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Preliminary communication

ASYMMETRIC HYDROSILYLATION OF KETONES CATALYSED BY A CHIRAL RHODIUM COMPLEX

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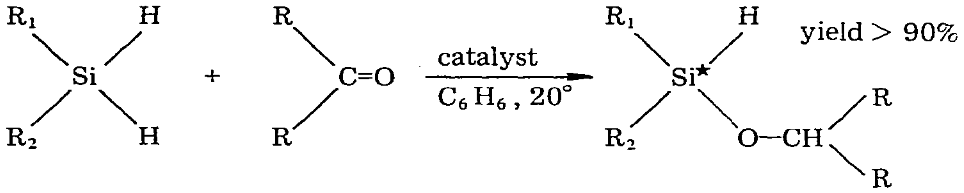
Summary

Synthesis of optically active alkoxysilanes by asymmetric hydrosilylation of ketones, in the presence of a chiral phosphine—rhodium complex, is described; optical yields up to 46% are observed.

In order to prepare chiral organosilanes directly, without resolution, we have studied asymmetric synthesis for organosilicon compounds. This has not yet been widely studied [1,2] and we have looked at the possibilities offered by asymmetric catalysis.

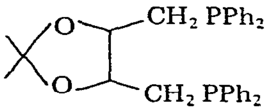
Alcoholysis of diarylsilanes [3] and hydrosilylation of ketones [3, 4] with a rhodium complex present gives direct preparation, in quantitative yields, of a variety of bifunctional alkoxysilanes. We have also shown [5] that alcoholysis of prochiral silanes by an asymmetric alcohol or with chiral catalyst catalysis leads to alkoxysilanes of up to 56% optical purity. We now report the asymmetric synthesis of organosilanes, by asymmetric hydrosilylation of ketones, in the presence of a catalyst containing a chiral phosphine.

We studied first of all the reaction of a ketone with a prochiral silane, catalysed by the asymmetric rhodium complex prepared by Kagan and coworkers [6]:

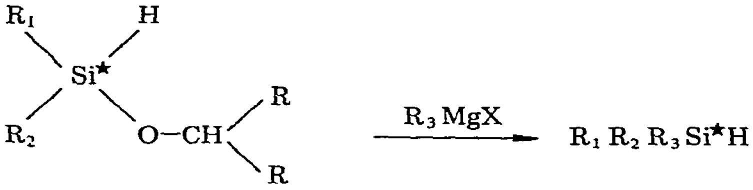


yield > 90%

catalyst: $[(C_8H_{14})_2RhCl]_2$ + (+)- or (—)-Diop, Diop =



The preferential addition of one of the SiH groups leads to an optically active alkoxysilane; its optical purity was measured by conversion to a trisubstituted silane of known maximum specific rotation:



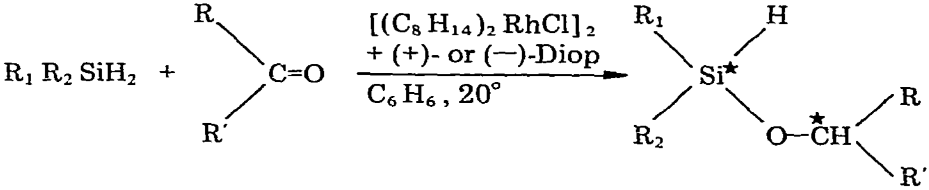
This reaction is both quantitative and stereospecific [1]. The principal results obtained are presented in Table 1. The optical yields obtained are slightly better than those given by the corresponding alcohols [5].

TABLE 1

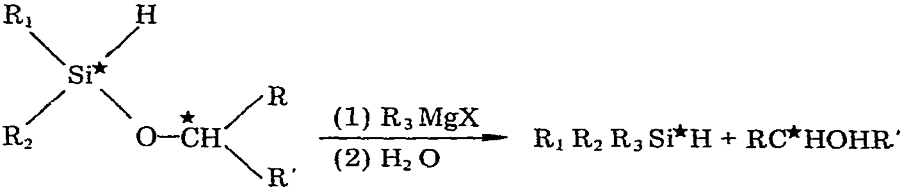
$R_1R_2SiH_2$	RRC=O	Catalyst [a]	$R_1R_2R_3SiH$	Optical purity (%)
1-NpPhSiH$_2$	Me$_2$C=O	(+)-cat.	(+)-1-NpPhEtSiH	30
1-NpPhSiH$_2$	Et$_2$C=O	(+)-cat.	(+)-1-NpPhMeSiH	46
1-NpPhSiH$_2$	n-Pr$_2$C=O	(+)-cat.	(+)-1-NpPhMeSiH	39
1-NpPhSiH$_2$	Ph$_2$C=O	(+)-cat.	(+)-1-NpPhMeSiH	31
1-NpPhSiH$_2$	cyclo-$C_6H_{10}O$	(+)-cat.	(+)-1-NpPhEtSiH	32
1-NpPhSiH$_2$	cyclo-C_5H_8O	(+)-cat.	(+)-1-NpPhMeSiH	35

[a] (+)-cat. = $[(C_5H_{14})_2RhCl]_2$ + (+)-Diop.

In the case of a non-symmetric ketone, the same catalyst leads to an asymmetric reaction at both the silicon and carbon centres:



Treatment of the reaction mixture by a Grignard reagent allows recovery of an organosilane and an alcohol of different optical purities.



The results obtained are given in Table 2.

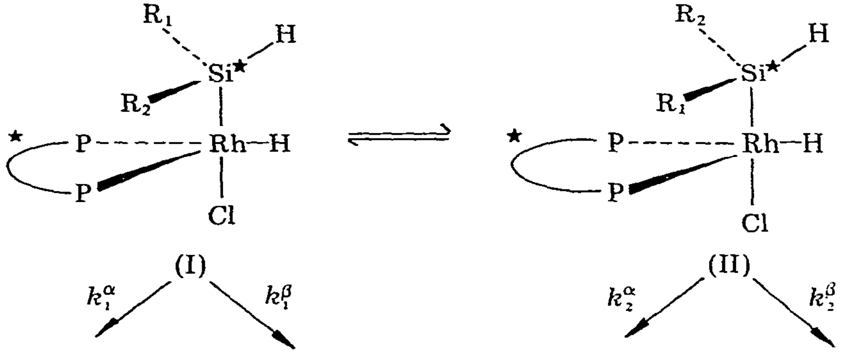
TABLE 2

$R_1R_2SiH_2$	RCOR′	Catalyst [a]	$R_1R_2R_3Si^{*}H$	Optical purity (%)	$RC^{*}HOHR'$	Optical purity (%)
1-NpPhSiH$_2$	MeCOEt	(—)-cat.	(—)-1-NpPhMeSiH	40	(—)-MeCHOHEt	42
1-NpPhSiH$_2$	PhCOMe	(—)-cat.	(—)-1-NpPhEtSiH	32	(+)-PhCHOHMe	55
1-NpPhSiH$_2$	PhCOEt	(+)-cat.	(+)-1-NpPhMeSiH	30	(—)-PhCHOHEt	42

[a] (—)-cat. = $[(C_8H_{14})_2RhCl]_2$ + (—)-Diop, (+)-cat = $[(C_8H_{14})_2RhCl]_2$ + (+)-Diop.

The organosilanes prepared are of similar optical purity to those in Table 1. The alcohols are obtained with a better optical yield than those reported for asymmetric reduction of ketones by hydrosilylation [7]. 1-NpPhSiH$_2$ seems to be a better reactant for such asymmetric reductions than the trisubstituted silanes; analogous observations were made by Kagan and coworkers [8];

To explain our results we envisage the following mechanism:



The oxidative addition of the silane to the chiral rhodium complex leads to two complexes (I) and (II), according to the silicon atom configuration. These two diastereoisomeric complexes exist in unequal proportions at equilibrium in the reaction medium; they can react at the two faces (α and β) of the ketone. The alkoxysilanes are then formed in proportions depending on the rate constants k_1^{α}, k_1^{β}, k_2^{α} and k_2^{β}. The optical purity of the silane depends on the factor $(k_1^{\alpha} + k_1^{\beta})/(k_2^{\alpha} + k_2^{\beta})$; it differs from that of the alcohol which is related to $(k_1^{\alpha} + k_2^{\alpha})/(k_1^{\beta} + k_2^{\beta})$. This explains the unequal optical results for the carbon and silicon centres.

Ketone hydrosilylation has already been used for asymmetric alcohol preparation. The present work shows its use in the preparation of organosilanes of sufficient optical purity for stereochemical studies.

Acknowledgement

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