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Asymmetric Hydroformylation of Conjugated Dienes Catalyzed by Chiral Phosphine-Phosphite–Rh(I) Complex

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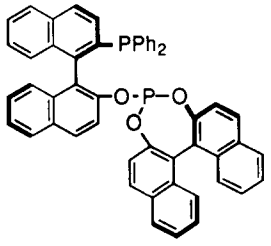
Abstract: Asymmetric hydroformylation of conjugated dienes has been investigated using (*R*,*S*)-BINAPHOS–Rh(I) complex as a catalyst [(*R*,*S*)-BINAPHOS = (*R*)-2-(diphenylphosphino)-1,1'-binaphthalen-2'-yl (*S*)-1,1'-binaphthalene-2,2'-diyl phosphite]. Optically active β,γ-unsaturated aldehydes were obtained in high regio- (78–94%) and enantioselectivities (80–97% ee) from 1-vinylcyclohexene, 4-methyl-1,3-pentadiene, and (*E*)-1-phenyl-1,3-butadiene. On the other hand, hydroformylation of 1,3-butadiene gave achiral product, (*E*)- and (*Z*)-3-pentenal, in up to 95% selectivity. (*R*)-(*E*)-2-Methyl-3-pentenal was formed as the major product from both (*E*)- and (*Z*)-1,3-pentadiene, but enantioselectivity of the reaction was low. Mechanistic aspects are also discussed. © 1997 Elsevier Science Ltd.

INTRODUCTION

Conjugated dienes have been investigated as substrates for hydroformylation to much less extent than monoolefins such as arylethenes and vinyl carboxylates. Most of the previous studies are concerned with the reaction of simple dienes such as 1,3-butadiene, isoprene, and 1,3-pentadiene. In these studies, the chemo- and regioselectivities are generally rather low, probably because of the high reaction temperature employed (95–130 °C). Fell and coworkers reported the systematic study on the hydroformylation of 1,3-dienes, mainly 1,3-butadiene.[1] According to the catalytic systems employed, various amounts of saturated monoaldehydes and dialdehydes were formed. Some attempts at preparing hexanedial by dihydroformylation of 1,3-butadiene have been made mainly on patent literatures.[2] This process leads to the production of adipic acid, one of the starting material of nylon-6,6. On the other hand, van Leeuwen was successful in the selective monohydroformylation of 1,3-butadiene catalyzed by 1,2-bis(diphenylphosphino)ethane–Rh(I) complex to give pentanal in over 90% selectivity, but the selectivity was lower than 60% for isoprene and 1,3-pentadiene with the same catalyst.[3] In this manner, saturated aldehydes were mainly formed in most cases.[4] It is suggested that β,γ-unsaturated aldehydes are formed as the first reaction products.[1,5,6] Saturated aldehydes may be formed *via* double-bond migration of the first products followed by hydrogenation.[1,6] The intermediate α,β-unsaturated aldehydes are much more susceptible to hydrogenation than hydroformylation.[7]

Asymmetric hydroformylation of conjugated dienes has been left almost unexplored. The best optical yield was obtained from the reaction of isoprene, in which 3-methylpentanal was formed in 32% optical purity with $HRh(CO)(PPh_3)_3$/(–)-DIOP system [DIOP = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino) butane].[6] In addition, regioselectivity of the reaction was low, and attention was paid only to the formation of the saturated aldehydes.

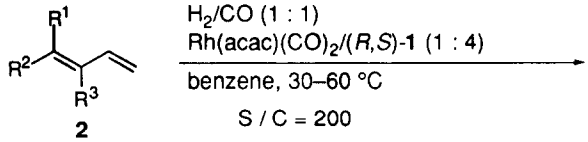
We have developed a chiral phosphine-phosphite ligand, (*R*,*S*)-BINAPHOS [= (*R*)-2-(diphenylphosphino)-1,1'-binaphthalen-2'-yl (*S*)-1,1'-binaphthalene-2,2'-diyl phosphite] [(*R*,*S*)-**1**] and its enantiomer, and successfully applied them to the enantioselective hydroformylation of a variety of prochiral olefins.[8] Here we report a highly selective asymmetric hydroformylation of 1,3-dienes catalyzed by (*R*,*S*)-BINAPHOS–Rh(I) complex under mild conditions to give optically active β,γ-unsaturated aldehydes, which are useful chiral building blocks for the stereocontrolled syntheses of natural products.[9,10]



(*R*,*S*)-BINAPHOS [(*R*,*S*)-**1**]

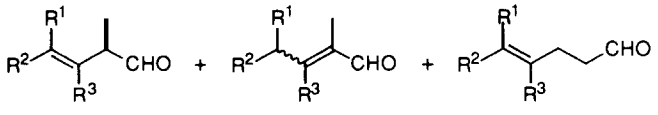
RESULTS AND DISCUSSION

First, asymmetric hydroformylation of 1-vinylcyclohexene (**2a**) was investigated (eq 1, Table 1). The catalyst species was prepared *in situ* by mixing $Rh(acac)(CO)_2$ and 4.0 equivalents of (*R*,*S*)-**1** in benzene. Reactions were carried out at 30–60 °C and at a total pressure of 100 atm (H_2/CO = 1/1). Unsaturated aldehydes (*R*)-2-(1-cyclohexenyl)propanal [(*R*)-**3a**] and 3-(1-cyclohexenyl)propanal (**5a**) were exclusively formed, and **3a** was the major product.[11,12] Saturated aldehydes were not formed. Regio- (86–88%) and enantioselectivities (96–97%) observed for **2a** are comparable to those observed for styrene (2-phenylpropanal/3-phenylpropanal = 88/12, 94% ee at 60 °C)[8a] and are almost independent of the reaction temperature (runs 1–3). Prolonged reaction time caused double-bond migration of **3a** and decrease in the ee of **3a** (run 4). The rate of hydroformylation was effectively improved by lowering the H_2/CO pressure (runs 5–7). The regio- and enantioselectivities did not change significantly. Thus, at 20 atm, the reaction was almost completed in 49 h without isomerization of **3a**, while isomerization of **3a** took place before completion of the hydroformylation at 40–100 atm (runs 4 and 6).



2

a: R^1 = H, R^2R^3 = $(CH_2)_4$
b: R^1 = R^2 = Me, R^3 = H
c: R^1 = R^3 = H, R^2 = Ph



3 **4** **5** (1)

Table 1. Asymmetric Hydroformylation of 1-Vinylcyclohexene (**2a**) Catalyzed by (*R*,*S*)-BINAPHOS–Rh(I) complex[a]

Run	Temp ℃	Press atm	Time h	% Conv[b]	**3a / 4a / 5a**[b]	% ee of **3a** (Config)
1	60	100	18	85	86 / 0 / 14	96 (*R*)
2	40	100	96	78	88 / 0 / 12	96 (*R*)
3	30	100	108	60	88 / 0 / 12	97 (*R*)
4	40	100	144	96	70 / 19 / 11	88 (*R*)
5	40	40	48	84	88 / 0 / 12	95 (*R*)
6	40	40	96	95	84 / 4 / 12	96 (*R*)
7	40	20	49	94	87 / 0 / 13	96 (*R*)

[a] Reactions were carried out with the substrate **2a** (4 mmol), $Rh(acac)(CO)_2$ (0.5 mol%) and (*R*,*S*)-**1** (4 equiv to Rh) in benzene (0.5 mL) in a 50-mL stainless-steel autoclave under a 1 : 1 mixture of H_2 and CO. [b] Determined by ^1H NMR spectroscopy.

Similarly, asymmetric hydroformylation of 4-methyl-1,3-pentadiene (**2b**) gave (*R*)-2,4-dimethyl-3-pentenal [(*R*)-**3b**] as the major product without double-bond migration or hydrogenation (Table 2). For this substrate, the reaction was faster than for **2a**. Although the regio- and enantioselectivities were somewhat lower than those for **2a**, the selectivities were slightly improved by lowering the reaction temperature. The reaction rate was improved by lowering the pressure without affecting the selectivity, similar to the case of **2a**.

Table 2. Asymmetric Hydroformylation of 4-Methyl-1,3-pentadiene (**2b**) Catalyzed by (*R*,*S*)-BINAPHOS–Rh(I) complex[a]

Run	Temp ℃	Press atm	Time h	% Conv[b]	**3b / 4b / 5b**[b]	% ee of **3b** (Config)
1	60	100	18	92	78 / 0 / 22	80 (*R*)
2	30	100	96	67	81 / 0 / 19	84 (*R*)
3	30	20	76	79	83 / 0 / 17	84 (*R*)

[a] Reactions were carried out with the substrate **2b** (4 mmol), $Rh(acac)(CO)_2$ (0.5 mol%) and (*R*,*S*)-**1** (4 equiv to Rh) in benzene (0.5 mL) in a 50-mL stainless-steel autoclave under a 1 : 1 mixture of H_2 and CO. [b] Determined by ^1H NMR spectroscopy.

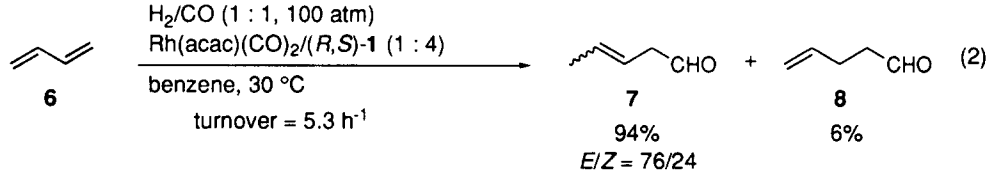
Asymmetric hydroformylation of (*E*)-1-phenyl-1,3-butadiene (**2c**) afforded (*R*)-(*E*)-2-methyl-4-phenyl-3-butenal [(*R*)-**3c**] in 91% selectivity and in 89% ee at 30 °C and at 100 atm (Table 3, run 2). Introduction of a formyl group at either the C1 or C2-position was not observed. Saturated aldehydes were not formed in all runs. As in the case of **2a**, prolonged reaction time or higher reaction temperature prompted the isomerization of **3c** to give a mixture of (*E*)- and (*Z*)-**4c** (runs 1 and 3). The isomerization of **3c** took place much more easily compared to **3a–b**. In addition, much larger drop in ee of the product was observed for the reaction of **2c**. The lower H_2/CO pressure effectively improved the yield of **3c**. Thus, the desired product **3c** was obtained in good yield and in high enantioselectivity (run 4). When the reaction at 20 atm was stopped after 12 h, the isomerization product **4c** was not observed (run 5).

Table 3. Asymmetric Hydroformylation of (*E*)-1-Phenyl-1,3-butadiene (**2c**) Catalyzed by (*R*,*S*)-BINAPHOS–Rh(I) complex[a]

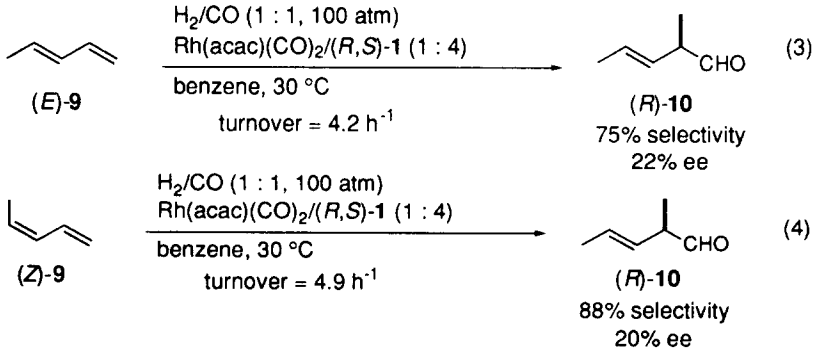
Run	Temp ℃	Press atm	Time h	% Conv[b]	**3c** / **4c** / **5c**[b]	% ee of **3c** (Config)
1	60	100	18	> 99	57 / (28 + 13)[c] / 2	64 (*R*)
2	30	100	48	62	91 / (2 + 2)[c] / 5	89 (*R*)
3	30	100	72	90	42 / (56 + 1)[c] / 1	56 (*R*)
4	30	40	24	88	92 / (2 + 1)[c] / 5	90 (*R*)
5	30	20	12	47	94 / 0 / 6	92 (*R*)

[a] Reactions were carried out with the substrate **2c** (4 mmol), $Rh(acac)(CO)_2$ (0.5 mol%) and (*R*,*S*)-**1** (4 equiv to Rh) in benzene (0.5 mL) in a 50-mL stainless-steel autoclave under a 1 : 1 mixture of H_2 and CO. [b] Determined by ^1H NMR spectroscopy. [c] Described as ((*E*)-**4c** + (*Z*)-**4c**).

In contrast to the results with **2a–c**, hydroformylation of 1,3-butadiene (**6**), the simplest conjugated diene, afforded an *E*/*Z* mixture (*E*/*Z* = 76/24) of 3-pentenal (**7**) in 94% selectivity at 30 °C (eq 2). No product corresponding to **3** or **4** was formed. At 60 °C, **7** was still the predominant product, although a more complex mixture was obtained.



When (*E*)-1,3-pentadiene [(*E*)-**9**] was subjected to the asymmetric hydroformylation, (*R*)-(*E*)-2-methyl-3-pentenal [(*R*)-**10**] was formed as the major product in 75% selectivity at 30 °C (eq 3). Interestingly, the same (*E*)-configurated product **10** was obtained in 88% selectivity even from (*Z*)-**9** (eq 4). The enantioselectivity and reaction rate are also similar from both substrates. These results suggest that the same intermediate is formed from the hydroformylation of both (*E*)- and (*Z*)-**9** (*vide infra*). The enantioselectivities are much lower than that



from **2a–c** and terminal aliphatic monoolefins such as 1-hexene (83% ee for 2-methylhexanal).[8d] The results obtained from the hydroformylation of these simple conjugated dienes clearly demonstrate that the substituents on the C3 and C4-position (R^1–R^3 of **2**) play a crucial role for the selectivity of the reaction.

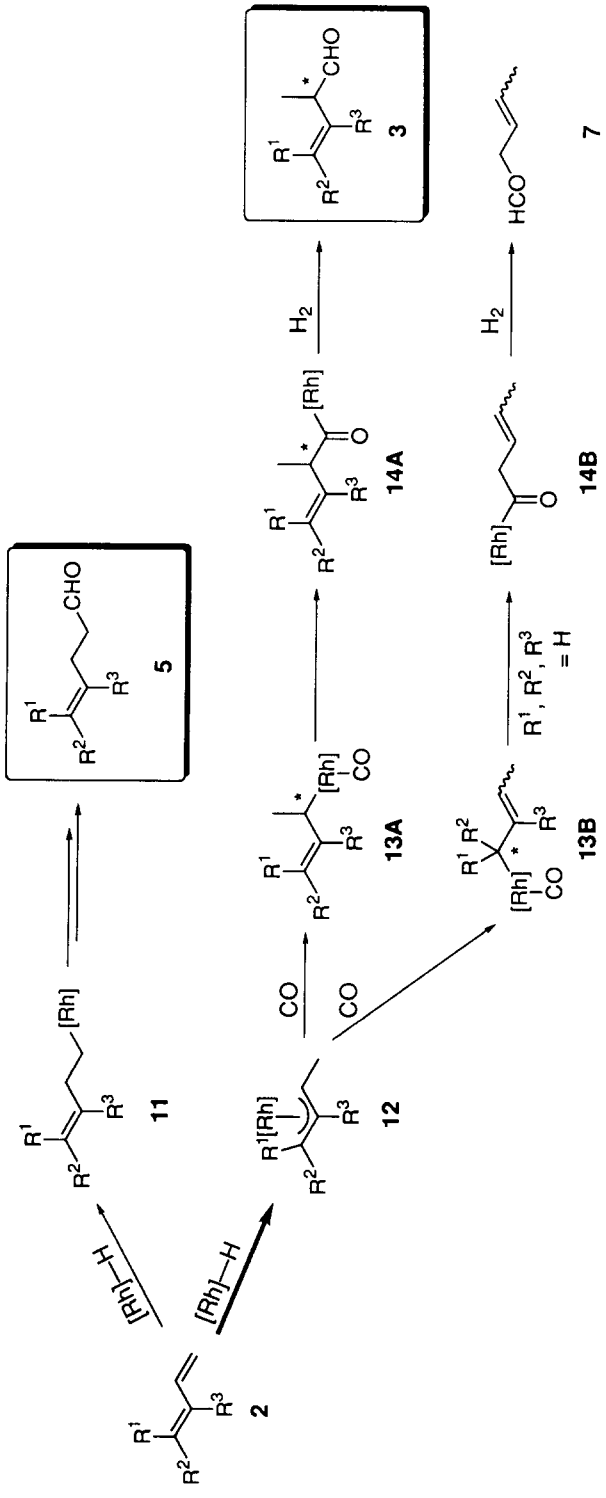
Mechanistic Considerations

The exceptionally high regioselectivity of the hydroformylation of **2a–c** compared with the simple aliphatic olefins can be rationalized by the formation of η^3-allylrhodium complex **12** as an intermediate (Scheme 1).[3,4] Rhodium(I) allyl complexes have been prepared stoichiometrically from hydridorhodium complexes and conjugated dienes.[5,13] It appears that they do not readily insert CO, but instead, form η^1-allylrhodium species, prompted by coordination of CO.[14] Thus, it is likely that an η^1-allyl species as **13** should be formed before insertion of CO.

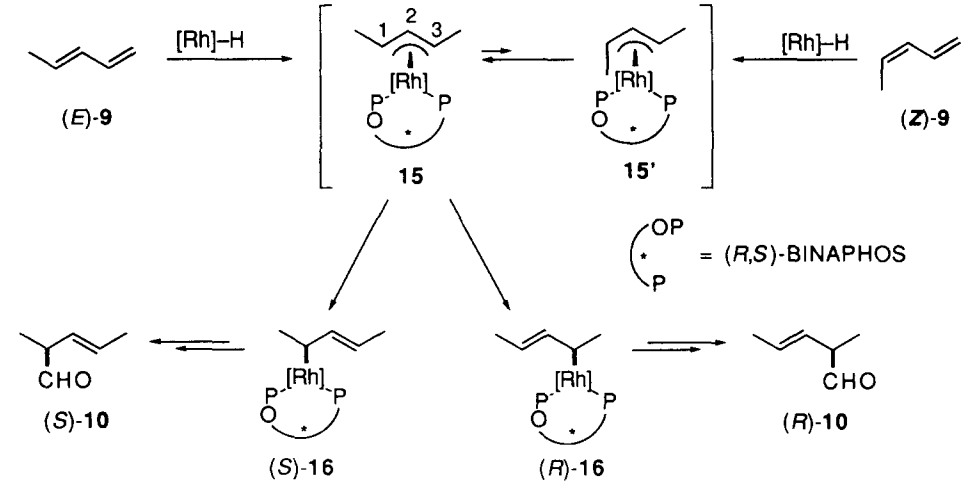
From the reaction of **2**, the η^3-allylrhodium complex **12** should be preferentially formed by insertion of the sterically less hindered olefinic bond of **2** into hydridorhodium species. When the η^1-allyl species is formed, there should be a strong preference for producing **13A** because of the smaller steric repulsion between the BINAPHOS–Rh(I) moiety and the substituents on the η^1-allyl group. Consequently, the chiral β,γ-unsaturated aldehyde **3** is formed through CO insertion followed by hydrogenolysis of the resulting acylrhodium species **14A**. A similar preference for insertion of CO at less hindered position was also documented for substituted η^3-allylrhodium[3] and iridium[5] complexes. From the reaction of 1,3-butadiene (**6**), the η^3-butenylrhodium complex (**12**, $R^1 = R^2 = R^3 = H$) should be formed. In this case, formation of **13B** would be preferred due to the sterical requirement, and thus 3-pentenal (**7**) is formed.

In the case of (*E*)-1,3-pentadiene [(*E*)-**9**], a symmetrical η^3-allylrhodium species **15** should be formed by insertion of the vinyl group of (*E*)-**9** into Rh–H bond (Scheme 2). Also from (*Z*)-**9**, **15** should be formed *via* syn-anti rearrangement of **15'** due to the steric repulsion between the methyl group on η^3-dimethylallyl ligand and the BINAPHOS–Rh(I) moiety.[14] The formation of such a symmetrical η^3-allylrhodium species in rhodium-catalyzed hydroformylation of **9** has been also documented.[4] Because of the symmetry of **15**, the enantioselectivity of asymmetric hydroformylation of **9** should be mainly determined by discrimination of the diastereotopic carbons C1 and C3, rather than the enantioface discrimination during the olefin insertion step. This assumption is supported by deuterioformylation experiment (eq 5), in which two possible isomers were obtained in *ca* 1.2 : 1 ratio.[15] This may be a reason for the much lower enantioselectivity of the hydroformylation of **9** compared to other conjugated dienes and aliphatic terminal olefins, that is, the (*R*,*S*)-**1**–Rh(I) system may not be suitable for this type of enantioselection.

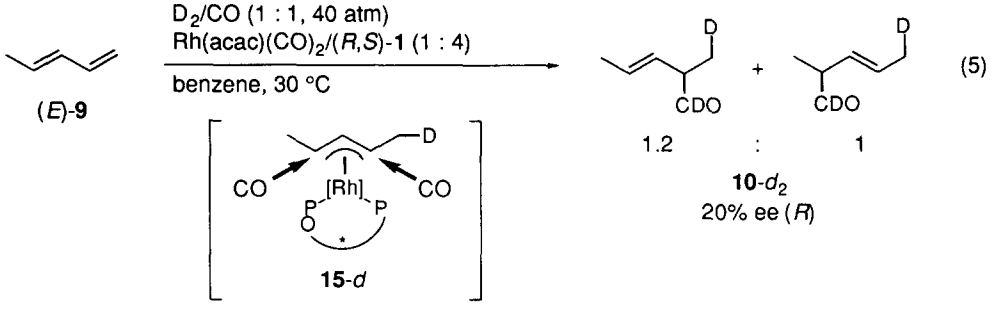
In conclusion, we have found that asymmetric hydroformylation of certain conjugated dienes catalyzed by BINAPHOS–Rh(I) complexes gives optically active β,γ-unsaturated aldehydes in high regio- and enantioselectivities. The present hydroformylation provides a new and direct route to optically active β,γ-unsaturated aldehydes, which are useful in organic synthesis and are difficult to obtain by other methods.



Scheme 1. A Plausible Mechanism for Regioselection.



Scheme 2



EXPERIMENTAL SECTION

General Methods

All manipulations of the oxygen- and moisture-sensitive materials were conducted under a purified argon atmosphere (BASF-Catalyst R3-11 column at 80 °C and molecular sieves 3A) with the standard Schlenk techniques.

Benzene was purified by distillation under argon over sodium benzophenone ketyl. Commercial reagents such as 4-methyl-1,3-pentadiene (**2b**), 1,3-butadiene (**6**), and (*E*)- and (Z)-1,3-pentadiene (**9**) were used without further purification. 1-Vinylcyclohexene (**2a**)[16] and (*E*)-1-phenyl-1,3-butadiene (**2c**)[17] were prepared by literature methods. (*R*,*S*)-BINAPHOS [(*R*,*S*)-**1**] was prepared by the known procedure.[8a,d] Commercial $Rh(acac)(CO)_2$ (Aldrich) was used as received.

Asymmetric Hydroformylation of 1-Vinylcyclohexene (2a): Typical Procedure for the Asymmetric Hydroformylation of Conjugated Dienes

A 20-mL Schlenk tube was charged with 1-vinylcyclohexene (**2a**) (424 mg, 3.92 mmol), diphenylmethane (internal standard, 48.7 mg, 0.289 mmol), and benzene (0.5 mL). The solution was degassed by three freeze-thaw cycles and transferred by a cannula into another 20-mL Schlenk tube containing $Rh(acac)(CO)_2$ (5.1 mg, 0.020 mmol) and (*R*,*S*)-**1** (61.3 mg, 0.0797 mmol). The resulting solution was degassed again by two freeze-

thaw cycles and then transferred into a 50-mL stainless-steel autoclave containing a magnetic stirring bar. Carbon monoxide (50 atm) and hydrogen (50 atm) were charged and the solution was stirred for 96 h at 40 °C. Conversion and regioselectivity of the reaction were determined by ^{1}H NMR analysis of the crude reaction mixture without evaporation of the solvent.

*(R)-(–)-2-(1-Cyclohexenyl)propanal [(R)-**3a**]:* Identification was completed by comparison of the following data with those in literature.[18] ^{1}H NMR ($CDCl_3$) δ 1.16 (d, J = 6.93 Hz, 3H), 1.5–1.8 (m, 4H), 1.8–2.2 (m, 4H), 2.91 (br q, J = 6.93 Hz, 1H), 5.60 (m, 1H), 9.50 (d, J = 1.65 Hz, 1H); ^{13}C NMR δ 12.0, 22.2, 22.8, 25.4, 27.2, 54.4, 126.0, 134.1, 202.3; $[\alpha]^{22}_D$ = -213 (*c* 2.40, Et_2O) at 89% ee.

*2-Cyclohexylidenepropanal (**4a**):* Identification was completed by comparison of the following data with those in literature.[19] ^{1}H NMR ($CDCl_3$) δ 1.5–1.8 (m, 6H), 1.76 (s, 3H), 2.35–2.45 (m, 2H), 2.7–2.8 (m, 2H), 10.19 (s, 1H); ^{13}C NMR δ 26.4, 27.9, 28.7, 29.1, 33.3, 129.4, 162.6, 190.5.

*3-(1-Cyclohexenyl)propanal (**5a**):* Identification was completed by comparison of the following data with those in literature.[20] ^{1}H NMR ($CDCl_3$) δ 1.4–1.8 (m, 4H), 1.8–2.1 (m, 4H), 2.27 (br t, J = 7.26 Hz, 2H), 2.52 (td, J = 7.25, 1.98 Hz, 2H), 5.42 (m, 1H), 9.76 (t, J = 1.98 Hz, 1H); ^{13}C NMR δ 22.3, 22.8, 25.1, 28.4, 30.2, 41.8, 121.9, 135.7, 202.8.

*Determination of Enantiomeric Excess and Absolute Configuration of **3a***

The reaction mixture was diluted with acetone and cooled with an ice bath. To this was slowly added Jones reagent, and the mixture was stirred at room temperature overnight. The reaction mixture was treated with $NaHSO_3$. After the orange color disappeared, the insoluble material was filtered off. The filtrate was diluted with brine, and extracted twice with ether. The combined organic layers were extracted with 1 *N* NaOH. The alkaline aqueous layer was acidified with concd HCl and extracted three times with ether. The combined organic layers were dried over $MgSO_4$ and concentrated. The residue was distilled in a Kugelrohr apparatus to afford (*R*)-(–)-2-(1-cyclohexenyl)propanoic acid[21] as a mixture with 3-(1-cyclohexenyl)propanoic acid. Enantiomeric excess was determined by HPLC analysis of the corresponding *N*-phenylamide[22] (Daicel Chiralcel OJ, hexane/2-propanol = 49/1, flow rate = 1.0 mL·min^{-1}). The absolute configuration of **3a** was determined by the specific rotation of 2-cyclohexylpropanoic acid,[23] derived by PtO_2-catalyzed hydrogenation of 2-(1-cyclohexenyl)propanoic acid.

*Determination of Enantiomeric Excess and Absolute Configuration of **3b***

The reaction mixture (containing **3b**[9a] and **5b**[24]) was treated by Jones reagent as described above to afford (*R*)-(–)-2,4-dimethyl-3-pentenoic acid as the major product.[25] Enantiomeric excess was determined by HPLC analysis of the corresponding *N*-phenylamide[22] (Daicel Chiralcel OD, hexane/2-propanol = 97/3, flow rate = 1.0 mL·min^{-1}). The absolute configuration of **3b** was determined by the specific rotation of 2,4-dimethylpentanoic acid, derived by PtO_2-catalyzed hydrogenation of 2,4-dimethyl-3-pentenoic acid. $[\alpha]_D^{22}$ for a 79:21 mixture of (*R*)-2,4-dimethyl-3-pentanoic acid and 5-methyl-4-hexanoic acid (80% *ee*) was -16.5 (*c* 2.04 for 2,4-dimethyl-3-pentanoic acid, Et_2O). $[\alpha]_D^{20}$ for (*S*)-2,4-dimethyl-3-pentanoic acid (98±2% *ee*) was reported to be +20±0.5 (*c* 0.86, Et_2O).[26]

*Determination of Enantiomeric Excess and Absolute Configuration of **3c***

The reaction mixture (containing **3c**,[9c] **4c**,[27] and **5c**[28]) was treated by Jones reagent as described above to afford (*R*)-(–)-(*E*)-2-methyl-4-phenyl-3-butenoic acid as the major product.[9c] Enantiomeric excess was determined by HPLC analysis of the corresponding methyl ester[9c] derived by the treatment of the acid with diazomethane (Daicel Chiralcel OD, hexane/2-propanol = 199/1, flow rate = 1.0 mL·min^{-1}). The absolute

configuration of **3c** was determined by the specific rotation of the methyl ester. $[\alpha]_D^{22}$ for a 88:7:3:2 mixture of (*R*)-(–)-methyl (*E*)-2-methyl-4-phenyl-3-butenoate (85% *ee*), methyl (*E*)-2-methyl-4-phenyl-2-butenoate, (*Z*)-2-methyl-4-phenyl-2-butenoate, and methyl 5-phenyl-pentanoate was –40.4 (*c* 1.75 for methyl (*E*)-2-methyl-4-phenyl-3-butenoate, MeOH). $[\alpha]_D$ for (*R*)-(–)-methyl (*E*)-2-methyl-4-phenyl-3-butenoate (>96% *ee*) was reported to be –52.5 (*c* 5.2).[9c]

Hydroformylation of 1,3-Butadiene (6)

In a 20-mL Schlenk tube were dissolved $Rh(acac)(CO)_2$ (3.0 mg, 0.012 mmol), (*R,S*)-**1** (37 mg, 0.048 mmol), diphenylmethane (39.4 mg, 0.234 mmol), and a small amount of 2,6-di-*tert*-butyl-4-methylphenol in benzene (10.0 mL). The solution was degassed by three freeze-thaw cycles and transferred into a 50-mL stainless-steel autoclave. To this was added 1,3-butadiene (*ca.* 3 mL). The system was pressurized with hydrogen (50 atm) and carbon monoxide (50 atm). The turnover frequency of the reaction and selectivity toward the products (*E*)- and (*Z*)-3-pentane (**7**)[4] and 4-pentane (**8**)[4] were determined by ^1H NMR using diphenylmethane as an internal standard. Asymmetric hydroformylation of (*E*)- and (*Z*)-1,3-pentadiene (**9**) was carried out by a similar procedure.

Determination of Enantiomeric Excess and Absolute Configuration of 10

The reaction mixture (containing **10**[29]) was treated by Jones reagent as described above to afford (*R*)-(*E*)-2-methyl-3-pentenoic acid as the major product. Enantiomeric excess was determined by GLC analysis of the corresponding carboxylic acid derived by Jones oxidation of the product (astec chiraldex B-PH, 120 °C, He 1.0 $kg \cdot cm^{-2}$). Absolute configuration was determined by the specific rotation of (*R*)-(*E*)-2-methyl-3-pentenoic acid. $[\alpha]_D^{22}$ for a 84:16 mixture of (*R*)-(*E*)-2-methyl-3-pentenoic acid (24% *ee*) and other achiral carboxylic acids ((*E*)- and (*Z*)-4-hexenoic acid, (*E*)- and (*Z*)-2-hexenoic acid, and hexanoic acid) was –14.5 (*c* 0.031 for (*E*)-2-methyl-3-pentenoic acid, Et_2O). $[\alpha]_D$ for (*S*)-(*E*)-2-methyl-3-pentenoic acid was reported to be +63.6 (Et_2O).[30]

REFERENCES AND NOTES

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‡ Deceased on October 4, 1995

1. (a) Fell, B.; Bahrmann, H. *J. Mol. Catal.* **1977**, *2*, 211–218. (b) Bahrmann, H.; Fell, B. *J. Mol. Catal.* **1980**, *8*, 329–337.
2. (a) Kummer, R.; Weiss, F. J. *Symp. Rhodium Homogeneous Catal.* **1978**, 87–93; *Chem Abstr.* **1979**, *90*, 38503n. (b) Packett, D. L. Eur. Pat. Appl. EP 577,042; *Chem. Abstr.* **1994**, *120*, 298075j. (c) Packett, D. L. U.S. US 5,312,996; *Chem. Abstr.* **1995**, *123*, 82828w.
3. van Leeuwen, P. W. N. M.; Roobeek, C. F. *J. Mol. Catal.* **1985**, *31*, 345–353.
4. Recently, Bertozzi *et al.* reported the selective formation of β,γ-unsaturated aldehydes by hydroformylation of conjugated dienes such as 1,3-butadiene, isoprene, and 1,3-pentadiene using rhodium vapor–mesitylene cocondensates as a catalytic precursor: Bertozzi, S.; Campigli, N.; Vitulli, G.; Lazzaroni, R.; Salvadori, P. *J. Organomet. Chem.* **1995**, *487*, 41–45.
5. Brown, C. K.; Mowat, W.; Yagupsky, G.; Wilkinson, G. *J. Chem. Soc. (A)* **1971**, 850–859.
6. Botteghi, C.; Branca, M.; Saba, A. *J. Organomet. Chem.* **1980**, *184*, C17–C19.
7. Botteghi, C.; Salomon, C. *Tetrahedron Lett.* **1974**, 4285–4288.

8. (a) Sakai, N.; Mano, S.; Nozaki, K.; Takaya, H. *J. Am. Chem. Soc.* **1993**, *115*, 7033–7034. (b) Sakai, N.; Mano, S.; Nozaki, K.; Takaya, H. *J. Chem. Soc., Chem. Commun.* **1994**, 395–396. (c) Nanno, T.; Sakai, N.; Nozaki, K.; Takaya, H. *Tetrahedron: Asymmetry* **1995**, *6*, 2583–2591. (d) Nozaki, K.; Sakai, N.; Nanno, T.; Higashijima, T.; Mano, S.; Horiuchi, T.; Takaya, H. *J. Am. Chem. Soc.*, in press.
9. (a) Heathcock, C. H.; Young, S. D.; Hagen, J. P.; Pilli, R.; Badertscher, U. *J. Org. Chem.* **1985**, *50*, 2095–2105. (b) Evans, D. A.; DiMare, M. *J. Am. Chem. Soc.* **1986**, *108*, 2476–2478. (c) Salamonczyk, G. M.; Han, K.; Guo, Z.; Sih, C. J. *J. Org. Chem.* **1996**, *61*, 6893–6900.
10. We have already reported a part of this work as a communication, see: Horiuchi, T.; Ohta, T.; Nozaki, K.; Takaya, H. *Chem. Commun.* **1996**, 155–156.
11. Efficient stirring of the reaction mixture is indispensable for obtaining high regio- and enantioselectivities. Otherwise, variable amounts of **4a** were formed *via* isomerization of **3a**, and the ee of **3a** has dropped to some extent (80–90% ee).
12. Recently, hydroformylation of 17-vinyl-16-androstene (containing 1-vinylcyclopentene moiety) has been carried out to give the product corresponding to **3** using $[Rh(norbornadiene)Cl]_2/PPh_3$ system: Skoda-Földes, R.; Kollár, L.; Heil, B.; Gálik, G.; Tuba, Z.; Arcadi, A. *Tetrahedron: Asymmetry* **1991**, *2*, 633–634.
13. Reilly, C. A.; Thyret, H. *J. Am. Chem. Soc.* **1967**, *89*, 5144–5149.
14. Hughes, R. P. *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press Ltd.: Oxford, 1982; Vol. 5, pp. 493–506.
15. This value corresponds to 10% ee. The deviation from the observed ee can be explained by assuming that the selectivity of the formation of (*R*)- or (*S*)-**16** may slightly depend on the enantioface discrimination during the formation of **15**.
16. Liu, H.-J.; Browne, E. N. C. *Can. J. Chem.* **1987**, *65*, 1262–1278.
17. Okamoto, T.; Kobayashi, K.; Oka, S.; Tanimoto, S. *J. Org. Chem.* **1988**, *53*, 4897–4901.
18. Maruoka, K.; Itoh, T.; Sakurai, M.; Nonoshita, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 3588–3597.
19. Corey, E. J.; Enders, D.; Bock, M. G. *Tetrahedron Lett.* **1976**, 7–10.
20. Boger, D. L.; Mathvink, R. J. *J. Org. Chem.* **1992**, *57*, 1429–1443.
21. Black, T. H.; Eisenbeis, S. A.; McDermott, T. S.; Maluleka, S. L. *Tetrahedron* **1990**, *46*, 2307–2316.
22. Uemura, T.; Zhang, X.; Matsumura, K.; Sayo, N.; Kumobayashi, H.; Ohta, T.; Nozaki, K.; Takaya, H.*J. Org. Chem.* **1996**, *61*, 5510–5516.
23. Rangaishenvi, M. V.; Singaram, B.; Brown, H. C. *J. Org. Chem.* **1991**, *56*, 3286–3294.
24. Harris, N. J.; Gajewski, J. J. *J. Am. Chem. Soc.* **1994**, *116*, 6121–6129.
25. Henin, F.; Mortezaei, R.; Muzart, J.; Pete, J.-P.; Piva, O. *Tetrahedron* **1989**, *45*, 6171–6196.
26. Mortezaei, R.; Henin, R.; Muzart, J.; Pete, J.-P. *Tetrahedron Lett.* **1985**, *26*, 6079–6080.
27. Masaki, Y.; Sakuma, K.; Kaji, K. *Chem. Pharm. Bull.* **1985**, *33*, 2531–2534.
28. Nonoshita, K.; Banno, H.; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1990**, *112*, 316–322.
29. Kovács, I.; Ungváry, F.; Garst, J. F. *Organometallics* **1993**, *12*, 389–396.
30. Corey, E. J.; Hasw, T. *Tetrahedron Lett.* **1979**, 335–338.

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