THE JOURNAL OF Organic Chemistry®

VOLUME 42, NUMBER 10

MAY 13, 1977

Reduction of Carbonyl Compounds via Hydrosilylation. 3. Asymmetric Reduction of Keto Esters via Hydrosilylation Catalyzed by a Rhodium Complex with Chiral Phosphine Ligands

Iwao Ojima,* Tetsuo Kogure, and Miyoko Kumagai

Sagami Chemical Research Center, Nishi-Ohnuma 4-4-1, Sagamihara, Kanagawa 229, Japan

Received October 5, 1976

Asymmetric reduction of α-, β- and γ-keto esters via hydrosilylation catalyzed by rhodium complexes with chiral phosphines, (+)-BMPP, (+)- or (−)-DIOP, was investigated. High optical yields around 80% (72–85% ee) were attained in the case of pyruvates. Clear double asymmetric induction was observed in the asymmetric hydrosilylation of (−)-menthyl phenylglyoxylate. Under optimum conditions, the optical purity of the mandelate was 77%. Transfer hydrogenation instead of hydrosilylation is proposed to be involved in the reaction of an acetoacetate and a benzoylacetate. Asymmetric hydrosilylation of various levulinates followed by acid hydrolysis afforded 4-methyl-γ-butyrolactone (76–85% ee) in nearly quantitative yield. A combination of DIOP ligand with α-naphthylphenylsilane was found to be quite effective for the asymmetric induction. High efficiency of asymmetric induction for the keto esters compared with simple prochiral ketones may be due to an attractive interaction between the ester carbonyl and rhodium center in the transition state. Possible mechanisms for the induction of asymmetry are discussed using Dreiding models of the intermediate α-silyloxyalkyl–rhodium complexes.

Among many asymmetric reactions, the synthesis of optically active α-hydroxycarboxylic acids has gathered much interest for a long time, and a large number of reports has been made on the Grignard reaction and the reduction of α-keto esters.[1] The asymmetric reductions of chiral α-keto esters by catalytic hydrogenation and metal hydride reduction have been extensively studied. Relatively little is known, however, about the asymmetric reduction of α-keto esters by chiral reducing agents, although reductions of phenylglyoxylic acid and its esters by the use of chiral magnesium alkoxides[2] and lithium aluminum hydride–chiral alcohol complexes[3] have been reported. The optical yield attained by the former agents was reported to be 15–33%, and that obtained by the latter systems was 4–17%. Ohgo et al. have recently reported[4] the catalytic asymmetric hydrogenation of phenylglyoxylates using Co(dimethylglyoxymato)$_2$–quinine complex to give mandelates in 11.5–19.5% optical yield. As for β-keto esters, an effective asymmetric hydrogenation of methyl acetoacetate has been reported by Solodar using a cationic rhodium complex with chiral phosphines.[5]

Recently, we reported the first and quite effective catalytic asymmetric reductions of α-keto esters using hydrosilylation.[6] We describe here a full account of our research on the asymmetric reductions of α-, β- and γ-keto esters[7] as an application of our work on the reduction of carbonyl[8] and imino[9] functionalities using hydrosilylation catalyzed by rhodium(I) complexes with phosphine ligands. We also discuss the mechanism of the induction of asymmetry in these reactions.

Results and Discussion

Asymmetric Reduction of α-Keto Esters via Hydrosilylation. The asymmetric reduction of α-keto esters, typically alkyl pyruvate and phenylglyoxylate, was carried out via hydrosilylation catalyzed by rhodium(I) complexes with (*R*)-(+)-benzylmethylphenylphosphine (BMPP), and 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane (DIOP)[10] as chiral ligands. Reactions were performed in accordance with a general procedure as shown in eq 1.

$$R^1COCOOR^2 + R^3R^4SiH_2 \xrightarrow[\text{benzene}]{[Rh]^*} \underset{\displaystyle OSiHR^3R^4}{\overset{\displaystyle *}{R^1CHCOOR^2}} \xrightarrow[MeOH-C_6H_6]{H^+} \underset{\displaystyle OH}{\overset{\displaystyle *}{R^1CHCOOR^2}} \quad (1)$$

Results are summarized in Table I. As is seen from Table I, optical yields depend on the nature of hydrosilane used, and the configuration of *n*-propyl lactate derived by the use of (+)-BMPP is opposite to that derived by using (+)-DIOP. The substituent of the ester moiety has a considerable effect on the extent of asymmetric induction. The optical yields realized for the asymmetric reduction of pyruvates by this method are much higher than those obtained by other methods. In the optimum conditions, *n*-propyl and *n*-butyl pyruvate were effectively converted to *n*-propyl and *n*-butyl lactate in 85.4 and 83.1% optical yields, respectively. The optical yield attained in the case of *n*-propyl pyruvate by the

Table I. Asymmetric Reductions of Pyruvates and Phenylglyoxylates

Registry no.	α-Keto ester	Hydrosilane[n]	Chiral ligand[o]	α-Hydroxy ester Yield, %[a]	$[\alpha]^{17-25}_D$[b]	Optical purity, %[c]	Registry no.
20279-43-0	$CH_3COCOOPr$-*n*	Et_2SiH_2	(+)-BMPP	85	+3.67[d]	30.3 (*R*)	
		$PhMeSiH_2$	(+)-BMPP	80	+6.05[d]	50.0 (*R*)	
		Ph_2SiH_2	(+)-BMPP	84	+7.30[d]	60.3 (*R*)	
		Ph_2SiH_2	(+)-DIOP	82	−9.26	76.5 (*S*)	53651-69-7
		α-$NpPhSiH_2$	(−)-DIOP	90	+10.33	85.4[k] (*R*)	53651-70-0
20279-44-1	$CH_3COCOOBu$-*n*	Ph_2SiH_2	(+)-DIOP	82	−8.68	74.2 (*S*)	
		α-$NpPhSiH_2$	(+)-DIOP	83	−9.73	83.1[l] (*S*)	34451-19-9
13051-48-4	$CH_3COCOOBu$-*i*	Ph_2SiH_2	(−)-DIOP	85	+9.72	63.1 (*R*)	
		α-$NpPhSiH_2$	(−)-DIOP	84	+11.11	72.1[m] (*R*)	61597-96-4
1603-79-8	PhCOCOOEt	Et_2SiH_2	(+)-BMPP	80	+8.20[d,e]	6.4 (*S*)	13704-09-1
		Ph_2SiH_2	(+)-BMPP	82	−13.24[d,f]	10.3 (*R*)	10606-72-1
		Ph_2SiH_2	(+)-DIOP	80	+12.30[g]	9.7 (*S*)	
		α-$NpPhSiH_2$	(+)-DIOP	87	+49.50[h]	39.2 (*S*)	
61598-01-4	$PhCOCOOC_6H_{11}$-c	Ph_2SiH_2	(+)-DIOP	89	+31.11[i]	42.5 (*S*)	
		α-$NpPhSiH_2$	(+)-DIOP	85	+34.62[j]	47.2 (*S*)	61597-97-5

[a] GLC yield. [b] Optical rotations are for the neat liquid unless otherwise noted. [c] Optical purity for lactates or ethyl mandelate is calculated from the specific rotation of the pure enantiomer which is reported in the literature: for lactates see ref 11 [*n*-Pr ester, $[\alpha]^{18}_D$ 12.1° (neat); *n*-Bu ester, $[\alpha]^{17}_D$ 11.7° (neat); *i*-Bu ester, $[\alpha]^{18}_D$ 15.4° (neat)], for mandelate see ref 12 [Et ester, $[\alpha]^{25}_D$ 126.2° ($CHCl_3$, *c* 2.012)]. Since the maximum rotation of cyclohexyl mandelate was unknown as far as we were concerned, we prepared the authentic sample of (*S*)-(+)-cyclohexyl mandelate by condensation of (*S*)-(+)-mandelic acid with cyclohexanol and estimated the value: $[\alpha]^{20}_D$ +73.27° (EtOH, *c* 2) (see Experimental Section). [d] Optical rotation is calibrated by the purity of (+)-BMPP (77.7%). [e] $CHCl_3$, *c* 1.57. [f] $CHCl_3$, *c* 7.07. [g] $CHCl_3$, *c* 1.98. [h] $CHCl_3$, *c* 1.98. [i] EtOH, *c* 2.03. [j] EtOH, *c* 2.00, [k] 83.5% ee based on the NMR measurement using Eu(facam)$_3$. [l] 82% ee based on NMR using Eu(facam)$_3$. [m] 73% ee based on NMR using Eu(facam)$_3$. [n] Registry no. are, respectively, 542-91-6, 766-08-5, 775-12-2, 21701-61-1. [o] Registry no. are, respectively, 25140-53-8, 37002-48-5, 32305-98-9.

Table II. Double Asymmetric Reduction of (−)-Menthyl Phenylglyoxylate

Method	Hydrosilane	Ligand	Yield, %[a]	Optical purity, %[b]	Config[c]
a	Ph_2SiH_2	Ph_3P[d]	99	21	*S*
b	Ph_2SiH_2	(−)-DIOP	98	37	*R*
c	Ph_2SiH_2	(+)-DIOP	98	60	*S*
a	α-$NpPhSiH_2$	Ph_3P	99	17	*S*
c	α-$NpPhSiH_2$	(+)-DIOP	99	77	*S*

[a] GLC yield. [b] Optical purity on the α carbon is estimated on the basis of NMR spectra (100 MHz, C_6D_6); see ref 3 and note 14. [c] See note 14. [d] Registry no., 603-35-0.

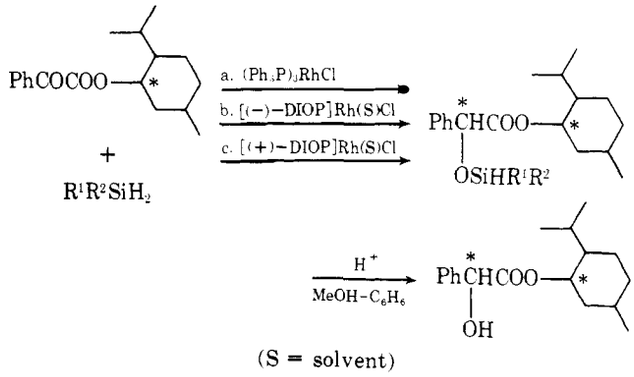
use of α-naphthylphenylsilane (85.4%) is the highest one ever known. A similar asymmetric reduction of ethyl phenylglyoxylate resulted in rather low optical yield although the optical yield was considerably improved when α-naphthylphenylsilane was employed. On the other hand, cyclohexyl ester afforded by far better results than ethyl ester. These results clearly indicate that the bulkiness of the ester group is an essential factor for determining the effectiveness and the direction of the asymmetric induction. A possible mechanism which can accommodate these results will be presented (vide post). In every case, the combination of α-naphthylphenylsilane and DIOP ligand displayed the best result.

"Double Asymmetric Reduction" of (−)-Menthyl Phenylglyoxylate and Pyruvate Using Catalytic Hydrosilylation. We also carried out the "double asymmetric reduction" of (−)-menthyl esters of phenylglyoxylic acid and pyruvic acid using the DIOP–rhodium complexes. Conceptually, there are several distinct ways in which the asymmetric reduction of an α-keto ester to give the corresponding optically active α-hydroxy ester can be achieved: (a) by the reduction of a chiral ester with an achiral reducing agent; (b) by the reduction of an achiral ester with a chiral reducing agent; (c) by a combination of chiral ester and chiral reducing agent.

Horeau and co-workers have investigated these possibilities with (−)-menthyl and ethyl phenylglyoxylate.[3] Either a simple asymmetric reduction of (−)-menthyl phenylglyoxylate with an achiral agent, $LiAlH_4$–cyclohexanol, process a, or of ethyl phenylglyoxylate with a chiral reducing agent, $LiAlH_4$–(+)-camphor, process b, gives (*R*)-(−)-mandelate (10 and 4% ee, respectively). However, "double asymmetric reduction" using both chiral ester and chiral reducing agent, process c, results in 49% asymmetric synthesis. This "double asymmetric induction" is higher than would be anticipated on the basis of any simple additive effect. Although this discussion seems to overlook the effect of the bulkiness of ester substituent on the extent of asymmetric induction (vide supra), "double asymmetric induction" was found to be an effective way of asymmetric synthesis. Accordingly, we applied this concept to a catalytic system.

In the first place, we performed the catalytic asymmetric reduction of (−)-menthyl phenylglyoxylate using diphenylsilane as reducing agent in the following ways (Scheme I):

Scheme I



(S = solvent)

(a) a simple asymmetric reduction by the hydrosilylation catalyzed by a rhodium complex with achiral phosphine ligands, $(Ph_3P)_3RhCl$; (b) double asymmetric reduction using a rhodium complex with a chiral phosphine ligand, [(−)-DIOP]Rh(S)Cl (S = solvent); (c) double asymmetric reduction using a rhodium complex with (+)-DIOP as chiral ligand, [(+)-DIOP]Rh(S)Cl. Results are summarized in Table II.

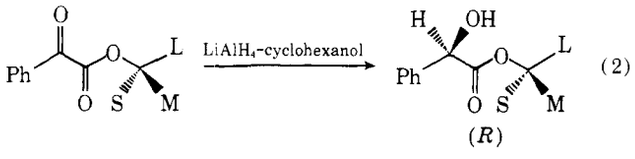
Table III. Double Asymmetric Reduction of (−)-Menthyl Pyruvate

Entry no.	Hydrosilane	Ligand	Final product	Yield, %[a]	$[\alpha]^{18-20}D$[b]	Optical yield, %[c]
1	Et_2SiH_2	(+)-BMPP	$CH_3\overset{*}{C}HCOOPr$ (OH)	50	+1.99	16.4 (*R*)
2	Et_2SiH_2	(+)-DIOP		48	−5.12	42.3 (*S*)
3	Ph_2SiH_2	(+)-DIOP		40	−7.55	62.4 (*S*)
4	Ph_2SiH_2	(−)-DIOP		45	+7.96	65.8 (*R*)
5	Ph_2SiH_2	(+)-DIOP	$CH_3\overset{*}{C}HCOO$–(*) (OH)	85 (98)	−79.21[d]	65.3 (*S*)[h]
6	Ph_2SiH_2	(−)-DIOP		82 (98)	−72.42[e]	62.1 (*R*)[i]
7	α-NpPhSiH$_2$	(+)-DIOP		81 (95)	−80.23[f]	85.6 (*S*)
8	α-NpPhSiH$_2$	(−)-DIOP		80 (96)	−71.23[g]	82.8 (*R*)

[a] Isolated yield unless otherwise noted. The values in parentheses are GLC yield. [b] Optical rotations are for the neat liquid unless otherwise noted. Optical rotation of (−)-menthyl *dl*-lactate was reported to be −75.9° (EtOH, *c* 5.0488) (ref 18). [c] Optical yield is calculated on the basis of the reported maximum rotation of the pure enantiomer (see Table I). As for (−)-menthyl lactate, optical yield is estimated based on NMR spectrum using $Eu(fod)_3$. [d] EtOH, *c* 2.256. [e] EtOH, *c* 1.933. [f] EtOH, *c* 2.004. [g] EtOH, *c* 2.307. [h] Registry no., 61597-98-6. [i] Registry no., 59259-38-0.

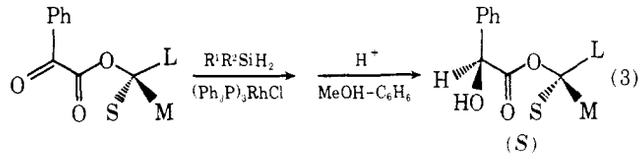
Based on the results from experiment a, we can estimate the influence of (−)-menthyl group on the induction of asymmetry. Namely, the stereochemical control by (−)-menthyl group operated to produce (−)-menthyl (*S*)-(+)-mandelate predominantly. The attained optical yield (21%) is a little higher than that obtained with the use of $LiAlH_4$–cyclohexanol. In an experiment b, it was shown that the opposing double asymmetric induction by the chiral catalyst and (−)-menthyl group afforded (*R*)-(−)-mandelate with rather low stereoselectivity (37% ee).[13] Accordingly, the rhodium catalyst with (−)-DIOP as chiral ligand may favor the production of (*R*)-mandelate also in this system,[13] and therefore, the direction of asymmetric induction is opposite to that by (−)-menthyl group. In an experiment c, it was demonstrated that the effective double asymmetric induction was realized (60% ee) when the rhodium complex with (+)-DIOP as chiral ligand was employed as a catalyst, which favored the production of (*S*)-mandelate. Thus, in this case, the direction of asymmetric induction by [(+)-DIOP]Rh(S)Cl matched well to the effect of (−)-menthyl group. As is also shown in Table II, α-naphthylphenylsilane displayed a considerable effect on the extent of asymmetric induction. Namely, α-naphthylphenylsilane–[(+)-DIOP]Rh(S)Cl combination afforded (*S*)-mandelate with 77% optical purity on the α-carbon, which was easily purified by recrystallization from *n*-hexane to provide the pure (*S*)-mandelate. The increase of the optical purity should be due to better matching of α-naphthylphenylsilane with the chiral ligand in the coordination sphere since a simple asymmetric induction using α-naphthylphenylsilane and $(Ph_3P)_3RhCl$ resulted in the formation of (*S*)-mandelate with only 17% optical purity.

As for the effect of (−)-menthyl group, the hydrosilylation with the rhodium complex showed an asymmetric induction of opposite direction compared with $LiAlH_4$–cyclohexanol reduction. Namely, the former favored the formation of (*S*)-mandelate, while the latter did (*R*)-mandelate. The latter case can be well understood by Prelog's generalization[15] in which the two carbonyl groups of the α-keto ester are in the anti-coplanar conformation (eq 2). If one follows Prelog's

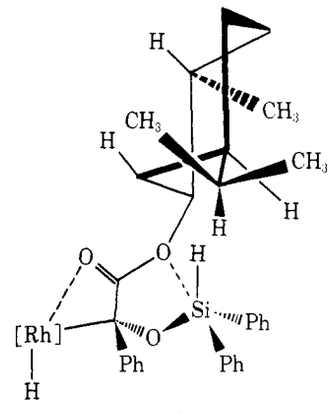


(*R*) (2)

stereochemical consideration of the effect of a chiral center, the two carbonyl groups of (−)-menthyl phenylglyoxylate should be in the unfavorable syn-coplanar conformation for the former case in order to accommodate the results (eq 3). However, it has previously been shown that the stereochemical course of the hydrosilylation catalyzed by rhodium complexes



(*S*) (3)



I

[Rh]: $(Ph_3P)_3RhCl$, [(+)- or (−)-DIOP]Rh(S)Cl

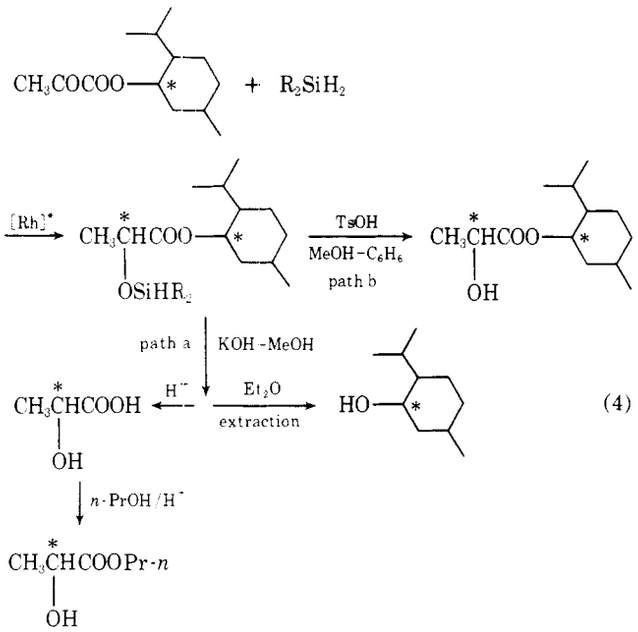
does not follow *steric approach control*,[16] and that the reaction proceeds via α-silyloxyalkyl–rhodium complex.[8c,j,17] Consequently, the former results may be best explained by a model depicted as I, which shows the most favorable structure of the intermediate complex based on the inspection of the Dreiding model. A possible attractive interaction between menthoxy oxygen and silyl moiety is indicated in I. Hydride shift from this conformation should afford (*S*)-mandelate.

In a similar manner, (−)-menthyl pyruvate was hydrosilylated using rhodium complexes with (+)-BMPP, (+)-DIOP, and (−)-DIOP as chiral phosphine ligand. The silylated (−)-menthyl lactate was hydrolyzed by KOH–MeOH, and both lactic acid and (−)-menthol were obtained. Lactic acid thus obtained was further esterified to *n*-propyl lactate (eq 4, path a). The results of the "double asymmetric induction" in (−)-menthyl pyruvate are listed in Table III (entry no. 1–4). The optical yields attained by this system are not so high as expected, and are rather low compared with those obtained in the case of the asymmetric reduction of alkyl pyruvates as far as diphenylsilane is concerned. Thus, the effect of (−)-menthyl group was by no means remarkable in these cases. However, a possibility of a partial racemization or a partial kinetic resolution during the alkaline hydrolysis cannot be excluded. Therefore, more direct estimation of the optical yield of the reaction was performed without alkaline hydrolysis. Namely, the hydrosilylated product, the silyl ether of (−)-menthyl lactate, was converted to (−)-menthyl lactate

Table IV. Asymmetric Reduction of Acetoacetates via Hydrosilylation Catalyzed by [(+)DIOP]Rh(S)Cl (S = Solvent)

Registry no.	Ester R	Hydrosilane	Yield, %[a]	$[\alpha]^{20}_D$[b]	Optical Purity, %[c]	Config[d]	Registry no.
105-45-3	Me	Ph_2SiH_2	84	+2.89	12 (13.7)	S	53562-86-0
		α-NpPhSiH$_2$	89	+4.96	21 (23.5)	S	
141-97-9	Et	Ph_2SiH_2	80	+2.16	11	S	58616-01-4
		α-NpPhSiH$_2$	86	+5.03	26	S	
591-60-6	*n*-Bu	Ph_2SiH_2	83	+1.77	12	S	61597-99-7
		α-NpPhSiH$_2$	92	+3.66	24	S	

[a] GLC yield. [b] Optical rotations are for the neat liquid. [c] Optical purity was determined on the basis of NMR measurement using Eu(facam)$_3$ in CCl_4. The values in parentheses are optical purity calculated from the reported specific rotation of the pure enantiomer [$[\alpha]^{20}_D$ −21.09° (neat)] (ref 19). [d] Configuration of ethyl and *n*-butyl 3-hydroxylbutyrate is unknown. Thus, *S* configuration is tentatively assigned on the basis of the fact that the sign of optical rotation of *S* acid is same to that of *S* ethyl ester. See ref 20.

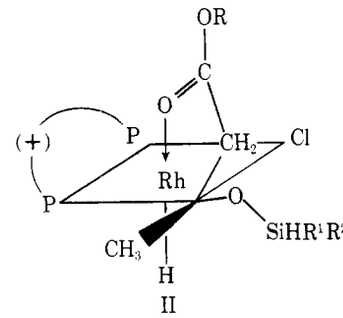


(4)

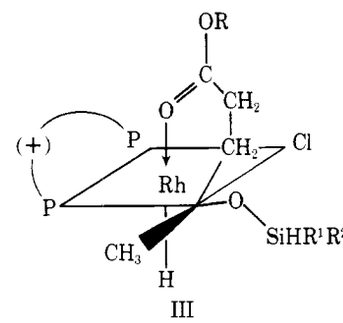
by using a 0.5% methanol solution of *p*-toluenesulfonic acid (TsOH) (eq 4, path b). The optical yield was determined on the basis of the NMR spectrum of the reaction mixture using a shift reagent, Eu(fod)$_3$. Results are listed in Table III (entry no. 5–8). Optical rotations of the isolated samples of (−)-menthyl lactate are also shown in Table III. The NMR spectra of isolated samples using the shift reagent revealed that a partial resolution during the isolation process, i.e., chromatography on silica and distillation, was negligible.

As is immediately seen from Table III, the experiments involving alkaline hydrolysis (entry no. 3–4) give largely reliable results, but may include a slight partial resolution since an opposite trend in the extent of asymmetric induction, on employing both (+)- and (−)-DIOP, was observed in the latter experiments (entry no. 5–6 and 7–8) where optical yields were directly estimated. A remarkable increase of optical yield was observed by the entry of α-naphthylphenylsilane, i.e., α-naphthylphenylsilane–[(+)-DIOP]Rh(S)Cl combination afforded the (*S*)-lactate with high optical purity such as 85.6% ee, and α-NpPhSiH$_2$–[(−)-DIOP]Rh(S)Cl system gave the (*R*)-lactate with 82.8% ee. Accordingly, it is concluded that (−)-menthyl has only a slight effect on asymmetric induction and behaves only as a bulky substituent in the given reaction.

Asymmetric Reduction of Acetoacetates and Levulinates via Hydrosilylation. The optical yields attained in the asymmetric reduction of α-keto esters are much higher than those obtained in the case of simple prochiral ketones.[8e,f,17a,b,21] The marked increase of the optical yield for the reaction may be due to a ligand effect, i.e., an attractive interaction, of the ester moiety in the transition state. In this point of view, we have investigated the effects of the ester moiety on the optical yield of the asymmetric hydrosilylation of other keto esters catalyzed by the rhodium complex with DIOP as chiral ligand. We chose acetoacetates and levulinates as substrates since these compounds seemed to be appropriate to estimate such an effect of the ester moiety. In the transition state, an acetoacetate may form a five membered ring chelate complex II, while a levulinate may afford a six membered ring chelate III.

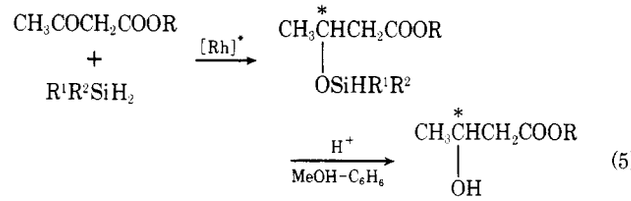


II

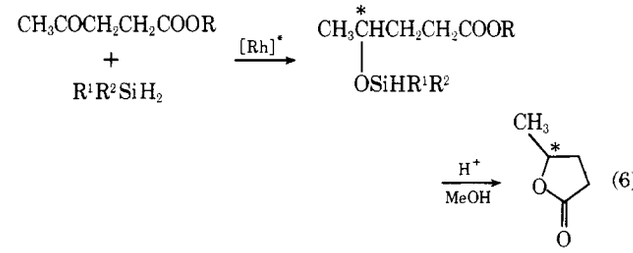


III

The catalytic asymmetric hydrosilylation followed by hydrolysis of acetoacetates afforded the corresponding optically active 3-hydroxybutyrates (eq 5), while that of levulinates



(5)



(6)

Table V. Asymmetric Reduction of Levulinates via Hydrosilylation Catalyzed by [(+)DIOP]Rh(S)Cl (S = Solvent)

Registry no.	Ester R	Hydrosilane	4-Methyl-γ-butyrolactone Yield, %[a]	$[\alpha]^{22}_D$ (neat)	Optical purity, %[b]	Confign
624-45-3	Me	Ph_2SiH_2	99	−11.01	39.6	S[c]
		α-NpPhSiH$_2$	99	−21.14	76.2	S
539-88-8	Et	Ph_2SiH_2	100	−10.56	38.1	S
		α-NpPhSiH$_2$	99	−22.34	80.5	S
645-67-0	*n*-Pr	Ph_2SiH_2	96	−9.61	34.6	S
		α-NpPhSiH$_2$	94	−22.96	82.7	S
3757-32-2	*i*-Bu	Ph_2SiH_2	96	−10.88	39.2	S
		α-NpPhSiH$_2$	96	−23.43	84.4	S
3063-69-2	c-C_6H_{11}	Ph_2SiH_2	94	−11.16	43.1	S
		α-NpPhSiH$_2$	98	−23.17	83.5	S
6939-75-9	$PhCH_2$	Ph_2SiH_2	95	−10.56	38.1	S
		α-NpPhSiH$_2$	100	−20.86	75.1	S

[a] GLC yield. [b] Optical purity is calculated from the reported specific rotation of the pure enantiomer (ref 20): $[\alpha]^{22}_D$ −27.75° (neat). [c] Registry no., 19041-15-7.

Table VI. Asymmetric Reductions of (−)-Menthyl and (−)-Bornyl Levulinate via Hydrosilylation Catalyzed by Rhodium(I) Complex with (+)-DIOP or (−)-DIOP

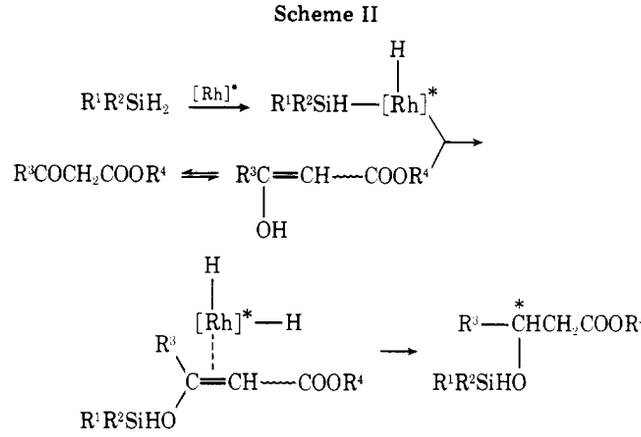
Registry no.	Ester	Hydrosilane	Ligand	4-Methyl-γ-butyrolactone Yield, %[a]	$[\alpha]^{20}_D$ (neat)	Optical purity, %[b]
61604-72-6	(−)-Menthyl	Ph_2SiH_2	(+)-DIOP	93	−10.29	37.1 (*S*)
		Ph_2SiH_2	(−)-DIOP	90	+13.27	47.8 (*R*)[c]
		α-NpPhSiH$_2$	(+)-DIOP	92	−23.02	82.9 (*S*)
		α-NpPhSiH$_2$	(−)-DIOP	98	+22.14	79.8 (*R*)
61598-00-3	(−)-Bornyl	Ph_2SiH_2	(+)-DIOP	97	−11.58	41.7 (*S*)
		Ph_2SiH_2	(−)-DIOP	98	+10.74	38.7 (*R*)
		α-NpPhSiH$_2$	(+)-DIOP	99	−20.12	72.5 (*S*)
		α-NpPhSiH$_2$	(−)-DIOP	98	+18.84	67.9 (*R*)

[a] GLC yield. [b] See Table V. [c] Registry no., 58917-25-2.

gave optically active 4-methyl-γ-butyrolactone through the silyl ether of 4-hydroxypentanoates (eq 6). Results of the asymmetric reduction of acetoacetates are listed in Table IV, and those of levulinates are summarized in Table V.

In order to estimate the effect of the ester moiety, the asymmetric reduction of hexan-2-one was carried out under similar conditions for comparison: the optical purity of (*S*)-hexan-2-ol thus obtained was 15.1% ee when diphenylsilane was employed, and 26.6% ee when α-naphthylphenylsilane was used.[22] As is immediately seen from Table V, a remarkable increase of optical yield is observed in the case of levulinates. Thus, the results may suggest the existence of the postulated ligand effect of the ester moiety in the transition state. However, such an effect cannot be observed in the case of acetoacetates. Accordingly, the asymmetric hydrosilylation of ethyl benzoylacetate followed by hydrolysis using α-naphthylphenylsilane and (+)-DIOP–rhodium catalyst was performed for comparison. The optical purity of the obtained ethyl (*S*)-3-hydroxy-3-phenylpropionate was 62.8% ee,[23] which was a little higher than that realized for simple alkyl phenyl ketones.[21c] At any rate, the expected large attractive interaction cannot be observed also in this case. For a possible explanation of these results, we suppose at this stage that transfer hydrogenation of the preformed silyl enol ether of acetoacetate or benzoylacetate, which would be formed by dehydrogenative coupling[24] of the enol with the hydrosilane and would be a mixture of *E* and *Z* isomer, may take place (Scheme II) together with hydrosilylation. Namely, if the asymmetric induction by transfer hydrogenation is considerably lower than that by hydrosilylation or if the direction of asymmetric induction by the former reaction is opposite to that by the latter, the apparently obtained optical yield of the given reaction may be unexpectedly low.

Scheme II



From a synthetic point of view, a preparation of optically active γ-valerolactones is important for the synthesis of optically active terpenes or alkaloids via optically active amino alcohols or diols. However, little is known about the effective route to the optically active γ-valerolactone except an optical resolution. Accordingly, the facile asymmetric synthesis of 4-methyl-γ-butyrolactone via hydrosilylation has a significant value. Recently, Meyers and Mihelich reported[25] an effective asymmetric synthesis of 2-substituted γ-butyrolactones using optically active oxazolines in 64–73% optical yields. It should be noted, as shown in Tables V and VI, that 4-methyl-γ-butyrolactone with high optical purity such as 76–84% ee was easily obtained via catalytic asymmetric hydrosilylation of levulinates followed by hydrolysis in excellent yields.

As is seen from Table V, the effect of the bulkiness of ester substituent on the asymmetric induction is not so remarkable, but a relatively bulky substituent afforded a better result. On

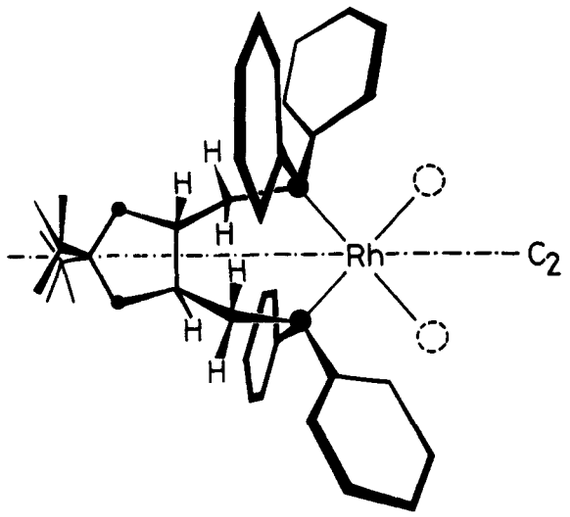


Figure 1. Illustration of the most preferable conformation of (+)-DIOP–rhodium complex in solution based on the Dreiding model.

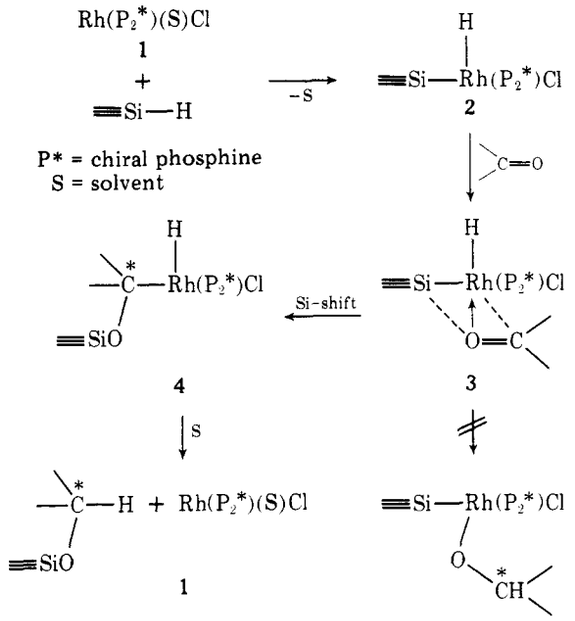
the other hand, the bulkiness of dihydrosilane exerts a large influence on the extent of asymmetric induction, i.e., α-naphthylphenylsilane is by far a better reagent than diphenylsilane. These results clearly indicate that α-naphthylphenylsilane has an appropriate bulkiness which satisfies the steric requirement for the effective asymmetric induction in the chiral coordination sphere. In all cases, *S* configuration of the lactone was preferred when (+)-DIOP was employed as a chiral ligand.

(−)-Menthyl and (−)-bornyl levulinate were also chosen as substrate. As Table VI shows, the effect of (−)-menthyl group on the extent of asymmetric induction was not remarkable. However, a considerable effect was observed when diphenylsilane was employed: (−)-menthyl levulinate–[(−)-DIOP]Rh(S)Cl combination gave a better result (ca. 10% ee difference) than the ester–[(+)-DIOP]Rh(S)Cl combination did. The bulkier (−)-bornyl group has a negative effect on the extent of asymmetric induction, especially when α-naphthylphenylsilane was employed. The results may be due to the fact that the coordination sphere is much too crowded by the entry of the bulky silane and the ester group. A similar phenomenon was observed when the (−)-menthyl ester was reduced by using α-$NpPhSiH_2$–[(−)-DIOP]Rh(S)Cl system.

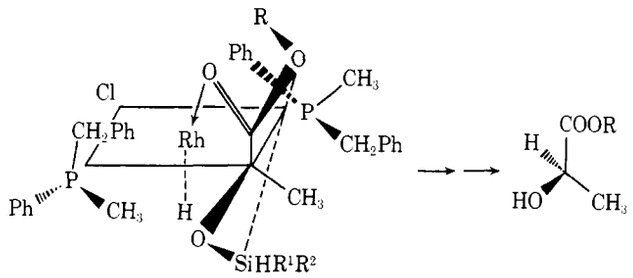
On the Mechanism of Asymmetric Induction. As for the induction of asymmetry, we already proposed[8f,j] in a previous paper a probable mechanism for the BMPP–rhodium(I) complex system based on the stereochemical inspection of the relationship between the configuration of the chiral phosphine and that of the resulting alcohol. According to the proposed mechanism, the intermediate α-silyloxyalkyl–rhodium complex plays a key role for the asymmetric induction, and the following steps are involved as shown in Scheme III: (a) oxidative addition of the hydrosilane to the rhodium(I) complex; (b) insertion of the ketone carbonyl into the resulting silicon–rhodium bond to form diastereomeric α-silyloxyalkyl–rhodium intermediate 4 in accordance with *product development control;*[16] (c) formation of an optically active silyl ether of secondary alcohol by reductive elimination. Among these steps, step b must play the most important role in inducing asymmetry at the carbonyl carbon because this step determines a predominant configuration and the extent of enantiomeric excess of the product.

In a previous paper,[8f,j] we reported that the predominant configuration of the produced secondary alcohol was satisfactorily predicted by the inspection of the most preferable conformation of the intermediate complex 4 using Dreiding

Scheme III



models. This prediction is also successfully applied to the reaction of α-keto esters, where certain electronic attractive interaction between the ester group and the central rhodium metal is taken into account. For instance, the most preferable conformation of the intermediate complex 4 for a pyruvate[26] is the one depicted as IV, which enables attractive interactions



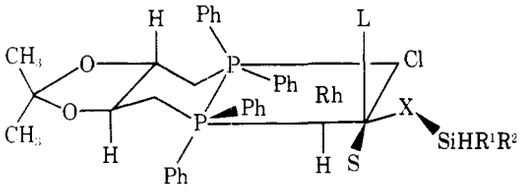
IV [4, P* = (+)-BMPP] (*R*)-lactate

between the ester carbonyl and rhodium, and between alkoxy oxygen and silyl group, to occur. The hydride shift in this conformation should afford (*R*)-lactate. The prediction matches well to the observed results as shown in Table I.

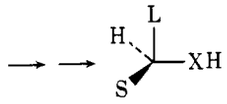
On the other hand, *the steric requirements in the coordination sphere of the DIOP–rhodium complex are quite different from those of the BMPP–rhodium complex;* nevertheless the intermediate α-silyloxyalkyl–rhodium complex 4 may also play a key role for the induction of asymmetry. The difference may principally be due to cis configuration in the former complex and trans in the latter. Although the coordinated DIOP ligand can take several conformations, the most preferable conformation in solution based on the Dreiding model is the one depicted in Figure 1[27] where steric repulsion between substituents, concerning especially four phenyl groups, is the smallest. In this conformation DIOP–rhodium metal moiety has a C_2 axis as shown in Figure 1.[28] *It should be noted that the proposed conformation corresponds exactly to the averaged one of possible conformations.* Inspection of the Dreiding model of the intermediate complex 4 indicates that the most preferable structure of the complex 4 is the one depicted in Figure 2 on account of the attractive interaction mentioned above. Accordingly, the ester group takes a *quasi-apical* position; methyl occupies the most congested site, and then bulkier silyloxy group occupies the least hindered site. The hydride shift in this conformation should af-

ford (*S*)-lactate. This model explains well the observed results, and is also successfully applied to the case of levulinates.

The proposed model also works very well for the prediction of the preferred configuration in the case of simple alkyl phenyl ketones[21c] or Schiff bases[29] by postulating the most favorable structure of the intermediate complex **4** in a manner similar to that of keto esters as shown as V. The predicted



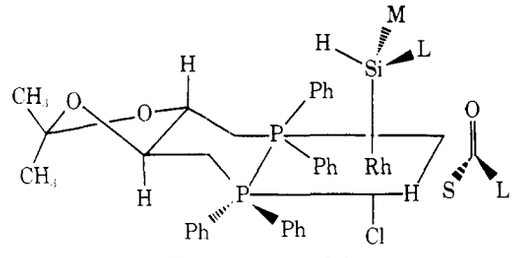
V [4, P^*_2 = (+)-DIOP]



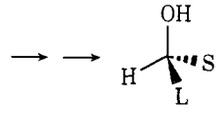
(*S*)-alcohol (X = O)
or
(*S*)-amine (X = R—N═)

configuration matches well the observed one. In these cases, the silyloxy (or silylamino) moiety is the bulkiest substituent in the coordination sphere on (+)-DIOP–rhodium complex and should occupy the least hindered *quasi-equatorial* position based on the inspection of Dreiding models.

An alternative mechanism for the induction of asymmetry in asymmetric hydrogenation and hydrosilylation has been reported by Glaser.[30] According to the proposed mechanism, a diastereomeric silylhydridorhodium(III) complex having octahedral (or trigonal bipyramidal) structure is assumed as an intermediate, which distinguishes enantiotopic faces of a prochiral ketone in terms of *steric approach control*, and the complex VI is proposed to be the most favorable model in



VI (Glaser's model)



(*S*)-alcohol

asymmetric addition of silylhydridorhodium complex to a prochiral carbonyl on the basis of the inspection of CPK model for the (+)-DIOP–rhodium complex system. In spite of an approximation and rather arbitrary choice about the conformations of DIOP, the model VI can be used successfully to predict the configuration of the major enantiomer produced.

As for the asymmetric hydrosilylation, however, Glaser's model has some disadvantages and seems not to be appropriate. (1) Although a similarity is assumed between the mechanism of hydrosilylation and that of hydrogenation in accordance with the *steric approach control* conception, it has been shown that the mechanisms of these reactions are quite different from each other when carbonyl compounds are employed as substrate, and it is strongly suggested that *product development control* is operative for the formation

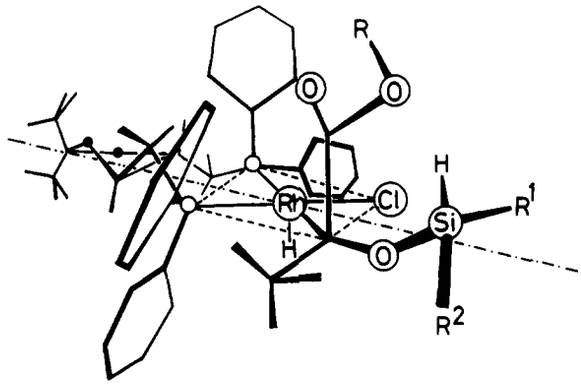
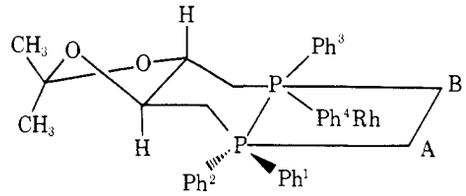
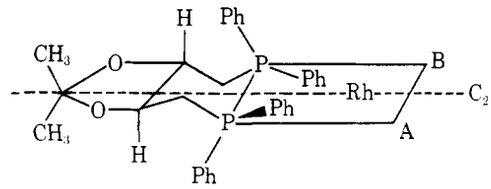


Figure 2. Illustration of the most favorable structure of the key intermediate complex **4** when pyruvate is chosen as substrate for the reaction.

of α-silyloxyalkyl–rhodium complex **4** in the former reaction. (2) According to the proposed mechanism, the silyl moiety occupies the upper *apical* position. However, this assumption seems to be inconsistent with his logic which is employed for the dihydridorhodium complex in hydrogenation. Namely, the upper position is more congested than the lower one. That is the reason why the larger chlorine ligand is assumed to occupy the lower *apical* position. However, silyl moiety is by far bulkier than chlorine ligand. Thus, the silyl group should be placed in the lower *apical* position. Then, the predicted configuration becomes opposite. (3) Although it is concluded on the basis of the inspection of CPK model that the coordination site B in VII is less hindered than the site A. However, we cannot reach the same conclusion. The steric hindrance caused by phenyl(1), Ph^1, seems to be estimated to be too much in his inspection. If a substrate occupies the site A, all of his predictions should be reverse. As described above, our proposed model can overcome these disadvantages. Note especially that, in our model VIII (see also Figure 1), there are no differences



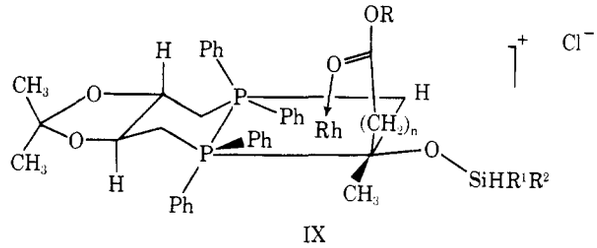
VII (Glaser's model)



VIII

between the coordination site A and B. This factor is very important to make stereochemical inspection clear and simple.

As for the structure of the intermediate complex **4**, we have postulated a neutral species in the discussion. However, there



IX

is another possibility, namely, that the attractive interaction, i.e., ligand effect, of the ester carbonyl with the central rhodium removes the chlorine ligand to the outer sphere as a counteranion, and makes the rhodium complex cationic as depicted as IX, which also works very well for the prediction of the preferred configuration in the case of keto esters in a similar manner to that described above. This idea is fascinating to explain the remarkable effect of ester group in the asymmetric induction, but must await further investigation.

Experimental Section

Measurement. The boiling points and melting points were uncorrected. The infrared spectra were recorded on a Hitachi EPI-G3 spectrophotometer, using samples as neat liquid or KBr disks. The nuclear magnetic resonance spectra were obtained by the use of Varian HA-100 or Varian T-60 spectrometers, using Me_4Si as the internal standard. Analytical gas chromatography (GLC) was carried out on Shimadzu GC-3BT, GC-3BF, or GC-5A using columns packed with 3%, 20% SE-30, 3% OV-17, 3% PEG-20M and 15% PEG-1000. Optical rotations were measured with Yanagimoto OR-50 automatic polarimeter.

Materials. Dihydrosilanes were prepared from chlorosilanes by known methods. Keto carboxylates were prepared from ketocarboxylic acids and the corresponding alcohols by condensation. Optically active keto carboxylates were also prepared by condensation of ketocarboxylic acids with optically active alcohols:[31] (−)-menthyl pyruvate, bp 100 °C (0.85 mmHg), $[\alpha]^{20}_D$ −91.73° (neat) [lit.[32] bp 131–132 °C (10 mmHg), $[\alpha]^{19.6}_D$ −92.8° (neat)]; (−)-menthyl phenylglyoxylate, mp 73–74 °C, $[\alpha]^{20}_D$ −44.32° (EtOH, c 4.58) [lit.[33] mp 73 °C, $[\alpha]^{20}_D$ −44.4° (EtOH, c 4,7832)]; (−)-menthyl levulinate, bp 138 °C (1.5 mmHg), $[\alpha]^{20}_D$ −60.90° (neat) [lit.[34] bp 151 °C (2 mmHg), $[\alpha]^{20.5}_D$ −61.14° (neat)]; (−)-bornyl levulinate, bp 124 °C (0.5 mmHg), $[\alpha]^{20}_D$ −32.52° (neat). (−)-Menthol and (−)-borneol were used as purchased from Aldrich Chemical Co. Methyl, ethyl and *n*-butyl acetoacetate were commercially available, and purified by distillation before use.

(*R*)-(+)-Benzylmethylphenylphosphine [(*R*)-(+)-BMPP] was prepared in accordance with Mislow's method[35b] using triethylamine as a base. The optical purity of the chiral phosphine was determined by quaternization using *n*-propyl bromide: [(+)-$PhMe(PhCH_2)P^+Pr$-*n*] Br^-, $[\alpha]^{25}_D$ + 28.59° (MeOH, c 1.63, 77.7% ee). The value for the pure (+) enantiomer was reported by Horner et al.,[35] $[\alpha]^{25}_D$ +36.8° (MeOH, c 1.507). (+)- and (−)-2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane [(+)- and (−)-DIOP] were commercially available from Strem Chemical Inc.

Shift reagents for NMR measurements, tris[3-(trifluoromethylhydroxymethylene)-*d*-camphorato]europium(III) [Eu(facam)$_3$] and tris[1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octadionato]europium(III) [Eu(fod)$_3$], were commercially available from Willow Brook Laboratories Inc.

(*S*)-(+)-Cyclohexyl Mandelate. (*S*)-(+)-Mandelic acid [7.6 g, 50 mmol, Aldrich Chemical Co., $[\alpha]^{20}_D$ +154.7° (H_2O, c 2.800)], cyclohexanol (5.0 g, 50 mmol), and *p*-toluenesulfonic acid (100 mg) were dissolved in benzene (150 mL) and the mixture was refluxed for 3 h with a Dean-Stark separator. After the generation of water ceased, the benzene solution was washed with a 5% aqueous solution of sodium bicarbonate and dried over anhydrous magnesium sulfate, and then the solvent was evaporated. The residue was distilled to give 8.8 g (75%) of (*S*)-(+)-cyclohexyl mandelate, bp 127–130 °C (0.9 mmHg), $[\alpha]^{20}_D$ +71.97° (EtOH, c 2.041). Anal. ($C_{14}H_{18}O_3$): C, H.

Since the maximum rotation, $[\alpha]^{20}_D$, of mandelic acid was reported[36] to be 157.5° (H_2O, c 2.1875), the optical purity of the employed acid is estimated to be 98.22%. Accordingly the maximum rotation, $[\alpha]^{20}_D$, of cyclohexyl mandelate is calculated to be 73.27° (EtOH, c 2).

Preparation of Catalyst Solution. The optically active catalyst was prepared in situ by the reaction of [Rh(1,5-cyclooctadiene)Cl]$_2$ with chiral phosphine in degassed benzene at ambient temperature. In a typical experiment, 25 mg (5.07×10^{-5} mol) of [Rh(1,5-cyclooctadiene)Cl]$_2$ and 75 mg (1.50×10^{-4} mol) of (+)-DIOP were dissolved in 5 mL of benzene under argon and stirred for 15 min. Similarly, the BMPP–rhodium complex catalyst was prepared from 25 mg (5.07×10^{-5} mol) of [Rh(1,5-cyclooctadiene)Cl]$_2$ and 70 μL (3.27×10^{-4} mol) of (*R*)-(+)-BMPP in 5 mL of benzene in a typical run.

Asymmetric Reduction of Pyruvates. A typical procedure is described for the asymmetric reduction of *n*-propyl pyruvate using α-naphthylphenylsilane and (−)-DIOP. To a 5-mL degassed benzene solution of the chiral catalyst (1.01×10^{-2} mmol, 0.34 mol %), cooled with an ice–water bath, was added a mixture of 3.90 g (30 mmol) of *n*-propyl pyruvate and 8.21 g (35 mmol) of α-naphthylphenylsilane in 15 mL of benzene, which was sufficiently cooled before adding. The mixture was stirred for 6 h and then the reaction completed. The temperature of the reaction mixture gradually rose up to ambient temperature during the course. The completion of the reaction was checked by GLC analysis and/or NMR spectroscopy. The reaction mixture was cooled to 0 °C and 30 mL of a cold methanol solution of *p*-toluenesulfonic acid (0.1%) was added. Methanolysis proceeded readily within 10 min at 0 °C. GLC analysis using *n*-pentadecane as internal standard revealed that *n*-propyl lactate was produced in 90% yield. Benzene (100 mL) was added to the mixture and then the solvents were evaporated. The residue was submitted to a column chromatography on silica and (*R*)-(+)-*n*-propyl lactate (2.96 g, 75%) was obtained from benzene–ether eluate. NMR (100 MHz) measurement using Eu(facam)$_3$ displayed that the purity of the enantiomer thus formed was 83.5% ee. For the measurement of optical rotation the obtained ester was further distilled under reduced pressure: bp 62 °C (12 mmHg) [lit.[11] bp 60–61 °C (10–11 mmHg)], $[\alpha]^{18}_D$ +10.33° (neat).

Asymmetric Reduction of Phenylglyoxylates. In a manner similar to that described above, 30 mmol of ethyl or cyclohexyl phenylglyoxylate was hydrosilylated by using 33 mmol of diphenylsilane or α-naphthylphenylsilane and the chiral catalyst (0.1–0.3 mol % based on the ester) in 20 mL of benzene. The produced silyl ether was methanolyzed and submitted to a column chromatography on silica. Ethyl or cyclohexyl mandelate was obtained from benzene eluate in 79–87% yield. A further distillation was carried out for the measurement of optical rotation.

Double Asymmetric Reduction of (−)-Menthyl Phenylglyoxylate. A typical procedure is described for the double asymmetric reduction of (−)-menthyl phenylglyoxylate using α-naphthylphenylsilane and (+)-DIOP. A mixture of (−)-menthyl phenylglyoxylate (2.88 g, 10 mmol) and α-naphthylphenylsilane (2.50 g, 10.7 mmol) in 10 mL of benzene was added to a benzene solution (5 mL) of the (+)-DIOP–rhodium catalyst (3.04×10^{-2} mmol, 0.304 mol %) under argon, and the mixture was stirred at 11 °C for 4 h. The completion of the reaction was checked by GLC analysis and then 80 mL of a 0.1% methanol solution of *p*-toluenesulfonic acid was added. Methanolysis was completed within 1.5 h at 30 °C and the solvent was evaporated. GLC analysis showed that (−)-menthyl mandelate was produced in 96.5% yield. NMR spectrum (100 MHz) of the reaction mixture revealed that the optical purity of the mandelate was 77% ee. The mixture was submitted to a column chromatography on silica and from *n*-hexane–benzene eluate, 2.73 g (94.1%) of (−)-menthyl (*S*)-(+)-mandelate was obtained, $[\alpha]^{25}_D$ −24.78° (EtOH, c 2.68).

Double Asymmetric Reduction of (−)-Menthyl Pyruvate. Procedure A (for Entry No. 1–4 in Table III). The reaction using diphenylsilane and (+)-DIOP is typically described. A mixture of (−)-menthyl pyruvate (11.3 g, 50 mmol) and diphenylsilane (11.0 g, 59.8 mmol) in 15 mL of degassed benzene was added to a benzene solution (5 mL) of the (+)-DIOP–rhodium catalyst (0.101 mmol, 0.202 mol %) under argon, and the mixture was stirred for 4 h at 18–20 °C. The completion of the reaction was checked by GLC analysis, and the solvent was evaporated. To the residue was added a methanol solution (100 mL) of potassium hydroxide (3 g) and the mixture was heated under reflux for 1 h. Precipitated rhodium metal species was filtered off and the filtrate was concentrated. Then 70 mL of water was added and the aqueous solution was extracted by ether in order to take out (−)-menthol. The aqueous solution was acidified (pH 1) by adding concentrated hydrochloric acid, and precipitated polydiphenylsiloxanes were filtered off. The filtered aqueous solution was concentrated until potassium chloride precipitated (ca. 20 mL) by using a suction pump at ambient temperature. The residue was extracted by 200 mL of ether several times. The ether extract was dried over anhydrous magnesium sulfate and concentrated. To the residue was added 3.0 g (50 mmol) of *n*-propyl alcohol, 50 mg of *p*-toluenesulfonic acid, and 120 mL of benzene. Esterification was readily made by azeotrope. The benzene solution was concentrated and submitted to a distillation under reduced pressure to afford (*S*)-*n*-propyl lactate (2.68 g, 40%), $[\alpha]^{20}_D$ −7.55° (neat), 62.4% ee.

Procedure B (for Entry No. 5–8 in Table III). The reaction using diphenylsilane and (+)-DIOP is typically described. To a degassed benzene solution (5 mL) of the (+)-DIOP–rhodium catalyst (6.09×10^{-2} mmol, 0.305 mol %) was added a mixture of (−)-menthyl pyruvate (4.52 g, 20 mmol) and diphenylsilane (4.00 g, 21.7 mmol) in 5 mL of degassed benzene under argon, and the mixture was stirred at 11 °C. After 1.5 h the reaction was completed (GLC analysis) and then a 0.1% methanol solution of *p*-toluenesulfonic acid was added to the

reaction mixture and the mixture was stirred at 30 °C for 1 h. GLC analysis revealed that (−)-menthyl lactate was produced in 97.5% yield. The solution was divided into two fractions by using volumetric flasks, and 1/5 portion was concentrated and submitted to NMR measurement using a shift reagent $Eu(fod)_3$, which revealed that the optical purity of the lactate was 65.3% ee, while 4/5 portion was also concentrated and submitted to a column chromatography on silica. *n*-Hexane–benzene eluates which contained (−)-menthyl lactate (checked by GLC) were collected and submitted to a distillation under reduced pressure to afford 3.095 g (85% yield) of (−)-menthyl lactate, bp 92–92.5 °C (0.6 mmHg), $[\alpha]^{20}_D$ −79.21° (EtOH, *c* 2.256). The NMR measurement of the lactate using $Eu(fod)_3$, thus obtained, displayed that the optical purity of the ester was 65.2% ee. This value clearly indicates that no racemization and partial kinetic resolution occurred during the isolation processes.

Asymmetric Reduction of Esters of Acetoacetic Acid and Benzoylacetic Acid. The asymmetric reduction of *n*-butyl acetoacetate using α-naphthylphenylsilane and (+)-DIOP is typically described. A mixture of *n*-butyl acetoacetate (4.76 g, 30 mmol) and α-naphthylphenylsilane (8.45 g, 36 mmol) in 15 mL of degassed benzene was added to a benzene solution (5 mL) of the (+)-DIOP–rhodium catalyst (0.089 mmol, 0.30 mol %) under argon, and the mixture was stirred for 1.5 h at 20 °C. The completion of the reaction was checked by GLC analysis. To the reaction mixture was added a 0.1% methanol solution of *p*-toluenesulfonic acid (30 mL) and benzene (30 mL), and the mixture was stirred for 0.5 h at ambient temperature. GLC analysis displayed that *n*-butyl 3-hydroxybutyrate was produced in 92% yield. Then the mixture was concentrated and submitted to a column chromatography on silica, and (*S*)-(+)-*n*-butyl 3-hydroxybutyrate (4.04 g, 83%) was obtained from ether eluate. The NMR spectrum using a chiral shift reagent, $Eu(facam)_3$, revealed that the optical purity of the ester thus obtained was 24% ee. For the measurement of optical rotation a further distillation was carried out: bp 81 °C (5 mmHg); $[\alpha]^{20}_D$ +3.66° (neat); $[\alpha]^{20}_D$ +8.55° ($CHCl_3$, *c* 3.02).

Asymmetric Synthesis of 4-Methyl-γ-butyrolactone. Typically, a mixture of isobutyl levulinate (5.16 g, 30 mmol) and α-naphthylphenylsilane (7.72 g, 33 mmol) in 10 mL of benzene was added to the catalyst solution (0.099 mmol, 0.33 mol %), and the mixture, which was cooled initially with an ice–water bath, was stirred for 12 h. To the reaction mixture was added 50 mL of a 0.1% methanol solution of *p*-toluenesulfonic acid and the mixture was stirred for 2 h at ambient temperature. GLC analysis showed that 4-methyl-γ-butyrolactone was formed in 96% yield. The reaction mixture was submitted to column chromatography on silica after the solvent was evaporated, and the lactone was obtained from benzene eluate. The pure sample of the lactone for the measurement of optical rotation was obtained by a distillation under reduced pressure (2.46 g, 82%): bp 89 °C (15 mmHg) [lit.[20] bp 78–80 °C (8 mmHg)]; $\nu_{C=O}$ 1770 cm^{-1}; $[\alpha]^{20}_D$ −23.43° (neat).

Acknowledgment. We are grateful to Professor Yoichiro Nagai of Gunma University for his encouragement. We also thank Mr. Kenichi Sato of our institute for his cooperation in the NMR measurements using shift reagents.

Registry No.—(−)-Menthyl phenylglyoxylate, 25966-98-9; (−)-menthyl pyruvate, 951-98-4; rhodium, 7440-16-6; (*S*)-(+)-mandelic acid, 17199-29-0.

References and Notes

(1) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, N.J., 1971, Sections 2 and 5, and references cited therein.
(2) G. Vavon and A. Antonini, *C. R. Acad. Sci.*, **230,** 1870 (1950); **232,** 1120 (1951).
(3) A. Horeau, H. B. Kagan, and J. P. Vigneron, *Bull. Soc. Chim. Fr.*, 3795 (1968).
(4) Y. Ohgo, Y. Natori, S. Takeuchi, and J. Yoshimura, *Chem. Lett.*, 709 (1974).
(5) J. Solodar, *CHEMTECH*, 421 (1975).
(6) (a) I. Ojima, T. Kogure, and Y. Nagai, *Tetrahedron Lett.*, 1889 (1974); (b) I. Ojima and Y. Nagai, *Chem. Lett.*, 191 (1975).
(7) A part of this work was presented in the 7th International Conference on Organometallic Chemistry, Venice, Sept 1975, Abstract No. 45.
(8) (a) I. Ojima, M. Nihonyanagi, and Y. Nagai, *J. Chem. Soc., Chem. Commun.*, 938 (1972); (b) I. Ojima, T. Kogure, M. Nihonyanagi, and Y. Nagai, *Bull. Chem. Soc. Jpn.*, **45,** 3506 (1972); (c) I. Ojima, M. Nihonyanagi, and Y. Nagai, *ibid.*, **45,** 3722 (1972); (d) I. Ojima, T. Kogure, and Y. Nagai, *Tetrahedron Lett.*, 5035 (1972); (e) *Chem. Lett.*, 541 (1973); (f) I. Ojima and Y. Nagai, *ibid.*, 223 (1974); (g) I. Ojima, T. Kogure, and Y. Nagai, *ibid.*, 985 (1975); (h) I. Ojima, M. Nihonyanagi, T. Kogure, M. Kumagai, S. Horiuchi, K. Nakatsugawa, and Y. Nagai, *J. Organomet. Chem.*, **94,** 449 (1975); (i) I. Ojima, M. Kumagai, and Y. Nagai, *ibid.*, **111,** 43 (1976); (j) I. Ojima, T. Kogure, M. Kumagai, S. Horiuchi, and T. Sato, *ibid.*, **122,** 83 (1976).
(9) I. Ojima, T. Kogure, and Y. Nagai, *Tetrahedron Lett.*, 2475 (1973).
(10) H. B. Kagan and T-P. Dang, *J. Am. Chem. Soc.*, **94,** 6429 (1972).
(11) E. Wassmer and P. A. Guye, *Chem. Zentralbl.*, **2,** 1418 (1903).
(12) R. Roger, *J. Chem. Soc.*, 2178 (1932).
(13) As is seen from Table I, the production of (*R*)-mandelate is favored when [(−)DIOP]Rh(S)Cl and diphenyl- or α-naphthylphenylsilane are employed for the reaction.
(14) To determine the optical purity of (−)-menthyl mandelate the 100-MHz NMR spectrum of the crude reaction mixture was employed, in which the methine protons of two diastereomers appeared as well-separated singlets at δ 5.00 and 5.10 in C_6D_6. Thus, the possibility of any fractionation during the purification process can be excluded in the estimation of asymmetric induction. The (−)-menthyl mandelate which displayed the signal of the methine proton at δ 5.10 was found to be the (*S*)-mandelate based on the fact that a pure sample of the (*S*)-mandelate showed the methine proton signal at δ 5.10, which was obtained by the fractional recrystallization of the reduction products using *n*-hexane [$[\alpha]^{25}_D$ −7.55° (etOH, *c* 4.85)], and then the other one was identified as (*R*)-mandelate.
(15) V. Prelog, *Helv. Chim. Acta*, **36,** 308 (1953); *Bull. Soc. Chim. Fr.*, 987 (1956).
(16) W. G. Dauben, G. J. Fonken, and D. S. Noyce, *J. Am. Chem. Soc.*, **78,** 2579 (1956).
(17) (a) K. Yamamoto, T. Hayashi, and M. Kumada, *J. Organomet. Chem.*, **54,** C45 (1973); (b) T. Hayashi, K. Yamamoto, K. Kasuga, H. Omizu, and M. Kumada, *ibid.*, **113,** 127 (1976).
(18) A. McKenzie and H. B. Thompson, *J. Chem. Soc.*, **87,** 1016 (1905).
(19) E. Fischer and H. Scheibler, *Chem. Ber.*, **42,** 1221 (1909).
(20) P. A. Levene and H. L. Haller, *J. Biol. Chem.*, **69,** 165 (1926).
(21) (a) K. Yamamoto, T. Hayashi, and M. Kumada, *J. Organomet. Chem.*, **46,** C65 (1972); (b) J-C. Poulin, W. Dumont, T-P. Dang, and H. B. Kagan, *C. R. Acad. Sci.*, **277,** C41 (1973); (c) *J. Am. Chem. Soc.*, **95,** 8295 (1973); (d) R. J. P. Corriu and J. J. E. Moreau, *J. Organomet. Chem.*, **64,** C51 (1974); (e) *ibid.*, **85,** 19 (1975).
(22) Optical rotations, $[\alpha]^{18}_D$ (neat), for the obtained hexan-2-ol were +1.76 and +3.11°, respectively. The optical purity was calculated from the reported specific rotation of the pure *S* enantiomer, $[\alpha]^{18}_D$ +11.68° (neat) [T. D. Stewart and D. Lipkin, *J. Am. Chem. Soc.*, **61,** 3299 (1939)].
(23) Optical purity of the ester was determined on the basis of NMR measurement using $Eu(facam)_3$ in CCl_4: $[\alpha]^{20}_D$ −17.6° (neat). The specific optical rotation, $[\alpha]^{17}_D$, of ethyl (*R*)-3-hydroxy-3-phenylpropionate, reported in the literature [J. Kenyon, H. Phillips, and G. R. Shutt, *J. Chem. Soc.*, 1663 (1935)] was +19.17° (neat), but this value was not a maximum rotation since the maximum rotation, $[\alpha]^{20}_D$, calculated from our result is 28.03° (neat).
(24) For example, (a) E. Frainnet, *Pure Appl. Chem.*, **19,** 489 (1965); (b) Y. Nagai, K. Uetake, T. Yoshikawa, and H. Matsumoto, *J. Synth. Org. Chem. Jpn.*, **31,** 759 (1973); (c) R. J. P. Corriu and J. J. E. Moreau, *J. Chem. Soc., Chem. Commun.*, 38 (1973); (d) I. Ojima, T. Kogure, M. Nihonyanagi, H. Kono, S. Inaba, and Y. Nagai, *Chem. Lett.*, 501 (1973); (e) T. Hayashi, K. Yamamoto, and M. Kumada, *J. Organomet. Chem.*, **112,** 253 (1976).
(25) A. I. Meyers and E. D. Mihelich, *J. Org. Chem.*, **40,** 1186 (1975).
(26) When phenylglyoxylate is employed as substrate, phenyl is the bulkiest substituent and occupies the *quasi-apical* position instead of ester moiety. Thus, the attractive interaction between the ester carbonyl and rhodium is no more effective. Accordingly, the observed results are well explained by the simple steric repulsion model where bulkiness order is estimated in accordance with the manner reported previously.[8j]
(27) Although the crystalline structure of (DIOP)$NiCl_2$ [V. Gramlich and C.Salomon, *J. Organomet. Chem.*, **73,** C61 (1974)] and (DIOP)IrCl(COD), where COD stands for 1,5-cyclooctadiene [S. Brunie, J. Mazan, N. Langlois, and H. B. Kagan, *J. Organomet. Chem.*, **114,** 225 (1976); H. B. Kagan, *Pure Appl. Chem.*, **43,** 401 (1975)] were determined to be tetrahedral and distorted trigonal bipyramidal, respectively, by x-ray analysis, it is not necessarily true that the structure for the crystalline state represents the most preferable structure in solution, especially in the case of these flexible molecules.
(28) Of course, a square-planar complex, (DIOP)Rh(S)Cl, does not have C_2 axis, but if DIOP–rhodium metal moiety of the complex is picked up, it has a C_2 axis.
(29) N. Langlois, T-P. Dang, and H. B. Kagan, *Tetrahedron Lett.*, 4865 (1973).
(30) R. Glaser, *Tetrahedron Lett.*, 2127 (1975).
(31) K. Matsumoto and K. Harada, *J. Org. Chem.*, **31,** 1956 (1966).
(32) A. McKenzie, *J. Chem. Soc.*, **87,** 1380 (1905).
(33) A. McKenzie, *J. Chem. Soc.*, **85,** 1254 (1904).
(34) J. A. Reid and E. E. Turner, *J. Chem. Soc.*, 3219 (1951).
(35) (a) L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffman, and D. Beck, *Tetrahedron Lett.*, 161 (1961); (b) K. Naumann, G. Zon, and K. Mislow, *J. Am. Chem. Soc.*, **91,** 7012 (1969).
(36) R. Roger, *J. Chem. Soc.*, 2168 (1932).