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ASYMMETRIC SYNTHESIS AT SILICON

II *. ALCOHOLYSIS OF PROCHIRAL ORGANOSILICON COMPOUNDS CATALYSED BY RHODIUM COMPLEXES

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Summary

The asymmetric alcoholysis of prochiral organosilanes catalysed by certain rhodium complexes, whether optically active or not, gives rise to alkoxysilanes with an optical purity of up to 57%. The nature of the ligands in the rhodium complex has little influence on the optical yields, but the structures of the organosilane and of the alcohol are very important. A mechanism involving rapid and reversible activation of the organosilane, followed by slow reaction with the alcohol, is proposed to account for the results. The small influence of the catalyst ligands is attributed to direct nucleophilic attack of the alcohol on the silicon atom.

Introduction

We have recently discussed the value of asymmetric synthesis at silicon and have shown that asymmetric hydrosilylation of ketones leads to the formation of organosilanes with an optical purity as high as 82% [1,2]. We now wish to report the results of the alcoholysis of diorganosilanes catalysed by rhodium complexes:

$$R^1R^2SiH_2 + ROH \xrightarrow{(PPh_3)_3RhCl} R^1R^2Si\begin{matrix}H\\OR\end{matrix} + H_2$$

Chlorotris(triphenylphosphine)rhodium gives quantitative reaction under mild conditions, even with very hindered alcohols [3]. Such homogeneous catalysis also allows the use of asymmetric complexes of rhodium of the type widely exploited in organic synthesis [4].

* For a preliminary report of this work see ref. 2a; for part I see ref. 1a.

Results and discussion

The reaction of chiral alcohols with prochiral organosilanes

We first examined the catalysed reactions of prochiral organosilanes with asymmetric alcohols (eq. 1):

$$R^1R^2SiH_2 + R^*OH \xrightarrow[C_6H_6,\ 20^\circ C]{\text{catalyst}} R^1R^2Si^*H(OR^*) + H_2 \quad (1)$$

The optical purity of the product with respect to the configuration at the silicon atom was determined by treatment of the mixture of diastereoisomeric alkoxysilanes with a Grignard reagent (eq. 2).

$$R^1R^2Si^*H(OR^*) \xrightarrow[Et_2O]{R_3MgX} R^1R^2R^3Si^*H \quad (2)$$

This reaction gives with retention of configuration a quantitative yield of the trisubstituted organosilane [5] (see also Footnote *c*, Table 2), for which the absolute configuration and maximum specific rotation are known.

The results obtained are shown in Table 1.

It can be seen that the nature of the chiral reagent is important. Ephedrine and menthol give optical yields of around 50%, whereas the other alcohols utilised give low optical yield with the same organosilane. The substituents attached to the silicon atom also have considerable influence on the optical yield, and as we observed previously, α-naphthylphenylsilane gives the best results.

The value of catalysis by complexes of rhodium is well illustrated by comparison with asymmetric alcoholysis catalysed by Raney nickel [9] or by an amine [10], which yield racemic organosilanes. On the other hand, dichlorotetrakis(cyclooctene)dirhodium gives results which differ little from those ob-

TABLE 1

REACTIONS OF ASYMMETRIC ALCOHOLS WITH PROCHIRAL ORGANOSILANES [a]

$R^1R^2SiH_2$	R*OH	Catalyst	$R^1R^2R^3Si^*H$ [c]	$[\alpha]_D$ (°)	Configuration	Optical purity (%)
α-NpPhSiH$_2$ [b]	(—)-Menthol	$(PPh_3)_3RhCl$	α-NpPhMeSiH	+17.2	*R*	48
α-NpPhSiH$_2$	(—)-Cholesterol	$(PPh_3)_3RhCl$	α-NpPhMeSiH	+ 1.1	*R*	3
α-NpPhSiH$_2$	(+)-Cinchonine	$(PPh_3)_3RhCl$	α-NpPhEtSiH	— 3.2	*S*	13
α-NpPhSiH$_2$	(—)-Borneol	$(PPh_3)_3RhCl$	α-NpPhEtSiH	— 1.4	*S*	6
α-NpPhSiH$_2$	(—)-Ephedrine	$(PPh_3)_3RhCl$	α-NpPhMeSiH	+19.2	*R*	54
α-NpPhSiH$_2$	(+)-Ephedrine	$(PPh_3)_3RhCl$	α-NpPhMeSiH	—19.3	*S*	54
α-NpEtSiH$_2$	(—)-Menthol	$(PPh_3)_3RhCl$	α-NpPhEtSiH	— 5.1	*S*	21
α-NpPhCH$_2$SiH$_2$	(—)-Menthol	$(PPh_3)_3RhCl$	α-NpPhPhCH$_2$SiH	+ 1.2	*S*	20
Ph-i-BuSiH$_2$	(—)-Menthol	$(PPh_3)_3RhCl$	α-NpPh-i-BuSiH	— 3.0	*S*	16
PhMeSiH$_2$	(—)-Menthol	$(PPh_3)_3RhCl$	α-NpPhMeSiH	— 0.8	*S*	2
α-NpPhSiH$_2$	(—)-Menthol	Ni Raney	α-NpPhMeSiH	0.0		0
α-NpPhSiH$_2$	(—)-Ephedrine	Neant [d]	α-NpPhEtSiH	+ 0.5	*R*	2
α-NpPhSiH$_2$	(—)-Ephedrine	$[(C_8H_{14})_2RhCl]_2$ [e]	α-NpPhMeSiH	+18.0	*R*	50
α-NpPhSiH$_2$	(—)-Menthol	$[(C_8H_{14})_2RhCl]_2$ [e]	α-NpPhMeSiH	+13.7	*R*	38

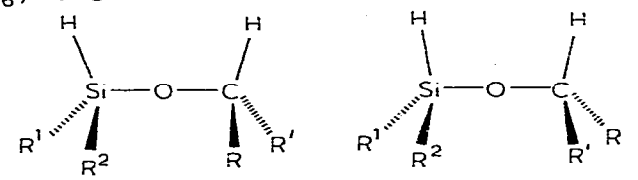
[a] Benzene solvent at 20°C. [b] α-Np = α-Naphthyl. [c] *R* (+)-α-NpPhMeSiH, $[\alpha]_D$ + 36.0° (pentane) [6]; *R* (+)-α-NpPhEtSiH, $[\alpha]_D$ + 24.6° (CCl_4) [7]; *S* (+)-α-NpPhPhCH$_2$SiH, $[\alpha]_D$ + 5.9° (pentane) [8]; *S* (—)-α-NpPh-i-BuSiH, $[\alpha]_D$ —18.7° (pentane) [5]. [d] The amino group on ephedrine is sufficient to catalyse the alcoholysis reaction [10]. [e] C_8H_{14} = cyclooctene.

tained with chlorotris(triphenylphosphine)rhodium.

We would emphasise that the reaction of ephedrine with α-naphthylphenylsilane followed by treatment with methylmagnesium bromide constitutes a useful method for the preparation of optically active α-naphthylphenylmethylsilane, which can be isolated optically pure after a single recrystallisation [2,b].

We also studied the asymmetric alcoholysis by racemic alcohols, following the method developed by Horeau and coworkers [11] (eq. 3).

$$R^1R^2SiH_2 + RR'CHOH \xrightarrow[C_6H_6,\ 20°C]{(PPh_3)_3RhCl}$$



(d,l) (d,l) (3)

The relative yield of the two diastereoisomers were determined by VPC or NMR and the results obtained are given in Table 2. Only the very sterically hindered alcohol, mesitylisopropylcarbinol gave results comparable to those obtained with menthol or ephedrine.

Utilisation of a chiral catalyst

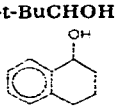
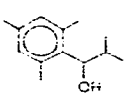
We subsequently investigated the effect of catalyst configuration on the reaction with achiral alcohols:

$$R^1R^2SiH_2 + ROH \xrightarrow[C_6H_6,\ 20°C]{\text{catalyst}} R^1R^2Si^*H(OR) + H_2 \quad (4)$$

catalyst = $[(C_8H_{14})_2RhCl]_2$ + chiral phosphine ((+)- or (—)-diop [12], menthyl- and neomenthyl-diphenylphosphine [13]).

TABLE 2

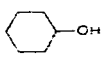
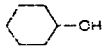
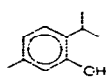
REACTIONS OF RACEMIC ALCOHOLS WITH PROCHIRAL ORGANOSILANES [a]

$R^1R^2SiH_2$	RR'CHOH	Catalyst	Diastereomer ratio	Optical yield [b] (%)
α-NpPhSiH$_2$	PhMeCHOH	$(PPh_3)_3RhCl$	60 : 40	20
α-NpPhSiH$_2$	Ph-t-BuCHOH	$(PPh_3)_3RhCl$	57 : 43	14
α-NpPhSiH$_2$		$(PPh_3)_3RhCl$	50 : 50	0
α-NpPhSiH$_2$		$(PPh_3)_3RhCl$	75 : 25	50
α-NpPhSiH$_2$	(—)-Ephedrine [c]	$(PPh_3)_3RhCl$	78 : 22	56 [c]
α-NpPhSiH$_2$	(+)-Ephedrine [c]	$(PPh_3)_3RhCl$	79 : 21	57 [c]

[a] Benzene solvent at 20°C. [b] Optical yield which could be obtained by reaction of a chiral alcohol [11]. [c] The reaction of methylmagnesium bromide on the mixture of diastereomers yields an organosilane with 54% optical purity (cf. Table 1). The results reported here with optically active alcohols show that the action of the Grignard reagent is stereospecific (respectively 96 and 95% stereoselectivity).

TABLE 3

REACTIONS OF ACHIRAL ALCOHOLS CATALYSED BY OPTICALLY ACTIVE RHODIUM COMPLEXES [a]

$R^1R^2SiH_2$	ROH	Catalyst [b]	$R^1R^2R^3SiH$	$[\alpha]_D$ (°)	Configuration	Optical purity (%)
α-NpPhSiH$_2$ [c]	MeOH	[(+)-diop]RhCl	α-NpPhMeSiH [d]	+1.0	*R*	3
α-NpPhSiH$_2$	i-PrOH	[(+)-diop]RhCl	α-NpPhEtSiH [d]	+1.9	*R*	8
α-NpPhSiH$_2$	t-BuOH	[(—)-diop]RhCl	α-NpPhMeSiH	—2.5	*S*	7
α-NpPhSiH$_2$		[(+)-diop]RhCl	α-NpPhEtSiH	+4.3	*R*	17
α-NpPhSiH$_2$		(NMDPP)$_2$RhCl	α-NpPhEtSiH	—0.5	*S*	2
α-NpPhSiH$_2$	Ph$_2$CHOH	[(—)-diop]RhCl [e]	α-NpPhMeSiH	—6.5	*S*	18 [e]
α-NpPhSiH$_2$	Ph$_2$CHOH	[(+)-diop]RhCl [e]	α-NpPhMeSiH	+6.7	*R*	19 [e]
α-NpPhSiH$_2$		[(—)-diop]RhCl	α-NpPhEtSiH	—2.3	*S*	9

[a] Benzene solvent at 20°C. [b] Prepared by reaction of a chiral phosphine with $[(C_8H_{14})_2RhCl]_2$; diop = 2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [12]; NMDPP = neomenthyldiphenylphosphine [13]. [c] α-Np = α-naphthyl. [d] Cf. footnote *c*, Table 1. [e] These two products are of course enantiomeric, the different optical purities observed are identical within the limits of experimental error.

The optical purity of the alkoxysilane was determined as before by treatment with a Grignard reagent (eq. 2). The results are presented in Table 3.

The optical yields observed here were low, not exceeding 19%, significantly inferior to those obtained by the hydrosilylation of ketones, which varied between 30% and 46% [1,a]. The latter method is still to be prefered for the preparation of bifunctionnal enantiomers therefore.

TABLE 4

REACTIONS OF CHIRAL ALCOHOLS CATALYSED BY OPTICALLY ACTIVE RHODIUM COMPLEXES [a]

$R^1R^2SiH_2$	R*OH	Catalyst [b]	$R^1R^2R^3SiH$	$[\alpha]_D$ (°)	Configuration	Optical purity (%)
α-NpPhSiH$_2$ [c]	(—)-Menthol	[(—)-diop]RhCl	α-NpPhMeSiH [d]	+11.0	*R*	31
α-NpPhSiH$_2$	(—)-Menthol	[(+)-diop]RhCl	α-NpPhMeSiH	+17.6	*R*	49
α-NpPhSiH$_2$	(—)-Menthol	(NMDPP)$_2$RhCl	α-NpPhMeSiH	+ 8.1	*R*	22
α-NpPhSiH$_2$	(—)-Menthol	(MDPP)$_2$RHCl	α-NpPhMeSiH	+16.0	*R*	44
α-NpPhSiH$_2$	(—)-Ephedrine [e]	[(—)-diop]RhCl	α-NpPhMeSiH	+15.1	*R*	42
α-NpPhSiH$_2$	(—)-Ephedrine [e]	[(+)-diop]RhCl	α-NpPhMeSiH	+16.5	*R*	46
α-NpPhSiH$_2$	(+)-Ephedrine [e]	[(—)-diop]RhCl	α-NpPhMeSiH	—15.7	*S*	44
α-NpPhSiH$_2$	(+)-Ephedrine [e]	[(+)-diop]RhCl	α-NpPhMeSiH	—14.3	*S*	40
α-NpPhSiH$_2$	(—)-Ephedrine	(NMDPP)$_2$RhCl	α-NpPhEtSiH [d]	+13.1	*R*	53
α-NpPhSiH$_2$	(—)-Ephedrine	(MDPP)$_2$RhCl	α-NpPhEtSiH	+12.9	*R*	52
α-NpPhSiH$_2$	(+)-Ephedrine	(NMDPP)$_2$RhCl	α-NpPhEtSiH	—13.4	*S*	54
α-NpPhSiH$_2$	(+)-Ephedrine	(MDPP)$_2$RhCl	α-NpPhEtSiH	—13.3	*S*	54

[a] Benzene solvent at 20°C. [b] Prepared by reaction of a chiral phosphine with $[(C_8H_{14})_2RhCl]_2$; diop = 2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [12]; NMDPP = neomenthyldiphenylphosphine; MDPP = menthyldiphenylphosphine [13]. [c] α-Np = α-naphthyl. [d] Cf. footnote *c*, Table 1. [e] Cf. footnote *c*, Table 3.

Finally, we studied the reaction of chiral alcohols in the presence of an asymmetric catalyst (eq. 4). The results are given in Table 4.

It is evident that the optical purities of the organosilanes obtained is not increased by the utilisation of an asymmetric catalyst instead of the achiral catalysts such as $(PPh_3)_3RhCl$ or $[(C_8H_{14})_2RhCl]_2$. In any event the configuration of the organosilane obtained is mainly determined by that of the alcohol taken. The configuration of the catalyst has a smaller influence on the optical purity. These two facts are particularly well illustrated by the series of experiments with ephedrine. Whatever asymmetric catalyst was used, the optical yields were similar to and at best equal to those obtained with $(PPh_3)_3RhCl$. This behaviour is significantly different from that observed for the hydrosilylation of (—) menthone [1b]. Then there were considerable variation in the optical yield and even changes in the configuration of the product, according to the catalyst used.

Mechanism

The activation of the organosilane by the catalyst is brought about by reversible oxidative addition of —Si—H to the rhodium complex, giving a pentacoordinate complex [14]:

$$L_3RhCl + R_3SiH \rightleftharpoons L_2ClHRhSiR_3 + L \qquad (5)$$

$(L = PPh_3)$

We have suggested that the asymmetric synthesis proceeds through the rapid establishment of a pre-equilibrium between two enantiomeric or diatereoisomeric complexes [1,2]. This implies that oxidative addition to the rhodium is fast and may be followed by an equally fast reductive elimination of the organosilane (eq. 5). With a view to substantiating the existence of this equilibrium we examined the isotopic exchange between the organosilanes R_3SiH and R'_3SiD (eq. 6).

$$Et_3SiH + Ph_3SiD \xrightleftharpoons[C_6H_6,\ 20°C]{0.5 \times 10^{-2}\ mol\ (PPh_3)_3RhCl} Et_3SiD + Ph_3SiH \qquad (6)$$

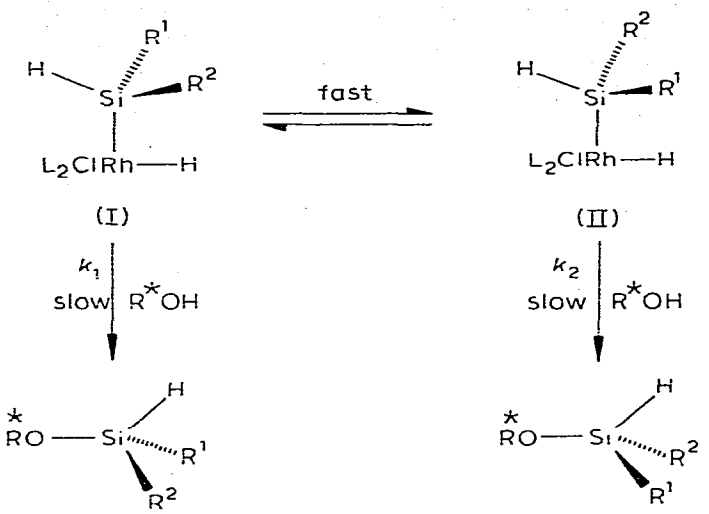
Exchange of protium and deuterium is instantaneous in the presence of 0.5% chlorotris(triphenylphosphine)rhodium, requiring a rapid and reversible activation of the organosilane, a process which has also been demonstrated in the case of iridium complexes [15].

Such exchanges must necessarily occur with complete retention of configuration at the silicon atom. Stereospecific reactions of optically active organosilanes, catalysed by $(PPh_3)_3RhCl$ [1,2] are not compatible with rapid exchange involving racemisation or inversion. Similar retention of stereochemistry has been shown in other exchange reactions of silanes catalysed by transition metals [16].

The results obtained are consistent with a slow reaction of the alcohol with the coordinated organosilane as the rate determining step in the proposed mechanism [3]. For the prochiral organosilanes, we can thus write a kinetic scheme analogous to that proposed for the hydrosilylation of ketones (Scheme 1) [1].

The complexes I and II, the structure of which have been studied [14,17,18], are enantiomeric when $L = PPh_3$. The optical yield depends on the relative rates of the reactions of the alcohol on the complexes I and II, that is the ratio k_1/k_2. When L is a chiral phosphine the optical yield depends in addition on the relative

SCHEME 1



stabilities of the two complexes, which in this case are diastereoisomeric and so do not have the same concentration in the mixture. The optical yield is then given by $k_1[I]/k_2[II]$, a function of three variables which do not all necessarily tend in the direction of maximum optical yield.

For the reaction of the alcohol with the complexes I and II, our results are consistent with nucleophilic attack on the silicon without prior coordination of the alcohol to the rhodium atom. The much greater effect on the optical yield of the configuration of the alcohol and of the substituents attached to the silicon atom, compared with the influence of the catalyst structure, suggests that during the reaction the interactions between alcohol and catalyst are weak, implying that there is no specific activation of the alcohol by the catalyst.

Conclusion

The asymmetric alcoholysis of prochiral organosilanes is a useful method for the preparation of optically active silanes. It provides a very attractive route to *R* or to *S*. α-Naphthylphenylmethylsilane [2,b] and permits stereochemical studies not otherwise feasible [19].

Experimental

All the manipulations were carried out under dry nitrogen. The Grignard reagents were prepared in the usual manner and titrated by iodometry. The NMR spectra were recorded on Varian A60 and T60 spectrometers. The chemical shifts δ are given in ppm relative to TMS. After the δ, the number of protons (nH) and the nature of the signal (s, singlet; d, doublet; t, triplet; q, quadruplet; m, multiplet) are indicated. The IR spectra were recorded on a Perkin—Elmer 257 spectrophotometer. The specific rotations were measured on a Perkin—Elmer 141 polarimeter.

(1) Preparation of the organosilanes and of the catalyst

All the starting materials were obtained by methods already described (see ref. 1 and references cited therein).

(2) Reactions of optically active alcohols

General technique

All the alcoholysis reactions were carried out in the same way at 20°C. 4.6×10^{-3} g (0.5×10^{-5} mol) of chlorotris(triphenylphosphine)rhodium was dissolved in 5 ml of anhydrous degassed benzene, 5×10^{-3} mol of an asymmetric alcohol dissolved in 5 ml of benzene was introduced by a syringe. The organosilane (5×10^{-3} mol) also dissolved in 5 ml of benzene was finally added. The reaction mixture was stirred until the evolution of gas stopped. The disappearance of the starting organosilane was monitored by TLC and when the reaction appeared to be complete the solvent removed under vacuum. It was confirmed by comparison of the NMR spectrum of the crude reaction product with that of an authentic sample [3,20] that formation of the alkoxysilane was quantitative. The residue was dissolved in 5 ml of anhydrous ether and added to a solution containing 10^{-2} mol of the appropriate Grignard reagent. The reaction mixture was stirred at room temperature and the formation of the trisubstituted silane was detected by TLC. The reaction mixture was then poured on to 50 ml of aqueous HCl ($\simeq 4$ *N*). After extraction with ether, the organic layer was washed with water and dried over anhydrous magnesium sulphate. After removal of the solvent, the residu was purified by preparative thin-layer chromatography (silica gel, eluant pentane/benzene 9 : 1). The isolated organosilane was identified by comparison of its NMR and IR spectra with those of samples already described [5,6,8].

α-Naphthylphenylsilane and (—)-menthol. The earlier method leads after treatment with methylmagnesium bromide to α-naphthylphenylmethylsilane ($[\alpha]_D$ + 17.2, *c* 10.6 (pentane), yield 92%).

α-Naphthylphenylsilane and (—)-cholesterol. α-Naphthylphenylmethylsilane was isolated ($[\alpha]_D$ + 1.1, *c* 8.3 (pentane), yield 85%).

α-Naphthylphenylsilane and (+)-cinchonine. α-Naphthylphenylethylsilane was isolated ($[\alpha]_D$ — 3.2, *c* 12.5 (CCl_4), yield 83%)

α-Naphthylphenylsilane and (—)-borneol. α-Naphthylphenylethylsilane was isolated ($[\alpha]_D$ — 1.4, *c* 36.2 (CCl_4), yield 89%).

α-Naphthylphenylsilane and (+)- or (—)-ephedrine. These two experiments have been already described (see ref. 2b).

α-Naphthylethylsilane and (—)-menthol. α-Naphthylphenylethylsilane was isolated ($[\alpha]_D$ — 5.1, *c* 7.6 (CCl_4), yield 89%).

α-Naphthylbenzylsilane and (—)-menthol. α-Naphtylphenylbenzylsilane was isolated ($[\alpha]_D$ + 1.2, *c* 30.6 (pentane), yield 82%).

Phenylisobutylsilane and (—)-menthol. α-Naphthyiphenylisobutylsilane was isolated ($[\alpha]_D$ — 3.0, *c* 12.3 (pentane), yield 79%).

Phenylmethylsilane and (—)-menthol. α-Naphthylphenylmethylsilane was isolated ($[\alpha]_D$ — 0.8, *c* 15.0 (pentane), yield 91%).

Ni Raney as catalyst. The reaction of α-naphthylphenylsilane and (—)-men-

thol followed by treatment with methylmagnesium bromide yielded α-napthylphenylmethylsilane ($[\alpha]_D$ 0, yield 67%).

Without catalyst. The reaction of α-naphthylphenylsilane and (—)-ephedrine followed by treatment with ethylmagnesiumbromide yielded α-naphthylphenylethylsilane ($[\alpha]_D$ + 0.5, *c* 10.5 (pentane), yield 70%).

Dichlorotetrakiscyclooctene dirhodium as catalyst. The menthanolysis of α-naphthylphenylsilane followed by treatment with methylmagnesium bromide yielded α-naphthylphenylmethylsilane ($[\alpha]_D$ + 13.7, *c* 21.2 (pentane), yield 91%).

The reaction of (—)-ephedrine and α-naphthylphenylsilane followed by action of methylmagnesium bromide lead to α-naphthylphenylmethylsilane ($[\alpha]_D$ + 18.0, *c* 23.8 (pentane), yield 85%).

(3) Reactions of α-naphthylphenylsilane and racemic alcohols

The reactions of racemic alcohols are carried out as above (cf. §2 general technique). The diastereomeric alkoxysilanes were isolated after distillation and the mixture was analysed by VPC or NMR. The diastereomer ratio was the same before and after distillation.

1-Phenylethanol. The α-naphthylphenyl(phenyl-1-ethoxy)silanes diastereomers were isolated in a 89% yield and had similar properties to those already described [3]. Diastereomer ratio 2 : 3.

1-Phenyl-2,2-dimethylpropanol. The α-naphthylphenyl(phenyl-t-butyl methoxy)silanes were isolated in a 86% yield. NMR: δ 7.7 ppm (17 H, m), 5.65 (0.43H, s), 5.55 (0.57H, s), 4.45 (0.43H, s) 4.35 (0.57H, s), 0.9 (9H, m).

α-Hydroxytetraline. The diastereomeric alkoxysilane were obtained in 75% yield (Eb. 220—230/0.4 mmHg). NMR: δ 7.6 ppm (16H, m), 5.85 (0.5H, s) 5.80 (0.5H, s), 4.9 (1H, m), 2.6 (2H, m), 1.8 (4H, m). Analysis: Found: C, 81.82; H, 6.32; Si, 7.11. $C_{26}H_{24}SiO$ calcd.: C, 82.49; H, 6.39; Si, 6.89%.

1-Mesityl-2-methylpropanol. The alkoxysilanes were produced in a 91% yield: NMR: δ 7.5 ppm (solvent C_6D_6 (14H, m), 5.8 (0.25H, s), 5.65 (0.75H, s), 4.85 (0.25H, d), 4.75 (0.75H, d), 2.7 (1.55H, s), 2.6 (0.75H, s), 2.4 (1H, m), 2.1 (1.55H, s), 2.05 (0.75H, s), 1.75(0.75H, s), 1.65 (1.55H, s) 1.35 (1.55H, d), 1.3 (0.75H, d), 0.65 (0.75H, d), 0.55 (1.55H, d). VPC (capillary column OV.17, 20 m, 240°C): 2 peaks 25 : 75. Analysis: Found: C, 81.96; H, 7.57; Si, 6.82. $C_{28}H_{32}SiO$ calcd.: C, 82.02; H, 7.60; Si, 6.61%.

Ephedrine. see ref. 2b.

(4) Reactions in the presence of an asymmetric catalyst

All these experiments were carried out in the same way as above (cf. § 2 general technique). The asymmetric catalyst was formed "in situ" by dissolving 0.5×10^{-5} mol of $[(C_8H_{14})_2RhCl]_2$ and 10^{-5} mol of (+)- or (—)-diop, or 2×10^{-5} mol of MDPP or NMDPP, in 5 ml of anhydrous degassed benzene. The mixture was stirred during 10 min at room temperature before adding the reagents.

Methanol and (+)-diop. α-Naphthylphenylmethylsilane ($[\alpha]_D$ + 1.0, *c* 34.0 (pentane), yield 92%).

Isopropanol and (+)-diop. α-Naphthylphenylethylsilane ($[\alpha]_D$ + 1.9, *c* 21.8 (CCl_4), yield 88%).

Tertiobutanol and (—)-diop. α-Naphthylphenylmethylsilane ($[\alpha]_D$ — 2.5, *c* 29.2 (pentane), yield 91%).

Cyclohexanol and (+)-diop. α-Naphthylphenylethylsilane ($[\alpha]_D$ + 4.3, *c* 13.0 (CCl_4), yield 86%).

Cyclohexanol and NMDPP. α-Naphthylphenylethylsilane ($[\alpha]_D$ — 0.5, *c* 12.5 (CCl_4), yield 83%).

Diphenylmethanol and (—)-diop. α-Naphthylphenylmethylsilane ($[\alpha]_D$ — 6.5, *c* 16.5 (pentane), yield 90%).

Diphenylmethanol and (+)-diop. α-Naphthylphenylmethylsilane ($[\alpha]_D$ + 6.7, *c* 20.3 (pentane) yield 92%).

Thymol and (—)-diop. α-Naphthylphenylethylsilane ($[\alpha]_D$ — 2.3, *c* 33.3 (CCl_4), yield 85%).

(—)-Menthol. α-Naphthylphenylmethylsilane: (—)-diop, $[\alpha]_D$ + 11.0, *c* 28.2 (pentane), yield 91%; (+)-diop, $[\alpha]_D$ + 17.6, *c* 27.9 (pentane), yield 90%; NMDPP, $[\alpha]_D$ + 8.1, *c* 10.8 (pentane), yield 87%; MDPP, $[\alpha]_D$ + 16.0, *c* 9.1 (pentane), yield 90%.

(—)-Ephedrine. α-Naphthylphenylmethylsilane: (—)-diop, $[\alpha]_D$ + 15.1, *c* 10.8 (pentane), yield 93%; (+)-diop, $[\alpha]_D$ + 16.5, *c* 14.8 (pentane), yield 89%; α-naphthylphenylethylsilane: NMDPP, $[\alpha]_D$ + 13.1 (*c* 13.9 (CCl_4), yield 91%, MDPP, $[\alpha]_D$ + 12.9, *c* 19.9 (CCl_4), yield 91%.

(+)-Ephedrine. α-Naphthylphenylmethylsilane: (—)-diop, $[\alpha]_D$ — 15.7, *c* 12.7 (pentane), yield 87%; (+)-diop, $[\alpha]_D$ — 14.3, *c* 9.9 (pentane), yield 89%; α-naphthylphenylethylsilane: NMDPP, $[\alpha]_D$ — 13.4, *c* 25,8 (CCl_4), yield 90%; MDPP, $[\alpha]_D$ — 13.3, *c* 15,6 (CCl_4), yield 90%.

(5) Hydrogen—deuterium exchange reaction

0.116 g (10^{-3} mol) of triethylsilane and 0.261 g of triphenyldeuterosilane were dissolved in 2 ml of C_6D_6. Then, 4.7×10^{-3} g (0.5×10^{-5} mol) of chlorotris(triphenylphosphine)rhodium was added and the mixture straightaway analysed by NMR: Two signals of equal intensities were observed: δ 5.65 (Ph_3SiH, s) and 3.85 ppm (Et_3SiH, m).

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