Thioboranes: Their Use in the Synthesis of Unsymmetrical Disulphides

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Summary Unsymmetrical disulphides have been prepared in high yields and under mild conditions from the reaction of a thioborane with a sulphenic ester.

THIOBORANES, obtained by the interaction of boron halides with lead hydrogen sulphide, are useful intermediates in the preparation of organosulphur compounds. Thioacetals are formed by the reactions of ketones[1] and aldehydes[2] with thioboranes. Recently the preparation of unsymmetrial disulphides, by the reaction of thiophthalimides with thiols, has been reported.[3,4]

We now report a convenient synthesis of unsymmetrical disulphides by the reaction of a thioborane with a sulphenic ester.

A series of thioboranes was heated under reflux with PhSOMe, in petroleum (b.p. 40—60°), for up to 2 h [reaction (1)]. The solvent and $(MeO)_3B$, produced in the reaction, were pumped off leaving the unsymmetrical disulphide, (Table).

$$(RS)_3B + PhSOMe \rightarrow (MeO)_3B + RSSPh \qquad (1)$$

The presence of $(MeO)_3B$ was shown by carrying out one of the reactions in the absence of solvent. Lower yields of the unsymmetrical disulphides were obtained when substituted thioboranes were used, because of the separation of the reaction products. The driving force of the reaction can be attributed to the higher affinity of boron for oxygen than sulphur.

Reactions of thioboranes with PhSOMe

Reactants	Products	Yield of disulphide (%)
$PhSOMe + (MeS)_3B$	$MeSSPh + (MeO)_3B$	82
$PhSOMe + (EtS)_3B$	$EtSSPh + (MeO)_3B$	81
$PhSOMe + Ph_2BSEt$	$EtSSPh + Ph_2BOMe$	55
$PhSOMe + PhB(SPr^n)_2$	$Pr^nSSPh + PhB(OMe)_2$	47
$PhSOMe + (Bu^tS)_3B$	$Bu^tSSPh + (MeO)_3B$	75

The unsymmetrical disulphides were characterised by ^1H n.m.r. and mass spectrometry. An interesting feature of the fragmentation pattern of MeSSPh is a re-arrangement process leading to the formation of a species assigned as the tropylium ion.

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