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Optimization of asymmetric hydrogenation of 3-phenyl-3-butenoic acid catalyzed by rhodium(I)-4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyldioxolane (DIOP) *, **

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Abstract

Enantioselective, homogeneous hydrogenation of 3-phenyl-3-butenoic acid (**1**) has extensively been examined in the presence of the rhodium(I)/4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyldioxolane (DIOP) catalyst systems. Optimization of the reaction conditions was undertaken mainly by controlling effects of added tertiary amines as well as solvent polarities on the enantio-selectivity of the product. The best asymmetric yield (85.1% e.e.) was attained when the hydrogenation was carried out in the presence of triethylamine (5 mol%) in 75% aqueous methanol using a neutral rhodium-DIOP catalyst.

Optically active 3-phenylbutanoic acid and its derivatives are often useful building blocks in organic synthesis. Many different asymmetric syntheses of the acid have therefore been carried out mainly using a diastereoface-differentiating alkylation methodology from the corresponding α,β-unsaturated acid, which is modified to esters or amides with a stoichiometric quantity of chiral auxiliaries [2].

There is another approach to the preparation of the chiral acid. Catalytic hydrogenation is evidently a choice and one of the important advantages of homogeneous over heterogeneous catalysis may be the selectivity of the former. At present, however, efficient asymmetric hydrogenation is rarely used except in syntheses of amino acids and closely related compounds [3].

Homogeneous asymmetric hydrogenation of β-methylcinnamic acid has been carried out by a few research groups. While various kinds of optically active phosphines and amides have been examined as chiral ligands of rhodium(I) catalyst

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[4], hydrogenation of this trisubstituted-type of olefin seemed only to proceed under rather severe conditions with only a moderate level of enantioselectivity (24–76% e.e.). Very recently, Noyori and coworkers [5] have found that $Ru(OAc)_2$-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP) is an excellent chiral catalyst for the enantioselective hydrogenation of various acrylic acids including β-methylcinnamic acid (85% e.e.).

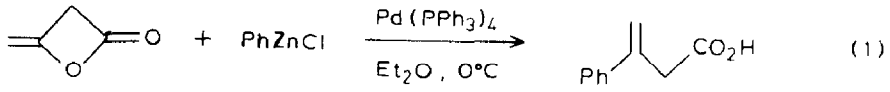
Highly enantioselective hydrogenation of α-acylaminoacrylic acids has been achieved by use of rhodium(I) complexes with a variety of chiral diphosphines, relying primarily on the structural features involved in these prochiral olefin substrates [3]. It is well known that the hydrogenation is facilitated by forming a strong chelation of the substrate with the metal at both C=C and amide C=O and that such a chelation is effective for the enantioface-differentiation by the formal 12 electron RhL_2^+ fragment, where L_2 stands for a specific chiral diphosphine ligand [3a,c].

Bearing in mind an existing difference in coordination stability of the olefin-rhodium(I) complexes between acrylic acids and styrenes, with the stability constant of the latter being known to be lower than that of the former [6], we have investigated homogeneous asymmetric hydrogenation of 3-phenyl-3-butenoic acid (**1**), its esters (**2**), or 3-phenyl-3-butenol (**3**) in the presence of neutral or cationic rhodium(I) complexes with conventional chiral diphosphines. Optimization of the reaction conditions was achieved for the asymmetric hydrogenation of **1** in the presence of rhodium(I) 4,5-bis[(diphenylphosphino)methyl]-2,2-dimethyldioxolane (DIOP) as a catalyst mainly by controlling the known effects, in some cases, of added triethylamine [7] as well as solvent polarities on the enantioselectivity of the product.

The other two substrates, **2** and **3** are also expected to hold even weaker chelation with the catalyst. Thus, these studies of hydrogenation seem to be on a similar line of research to the hydroxy-directed hydrogenation of olefinic alcohols [8].

Results and discussion

The prochiral olefin substrate, 3-phenyl-3-butenoic acid (**1**), can easily be prepared in one step by a palladium(0)-catalyzed reaction of diketene with phenylzinc chloride in moderate yield (eq. 1) [9].



(1) (1)

The simplicity of obtaining **1** and the anticipated mild conditions for its hydrogenation should make the present approach attractive.

Effect of chiral diphosphines of rhodium(I) catalysts

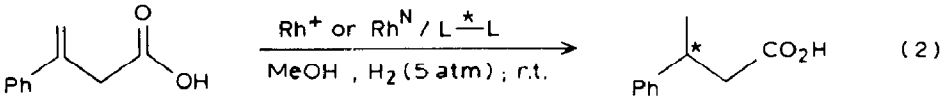
In fact, homogeneous hydrogenation of **1** proceeded readily at room temperature under low pressure of hydrogen (1–5 atm) in the presence of rhodium(I)-diphosphine(L–L*) as catalyst (eq. 2).

Table 1

Asymmetric hydrogenation of 3-phenyl-3-butenoic acid (**1**) with various chiral diphosphine-rhodium(I) catalysts [a]

Entry	Cat. system [b]	Et_3N (mol%)	Yield [c] (%)	$[\alpha]_D^{25}$(PhH) (deg.)	%e.e. [d] (Confgn.)
1	Rh^N-(*S*,*S*)-DIOP	0	77	+16.4 (*c* 2.25)	28.5 (*S*)
2	Rh^N-(*S*,*S*)-DIOP	5	71	+41.2 (*c* 2.08)	71.5 (*S*)
3	Rh^+-(*S*,*S*)-DIOP	0	(6) [e]	+9.6 (*c* 1.66)	16.7 (*S*)
4	Rh^+-(*S*,*S*)-DIOP	10	78	+40.5 (*c* 2.09)	70.3 (*S*)
5	Rh^N-(*S*,*S*)-BPPM	5	79	+12.7 (*c* 2.42)	22.0 (*S*)
6	Rh^N-(*R*)-BINAP	5	78	+1.0 (*c* 2.33)	1.7 (*S*)
7	Rh^+-(*R*)-BINAP	10	80	−1.7 (*c* 2.27)	3.0 (*R*)
8	Rh^N-(*S*,*S*)-CHIRAPHOS	5	(63) [f]	[−13.3 (*c* 1.53)] [g]	35.5 (*R*)
9	Rh^+-(*S*,*S*)-CHIRAPHOS [h]	10	(59) [i]		
10	Rh^N-(*R*)-(*S*)-BPPFA	5	76	+8.6 (*c* 2.20)	14.9 (*S*)
11	Rh^+-(*R*)-DEGPHOS [j]	5	85	+5.5 (*c* 2.16)	9.5 (*S*)
12 [k]	Rh^N-(*S*,*S*)-DIOP	5	76	+43.5 (*c* 2.03)	67.0 (*S*)

[a] $Rh^N = \frac{1}{2}[Rh(1,5\text{-}C_6H_{10})Cl]_2 + L^*L$; $Rh^+ = [Rh(COD)L^*L]^+ ClO_4^-$. Reactions were carried out with 1.0 mmol of **1** in MeOH (0.1 *M*) in the presence of 2 mol% Rh catalyst at room temperature for 20 h under an initial hydrogen pressure of 5 atm. [b] For abbreviation of chiral diphosphines, see ref. 3a. [c] Isolated yield. [d] Enantiomeric excess was calculated with respect to the following value for the optically pure (*R*)-3-phenylbutanoic acid: $[\alpha]_D^{25}$ −57.6° (*c* 2.7, PhH) (ref. 10) (Also, see Experimental). [e] Slow reaction. [f] Conversion (GLC) in 6 days. [g] Determined by its methyl ester, which was prepared by esterification with diazomethane (see Table 5 footnote *c*)). [h] $[Rh(NBD)(CHIRAPHOS)]^+ ClO_4^-$. [i] Conversion (GLC) in 3 days. [j] $[Rh(COD)(DEGPHOS)]^+ BF_4^-$. [k] Asymmetric hydrogenation of 3-*p*-tolyl-3-butenoic acid. (*S*)-3-*p*-tolylbutanoic acid: $[\alpha]_D^{25}$ +65° (*c* 4.6, PhH); V.K. Honwad and A.S. Rao [25].



(1) (2)

In Table 1 is shown the effect of conventional chiral diphosphines on the enantioselectivity of the hydrogenation product by using either a neutral (prepared in situ) or a cationic rhodium catalyst with or without added triethylamine.

As can be seen from Table 1, it is noteworthy that (i) addition of triethylamine (5–10 mol% to **1**) was essential for appreciably enantioselective hydrogenation to take place (entries 1 and 2; 3 and 4), (ii) among chiral diphosphines examined, only the DIOP complex was satisfactorily effective for both catalytic activity and enantioselectivity, and (iii) significant differences in catalysis between neutral and cationic rhodium(I) species in methanol appeared to be reflected in the extent and even the sense of enantioface-differentiation (entries 1 and 3; 6 and 7).

By taking entry 4 in Table 1 as standard conditions ([Rh] 2 m*M*, [Substrate **1**] 0.1 *M* in MeOH) but under atmospheric hydrogen pressure, the turnover rate was measured to be 19 mol H_2/mol Rh · h.

The value may be roughly compared with 2300 mol H_2/mol Rh · h given for α-acetamidocinnamic acid under the conditions ([Rh] 5 m*M*, [Substrate] 0.5 *M* in

PhH/EtOH (1/2 v/v)) [11], indicating 1/120 decrease in turnover rate of hydrogenation for **1**.

Presumably, the overall rate differences stem from the marked difference in equilibrium constants between coordination of α-acetamidocinnamic acid and coordination of **1**, with Rh^I complexes [6b]. It is suggested that as the coordination of a prochiral olefin moiety to the chiral catalyst becomes weaker, the harder overall enantioface differentiation becomes, even though the present substrate (**1**) holds chelation with the catalyst center.

The function of chiral display of all conventional diphosphines employed here arises from the conformational array of phenyl rings in diphenylphosphino groups of a given chiral diphosphine which is forming a chelate with rhodium [3]. The reason why most chiral diphosphines other than DIOP are not effective in the present hydrogenation may stem from the fact that the seven-membered chelate ring formed with DIOP is flexible enough to allow coordination of the substrate **1** to exhibit moderate enantioface-differentiating ability [7a,12], whereas the rigid five-membered chelate ring with 1,2-dimethyl-1,2-bis(diphenylphosphino)ethane (CHIRAPHOS) (or equally rigid one with BINAP) does not effectively fit with the substrate **1**, differentiating poorly the enantioface of this substrate.

It is assumed that Rh^I species which contain more basic phosphine ligands may help coordination of **1** because of a favorable back donation from the metal to the olefin. Attempted derivation of DIOP, by introducing an electron-donating substituent (Me, MeO, or Me_2N) into the *para* position of diphenylphosphino groups, however, resulted in less effective asymmetric hydrogenation of **1** (for Rh^+ catalyst, 38.2, 30.6, and 63.7% e.e., respectively). It is concluded that as the phosphorus atoms in DIOP derivatives have a more basic nature than in the parent DIOP, they can hardly operate efficiently because of the change in steric environments even at the *para* positions. Thus our attention was focused on the use of DIOP itself.

Effects of solvents

In order to optimize the reaction conditions under which the best enantioselectivity in the present asymmetric hydrogenation of **1** would be attained, we examined effects of solvents and triethylamine added for both neutral and cationic rhodium-DIOP catalyst systems. Results are summarized in Table 2, concentrations of reagents being essentially the same as in entry 4, Table 1.

Characteristic features in Table 2 are: (i) Neutral rhodium(I)-DIOP behaved quite differently in methanol and in benzene regardless of the presence or absence of triethylamine: (*S*)-3-phenylbutanoic acid was obtained in methanol with a marked effect of the amount of added triethylamine on the enantiomeric excess (entries 1–3) (vide infra), whereas (*R*)-isomer was the product in benzene solution (entries 4 and 5). (ii) This is not the case with the cationic catalyst but a very low level of enantioselectivity in benzene solution was observed (entries 7 and 8). (iii) Dichloromethane was found to be a satisfactory solvent for the cationic catalyst (entry 10). (iv) Hydrogenation at high pressure (80 atm) affected enantioselectivity differently for neutral and cationic rhodium catalysts (footnote *d* for entries 2 and 7). These results can be explained by assuming that the neutral rhodium(I)-DIOP species must be converted in methanol into cationic species, chloride ion still retaining substantial effect on both catalytic activity and selectivity of RhL_2^+ fragment (i.e. difference in Cl^- vs. ClO_4^-).

Table 2

Effects of solvent and triethylamine added on the asymmetric hydrogenation of **1** [a]

Entry	Catalyst	Solvent	Et_3N (mol%)	Yield [b] (%)	%e.e. [c] (Confgn.)
1	Rh^N-(*S*,*S*)-DIOP	MeOH	0	77	28.5 (*S*)
2	Rh^N-(*S*,*S*)-DIOP	MeOH	5	71	71.5 (*S*) [d]
3	Rh^N-(*S*,*S*)-DIOP	MeOH	50	76	77.6 (*S*)
4	Rh^N-(*S*,*S*)-DIOP	PhH	0	72	16.7 (*R*)
5	Rh^N-(*S*,*S*)-DIOP	PhH	5	80	11.8 (*R*)
6	Rh^N-(*S*,*S*)-DIOP	PhH/MeOH (1/3 v/v)	5	78	64.6 (*S*)
7	Rh^+-(*S*,*S*)-DIOP	MeOH	10	78	70.3 (*S*) [d]
8	Rh^+-(*S*,*S*)-DIOP	PhH	10	85	1.7 (*S*)
9	Rh^+-(*S*,*S*)-DIOP	THF	10	(76) [e]	9.7 (*S*)
10	Rh^+-(*S*,*S*)-DIOP	CH_2Cl_2	10	75	72.4 (*S*)

[a] For reaction conditions, see Table 1, footnote *a*. [b] Isolated yield. [c] Based on the optical rotation of (*R*)-3-phenylbutanoic acid. [d] High initial hydrogen pressure (80 atm) affects enantioselectivity differently for Rh^N (57.9% e.e.) and Rh^+ (76.6% e.e.). [e] Slow reaction. Stirred at r.t. for 3 days.

Effects of addition of tertiary amines

Although the enantioselectivity in the asymmetric hydrogenation of **1** with the Rh^I-DIOP catalyst system was improved dramatically by the addition of triethylamine, its role is still unclear. There has been an argument that tertiary amines may help dissociation of a chloro ligand from the so-called neutral rhodium catalyst, which is obtained in situ by mixing $[Rh(diene)Cl]_2$ and an appropriate chiral diphosphine in a conventional method [7a].

Since 3-phenyl-3-butenoic acid (**1**) forms an ammonium carboxylate with an added tertiary amine, and the olefinic carboxylate ion, in turn, may form a stronger chelate with the rhodium center than **1**, it must be informative to examine the effects of various tertiary amines including optically active ones on the observed enantioselectivity of the product. Results are summarized in Table 3.

The steric effect of tertiary amines used was neither straightforward nor significant, quinuclidine and 1,4-diazabicyclo[2.2.2]octane (DABCO) giving rise to only slightly higher enantioselectivity. At the moment, the best selectivity reached nearly 79% e.e. (entries 2, 3 and 7, 8).

It is, however particularly worthy of note that double asymmetric induction was observed by using (*S*)-*N*,*N*-dimethyl-α-methylbenzylamine. Catalytic hydrogenation of **1** with use of Rh^+/(*R*,*R*)-DIOP and the (*S*)-amine was found to result in an ordinary enantioselectivity (entry 14), while that with Rh^+/(*S*,*S*)-DIOP and the (*S*)-amine gave rise to much inferior selectivity (entry 13). The results must indicate the formation of an intimate ammonium salt between **1** and the chiral amine, the olefinic prochiral faces now becoming diastereotopic. Consequently, diastereofacial differentiation of the (*S*)-ammonium carboxylate of **1** with Rh^+/(*R*,*R*)-DIOP as a "matched pair" took place advantageously compared with Rh^+/(*S*,*S*)-DIOP ("mismatched pair") [13].

The same trend as above was clearly observed with the neutral Rh^I-DIOP catalyst and three different but related chiral amines (entry 10–12).

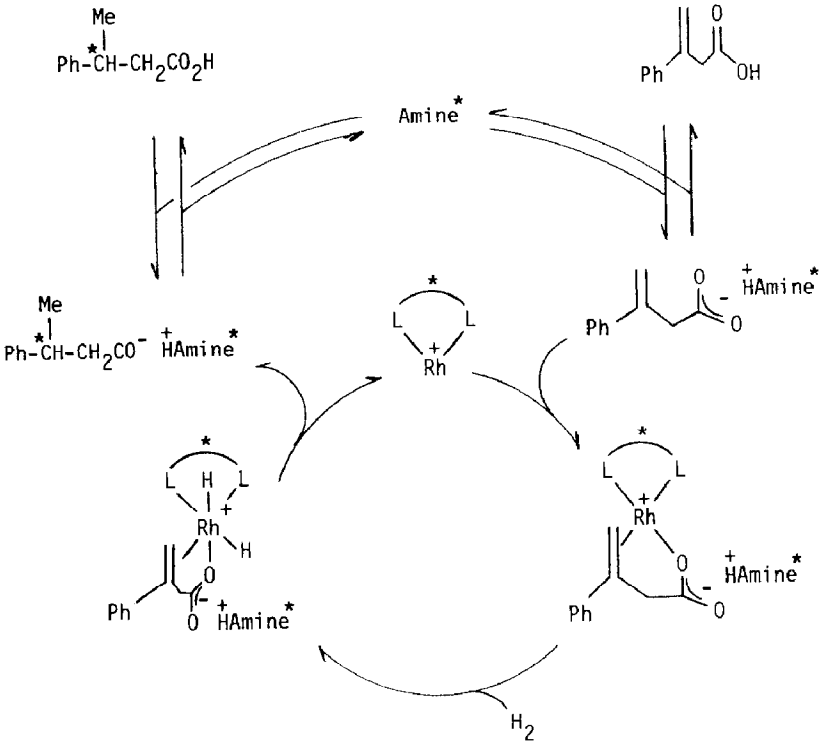
It may be appropriate to discuss here the role of added amines in asymmetric hydrogenation of **1**; the olefinic ammonium carboxylate of **1** does assist stronger

Table 3

Effects of tertiary amines on the asymmetric hydrogenation of **1** [a]

Entry	Rh/DIOP +or N	Additive (mol%)	Yield [b] (%)	%e.e. [c] (Confign.)
1	N/(*S*,*S*)	Et_3N (5)	71	71.5 (*S*)
2	N	DABCO (5)	80	74.5 (*S*)
3	N	Quinuclidine (5)	85	70.5 (*S*)
4	+	Et_3N (10)	78	70.3 (*S*)
5	+	i-Pr_2EtN (10)	86	49.8 (*S*)
6	+	$PhCH_2NMe_2$ (10)	83	54.9 (*S*)
7	+	DABCO (10)	85	78.9 (*S*)
8	+	Quinuclidine (10)	81	45.3 (*S*)
9	+	TDA-1 [d] (10)	84	45.3 (*S*)
10	N/(*R*,*R*)	(*S*)-PhCHMeNMe_2 (5)	84	74.0 (*R*)
11	N/(*S*,*S*)	(*R*)-1-NpCHMeNMe_2 (5)	89	66.8 (*S*)
12	N/(*R*,*R*)	(*S*)-2-NpCHMeNMe_2 (5)	80	79.2 (*R*)
13	+/(*S*,*S*)	(*S*)-PhCHMeNMe_2 (10)	84	33.9 (*S*)
14	+/(*R*,*R*)	(*S*)-PhCHMeNMe_2 (10)	82	75.3 (*R*)

[a] Rh^+ = [Rh(COD)(+) or (−)-DIOP]$^+$ ClO_4^-; $Rh^N = \frac{1}{2}[Rh(1,5\text{-}C_6H_{10})Cl]_2$ + (+)- or (−)-DIOP. Reactions were carried out with 1 mmol of substrate **1** in MeOH (0.1 *M*) in the presence of 2 mol% of Rh catalyst at room temperature for 20 h under an initial hydrogen pressure of 5 atm. [b] Isolated yield. [c] Enantiomeric excess was based on the optical rotation of pure (*R*)-3-phenylbutanoic acid (ref. 3a). [d] Tris(3,6-dioxaheptyl)amine.



Scheme 1. Catalytic cycle.

Table 4

Effect of solvent polarity of aqueous methanol on the asymmetric hydrogenation of **1** [a]

Entry	Rh +or N	Solvent $MeOH/H_2O$	Et_3N (mol.%)	Yield [b] (%)	%e.e. [c] (Confign.)
1	N	1/0	5	71	71.5 (*S*)
2	N	10/1	5	79	72.5 (*S*)
3	N	5/1	5	84	74.5 (*S*)
4	N	3/1	5	73 (83) [d]	85.1 (*S*) (83.9) [d]
5	N	2/1	5	83 [e]	7.9 (*S*)
6	+	1/0	10	78	70.3 (*S*)
7	+	3/1	10	77	77.6 (*S*)

[a] $Rh^+ = [Rh(COD)(S,S)\text{-DIOP}]^+ ClO_4^-$; $Rh^N = \frac{1}{2}[Rh(1,5\text{-}C_6H_{10})Cl]_2 + (S,S)$-DIOP. For reaction conditions, see Table 1, footnote *a*). [b] Isolated yield. [c] On the same basis as in Tables 1–3. [d] Duplicated runs. [e] Catalyst deteriorated.

chelation to the chiral catalyst center than **1** itself, resulting in higher enantioselection as a whole. A plausible cycle for rhodium-catalyzed selective hydrogenation of **1** is depicted in Scheme 1 in which an added amine plays a role in reversible formation of the ammonium salt of **1** that actually undergoes hydrogenation.

The amount of triethylamine up to 50 mol% with respect to **1** did affect significantly the asymmetric yield as mentioned above (Table 2, entries 1–3). This may be not simply due to a plenty of the ammonium salt to be formed, but also due to the polarity of the reaction medium which must play a role in determining the critical step for enantioselectivity by the cationic rhodium(I) species.

Thus, we have further examined the solvent effect on the asymmetric hydrogenation of **1**, where aqueous methanol was used as solvent. The polarizing ability of the mixed solvent (the *Y*-value of which is known to be measure [14]) was found to be indeed of significance as summarized in Table 4.

The best asymmetric yield (85.1% e.e.) for the present hydrogenation of **1** was attained when triethylamine (5 mol%) was added in 75% aqueous methanol containing a neutral rhodium-DIOP catalyst under otherwise the standard conditions as described above.

It is quite interesting to find that, as far as the homogeneity of the reaction mixture is maintained, the observed enantiomeric excess tends to be proportional to the increase in *Y*-value of aqueous methanol.

It is thus presumed that the more polar the solvent is, the better the cationic rhodium(I) species operates as a RhL_2^+ fragment. Generation of the latter free from the gegenanion (Cl^- or ClO_4^-) could be advantageous for efficient enantioselective hydrogenation of **1**.

Another double asymmetric induction during hydrogenation was examined by using *N*-[(*S*)-α-methylbenzyl]-3-phenyl-3-butenamide as a substrate. Hydrogenation of the (*S*)-butenamide with a Rh^+-(*S,S*)-DIOP catalyst under the standard conditions gave *N*-[(*S*)-α-methylbenzyl]-3-phenylbutanamide quantitatively in 74% d.e. (*S,S*), while hydrogenation with a Rh^+-(*R,R*)-DIOP catalyst resulted in giving the diastereomer in 60% d.e. (*R,S*). Thus, diastereofacial differentiation of the (*S*)-butenamide with chiral Rh^+/DIOP catalyst systems exhibited an inverse matching as compared with the (*S*)-ammonium carboxylate of **1** discussed earlier.

Table 5

Asymmetric hydrogenation of 3-phenyl-3-butenoate esters, $PhC(CH_2CO_2R)=CH_2$ (**2**) [a]

Entry	R	Yield [b] (%)	$[\alpha]_D^{25}$ (EtOH) [c] (deg.) of Me ester	%e.e. (Confgn.)
1	Me (**2a**)	94	+8.8 (*c* 1.05) [d]	23 (*S*) [d]
2	Et (**2b**)	92	+8.3 (*c* 1.04)	22 (*S*)
3	i-Pr (**2c**)	95	+8.4 (*c* 2.20)	22 (*S*)
4	i-Bu (**2d**)	95	+9.5 (*c* 1.58)	25 (*S*)
5	t-Bu (**2e**)	93	+9.5 (*c* 1.89)	25 (*S*)

[a] $Rh^N = \frac{1}{2}[Rh(1,5\text{-}C_6H_{10})Cl]_2 + (R,R)$-DIOP. Reactions were carried out with 1 mmol of **2** in benzene (0.1 *M*) in the presence of 2 mol% of Rh^N at room temperature for 20 h under H_2 (5 atm). [b] Isolated yield. [c] Product was converted to the methyl ester by transesterification (*p*-TsOH in MeOH, heated for 5 h): (*S*)-methyl 3-phenylbutanoate: $[\alpha]_D^{25}$ +37.5° (*c* 2.06, EtOH) (See Experimental). [d] HPLC analysis of diastereomeric mixture of *N*-[(*S*)-α-methylbenzyl]-3-phenylbutanamide.

Asymmetric hydrogenation of 3-phenyl-3-butenoate esters (2)

In order to examine the foregoing arguments on the role of ammonium carboxylate function, asymmetric hydrogenation of a series of 3-phenyl-3-butenoate esters, including methyl (**2a**), ethyl (**2b**), isopropyl (**2c**), isobutyl (**2d**), and t-butyl (**2e**) esters, was carried out under standard conditions similar to those for **1**. The results given in Table 5 show only moderate asymmetric yield (22–25% e.e.) regardless of the bulkiness of the ester groups.

Such an insensitivity to steric effect of the esters (**2**) on the asymmetric yields reflects only a weak chelation, if any, of the esters. They undergo hydrogenation by experiencing almost similar chiral environments provided by the Rh^I-DIOP catalyst, substantiating the above-mentioned strong chelation of the olefinic ammonium carboxylate of **1**.

Also, asymmetric hydrogenation of 3-phenyl-3-butenol (**3**) proceeded smoothly to give 3-phenylbutanol in at best 35% e.e.

Experimental

General

^1H NMR and IR spectra were recorded on a JEOL FX 90Q FT spectrometer and with a JASCO IRA-2 spectrometer. GLC and HPLC analyses were performed on a Shimazu GC-4CPT with dual columns (Silicone DC-550 and PEG 20M) and on a Nihon Seimitsu NP-DX, with a UV and RI detector.

Materials

Chiral phosphines and rhodium(I) complexes. *p*-Substituted phenyl DIOP analogs were prepared by the reported procedure [15] using the corresponding tris(*p*-substituted phenyl)phosphines.

(*R,R*)-(4-Me)-DIOP [11]: $[\alpha]_D^{25}$ −1.8° (*c* 2.01, PhH). (*R,R*)-(4-MeO)-DIOP: $[\alpha]_D^{25}$ −5.47° (*c* 2.23, PhH). ^1H NMR (90 MHz, $CDCl_3$, TMS) 1.35 (s, 6H), 2.2–2.4 (m, 4H), 3.7–4.0 (m, 2H), 6.84 (dd, *J*(H–H) 8.8 Hz, *J*(H–P) 0.7 Hz, 8H), 7.34 (dd, *J*(H–H) 8.8 Hz, *J*(H–P) 3.7 Hz, 8H).

(*R,R*)-(4-Me_2N)-DIOP: $[\alpha]_D^{25}$ +7.61° (*c* 2.26, PhH). ^1H NMR; 1.35 (s, 6H), 2.2–2.4 (m, 4H), 2.94 (s, 24H), 3.7–4.0 (m, 2H), 6.66 (d, *J* 8.1 Hz, 8H), 7.2–7.4 (m, 8H).

(*2S,4S*)-*N*-t-Butoxycarbonyl-2-(diphenylphosphino)methyl-4-(diphenylphosphino)pyrrolidine (BPPM) [16] and (*R*)-*N,N*-dimethyl-1-[(*S*)-1′,2-bis(diphenylphosphino)ferrocenyl]ethylamine (BPPFA) [17] were also prepared according to the methods given in the literature. (*R,R*)- and (*S,S*)-DIOP, and (*S,S*)-CHIRAPHOS were purchased. (*R*)-BINAP and (*R*)-*N*-benzyl-3,4-bis(diphenylphosphino)pyrrolidine (DEGPHOS) (as a rhodium(I) complex) were kindly supplied by Dr. Akutagawa (Takasago Research Institute) and Degussa A.G., respectively. $[Rh(1,5\text{-}C_6H_{10})Cl]_2$ [18], $[Rh(COD)Cl]_2$ [18], and [Rh(COD)(acac)] [19] were prepared by standard methods. Cationic rhodium(I) complexes $[Rh(COD)(L\text{-}L)]^+ ClO_4^-$ were prepared by either of the two methods: (A) [11] [Rh(COD)(acac)] + L-L + $HClO_4$; (B) [20] $\frac{1}{2}[Rh(COD)Cl]_2$ + L-L + $AgClO_4$. These complexes and phosphines were stored in a desiccator under an argon atmosphere.

Chiral amines. (*S*)-α-Methylbenzylamine was purchased, $[\alpha]_D^{20}$ −39° (neat), and converted to an (*S*)-*N,N*-dimethyl derivative by formic acid and 38% formalin [21], $[\alpha]_D^{25}$ −41.7° (*c* 2.06, MeOH). Partially active (*R*)-α-(1-naphthyl)ethylamine (39% e.e.) [22a,b] was resolved by using (+)-tartaric acid, $[\alpha]_D^{25}$ +60.7° (*c* 2.19, MeOH) and converted to an (*R*)-*N,N*-dimethyl derivative [21], b.p. 110–115°C/3 Torr (Kugelrohr), $[\alpha]_D^{25}$ +41.7° (*c* 2.06, MeOH). Partially active (*S*)-α-(2-naphthyl)ethylamine (34% e.e.) [22b,c] was also resolved in essentially the same manner as above, $[\alpha]_D^{25}$ −20.0° (*c* 2.02, EtOH) (92.5% e.e.), and converted to an (*S*)-*N,N*-dimethyl derivative [21], b.p. 115–120°/3 Torr (Kugelrohr], $[\alpha]_D^{25}$ −59.5° (*c* 2.04, EtOH). Tris(3,5-dioxaheptyl)amine (TDA-1) was supplied by Rhone Poulenc, Japan.

Preparation of 3-phenyl-3-butenoic aid (1), its esters (2), and 3-phenyl-3-butenol (3)

According to the literature [9], with a slight modification, diketene (4.20 g, 50 mmol) and freshly prepared $Pd(PPh_3)_4$ (1.5 mmol, 3 mol%) were dissolved in dry THF (50 ml) under nitrogen, and the solution was cooled to 0°C. To the solution was added dropwise a suspension of phenylzinc chloride, prepared from phenylmagnesium bromide in ether (1.7 *M*, 60 mmol) and a solution of zinc chloride (8.99 g, 66 mmol) in THF (70 ml), with ice-cooling and the resulting mixture was stirred for an additional 3 h at 0°C. Usual work-up to remove Pd catalyst and extractive purification and recrystallization from pentane gave 3-phenyl-3-butenoic acid: m.p. 46–47°C (lit. [9] m.p. 46–47°C), 56–67% yield. ^1H NMR 3.54 (d, *J* 0.9 Hz, 2H), 5.25 (d, *J* 0.9 Hz, 1H), 5.57 (s, 1H), 7.3–7.5 (m, 5H), 10.5 (bs, 1H). IR (Nujol) 1720, 1640 cm^{-1}. In exactly the same procedure a above, palladium(0)-catalyzed reaction of diketene with *p*-tolylzinc chloride afforded 3-*p*-tolyl-3-butenoic acid in 50% yield, mp. 113–114°C, (lit. [9] m.p. 113–114°C). ^1H NMR 2.32 (s, 3H), 3.51 (d, *J* 0.9 Hz, 2H), 5.19 (d, *J* 0.9 Hz, 1H), 5.53 (s, 1H), 7.10–7.4 (m, 4H), 11.0 (bs, 1H). IR (Nujol) 1700, 1640 cm^{-1}.

Methyl 3-phenyl-3-butenoate (**2a**) was prepared by methylation of **1** (1.62 g, 10 mmol) with diazomethane in 90% yield; b.p. 70–75°C/2 Torr.

General procedure for the preparation of starting carbonates. A mixture of 2-phenylpropenol (4.75 g, 60 mmol) and excess pyridine in dry ether (100 ml) was treated with an alkyl chloroformate (60 mmol) at 0°C for 2 h and at room

temperature overnight. Usual aqueous work-up followed by fractional distillation gave pure carbonate esters, $PhC(CH_2OCO_2R)=CH_2$. R = Me (58% yield), b.p. 81–85 °C/3 Torr; R = Et (72%), b.p. 86–87 °C/3 Torr; R = i-Pr (61%), b.p. 98–99 °C/3 Torr; and R = i-Bu (68%), b.p. 102–103 °C/3 Torr.

General procedure for the preparation of alkyl 3-phenyl-3-butenoates (2). Methyl (**2a**), ethyl (**2b**), isopropyl (**2c**), isobutyl (**2d**), and t-butyl (**2e**) esters were prepared by way of palladium(0)-catalyzed decarboxylation-carbonylation [23] of the corresponding 2-phenylpropenyl carbonates obtained as described above.

General procedure for the carbonylation of allylic carbonates

In a 50-ml microautoclave equipped with a magnetic stirrer were placed $Pd(OAc)_2$ (44.9 mg, 0.2 mmol), PPh_3 or 1-methyl-2,6,7-trioxa-4-phospha-bicyclo[2.2.2]octane (0.4 mmol) and an allylic carbonate (10 mmol). The autoclave was purged three times by filling and evacuating with CO (15 atm), and filled with CO (12–30 atm). The mixture was heated at 50 °C overnight with stirring. After the reaction was complete (GLC analysis), the palladium catalyst was triturated by adding ether and filtered though a florisil plug. The filtrate was concentrated by evaporation and the residue was purified by distillation to give 3-phenyl-3-butenoates. Methyl ester (**2a**) (73% yield), b.p. 75–77 °C/2 Torr; ethyl (**2b**) (72%), b.p. 80–82 °C/3 Torr; isopropyl (**2c**) (66%), b.p. 92–95 °C/3 Torr; isobutyl (**2d**) (68%), b.p. 80–82 °C/2 Torr; and t-butyl (**2e**) (53%), b.. 77–79 °C/2 Torr.

One exceptional case was the preparation of t-butyl 2-phenylpropenyl carbonate, which was obtained by a reaction of 2-phenylpropenyl chloroformate (30 mmol) with sodium t-butyl alcoholate (45 mol) in dry THF in 52% yield, b.p. 85–86 °C/0.6 Torr. ^1H NMR spectra and analytical data for allylic carbonates and 3-phenyl-3-butenoates (**2a–2e**) are tabulated in Table 6.

Preparation of 3-phenyl-3-butenol (3). To a solution of **2a** (2.64 g, 15 mmol) in dry ether (30 ml) was added diisobutylaluminum hydride (1.55 *M* in pentane, 21 ml, 33 mmol) at 0 °C and the resulting mixture was stirred at 0 °C for 15 min. After usual workup, **3** was obtained by distillation in 84% yield, b.p. 79–80 °C/2 Torr. ^1H NMR: 1.6 (bs, 1H), 2.77 (t, *J* 6.4 Hz, 2H), 3.72 (t, *J* 6.4 Hz, 2H), 5.15 (d, *J* 0.3 Hz, 1H), 5.00 (d, *J* 1.3 Hz, 1H), 7.3–7.5 (m, 5H).

Hydrogenation procedures

All solvents were cleared of air by a stream of nitrogen for at least 15 min before use. A typical procedure for the asymmetric hydrogenation is as follows;

(A) Cationic rhodium catalyst. In a 50-ml microautoclave lined with a glass tube and equipped with a magnetic stirrer was placed a cationic rhodium-bisphosphine complex (0.02 mmol) under nitrogen. In the case of acid **1**, the autoclave was then charged with the substrate (1.0 mmol), Et_3N (0.1 mmol; 10 mol%), and solvent (10 ml). The autoclave containing the solution was purged three times by filling and evacuating with hydrogen (10 atm) to remove any trace of oxygen, and the hydrogenation was carried out under an initial hydrogen pressure of, usually, 5 atm at room temperature with stirring for 20 h. After the hydrogenation was complete (GLC analysis), the mixture was worked up in two different ways depending on the substrate (vide infra) to give a pure hydrogenation product.

(B) Neutral rhodium catalyst. In the same 50-ml microautoclave as above were placed $[Rh(1,5\text{-}C_6H_{10})Cl]_2$ (4.4 mg, 0.01 mmol) and a given chiral bisphosphine

Table 6

^{1}H NMR spectral and analytical data for alkyl 2-phenylpropenyl carbonates and alkyl 3-phenyl-3-butenoates (**2a–2e**)

	^{1}H NMR (90 MHz, $CDCl_3$, TMS) δ	Anal. (Found (calcd.)(%))		
		form	C	H
PhC(CH_2OCO_2R)=CH_2				
R = Me	3.78 (s, 3H), 5.03 (d, *J* 1.1 Hz, 2H), 5.40 (d, *J* 1.1 Hz, 1H), 5.56 (s, 1H), 7.3–7.5 (m, 5H)	$C_{11}H_{12}O_3$	68.44 (68.73)	6.29 (6.29)
R = Et	1.29 (t, *J* 7.0 Hz, 3H), 4.20 (q, *J* 7.0 Hz, 2H), 5.02 (d, *J* 0.9 Hz, 2H), 5.40 (d, *J* 0.9 Hz, 1H), 5.56 (s, 1H), 7.3–7.5 (m, 5H)			
R = i-Pr	1.29 (d, *J* 6.2 Hz, 6H), 4.89 (septet, *J* 6.2 Hz), 1H), 5.01 (d, *J* 0.9 Hz, 2H), 5.40 (d, *J* 0.9 Hz, 1H), 5.56 (s, 1H), 7.3–7.5 (m, 5H)	$C_{13}H_{15}O_3$	70.74 (70.89)	7.34 (7.32)
R = i-Bu	0.93 (d, *J* 6.6 Hz, 6H), 1.96 (m, *J* 6.6 Hz, 1H), 3.93 (d, *J* 6.6 Hz, 2H), 5.03 (d, *J* 0.9 Hz, 2H), 5.40 (d, *J* 0.9 Hz, 1H), 5.56 (s, 1H), 7.3–7.5 (m, 5H)	$C_{14}H_{18}O_3$	71.57 (71.77)	7.61 (7.32)
R = t-Bu	1.47 (s, 9H), 4.96 (d, *J* 1.1 Hz, 2H), 5.38 (d, *J* 1.1 Hz, 1H), 5.54 (d, *J* 0.9 Hz, 1H), 7.2–7.5 (m, 5H)			
*PhC(CH_2CO_2R)=CH_2 (**2a–2e**)*				
R = Me (**2a**)	3.52 (d, *J* 1.1 Hz, 2H), 3.64 (s, 3H), 5.23 (d, *J* 1.1 Hz, 1H), 5.55 (d, *J* 0.9 Hz, 1H), 7.3–7.5 (m, 5H)	$C_{11}H_{12}O_2$	74.77 (74.98)	6.90 (6.86)
R = Et (**2b**)	1.18 (t, *J* 7.3 Hz, 3.51 (d, *J* 1.1 Hz, 2H), 4.11 (q, *J* 7.3 Hz, 2H), 5.23 (d, *J* 1.1 Hz, 1H), 5.53 (s, 1H), 7.3–7.5 (m, 5H)			
R = i-Pr (**2c**)	1.14 (d, *J* 6.2 Hz, 6H), 3.48 (d, *J* 1.1 Hz, 2H), 5.49 (septet, *J* 6.2 Hz, 1H), 5.22 (d, *J* 1.1 Hz, 1H), 5.52 (s, 1H), 7.3–7.5 (m, 5H)	$C_{13}H_{16}O_2$	76.06 (76.44)	7.77 (7.90)
R = i-Bu (**2d**)	0.83 (d, *J* 6.6 Hz, 6H), 1.84 (m, *J* 6.6 Hz, 1H), 3.54 (d, *J* 1.1 Hz, 2H), 3.83 (d, *J* 6.6 Hz, 2H), 5.24 (d, *J* 1.1 Hz, 1H), 5.54 (d, *J* 0.9 Hz, 1H), 7.3–7.5 (m, 3H)	$C_{14}H_{18}O_2$	76.58 (77.03)	8.38 (8.31)
R = t-Bu (**2e**)	1.35 (s, 9H), 3.43 (d, *J* 1.1 Hz, 2H), 5.20 (d, *J* 1.1 Hz, 1H), 5.49 (d, *J* 0.9 Hz, 1H), 7.3–7.5 (m, 5H)	$C_{14}H_{18}O_2$	76.94 (77.03)	8.40 (8.31)

(0.021 mmol) under nitrogen. To this was added a given solvent (5 ml) and the solution was stirred for 10 min at room temperature. In the case of acid **1**, a solution of the substrate (1.0 mmol) and Et_3N (0.05 mmol, 5 mol%) dissolved in the same solvent (5 ml) was then added to the in-situ catalyst solution. After the same procedure for purging any trace of oxygen as described above, the hydrogenation was carried out at room temperature for 20 h under hydrogen (5 atm). Workup followed.

(C) Work-up procedure. (i) For carboxylic acid **1**. After removal of the solvent by evaporation, the residue was dissolved in 30 ml of ether. The resulting solution was extracted with cold saturated $NaHCO_3$ (15 ml × 2). The alkaline extracts were acidified with 6N HCl and the organic material was extracted with ether (15 ml × 2). The ether extracts were washed with brine, dried ($MgSO_4$) and con-

Table 7

Turnover rate [a] measurements

Substrate **1** (1.0 mmol)	NO.	t(min)	$V(H_2)$ (ml)	Conversion (%)
Catalyst [Rh(COD)(*S*,*S*)-DIOP]$^+$ ClO_4^-	0	0	0	0
	1	26	5.1	24.6
Solvent MeOH (10 ml)	2	54	10.1	47.4
Additive Et_3N (0.10 mmol)	3	88	16.1	71.5
	4	120	21.3	90.3
H_2 1 atm	5	156	25.7	> 99
Temperature 20 °C	6	240	28.0	> 99

[a] Turnover rate = 19 mol H_2/mol Rh·h.

centrated by evaporation. The residue was distilled (Kugelrohr) to give a pure product.

(ii) For esters **2** and alcohol **3**. After removal of the solvent, the residue was diluted with ether and the solution was filtered through a short florisil column to remove a rhodium complex. The filrate was concentrated by evaporation and the residue was distilled (Kugelrohr) to give a colorless oil. Further purification was carried out by preparative GLC, if required.

(D) Turnover rate measurements. Asymmetric hydrogenation of **1** was carried out by using [Rh(COD)(*S*,*S*)-DIOP]$^+$ ClO_4^- as a catalyst precursor (condition A) under a normal hydrogen pressure (gas burette) at 20 °C. The extent of hydrogenation was monitored by both uptake of H_2 and GLC analysis of aliquots (50 μl sampling at every ca. 5 ml of hydrogen uptake) after methylation by diazomethane. The results are given in Table 7.

(E) Preparation of N-[(S)-α-methylbenzyl]-3-phenyl-3-butenamide. To a stirred suspension of 2-chloro-1-methylpyridinium iodide (3.07 g, 12 mmol) and **1** (1.62 g, 10 mmol) in CH_2Cl_2 (5 ml) was added a solution of (*S*)-α-methylbenzylamine (2.41 g, 20 mmol) and Et_3N (4.05 g, 40 mmol) in CH_2Cl_2 (5 ml) under argon. The mixture was heated under refluxing for 5 h. After removal of the solvent, the residue was purified by column chromatography (silica gel). Recrystallization (benzene-hexane) gave pure amide 1.27 g (48%).

^{1}H NMR 1.33 (d, *J* 7.0 Hz, 3 H), 3.48 (d, *J* 1.5 Hz, 2H), 5.06 (quint, *J* 7.3 Hz, 1H), 5.27 (d, *J* 1.1 Hz, 1H), 5.64 (d, *J* 1.1 Hz, 1H), 5.9 (bd, *J* 7 Hz, 1H), 7.0–7.5 (m, 10H).

Double asymmetric induction during hydrogenation was detected with the (*S*)-butenamide (0.65 mmol) and [Rh$^+$(COD)(*S*,*S*)-DIOP]$^+$ ClO_4^- (2 mol%) in MeOH (6.5 ml) at room temperature for 20 h under H_2 (5 atm). *N*-[(*S*)-α-Methylbenzyl]-3-phenylbutanamide was obtained after a short column chromatography in 94% yield. Diastereomeric excess was directly determined to be 74% d.e. (*S*,*S*) by HPLC analysis (silica gel, 100 mm ×5 mm; 2% isopropyl alcohol/hexane, 2 ml/min). In exactly the same manner as above by using Rh$^+$-(*R*,*R*)-DIOP catalyst, the 3-phenylbutanamide was obtained (90% yield) with 60% e.e. (*R*,*S*) (See below).

N-[(*S*)-α-Methylbenzyl)-(*S*)-3-phenylbutanamide: ^{1}H NMR 1.30 (d, *J* 6.8 Hz, 3H), 1.38 (d, *J* 7.0 Hz, 3H), 2.42 (d, *J* 7.5 Hz, 2H), 3.24 (sextet, *J* 7.3 Hz, 1H), 5.02 (quinted, *J* 7.1 Hz, 1H), 5.6 (bd, *J* 7 Hz, 1H), 6.9–7.4 (m, 10H).

N-[(*S*)-α-methylbenzyl]-(*R*)-3-phenylbutanamide: ^{1}H NMR 1.24 (d, *J* 6.1 Hz, 3H), 1.29 (d, *J* 7.0 Hz, 3H), 2.41 (d, *J* 7.4 Hz, 2H), 3.28 (sextet, *J* 7.1 Hz, 1H), 5.01 (quinted, *J* 7.3 Hz, 1H), 5.4 (bd, *J* 7 Hz, 1H), 7.2–7.4 (m, 10H).

Partially active (*S*)-3-phenylbutanoic acid, $[\alpha]_D^{25}$ +31.6° (*c* 2.06, PhH), 54.9% e.e., was converted into the corresponding (*S*,*S*)-amide in exactly the same manner as above to record 54.3% e.e. by HPLC analysis. This is in excellent agreement with the starting % e.e. on the basis of literature data on maximum rotation [10].

Partially active (*S*)-3-phenylbutanoic acid, $[\alpha]_D^{25}$ +37.3° (*c* 2.07, PhH), 64.8% e.e., was converted by methylation with diazomethane into the corresponding methyl ester, $[\alpha]_D^{25}$ +24.3° (*c* 2.06, EtOH). Calculated maximum rotation should be +37.5° (EtOH). (See Table 5).

(F) Asymmetric hydrogenation of 3-phenyl-3-buten-1-ol (3). According to the general procedure for neutral rhodium catalyst, **3** was hydrogenated in THF by using either (*S*,*S*)-DIOP or (*R*)-BINAP as a chiral ligand under high hydrogen pressure (80 atm) to afford 3-phenylbutanol in almost quantitative yield, enantiomeric excess of the product being 25%(*R*) and 35%(*S*), respectively, on the basis of the rotation of optically pure (*R*)-3-phenylbutanol, $[\alpha]_D^{25}$ −28.4° (*c* 2.14, dioxane) [24]. ^{1}H NMR 1.27 (d, *J* 7.0 Hz, 3H), 1.40 (bs, 1H), 1.84 (q, *J* 7.0 Hz, 2H), 2.88 (sextet, *J* 7.0 Hz, 1H), 3.54 (t, *J* 7.0 Hz, 2H), 7.1–7.4 (m, 5H).

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