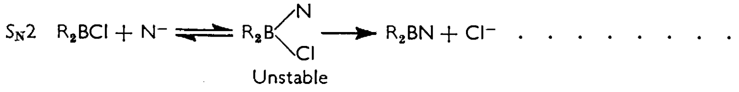
229. *Mechanism of Substitution at a Boron Atom. Part I.*

By J. C. Lockhart.

Possible mechanisms of nucleophilic substitution at boron are discussed. Some proof is offered of a mechanism involving an intermediate complex similar to that in aromatic chemistry. Relative reactivities in such reactions are qualitatively evaluated.

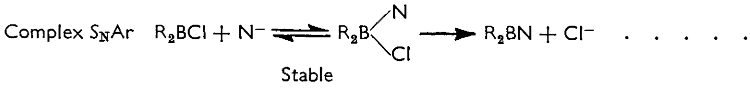
Various mechanisms of substitution at boron can be considered in the light of current knowledge of nucleophilic substitution at carbon. Reaction paths based on the S_N1 and S_N2 mechanisms of aliphatic chemistry[1] and the intermediate-complex mechanism[2] of aromatic chemistry, modified to the stereochemistry and electronic requirements of boron, are set out in equations 1—3. The S_N1 type will almost certainly be found in reactions

$$S_N1 \qquad R_2BCl \rightleftharpoons R_2B^+ + Cl^- \qquad R_2B^+ + N^- \longrightarrow R_2BN \qquad (1)$$



$$S_N2 \quad R_2BCl + N^- \rightleftharpoons R_2B\begin{smallmatrix} N \\ Cl \end{smallmatrix} \longrightarrow R_2BN + Cl^- \qquad (2)$$

Unstable



$$\text{Complex } S_NAr \quad R_2BCl + N^- \rightleftharpoons R_2B\begin{smallmatrix} N \\ Cl \end{smallmatrix} \longrightarrow R_2BN + Cl^- \qquad (3)$$

Stable

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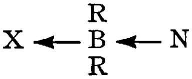
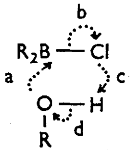
[1] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, p. 306.

[2] Gould, " Mechanism and Structure in Organic Chemistry," Henry Holt and Co., New York, 1959, p. 452.

of diphenylboron halides which ionise to the orange diphenylboronium cation in nitrobenzene containing aluminium chloride:[3] $Ph_2BCl \rightleftharpoons Ph_2B^+ + Cl^-$. The diphenylcarbonium ion is not formed to the same extent under these conditions.[3]

The stereochemistry of an S_N2 or synchronous bond-making and -breaking reaction would be different from that in aliphatic carbon. Both attacking and leaving group could be tetrahedrally disposed around the boron and therefore adjacent. A transition state  $X \leftarrow \overset{R}{\underset{R}{B}} \leftarrow N$ in which all four groups attached to boron lie in a plane would be the nearest equivalent of the carbon S_N2 transition state, but the strain in such a model would be considerable. Neutral boron having the *sp*^{2}-planar configuration, the analogy is perhaps closer to the carbon of aromatic systems. Each is capable of sustaining a negative charge on change to an *sp*^{3}-tetrahedral configuration, negatively charged boron being stable, and the aromatic ring in the other systems sharing the charge. The type of intermediate complex mechanism shown by Bunnett and Randall[4] for nucleophilic aromatic substitution may thus be expected.



(I)

Another viewpoint, that of Gerrard,[5] called the four-centre approach or broadside elimination, can be reconciled with mechanism (1), (2), or (3). This approach consists of two bond-forming steps (I; a and c) and two bond-breaking steps b and d. If b occurs first we have an ionisation S_N1. If a, b, c, and d, or a and b, are synchronous we have an S_N2 reaction. If a occurs first, we have a complex as required in mechanism (3).

$$C_5H_5N + BCl_3 \longrightarrow C_5H_5N,BCl_3 \text{ (ref. 6)} \quad (4)$$

$$Et_2O + BCl_3 \longrightarrow Et_2O,BCl_3 \text{ (ref. 7)} \longrightarrow EtCl + EtO{\cdot}BCl_2 \quad (5)$$

$$Bu_2S + BCl_3 \longrightarrow Bu_2S,BCl_3 \text{ (ref. 8)} \quad (6)$$

Consider reactions (4—6). In each, stable 1 : 1 complexes can be isolated, somewhat reminiscent of the Menschutkin reaction. Only reaction (5) is known to proceed further. Under more vigorous conditions chlorine is expelled and replaced by ethoxyl. When the attacking molecule has a reactive hydrogen, amines form a complex (reaction 7), substitution occurs instantly with alcohols or phenols (8), and there is no detectable reaction with thiols (9) at room temperature:

$$C_5H_{10}NH + PhBCl_2 \longrightarrow C_5H_{10}NH,PhBCl_2 \quad (7)$$

$$BuOH + PhBCl_2 \longrightarrow PhBCl{\cdot}OBu + HCl \text{ (ref. 9)} \quad (8)$$

$$PhSH + PhBCl_2 \quad \text{No reaction} \quad (9)$$

When, however, a mole of triethylamine is used in reaction (7) to remove hydrogen chloride the substitution product is formed:[10]

$$C_5H_{10}NH + PhBCl_2 + Et_3N \longrightarrow C_5H_{10}N{\cdot}BPhCl + Et_3NHCl$$

Triethylamine was instantly precipitated as its hydrochloride when added in equimolar quantity to the mixture of phenylboron dichloride and thiophenol (reaction 9), and the reaction of butoxyphenylboron chloride with thiophenol was similar. Presumably the amine first released the thiophenoxide ion, which is known to be a very powerful nucleophile; the other product was probably the simple thio-replacement product, but attempted isolation caused pyrolysis and tri(phenylthio)boron was obtained in low yield.

Intermediate complexes of great stability are certainly formed in reactions of amines,

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[3] Davidson and French, *J.*, 1958, 114.
[4] Bunnett and Randall, *J. Amer. Chem. Soc.*, 1958, **80**, 6020.
[5] Gerrard, *Chem. and Ind.*, 1951, 463.
[6] Gerrard and Lappert, *J.*, 1951, 1020.
[7] Wiberg, *Z. anorg. Chem.*, 1931, **195**, 288.
[8] Lappert, *J.*, 1953, 2784.
[9] Daudegaonker, Gerrard, and Lappert, *J.*, 1957, 2872.
[10] Niedenzu and Dawson, *J. Amer. Chem. Soc.*, 1960, **82**, 4223.

and a second mole of amine (the same or a tertiary one) is required to break the complex by abstracting a proton and removing the leaving halide group. The much greater stability of this intermediate complex than of that in aromatic substitution is demonstrable. An equimolar mixture of piperidine and chlorodinitrobenzene gives half a mole of substitution product and half a mole of amine hydrochloride. An equimolar mixture of piperidine and phenylboron dichloride forms a 1 : 1 complex. In terms of an energy profile the boron complex is at a pronounced minimum, whereas the aromatic one is at a slight dip. The boron reaction could be considered simply as two successive bimolecular reactions. Complexes of alcohols and phenols with phenylboron dichloride were not isolable (because reaction was complete and very fast), but their formation cannot be excluded in view of the stable complex obtained with ethers (reaction 5) and the alcohol–boron trifluoride complexes.[11] No complex of phenylboron dichloride with thiophenol was observed in this work, but boron trichloride formed a complex at low temperatures which disproportionated just above room temperature to give tri(phenylthio)boron. Alkanethiols were found by Goubeau and Wittmeier [12] to co-ordinate to boron trichloride and boron tribromide before splitting off hydrogen halide to form the thioboron compound.

By analogy with the work of Ingold, Hughes, *et al.* on nucleophilic substitution at carbon, it was hoped to investigate the problems kinetically. Many reactions of boron compounds were screened in the hope of finding one suitable. Most of the reactions considered, such as that of alcohol with a halogenoboron compound, were very fast in dilute solution in inert solvent at room temperatures. An experimental technique such as that of Prince [13] will be necessary for a full enquiry. Reaction of a very weak nucleophile such as 2,4-dinitronaphthylamine with boron halides is visibly slow and future work will be concerned with this. The thiol reactions previously mentioned are extremely slow and the boron compounds are often unstable under the conditions required.

An approach other than the formal kinetic one was sought. The technique of competitive reactions was useful within certain limitations. The mechanisms of competing reactions cannot be said to be identical without the backing of kinetic evidence but qualitative comparisons of similar reactions can be made.

Competitive reactions between various nucleophiles and compounds in the phenylboron dihalide and butoxyphenylboron halide series have led us to the general conclusion that both the entering and the leaving group are kinetically important, and an S_N1 mechanism is excluded.

Groups are displaced in a certain order. With water, butanol, phenol, or *o*-nitrophenol as nucleophile the order is Br > Cl > F; Cl > NCS > *o*-nitroanilino > *o*-nitrophenoxy. With piperidine as nucleophile, butoxyphenylboron bromide formed the initial complex more readily than did the chloride. Goubeau and Wittmeier's work [12] indicates that boron tribromide reacts more rapidly than boron trichloride with alkanethiols. Relative nucleophilicities are butanol, water, phenol, or *p*-toluidine > *o*-nitrophenol > *o*-nitroaniline > dinitronaphthylamine > thiophenol. The reactivities of boron halides to complex-formation and displacement are in the expected order,[14] and the nucleophilicities are similar to those found for aliphatic substitution.

Some competitive reactions were run between mixtures of two phenylboron dihalides and butanol. It was of interest to consider whether such phenylboron halide mixtures rearrange to give two different halogen substituents on the boron, as can happen with mixtures of boron trihalides,[15] and infrared evidence for such equilibria was sought:

$$\mathrm{PhBF_2 + PhBCl_2 \rightleftharpoons PhBFCl} \quad \ldots\ldots\ldots\ldots \quad (10)$$

$$\mathrm{PhBCl_2 + PhBBr_2 \rightleftharpoons PhBClBr} \quad \ldots\ldots\ldots\ldots \quad (11)$$

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[11] Topchiev, Zavgorodriu, and Paushkin, " Boron Trifluoride and its Compounds as Catalysts in Organic Chemistry," Pergamon Press Ltd., London, 1959, p. 67.

[12] Goubeau and Wittmeier, *Z. anorg. Chem.*, 1952, **270**, 16.

[13] Prince, *Trans. Faraday Soc.*, 1958, **54**, 838.

[14] Cotton and Leto, *J. Chem. Phys.*, 1959, **30**, 993.

Spectra of these mixtures in carbon tetrachloride solution were measured. The spectrum of each mixture was not quite superposable on the two component spectra. Two new weak bands in the boron–halogen asymmetric stretching frequency region were observed, displaced in the direction expected for the mixed halides.[15] The equilibrium could not be quantitatively investigated on the instrument used but appears to lie very much to the left in carbon tetrachloride. The new bands were at about 910—900 (B–Cl) and 855—865 (B–Br) wave numbers in the bromide–chloride mixture, and at 935—945 (B–Cl) and 1310—1320 (B–F) wave numbers in the fluoride–chloride mixture. Assignments are complicated because of the possibility of isotopic splitting introduced by boron, chlorine, and bromine bonds. No attempt was made to isolate the mixed halides.

EXPERIMENTAL

Phenylboron halides, etc., were prepared by standard routes. M. p.s were taken in sealed capillary tubes, and operations with moisture-sensitive compounds conducted in a dry-box.

Piperidine–Phenylboron Dichloride Adduct.—Phenylboron dichloride (4 ml.) and piperidine (3 ml.) were mixed at −80° in toluene (30 ml.). The mixture was allowed to warm to room temperature and filtered. White needles, stable to atmospheric moisture, were obtained and recrystallised from ether without decomposition. The m. p. was indistinct (165—175°). Many features of the infrared spectrum (Nujol mull) resemble those noted for the piperidine–boron trichloride complex isolated by Greenwood.[16] The yield of *piperidine-phenylboron dichloride complex* was 7 g. (96%) (Found: C, 53·7; H, 6·6; N, 6·0; Cl, 27·4; B, 4·2. $C_{11}H_{16}BCl_2N$ requires C, 54·5; H, 6·6; N, 5·8; Cl, 29·1; B, 4·4%).

The adduct (3·7 g.) was made into a slurry in benzene, and triethylamine (2·1 ml.) was added. Heat was evolved. The mixture was refluxed for 3 hr. and filtered. Triethylammonium chloride (2·2 g; m. p. 252—254°) was recovered. Evaporation of the benzene left a liquid which was distilled to give phenylpiperidinoboron chloride [10] (112 g., 38%), b. p. 78—80°/0·02 mm., n_D^{25} 1·5468 (Found: B, 5·0. Calc. for $C_{11}H_{15}BClN$: B, 5·2%). This solidified, as noted by Niedenzu and Dawson.[10] A more viscous, higher-boiling fraction (0·6 g.) was perhaps a dimer or polymer.

N-*Methylaniline–Phenylboron Dichloride Adduct.*—Phenylboron dichloride (4 ml.) and *N*-methylaniline (3 ml.), reacting as did piperidine, gave a *complex* (7·5 g., 100%), that was sensitive to moisture and readily decomposed on being heated. A sample recrystallised from ether and hexane was analysed (Found: C, 55·6; H, 5·4; B, 4·0; Cl, 25·7; N, 5·3. $C_{13}H_{14}BCl_2N$ requires C, 58·7; H, 5·3; B, 4·0; Cl, 26·7; N, 5·3%).

N-Methylanilinophenylboron chloride was prepared from the adduct by reaction with triethylamine as above. It had b. p. 100—103°/0·1 mm. and solidified but was not analysed.

Reaction of Phenylboron Dichloride and Thiophenol.—Thiophenol (3 ml.) was added dropwise at 0° to phenylboron dichloride (4 ml.). There was no apparent reaction and the infrared spectrum of the mixture showed no alteration from that of the two component spectra superimposed. Addition of triethylamine (4·1 ml.) caused a violent reaction. Triethylammonium chloride was filtered off (m. p. 250°). Infrared spectrum showed that the residue had no S–H group left. Distillation under reduced pressure caused decomposition.

Reaction of Thiophenol and Boron Trichloride.—To boron trichloride (10 g.) at −80° was added thiophenol (8·2 ml.); a yellow solid was precipitated. This was allowed to warm slowly to room temperature. A little hydrogen chloride (5%) was evolved. The mixture evolved hydrogen chloride rapidly at 35°. When the pressure was reduced to 0·1 mm. liquefaction occurred. On warming, a sublimate of *tri(phenylthio)boron*, m. p. 57°, was isolated (Found C, 65·05; H, 4·3; B, 3·3; S, 27·9. $C_{18}H_{15}BS_3$ requires C, 63·9; H, 4·5; B, 3·2; S, 28·4%).

Reaction of Sodium Thiophenoxide and Butoxyphenylboron Chloride.—Butoxyphenylboron halide (3·2 ml.) was added to sodium thiophenoxide (2·2 g.) in ethylene glycol dimethyl ether (10 ml.). Reaction was very exothermic. After being stirred for 48 hr. the mixture was filtered and evaporated. The liquid residue was apparently pyrolysed on distillation at reduced pressure, thiophenol and butanol being formed. A small quantity of fairly pure tri(phenylthio)boron, m. p. 57°, sublimed.

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[15] Long and Dollimore, *J.*, 1954, 4487.

[16] Greenwood and Wade, *J.*, 1960, 1130.

Butoxyphenylboron Isothiocyanate.—A solution of potassium thiocyanate (3·2 g.) in ethylene glycol dimethyl ether was kept at 0° during addition of butoxyphenylboron chloride (6 g.). The mixture was stirred for 1 hr., then filtered and evaporated, and the residue distilled at 98—108°/0·5 mm. (yield, 6 g., 90%). Redistillation afforded pure *butoxyphenylboron isothiocyanate,* b. p. 94—100°/0·6 mm. (Found: C, 60·25; H, 6·5; B, 4·9. $C_{11}H_{14}BNOS$ requires C, 60·3; H, 6·4; B, 4·9%). The infrared spectrum showed absorption about 2080 cm.$^{-1}$ (very broad), indicative of its isothiocyanate character.[17] A characteristic broad band also occurs at about 845 and another sharp band at about 1095 cm.$^{-1}$.

Competitive Reactions.—These were generally done in carbon tetrachloride solution at room temperature. The reagents (generally 0·25M) were dissolved in carbon tetrachloride, and the substrate was quickly added. For soluble products infrared or visible absorption was used to analyse the mixtures. Insoluble amine complexes were analysed for halogen content. The spectroscopic method of analysis was accurate to only 5%. However, within this margin relative rates could be estimated on the assumption of mechanistic identity of the competing reactions. These relative rates are given in the Table.

	Br	Cl	F	NCS
BuOH, PhOH, or H_2O	95	1		
BuOH		95	1	
,,		95		1
Piperidine	95	1		

Infrared Absorption.—Spectra of many of the compounds have been recorded from 3500 to 400 wave numbers and will be discussed in a future publication. Spectra reported or used in this publication were recorded on a Perkin-Elmer Infracord instrument.

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