New, High-yield Synthesis of 'Mixed' Trialkylboranes ($R^A{}_2R^BB$)

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Summary Dialkylbromoboranes may be converted into 'mixed' trialkylboranes ($R^A{}_2R^BB$) in high yield using sodium hydride reduction in the presence of an alkene, a method with excellent functional group tolerance.

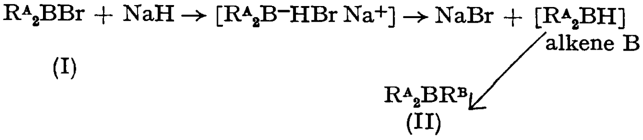
THE many organic syntheses using organoboranes[1] require the availability of derivatives where different alkyl groups are bonded to boron ('mixed' organoboranes). However, although such derivatives are stable, their preparation is in general a difficult operation.[2] We here report the preparation of partly mixed trialkylboranes ($R^A{}_2R^BB$) in high yield by a mild procedure starting from dialkylbromoboranes which we have shown[3] to be readily available substances.

The best methods currently available for the preparation of $R^A{}_2R^BB$ involve reduction of $R^A{}_2BX$ (X = OR,[4] SR[5]) with $LiAlH_4$ or 'AlH_3' (X = OMe[6]) in the presence of alkene. When the alkyl groups are simple these methods give reasonable results but the use of such strong reducing agents clearly limits the functional groups that may be accommodated and hence obviates one of the major advantages associated with the use of organoboranes. Furthermore the soluble lithium and aluminium salts produced may hinder purification or interfere with further reactions if the organoborane is utilised directly.[7]

TABLE 1

$R^A{}_2BBr$	Alkene B	Product	Yield[a] (%)
$(n\text{-}C_5H_{11})_2BBr$	Oct-1-ene	Octanol	99
,,	Hex-1-ene	Hexanol	96
,,	Cyclohexene	Cyclohexanol	97
,,	Cyclopentene	Cyclopentanol	93
,,	$CH_2{=}CH{\cdot}[CH_2]_6Cl$	$HO[CH_2]_8Cl$	81
,,	Norbornene	Norbornan-2-ol	88
(Cyclopent)$_2$ BBr	Oct-1-ene	Octanol	98
,,	Hex-1-ene	Hexanol	95
,,	Cyclohexene	Cyclohexanol	98
,,	$CH{\equiv}C{\cdot}[CH_2]_6Cl$[b]	$CH_2{=}CH[CH_2]_6Cl$	91[c]

[a] Based on a maximum possible 5 mmol conversion. [b] Alkyne (5 mmol) drip-fed to the stirred reaction mixture over 6 h. [c] Yield is of isolated product.



$$R^A{}_2BBr + NaH \rightarrow [R^A{}_2B^-HBr\,Na^+] \rightarrow NaBr + [R^A{}_2BH] \xrightarrow{\text{alkene B}} R^A{}_2BR^B$$

(I) (II)

SCHEME

The Scheme shows the route by which bromoboranes (I) are converted into the mixed boranes (II). The only side product is sodium bromide, which may be filtered off if desired, but which we have found does not interfere with subsequent reactions. The reducing agent is sodium hydride which will tolerate very many functional groups, and by analogy[8] it probably acts first to produce an 'ate' complex which subsequently eliminates sodium bromide. Table 1 shows the results when the reactions are carried out by addition at −63 °C of (I) (5 mmol) to a stirred suspension of NaH (6 mmol) and alkene B (7 mmol) in diglyme (8 ml), followed by stirring at 23 °C for 7h. The production of R^B–B bonds was estimated by oxidation followed by g.l.c. estimation of the product alcohol.

It is evident from Table 1 that the reaction proceeds essentially quantitatively for a variety of structural types and the tolerance to steric hindrance is particularly noteworthy. Equally notable is that by a slight change of procedure a terminal alkyne may be used in the synthesis, even though this functional group is reactive towards NaH. This reaction allows the preparation of dialkylvinylboranes.

Table 1 does not, of course, establish the degree of redistribution of the mixed product $R^A{}_2R^BB$, and to do this the cyanoborate process for trialkylmethanols[9] was applied directly to a number of representative reactions, without purification of the mixed boranes. Table 2 shows the isolated yields for the overall process $R^A{}_2BBr \rightarrow\rightarrow\rightarrow R^A{}_2R^BCOH$.

TABLE 2

Triple migration product[a]	Yield(%)	Proportion of redistributed product(%)[b]
Hex^n(Pent^n)$_2$C·OH	86	2
Cyclopent(pent^n)$_2$C·OH	83	<2
(Cyclohex)$_2$cyclopent-C·OH	81	7

[a] The initial tertiary alcohol contained no olefin, but on purification by column chromatography some dehydration product was produced. Yield of total triple-migration product is given. [b] The degree of redistribution was estimated by g.l.c.

The overall yield for this long series of reactions is most satisfactory and redistribution is negligible except for the most hindered case, where it still only amounted to 7% of the product.

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