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THIOBORANES: THEIR USE IN THE SYNTHESIS OF THIOACETALS

R. H. Cragg and J. P. N. Husband

The Chemical Laboratory, University of Kent at Canterbury

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Thioacetals are widely used in synthetic organic chemistry but their preparation involves the use of mercaptans which necessitates careful handling techniques.

We wish to report a convenient synthesis of thioacetals, in good yields and at ambient temperatures, which entails the reaction of an aldehyde with a thioborane (readily obtained by the interaction of a boron halide and lead mercaptide) in an inert solvent such as petroleum spirit. With the exception of benzaldehyde no reactions of aldehydes and thioboranes have been reported. (1)

The types of reaction studied are shown in equations 1 and 2.

$$2(RS)_3B + 3 - C\begin{matrix}H\\ \diagup\\ \diagdown\\ O\end{matrix} \longrightarrow B_2O_3 + 3 - C\begin{matrix}H\\ \diagup\\ \diagdown\\ SR\end{matrix}\!\!SR \qquad (1)$$

$$PhB(SR)_2 + - C\begin{matrix}H\\ \diagup\\ \diagdown\\ O\end{matrix} \longrightarrow \tfrac{1}{3}(PhBO)_3 + - C\begin{matrix}H\\ \diagup\\ \diagdown\\ SR\end{matrix}\!\!SR \qquad (2)$$

The boron-containing products being insoluble in petroleum spirit are easily removed by filtration.

Some idea of the scope of the reaction can be seen by the examples given in the table. All compounds have been characterised by analysis and ^1H n.m.r.

TABLE

Reactants	Products	Yield %
$C_6F_5CHO + Ph(SEt)_2$	$C_6F_5CH(SEt)_2 + (PhBO)_3$	45
$CH_3CH=CHCHO + PhB(SEt)_2$	$CH_3CH=CHCH(SEt)_2 + (PhBO)_3$	67
$C_6H_5CH=CHCHO + (EtS)_3B$	$C_6H_5CH=CHCH(SEt)_2 + B_2O_3$	59
p $CH_3OC_6H_4CHO + (MeS)_3B$	p $CH_3OC_6H_4CH(SMe)_2 + B_2O_3$	56
p $CH_3OC_6H_4CHO + (EtS)_3B$	p $CH_3OC_6H_4CH(SEt)_2 + B_2O_3$	78

A typical reaction was as follows:- Crotonaldehyde (0.74 g.) and bis(ethylthio)phenylborane (2.2 g.) were mixed in petroleum spirit (b.p. 60-68°, 25 ml.). An exothermic reaction took place and the mixture was refluxed for four hours to bring the reaction to completion. On cooling phenylboroxine (1.1 g., 98%) was filtered off and after the removal of the solvent the residue afforded on distillation crotonaldehyde diethylthioacetal (1.24 g., 67%).

The ease of the reaction can be attributed to the higher affinity of boron for oxygen than sulphur.

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Reference

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