## Preliminary communication

## Aminoboranes: their use in the synthesis of sulphenamides

R.H. CRAGG, J.P.N. HUSBAND, G.C.H. JONES and A.F. WESTON The Chemical Laboratory, University of Kent at Canterbury, Kent (Great Britain) (Received October 2nd, 1972)

### SUMMARY

Sulphenamides have been prepared in good yields and under mild conditions from the reaction of an aminoborane with a sulphenic ester.

Aminoboranes are readily obtained from the reaction of a haloborane and an amine and due to the ease of their synthesis they are useful synthetic intermediates, We wish to describe the use of aminoboranes in a convenient synthesis of sulphenamides.

A series of aminoboranes were heated under reflux with PhSOMe, in petroleum ether (b.p.  $60-80^{\circ}$ ), for up to 6 hours (Eqn. 1). The solvent and methyl borate, produced in the reaction were pumped off leaving the sulphenamide. The presence of methyl borate was demonstrated by carrying out one of the reactions in the absence of solvent.

$$(\mathbf{R}_2\mathbf{N})_3\mathbf{B} + 3PhSOMe \rightarrow (MeO)_3\mathbf{B} + 3R_2NSPh$$
(1)

# TABLE 1

#### **REACTIONS OF AMINOBORANES WITH PhSOMe**

Reactants	Products	Yield of sulphenamide (%)
PhSOMe + Ph <sub>2</sub> BNMe <sub>2</sub>	PhSNMe + Ph <sub>2</sub> BOMe	50 <sup>a</sup>
PhSOMe + B(NEt <sub>2</sub> ) <sub>3</sub>	PhSNEt <sub>2</sub> + B(OMe) <sub>3</sub>	55
PhSOMe + PhB(NEt <sub>2</sub> ) <sub>2</sub>	PhSNEt <sub>2</sub> + PhB(OMe) <sub>2</sub>	74
PhSOMe + PhB(N-n-Bu <sub>2</sub> ) <sub>2</sub>	PhSN-n-Bu <sub>2</sub> + PhB(OMe) <sub>2</sub>	69
PhSOMe + B(NH-t-Bu) <sub>3</sub>	PhSN-n-Bu <sub>2</sub> + PhB(OMe) <sub>3</sub>	74

<sup>a</sup> A mixture was obtained and the % yield estimated by <sup>1</sup>H NMR.

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Higher yields of sulphenamides were obtained when substituted aminoboranes were used, because although careful distillation of the products was necessary in order to obtain the sulphenamide in a pure form, milder reaction conditions could be used (reflux in petroleum ether b.p.  $40-60^{\circ}$ , for up to 4 h.)

Some idea of the scope of this reaction is demonstrated by the examples in Table 1.

The driving force of the reaction can be attributed to the higher affinity of boron for oxygen than for nitrogen and, where applicable, the high volatility of methyl borate. The sulphenamides were characterised by <sup>1</sup>H NMR analysis and mass spectrometry.

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