The First Phase-transfer catalysed Reactions of Trialkylboranes. A Highly Facile Synthesis of Trialkylmethanols from Alkenes

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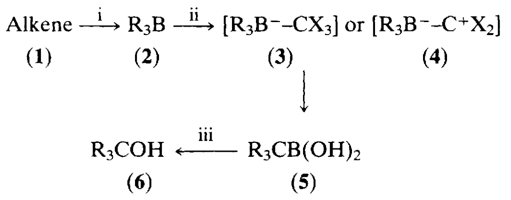
The phase-transfer catalysed reactions of trialkylboranes, generated *in situ via* hydroboration of alkenes, with chloroform and aqueous sodium hydroxide, followed by treatment with hydrogen peroxide, provide an economic and convenient method for the synthesis of trialkylmethanols.

There have been many important applications of phase-transfer catalysis in organic chemistry,[1] and recently in organometallic chemistry.[2] However, at present, relatively little is known about the phase-transfer catalysed reactions involving boron, (apart from reduction with sodium borohydride using a phase-transfer catalyst[3] and the alkylation of carborane by an alkyl halide in the presence of an alkali under phase-transfer catalysis conditions[4]), even though organoboranes have become most useful intermediates in organic synthesis.[5] This paper describes the first application of phase-transfer catalysis to organoboranes to form carbon–carbon bonds.

We have found that the treatment of trialkylboranes (**2**), prepared *in situ via* the hydroboration of alkenes (**1**) with dimethylsulphide–borane,[5] with haloform (chloroform, bromoform, and iodoform), 50% aqueous sodium hydroxide, and a phase-transfer catalyst could produce trialkylmethanols (**6**), with some dialkylketones on oxidation with hydrogen peroxide (Scheme 1). The reaction with cloroform in dichloromethane and tetrahydrofuran (THF) at 40 °C, or better, in benzene at 70 °C, favoured the formation of trialkylmethanols. A number of representative alkenes were hydroborated and the resulting trialkylboranes were readily converted into the corresponding trialkylmethanols under these reaction conditions. The results are summarized in Table 1.



$$\begin{tikzcd}
\underset{(1)}{\text{Alkene}} \arrow[r, "i"] & \underset{(2)}{R_3B} \arrow[r, "ii"] & \underset{(3)}{[R_3B^{-}\text{–}CX_3]} \text{ or } \underset{(4)}{[R_3B^{-}\text{–}C^{+}X_2]} \arrow[d] \\
\underset{(6)}{R_3COH} & & \underset{(5)}{R_3CB(OH)_2} \arrow[ll, "iii"']
\end{tikzcd}$$

Scheme 1. *Reagents and conditions*: i, BH_3-SMe_2 in benzene (or THF); ii, $CHCl_3$, aq. NaOH; iii, H_2O_2.

Table 1.

Alkene	Product[a]	R	Yield/%[b]
Hexene[c]	(**6a**)	Hexyl	70
Octene[c]	(**6b**)	Octyl	72
Dodecene[c]	(**6c**)	Dodecyl	63
Cyclohexene[c]	(**6d**)	Cyclohexyl	70
Cyclopentene[d]	(**6e**)	Cyclopentyl	46
α-Methylstyrene[d]	(**6f**)	2′-Phenylpropyl	40

[a] All products were identified by ^1H NMR and IR spectroscopy, and MS. [b] Isolated yields calculated on the alkene added at the beginning of the process. [c] The alkene was hydroborated with BH_3-SMe_2 in benzene, and the phase-transfer catalysis was carried out at 70 °C for 4 h. [d] The alkene was hydroborated with BH_3-SMe_2 in THF and CH_2Cl_2, and the phase-transfer catalysis was carried out at 40 °C for 4 h.

A typical procedure is as follows (all manipulations, except oxidation, are carried out under dry nitrogen). To trioctylborane (5.4 mmol), prepared *via* the hydroboration of octene (1.82 g, 16.2 mmol) in benzene (5 ml) with dimethylsulphide–borane (9.8 M, 0.56 ml, 5.5 mmol),[5] was added chloroform (1.0 ml, 12 mmol), aqueous sodium hydroxide (50%, 3.0 ml), and triethylamine (0.050 ml). The mixture was stirred at 70 °C for 4 h, then cooled to *ca.* 0 °C, and water (10 ml), ethanol (5 ml), and H_2O_2 (30%, 2.0 ml) added. The oxidation was effected at 25 °C for 2 h, then at 50 °C for 1 h. The product was extracted into diethyl ether. The residue was concentrated under vacuum and purified by column chromatography (silica gel, elution with hexane, and then with dichloromethane) to give trioctylmethanol (1.43 g, 72%).

The mechanism is not very clear. However, it is possible that the trichloromethyl anion or dichlorocarbene, produced from chloroform under basic phase-transfer conditions,[1] is combined with trialkylborane to form the borate (**3**) or (**4**),[6] which leads to the intermediate (**5**) *via* the three alkyl migrations.

The reactions of trialkylboranes with carbon monoxide[7] or with sodium cyanide[8] yield trialkylcarbinols, but relatively drastic conditions are required. The lithium triethylcarboxide induced reactions of trialkylboranes with haloform or with dichloromethyl methyl ether could be used as a smooth way for synthesis of trialkylmethanols.[9] However, the base is expensive, and can be accompanied by troublesome isolation. The present reaction has potential to provide a more convenient and especially more economic means of preparing these compounds from alkenes.

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