325. *Pseudohalides. Part I. Preparation, Characterisation, and Reactions of Iso- and Isothio-cyanatoborazoles.*

By M. F. LAPPERT and H. PYSZORA.

Interaction of chloroborazoles and metal salts of cyanic or thiocyanic acid afforded iso- or isothio-cyanatoborazoles. These compounds have been characterised and the behaviour of selected examples with amines and alcohols has been investigated. Both substitution and addition were observed. From the latter, a new class of boron compound, ureidoborazoles, was obtained. The results are discussed and compared with those on pseudohalides of elements other than boron.

THIS paper begins a series dealing with covalent pseudohalides. Initially, we have studied the isocyanates and isothiocyanates of boron and have communicated our preliminary findings.[1] We now describe in more detail the preparation, characterisation, and selected reactions of borazole derivatives, and hope shortly to report mononuclear 3- and 4-co-ordinate boron compounds and the infrared spectra of all these derivatives.

The compounds in Tables 1—3 were prepared from corresponding chlorides by metathesis of trichloroborazole with silver, sodium, potassium, or lead cyanate or thiocyanate in solvents such as benzene, methylene dichloride, pentane, and acetonitrile. Only with the silver salts were non-polar solvents effective, and sodium or potassium salts reacted very slowly if at all, either when no solvent, or when pentane or benzene, was used.

By adjusting the ratio of chloroborazole to metal salt, mono- and di-pseudohalogenoborazoles, $Cl(OCN)_2B_3N_3R_3$ and $Cl_2(OCN)B_3N_3R_3$, were also synthesised (see Table 3). Such unsymmetrical borazoles are rare.[2] The evidence for their structure is primarily spectroscopic; their infrared spectra showed absorption bands additional to those to be expected from a mixture of symmetrical products.

Reactions of isocyanatoborazoles with primary or secondary aliphatic amines led to rapid and quantitative formation of addition products, the ureidoborazoles of Table 4. Aromatic primary amines reacted much more slowly and there was no reaction between *N*-methylaniline and *B*-tri-isocyanatoborazole after 4 hr. in refluxing benzene. Thus, an

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

[2] Cf. Lappert and Majumdar, *Proc. Chem. Soc.*, 1961. 425.

TABLE 1.

Symmetrical isocyanatoborazoles.

R in (OCN·BNR)$_3$	B. p./mm.	M. p.	Yield %	Found (%)					Formula	Required (%)				
				C	H	N	B	*M*		C	H	N	B	*M*
H *	—	166°	92·5	17·3	1·6	41·0	15·9	¶	$C_3H_3B_3N_6O_3$	17·7	1·5	41·3	15·9	204
Me	112°/0·03	85—86	90	29·0	3·5	34·3	13·2	240	$C_6H_9B_3N_6O_3$	29·3	3·7	34·2	13·2	246
Et	102°/0·01	36	87	37·6	5·3	29·1	11·1	280	$C_9H_{15}B_3N_6O_3$	37·5	5·2	29·0	11·2	289
Pr^n ‡	118°/0·003	—	85·5	43·4	6·3	25·8	9·78	338	$C_{12}H_{21}B_3N_6O_3$	43·7	6·4	25·5	9·8	330
Bu^n	140°/0·02	30	75	48·8	7·0	22·4	8·7	367	$C_{15}H_{27}B_3N_6O_3$	48·48	7·3	22·6	8·7	372
Bu^s †	134°/0·01	—	88·5	49·3	6·9	22·3	8·7	380	$C_{15}H_{27}B_3N_6O_3$	48·48	7·3	22·6	8·7	372
Ph	—	151—152	95·5	58·6	3·6	19·5	7·59	422	$C_{21}H_{15}B_3N_6O_3$	58·37	3·5	19·45	7·5	432

* Melts sharply at 166°, and then on further heating solidifies again. † n_D^{20} 1·4901, d_4^{20} 1·060. ¶ Not determined, owing to low solubility in benzene. ‡ n_D^{20} 1·4499, d_4^{20} 1·094.

TABLE 2.

Symmetrical isothiocyanatoborazoles.

R in (SCN·BNR)$_3$	M. p.	Yield (%)	Found (%)						Formula	Required (%)					
			C	H	N	B	S	*M*		C	H	N	B	S	*M*
H *	154°	99	14·0	1·2	33·4	12·5	38·0	259	$C_3H_3B_3N_6S_3$	14·3	1·2	33·4	12·9	38·2	252
Me	202—204	92	24·0	3·1	28·6	11·1	32·4	‡	$C_6H_9B_3N_6S_3$	24·5	3·1	28·6	11·1	32·7	294
Et †	87—88	82·5	32·2	4·5	25·0	9·67	28·2	328	$C_9H_{15}B_3N_6S_3$	32·15	4·5	25·0	9·7	28·6	336
Pr^n	121	86·5	38·8	5·2	21·8	8·57	25·6	372	$C_{12}H_{21}B_3N_6S_3$	38·1	5·6	22·2	8·6	25·4	378
Bu^s	54	91·5	42·6	6·4	19·8	7·7	22·8	432	$C_{15}H_{27}B_3N_6S_3$	42·9	6·5	20·0	7·7	22·9	420
Ph	212—214	85·6	53·0	2·9	17·6	6·8	19·8	473	$C_{21}H_{15}B_3N_6S_3$	52·5	3·15	17·52	6·8	20·0	480

* Ref. 3, m. p. 147—150° (decomp.); 176°, softening range 15°. † B. p. 130°/0·01 mm. ‡ Not determined.

TABLE 3.

Unsymmetrical isocyanatoborazoles.

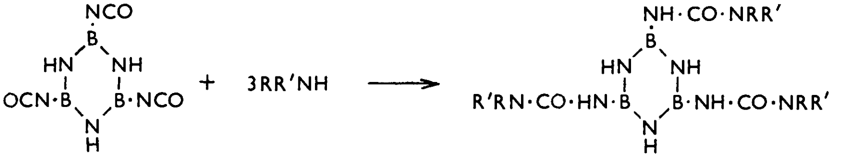
Compound	M. p. or b. p./mm.	Found (%)					Formula	Required (%)				
		C	H	B	N	Cl		C	H	B	N	Cl
$(OCN)_2ClB_3N_3Me_3$	95°	25·0	3·6	13·6	28·95	15·1	$C_5H_9B_3ClN_5O_2$	25·1	3·8	13·6	29·3	14·8
$(OCN)Cl_2B_3N_3Me_3$	56—57°	20·5	3·7	13·3	24·1	29·1	$C_4H_9B_3Cl_2N_4O$	20·65	3·9	14·0	24·1	30·5
$(OCN)_2ClB_3N_3Et_3$	98°/0·025	34·6	5·4	11·4	24·5	12·5	$C_8H_{15}B_3ClN_5O_2$	34·2	5·38	11·5	24·9	12·6

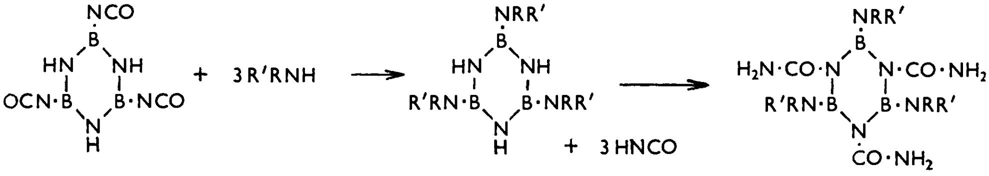
TABLE 4.

Symmetrical ureidoborazoles.

Compound	M. p.	Yield (%)	Found (%)				Formula	Required (%)			
			C	H	N	B		C	H	N	B
(EtNH·CO·NH·B·NH)$_3$	128—130°	94	31·2	7·0	37·1	9·6	$C_9H_{24}B_3N_9O_3$	31·8	7·1	37·2	9·6
(Bu^{n}NH·CO·NH·B·NH)$_3$	120—121	85	41·8	8·5	29·7	7·66	$C_{15}H_{36}B_3N_9O_3$	42·6	8·5	29·8	7·7
(Bu^{s}NH·CO·NH·B·NH)$_3$	133—136	92	41·9	8·6	29·3	7·65	$C_{15}H_{36}B_3N_9O_3$	42·6	8·5	29·8	7·7
(Et$_2$N·CO·NH·B·NH)$_3$	74—76	98	41·8	8·6	28·9	7·6	$C_{15}H_{36}B_3N_9O_3$	42·6	8·5	29·8	7·7
(Bu$^n_2$N·CO·NH·B·NH)$_3$	88—90	95	54·6	9·7	21·2	5·5	$C_{27}H_{60}B_3N_9O_3$	54·9	9·7	21·3	5·5
(Bu^{n}NH·CO·NH·B·NMe)$_3$	78—81	90	46·5	9·1	27·2	6·85	$C_{18}H_{42}B_3N_9O_3$	46·5	9·3	27·1	7·0
(Pr$^i_2$N·CO·NH·B·NH)$_3$	124—129	100	49·8	9·5	24·7	6·34	$C_{21}H_{48}B_3N_9O_3$	49·8	9·5	24·9	6·4

order of reactivity similar to that found for organic isocyanates[4] and silicon isocyanates[5] is found with borazole compounds: $R{\cdot}NH_2 > R_2NH \gg Ar{\cdot}NH_2 \gg Ar{\cdot}RNH$. In most of the reactions with aliphatic amines *B*-tri-isocyanatoborazole was used and this can, in principle, lead to two products, depending on whether reaction route (1) or (2) is followed.

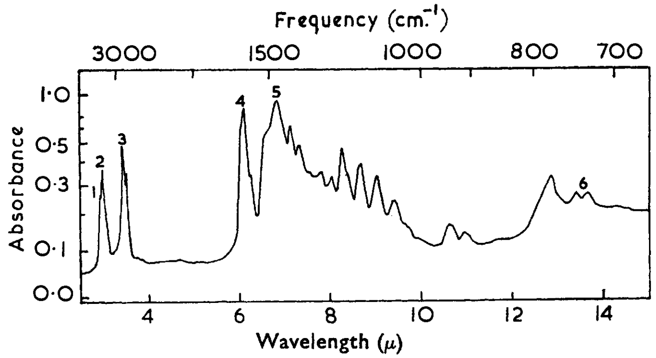

(1)


(2)

Route (2), though less likely, was feasible since addition of organic isocyanates to the NH group in *B*-substituted borazoles has been reported.[6] That the reaction proceeded according to scheme (1) has been established spectroscopically (infrared) and by alcoholysis of the final products, which gave borates, ammonia, and disubstituted ureas.

Reactions between aliphatic ($NH_2{\cdot}[CH_2]_6{\cdot}NH_2$) or aromatic [$p$-$C_6H_4(NH_2)_2$] diamines with isocyanatoborazoles led to polymeric, highly cross-linked poly(ureidoborazoles), insoluble in organic solvents and boiling water.

The infrared spectra of ureidoborazoles and polymers therefrom showed absorption bands as follows: 3485—3436m (νNH, borazole); 3356—3215m (νNH, urea); 1658—1639s (C=O, amide I); 1462—1449vs (B–N ring); and 744—721m cm.$^{-1}$ (borazole ring deformation). A typical spectrum is reproduced in the Figure.



Infrared spectrum of trisdibutylureidoborazole in methylene dichloride solution (to 12 μ) and liquid paraffin mull (above 12 μ).

Assignments: (1) 3436 (NH borazole); (2) 3356 (NH urea); (3) 2941, 2857 (CH); (4) 1639 (C=O); (5) 1462 (BN ring); (6) 744, 730 cm.$^{-1}$ (borazole ring deformation).

In contrast to the addition observed with amines, isocyanatoborazoles afforded substitution products when treated with alcohols, this being accompanied by ring cleavage. It is very unlikely that initial addition (and subsequent elimination) takes place; thus,

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[3] Green, Sowerby, and Wihksne, *Chem. and Ind.*, 1960, 1306; Brennan, Dahl, and Schaeffer, *J. Amer. Chem. Soc.*, 1960, **82**, 6248.

[4] Saunders and Slocombe, *Chem. Rev.*, 1948, **43**, 203; Arnold, Nelson, and Verbane, *ibid.*, 1957, **57**, 47.

[5] Goubeau and Heubach, *Chem. Ber.*, 1960, **93**, 1117.

[6] Korshak, Zamyatina, and Bekasova, *Vysokomol. Soedineniya*, 1960, **2**, 1287; McCloskey, " Research on Inorganic Polymer Systems," WADD-TR 60—911, 1961, Parts 1, 3, and 4.

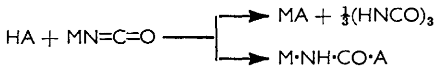
even when a deficiency of alcohol was used, no alkoxyborazole or alkoxycarbonylaminoborazole was isolated. Similar observations, relating to ring cleavage, have been made about alcoholysis of chloroborazoles.[7] Using an excess of alcohol led to quantitative yields of borate and urea. Mr. M. Rieber has shown that even with branched alkyl groups [$Pr^i_3N_3B_3(NCO)_3$ + ROH, where R = Bu^t or C_6H_{11}] urethane formation was not achieved.

Alcohol–isothiocyanatoborazole interaction led again to substitution, yielding borates and substituted ammonium thiocyanates. The latter were differentiated from the isomeric thioureas by their infrared spectra. The reaction conditions were very mild (½ hour's refluxing in light petroleum of b. p. 80—100°) and heating is usually necessary to convert an ammonium thiocyanate into a thiourea.

Reactions of amines with isothiocyanatoborazoles were very much slower than with the corresponding isocyanatoborazoles and the products were not thioureidoborazoles but were aminoborazoles, ammonium thiocyanates, and some triaminoboranes, the last resulting from some ring cleavage.[11]

There was no reaction between isocyanatoborazole and ethanethiol after 5½ hours' refluxing.

Discussion.—The term pseudohalide was introduced[9] for groups such as cyanide, thiocyanate, azidothiocarbonate, selenocyanate, tellurocyanate, cyanate, azide, and their structural isomers in order to emphasize the physical and chemical resemblances between them and halogens. In addition they are linear, electronegative (*i.e.*, exert a $-I$ effect), and capable of participating in intramolecular π-bonding with a neighbouring electron-deficient centre (*i.e.*, may exert a $+M$ effect). However, as they are unsaturated, the possibility of addition is present and such reactions are likely to be nucleophilic. From the point of view of covalent derivatives, the interest in the chemistry, for a given class, is primarily that of decision whether or not there is a prevalence of substitution (pseudohalide behaviour), or addition. This may be illustrated for isocyanates and active-hydrogen compounds, HA, by scheme (3):

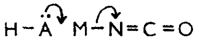


$$\mathrm{HA + MN{=}C{=}O} \longrightarrow \begin{cases} \mathrm{MA} + \tfrac{1}{3}\mathrm{(HNCO)_3} \\ \mathrm{M{\cdot}NH{\cdot}CO{\cdot}A} \end{cases} \qquad (3)$$

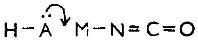
Under S_N1 conditions, when M–N heterolysis is rate-determining, substitution will of necessity prevail, but under bimolecular conditions product control is determined by competition between the two electrophilic sites, the central carbon atom (see 4) and M.

$$\mathrm{M{\cdot}N{:}C{:}O} + \mathrm{\ddot{A}H} \rightleftharpoons \mathrm{M{\cdot}\bar{N}{\cdot}CO{\cdot}AH^+} \qquad (4)$$

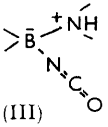
The nature of the transition state in the latter case depends on M but it may, in general, require initial formation of a complex (as in II), or it may involve synchronous bond-making and bond-breaking (as in I). The former is the relevant mechanism in the case



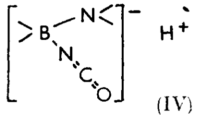
(I)



(II)



(III)



(IV)

of a trigonal boron pseudohalide, and the complex with a primary or secondary amine as the reagent, may be pictured as in (III) or (IV). The competition between the boron atom and the carbon atom for the attacking nucleophile is affected also by the nature of the attacking reagent. This is so, because substitution at trigonal boron depends on both basicity and steric factors,[10] whereas attack at digonal carbon is likely to be controlled

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[7] Bradley, Ryschkewitsch, and Sisler, *J. Amer. Chem. Soc.*, 1959, **81**, 2635.

[8] Aubrey, Lappert, and Majumdar, *J.*, 1962, 4088.

[9] Birckenbach and Kellermann, *Ber.*, 1925, **58**, 786, 2377; Browne, Hoel, Smith, and Swezey, *J. Amer. Chem. Soc.*, 1923, **45**, 2541.

[10] Aubrey and Lappert, *Proc. Chem. Soc.*, 1960, 148.

largely by a combination of basicity and polarizability of the nucleophile[11] [a simple illustration is the relative reactivity, generally $H_2O > NH_3 > R{\cdot}NH_2 > R_2NH$ for trigonal boron compounds,[10] but $NH_3 > H_2O$ for carbonyl-carbon (in *p*-nitrophenyl acetate[12])].

In order to have effective competition for the substitution, steric hindrance both in the substrate and in the reagent are helpful. From the electronic aspect, either M should not have available vacant low-energy orbitals, or the reorganisation energy for change in hybridisation should be high. This analysis appears to explain satisfactorily the results, not only for the boron pseudohalides, but also for derivatives of other elements (for a summary of isocyanate and isothiocyanate behaviour, see Table 5). The lower additive reactivity of isothiocyanates than of isocyanates is attributed to the low polarity of the thiocarbonyl compared with the carbonyl bond.

TABLE 5.

Behaviour of isocyanates and isothiocyanates with alcohols and amines.

Class	With ROH	With $R{\cdot}NH_2$	Note
$>$B·NCO	$>$B·OR	$>$B·NHR	*a*
$\geq\overset{-}{\mathrm{B}}$·NCO	$>$B·OR	$>$B·NH·CO·NHR	*a*
$(R'{\cdot}N{\cdot}B{\cdot}NCO)_3$	$>$B·OR	$(R'N{\cdot}B{\cdot}NH{\cdot}CO{\cdot}NHR)_3$	*b*
$(R'N{\cdot}B{\cdot}NCS)_3$	$>$B·OR	$(R'N{\cdot}B{\cdot}NHR)_3$	*b*
$\geq$C·NCO	$\geq C{\cdot}NH{\cdot}CO_2R$	$\geq$C·NH·CO·NHR	*c*
$\geq$C·NCS	$\geq$C·NH·CS·OR	$\geq$C·NH·CS·NHR	*d*
$\geq$Si·NCO	$\geq$Si·OR	$\geq$Si·NH·CO·NHR	*e*, *f*
$\geq$Ge·NCO	$\geq$Ge·OR	—	*g*
$>$PO·NCO	$>PO{\cdot}NH{\cdot}CO_2R$	$>$PO·NH·CO·NHR	*h*, *i*
$>$PO·NCS	$>$PO·NH·CS·OR	$>$PO·NH·CS·NHR	*j*
$[PN(NCS)_2]_{3,4}$	Addition	Addition	*k*
$S^{VI}{\cdot}NCO$	$S^{VI}{\cdot}NH{\cdot}CO_2R$	$S^{VI}{\cdot}NH{\cdot}CO{\cdot}NHR$	*l*

Notes: (*a*) Lappert, Pyszora, and Rieber, unpublished work. (*b*) This work. (*c*) Arnold, Nelson, and Verbanc, *Chem. Rev.*, 1957, **57**, 47. (*d*) Kharasch, in "Organic Sulfur Compounds," Pergamon Press, London, 1961, Vol. I, p. 326—339. (*e*) Goubeau and Paulin, *Chem. Ber.*, 1960, **93**, 1111. (*f*) Goubeau and Heubach, *ibid.*, p. 1117. (*g*) Anderson, *J. Amer. Chem. Soc.*, 1949, **71**, 1799. (*h*) Kirsanov and Marenets, *Zhur. obshchei Khim.*, 1959, **29**, 2256. (*i*) Shevchenko, Shtepanek, and Kirsanov, *ibid.*, 1961, **31**, 3062. (*j*) Elmore and Ogle, *J.*, 1959, 2286. (*k*) Tesi, Otto, Sherif, and Audrieth, *J. Amer. Chem. Soc.*, 1958, **80**, 5894. (*l*) Appel and Gerber, *Chem. Ber.*, 1958, **91**, 1200. Only the latest references are given.

EXPERIMENTAL

General Procedures.—n-Butyl alcohol was dried by distillation from metallic calcium. Amines were dried by heating them under reflux with, and fractionating them from, barium oxide. Analyses, except of 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.[13] Molecular weights were determined cryoscopically in benzene. Chloroborazoles used as starting materials were prepared by known methods;[14] chloro-n-propyl- and s-butylborazole were mentioned only in a Lecture.[15]

Trichlorotri-n-propylborazole (69·5% yield) had b. p. 110°/0·01 mm., m. p. 79—80° (Found: C, 34·8; H, 6·8; N, 13·6; B, 10·45; Cl, 34·0%; *M*, 318. $C_9H_{21}B_3Cl_3N_3$ requires C, 34·85; H, 6·8; N, 13·6; B, 10·5; Cl, 34·3%; *M*, 310); the *s-butyl analogue* had b. p. 102°/0·005 mm., n_D^{20} 1·4841, d_4^{20} 1·090, $[R_L]_D$ 92·3 (calc., 93·0) (Found: C, 41·0; H, 7·3; N, 12·0; B, 9·1; Cl, 30·2%; *M*, 354. $C_{12}H_{27}B_3Cl_3N_3$ requires C, 40·9; H, 7·7; N, 11·9; B, 9·2; Cl, 30·2%; *M*, 352).

Infrared spectra were recorded on Perkin-Elmer model 21 (2—15 μ) and Infracord K14

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[11] Edwards and Pearson, *J. Amer. Chem. Soc.*, 1962, **84**, 16.

[12] Jencks and Carriulo, *J. Amer. Chem. Soc.*, 1960, **82**, 1778.

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

[14] Turner and Warne, *Chem. and Ind.*, 1958, 526; Hohnstedt and Haworth, *J. Amer. Chem. Soc.*, 1960, **82**, 89; Brown and Laubengayer, *ibid.*, 1955, **77**, 3699.

[15] Turner, Chem. Soc. Anniversary Meeting, Liverpool, April 12—14th, 1961.

(15—25 μ) instruments equipped, respectively, with sodium chloride and potassium bromide optics.

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

Preparation of Borazole Pseudohalides.—The general procedure is illustrated by the preparation of *B*-tri-isocyanato-*N*-tri-n-propylborazole. Solid silver cyanate (20·9 g., 4·5 mol.), dried for 2 hr. at 130°, was added in a dry-box to a solution of *B*-trichloro-*N*-tri-n-propylborazole (9·65 g., 1 mol.) in dry benzene (25 ml.). An exothermal reaction took place. The mixture was refluxed for 1 hr. and allowed to attain room temperature, and solid silver chloride and excess of silver cyanate were filtered off and washed with dry benzene (2 × 15 ml.). Solvent was removed first at 20°/15 mm. and then at 20°/0·1 mm., and the liquid residue (10·11 g., 98·5%) was fractionally distilled, to give B-*tri-isocyanato*-N-*tri-n-propylborazole* (8·76 g., 85·5%) (see Table 1) and an undistilled residue (1·03 g.).

Preparation of Ureidoborazoles.—The general procedure is illustrated by one example. Di-n-butylamine (6·04 g., 3·05 mol.) in dry benzene (20 ml.) was added dropwise (15 min.) at room temperature to *B*-tri-isocyanatoborazole (3·124 g., 1 mol.) in the same solvent (40 ml.). The reaction was exothermic. The mixture was refluxed for 0·5 hr. and solvent was removed first at 20°/15 mm. and finally at 80°/0·002 mm., leaving a solid residue (9·065 g., 100%) of the *ureidoborazole*. This recrystallised from isopentane–methylene dichloride (8·61 g., 95%) (see Table 4).

Reaction of a Ureidoborazole with n-Butyl Alcohol.—The alcohol (3·445 g., 9 mol.) in methylene dichloride (20 ml.) was added dropwise in 5 min. to a solution of the tri-(*N'N'*-dibutylureido)-borazole (3·05 g., 1 mol.) in the same solvent (20 ml.). The mixture was boiled for 1 hr. and the ammonia evolved (2·85 mol.) was absorbed into 0·1N-sulphuric acid. Solvent was removed at 20°/15 mm., to leave a liquid (6·23 g., 100%), which was spectroscopically (infrared) identified as a mixture of borate and dibutylurea. Separation was not achieved by solvent-extraction and the mixture was fractionally distilled, to yield tri-n-butyl borate (3·34 g., 91%), b. p. 106°/9 mm., n_D^{20} 1·4086 (authentic infrared spectrum), and *NN*-di-n-butylurea (2·47 g., 92·5%), b. p. 130—135°/2 mm. (cf.[16] b. p. 118—119°/2—3 mm.) (Found: N, 16·3. Calc. for $C_9H_{20}N_2O$: N, 16·3%) [$\nu(NH_2)$ 3342, 3210; $\nu(C{=}O)$ (amide I) 1654; (amide II) 1605 cm.$^{-1}$].

Interaction of N-*Triethyl*-B-*tri-isothiocyanatoborazole and n-Butyl Alcohol.*—The alcohol (4·27 g., 9 mol.) in light petroleum (b. p. 80—100°; 10 ml.) was added dropwise in 10 min. at 20° to the borazole (2·15 g., 1 mol.) in the same solvent (20 ml.). After ~10 min., an exothermal reaction set in, accompanied by formation of a white solid and a heavy yellow liquid. An infrared spectrum of the supernatant liquor showed absence of NCS absorption at ~2080 cm.$^{-1}$. The mixture was refluxed for ½ hr., the solid (2·01 g., 100%) filtered off and washed with light petroleum (2 × 10 ml.), and the solvent removed from the filtrate at 20°/15 mm. The liquid residue of tri-n-butyl borate (4·42 g., 100%) was distilled (b. p. 114°/15 mm.), to give the pure product (4·25 g., 96·3%), n_D^{20} 1·4082 (Found: B, 4·7. Calc. for $C_{12}H_{27}BO_3$: B, 4·7%).

A mixture of benzene and alcohol was added to the solid product, giving an oily suspension. On addition of ether and cooling (−40°), the crystalline (needles) *ethylammonium thiocyanate* (1·89 g., 94·5%), m. p. 53—54° (Found: C, 34·6; H, 7·8; N, 27·0; NCS, 55·0. $C_3H_8N_2S$ requires C, 34·6; H, 7·7; N, 26·9; NCS, 55·7%), separated, was filtered off, washed with light petroleum (2 × 10 ml.), and freed from solvent under a vacuum. It had thiocyanate bands[17] as follows: ν_1 2043vs, $2\nu_2$a 965s, $2\nu_2$b 935w, ν_3 755m, ν_2a 484m, and ν_2b 468m cm.$^{-1}$.

Reaction of B-*Tri-isothiocyanato*-N-*tri-n-propylborazole with n-Propylamine.*—The amine (2·59 g., 6 mol.) in light petroleum (b. p. 80—100°; 10 ml.) was added dropwise in 10 min. at 20° to the borazole (2·75 g., 1 mol.) in the same solvent (25 ml.). The mixture was refluxed for 15 min., and on cooling to 20° a heavy, yellow oil separated. Solvent was removed at 20°/15 mm., and then at 20°/2 mm., to leave a liquid residue (4·98 g.) in two layers of which the lower was insoluble in light petroleum (3 × 25 ml.); from the soluble extract, solvent was removed at 20°/15 mm., to afford a liquid residue (2·60 g.), which yielded *tris-n-propylaminoborane* (0·3 g.), b. p. 40—42°/1 mm., $n_D^{20.5}$ 1·4391 (Found: C, 58·0; H, 13·3; N, 23·0; B, 5·8. $C_9H_{24}BN_3$ requires C, 58·4; H, 13·1; N, 22·7; B, 5·8%), $\nu_{max.}$ (liquid) 3477m (NH), 2967sh, 2950s, 2874s, 2747vw, 1511sh (B–N), 1497vs (B–N), 1468sh, 1445sh, 1377m, 1337w, 1297sh, 1280s, 1261sh, 1225s, 1139s (C–N), 1074vb, 1015w, 988vw, 878w, 852w, 800wb, 769vw, 755wv,

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[16] Davis and Blanchard, *J. Amer. Chem. Soc.*, 1929, **51**, 1790.

[17] Kinell and Strandberg, *Acta Chem. Scand.*, 1959, **13**, 1607.

645sh, 624m cm.$^{-1}$ (cf. ref. 18), and B-*isothiocyanato-propyl*-B′B″-*bis-n-propylamino*-NN′N″-*tri-n-borazole* (1·4 g.), b. p. 136—141°/0·005 mm., n_D^{21} 1·4866 (Found: C, 51·4; H, 9·6; N, 22·1; B, 8·6%; *M*, 362. $C_{16}H_{37}B_3N_6S$ requires C, 50·8; H, 9·9; N, 22·25; B, 8·6%; *M*, 378), $\nu_{max.}$ (liquid) 3472m, 2967sh, 2941s, 2890s, 2114vs (NCS), 1493vs (B–N), 1466sh, 1445sh, 1408s, 1377s, 1355s, 1295s, 1233s, 1170s, 1143m, 1110wb (C–N), 1015w, 971vw, 889m, 851wb, 810vw (ω_{10}), 750w, 714s (ω_6), and 709s (ω_7) cm.$^{-1}$ (cf. ref. 19). There was a distillation residue (0·85 g.).

From the petroleum-insoluble fraction traces of solvent were removed at 20°/15 mm., whereafter the oil solidified. Recrystallisation from ether–alcohol gave *n-propylammonium thiocyanate* (1·90 g.), m. p. 66—68° (Found: C, 40·6; H, 8·5; N, 23·5; NCS, 49·1. $C_4H_{10}N_2S$ requires C, 40·6; H, 8·5; N, 23·7; NCS, 49·2%), $\nu_{max.}$ (NCS) (cf. ref. 17), ν_1 2066vs, $2\nu_2$a 980m, $2\nu_2$b 935w, ν_3 754s, ν_2a 489m, and ν_2b 467m cm.$^{-1}$.

Lack of Reaction between B-*Isocyanato*-N-*propylborazole and Ethanethiol.*—The thiol (7·35 g., 9 mol.) and the borazole (4·335 g., 1 mol.) were refluxed (−78°, cold-finger) for 5½ hr., whereafter the thiol (7·32 g., 99%) was removed at 20°/15 mm. and the residue was identified spectroscopically as unchanged isocyanatoborazole (4·33 g., 100%).

Interaction of B-*Tri-isocyanato*-N-*tri-n-propylborazole and n-Butyl Alcohol.*—The alcohol (4·046 g., 9 mol.) in light petroleum (b. p. 40—60°; 20 ml.) was added dropwise in 5 min. at 20° to the borazole (2·02 g., 1 mol.) in the same solvent (25 ml.). An exothermal reaction ensued and a white solid was formed. The mixture was refluxed for ½ hr., cooled to 20°, and filtered. The solid was washed with light petroleum (2 × 15 ml.) and then freed from solvent under a vacuum. Solvent was removed from the filtrate at 20°/15 mm., leaving tri-n-butyl borate (3·89 g., 93%), b. p. 78°/1·5 mm., n_D^{20} 1·4081 (Found: B, 4·7%). The solid *N*-n-propylurea (1·79 g., 96·4%), when recrystallised from ethyl alcohol–ether, had m. p. 106° (lit.,[20] 107°) (Found: N, 27·4. Calc. for $C_4H_{10}N_2O$: N, 27·4%), $\nu(NH_2)$ 3440, 3230, $\nu(C{=}O)$ (amide I), 1670 (amide II) 1600 cm.$^{-1}$ (cf. ref. 20).

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[18] Aubrey, Lappert, and Pyszora, *J.*, 1960, 5239.
[19] Aubrey, Lappert, and Pyszora, *J.*, 1961, 1931.
[20] Boivin and Boivin, *Canad. J. Chem.*, 1951, **29**, 478; 1954, **32**, 561.