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# Stereochemical Studies of the Hydrogenation with an Asymmetrically Modified Raney Nickel Catalyst. The Hydrogenation of Acetylacetone

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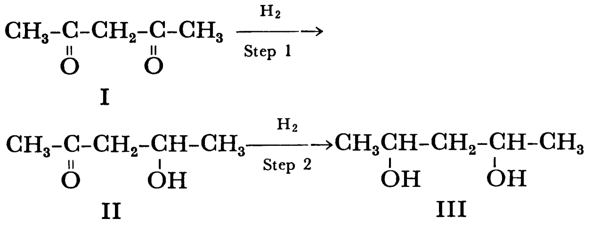
The hydrogenation of acetylacetone (I) over asymmetrically modified Raney nickel (MRNi) proceeded, step by step, as follows: acetylacetone (I) $\xrightarrow{\text{Step 1}}$ 4-hydroxy-2-pentanone (II) $\xrightarrow{\text{Step 2}}$ 2,4-pentanediol (III). It was demonstrated that the optical yield of Step 1 and the diastereomer excess of Step 2 are governed by the ratio of the stereo-differentiating reaction site to the non-stereo-differentiating reaction site on the catalyst. The stereochemistry of each step was also discussed based on the mode of the intermolecular hydrogen bondings between the substrate and tartaric acid adsorbed on the catalyst. RNi modified with a mixture of tartaric acid and NaBr (TA–NaBr–MRNi) gave the best result with respect to both Step 1 and Step 2.

In a previous communication, we have briefly reported that the modification of Raney nickel (RNi) with an aqueous solution of tartaric acid (TA) and NaBr gave an excellent catalyst (TA–NaBr–MRNi) for the stereo-differentiating (asymmetric) hydrogenation of acetylacetone (I) to 2,4-pentanediol (III).[1]

Although the hydrogenation of I over various MRNi's has been conducted by our research group[2] and others,[3] and although some important features of the reaction have been reported, the details of the mechanism of the stereo-differentiation have not yet been made clear.

The stereochemical studies of this reaction with the use of the effective enantio-differentiating catalyst (TA–NaBr–MRNi) enable us to obtain clear-cut information for understanding the reaction mechanism of the modified catalyst.

As has been reported,[2] the hydrogenation of I over RNi proceeds by a successive two-step process, as is shown in Scheme 1:



$$\underset{\mathbf{I}}{\mathrm{CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_3}} \xrightarrow[\text{Step 1}]{H_2}$$

$$\underset{\mathbf{II}}{\mathrm{CH_3\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_3}} \xrightarrow[\text{Step 2}]{H_2} \underset{\mathbf{III}}{\mathrm{CH_3\underset{\underset{OH}{|}}{CH}\text{-}CH_2\text{-}\underset{\underset{OH}{|}}{CH}\text{-}CH_3}}$$

Scheme 1.

In this report, the study of each step will be described first, and then the relation of the two steps will be discussed.

## Results and Discussion

*Enantioface-differentiating Hydrogenation of I to II.* The reaction of Step 1 with an asymmetrically modified catalyst is classified as an enantioface-differentiating reaction.[4] When the hydrogenation of I was stopped at the stage when the consumption of hydrogen reached a 1.1 molar equivalent to I, a mixture of I, II, and III was obtained. The results of the reactions carried out over three types of catalyst (RNi, TA–MRNi, and TA–NaBr–MRNi) are summarized in Table 1. The use of TA–NaBr–MRNi gave a higher optical yield than that of TA–MRNi. A comparable result has been obtained in the hydrogenation of methyl acetoacetate (MAA) to methyl 3-hydroxybutyrate (MHB).[5]

Our recent study[6] has shown that the optical yield of the MAA to MHB reaction is closely related to the ratio of the stereo-differentiating reaction site (the site where the substrate is converted to an optically active product by the aid of TA) to the non-stereo-differentiating reaction site (the site where a racemic product is produced) on the catalysts (hereafter, the abbreviations s.d. and non-s.d. will refer to the stereo-differentiating and non-stereo-differentiating reaction sites respectively). Furthermore, it has also been made clear that the proportion of the s.d. on the catalyst increases in the following order: RNi<TA–MRNi<TA–NaBr–MRNi. The NaBr on TA–NaBr–MRNi is considered to be adsorbed on the non-s.d. and to block the activity of the non-s.d. From the resemblance of the present results to those of MAA to MHB, the s.d. for the hydrogenation of MAA may also be said to function as the s.d. for the hydrogenation of I to II.

As may be found in Table 1, the catalyst giving a higher optical yield gives II in a larger proportion. This fact strongly suggests that both the optical purity and the proportion of II are governed by the ratio of the s.d. to non-s.d. The predominant formation of II in the case of TA–NaBr–MRNi indicates that the rate of Step 2 is appreciably slower than the rate of Step 1 at the s.d. From a comparison of the results with three catalysts (Table 1, Entries 1, 2, and 3), it is also evident that the rate of Step 2 at non-s.d. is higher than that at the s.d. That is, the s.d. and non-s.d. have different kinetics features.

I and MAA give (*R*)-II and (*R*)-MHB respectively in the hydrogenations with the catalyst modified with (*R*,*R*)-TA. When the structural similarity of I to MAA is taken into account, the mode of enantioface-differentiation of I with TA can be expected to be the same as that of MAA reported before.[7] The mode of the interaction between I and (*R*,*R*)-TA on the s.d. of the catalyst is shown in Figs. 1a and 1b. As may be found in Fig. 1b, one of the carbonyl groups in I to be hydrogenated comes close to the catalyst surface, with its si-face facing the catalyst, while the other, which remains unchanged, is located far from the catalyst. The considerable optical yield in the

TABLE 1. HYDROGENATION OF I TO II

| | Catalyst | Products (molar %) | | | Optical purity (%) and configuration of II |
|---|---|---|---|---|---|
| | | I | II | III | |
| 1 | RNi | 22 | 34 | 44 | — |
| 2 | (*R*,*R*)-TA-MRNi | 9 | 60 | 31 | 35 (*R*) |
| 3 | (*R*,*R*)-TA-NaBr-MRNi | 0 | 91 | 9 | 74 (*R*) |
| 4 | (*S*,*S*)-TA-NaBr-MRNi | 0 | 90 | 10 | 73 (*S*) |

TABLE 2. HYDROGENATION OF II TO III

| | Catalyst | Substrate | Products (molar %) | | d.e. (%) |
|---|---|---|---|---|---|
| | | | $(R^*,R^*)$-III | $(R^*,S^*)$-III | |
| 1 | RNi | racemic-II | 61 | 39 | 21 |
| 2 | RNi | (*R*)-II | 49 | 51 | −2[a] |
| 3 | (*R*,*R*)-TA-MRNi | (*R*)-II | 64 | 36 | 28 |
| 4 | (*R*,*R*)-TA-NaBr-MRNi | (*R*)-II | 90 | 10 | 80 |
| 5 | (*S*,*S*)-TA-NaBr-MRNi | (*R*)-II | 45 | 55 | −10[a] |

a) The sign, (−) indicates excess $(R^*,S^*)$-III.

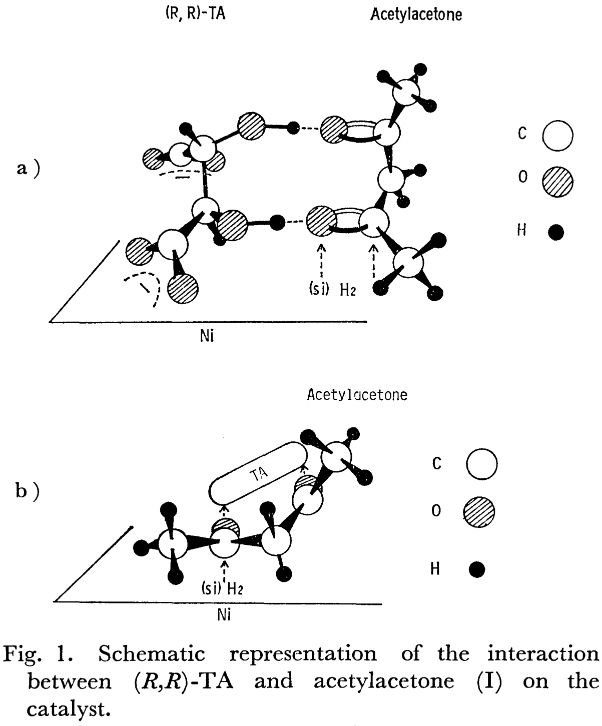


Fig. 1. Schematic representation of the interaction between (*R*,*R*)-TA and acetylacetone (I) on the catalyst.
a) Front view of coadsorbed species, b) side view of coadsorbed species.

reaction of I to II suggests that almost all of the I which has been adsorbed on the catalyst by interacting with (*R*,*R*)-TA is hydrogenated to (*R*)-II.

*Diastereoface-differentiating Hydrogenation of II to III.* 4-Hydroxy-2-pentanone, a substrate of Step 2, is a chiral compound. Therefore, the reaction of II to III is classified as a "diastereoface-differentiating reaction."[4] The efficiency of the reaction is expressed by the diastereomer excess (d.e. $= |(R^*,R^*)-(R^*,S^*)|/\{(R^*,R^*)+(R^*,S^*)\}$) of the product.

The results of the hydrogenation of II over various nickel catalysts are listed in Table 2. In the diastereo-differentiating reaction, the use of either an optically pure substrate or a racemic substrate can be expected to give a product with the same d.e. in principle so long as an achiral reagent or catalyst is used.[4]

In the hydrogenation with an unmodified RNi (Entries 1 and 2, Table 2), however, racemic II produces $(R^*,R^*)$-III in excess, while (*R*)-II gives $(R^*,R^*)$-III and $(R^*,S^*)$-III in almost the same ratio. This unusual result indicates that at least two chiral molecules, such as a substrate and a substrate, or a substrate and a product, are involved in the diastereo-differentiation step of the reaction. From the results presented above, the estimation of the inherent diastereoface-differentiating ability of RNi is found to be impossible. At any rate, a high d.e. is not expected in the reaction of II over unmodified RNi.

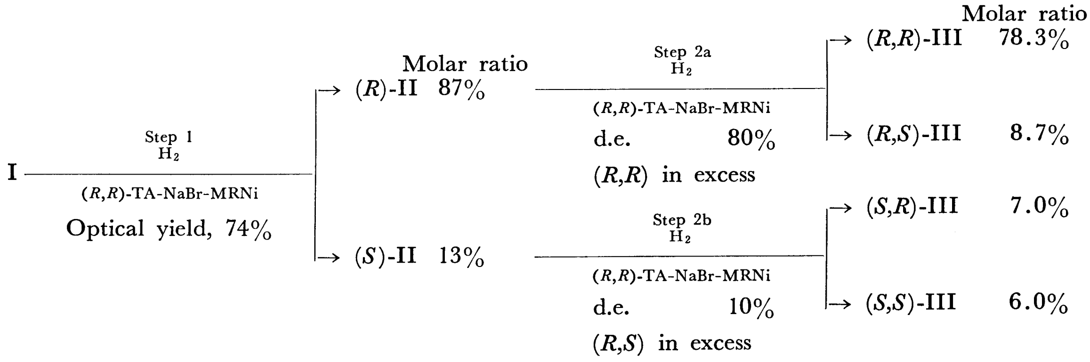
Entries 3 and 4, Table 2, show the results of the hydrogenation of (*R*)-II over (*R*,*R*)-TA–MRNi and (*R*,*R*)-TA–NaBr–MRNi. When (*R*,*R*)-TA–NaBr–MRNi was used, (*R*)-II was converted to (*R*,*R*)-III with 80% d.e.

On the other hand, the use of (*R*,*R*)-TA–MRNi resulted in the formation of (*R*,*R*)-III with a considerably low d.e. (28%). This great decrease in the d.e. is attributed to two characteristics of the non-s.d. remaining in the catalyst: 1) the d.e. at the non-s.d. is almost zero, as is expected from the result for RNi (Entry 2, Table 2) and 2) the hydrogenation rate at the non-s.d. is higher than that at the s.d., as has been mentioned in the previous section, so that a large portion of the substrate is hydrogenated at the non-s.d.

As is shown in Entries 4 and 5, Table 2, the hydrogenation of (*R*)-II over (*S*,*S*)-TA–NaBr–MRNi gave an extremely low d.e., in contrast with the high d.e. of the reaction of (*R*)-II over (*R*,*R*)-TA–NaBr–MRNi. That is, (*R*,*R*)-TA–NaBr–MRNi has a much higher diastereoface-differentiating ability than (*S*,*S*)-TA–NaBr–MRNi toward (*R*)-II. The origin of the high

Table 3. Enantiomer-differentiating hydrogenation of racemic-II

| Catalyst | | $(R,R)$-TA-NaBr-MRNi | $(S,S)$-TA-NaBr-MRNi |
|---|---|---|---|
| Conversion of hydrogenation (%) | | 55 | 43 |
| Recovered-II, | Optical purity (%) | 30 | 29 |
| | Configuration | $(S)$ | $(R)$ |
| Hydrogenation products (molar %), | | | |
| | $(R,R)$-III | 80 | 77 |
| | $(R,S)$-III | 20 | 23 |
| $(R^*,R^*)$-III, | Optical purity (%) | 48 | 61 |
| | Configuration | $(R,R)$ | $(S,S)$ |



Scheme 2.

d.e. in the combination of *(R)*-II and *(R,R)*-TA–NaBr–MRNi will be explained in the following section.

*Enantiomer-differentiating Hydrogenation of Racemic II over TA–NaBr–MRNi.* Since II is a chiral compound and TA–NaBr–MRNi is an optically active catalyst, an enantiomer-differentiating hydrogenation could be involved in the course of the reaction of Step 2 if II is a mixture of *(R)*- and *(S)*-II.

As the enantiomer-differentiating reaction and the diastereoface-differentiating reaction are intimately related to each other from the stereochemical viewpoint, a comparison of these two reactions should provide useful information about the stereo-differentiation of the reaction, II to III. In this regard, the partial hydrogenation of racemic II was carried out over *(R,R)*- and *(S,S)*-TA–NaBr–MRNi. The optical purity of the II recovered and the d.e. of the III produced around 50% conversion are listed in Table 3.

As may be found in Table 3, *(R,R)*-TA–NaBr–MRNi hydrogenated *(R)*-II much faster than *(S)*-II. The reaction with *(S,S)*-TA–NaBr–MRNi gave the same results except for the reverse stereochemistry.

The existence of a large enantiomer-differentiation is attributed to the selective adsorption of *(R)*-II on *(R,R)*-TA–NaBr–MRNi, which is brought about by the preferential interaction between *(R)*-II and *(R,R)*-TA. The results in Table 3 also indicate that, if the stereochemistry of II and TA is compatible, thus making for interaction between them, *(R*,R*)*-III is obtained in a high d.e.

From the fact that the hydrogenations of both I and *(R)*-II over *(R,R)*-TA–NaBr–MRNi produce chiral centers with an *R* configuration, the interaction between *(R)*-II and *(R,R)*-TA is expected to be close to that between I and *(R,R)*-TA.

The mode of interaction between *(R)*-II and *(R,R)*-TA is shown in Fig. 2. In this case, two components are brought into a well-fitting interaction by making two hydrogen bondings between them. On the other hand, *(R)*-II and *(S,S)*-TA could not interact well, as is the case of *(R,R)*-TA in any type of arrangemant. The lack of interaction with two hydrogen bondings between TA and II should cause a loss not only of the rigorous stereo-differentiation, but also of the potency of the associative adsorption of II on the catalyst.

From the all discussion presented above, the ratio of diastereomers in the reaction of II to III is governed by both the ratio of s.d. to non-s.d. on the catalyst and the stereochemical compatibility of II and TA.

*The Participations of the Enantioface-, Diastereoface-, and Enantiomer-differentiating Reactions in the Process of the I to III Reaction.* Based on the data of the separate reactions, I to II and II to III (Entry 3 in Table 1 and Entries 4 and 5 in Table 2), the material balance of the I to III reaction over *(R,R)*-TA–NaBr–MRNi is estimated to be as is shown in Scheme 2. Table 4 shows the proportion of diastereomers and the optical purity of *(R*,R*)*-III observed in the hydrogenation of I to III at a 100% conversion (Entry 2) and those calculated from the figures in Scheme 2 (Entry 3). The good agreement between the observed and calculated values clearly shows that the hydrogenation of the first and second carbonyl group proceeds step by step.

As may be found in Scheme 2, both the enantio-differentiation in Step 1 and the diastereo-differentiations in Steps 2a and 2b serve to give *(R*,R*)*-III with a high optical purity and a high d.e. In the hydrogenation of II to III, the reaction of Step 2a is

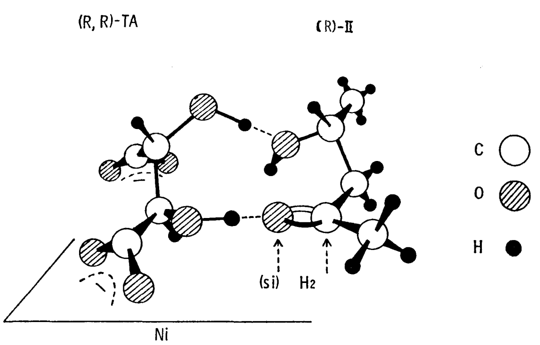


Fig. 2. Schematic representation of the interaction between (*R*,*R*)-TA and 4-hydroxy-2-pentanone (II).

Table 4. Hydrogenation of I to III over (*R*,*R*)-TA–NaBr–MRNi

| | Conversion % | Hydrogenation products (molar %) | | Optical purity of (*R**,*R**)-III |
|---|---|---|---|---|
| | | (*R**,*R**)-III | (*R**,*S**)-III | |
| 1 | 70 | 92 | 8 | 98 |
| 2 | 100 | 87 | 13 | 86 |
| 3 | Calculated values based on the data in Scheme 2 | 84 | 16 | 86 |

expected to proceed predominantly at the early stage of the reaction for the sake of the enantiomer-differentiating reaction with *(R,R)*-TA–NaBr–MRNi, as has been mentioned in the previous section. Therefore, the *(R*,R*)*-III produced at the early stage of the reaction should consist exclusively of *(R,R)*-III.

As is shown in Entry 1, Table 4, the optical purity of *(R*,R*)*-III in the reaction product had reached 98% when the reaction was discontinued at conversion of 70%.

It is evident that the hydrogenation of I to III over TA–NaBr–MRNi is the ideal stereo-differentiating reaction; that is, all three types of the stereo-differentiating reactions, enantioface-differentiation in Step 1, and diastereoface- and enantiomer-differentiations in Step 2, serve to increase the optical purity of *(R*,R*)*-III, the final hydrogenation product.

## Experimental

The analytical GLC was carried out with a Shimadzu GC-4A-PF gas chromatograph using a 3 m-5 mm o.d. glass column packed with 15% Ucon 50-HB-2000 on Chromosorb W. The $^1$H-NMR spectra were taken with a JEOL-FX-100 instrument. The optical rotations were measured with a Perkin Elmer 241 polarimeter.

All the chemicals except for those listed below were obtained from commercial sources and were used without further purification.

The catalysts used in this study were prepared by the method reported before.[5] The THF employed as a solvent of the hydrogenation was prepared as follows: commercial THF was dried over NaH overnight and was then distilled under a nitrogen atmosphere. (*R*,*R*)- and (*S*,*S*)-2,4-pentanediol (III) were prepared by the method previously reported.[1] *(R,R)*-III, mp 50.5 °C, bp 111—113 °C/19 mmHg, Found: C, 56.50; H, 11.77%. Calcd for $C_5H_{12}O_2\cdot(0.1\ H_2O)$: C, 56.67; H, 11.62%, $[\alpha]_D^{20}$ −54.5° (*c* 10, ethanol), NMR ($CDCl_3$, TMS) δ, 1.30 (d, *J*=6.3 Hz, 6H, two $\mathrm{C\underline{H}_3}$-CH(OH)–), 1.65 (t, *J*=6.2 Hz, 2H, –CH(OH)–$\mathrm{C\underline{H}_2}$–CH(OH)–) 2.75 (broad signal, 2H, two O$\underline{\mathrm{H}}$), 4.23 (m, 2H, two $CH_3$–C$\underline{\mathrm{H}}$(OH)–). The IR spectra of the sample were almost identical to those listed in the literature.[8] The analytical GLC (Ucon/80 °C) showed a single peak. *(S,S)*-III, $[\alpha]_D^{20}$ +54.2° (*c* 10, ethanol). All the other data of this compound were identical to those of *(R,R)*-III. *(R,R)*- and *(S,S)*-2,4-diacetoxypentane (V) were prepared by the treatment of acetic anhydride to III in the presence of pyridine, followed by purification with the preparative GLC of the sample. *(R,R)*-V, $[\alpha]_D^{20}$ −40.5° (*c* 10, ethanol). The analytical GLC (NPGS/80 °C) showed a single peak (retention time 79 min). The NMR spectra (TMS, $CDCl_3$) of V showed signals at δ, 1.22 (d, *J*=6 Hz, 6H, two $\mathrm{C\underline{H}_3}$–CHOAc–), 1.71 and 1.77 (two d, *J*=7 Hz, 2H, $-\underset{\mathrm{OAc}}{\mathrm{CH}}-\mathrm{C\underline{H}_2}-\underset{\mathrm{OAc}}{\mathrm{CH}}-$), 2.00 (s, 6H, two $\mathrm{C\underline{H}_3}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{-O-}$), and 4.98 (m, 2H, two $-\underset{\mathrm{OAc}}{\mathrm{C\underline{H}}}-$). The NMR spectra were also measured with a solution of V (10 mg) and Eu(hfmc)$_3$ (130 mg) in $CDCl_3$ (0.4 ml). V derived from *(R,R)*-III showed no detectable signal of the antipode. The difference in the chemical shift for acetyl groups (singlet) of *(R,R)*- and *(S,S)*-V was 4 Hz. *(S,S)*-V was obtained from *(S,S)*-III by the procedure described above. All the data were identical with those for *(R,R)*-V except for the value of $[\alpha]_D^{20}$ +40.2° (*c* 10, ethanol). *(R)*- and *(S)*-4-hydroxy-2-pentanone (II) were prepared by the partial oxidation of optically pure *(R,R)*- and *(S,S)*-III as follows: into a slurry of pyridinium chlorocromate (86 g) in 500 ml of $CH_2Cl_2$, a 40-g portion of *(R,R)*- or *(S,S)*-III, dissolved in 100 ml of $CH_2Cl_2$, was added all at once, after which the mixture was kept for 2 h with stirring at room temperature. The reaction mixture was then added to dry ether (3 l), and the resulting slurry was kept for another hour under stirring. The slurry was then passed through a column packed with 400 ml of Florisil, and the elute was concentrated under reduced pressure at room temperature. The distillation of the condensate under reduced pressure gave II in a yield of 12 g. *(R)*-II, bp 59—60 °C/20 mmHg, $[\alpha]_D^{20}$ −23.5° (neat), NMR ($CDCl_3$, TMS) δ 1.18 (d, *J*=0.6 Hz, 3H, $\mathrm{C\underline{H}_3}$–CH(OH)–), 2.17 (s, 3H, $\mathrm{C\underline{H}_3}\text{–}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\text{–}$), 2.56, 2.58 (two d, *J*=7.1 and 4.70 $-\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{C\underline{H}_2}\text{–CH(OH)–}$), 4.22 (m, –C$\underline{\mathrm{H}}$(OH)–), IR (neat), 3300 (OH) and 1700 cm$^{-1}$ (C=O). The GLC analysis showed a 99% purity. *(S)*-II, $[\alpha]_D^{20}$ +23.4° (neat). All the data of this compound were the same as those of *(R)*-II. A small portion of the sample was treated with acetic anhydride in the presence of pyridine. The resulting 4-acetoxy-2-pentanone (IV) was purified by preparative GLC (Ucon/20 min/100 °C). The analytical GLC (Ucon/85 °C) of the purified sample showed a single peak (retention time, 44 min). The purified IV showed NMR (TMS, $CDCl_3$), δ 1.22 (d, *J*=6.0 Hz, 3H, $\mathrm{C\underline{H}_3}$–CH(OAc)–), 2.00 (s, 3H, $\mathrm{C\underline{H}_3}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{-O-}$), 2.18 (s, 3H, $\mathrm{C\underline{H}_3}\underset{\underset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{-CH_2-}$), 2.62 and 2.80 (two d, *J*=7 Hz each, 2H, $-\underset{\mathrm{OAc}}{\mathrm{CH}}-\mathrm{C\underline{H}_2}-\underset{\mathrm{OAc}}{\mathrm{CH}}-$), and 4.95 (m, 2H, $-\underset{\mathrm{OAc}}{\mathrm{C\underline{H}}}-$). Racemic II was prepared by the partial hydrogenation of I over racemic-TA–NaBr–MRNi, as will be described below, and the fractional distillation of the product (bp 90—91 °C/38 mmHg).

*Partial Hydrogenation of I.* Into an autoclave (100-ml capacity), 11.5 ml (0.112 mol) of I, 0.2 ml of acetic acid, and 1.2 g of a catalyst suspended in 23 ml of THF were introduced. Thus, the volume to be occupied by hydrogen became *ca.* 65 ml. (The depression of 1 kg/cm$^2$ of the hydrogen pressure corresponds to 0.0021 mol of the consumption of $H_2$ at 100 °C.) After the evacuation of air from the autoclave, $H_2$ was charged to a pressure of 95 kg/cm$^2$ at room temperature (this value corresponded to 121 kg/cm$^2$ at 100 °C), and then heating was commenced. After the temperature of the reaction mixture had become 100 °C, this temperature was maintained until the hydrogen pressure became 58 kg/cm$^2$ (the consumption of $H_2$ amounts to 0.135 mol).

The autoclave was quickly cooled in an ice–water bath, and the $H_2$ was evacuated. After the removal of the catalyst from the reaction mixture, the filtrate was concentrated under reduced pressure to give a crude product. The relative amounts of I, II, and III in the crude product were determined by analytical GLC (Ucon/100 °C). The retention times of I, II, and III (the *(R*,R*)* and *(R*,S*)* isomers were partially resolved into two peaks) were 8, 24, 79, and 84 min respectively. A major portion of the crude product was distilled through a short column (a 5 cm × 10 mm o.d. glass column packed with a small glass helix 3 mm in diameter) under reduced pressure and fractionated into eight fractions. A fraction of pure II (bp 90—91 °C/38 mmHg) was found by the aid of the GLC analysis of each fraction. From the optical rotation of the purified II, the optical yield of the reaction, I to II, was calculated based on the $[\alpha]_D^{20}$ $-23.5°$ (neat) for optically pure *(R)*-II.

*Hydrogenation of I to III.* The hydrogenation of I was carried out under the same conditions as before until no more consumption of hydrogen was observed. After removing the catalyst from the reaction product by filtration, the filtrate was concentrated under reduced pressure to give a crude product. The ratio of *(R*,R*)*-III to *(R*,S*)*-III in the crude product was determined by analytical GLC (Ucon/85 °C). The retention times of *(R*,R*)*-III and *(R*,S*)*-III were 174 and 189 min respectively. The attempted separation of *(R*,R*)*-III and *(R*,S*)*-III by the preparative GLC failed. However, when they were converted to diacetate (V), the separation by preparative GLC was possible. Thus, the optical purity of *(R*,R*)*-III was evaluated from the optical purity of the *(R*,R*)*-V derived from the crude product.

A 1-g portion of the crude product was converted to V by the method described before. The preparative GLC (NPGS/80 °C) of the crude V gave pure *(R*,R*)*-V. From the optical rotation of the purified *(R*,R*)*-V, the optical purity of *(R*,R*)*-V was calculated based on the $[\alpha]_D^{20}$ $-40.5°$ (*c* 10, ethanol) for optically pure *(R,R)*-V.

*Hydrogenation of II to III.* The hydrogenation of II was carried out under the conditions described before. After removing the catalyst by filtration, the filtrate was subjected to analytical GLC (Ucon/85 °C). The ratio of *(R*,R*)*-III to *(R*,S*)*-III was evaluated from the peak areas of the corresponding compounds.

*Partial Hydrogenation of Racemic II.* The hydrogenation of racemic II (0.112 mol) was carried out under the same conditions as above until the consumption of hydrogen became 0.062 mol. After the removal of the catalyst by filtration, the filtrate was concentrated under reduced pressure to give a crude product.

The relative amounts of II, *(R*,R*)*-III, and *(R*,S*)*-III in the crude product were determined by analytical GLC (Ucon/85 °C). A major part of the crude product was distilled through a short column, as mentioned before, under a vacuum, and then fractionated into five fractions. A fraction of pure II (bp 59—60 °C/10 mmHg) was picked out of each fraction by the aid of GLC analysis. The pure II thus isolated from the reaction mixture was subjected to the determination of its optical purity by polarimetry. The optical purity of *(R*,R*)*-III was determined by the procedure previously described.

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