Novel Approach to the High-yield Synthesis of Tertiary Alcohols using Organoboranes

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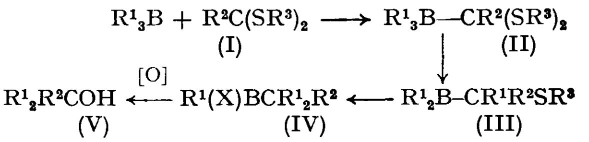
Summary Trialkylmethanols ($R^1_2R^2COH$) are produced in essentially quantitative yields by treatment of trialkylboranes successively in the same vessel with 1-lithio-1,1-bis(phenylthio)alkane (−30 to 20°), $HgCl_2$ (−78 to 0°) and alkaline hydrogen peroxide (20°).

Trialkylmethanols may be produced from trialkylboranes by reactions in which all three alkyl groups of the methanol originate in the trialkylborane.[1–3] In connection with our studies on organoborates,[1,2,4] we have studied a new approach in which two alkyl groups of the methanol originate in the trialkylborane, whilst the third is derived from an acyl anion equivalent (I)[5] (Scheme). The overall result is synthetically equivalent to the reactions of Grignard reagents with ketones or esters, which are often complicated by side-reactions and have a low functional group tolerance.[6]



$$\begin{tikzcd} & \underset{(I)}{R^1_3B + R^2\bar{C}(SR^3)_2} \arrow[r] & \underset{(II)}{R^1_3\bar{B}\text{—}CR^2(SR^3)_2} \arrow[d] \\ \underset{(V)}{R^1_2R^2COH} & \underset{(IV)}{R^1(X)BCR^1_2R^2} \arrow[l, "{[O]}"'] & \underset{(III)}{R^1_2B\text{–}CR^1R^2SR^3} \arrow[l] \end{tikzcd}$$

Scheme

We studied benzenethiol derivatives (I; $R^3 = Ph$) because it is known that in these cases the initial organoborates (II) spontaneously rearrange to (III) at 20°.[7] For these initial investigations R^2 was Pr^n. $HgCl_2$ induced an essentially quantitative conversion of (III) into (IV) (−78 to 0°). Oxidation of (IV), without isolation, gave the methanol (V), which was purified by chromatography as previously described.[2] A slight excess over 1 mol. equiv. of $HgCl_2$ was required for complete reaction, but in the standard procedure it was convenient to use 50% excess. Yields were excellent (Table).

Table

R^1 in R^1_3B	Yield(%)[a]
n-Octyl	90
n-Hexyl	96
Cyclohexyl	98
Cyclopentyl	85
[n-Octyl][b]	80

[a] Yield of the methanol $R^1_2Pr^nCOH$ after chromatographic isolation based on initial alkene added. [b] The trialkylborane used was 1,1,2-trimethylpropyldi-n-octylborane (thexyldioctylborane), but only octyl migration was observed. The product was 9-propylheptadecan-9-ol, as from trioctylborane.

Excess of methyl fluorosulphonate also induces the quantitative rearrangement of (III) to (IV)[8] but it causes polymerisation of tetrahydrofuran, the most favourable solvent for preparation of both trialkylborane and acyl anion equivalent. $HgCl_2$ does not suffer from this disadvantage.

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[8] Negishi has studied a similar reaction using dithiane derivatives, but the yields are poorer (⩽ 62%); E. Negishi and T. Yoshida, A.C.S. meeting, Chicago, August 1973; we thank Professor Negishi for a copy of the long abstract.