued and a white crystalline solid formed. An infrared spectrum, recorded on the supernatant liquor, showed absence of –NCO absorption at 2278 cm.$^{-1}$. The mixture was left overnight. Solvent was removed at 20°/15 mm., until only about 10 ml. remained. The solid was filtered off and washed with light petroleum (2 × 5 ml.). From the filtrate and washings, solvent was removed first at 20°/15 mm., and then at 20°/0·1 mm., leaving a liquid (3·26 g., 100%), which on fractional distillation afforded 2-n-butoxy-1,3,2-benzodioxaborole [19d] (2·69 g., 82·6%), b. p. 102°/5 mm., n_D^{20} 1·4890 (Found: B, 5·60. Calc for $C_{10}H_{13}BO_3$: B, 5·64%) (authentic infrared spectrum) and an undistilled residue (0·5 g.).

The solid was recrystallised from light petroleum (b. p. 60—80°), to give n-butylurethane (1·78 g., 93·6%), m. p. 51·5° (cf.[20] 51·6°) (Found: C, 51·3; H, 9·3; N, 12·1. Calc. for $C_5H_{11}NO_2$: C, 51·3; H, 9·5; N, 12·0%). An infrared spectrum of the urethane, as a suspension in liquid paraffin and hexachlorobutadiene, showed the following absorption bands (cm.$^{-1}$), for some of which assignments are indicated: [21] 3497, 3390, 3322 all vs (νNH_2), 2976s, 2899s (ν CH_2 and ν CH_3), 1712vs (C=O, Amide I), 1603s (Amide II), 1451s (δ CH_2), 1412s, 1357sh (δ CH_3), 1337vs, 1264w, 1232w, 1168w, 1124s, 1078vs, 1041m, 1018w, 940m, 888m, 788s, 755w, 741m, and 676wb.)

Interaction of Isocyanatobisdiethylaminoborane (1 mol.) and n-Butyl Alcohol (2 mol.).—n-Butyl

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[20] W. M. D. Bryant, *J. Amer. Chem. Soc.*, 1941, **63**, 511.

[21] L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, pp. 296 and 222.

alcohol (2·07 g., 2 mol.) in light petroleum (b. p. 30—40°) (10 ml.) was added at room temperature to a solution of isocyanatobisdiethylaminoborane (2·75 g., 1 mol.) in the same solvent (25 ml.). An exothermal reaction took place and, upon cooling, a crystalline solid separated. The white solid was filtered off, washed with light petroleum (2 × 15 ml.), and solvent was removed from the filtrate and washings at 20°/15 mm., to leave a liquid (3·10 g., 97·5%), which on fractional distillation yielded di-n-butoxydiethylaminoborane [22] (2·34 g., 73·6%), b. p. 56°/0·2 mm., n_D^{20} 1·4232, d_4^{20} 0·856 (Found: C, 62·4; H, 12·0; N, 5·9; B, 4·78. Calc. for $C_{12}H_{28}BNO_2$: C, 62·8; H, 12·3; N, 6·1; B, 4·72%). The solid (0·95 g., 58·7%) was recrystallised from ether to give *NN*-diethylurea (0·90 g.), m. p. 71° (cf.[23] 71°) (Found: N, 24·2. Calc. for $C_5H_{12}N_2O$: N, 24·15%) (νNH_2 at 3425, 3356, 3226 cm.$^{-1}$; C=O, Amide I, 1656 cm.$^{-1}$; Amide II, 1613 cm.$^{-1}$).

Interaction of Isothiocyanatobisdiethylaminoborane (1 *mol.*) *and n-Butyl Alcohol* (2 *mol.*).—n-Butyl alcohol (2·26 g., 1·02 mol.) in light petroleum (b. p. 30—40°) (20 ml.) was added dropwise (10 min.) at 20° to isothiocyanatobisdiethylaminoborane (3·20 g., 1 mol.). An exothermal reaction occurred and a yellow liquid separated at the bottom of the flask. An infrared spectrum of the supernatant liquor showed absence of –NCS absorption at 2083 cm.$^{-1}$. Solvent was removed at 20°/15 mm., to leave a liquid (5·47 g., 100%) of di-n-butoxydiethylaminoborane and diethylammonium thiocyanate. These were separated by addition of light petroleum (b. p. 30—40°) (50 ml.), transferred to a separating funnel, and removal of the heavy diethylammonium salt. From the solution of the borane, solvent was removed at 20°/15 mm., and the residue (3·44 g., 100%) was distilled to give di-n-butoxydiethylaminoborane (3·03 g., 88·3%), b. p. 60°/0·5 mm., n_D^{21} 1·4232 (Found: B, 4·8. Calc. for $C_{12}H_{28}BNO_2$: B, 4·72%). A mixture of benzene and alcohol was added to the yellow liquid (1·97 g., 99%) and the contents were cooled to −40°. Crystallisation was not effected. Solvent was removed at 20°/15 mm., and the crude diethylammonium thiocyanate was distilled to give *diethylammonium thiocyanate* (1·23 g., 61·8%), b. p. 128—134°/0·005 mm., n_D^{20} 1·5136 (Found: N, 21·3; NCS, 43·9. $C_5H_{12}N_2S$ requires N, 21·2; NCS, 43·9%). An infrared spectrum of this compound was recorded on a liquid film in the region 5000—400 cm.$^{-1}$, and the following values (cm.$^{-1}$) for the vibration [24] of the –NCS were found: ν_1 2079vs; $2\nu_2 b$ 935wb; ν_3 798m; $\nu_2 a$ 492w; and $\nu_2 b$ 472wb.

Interaction of Bisdi-isopropylaminoisocyanatoborane and n-Butyl Alcohol.—n-Butyl alcohol (2·32 g., 1 mol.) was added dropwise to bisdi-isopropylaminoisocyanatoborane (7·94 g., 1 mol.). A slightly exothermal reaction occurred. The mixture was refluxed for 45 min. and, after attaining room temperature, di-isopropylamine (2·89 g., 93·8%), b. p. 83°, n_D^{20} 1·3923 (authentic infrared spectrum) was removed at 20°/0·1 mm., and collected at −78°. The product was distilled to give *n-butoxydi-isopropylaminoisocyanatoborane* (4·76 g., 67%) (see Table 1), and an undistilled residue (2·1 g.).

Similarly, n-butyl alcohol (1·59 g., 2 mol.) was added to bisdi-isopropylaminoisocyanatoborane (2·71 g., 1 mol.). Di-isopropylamine (1·45 g., 68%) was removed at 20°/15 mm., and collected at −78°. The residue gave tri-n-butoxyborane [19a] (1·6 g., 66·6%), b. p. 77°/1·5 mm., n_D^{20} 1·4087 (Found: B, 4·8. Calc. for $C_{12}H_{27}BO_3$: B, 4·72%), and a solid (0·87 g.).

Interaction of Bisdi-isopropylaminoisocyanatoborane (1 *mol.*) *and Cyclohexanol* (1 *mol.*).—Cyclohexanol (2·29 g., 1 mol.) was added dropwise to bisdi-isopropylaminoisocyantoborane (5·80 g., 1 mol.). The mixture was refluxed for 45 min. and, after attaining room temperature, di-isopropylamine (2·12 g., 92·1%) (authentic infrared spectrum) was removed at 20°/0·2 mm., and collected at −78°. The remaining product gave *cyclohexoxydi-isopropylaminoisocyanatoborane* (3·15 g., 55·2%) (see Table 1), and a solid residue (2·4 g.).

Similarly, t-butyl alcohol (2·02 g., 1 mol.) and bisdi-isopropylaminoisocyanatoborane (6·9 g., 1 mol). gave *t-butoxydi-isopropylaminoisocyanatoborane* (3·27 g., 53%) (see Table 1), di-isopropylamine (2·45 g., 89%) (authentic infrared spectrum), and a solid residue (2·6 g.).

Interaction of Isocyanatobisdi-isopropylaminoborane (1 *mol.*) *and t-Butylamine.*—t-Butylamine (0·707 g., 1 mol.) was added dropwise (5 min.) to isocyanatobisdi-isopropylaminoborane (2·44 g., 1 mol.), and the mixture was refluxed for 2½ hr. Di-isopropylamine (0·96 g., 0·99 mol.) was removed at 20°/15 mm., and trapped at −78°. The liquid residue (2·0 g., 92·3%) was fractionally distilled to yield *isocyanatodi-isopropylamino-t-butylaminoborane* (1·5 g., 69%) (see Table 1) and a solid residue (0·42 g.). An infrared spectrum recorded on a liquid sample showed

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[22] W. Gerrard, M. F. Lappert, and C. A. Pearce, *Chem. and Ind.*, 1958, 292.

[23] J. H. Robson and J. Reinhart, *J. Amer. Chem. Soc.*, 1955, **77**, 2453.

[24] P. O. Kinell and B. Strandberg, *Acta Chem. Scand.*, 1959, **13**, 1607.

the following absorption bands (cm.$^{-1}$): 3425w (NH), 2963s (CH), 2933sh (CH), 2874m (CH), 2294vs (NCO), 1513sh (NCO), 1499vs (BN), 1471sh, 1447s (CH), 1412m, 1389s, 1377m (CH_3), 1362s, 1325vs, 1307sh, 1282w, 1242 and 1235s, doublet, 1215sh, 1186s, 1151s (CN), 1136s, 1079m, 1057vw, 1032vw, 1010s, 985vw, 963m, 931m, 857w, 810m, 792w, 643m, 613s (NCO), 601sh, 587m, and 521vwb.

Similarly, t-butylamine (1·61 g., 2 mol.) was added to the isocyanatoborane (2·80 g., 1 mol.) and the solution refluxed for 4 hr. Di-isopropylamine (2·04 g., 91·2%) was removed at 20°/0·03 mm., to leave a liquid residue (2·34 g. Calc. for $C_{10}H_{20}BN_3O$: 2·18 g.) of impure isocyanatobis-t-butylaminoborane with traces of di-isopropylamine. This was fractionally-distilled to afford *isocyanatobis-t-butylaminoborane* (1·31 g., 59·6%) (see Table 1) and an undistilled solid residue (0·8 g.). An infrared spectrum was recorded and the following absorption bands are assigned to the vibration of the –NCO function and the BN stretching mode: ν_{as}-NCO, 2288 cm.$^{-1}$, ν_s-NCO, 1504 cm.$^{-1}$; δ-NCO, 610 cm.$^{-1}$, and B–N, 1495 cm.$^{-1}$.

Interaction of Isothiocyanatobisdiethylaminoborane (1 mol.) and Diethylamine (2 mol.).—Diethylamine (1·56 g., 2 mol.) was added during 5 min. to liquid isothiocyanatobisdiethylaminoborane (2·28 g., 1 mol.). An exothermal reaction took place and a yellow liquid separated at the bottom of the flask. Addition of light petroleum (b. p. 30—40°) (25 ml.) and cooling to –40° failed to induce crystallisation. The supernatant liquor was therefore decanted, the yellow liquid extracted with light petroleum (2 × 20 ml.), and from the combined extracts solvent was removed at 20°/15 mm., to leave a liquid (2·23 g., 92·7%). This, on distillation, afforded trisdiethylaminoborane[25] (1·87 g., 77%), b. p. 53°/0·4 mm., n_D^{20} 1·4452 (Found: B, 4·8. Calc. for $C_{12}H_{30}BN_3$: B, 4·72%) (authentic infrared spectrum). The yellow liquid (1·35 g., 95·7%) was distilled to yield diethylammonium thiocyanate (1·06 g., 75·2%), b. p. 124°/0·005 mm., n_D^{20} 1·5135 (Found: N, 21·3; NCS, 43·6. Calc. for $C_5H_{12}N_2S$: N, 21·2; NCS, 43·9%).

Interaction of 2-*Isocyanato*-1,3,2-*benzodioxaborole and Di-n-butylamine.*—Di-n-butylamine (4·42 g., 2 mol.) was added dropwise (10 min.) to a solution of 2-isocyanato-1,3,2-benzodioxaborole (2·75 g., 1 mol.) in light petroleum (b. p. 40—60°) (25 ml.) at 20°. An exothermal reaction took place and a white crystalline solid separated. An infrared spectrum recorded on the supernatant liquor showed absence of –NCO absorption at 2278 cm.$^{-1}$. The mixture was refluxed for ½ hr.; the solid (2·33 g.) was filtered off, washed with light petroleum (2 × 10 ml.), and solvent was removed from the combined filtrate and washings at 20°/15 mm. The liquid residue (4·80 g.) was distilled to give 2-di-n-butylamino-1,3,2-benzodioxaborole[19d] (1·45 g.), b. p. 102°/0·003 mm., n_D^{20} 1·4972 (authentic infrared spectrum), and an undistilled liquid (3·30 g.). The solid (2·33 g.) was recrystallised (benzene) to give *di-n-butylamino-2-di-n-butylamino*-1,3,2-*benzodioxaborole* (2·30 g.), m. p. 173° (Found: C, 70·3; H, 11·1; N, 7·3; B, 2·9. $C_{22}H_{41}BN_2O_2$ requires C, 70·2; H, 11·0; N, 7·4; B, 2·8%). An infrared spectrum of this compound, recorded in the 5000—400 cm.$^{-1}$ region, showed the following absorption bands, (cm.$^{-1}$): 3077s, (2941s and 2881sh, liquid paraffin), 1866vw, 1754vw, 1613s, 1493vs, 1471vs, 1429sh, 1370m, 1323w, 1277sh, 1241vs, 1222vs, 1178vw, 1153m, 1117sh, 1104vs, 1074vsb, 1013m, 916sb, 872vw, 800m, 767sh, 741vs, 733vs, 703s, 556mb, and 434mb.

Similarly, 2-isocyanato-1,3,2-benzodioxaborole (5·70 g., 1 mol.) in light petroleum (b. p. 30—40°) (50 ml.) was added to a solution of di-n-butylamine (18·32 g., 4 mol.) in the same solvent (25 ml.) at 20°. The mixture was left for 18 hr., whereupon a crystalline solid separated. Solvent was removed at 20°/15 mm., to leave a residue (24·00 g., 100%), which on filtration yielded di-n-butylamino-2-di-n-butylamino-1,3,2-benzodioxaborole (5·02 g.), m. p. 172° (benzene). From the filtrate, excess of di-*n*-butylamine (10·13 g.) (authentic infrared spectrum) was removed at 30°/0·005 mm. Distillation of the remainder afforded 2-di-n-butylamino-1,3,2-benzodioxaborole[19d] (1·80 g.), b. p. 102°/0·003 mm., n_D^{20} 1·4972, and an undistillable residue (6·63 g.) which contained both boron and nitrogen; attempts to purify it failed.

Interaction of Isocyanatobisdi-isopropylaminoborane (1 mol.) and N-*Methylaniline (1 mol.).*—*N*-Methylaniline (1·14 g., 1 mol.) was added dropwise to isocyanatobisdi-isopropylaminoborane (2·7 g., 1 mol.). After refluxing (1 hr.), the mixture was brought to room temperature and di-isopropylamine (1·04 g., 99%) (authentic infrared spectrum) was removed at 20°/0·1 mm., and collected at –78°. The residue was distilled to afford *isocyanatodi-isopropylamino*(N-*methylanilino*)*borane* (2·33 g., 82·4%) (see Table 1).

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[25] D. W. Aubrey, M. F. Lappert, and H. Pyszora, *J.*, 1960, 5239.

Interaction of Isocyanatobisdi-isopropylaminoborane (1 *mol.*) *and NN′-Di-n-propylethylenediamine* (1 *mol.*).—*NN′*-Di-n-propylethylenediamine (2·5 g., 1 mol.) was added dropwise to isocyanoatobisdi-isopropylaminoborane (4·4 g., 1 mol.), and the mixture was refluxed for 1 hr. After attaining room temperature, di-isopropylamine (3·4 g., 94·4%) (authentic infrared spectrum) was removed at 20°/0·6 mm., and collected at −78°. The remaining liquid was fractionally distilled to yield 2-*isocyanato*-1,3,2-*diaza*-(NN′-*n-propyl*)*borolane* (1·7 g., 51·5%) (see Table 1) and a solid residue (1·2 g.).

Lack of Reaction between Isocyanatobisdi-isopropylaminoborane and Di-isopropylamine, and between 2-*Isocyanato*-1,3,2-*diaza*(NN′-*n-propyl*)*borolane and Di-isopropylamine.*—Neither isocyanatobisdi-isopropylaminoborane [upon refluxing in light petroleum (b. p. 60—80°) (25 ml.) for 11 hr.], nor 2-isocyanato-1,3,2-diaza(*NN′*-n-propyl)borolane (by refluxing in the absence of solvent for 2 hr.) reacted with di-isopropylamine. Quantitative amounts of unchanged materials were recovered.

Interaction of 2-*Isothiocyanato*-1,3,2-*benzodioxaborole, or* 2-*Isocyanato*-1,3,2-*benzodioxaborole, and Mercuric Oxide.*—Mercuric oxide (4·04 g., 1·1 mol.), previously dried (2 hr. at 120°), was added to a solution of 2-isothiocyanato-1,3,2-benzodioxaborole (3·0 g., 1 mol.) in benzene (30 ml.) at 20°. An exothermal reaction took place. After 30 min. at room temperature, an infrared spectrum was recorded on the supernatant liquor and there was no absorption in the 2000—2500 cm.$^{-1}$ region (*i.e.*, −NCS and −NCO absent). The mercuric thiocyanate and mercuric oxide were filtered off, washed with benzene (2 × 10 ml.), and solvent was removed from the filtrate and washings at 20°/15 mm., to leave a solid (2·1 g., 98%). This, after recrystallisation (hexane–benzene), yielded pure 2-oxobis(1,3,2-benzodioxaborole) (1·51 g., 70·4%), m. p. 156—158° (cf.[19d, 26] b. p. 160°/0·1 mm.) (authentic infrared spectrum) [27] (Found: B, 8·4. Calc. for $C_{12}H_8B_2O_5$: B, 8·5%).

Similarly, from reaction of mercuric oxide (1·35 g., 0·5 mol.) and 2-isocyanato-1,3,2-benzodioxaborole (2·0 g., 1 mol.) in benzene (10 ml.) at 20°, 2-oxobis(1,3,2-benzodioxaborole) (1·38 g., 87·4%), m. p. 156—158° (Found: B, 8·4%) was obtained.

Lack of Reaction between 2-*Isocyanato*-1,3,2-*benzodioxaborole and either Mercuric Sulphide or Phosphorus Pentasulphide.*—Neither mercuric sulphide nor phosphorus pentasulphide reacted with 2-isocyanato-1,3,2-benzodioxaborole in benzene solution, when they were refluxed for 6 and 12 hr., respectively. The starting materials were recovered.

Lack of Reaction between Di-n-butylamino-2-di-n-butylamino-1,3,2-*benzodioxaborole and Alcohols.*—n-Butyl alcohol (0·94 g., 1 mol.) in chloroform (10 ml.) was added dropwise (10 min.) to a solution of the " complex " (4·80 g., 1 mol.) in the same solvent (30 ml.). The mixture was refluxed for 1½ hr. and then allowed to attain room temperature. Solvent was removed at 20°/15 mm., and to the solid residue (4·76 g., 99%) light petroleum (b. p. 60—80°) (50 ml.) was added. The mixture, after refluxing for ½ hr. and then cooling to 20°, was filtered. The unchanged " complex " (4·74 g., 98·8%), m. p. 166—167° was recovered.

Similarly, when the " complex " was refluxed (½ hr.) with a large excess of methanol, the reagents were recovered quantitatively.

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[26] H. Schäfer and O. Braun, *Naturwiss.*, 1953, **39**, 280.

[27] J. A. Blau, W. Gerrard, M. F. Lappert, B. A. Mountfield, and H. Pyszora, *J.*, 1960, 380.