Journal of Organometallic Chemistry, 146 (1978) C8—C10

Preliminary Communication

A SYNTHESIS OF α-HYDROXYSILANES FROM ORGANOBORANES

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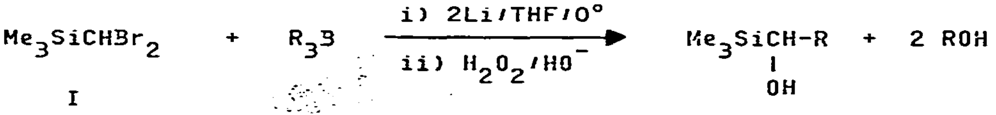
(Received December 16th, 1977)

Summary

A convenient synthesis of α-hydroxysilanes from trimethyl(dibromomethyl)silane, lithium and trialkylboranes in THF is described.

In our continuing interest in the preparation and reactions of carbo-functional organosilanes we have begun to investigate organoborane entries into such systems. Our interest in the organoborane approach stems from the possibility of utilizing the generally high yields and high regio and stereospecificity of the organoborane reactions (1) in the synthesis of carbo-functional organosilanes. We wish to report here the preliminary results of one aspect of this work, namely the synthesis of α-hydroxysilanes (2) from trialkylboranes.

The dropwise addition of trimethyl(dibromomethyl)silane (3), I, to a mixture of a trialkylborane (prepared via hydroboration) and lithium metal in THF results in a rapid consumption of the lithium. Alkaline hydrogen peroxide oxidation of the reaction mixture yields



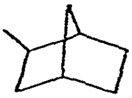
$$\underset{\text{I}}{Me_3SiCHBr_2} + R_3B \xrightarrow[\text{ii) } H_2O_2/HO^-]{\text{i) } 2Li/THF/0^\circ} \underset{\text{II}}{\underset{\displaystyle OH}{Me_3SiCH\text{-}R}} + 2\ ROH \qquad (1)$$

the α-hydroxysilane, II, in moderate to good yield. (eqn 1) The results of this reaction are given in Table I.

Several observations concerning the reaction should be noted. (a) The reaction occurs equally well with either lithium dispersion or lithium wire, the wire having the advantage of being easier to remove any excess if necessary. (b) The reaction proceeds well at 0°, and raising the temperature to 25° does not increase the yield or give appreciably faster reaction times. (c) The use of magnesium rather than lithium results in considerably lower yields and more complex reaction mixtures. (e.g. 15% versus 72% of 1-trimethylsilyl-1-heptanol) (d) The use of B-n-hexyl-9-BBN in an attempt to avoid the loss of two of the alkyl groups of the borane gave poor results and a mixture of products. (e) An analogous reaction carried out with either dibromomethane or dichloromethane and trihexylborane gave only 1-hexanol with no evidence for 1-heptanol. (f) The more hindered tricyclohexyl and tri-exo-norbornylboranes gave lower yields, presumably due to a steric effect.

The preparation of 1-trimethylsilyl-1-heptanol is representative. of the procedure. In a dry, 100 ml flask was prepared 10 mmoles of tri-n-hexylborane (from 2.52 g (30 mmol) of 1-hexene and 4.88 ml of 2.05 M borane in THF) in 25 ml of THF. To this was added 0.3 g (0.43 mmol) of lithium wire or dispersion, the reaction mixture cooled to 0° and 2.36 g (10 mmol) of trimethyl(dibromomethyl)silane in 10 ml of THF added over 20 min. The reaction mixture was stirred at 0° for 1 h and an additional hour at 25°. A small amount of water was added to destroy the excess lithium present, followed by the careful addition of 7 ml of 3 N sodium hydroxide and 7 ml of 30 % hydrogen peroxide. The oxidation was completed by heating to 40-50° for 1 h. The two phase system was saturated with sodium chloride and the organic layer removed, the aqueous layer extracted with ether (2 x 20ml) and the combined organic layers dried ($MgSO_4$) and the solvents removed by distillation. The residue, which showed essentially only two peaks, was subjected to preparative GLC using a 10 foot, 10% UCON Polar column.

Table I. α-Hydroxysilanes from Trialkylboranes.

R of R_3B	Product	% Yield[a]	n_D(T°C)
n-pentyl	$Me_3SiCH(OH)$-n-C_5H_{11}	79	1.4381(23)
n-hexyl	$Me_3SiCH(OH)$-n-C_6H_{13}	72	1.4421(24)
n-octyl	$Me_3SiCH(OH)$-n-C_8H_{17}	69	1.4443(23)
c-pentyl	$Me_3SiCH(OH)$-c-C_5H_9	63	1.4665(23)
c-hexyl	$Me_3SiCH(OH)$-c-C_6H_{11}	43	1.4711(23)
exo-norbornyl	$Me_3SiCH(OH)$ 	46	--

a. GLC yields using an internal standard. b. An apparent mixture of isomers, possible mixture of the two diastereomers, RR:SS and RS:SR. We thank referee B for this observation.

Acknowledgements

We thank the NSF (grant No. SER 77-04601) for financial support of this work and Bristol and Pfizer Pharmaceuticals for generous gifts of chemicals. One of us (O.R.) wishes to thank Pfizer and Abbott Pharmaceuticals and the Ford Foundation for graduate fellowships.

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