CHEMISTRY LETTERS, pp. 315-316, 1982.

ENANTIOFACE-DIFFERENTIATING HYDROGENATION OF 2-OCTANONE OVER MODIFIED RANEY NICKEL IN THE REACTION MEDIA CONTAINING ORGANIC ACID

Tsutomu OSAWA* and Tadao HARADA

Institute for Protein Research, Osaka University, Yamadaoka, Suita, Osaka 565

The use of a mixture of THF and carboxylic acid as the reaction medium resulted in drastic increase in the optical yield of the hydrogenation of 2-octanone to optically active 2-octanol over tartaric acid-NaBr-modified Raney nickel (TA-NaBr-MRNi). Among the carboxylic acids examined, pivalic acid gave the highest optical yield (65.6%).

The catalytic enantioface-differentiating (asymmetric) hydrogenation of carbonyl compounds to optically active alcohols have widely been studied. Generally, the optical yield was rather low except for the ketones with polar functional groups or unsaturated ketones. So far as we know, the maximum optical yield recorded in the catalytic hydrogenation of dialkyl ketones is up to 43%, which was achieved in the hydrogenation of 3,3-dimethyl-2-butanone.[1)]

In the previous communications we reported that the asymmetric modification of Raney nickel with an aqueous solution of tartaric acid and NaBr gave an excellent catalyst (TA-NaBr-MRNi) for the enantioface-differentiating hydrogenation of β-keto-esters,[2)] β-diketones,[3)] β-ketoalcohols,[4)]and β-ketosulfones.[5)] However, the use of this catalyst in the hydrogenation of dialkyl ketone resulted in a rather low optical yield (28%).[6)] As for the hydrogenation of Methyl acetoacetate, the additives in the reaction media have been reported to influence the optical yield by Izumi[7)] and also Orito et al.[8)] Now we found that TA-NaBr-MRNi also provided the good results for the enantioface-differentiating hydrogenation of 2-octanone when carboxylic acid was added to the reaction system. The optical yields and the acids employed for the hydrogenation with (R,R)-TA-NaBr-MRNi are listed in Table 1. There is a tendency that α-branched

Table 1 Hydrogenation of 2-octanone over (R,R)-TA-NaBr-MRNi in the presence of carboxylic acid (R-COOH)

NaBr in modifying solution (g) [a)]	Carboxylic acid (R-/ml)	Product $[\alpha]_D^{20}$	Oprical yield (%)	Configuration
4	CH_3-/3	3.24	33.2	S
4	C_2H_5-/11.9	4.22	43.2	S
4	n-C_6H_{11}-/13.2	4.23	43.4	S
4	$(CH_3)_2CH$-/14.8	5.57	57.0	S
0	$(CH_3)_3C$-/18	3.93	40.4	S
4	$(CH_3)_3C$-/18	6.17	63.3	S
12	$(CH_3)_3C$-/18	6.40	65.6	S

a) The modifying sloution contained 2g of tartaric acid. The modification was carried out at pH 3.2, 100°C.

aliphatic acids give better optical yields than unbranched ones. The best result was obtained by the use of pivalic acid. Figure 1 shows the effects of the amount of pivalic acid on the optical yield. The optical yield increased with the increase of amount of pivalic acid to settle down at a constant value.

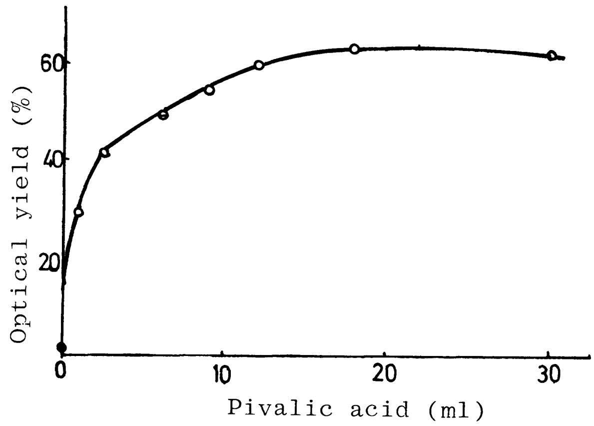

Figure 1 Relation between the amount of pivalic acid and optical yield

A typical procedure for the hydrogenation of 2-octanone is as follows: A 3.8g portion of the Raney nickel alloy (Ni:Al=42:58) was leached at 100°C for 1h, using 40ml of a 20% aqueous solution of sodium hydroxide. The catalyst was modified at 100°C for 1h with 200ml of an aqueous solution of tartaric acid(2g) and NaBr(12g) adjusted to pH 3.2 with 1M sodium hydroxide. The hydrogenation of 2-octanone(10ml) was carried out at 100°C with TA-NaBr-MRNi in THF(20ml) and pivalic acid(18ml) under 100kg/cm^2 of initial hydrogen pressure. The reaction was completed within 8h. After removal of the catalyst by decantation and evaporation of solvent, the residue was dissolved in 100ml of ether and washed with aqueous alkali solution to remove pivalic acid. The ether solution was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The vacuum distilation of the residue gave 2-octanol (bp 81°C/18 mmHg). Yield 6.2g, $[\alpha]^{20}_{D}$ +6.40(neat). Found:C, 73.59%; H,14.09%. Calcd for $C_8H_{18}O$: C,73.78%; H,13.92%. The IR and NMR spectra were identiacl with those of the authentic sample (Wako Pure Chemical Co., Ltd). Optical yield of the product was calculated based on the value of $[\alpha]^{20}_{D}$+9.76(neat) for the optically pure 2-octanol.9)

The applications of the present method to other ketones and detailed studies on the mode of enantioface-differentiating hydrogenation are under way.

The authors would like to thank Professors Yoshiharu Izumi and Akira Tai, and Dr. Hiroshi Ozaki, Osaka University for their many helpful discussions in the course of this work. Thanks are also due to Mrs. Aiko Kobatake for the elemental analyses.

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(Received December 23, 1981)