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CATALYTIC ASYMMETRIC HYDROSILYLATION OF KETONES

II *. CHIRAL PHOSPHINE–RHODIUM COMPLEX-CATALYZED HYDROSILYLATION **,***

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Summary

A cationic rhodium complex with (*R*)-benzylmethylphenylphosphine as ligand was found to be an effective catalyst for asymmetric hydrosilylation of a variety of prochiral ketones. The optical yield markedly depends on the structure of hydrosilanes as well as on that of ketones employed. Optical yields up to 61.8% have been achieved. A mechanism involving the formation of diastereomeric α-siloxyalkyl-rhodium intermediates is proposed for the asymmetric hydrosilylation of ketones.

The asymmetric hydrosilylation was also found to be catalyzed by ((−)-DIOP)Rh(S)Cl, where DIOP stands for 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.

Introduction

Asymmetric reduction of prochiral carbonyl compounds continues to be of interest from both practical and theoretical points of view. Many reports [2] of studies on the asymmetric Meerwein–Ponndorf–Verley reduction, asymmetric Grignard reduction, and reductions by chiral metal hydride complexes have appeared. Izumi and corworkers have extensively studied [3] heterogeneous asymmetric hydrogenation of carbonyl compounds, especially acetoacetic acid esters, with a modified Raney nickel catalyst. When we began our investigation of the catalytic asymmetric hydrosilylation of simple ketones using chiral transition metal complexes as catalysts, definite evidence for an activation of the carbonyl

* For Part I see [5].
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group by transition metal complexes was unknown except for the rather special case of hexafluoroacetone [4].

In the preceding paper [5] we reported that the catalytic hydrosilylation of ketones with methyldichlorosilane proceeds under mild conditions when dichlorobis(dimethylphenylphosphine)-di-μ-chlorodiplatinum(II) is used as a catalyst, and that its chiral phosphine analogs catalyze the asymmetric hydrosilylation of a series of alkyl phenyl ketones to give, after hydrolysis, partially active 1-phenylalkanols. Although the optical yields obtained were rather low, we were convinced that with a proper choice of catalyst much greater asymmetric induction might be realized.

In 1970, Schrock and Osborn reported [6] that a cationic rhodium complex of the type $[RhL_2H_2S_2]^+$, where L is a relatively basic phosphine and S is a solvent molecule, catalyzes the hydrogenation not only of olefinic compounds but also of simple ketones under mild conditions. The findings that the cationic complex activates carbonyl groups of ketones under conditions of hydrogenation greatly influenced our choice of complex. Accordingly, we have prepared a cationic rhodium complex with (*R*)-benzylmethylphenylphosphine (BMPP) as ligand, and catalytic asymmetric hydrosilylation of prochiral ketones has been carried out in the presence of this chiral cationic rhodium complex. Reactions involving it as catalyst were found to proceed with much higher enantioselectivity than in the platinum(II) system. In this paper, we describe in detail the catalytic asymmetric hydrosilylation of ketones, focusing our attention on the dependence of optical yields on the structure of the hydrosilanes used. After this investigation had been completed, a similar rhodium complex-catalyzed asymmetric hydrosilylation of ketones was reported independently by three research groups [7—9].

Results and discussion

The cationic rhodium complex, $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2(NBD)]^+ClO_4^-$ (I) (NBD = 2,5-norbornadiene), was prepared according to the procedure reported by Schrock and Osborn [10], by the reaction of di-μ-chlorobis(NBD)dirhodium with (*R*)-benzylmethylphenylphosphine in the presence of sodium perchlorate. I was then treated with molecular hydrogen in benzene—dichloromethane (5 : 1) solution to give in situ $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ (II) (S = solvent), which was used as a catalyst precursor for the following hydrosilylations (eq. 1 and 2).

$$\tfrac{1}{2}[Rh(NBD)Cl]_2 + 2L^* \xrightarrow{NaClO_4} \underset{(I)}{[RhL^*_2(NBD)]^+ClO_4^-} \qquad (1)$$

$[\alpha]_D^{20}$ +29° (*c* 0.3, CH_2Cl_2)

$$\underset{(I)}{[RhL^*_2(NBD)]^+ClO_4^-} \xrightarrow[C_6H_6/CH_2Cl_2]{H_2} \underset{(II)}{[RhL^*_2H_2S_2]^+ClO_4^-} \qquad (2)$$

L^* = (*R*)-$(PhCH_2)MePhP$ (70 or 79% optical purity)

Attempts to prepare a cationic rhodium complex [Rh{(−)-DIOP}(NBD)]$^+$-ClO_4^- *, where DIOP stands for 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane, were unsuccessful, and known ((−)-DIOP)Rh(S)Cl (III) [11] was used. Recently, Kagan and coworkers have reported [8] that ((+)-DIOP)Rh(S)Cl is an effective catalyst for asymmetric hydrosilylation of ketones.

Asymmetric hydrosilylation of ketones catalyzed by [Rh{(R)-(PhCH$_2$)MePhP}$_2$-H$_2$S$_2$]$^+$ClO$_4^-$ (II)

All experiments were carried out in degassed sealed glass tubes. In typical runs the catalyst concentration was 5×10^{-4} mole per mole ketone, and an equivalent of a hydrosilane for the ketone was used. The mixture was heated at a given temperature for 40 h. The hydrosilylation proceeded almost quantitatively. The hydrosilylation product, a silyl ether of a sec-alcohol, was isolated by distillation and characterized by its IR and NMR spectra and elemental analyses. The silyl ether was then converted into the corresponding sec-alcohol by treatment with potassium hydroxide in aqueous methanol or with excess methyllithium followed by acid hydrolysis (eq. 3). The absolute configuration and optical purity of the sec-alcohol thus obtained were determined on the basis of the known

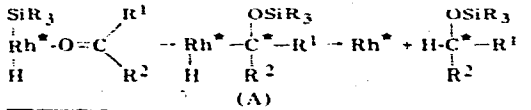
$$R^1COR^2 + HSiR_3 \xrightarrow{II} R^1R^2\overset{*}{C}HOSiR_3 \rightarrow R^1R^2\overset{*}{C}HOH \qquad (3)$$

maximum rotation of the pure enantiomer. All results obtained are summarized in Tables 1, 2, and 3.

In the first set of experiments (Table 1), the asymmetric addition of trialkylsilanes to a series of alkyl phenyl ketones in the presence of II was found to give predominantly (*S*)-1-phenylalkanols with one exception. Fairly good optical yields were obtained from the reaction of alkyl phenyl ketones, except for 2-phenylacetophenone, with phenyldimethylsilane. The optical yields of 31.6, 43.1, 56.3, and 61.8% for acetophenone, propiophenone, isobutyrophenone, and pivalophenone, respectively, are much higher than those observed in asymmetric hydrosilylation of the corresponding ketones catalyzed by the platinum-(II) [5] with the same chiral phosphine as used here. These values compare well with those reported in stoichiometric reductions of ketones using chiral Grignard reagents or chiral metal hydride complexes such as $LiAlH_m(OR^*)_n$ [2,12].

It should be noted that the extent of asymmetric hydrosilylation depends strongly upon the structure of the hydrosilanes employed. With phenyldimethylsilane optical yields are generally more than several times as high as with trimethylsilane. Most remarkable is the fact that the addition of phenyldimethylsilane to pivalophenone gave the silyl ether of (*S*)-2,2-dimethyl-1-phenylpropanol, while trimethylsilane led to the (*R*)-enantiomer. The marked effect of silane structure on a stereochemical outcome may be best rationalized as proceeding in the sequence depicted by Scheme 1.

SCHEME 1



(A)

* Preparation of the cationic complex has been reported recently [26].

TABLE 1

ASYMMETRIC HYDROSILYLATION OF ALKYL PHENYL KETONES WITH $HSiR_3$ CATALYZED BY $[RhCl\{(R)\text{-}(+)\text{-}CH_2CH_2MePhP\}_2]_2[S_2]^{2+}(ClO_4^-)_2$ (II) [a,b]

Ketone	Yield (%)	Silyl ether $[\alpha]_D^{20}$ (neat)	Alcohol [c] $[\alpha]_D^{20}$ (neat)	Optical yield [d] (%) (Configuration)
$HSiR_3$ = $HSiMe_2Ph$				
MeCOPh	97	−19.21	−9.61	51.6 (*S*)
EtCOPh	94	−24.54	8.47	13.1 (*S*)
i-PrCOPh	62	−28.48	−18.81 [e]	56.3 (*S*)
t-BuCOPh	84	−24.92	−11.20 [f]	61.8 (*S*)
$PhCH_2COPh$	44	−0.30	0 [g]	
$HSiR_3$ = $HSiMe_3$				
MeCOPh	100	−2.25	1.55	5.1 (*S*)
EtCOPh	92	−3.23	1.26	6.3 (*S*)
i-PrCOPh	98	−1.78	1.23 [e]	3.7 (*S*)
t-BuCOPh	81	+10.50	+5.10 [f]	28.1 (*R*)
$PhCH_2COPh$	70	0.37	0 [g]	
$HSiR_3$ = $HSiMePh_2$				
EtCOPh	65 [h]	−9.67	4.00	20.1 (*S*)
$HSiR_3$ = $HSiMeEt_2$				
EtCOPh	42 [i,j]	−0.55	−0.28	1.3 (*S*)

[a] The phosphine of 70% optical purity was used unless otherwise noted. [b] Reactions at 50 °C for 10 h in a sealed tube. [c] The specific rotations of pure enantiomers reported are: (*S*)-1-phenylethanol $[\alpha]_D^{19}$ −33.5 (neat) [16], (*S*)-1-phenylpropanol, $[\alpha]_D^{22}$ −28.1° (neat) [16], (*S*)-2-methyl-1-phenylpropanol $[\alpha]_D^{25}$ −8.7 (ether) [16], (*R*)-2,2-dimethyl-1-phenylpropanol, $[\alpha]_D^{20}$ +25.9° (benzene) [16], (*S*)-1,2-diphenylethanol $[\alpha]_D^{23}$ +56.1° (ethanol) [17]. The enantiomeric purities of these 1-phenylalkanols were also determined directly by NMR measurement with the aid of a chiral shift reagent, tris[3-(trifluoromethylhydroxymethylene)-(+)-camphorato]europium(III) [18]. [d] Corrected for the optical purity of the chiral phosphine used. [e] Specific rotation in ether. [f] In benzene. [g] In ethanol. [h] Heated at 80 °C for 120 h. [i] Heated at 70 °C for 50 h. [j] The phosphine of 79% optical purity was used.

The proposed mechanism involves the following steps. (*a*) Oxidative addition of the hydrosilane to the cationic rhodium complex to which a ketone is coordinated. (*b*) The ketone carbonyl, which is activated by its coordination with the rhodium complex, inserts into the resulting silicon—rhodium bond to form diastereomeric α-siloxyalkylrhodium intermediates A. (*c*) Finally, the product, an optically active silyl ether of a sec-alcohol, is formed from reductive elimination of the diastereomeric intermediates. Of these steps, step *b* must play the most important role in inducing asymmetry at the carbonyl carbon because of the formation of a pair of diastereomeric α-siloxyalkyl—rhodium intermediates, in which a predominant configuration and the extent of enantiomeric excess of the product already would have been determined. It is, therefore, reasonable that the steric demands of not only the chiral phosphine ligand but also of the substituents on the silicon atom bound to the rhodium catalyst exhibit a remarkable effect on the selection of enantiotopic faces of a prochiral ketone.

Such marked effects of the structure of hydrosilanes as mentioned above on the stereoselectivity have not been observed in the asymmetric hydrosilylation of prochiral olefins [13]. Since the key step in the hydrosilylation of olefins is the formation of alkylmetal intermediates which arise from the insertion of a coordinated olefin into a hydridometal moiety, the silyl group, which is still

bound to the metal throughout the course of formation of the alkylmetal intermediates, may not exert any significant steric effect on the stereoselectivity.

It is conceivably possible to argue that the hydrosilylation of ketones proceeds, by analogy to that of olefins, via alkoxyrhodium intermediates which arise from the insertion of ketone carbonyl into the hydridorhodium moiety. In fact, the intervention of an alkoxyrhodium has been proposed by Schrock and Osborn for the hydrogenation of ketones catalyzed by cationic rhodium complexes [6]. However, such a mechanism involving alkoxyrhodium intermediates would not give rise to the observed changes in optical yields on changing the silane structure. In addition, the fact that the asymmetric hydrogenation of acetophenone catalyzed by the same chiral rhodium complex II has been found to give (*R*)-1-phenylethanol in low optical yield [14] may reinforce the argument on the difference in the key steps between hydrogenation and hydrosilylation of ketones. Ojima and coworkers have reported previously [15] steric effects of hydrosilanes similar to those mentioned above in the stereoselective hydrosilylation of terpene ketones such as menthone or camphor.

Hydrosilylation of several dialkyl ketones with phenyldimethylsilane and trimethylsilane in the presence of II also was carried out (Table 2). The results show that no significant asymmetric induction was observed in the hydrosilylation of 3,3-dimethyl-2-butanone, 2-hexanone, and 2-butanone. On the other hand, the reactions of 1-phenyl-2-propanone with either hydrosilane gave the respective silyl ethers of (*S*)-1-phenyl-2-propanol in higher than 10% optical yield. Therefore, it may be said that the presence of a phenyl group in the ketone substrate, such as 1-phenyl-2-propanone and alkyl phenyl ketones, necessarily favors the asymmetric induction in the present reaction systems.

The addition of dialkylsilanes to ketones in the presence of II proceeded readily at 20 °C to give optically active silyl ethers, the results obtained being shown in Table 3. Several features of these reactions are seen in Table 3. With dialkylsilanes occasional formation of silyl enol ethers accompanying the asym-

TABLE 2

ASYMMETRIC HYDROSILYLATION OF DIALKYL KETONES WITH $HSiR_1$ CATALYZED BY [Rh(*R*-(PhCH(Me)NMePhP)$_2$H$_2$S)]$^+ClO_4^-$ (II)[a]

Ketone	Yield (%)	Silyl ether $[\alpha]_D^{25}$ (neat)	Alcohol[b] $[\alpha]_D^{25}$ (neat)	Optical yield[c] (%) (Configuration)
$HSiR_1$ = $HSiMe_2Ph$				
$PhCH_2COMe$	69	+3.74	+3.02	15.3 (*S*)
t-BuCOMe	46	0	0.10	1.8 (*R*)
n-BuCOMe	64	−0.23	0.44	5.4 (*R*)
$HSiR_1$ = $HSiMe_3$				
$PhCH_2COMe$	76	+3.68	+1.96	10.0 (*S*)
t-BuCOMe	75	0.15	0.09	1.6 (*R*)
n-BuCOMe	82	0.32	0.36	4.4 (*R*)
EtCOMe	79	+0.03	0	–

[a] Reactions at 50 °C for 40 h in a sealed tube. [b] The specific rotations of pure enantiomers are: (*R*)-1-phenylpropan-2-ol: $[\alpha]_D^{25}$ −28.1° (neat) [19]; (*S*)-3,3-dimethylbutan-2-ol: $[\alpha]_D^{20}$ +7.84° (neat) [20]; (*S*)-hexan-2-ol: $[\alpha]_D^{15}$ +11.68° (neat) [21]; (*S*)-butan-2-ol: $[\alpha]_D^{20}$ +13.83° (neat) [19]. [c] Corrected for the optical purity of the phosphine used (70%).

TABLE 3

ASYMMETRIC HYDROSILYLATION OF KETONES WITH H_2SiR_2 CATALYZED BY [Rh{(*R*)-(PhCH$_2$)MePhP}$_2$H$_2$S$_2$]$^+$ClO$_4^-$ (II) [a]

Ketone	Yield (%)	Silyl ether $[\alpha]_D^{20}$ (neat)	Alcohol $[\alpha]_D^{20}$ (neat)	Optical yield [b] (%) (Configuration)
H_2SiR_2 = H_2SiEt_2				
EtCOPh	91 [c]	+0.87	+0.45	2.0 (*R*)
t-BuCOPh	78	+1.06 [d]	+0.59 [e]	3.3 (*R*)
t-BuCOMe	90	−3.23	−1.42	23.0 (*R*)
H_2SiR_2 = H_2SiPh_2				
MeCOPh	84	+7.83	+6.34	14.6 (*R*)
EtCOPh	83	+2.11	+0.96	4.4 (*R*)
t-BuCOMe	84	−2.16	−1.39	22.5 (*R*)
H_2SiR_2 = $H_2SiMePh$				
EtCOPh	84 [f]	--	+2.59	11.7 (*R*)

[a] Reactions at 20°C for 40 h in a sealed tube. [b] Optical yield is calculated on the basis of specific rotation of pure enantiomer (see the footnotes of Tables 1 and 2), and corrected for the optical purity of the phosphine used (79%). [c] Including 17% of Ph(HSiEt$_2$O)C=CHCH$_3$. [d] The chiral phosphine of 70% optical purity was used. [e] In benzene. [f] A mixture of diastereoisomers associated with asymmetric silicon atom (ca. 1 : 1 by NMR analysis).

metric addition reaction was observed (see footnote *c* in Table 3). Of interest is that the reaction of propiophenone with any of the dialkylsilanes always gave a silyl ether of (*R*)-1-phenylpropanol in contrast to the reaction with trialkylsilanes. Furthermore, it is noteworthy that the optical yield in the hydrosilylation of 3,3-dimethyl-2-butanone was much improved by the use of dialkylsilanes, while the reaction with trialkylsilanes gave no appreciable asymmetric induction.

In conclusion, all results described here clearly indicate that an optimum match of ketone and hydrosilane with a given chiral catalyst does attain a high optical yield, although the choice of the catalyst is only empirical at the present time.

Asymmetric hydrosilylation of ketones catalyzed by ((−)-DIOP)Rh(S)Cl (III)

The ability of III to catalyze the asymmetric hydrosilylation of ketones also was examined. The addition of dialkylsilanes to alkyl phenyl ketones in the presence of III took place readily at 50°C to give predominantly the (*R*)-adduct, except for the case where the silyl ether of (*S*)-2,2-dimethyl-1-phenylpropanol was produced from the reaction between pivalophenone and diphenylsilane. Hydrosilylation of alkyl phenyl ketones with trialkylsilanes, on the other hand, required higher reaction temperatures, and the optical yields were generally much lower than with dialkylsilanes. The data obtained for asymmetric hydrosilylation catalyzed by III are summarized in Table 4. A marked dependence of the optical yields on the structure of hydrosilanes also was observed with this catalyst system.

Kagan and coworkers have reported [8] similar results using ((+)-DIOP)Rh(S)Cl or a polymer-supported rhodium complex related to it. α-Naphthylphenylsilane is found to be the most useful silane of those examined.

TABLE 4

ASYMMETRIC HYDROSILYLATION OF ALKYL PHENYL KETONES CATALYZED BY ((−)-DIOP)-Rh(S)Cl (III) [a]

Ketone	Yield (%)	Silyl ether $[\alpha]_D^{20}$ (neat)	Alcohol $[\alpha]_D^{20}$ (neat)	Optical yield (%) (Configuration)
Silane = H_2SiEt_2				
MeCOPh	90	+14.13	+11.59	26.6 (*R*)
EtCOPh	83	+26.97	+12.89	45.9 (*R*)
i-PrCOPh	89	+5.37	+4.69 [b]	9.8 (*R*)
t-BuCOPh	83	−12.02	−6.56 [c]	25.3 (*S*)
Silane = H_2SiPh_2				
MeCOPh	81	+16.43	+13.29	30.6 (*R*)
EtCOPh	81	+17.40	+7.92	28.2 (*R*)
i-PrCOPh	72	+16.63	+13.07 [b]	27.4 (*R*)
t-BuCOPh	75	+20.47	+10.63 [c]	41.0 (*R*)
Silane = $HSiMe_2Ph$				
MeCOPh [d]	35	+2.46	—	2.8 [e] (*R*)
EtCOPh [d]	54	+3.94	—	4.8 [e] (*R*)
t-BuCOPh [d]	41	+9.51	—	16.5 [e] (*R*)
Silane = $HSiMe_3$				
EtCOPh [d]	62	+3.21	—	4.4 [e] (*R*)
t-BuCOPh [f]	83	+7.57	—	14.2 [e] (*R*)

[a] Reactions at 50°C for 40 h in a sealed tube. Catalyst = 0.1 mol%. [b] Specific rotation in ether. [c] In benzene. [d] Heated at 70°C. [e] Optical yield was calculated on the basis of specific rotation of the optically pure silyl ethers which was estimated by data indicated in Table 1. [f] Heated at 90°C.

Experimental

General comments

A Varian Aerograph Model 90P, equipped with a 20 ft. column packed with Silicone DC550 (30% on Celite) or PEG 20M (30% on Celite), was used for isolation and purification of the products. NMR spectra were obtained on a Varian EM-360 spectrometer, IR spectra with a Hitachi EPI-G3 Grating spectrophotometer, and optical rotations were measured with a Yanagimoto OR-50 automatic polarimeter.

(*R*)-Benzylmethylphenylphosphine (BMPP) [22] and (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((−)-DIOP) [11] were prepared by reported methods.

Preparation of [Rh{(R)-(PhCH$_2$)MePhP}$_2$(NBD)]$^+$ClO$_4^-$ (I)

The procedure reported by Schrock and Osborn [10] for preparing the complexes of the type [RhP$_2$(NBD)]$^+$ClO$_4^-$ (P = tertiary phosphine) was modified as follows: Under an argon atmosphere 0.40 g (0.87 mmol) of di-μ-chlorobis(2,5-norbornadiene)dirhodium and 0.25 g (2.02 mmol) of sodium perchlorate were placed in a 30 ml flask, and 1.7 ml of degassed tetrahydrofuran was added. To the suspension, 0.77 g (3.62 mmol) of (*R*)-BMPP (79% optical purity) was added dropwise with stirring. The mixture was stirred for 10 min, and then 15 ml of anhydrous ether was added dropwise to the red cloudy solution. The orange

precipitate was collected by filtration and the cake thus obtained then was dissolved in dichloromethane, leaving sodium chloride behind. The dichloromethane solution was reduced to 1 ml in vacuo and 12 ml of anhydrous ether was added. The orange powder was filtered, washed with two portions of each 5 ml of ether, and dried in vacuo to give 1.20 g (95%) of I: $[\alpha]_D^{20}$ + 29° (*c* 0.275, dichloromethane). (Found: C, 56.54; H, 5.83; Cl, 5.19. $C_{35}H_{38}ClO_4P_2Rh$ calcd.: C, 58.15; H, 5.30; Cl, 4.90%.) The same complex but with the phosphine of 70% optical purity also was prepared.

I was treated with molecular hydrogen in benzene/dichloromethane (5 : 1) solution to generate $[Rh\{(R)\text{-}(PhCH_2)MePhP\}_2H_2S_2]^+ClO_4^-$ (II) with the elimination of norbornane. The solvated dihydride species was used as a catalyst for the present reaction.

Asymmetric hydrosilylation of ketones

All reactions were carried out in glass ampoules. A ketone (40 mmol), a hydrosilane (40 mmol), and a chiral catalyst (2 or 4 × 10^{-2} mmol) were placed in a glass ampoule, and the mixture was degassed by several freeze–thaw cycles under reduced pressure. The ampoule then was sealed in vacuo and heated over a period of 40 h. The product was isolated by fractional distillation or by preparative GLC after flash distillation to give an optically active silyl ether. The silyl ether was characterized by its IR and NMR spectra and elemental analyses. These data are listed in Tables 5 and 6. The silyl ether was converted into the corresponding alcohol by hydrolysis with potassium hydroxide in aqueous methanol where possible, or by methylation with excess methyllithium followed by acid hydrolysis. The optical yield was determined by comparison of specific rotation of the obtained alcohol with that of the pure enantiomer as reported in the literature (see footnotes of Tables 1 and 2).

All the results for asymmetric hydrosilylation of ketones are collected in Tables 1–4. Two examples of the typical procedure are given below.

Reaction of pivalophenone with phenyldimethylsilane catalyzed by II Through a solution of 14 mg (2 × 10^{-2} mmol) of I (70% optical purity) in 3.0 ml of degassed benzene/dichloromethane (5:1) molecular hydrogen was bubbled for 10 min, and to the catalyst solution 6.5 g (40 mmol) of pivalophenone and 5.5 g (40 mmol) of phenyldimethylsilane were added successively. The mixture was heated at 50°C over a period of 40 h in a sealed, degassed glass ampoule. The product was isolated by distillation through a short Vigreux column to give 10.0 g (84%) of 2,2-dimethyl-1-phenylpropylphenyldimethylsilyl ether, b.p. 118 °C/2.5 Torr, n_D^{20} 1.5218, d_4^{20} 0.9726, $[\alpha]_D^{20}$ −24.92° (neat). The NMR and analytical data are shown in Tables 5 and 6. To a tetrahydrofuran solution of the silyl ether, a slightly excess amount of methyllithium in ether solution was added. The mixture was heated at reflux for 3 h, and then hydrolyzed with dilute hydrochloric acid. After work-up in the usual manner, fractional distillation gave quantitatively 2,2-dimethyl-1-phenylpropanol, $[\alpha]_D^{20}$ −11.20° (*c* 4, benzene). Absolute configuration and optical purity were determined on the basis of the known values of $[\alpha]_D^{25}$ +25.9° (benzene) for (*R*)-2,2-dimethyl-1-phenylpropanol [16]. Taking account of an optical purity of the phosphine (70%), the optical yield is 61.8%.

Reaction of propiophenone with diphenylsilane catalyzed by III In a degassed

TABLE 5

PHYSICAL CONSTANTS AND ANALYTICAL DATA FOR HYDROSILYLATION PRODUCTS

Compound	B.p. (°C/Torr)	n_D^{20}	d_4^{20}	Found (calcd.)(%)	
				C	H
MePhCHOSiMe$_2$Ph	118/3	1.5314	0.9955	74.90(74.95)	7.81(7.86)
EtPhCHOSiMe$_2$Ph	123/3	1.5272	0.9863	75.74(75.50)	8.41(8.20)
i-PrPhCHOSiMe$_2$Ph	124/2.5	1.5233	0.9771	76.10(76.00)	8.57(8.50)
t-BuPhCHOSiMe$_2$Ph	118/2.5	1.5218	0.9726	76.20(76.45)	8.99(8.78)
PhCH$_2$PhCHOSiMe$_2$Ph	145–149/0.02	1.5622	1.0372	79.26(79.47)	7.13(7.28)
PhCH$_2$MeCHOSiMe$_2$Ph	137/5	1.5267	0.9850	75.80(75.50)	8.40(8.20)
t-BuMeCHOSiMe$_2$Ph	96/3	1.4783	0.9051	71.36(71.12)	10.42(10.23)
n-BuMeCHOSiMe$_2$Ph	97/4	1.4761	0.9018	71.24(71.12)	10.52(10.23)
MePhCHOSiMe$_3$ [a]	49.5/3	1.4704	0.9026	68.27(67.98)	9.60(9.33)
EtPhCHOSiMe$_3$	62/3.5	1.4697	0.8974	69.13(69.17)	9.87(9.67)
i-PrPhCHOSiMe$_3$	61/2.5	1.4697	0.8929	70.13(70.21)	10.21(9.97)
t-BuPhCHOSiMe$_3$	63/3	1.4711	0.8971	71.36(71.12)	10.27(10.23)
PhCH$_2$PhCHOSiMe$_3$	120.5/3.5	1.5230	0.9766	75.52(75.50)	8.41(8.20)
PhCH$_2$MeCHOSiMe$_3$ [b]	59/5	1.4691			
t-BuMeCHOSiMe$_3$	58/41	1.4030	0.7861	62.29(62.00)	12.71(12.72)
n-BuMeCHOSiMe$_3$ [c]	70/44	1.4026			
EtMeCHOSiMe$_3$ [d]	58/110	1.3895			
EtPhCHOSiMePh$_2$	150/0.03	1.5684	1.0422	79.60(79.47)	7.23(7.28)
EtPhCHOSiMeEt$_2$	84/3	1.4778	0.9062	71.24(71.12)	10.25(10.23)
MePhCHOSiHEt$_2$	41/2	1.4820	0.9147	69.18(69.17)	9.56(9.68)
EtPhCHOSiHEt$_2$	55/3	1.4872	0.9114	70.04(70.21)	10.04(9.97)
i-PrPhCHOSiHEt$_2$	86.5/3	1.4967	0.9062	71.37(71.12)	10.25(10.23)
t-BuPhCHOSiHEt$_2$	87/3	1.4796	0.9029	71.63(71.93)	10.58(10.46)
t-BuMeCHOSiHEt$_2$	100–102/70	1.4189	0.8086	63.54(63.76)	12.62(12.84)
MePhCHOSiHPh$_2$	139/0.03	1.5802	1.0625	78.61(78.90)	6.46(6.62)
EtPhCHOSiHPh$_2$	145/0.09	1.5741	1.0521	79.39(79.20)	7.15(6.96)
i-PrPhCHOSiHPh$_2$	160/0.2	1.5671	1.0394	79.32(79.47)	7.32(7.26)
t-BuPhCHOSiHPh$_2$	170–173/0.03	1.5655	1.0326	79.86(79.72)	7.47(7.56)
t-BuMeCHOSiHPh$_2$	124/3	1.5303	0.9798	76.24(76.00)	8.68(8.50)
EtPhCHOSiHMePh	115–125/3			74.68(74.95)	7.95(7.86)

[a] Lit. [23], b.p. 91°C/14 Torr, n_D^{20} 1.4702, d_4^{20} 0.9059. [b] Lit. [23], b.p. 102°C/18 Torr, n_D^{20} 1.4690, d_4^{20} 0.8974. [c] Lit. [24], b.p. 154–155°C/741 Torr, n_D^{20} 1.4020, d_4^{20} 0.7856. [d] Lit. [25], b.p. 112.3°C, n_D^{20} 1.3898, d_4^{20} 0.772.

glass ampoule a mixture of 5.4 g (40 mmol) of propiophenone and 7.4 g (40 mmol) of diphenylsilane was heated at 50°C for 40 h in the presence of 9 mg (2×10^{-2} mmol) of di-μ-chlorobis(1,5-hexadiene)dirhodium and 20 mg (4×10^{-2} mmol) of (−)-DIOP. Distillation gave 10.3 g (81%) of 1-phenylpropyl diphenylsilyl ether, b.p. 143-5°C/0.09 Torr, n_D^{20} 1.5741, d_4^{20} 1.0521, $[\alpha]_D^{20}$ +17.04° (neat). To a solution of the silyl ether thus obtained in 20 ml of methanol was added with stirring 15 ml of 2 *N* KOH at room temperature. The hydrolysis was completed within 10 min. After work-up, distillation gave 1-phenylpropanol in quantitative yield, $[\alpha]_D^{20}$ +7.29° (neat), which was of 28.2% enantiomeric excess of the *R* isomer, on the basis of the known value of $[\alpha]_D^{25}$ −28.1° (neat) for (*S*)-1-phenylpropanol [16].

In the reaction of propiophenone with diethylsilane catalyzed by II, the asymmetric addition reaction was accompanied by the formation of 17% of 1-diethylsiloxy-1-phenylpropene. The silyl enol ether was isolated by preparative GLC, NMR (CCl_4/TMS): δ 0.3-1.2 (m, $SiC\underline{H}_2C\underline{H}_3$), 1.77 (d, J = 6.8 Hz,

TABLE 6

^{1}H NMR DATA FOR HYDROSILYLATION PRODUCTS

(a) $R^1R^2CHOSiMe_2Ph$

R^1	R^2	$Si(CH_3)_2$ [a]	OCH	SiC_6H_5	Others
Me	Ph	0.24 0.31	4.75 (q, J = 6.0 Hz)	7.03–7.55 (m)	1.38 (d, J = 6.0 Hz, CCH_3) 7.16 (s, C_6H_5)
Et	Ph	0.19 0.25	4.45 (t, J = 6.6 Hz)	7.04–7.54 (m)	0.79 (t, J = 6.6 Hz, CH_2CH_3) 1.66 (5, ill-resolved, CH_2CH_3) 7.15 (s, C_6H_5)
i-Pr	Ph	0.17 0.21	4.23 (d, J = 6.2 Hz)	6.90–7.50 (m)	0.73 and 0.90 (a pair of d, J = 6.2 Hz, $C(CH_3)_2$) 1.79 (7, J = 6.2 Hz, CH) 7.12 (s, C_6H_5)
t-Bu	Ph	0.17	4.19 (s)	6.85–7.64 (m)	0.86 (s, $C(CH_3)_3$) 7.14 (s, C_6H_5)
$PhCH_2$	Ph	0.03 0.09	4.73 (t, J = 6.4 Hz)	6.9–7.4 (m)	2.88 (d, J = 6.4 Hz, CH_2) 7.23 (s, $2C_6H_5$)
$PhCH_2$	Me	0.15 0.19	3.93 (6, J = 6.4 Hz)	7.36 (broad s)	1.10 (d, J = 6.4 Hz, CCH_3) 2.66 (d, J = 6.4 Hz, CH_2) 7.17 (s, C_6H_5)
t-Bu	Me	0.37	3.49 (q, J = 6.2 Hz)	7.24–7.72 (m)	0.87 (s, $C(CH_3)_3$) 1.01 (d, J = 6.2 Hz, CH_3)
n-Bu	Me	0.31	3.74 (6)	7.19–7.72 (m)	0.6–1.5 (broad m, n-butyl) 1.02 (d, J = 6.6 Hz, $OCCH_3$)

(b) $R^1R^2CHOSiMe_3$

R^1	R^2	$Si(CH_3)_3$	OCH	Others
Me	Ph	0.03 (s)	4.77 (q, J = 6.0 Hz)	1.37 (d, J = 6.0 Hz, CCH_3), 7.22 (s, C_6H_5)
Et	Ph	0.12 (s)	4.60 (t, J = 6.4 Hz)	0.96 (t, J = 7.2 Hz, CH_2CH_3), 1.75 (5, ill-resolved, CH_2CH_3), 7.32 (s, C_6H_5)
i-Pr	Ph	0.09 (s)	4.36 (d, J = 6.2 Hz)	0.87 and 0.99 (a pair of d, J = 6.2 Hz, $C(CH_3)_2$), 1.59–2.20 (m, CH), 7.31 (s, C_6H_5)
t-Bu	Ph	0.02 (s)	4.31 (s)	0.92 (s, $C(CH_3)_3$), 7.92 (s, C_6H_5)
$PhCH_2$	Ph	−0.09 (s)	4.78 (t, J = 6.2 Hz)	2.94 (d, J = 6.2 Hz, CH_2), 7.23 (s, $CH_2C_6H_5$), 7.31 (s, OCC_6H_5)
$PhCH_2$	Me	−0.12 (s)	3.91 (6, J = 6.2 Hz)	1.11 (d, J = 6.2 Hz, CH_3), 2.64 (d, J = 6.4 Hz, CH_2), 7.25 (s, C_6H_5)
t-Bu	Me	0.14 (s)	3.44 (q, J = 6.4 Hz)	0.89 (s, $C(CH_3)_3$), 1.06 (d, J = 6.4 Hz, $OCCH_3$)
n-Bu	Me	0.08 (s)	3.62 (6, ill-resolved)	0.6–1.5 (broad m, n-butyl), 1.09 (d, J = 6.4 Hz, $OCCH_3$)

(c) $R^1R^2CHOSiHF_2$ [b]

R^1	R^2	SiH [c]	OCH	Others [d]
Me	Ph	4.32 (5)	4.57 (q, J = 6.4 Hz)	1.42 (d, J = 6.4 Hz, CH_3), 7.26 (s, C_6H_5)
Et	Ph	4.41 (5)	4.55 (t, J = 6.2 Hz)	0.89 (t, J = 6.8 Hz, CH_3), 1.70 (5, CH_2) 7.25 (s, C_6H_5)
i-Pr	Ph	4.32 (5)	4.26 (d, J = 6.4 Hz)	0.7–2.0 (m, $C(CH_3)_2$), 1.80 (7, J = 6.4 Hz, CH), 7.18 (s, C_6H_5)
t-Bu	Ph	4.34 (5)	4.28 (s)	0.83 (s, $C(CH_3)_3$), 7.23 (s, C_6H_5)
t-Bu	Me	4.36 (5)	3.40 (q, J = 6.4 Hz)	0.85 (s, $C(CH_3)_3$), 1.40 (d, J = 6.4 Hz, CH_3)

(d) $R^1R^2CHOSiHPh_2$ [e]

R^1	R^2	SiH	OCH	Others [f]
Me	Ph	5.39 (s)	4.91 (q, J = 6.2 Hz)	1.46 (d, J = 6.2 Hz, CH_3), 7.20 (s, C_6H_5)
Et	Ph	5.35 (s)	4.60 (t, J = 6.2 Hz)	0.84 (t, J = 7.2 Hz, CH_3), 1.78 (5, CH_2) 7.12 (s, C_6H_5)
i-Pr	Ph	5.27 (s)	4.37 (d, J = 6.2 Hz)	0.77 and 0.92 (a pair of d, J = 7.2 Hz, $C(CH_3)_2$), 1.92 (7, CH), 7.14 (s, C_6H_5)
t-Bu	Ph	5.24 (s)	4.34 (s)	0.97 (s, $C(CH_3)_3$), 7.14 (s, C_6H_5)
t-Bu	Me	5.41 (s)	3.57 (q, J = 6.2 Hz)	0.92 (s, $C(CH_3)_3$), 1.10 (d, J = 6.2 Hz, CH_3)

(Table continued)

TABLE 6 (continued)

(c) Others

Compound	
EtPhCHOSiMePh$_2$	0.44 (s, SiCH$_3$), 0.81 (t, J = 6.8 Hz, CH$_2$CH$_3$), 1.74 (s, CH$_2$CH$_3$), 4.59 (t, J = 6.0 Hz, OCH), 7.21 (s, CC$_6$H$_5$), 7.00–7.66 (m, SiC$_6$H$_5$)
EtPhCHOSiMeEt$_2$	−0.03 (s, SiCH$_3$), 0.20–1.22 (m, SiCH$_2$CH$_3$), 0.86 (t, J = 7.0 Hz, CH$_2$CH$_3$), 1.67 (s, CH$_2$CH$_3$), 4.52 (t, J = 6.0 Hz, OCH), 7.21 (s, C$_6$H$_5$)
EtPhCHOSiHMePh [g]	0.30 and 0.34 (d, J = 2.8 Hz, SiCH$_3$), 0.80 and 0.82 (t, J = 6.8 Hz, CH$_2$CH$_3$), 1.72 (s, CH$_2$CH$_3$), 4.52 (t, J = 6.0 Hz, OCH), 4.91 and 4.99 (q, J = 2.8 Hz, SiH), 7.14 and 7.17 (s, CC$_6$H$_5$), 6.89–7.56 (m, SiC$_6$H$_5$)

[a] Diastereotopic methyls (a pair of s). [b] ν(Si–H): 2100–2110 cm^{-1}. [c] J = 2.2 Hz. HSi–CH$_2$. [d] SiCH$_2$CH$_3$: δ 0.3–1.0 (diffused multiplet). [e] ν(Si–H): 2120–2125 cm^{-1}. [f] SiC$_6$H$_5$: δ 7.2–7.6 (m). [g] A mixture of two diastereomeric isomers.

–CCH$_3$), 4.58 (q, J = 2.0 Hz, SiH), 5.25 (q, J = 6.8 Hz, –CH), and 7.04–7.49 (m, C$_6$H$_5$). (Found: C, 70.76; H, 9.39. C$_{13}$H$_{20}$OSi calcd.: C, 70.85; H, 9.15%.)

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