CHEMISTRY LETTERS, pp. 265-266, 1973. Published by the Chemical Society of Japan

ASYMMETRIC HYDROGENATION OF OLEFINIC COMPOUNDS CATALYZED BY BIS(DIMETHYLGLYOXIMATO)COBALT(II)-OPTICALLY ACTIVE AMINE COMPLEX

Seiji TAKEUCHI, Yoshiaki OHGO, and Juji YOSHIMURA
Laboratory of Chemistry for Natural Products,
Tokyo Institute of Technology, Meguro-ku, Tokyo

Bis(dimethylglyoximato)cobalt(II)-quinine complex catalyzed asymmetric hydrogenation of olefinic compounds to afford optically active carboxylic acid and amino acid esters. α-Phenylacrylophenone gave higher optical yield (ca. 50%) than α,β-unsaturated esters (7-20%).

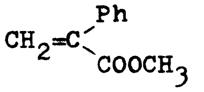
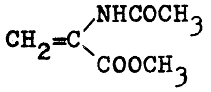
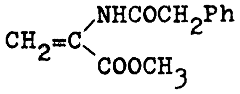
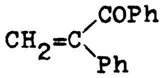
We reported that bis(dimethylglyoximato)cobalt(II)-base complex catalyzed the hydrogenation of activated α,β-unsaturated carboxylates; nitro-, azoxy- and azobenzenes; α-diketones; and α-ketocarboxylic acid esters1) and that the quinine complex catalyzed asymmetric hydrogenation of benzil.2) In this paper, asymmetric hydrogenation of olefinic compounds catalyzed by the same complex was examined.

Hydrogenation of olefinic compounds (1 - 4) in benzene was carried out under the best conditions used for the hydrogenation of benzil, and then treated by the same way. The products from methyl atropate (1), methyl α-acetamidoacrylate (2) and α-phenylacrylophenone (4) were purified by distillation, and that from methyl α-phenylacetamidoacrylate (3) by recrystallization. The product from (2) was distilled after fractionation of the reaction mixture by silica-gel column chromatography.

Optical yield was calculated from the specific rotation of the product. The specific rotation of (S)-(N-phenylacetyl)alanine methyl ester [mp 69.5 - 70.5°C; $[\alpha]_D$ -56.9° (c 2, methanol)] obtained by esterification of the corresponding acid3) ($[\alpha]_D$ -30°) with diazomethane was used as a standard for the product from (3).

The results (Table 1) indicated that: 1) Catalytic asymmetric hydrogenation of olefinic compounds clearly occurred to afford optically active ketone, carboxylic acid and amino acid esters, similarly as with the Wilkinson complex coordinating chiral phosphines.4) 2) (4) gave a higher optical yield than others, which

Table 1

Substrates		S/Co a)	Reaction		Yield	$[\alpha]_D$	Configuration	Optical Yield (%)
			Temp.	Time				
 $CH_2{=}C{<}^{Ph}_{COOCH_3}$	(1)	9	R.T. b)	4.3h	80%	+7.7° c)	S	7
〃		17	9°C	69h	92%	+11.3°	S	10.4
 $CH_2{=}C{<}^{NHCOCH_3}_{COOCH_3}$	(2)	8.4	R.T.	5h	62%	-17.0° d)	S	19
 $CH_2{=}C{<}^{NHCOCH_2Ph}_{COOCH_3}$	(3)	8	〃	2h	60%	-4.0°	S	7
 $CH_2{=}C{<}^{COPh}_{Ph}$	(4)	10	〃	1 day	95%	+99.4° e)	S	49.2

a) Molar ratio of substrate to cobalt. b) Room temperature. c) Pure (S)-isomer; $[\alpha]_D$ +109.2° (c 6.2, toluene).5) d) Pure (S)-isomer; $[\alpha]_D$ -91.7° (c 2, water).6) e) Pure (S)-isomer; $[\alpha]_D$ +202° (c 3.5, chloroform).7)

is consistent with the fact that the optical yield in the case of diketones (56 - 71%) were much higher than those in the case of α-ketocarboxylates (12 - 20%).8) These fact, in consideration of the fact that O-acetylquinine complex could scarcely induce the asymmetric hydrogenation8), suggest that some mode of attractive interaction involving the carbonyl group of substrates and the hydroxyl group of quinine plays an important role in the asymmetry-transfer.

Studies on the mechanism of this asymmetric hydrogenation are now in progress.

The authors wish to thank THE KAWAKAMI FOUNDATION for support of this work.

REFERENCES

1) Y. Ohgo, S. Takeuchi, and J. Yoshimura, Bull. Chem. Soc. Japan, 44, 283 (1971).
2) Y. Ohgo, S. Takeuchi, and J. Yoshimura, ibid., 44, 583 (1971).
3) T. Suyama, T. Toyoda, and S. Kanao, Yakugaku Zasshi, 85, 279 (1965).
4) T. D. Dang and H. B. Kagan, Chem. Commun., 481 (1971); W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, ibid., 10 (1972).
5) H. Pracejus, Ann. Chem., 634, 9 (1960).
6) J. P. Wolf, III, and C. Niemann, Biochim., 2, 493 (1963).
7) F. A. A. Elhafez and D. J. Cram, J. Amer. Chem. Soc., 74, 5846 (1952).
8) Y. Ohgo, Y. Natori, J. Yoshimura, 26th Annual Meeting of Chemical Society of Japan, Hiratsuka, April, 1972; Y. Ohgo, S. Takeuchi, J. Yoshimura, 19th Symposium on Organometallic Chemistry Abstracts, p55 (1971).

(Received December 28, 1972)