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PREPARATION OF SECONDARY ALCOHOLS BY REACTION OF TRIALKYLBORANES WITH BIS(PHENYLTHIO)METHYL-LITHIUM

Rosemary J. Hughes, Andrew Pelter, and Keith Smith,*
Department of Chemistry, University College of Swansea, Swansea SA2 8PP,
Ei-ichi Negishi and Takao Yoshida,
Department of Chemistry, Syracuse University, Syracuse, New York 13210.
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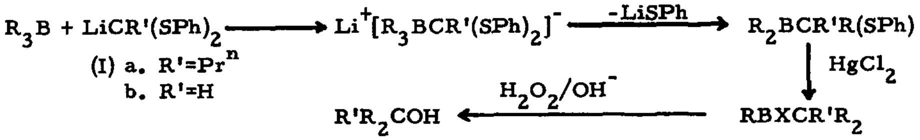
Summary. Reaction of trialkylboranes with bis(phenylthio)methyl-lithium (Ib), followed by $HgCl_2$ and oxidation of the intermediate organoborane, yields dialkylmethanols in good yields. (Ib) is thus a new one carbon insertion unit for trialkylboranes.

Reaction of 1-lithio-1,1-bis(phenylthio)butane (Ia) with trialkylboranes, followed by reaction with $HgCl_2$ and oxidation gives tertiary alcohols in high yield (Scheme, $R'=Pr^n$).[1] The reaction is, however, unsuccessful with hindered organoboranes such as tris-exo-2-norbornylborane or thexyldicyclopentylborane.


$$\begin{tikzcd} R_3B + LiCR'(SPh)_2 \arrow[r] & Li^+[R_3BCR'(SPh)_2]^- \arrow[r, "-LiSPh"] & R_2BCR'R(SPh) \arrow[d, "HgCl_2"] \\ & R'R_2COH & RBXCR'R_2 \arrow[l, "H_2O_2/OH^-"'] \end{tikzcd}$$

(I) a. $R'=Pr^n$
b. $R'=H$

Surprisingly, under the conditions used for tertiary alcohol preparation, little secondary alcohol is obtained from reaction of trialkylboranes with (Ib), although the first migration is known to proceed normally.[2] We now report that use of three equivalents of $HgCl_2$ satisfactorily induces the second migration, oxidation giving secondary alcohols in good yield (Table). Even the hindered organoboranes which do not react successfully with (Ia) are accommodated, though some modification of the standard conditions is necessary (cf. footnote b and c of Table).

Although easily prepared, bis(phenylthio)methane is not commercially available, so that 1,3-dithiane would be a more attractive starting material. However, under conditions similar to those used with (Ib), reaction of tri-n-hexylborane with 2-lithio-1,3-dithiane (II) followed by treatment with $HgCl_2$ and oxidation, gave only ca. 60% of tridecan-7-ol. Methylation (FSO_3Me) gave similar results.[3] The yield of tridecan-7-ol could be increased to 74% by use of two equivalents of (II) and four of $HgCl_2$, but even under these conditions the yield of dicyclopentylmethanol from tricyclopentylborane was only 32%.

Preparation of Secondary Alcohols, R^2R^3CHOH, from $R^1R^2R^3B$ and $(PhS)_2CHLi$

R^1	R^2	R^3	Yield (%)[a]
n-C_6H_{13}	n-C_6H_{13}	n-C_6H_{13}	85
cyclopentyl	cyclopentyl	cyclopentyl	88
cyclohexyl	cyclohexyl	cyclohexyl	88
1, 1, 2-trimethylpropyl(thexyl)	cyclopentyl	cyclopentyl	80[b]
exo-2-norbornyl	exo-2-norbornyl	exo-2-norbornyl	75[c]

a. Yield of R^2R^3CHOH after isolation by column chromatography.

b. The reaction mixture was stirred 2 h at 20° before cooling for addition of $HgCl_2$, and 30 min. at 20°C before oxidation.

c. Two equivalents of (Ib) were used; reaction conditions were as described in (b).

Thus, bis(phenylthio)methane is preferable to 1, 3-dithiane as a one-carbon insertion unit for the production of dialkylmethanols from trialkylboranes, and it may be added to the list of one-carbon units which are useful in organoborane chemistry.[4]

The following is a representative procedure (n.b. See Table for modifications).

To stirred bis(phenylthio)methane (0.23g, 1 mmol) in THF (10 cm^3) at -30°C under N_2 was added Bu^nLi (1.1 mmol). Stirring was maintained for 90 min. Tricyclopentylborane (1 mmol) in THF (10 cm^3) was added and the mixture was stirred for 1 h at -30°C and 1 h at 20°C before cooling to -78°C. $HgCl_2$ (0.81 g, 3 mmol) was added and the stirred mixture was allowed to warm to 0°C (ca. 15 mins). The mixture was oxidised by addition of NaOH (5 cm^3 of 5N solution) and H_2O_2 (3 cm^3 of 50%) at 20°C, followed by stirring overnight. The neutral products were extracted into pentane and separated by dry-column chromatography on silica. Dicyclopentylmethanol (0.15 g, 88%) was eluted with dichloromethane.

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1. R.J.Hughes, A.Pelter, and K.Smith, J.C.S.Chem.Comm., 1974, 863.
2. S.Yamamoto, M.Shiono, and T.Mukaiyama, Chemistry Letters, 1973, 961.
3. E.Negishi and T.Yoshida, A.C.S.Meeting, Chicago, August 1973.
4. (a) A.Pelter, M.G.Hutchings, K.Rowe, and K.Smith, J.C.S.Perkin I, 1975, p.129;
   (b) ibid., p.138; (c) H.C.Brown, Accounts Chem. Research, 1969, **2**, 65;
   (d) H.C.Brown and B.A.Carlson, J.Org.Chem., 1973, **38**, 2422;
   (e) E.Negishi, T.Yoshida, A.Silveira, and B.L.Chiou, J.Org.Chem., 1975, **40**, 814.