Thioboranes: their Use in the Synthesis of Organoboron Heterocycles

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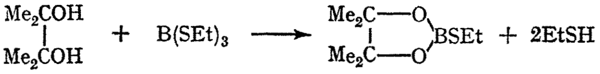
Summary Organoboron heterocycles have been synthesised, in high yields and at room temperature, by the interaction of a thioborane and a difunctional organic compound such as a diol.

THIOBORANES, for example bisethylthiophenylborane $\mathrm{PhB(SEt)_2}$, are highly reactive compounds and react readily with unsaturated substrates (*e.g.* isocyanates)[1] and protic species (*e.g.* alcohols).[2] Thioboranes are very useful as synthetic intermediates in the preparation of a wide range of organoboron heterocycles in high yields and at ambient temperatures.

Thioboranes react readily with difunctional organic compounds such as substituted diols, amino-alcohols, and thiol-alcohols to give high yields of the corresponding organoboron heterocycle:



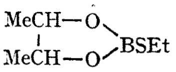
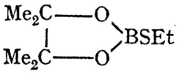
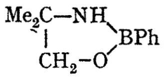
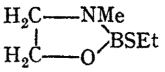
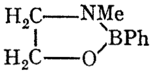
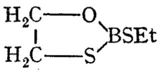
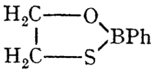
Some idea of the scope of this reaction can be seen from the examples of heterocycles, prepared by this method, quoted in the Table. All the compounds have been characterised by analysis and i.r. and n.m.r. spectra.

A typical reaction sequence is as follows. Butane-2,3-diol (2·79 g.) was added slowly to triethylthioborane (6·0 g.) at 0°. The mixture was allowed to stand at room temperature for 1 hr. Ethanethiol (3·9 g., 100%) was removed and the residue (4·5 g.) afforded on distillation 1-ethylthio-4,5-dimethyl-1,3,2-dioxaborolane.

The ease of the reaction can be attributed to (a) the volatility of the thiol formed in the reaction and (b) the high affinity of boron for oxygen.

I thank the S. R. C. for financial support.

TABLE

Reactants				Product	Yield (%)
MeCHOH MeCHOH	+	$\mathrm{B(SEt)_3}$	$\longrightarrow$		70
$\mathrm{Me_2COH}$ $\mathrm{Me_2COH}$	+	$\mathrm{B(SEt)_3}$	$\longrightarrow$		65
$\mathrm{Me_2CNH_2}$ $\mathrm{CH_2OH}$	+	$\mathrm{PhB(SEt)_2}$	$\longrightarrow$		60
$\mathrm{CH_2NHMe}$ $\mathrm{CH_2OH}$	+	$\mathrm{B(SEt)_3}$	$\longrightarrow$		83
$\mathrm{CH_2{\cdot}NHMe}$ $\mathrm{CH_2OH}$	+	$\mathrm{PhB(SEt)_2}$	$\longrightarrow$		86
$\mathrm{CH_2OH}$ $\mathrm{CH_2SH}$	+	$\mathrm{B(SEt)_3}$	$\longrightarrow$		85
$\mathrm{CH_2OH}$ $\mathrm{CH_2SH}$	+	$\mathrm{PhB(SEt)_2}$	$\longrightarrow$		77

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[1] R. H. Cragg, *J. Chem. Soc.* (*A*), 1968, 2962.

[2] M. F. Hawthorne, *J. Amer. Chem. Soc.*, 1961, **83**, 1345.