Boron–Sulphur Compounds. Part I. Thioboration of Isocyanates

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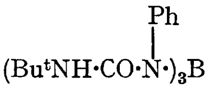
The reaction of substituted phenyl isocyanates with bis(ethylthio)phenylborane gives bis(*N*-aryl-*N*-ethylthiocarbonylamino)phenylboranes. In this reaction the relative migratory aptitude of groups attached to boron is SR > Ph.

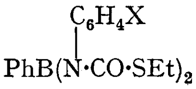
THE reaction of tris(t-butylamino)borane and phenyl isocyanate gives the corresponding ureidoborane (I).[1]


$(Bu^tNH\cdot CO\cdot \overset{Ph}{N}\cdot)_3B$

(I)

$PhB(SEt)_2$

(II)


$PhB(\overset{C_6H_4X}{N}\cdot CO\cdot SEt)_2$

(III)

Analogous reactions of corresponding thioboranes, however, have received little attention.[2-4] Dichlorophenylborane reacted with bis(ethylthio)lead to give bis(ethylthio)phenylborane (II). This added quantitatively to the N=C bond of aromatic isocyanates $XC_6H_4\cdot NCO$ (X = 2-Me, 4-MeO, 2-Cl, 4-Cl, and 3,4-Cl_2) to form the corresponding bis-(*N*-aryl-*N*-ethylthiocarbonylamino)phenylborane (III).

The i.r. absorption of the products showed that the insertion of the carbon–nitrogen group of the isocyanate had taken place between boron and sulphur. Bands in the region 1100—1000 cm.$^{-1}$ which are assigned to boron–sulphur bonds[4] were not observed in the i.r. spectra of the products. The relative migratory aptitude of the groups attached to boron in bis(ethylthio)phenylborane is accordingly EtS > Ph. The reaction probably takes place *via* a four-centre transition state involving the atoms BSCN.

EXPERIMENTAL

General Procedures and Starting Materials.—Diethyl ether and light petroleum (b.p. 40—60°) were stored over sodium wire and distilled before use. I.r. spectra were recorded as Nujol mulls using a Perkin-Elmer 227 (4000—400 cm.$^{-1}$), spectrophotometer. The usual precautions were taken with air-sensitive starting materials and products. As the experimental technique was the same in all cases only one example is described. All analytical and physical data, for the bis-(*N*-aryl-*N*-ethylthiocarbonylamino)phenylboranes, are given in the Table.

Preparation of Bis(ethylthio)phenylborane.—Dichlorophenylborane (15 g., 1 mol.) and bisethylthiolead (32 g., 1 mol.) were heated under reflux for 2 hr. in light petroleum (50 ml.). The insoluble lead chloride (25·8 g., 97%) was filtered off and washed with more solvent. The filtrate was freed from solvent under reduced pressure; distillation of the residue afforded bis(ethylthio)phenylborane[4] (13·2 g., 66%), b.p. 80–81°/0·2 mm., n_D^{29} 1·5689 (Found: C, 57·6; H, 6·8; B, 5·0. Calc. for $C_{10}H_{13}BS_2$: C, 57·2; H, 7·1; B, 5·1%).

Bis-(*N*-aryl-*N*-ethylthiocarbonylamino)phenylboranes [$PhB(NR\cdot CO\cdot SEt)_2$]

Compound R	Yield (%)	M.p.	Found * (%) C	Found * (%) H	Requires (%) C	Requires (%) H	Carbonyl stretching frequency cm.$^{-1}$
2-MeC_6H_4 ...	90	157—159°	65·7	5·7	65·6	6·1	1710
4-$MeOC_6H_4$	82	115—117	60·9	5·4	61·4	5·7	1718
2-ClC_6H_4 ...	86	172—176	55·5	4·3	55·7	4·5	1725
4-ClC_6H_4 ...	85	221—223	55·3	4·6	55·7	4·5	1730
2,4-$Cl_2C_6H_3$	78	205—208	48·6	3·4	49·0	3·6	1722

* C and H analyses in thioboranes, by standard microanalytical techniques, are often unsatisfactory due to incomplete combustion.[5]

Preparation of Bis-(N-o-*chlorophenyl*-N-*ethylthiocarbonylamino)phenylborane.*—A solution of bis(ethlythio)phenylborane (1·5 g., 1 mol.) and *o*-chlorophenyl isocyanate (2·3 g., 2·1 mol.) in ether (25 ml.) kept at room temperture for 2 days gave crystalline *bis-*(N-o-*chlorophenyl-*N-*ethylthiocarbonylamino)phenylborane* (3·2 g., 86%), m.p. 172—176° (Found: C, 55·5; H, 4·3. $C_{24}H_{21}BCl_2N_2O_2S_2$ requires C, 55·7; H, 4·5%).

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