Asymmetric Hydrogenation of C=O Double Bond with Modified Raney Nickel. XV. Asymmetric Hydrogenation of Metal Chelate Compound

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The asymmetric hydrogenation catalysts prepared from Raney nickel catalysts by modifications with aqueous solutions of optically-active compounds have been studied in terms of the relationships between the modifying reagent and the substrate in this series.[1,2] In the asymmetric hydrogenation of carbonyl compounds, it was found that the asymmetric yield of the product was much affected by the structure of the substrate and that the best substrate for the catalyst modified with an optically-active 2-hydroxy or 2-amino acid was a *β*-ketocarbonyl compound, such as a *β*-ketoester or a *β*-diketone.[1]

At an early stage of the hydrogenation of acetylacetone using the unmodified catalyst or a catalyst modified with D-tartaric acid, nickel acetylacetonate was detected in the reaction mixture, but nickel acetylacetonate was not detected at the end of hydrogenation. Moreover, it has been reported how the spectrum of acetylacetone chelating with nickel metal was observed by the exposure of the evaporated nickel film in the acetylacetone vapor.[3,4]

In view of the above-mentioned facts, the chelations of *β*-ketocarbonyl compounds onto the nickel surface of the catalyst might contribute to their excellent asymmetric yields of the products. Moreover, it is very important in the elucidation of the asymmetric hydrogenation mechanism of carbonyl compounds to examine the asymmetric hydrogenation of the nickel chelates of *β*-ketocarbonyl compounds with nickel.

In this respect, the asymmetric hydrogenation of the nickel complexes of *β*-ketocarbonyl compounds as the substrate, nickel methyl acetoacetate and nickel acetoacetonate,[5] were tested.

The modified Raney nickel catalysts were prepared and the optical rotation of the product was measured in ways which have been reported in a previous paper.[2] D-Tartaric acid and L-glutamic acid were used as the modifying reagents; the results are shown in Table 1.

From the results in Table 1, the asymmetric hydrogenations of the nickel chelate compounds of *β*-carbonyl compound are found to occur in fairly lower asymmetric yields compared with those in the asymmetric hydrogenation of methyl acetoacetate or of acetylacetone itself. These lower asymmetric yields might be caused by the change in asymmetric centers caused by the nickel metal deposited on the catalyst surface in the hydrogenation of the chelate compounds or by the difference in the structures of the *β*-carbonyl compound adsorbed on the catalyst surface and on the nickel chelate compound, which is a trimer in crystal and in a benzene solution. This study will be discussed in detail in this Bulletin in the near future.

Table 1. Optical rotation of product

No.	Substrate[*1] (g)	Amount of R-Ni (as alloy) (g)	Modifying reagent (mod. temp. and pH)	Product	Optical rotation $[\alpha]^{20}_{D}$
1	$Ni(MAA)_2\cdot 2H_2O$[*2] (3.0)	3	2%-D-Tartaric acid (0°C, 5.0)	Methyl 3-hydroxybutyrate	−0.04
2	$Ni(MAA)_2\cdot 2H_2O$ (3.0)	3	2%-D-Glutamic acid (0°C, 5.0)	Methyl 3-hydroxybutyrate	+0.15
3	$Ni(AA)_2\cdot H_2O$[*3] (5.0)	3	2%-D-Tartaric acid (0°C, 5.0)	2,4-Pentanediol	−2.88
4	$Ni(AA)_2\cdot H_2O$ (5.0)	3	2%-L-Glutamic acid (0°C, 5.1)	2,4-Pentanediol	−0.16
5	Acetylacetone (10.0)	1	2%-L-Glutamic acid (0°C, 5.0)	2,4-Pentanediol	−1.88

[*1] 50 m*l* of benzene was used as the solvent. [*2] MAA: methyl acetoacetate. [*3] AA: acetylacetone.

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