# Asymmetric Transfer Hydrogenation of Prochiral α,β-Unsaturated Acids and Their Esters by Achiral or Chiral Alcohols with Ruthenium Chiral Diphosphine Complexes

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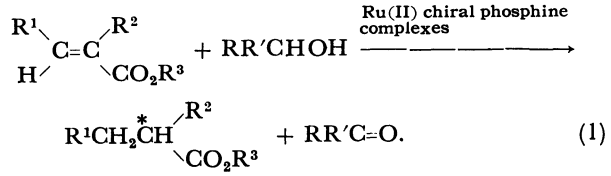
(Received September 30, 1982)

Asymmetric transfer hydrogenations of α,β-unsaturated acids ($MeCH=C(Me)CO_2H$, $PhCH=C(Me)CO_2H$, $CH_2=C(CH_2CO_2H)CO_2H$, and $HO_2CCH=C(Me)CO_2H$) and esters ($MeCH=C(Me)CO_2R$; R=achiral and chiral group) by alcohols ($PhCH_2OH$, (*RS*)-PhCH(Me)OH, and α-D-glucofuranose derivatives) were carried out with $RuCl_2(PPh_3)_3$ or $Ru_2Cl_4$((+) or (−)-diop)$_3$ (diop=2,3-*O*-isopropylidene-1,4-bis(diphenylphosphino)-2,3-butanediol) at 160—190 °C. The optical purity (3.4—16.4%) of hydrogenated acids obtained with $PhCH_2OH$ and $Ru_2Cl_4$((−)-diop)$_3$ is in the order $MeCH=C(Me)CO_2H > PhCH=C(Me)CO_2H > CH_2=C(CH_2CO_2H)CO_2H > HO_2CCH=C(Me)CO_2H$, suggesting that the substrates possessing two carboxyl groups would provide an asymmetrically unfavorable coordination to the Ru(II) complex for this asymmetric reaction. In the transfer hydrogenation of $MeCH=C(Me)CO_2R$ by $PhCH_2OH$ or (*RS*)-PhCH(Me)OH at 190 °C, the extent of asymmetric induction of $Ru_2Cl_4$((−)-diop)$_3$ (1.7—11.4% e.e. with $PhCH_2OH$ and 7.4—18.2% e.e. with (*RS*)-PhCH(Me)OH) decreases with increase in bulkiness of groups R (R=H, Me, Et, *n*-Bu, and $PhCH_2$) and is not enhanced by the introduction of any groups R with chiral carbon atoms into esters (maximum 15.4% e.e.). The structural change of hydrogen donors from $PhCH_2OH$ to (*RS*)-PhCH(Me)OH appreciably increases the optical purity of the saturated acids and esters, and the chiral α-D-glucofuranose derivatives afford optically active saturated products, even with achiral $RuCl_2(PPh_3)_3$. Features of the present reaction are discussed in relation to the reaction mechanism.

Catalytic asymmetric synthesis of optically active compounds is recently receiving considerable attention,[1] and rhodium chiral phosphine complexes have successfully been used in homogeneous hydrogenations for formation of α-amino acid derivatives.[2-4] Chiral ruthenium complexes, as compared with rhodium ones, have been subjected to limited investigations on their catalytic activity for the asymmetric synthesis.[5,6]

Since ruthenium chiral phosphine complexes are effective catalysts for enantiomer-differentiating dehydrogenation of racemic secondary alcohols as found in our laboratory,[7] we have investigated the catalytic efficiency of chiral ruthenium complexes for the asymmetric transfer hydrogenation of prochiral olefins by alcohols, to examine the asymmetric hydrogenation without molecular hydrogen at the atmospheric pressure.




$$R^1R^2C{=}CH(CO_2R^3) + RR'CHOH \xrightarrow{\text{Ru(II) chiral phosphine complexes}} R^1CH_2\overset{*}{C}H(R^2)(CO_2R^3) + RR'C{=}O. \quad (1)$$

In this paper, we describe effects of the chirality and bulkiness of substituent groups in reactants on the extent of asymmetric induction in the transfer hydrogenation of prochiral α,β-unsaturated acids and esters by alcohols with $RuCl_2(PPh_3)_3$ or $Ru_2Cl_4$((+) or (−)-diop)$_3$ (diop =2,3-*O*-isopropylidene-1,4-bis(diphenylphosphino)-2,3-butanediol), and discuss on the reaction mechanism with particular reference to the enantio-differentiating catalysis by the ruthenium complexes.

## Experimental

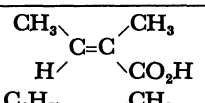
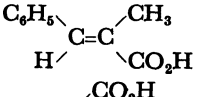
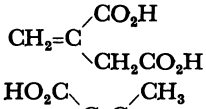
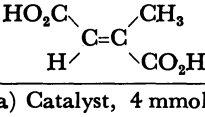
*Materials.* (+) and (−)-Diop and $Ru_2Cl_4$ ((+) or (−)-diop)$_3$ were prepared by Kagan's[8] and James'[5a] methods, respectively. α-D-Glucose derivatives, 1,2-*O*-isopropylidene-1,2 : 5,6-*O*-diisopropylidene-, 1,2-*O*-cyclohexylidene-, and 1,2 : 5,6-*O*-dicyclohexylidene-α-D-glucofuranose were synthesized by the methods reported.[9,10] Several α-methylcrotonates (1-phenylethyl, α-(ethoxycarbonyl)benzyl, (1*R*,2*R*)-1,2-bis(ethoxycarbonyl)-2-hydroxyethyl, and *l*-menthyl esters) were prepared *via* the reaction of α-methycrotonoyl chloride and the corresponding hydroxy compounds (1-phenylethanol, ethyl mandelate, diethyl (2*R*, 3*R*)-tartarate, and *l*-menthol, respectively). Alcohols, prochiral acids, and esters were purified by fractional distillation or recrystallization before use.

*Transfer Hydrogenation.* A mixture of prochiral olefin and alcohol was allowed to react in the presence of the chiral ruthenium complex in a sealed tube at the desired temperature controlled within ±1 °C in a nitrogen atmosphere. The reaction mixture was refluxed in a 10% NaOH–methanol solution, and the insoluble catalyst was separated from the solution by the filtration. The filtrate was washed with water, acidified with dilute HCl solution in the range of pH 3—4, and extracted with ether. The ethereal phase was washed with water, dried over magnesium sulfate, and evaporated to dryness. The unreacted prochiral olefin and hydrogenated product were identified by GLC analysis (at 170 °C using a 1 m column packed with 15% EGA on Uniport B) or by the proton NMR (100 MHz) method. The optical rotation of the hydrogenated product was measured with a high-sensitivity Union PM-101 polarimeter.

## Results and Discussion

*Asymmetric Transfer Hydrogenation of α,β-Unsaturated Carboxylic Acids and Esters.* The asymmetric reduction of the carbon-carbon double bond in prochiral α,β-unsaturated mono- and dicarboxylic acids by benzyl or *p*-methoxybenzyl alcohol was first carried out with $Ru_2Cl_4$((−)-diop)$_3$. The results are summarized in Table 1. The optical purity of hydrogenated products for the unsaturated monocarboxylic acids is relatively high as compared with that for the unsaturated dicarboxylic acids. The bulky carboxyl groups might hinder the

Table 1. Asymmetric transfer hydrogenation of prochiral unsaturated carboxylic acids by benzyl alcohol with $Ru_2Cl_4((-)\text{-diop})_3$ at 180 °C[a]

| Substrate | Time / h | Yield / % | $[\alpha]_D$ / ° | O.P.[b] / % |
|---|---|---|---|---|
|  | 6 | 10 | −1.99 | 16.4 |
|  | 6 | 36 | −3.29 | 15.9 |
|  | 6 | 31 | −0.86 | 6.1 |
|  | 9 | 9 | −0.59 | 3.4 |

a) Catalyst, 4 mmol dm$^{-3}$; substrate, 40 mmol; alcohol, 80 mmol. b) Calculated on the basis of the following values of optically pure acids: $[\alpha]_D^{23}+12.17°$ (*c* 5, $C_2H_5OH$) for (*S*)-(+)-$CH_3CH_2CH(CH_3)CO_2H$;[11] $[\alpha]_D^{25}+20.68°$ (neat) for (*S*)-(+)-$CH_3CH_2CH(CH_3)CO_2H$;[12] $[\alpha]_D^{20}+16.88°$ (*c* 2.16, $C_2H_5OH$) for (*R*)-(+)-$CH_3CH(CO_2H)CH_2CO_2H$;[13] $[\alpha]_D^{20}$ −17.27° (*c* 5.0, $C_2H_5OH$) for (*S*)-(−)-$HO_2CCH_2CH(CH_3)CO_2H$.[14]

asymmetrically favorable coordination of the carbon-carbon double bond in the substrate to the chiral Ru(II) complex in the step of asymmetric induction.

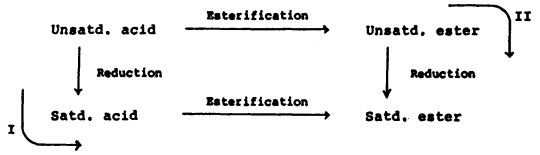
It is also noteworthy that the optical purity of the saturated products derived from α-methylcrotonic or α-methylcinnamic acid (16.4 and 15.4%, respectively) is higher than the reported values (maxima 6.9 and 1.5%, respectively)[6c] for transfer hydrogenations of the same species with $H_4Ru_4(CO)_8((-)\text{-diop})_8$ at 120 °C by 2-propanol, indoline, dioxane, *etc.*

Asymmetric transfer hydrogenation of a series of esters of α-methylcrotonic acid by benzyl alcohol or 1-phenylethanol was carried out with the Ru(II)-(−)-diop complex. The results are shown in Table 2. The ester derivatives of α-methylcrotonic acid, as compared with α-methylcrotonic acid itself, are easily hydrogenated to give their hydrogenated products with very low optical purities, which decrease with increasing bulkiness of the ester groups. The bulky ester moiety might decrease the extent of asymmetric induction considerably by suppressing the approach of the ester to the chiral catalyst during the enantio-face differentiating process.

The extent of asymmetric induction is also affected by the structure of hydrogen donor. Such an achiral alcohol as benzyl alcohol results in a low magnitude of asymmetric induction than 1-phenylethanol in the hydrogenation of α-methylcrotonic acid. Although benzyl alcohol gives saturated esters enriched in (*S*)-enantiomer, racemic 1-phenylethanol affords products enriched in the antipode with higher optical purity.

When a hydrogen transfer is effected with the Ru(II)-(−)-diop complex from alcohol to such an unsaturated acid as α-methylcrotonic acid, the reaction is considered to proceed *via* two courses I and II specified in Scheme 1. In course I, a partial esterification of the saturated acid is followed by a reduction of the carbon-carbon double bond of the unsaturated acid, and in course II, an unsaturated ester is formed before the corresponding acid is hydrogenated by alcohol in the presence of Ru(II) catalyst. In order to elucidate which course is predominant in the asymmetric transfer hydrogenation of unsaturated acid, we determined the time dependence of the chemical yield of products in the Ru(II)-(−)-diop complex catalyzed transfer hydrogenation of α-methylcrotonic acid or 1-phenylethyl α-methylcrotonate by 1-phenylethanol.

As can be seen from Fig. 1, α-methylcrotonic acid is




Scheme 1.

Table 2. Asymmetric transfer hydrogenation of α-methylcrotonic acid and its esters by achiral and racemic alcohols with $Ru_2Cl_4((-)\text{-diop})_3$ at 190 °C[a]

| Alcohol | $CH_3CH=C(CH_3)CO_2R$ R | Time / h | Yield / % | $[\alpha]_D^{23}$ / ° | O.P.[b] / % | Prevailing configuration |
|---|---|---|---|---|---|---|
| $C_6H_5CH_2OH$ | H | 8 | 10 | −1.39 | 11.4 | *R* |
| | $CH_3$ | 4 | 35 | +0.22 | 1.8 | *S* |
| | $C_2H_5$ | 5 | 53 | +0.28 | 2.3 | *S* |
| | *n*-$C_4H_9$ | 5 | 47 | +0.28 | 2.3 | *S* |
| | $C_6H_5CH_2$ | 5 | 41 | +0.20 | 1.7 | *S* |
| $C_6H_5CH(CH_3)OH$ | H[c] | 10 | 13 | −3.21 | 26.4 | *R* |
| | H | 4 | 10 | −2.21 | 18.2 | *R* |
| | $CH_3$ | 3 | 85 | −1.21 | 10.0 | *R* |
| | $C_2H_5$ | 22 | 59 | −1.19 | 9.8 | *R* |
| | *n*-$C_4H_9$ | 4 | 94 | −0.90 | 7.4 | *R* |
| | $C_6H_5CH_2$ | 5 | 75 | −1.02 | 8.4 | *R* |
| *p*-$CH_3OC_6H_4CH_2OH$ | H | 8 | 9 | −1.35 | 11.1 | *R* |
| | H[d] | 8 | 8 | +1.25 | 10.3 | *S* |

a) $Ru_2Cl_4((-)\text{-diop})_3$, 4 mmol dm$^{-3}$; alcohol, 33 mmol; olefin, 67 mmol. b) Optical purities of saturated esters were calculated for the α-methylbutyric acids obtained from the esters by base hydrolysis. c) The reaction was carried out at 170 °C. d) $Ru_2Cl_4((+)\text{-diop})_3$ was used.

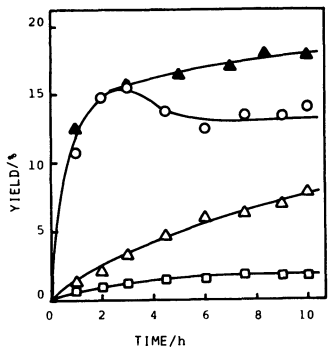



Fig. 1. Changes of product yields with time in the transfer hydrogenation of α-methylcrotonic acid (3.0 mol $dm^{-3}$) by 1-phenylethanol (5.8 mol $dm^{-3}$) with $Ru_2Cl_4$-(−)-diop)$_3$ (4.0 mmol $dm^{-3}$) at 190 °C.
Product: α-methylbutyric acid (○), 1-phenylethyl α-methylbutyrate (△), 1-phenylethyl α-methylcrotonate (□), 1-phenylethyl α-methylbutyrate (▲) obtained with 1-phenylethyl α-methylcrotonate (2.3 mol $dm^{-3}$) and 1-phenylethanol (4.7 mol $dm^{-3}$) at 190 °C.

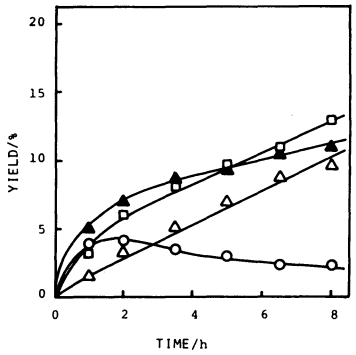



Fig. 2. Changes of product yields with time in the transfer hydrogenation of α-methylcrotonic acid (2.9 mol $dm^{-3}$) by benzyl alcohol (7.0 mol $dm^{-3}$) with $Ru_2Cl_4$-((−)-diop)$_3$ (4.0 mmol $dm^{-3}$) at 190 °C.
Product: α-methylbutyric acid (○), benzyl α-methylbutyrate (△), benzyl α-methylcrotonate (□); benzyl α-methylbutyrate (▲) obtained with benzyl α-methylcrotonate (1.5 mol $dm^{-3}$) and benzyl alcohol (6.8 mol $dm^{-3}$) at 190 °C.

hydrogenated smoothly by 1-phenylethanol with a small extent of esterification of the unsaturated acid, and rates of hydrogen transfers from 1-phenylethanol to α-methylcrotonic acid and to 1-phenylethyl α-methylcrotonate do not differ distinctly from each other. Strictly speaking, the hydrogenation of α-methylcrotonic acid includes a rate drop by the slow esterification of acid. Thus, the chiral Ru(II) complex catalyzed reaction of α-methylcrotonic acid with 1-phenylethanol proceeds mainly *via* course I with formation of α-methylbutyric acid as a main product.

On the other hand, the esterification of α-methylcrotonic acid by benzyl alcohol is relatively rapid, and benzyl α-methylcrotonate is easily reduced to benzyl α-methylbutyrate. From the gradual decrease in the yield of α-methylbutyric acid after the reaction period of 2 h (Fig. 2), it is evident that the saturated ester is produced from α-methylbutyric acid *via* course I, and that benzyl α-methylbutyrate is formed from α-methylcrotonic acid and benzyl alcohol *via* both courses I and II; the later path seems predominant. It should be stressed that in the transfer hydrogenation of α-methylcrotonate with benzyl alcohol or 1-phenylethanol, no hydrolysis of unsaturated or saturated esters was observed. Thus the difference in reactivity between hydrogen donors (alcohols) affects the transfer hydrogenation process, allowing 1-phenylethanol to give a higher optical purity (18.2%) than that (11.4%) obtained with benzyl alcohol in the hydrogenation of α-methylcrotonic acid (Table 2). Since the saturated product from benzyl α-methylcrotonate has a considerably low optical purity (1.7%) and contains the prevailing (*S*)-enantiomer, opposite to the predominant enantiomer found with α-methylcrotonic acid, the easy esterification of α-methylcrotonic acid by benzyl alcohol is taken to be responsible for the decreased optical purity of the saturated product.

For the present reaction the effective asymmetric induction by racemic 1-phenylethanol was actually recognized, and this is attributable to the chiral circumstances enriched in one specific enantiomer of the unreacted alcohol. In fact, in the transfer hydrogenation of α-methylcrotonic acid or its esters by racemic 1-phenylethanol, an enantiomer-differentiation of the alcohol was observed, and the optically active unreacted alcohol (maximum e.e. 4.2%) could be separated; the prevailing enantiomers are the (*S*)-isomer in the case of Ru(II)-(−)-diop complex and the (*R*)-isomer in the case of Ru(II)-(+)-diop complex. One of the enantiomers of 1-phenylethanol might contribute to the asymmetric induction through coordination to the chiral Ru(II) complex.

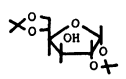
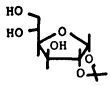
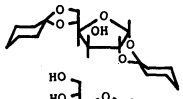
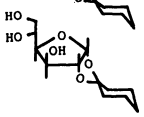
*Asymmetric Transfer Hydrogenation of α-Methylcrotonic Acid by Chiral Alcohol.* Since the chirality of hydrogen donors is anticipated to affect the extent of asymmetric induction in the transfer hydrogenation of unsaturated species with the chiral Ru(II) complex, we carried out a reaction of α-methylcrotonic acid with chiral alcohol as follows: (1) an asymmetric transfer hydrogenation using α-D-glucofuranose derivatives as chiral alcohols with an achiral catalyst $RuCl_2(PPh_3)_3$, and (2) a double asymmetric transfer hydrogenation by the chiral hydrogen donors with a chiral catalyst $Ru_2Cl_4$((+) or (−)-diop)$_3$. Results are listed in Table 3.

$$RR'\overset{*}{C}HOH + CH_2CH{=}C\begin{matrix}CH_3\\CO_2H\end{matrix} \xrightarrow[2.\ Ru_2Cl_4((+)\text{ or }(-)\text{-diop})_3]{1.\ RuCl_2(PPh_3)_3} CH_3CH_2\overset{*}{C}H\begin{matrix}CH_3\\CO_2H\end{matrix} + RR'C{=}O \qquad (2)$$

In the case of the transfer hydrogenation of α-methylcrotonic acid with the chiral alcohol and $RuCl_2(PPh_3)_3$, the optically active α-methylbutyric acid (0.3—8.9% e.e.) was produced with the prevailing (*R*)-enantiomer, and the use of 1,2 : 5,6-*O*-diisopropylidene- and 1,2-*O*-isopropylidene-α-D-glucofuranose gave rise to higher optical purities (6.7—8.9%) than those (0.3—3.1%) obtained with 1,2 : 5,6-*O*-dicyclohexylidene- and 1,2-*O*-cyclohexylidene-α-D-glucofuranose.

In the double asymmetric reaction with the chiral

TABLE 3. ASYMMETRIC TRANSFER HYDROGENATION OF α-METHYLCROTONIC ACID BY CHIRAL ALCOHOLS WITH $RuCl_2(PPh_3)_3$ OR $Ru_2Cl_4((+)$ OR $(-)$-diop$)_3$ AT 160 °C[a]

| Alcohol | Catalyst | Yield[b] % | $-[\alpha]_D^{23}$ ° | O.P. % |
|---|---|---|---|---|
|  | $RuCl_2(PPh_3)_3$ | 7 | 0.81 | 6.7 |
| | $Ru_2Cl_4((-)$-diop$)_3$ | 7 | 1.57 | 12.9 |
| | $Ru_2Cl_4((+)$-diop$)_3$ | 6 | 0.77 | 6.4 |
|  | $RuCl_2(PPh_3)_3$ | 18 | 1.08 | 8.9 |
| | $Ru_2Cl_4((-)$-diop$)_3$ | 14 | 2.74 | 22.5 |
| | $Ru_2Cl_4((+)$-diop$)_3$ | 13 | −0.47 | 3.9 |
|  | $RuCl_2(PPh_3)_3$ | 5 | 0.37 | 3.1 |
| | $Ru_2Cl_4((-)$-diop$)_3$ | 2 | 0.90 | 7.4 |
| | $Ru_2Cl_4((+)$-diop$)_3$ | 7 | 0.15 | 1.2 |
|  | $RuCl_2(PPh_3)_3$ | 19 | 0.04 | 0.3 |
| | $Ru_2Cl_4((-)$-diop$)_3$ | 3 | 0.23 | 1.9 |

a) $RuCl_2(PPh_3)_3$, 2.5 mmol dm$^{-3}$; $Ru_2Cl_4((+)$ or $(-)$-diop$)_3$, 1.25 mmol dm$^{-3}$; olefin, 40 mmol; alcohol, 40 mmol in diphenyl ether (300 ml); reaction time, 12 h. b) No products derived from the glucofuranose derivatives were investigated.

TABLE 4. ASYMMETRIC TRANSFER HYDROGENATION OF α-METHYLCROTONATES INCLUDING RACEMIC OR CHIRAL ESTER GROUPS BY 1-PHENYLETHANOL WITH $Ru_2Cl_4$ $((-)$diop$)_3$ AT 190 °C[a]

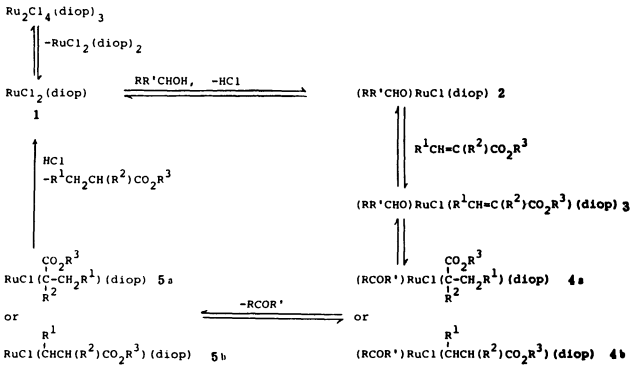
| $CH_3CH=C(CH_3)CO_2R$ R | Time h | Yield % | $[\alpha]_D^{23}$ ° | O.P.[b] % |
|---|---|---|---|---|
| 1-Phenylethyl | 10 | 71 | +0.10 | 0.8 |
| α-(Ethoxycarbonyl) benzyl | 9 | 93 | −1.88 | 15.4 |
| (1*R*, 2*R*)-1, 2-Bis(ethoxycarbonyl)-2-hydroxyethyl | 4 | 80 | −0.41 | 1.1 |
| *l*-Menthyl | 9 | 34 | −0.23 | 1.9 |
| | 12[c] | 43 | +0.06 | 0.6 |

a) Catalyst, 4 mmol dm$^{-3}$; alcohol, 33 mmol; ester, 67 mmol. b) Optical purities were determined in the same way as in Table 2. c) $Ru_2Cl_4((+)$-diop$)_3$ was used.

alcohol and $Ru_2Cl_4((-)$-diop$)_3$, the Ru(II) complex substantially increases the optical purity of α-methylbutyric acid enriched in (*R*)-enantiomer with a maximum optical purity of 22.5% in the case of 1,2-*O*-isopropylidene-α-D-glucofuranose. However, the Ru(II)-(+)-diop complex gave a lower optical purity of the saturated product than that obtained with $RuCl_2(PPh_3)_3$, and changed the enriched enantiomer in the product from (*R*)- to (*S*)-isomer in the case of 1,2-*O*-isopropylidene-α-D-glucofuranose.

At any rate, the chiral alcohols (α-D-glucofuranose derivatives) contribute to enhancing the extent of asymmetric induction, even though the maximum optical purity of 22.5% is lower than that (26.4%) attained with 1-phenylethanol.

*Asymmetric Transfer Hydrogenation of α-Methylcrotonate Including Racemic or Chiral Ester Groups.* In the present transfer hydrogenation, the double asymmetric induction, including the diastereo-face differentiation of unsaturated esters by the chiral catalyst, can also be expected by the use of unsaturated ester substrates containing chiral carbon atoms in the ester moiety,




Scheme 2. The sign of the optical rotation of diop is omitted.

achiral alcohol, and the Ru(II) complex.

When an asymmetric transfer hydrogenation of racemic or optically active α-methylcrotonate by 1-phenylethanol was effected with the Ru(II)-(−)-diop complex, no effective double asymmetric induction was realized (Table 4); optical purities of hydrogenated products were low (maximum 15.4%). Presumably, the steric bulkiness of the ester group in the substrates decreases the enantio-face differentiating ability of the chiral Ru(II) complex through depression of the substrate coordination to the complex.

*Reaction Mechanism.* It is obvious that the present asymmetric hydrogen transfer from alcohol (RR'CHOH) to unsaturated substrate ($R^1CH=C(R^2)CO_2R^3$) is effected by the coordination of both the reactants to the Ru(II) complex. From the fact that the chirality of the alcohol substantially affects the extent of asymmetric induction by the Ru(II)-(+) or (−)-diop catalyst, the asymmetric induction can be expected in the process of coordination of $R^1CH=C(R^2)CO_2R^3$ to the unsoluble ruthenium–alkoxide complex (*viz.*, the steric approach control over enantio-face differentiation[15]), which has previously been formed from the

active ruthenium species and the alcohol.

As for the catalytically active species in the present catalysis, $RuCl_2$((+) or (−)-diop) (**1**) has already been suggested as the plausible species by our previous $^{31}P$ NMR analysis of $Ru_2Cl_4$((−)-diop)$_3$ at −10—70°C;[16] $RuCl_2$((+) or (−)-diop)$_2$ simultaneously formed seems inactive for the present reaction because of the lack of active sites.

Therefore, the present transfer hydrogenation is thought to proceed along the catalytic cycle in Scheme 2, where the participation of HCl in the step of coordination of the alcohol to species **1** and of the elimination of the hydrogenated product has already been proposed by Sasson and Blum[17] in the transfer hydrogenation of unsaturated ketones by alcohols with $RuCl_2(PPh_3)_3$. Ruthenium–alkyl complexes **4a** and **5a** are more plausible than complexes **4b** and **5b** in the light of the contribution of the d-$\pi$ conjugation between the ruthenium metal and carbonyl group to the stabilization.[18] A more detailed study on the reaction mechanism, especially regarding the asymmetric induction of the Ru(II)-(+) or (−)-diop complex, is now in progress.

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