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IMPROVED SYNTHESIS OF TERTIARY ALCOHOLS FROM REACTIONS OF ORGANOBORANES WITH 2-LITHIO-1,3-BENZODITHIOLES

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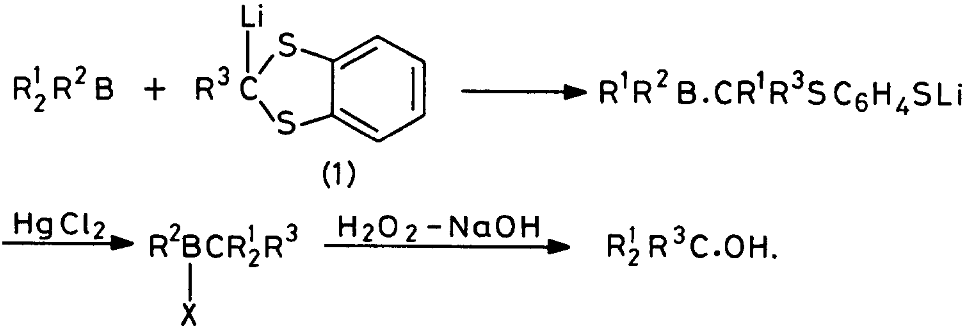
SUMMARY. Treatment of trialkylboranes with 2-lithio-1,3-benzodithioles and then mercuric chloride (or methyl fluorosulphonate) followed by oxidation gives tertiary alcohols in high yields. The method is applicable to reactions of hindered organoboranes that fail using 1-lithio-1,1-bis(phenylthio)alkanes.

We have previously reported the reactions of trialkylboranes with 1-lithio-1,1-bis-(phenylthio)butane followed by treatment with mercuric chloride and then oxidation, as a route to tertiary alcohols.[1]

Unfortunately the reactions were unsuccessful when hindered trialkylboranes such as trinorbornylborane and thexyldicyclopentylborane were used[1c]. In an attempt to overcome this problem we chose to examine 2-lithio-2-substituted-1,3-benzodithioles as electronically similar but less hindered alternatives for 1-lithio-1,1-bis(phenylthio)alkanes.

We have developed a convenient synthesis of 2-substituted-1,3-benzodithioles (1)[2] and demonstrated that they behave as useful acyl carbanion equivalents in reactions with organic electrophiles.[3] In the preceeding communication we show that anions (1) react with organoboranes to give intermediates that yield ketones on oxidation, and that the reaction is successful even with hindered organoboranes.[4] We now report that further treatment of these intermediates with mercuric chloride (and in one case with methyl fluorosulphonate), followed by oxidation gives tertiary alcohols (Scheme).



SCHEME.

The scope of the reaction is illustrated by examples (1) to (9) (Table.)

TABLE

Production of tertiary carbinols according to the Scheme

	Alkyl groups of organoborane R^1	R^2	Alkyl group of (1) R^3	Product	Yield[a](%)
i)	n-Hexyl		Pr^n	$R^1_2R^3COH$	79
ii)	Norbornyl		Pr^n	$R^1_2R^3COH$	74
iii)	n-Hexyl		c-Hexyl	$R^1_2R^3COH$	85
iv)	c-Pentyl		c-Hexyl	$R^1_2R^3COH$	67
v)	n-Octyl		H	$R^1_2R^3COH$	73
vi)	c-Pentyl	Thexyl	Pr^n	$R^1_2R^3COH$	74
vii)	c-Pentyl	Thexyl	c-Hexyl	$R^1_2R^3COH$	80
viii)	n-Octyl	Thexyl	Pr^n	$R^1R^2R^3COH$	35[b]
				$R^1_2R^3COH$	41
ix)	n-Octyl	Thexyl	Pr^n	$R^1R^2R^3COH$	59[c]

[a] All yields are of isolated, purified products each of which gave satisfactory C,H analysis and spectroscopic data.

[b] Hg(II) used to induce second migration.

[c] MeO_2SF used to induce migration. Low yield due to some polymerisation of solvent by the alkylating agent.

Not only do those reactions which failed using bis(phenylthio)alkane anions now give products in good yield (reactions (ii), (iii), (iv), (vi)) but even the most hindered combination of reactants (reaction (vii)) gives tertiary carbinol in excellent yield. When the migrating groups are secondary and the third migration is induced by Hg(II) then use of a dialkylthexylborane gives a clean product in which the secondary alkyl groups have been fully utilised (reactions (vi) and (vii)). However, a similar procedure involving primary alkyl groups gives mixtures in which the thexyl group has migrated competitively with the primary groups. (Reaction (viii)). When methyl fluorosulphonate was used to induce the second migration the thexyl group migrated cleanly, yielding finally the completely unsymmetrical alcohol. (reaction (ix)).

The following procedure is representative.

To a stirred solution of 2-lithio-2-n-propyl-1,3-benzodithiole (2 mmole) in THF (see preceding communication) at -30°C was added tri-n-hexylborane (2 mmole) in dry THF (5 cm^3). The solution was allowed to stand at -30°C for 1h. and then at 25°C for a further 1h. It was cooled to -78°C and mercuric chloride (2.1g., 6 mmole) was added by rotating a side arm.[1c] The mixture was allowed to warm to 0°C and then oxidised by addition of NaOH (5M., 10cm^3) followed by hydrogen peroxide (5 cm^3. 50%. CARE!) and stirring overnight. The product was taken into pentane, the pentane layer washed with water, dried (Na_2SO_4), filtered and evaporated. The crude product was placed on an alumina (activity III) column from which elution with dichloromethane gave di-n-hexyl-n-propylmethanol (7-n-propyltridecan-7-ol) 0.380g (79%), $n_D^{20^\circ}$ = 1.479, (lit.[1c] $n_D^{20^\circ}$ = 1.468.)

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