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A FACILE METHOD FOR THE PREPARATION OF OPTICALLY PURE 2,4-PENTANEDIOL; AN APPLICATION OF ASYMMETRICALLY MODIFIED NICKEL CATALYST FOR THE PREPARATION OF OPTICALLY ACTIVE COMPOUNDS

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The hydrogenation of acetylacetone over asymmetrically modified Raney nickel catalyst gave the chiral diastereomer of 2,4-pentanediol selectively with high optical purity. The recrystallization of the hydrogenation product from the ethereal solution gave optically pure (2R*,4R*)-2,4-pentanediol. Thus, (-)-(2R,4R)- and (+)-(2S,4S)-2,4-pentanediol were obtained from the hydrogenation products on using (R,R)- and (S,S)-tartaric acid-NaBr-modified Raney nickel, respectively.

Large scale preparation of optically pure (2R*,4R*)-2,4-pentanediol (II) has never been achieved because of the difficulty of optical resolution.[1]

In general, the catalytic hydrogenation of acetylacetone (I) gives a mixture of chiral diastereomer; (2R*,4R*)-II, and achiral diastereomer; (2R*,4S*)-II.

In the previous communication, we reported that the modification of Raney nickel catalyst with an aqueous solution of tartaric acid and NaBr gave an excellent catalyst (TA-NaBr-MRNi) for the enantioface-differentiating hydrogenation of methyl acetoacetate.[2] This catalyst was also found to be effective for the hydrogenation of I to II giving (2R*,4R*)-II selectively with high optical purity.

Table 1 shows the results of the hydrogenation of I under various reaction conditions. The product containing more than 85% of (2R*,4R*)-II with 87% of optical purity was obtained under the optimum conditions (entries 3 and 8 in Table 1).

Table 1 The hydrogenation of acetylacetone with MRNi[a]

	Catalyst	Solvent	Composition of Product		Yield and Optical Purity of Isolated (2R*,4R*)-II	
			(2R*,4R*)-II (%)	(2R*,4S*)-II (%)	Yield(%)	Optical Purity(%)
1	RNi (unmodified)	THF	63	37	—[b]	—
2	(R,R)-TA-MRNi	THF	67	33	—[b]	—
3	(R,R)-TA-NaBr-MRNi	THF	87	13	65	100[c]
4	(R,R)-TA-NaBr-MRNi	MeOH	63	37	—[b]	—
5	(R,R)-TA-NaBr-MRNi	EtOH	84	16	41	98
6	(R,R)-TA-NaBr-MRNi	*i*-PrOH	83	17	40	96
7	(S,S)-TA-NaBr-MRNi	THF	86	14	58	100[d]

a) Conditions for the hydrogenation are the same as described in the text except for the use of the catalyst and solvent listed in the table.

b) The compound could not be isolated, because of the difficulty of the crystallization of the product.

c) Calculated based on $[\alpha]_D^{20}$ $-53.7°$ (c 10, EtOH) for the optically pure (2R,4R)-II.

d) The configuration of the product is (2S,4S).

The (2R*,4R*)-II with high optical purity was found to be crystallized from ether at low temperature. Thus, optically pure (2R*,4R*)-II was easily isolated from the ethereal solution of the reaction product as crystals.

A typical procedure for the preparation of II is as follows: The TA-NaBr-MRNi was prepared from 38 g of Raney alloy by the same procedure as reported before except that the modification of RNi was conducted at 97°C instead of 100°C. In an autoclave (1000 ml capacity), were placed 97 g of I, 2 ml of acetic acid, 220 ml of THF, and TA-NaBr-MRNi prepared from 38 g of Raney alloy. Hydrogen was charged to a pressure of 95 kg/cm^2 and then heating was commenced. After the temperature of the reaction mixture had become 100°C, this temperature was maintained until no fall of the hydrogen pressure in the vessel was observed. After the evacuation of hydrogen and the removal of catalyst by filtration, the filtrate was concentrated under reduced pressure to give a crude product. The ratio of diastereomers determined by GLC (Ucon 50-HB-2000/15% on Chromosorb-W/3 mm x 3 m column/80°C) was listed in the table. A 1.5 g portion of the crude product was converted to 2,4-diacetoxypentane (III) by the treatment of acetic anhydride. (2R*,4R*)-III isolated by the preparative GLC (OV-17/2% on Chromosorb-W/6 mm x 3 m column/80°C) was subjected to determination of the optical purity by polarimetry. The calculated optical purity of this sample was 87 % based on the $[\alpha]_D^{20}$-40.5 (c 10, EtOH) for optically pure (2R,4R)-III.

The major part of the crude product was dissolved in 100 ml of ether and the mixture was cooled at -50°C for 3 h. The crystals precipitated were taken out at -50°C and the recrystallized from 100 ml of ether at -5°C. The distillation of the resulting crystals gave 65 g of II, bp. 111-113° C/19 mmHg, mp. 50.5°C. The analytical GLC (the same conditions as stated before) showed a single peak corresponding to (2R*,4R*)-II. The product was too hygroscopic for the elemental analysis to be performed with a completely dried sample. The results of a partially dried sample were as follows; 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 %. The optical rotation of the product is as follows; $[\alpha]_D^{20}$-53.7° (c 10, EtOH), $[\alpha]_D^{25}$-41.2°(c 10, $CHCl_3$) (lit[1] 41.3° ($CHCl_3$ c, not stated)). NMR and IR spectra of the sample were consistent with the structure of II. NMR spectra were measured with the solutions of III (10 mg) and $Eu(tfmc)_3$ (15 mg) in $CDCl_3$ (0.4 ml). III derived from the product showed no detectable signal of the antipode: The difference in chemical shift for the acetyl groups (singlet) of (2R,4R)- and (2S,4S)-III being 2.2 Hz.

References

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