# Reaction of Diborane with Benzoxazole and Its Sulphur and Selenium Analogues. A Novel Rearrangement to Benzoxazaboroles, Benzothiazaboroles, and Benzoselenazaboroles

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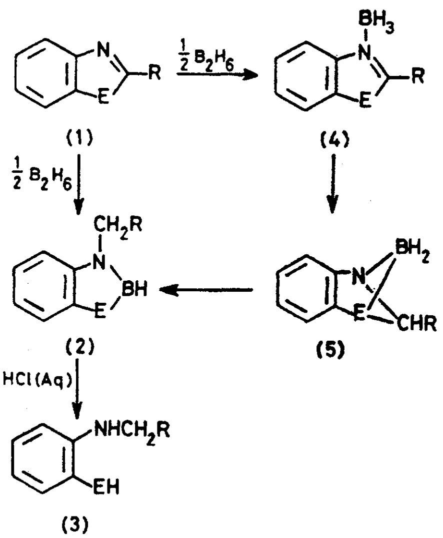
*Summary* Reaction of $B_2H_6$ with the benzo-fused heteroaromatic compounds (**1a**—**d**) produces the boroles (**2a**—**d**) *via* a rearrangement in which $BH_3$ adduct formation is the first step.

When monoglyme (1,2-dimethoxyethane) solutions of the heteroaromatic compounds (**1a**—**d**) are treated with $B_2H_6$ at 25 °C followed by aqueous hydrochloric acid, the ring opened products (**3a**—**d**) are obtained in high yield.

We have found that the stable boron intermediates in these systems are the boroles (**2a**—**d**). All the reactions are complete within 48 h and only 0·5 mol of $B_2H_6$ per mol of heterocycle is required for complete conversion. The boroles (**2b**—**d**) can be recovered in good purity after solvent evaporation; (**2a**) is sufficiently volatile to be isolated by trap-to-trap vacuum fractionation. Proof of structure rests upon spectroscopic characterization, boron analysis, stoicheiometry, and identity of the hydrolysis products (**3a**—**d**). In a typical case, benzoxazole (**1a**) consumed 0·97 equiv. $BH_3$ to give the benzoxazaborole (**2a**) in virtually quantitative yield. $^1$H N.m.r. spectroscopy in $CDCl_3$ showed $\delta$7·2—7·8 (4H, m, ArH) and 3·72 (3H, s, Me). Satisfactory boron analysis was obtained. Yields in the other cases are in the range 90—100%.

In the case of benzoxazole (**1a**) and benzothiazole (**1b**) we have followed the course of the reaction by $^{11}$B n.m.r. spectroscopy. In both studies we have detected two precursors to (**2a**—**b**). Immediately after mixing the only signal is a quartet [(**1a**): $\delta$ −20·3 p.p.m., *J* 81 Hz; (**1b**): $\delta$ −16·8 p.p.m., *J* 61 Hz]† which is replaced by a broad triplet [(**1a**): $\delta$ −16·0 p.p.m., *J* 125 Hz; (**1b**): $\delta$ −16·1 p.p.m., *J* 118 Hz] within a few minutes at the n.m.r. probe temperature. With (**1a**) the doublet signal of the product ($\delta$ 28·1 p.p.m., *J* 168 Hz) replaces the triplet within 15 min; the reaction is slower with (**1b**) requiring 48 h before conversion into the product (doublet: $\delta$ 22·3 p.p.m., *J* 156 Hz) is complete.



**a**, E = O, R = H; **b**, E = S, R = H; **c**, E = S, R = Me; **d**, E=Se, R= Me.

We assign the quartet to the borane adducts (**4a**—**b**). The identity of the intermediates associated with the triplet is less certain, but because the chemical shift implies four-co-ordinate boron, we propose the boron bridged compounds (**5a**—**b**) formed by possible intramolecular hydroboration of the CN double bond. The final rearrangement to (**2a**—**b**) could then occur *via* a hydride transfer from boron to carbon.

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† Chemical shift for $Et_2OBF_3$ is 0·0 p.p.m.; downfield shifts are positive.