

ASYMMETRIC SYNTHESIS OF BIFUNCTIONAL ORGANOSILICON COMPOUNDS via HYDROSILYLATION

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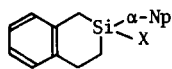
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The fundamental work of Sommer and his coworkers on the stereochemistry of organosilicon compounds¹ has originated from the preparation of optically pure methyl- α -naphthylphenylsilane (1a) and closely related compounds, which are obtained via fractional crystallization of diastereomeric menthoxyethyl- α -naphthylphenylsilane (1b). Another system having asymmetric silicon — cyclic one (2) — has been developed by Corriu et al.² using a similar technique as a probe of a different stereochemistry of some substitution reactions at silicon.

However, few examples of the preparation of optically active organosilanes by asymmetric synthesis or by kinetic resolution have been recorded so far in the literature. Corriu et al.³ have reported a kinetic resolution of bifunctional organosilanes during menthanolysis of chloro- α -naphthylphenylsilane (3), the latter being assumed to undergo extensive racemization under the conditions employed. Recently, Holt and coworkers⁴ have carried out partial reduction of various



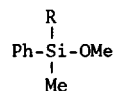
1 a: X = H
 ~ b: X = OMe



2



3



4

racemic methoxysilanes (4, R = α -naphthyl, ethyl, and benzyl) by a chiral reducing complex of lithium aluminum hydride to achieve a kinetic resolution.

The only asymmetric synthesis at a silicon center has been observed by Klebe et al.⁵ in the reaction of bis(N-methylacetamido)methylphenylsilane with optically active amino acids to form unequal amounts of diastereomeric pairs of 2-siloxazolidone-5, which are claimed to undergo a

second order asymmetric transformation. To our best knowledge, however, there are no data of asymmetric induction at a prochiral silicon center in a sense of catalytic asymmetric reactions, on which increasing attention has been focused recently.

The present paper describes an application of asymmetric catalytic hydrosilylation of ketones to the preparation of some new asymmetric bifunctional organosilanes. The initial work on homogeneous asymmetric hydrosilylation of ketones, which was achieved by catalysis of certain chiral rhodium complexes, has already been reported.^{6,7} Thus the use of optically active benzylmethylphenylphosphine as a chiral ligand in a cationic rhodium complex, $[\text{Rh}\{\text{(R)}-(\text{PhCH}_2)\text{MePhP}\}_2\text{H}_2\text{S}_2]^+\text{ClO}_4^-$ (S refers to a solvent molecule) is effective to cause stereoselective addition of a hydrosilane to a variety of alkyl phenyl ketones to give rise to silyl ethers of alkylphenylcarbinols with fairly high enantiomeric bias at the carbonyl carbon atom.

The asymmetric induction at a meso-silicon atom stems from similar hydrosilylation to that described above. Addition of certain dihydrosilane, $\text{H}_2\text{SiR}^1\text{R}^2$, having a meso-silicon atom to such symmetric ketones as diethyl ketone or benzophenone in the presence of the chiral rhodium complex gave silyl ethers in the optically active form associated with the silicon atom (eq. 1).⁸ The silyl ethers were converted into known methyl- α -naphthylphenylsilane (1a) in order to examine respective optical yield, although such conversion may be accompanied by considerable racemization.¹¹ Results are summarized in Table I.

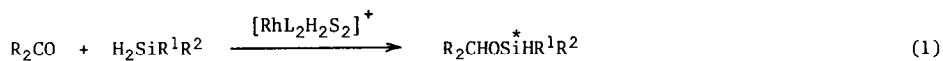
Table I. Asymmetric Induction at meso-Silicon Atom via Hydrosilylation of Ketones Catalyzed by $[\text{Rh}\{\text{(R)}-(\text{PhCH}_2)\text{MePhP}\}_2\text{H}_2\text{S}_2]^+$ at Room Temperature.

Ketone	Silyl ether, $[\alpha]_D$ (neat)	Yield (%)	α -NpPhMeSiH (<u>1a</u>) ^a , $[\alpha]_D$ (cyclohexane)	Optical yield ^b (%)	Configuration
α -NpMeSiH ₂ (<u>5a</u>)					
Me ₂ CO	-2.31	63	+2.05	7.4	<u>R</u>
Et ₂ CO	-4.40	69	+2.38	8.6	<u>R</u>
Ph ₂ CO	-4.33 ^c	72	+5.45	19.7	<u>R</u>
α -NpPhSiH ₂ (<u>5b</u>)					
Me ₂ CO	-0.09	76	-0.14	—	<u>S</u>
Et ₂ CO	-0.57	86	-1.98	7.2	<u>S</u>
Ph ₂ CO	—	—	-7.66	27.7	<u>S</u>

^a Optically pure (R)- α -NpPhMeSiH, $[\alpha]_D +35.0^\circ$ (c 15.6, cyclohexane).

^b Calibrated on the basis of the optical purity of phosphine used (79%).

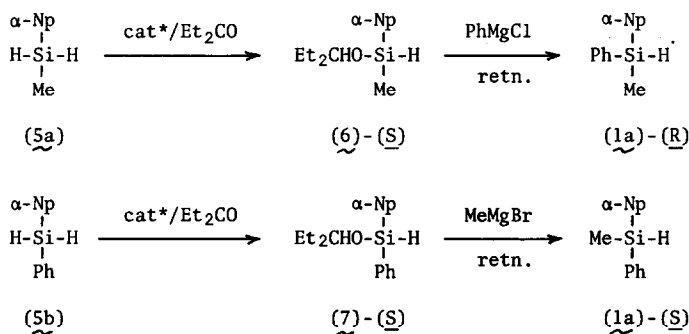
^c Measured in cyclohexane (c 10).



R = Me, Et, and Ph; R¹ = Me and Ph; R² = α-Np

L = (R)-(PhCH₂)MePhP (79% optical purity)

It is noteworthy that one enantiomer of 1a was produced in excess through the hydrosilylation of ketones using methyl-α-naphthylsilane (5a) while the other enantiomer was obtained in excess starting with α-naphthylphenylsilane (5b). If, for example, phenylation of 3-pentyloxy-α-naphthylmethylsilane (6) and methylation of 3-pentyloxy-α-naphthylphenylsilane (7) proceed largely with retention of configuration at the silicon center,^{3,11} the following scheme would be valid to rationalize the present results. This clearly suggests that, in both cases of forming 6 and 7, one enantiotopic hydrogen (pro S) attached to the silicon atom of the dihydrosilanes (5a and 5b) participates preferentially in the chiral complex-catalyzed hydrosilylation of symmetric ketones over the other (pro R).



Scheme I.

There is solid evidence that the oxidative addition of 1a to an appropriate platinum complex proceeds with retention of configuration.¹² The implication is that the configurational stability around a silicon atom during the activation of a dihydrosilane by the catalyst plays an important role to exert asymmetric induction at the meso-silicon atom.¹³

REFERENCES AND NOTES

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8. Ojima and coworkers⁹ and Corriu et al.¹⁰ have reported that chlorotris(triphenylphosphine)-rhodium(I) is very effective catalyst for the hydrosilylation of carbonyl compounds, providing a selective route to synthesize bifunctional alkoxy silanes.
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b) C. Eaborn, D. J. Tune, and D. R. M. Walton, J. C. S. Chem. Commun., 1223 (1972).
13. It should be mentioned that optically active bifunctional alkoxy silanes might be configurationally labile under the reaction conditions, because we have a problem in obtaining reproducible data of the optical activity of these compounds. We are investigating further in this respect.

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