A New Method for the Preparation of Mixed Organoboranes

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Summary A new rational synthesis of mixed alkyl boranes is described which involves the preparation of dialkylthioboranes followed by their reduction in the presence of an olefin.

WITH the rapid development of useful synthetic reactions starting from organoboranes there is a general need for methods for the preparation of organoboranes bearing two or more different primary groups. Brown has attacked this problem by the reduction of alkoxydialkylboranes or alkyldialkoxyboranes in the presence of olefins.[1,2]

TABLE

Olefin A	Olefin B	Product	Yield (%)
Oct-1-ene	Hept-1-ene	n-Heptyldi-n-octylborane	93
Hept-1-ene	Oct-1-ene	Di-n-heptyl-n-octylborane	96
Cyclohexene	Oct-1-ene	Dicyclohexyl-n-octylborane	70
Cyclopentene	Cyclohexene	—	0
Thioborane	Olefin		
Bu^n_2BSBu	Oct-1-ene	Di-n-butyl-n-octylborane	84
Bu^n_2BSBu	Cyclopentene	Di-n-butylcyclopentylborane	83
Bu^n_2BSBu	Cyclohexene	Di-n-butylcyclohexylborane	65

We have been greatly impressed by the thioalkyl group as a leaving group from boron[3] and also by the ease of preparation of thioboranes [*i.e.* reaction scheme (1)]. This

$$3\text{ Olefin A} + [BH_3] \rightarrow R^A_3B \rightarrow R^A_2BSR^1 \xrightarrow[\text{LiAlH}_4]{\text{Olefin B}} R^A_2BR^B \quad (1)$$

paper reports the results obtained by the route shown. The displacement of an alkyl group from boron by a thioalkyl residue has been shown to be a free-radical reaction, with marked steric control, primary groups being displaced *ca.* 100 times faster than secondary groups.[4] The latter observation is of particular interest as it has opened the way to a rational synthesis of completely unsymmetrical boranes which will be reported later.

Addition of either ethane- or butane-thiol to a trialkylborane readily gave the required thioborane. An olefin was then added to the reaction mixture followed by a solution of $LiAlH_4$. Reaction was extremely rapid and, in general, yields of the mixed boranes, which showed no tendency to undergo exchange of alkyl groups under the conditions of the reaction, were excellent. The yields were estimated by oxidation of the products and isolation and analysis of the resulting alcohols, after first checking that only a single trialkylborane was present in each case. The results of this procedure correlated well with those obtained by isolation of the borane. All experiments were reproducible, some results being shown in the Table. The Table shows that when cyclohexene is used as the second olefin the yields are depressed, and, in the case where olefin A is also a secondary olefin, no product is obtained. This is presumably due to the low rate of addition of cyclohexene to the dialkylborane intermediate, and gives one limit of the reaction.

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