BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 49(3), 823—824 (1976)

Heterogeneous Asymmetric Hydrogenation of Benzil Using Bis(dimethylglyoximato)cobalt Complexes as Catalysts

Hideaki FUJIKOSHI, Riichiro NAKAJIMA, and Tadashi HARA
Department of Chemical Engineering, Faculty of Engineering, Doshisha University, Kamikyo-ku, Kyoto 602

(Received March 19, 1975)

Synopsis. The asymmetric hydrogenation of benzil in the heterogeneous system was found to proceed not only in the presence of quinine soluble in benzene phase, but also of an optically active amino or ascorbic acids soluble in aqueous phase.

Although the asymmetric hydrogenation of benzil using the complexes of bis(dimethylglyoximato)cobalt and optically active amine(abbreviated to $Co(DMG)_2$–amine) as catalysts was exclusively carried out by Yoshimura *et al.*[1] in the homogeneous system, it was further extended by the authors to the heterogeneous system, which consists of the benzene phase containing benzil and the aqueous phase containing $Co(DMG)_2$–amine complex. The asymmetric hydrogenation of benzil was found to proceed not only in the presence of quinine soluble in benzene phase, but also of an optically active amino or ascorbic acids soluble in aqueous phase. This made possible the use of an optically active and water-soluble base as well as ascorbic acid, which did not react with ammonia and glycine under the experimental conditions,[2] instead of benzene-soluble quinine.

For the hydrogenation of benzil under atmospheric pressure, the conventional apparatus[3] was modified and used. All the reagents used were of guaranteed or purified in advance. Optical rotations were measured in a 1-dm cell with a Union PM-71 polarimeter. The method was as follows unless otherwise stated. In a 100-ml vessel of the hydrogenation apparatus, $CoCl_2 \cdot 6H_2O$ (0.238 g, 0.001 mol) and dimethylglyoxime (0.232 g, 0.002 mol) were placed. The vessel was replaced by nitrogen and added with 10 ml of ethanol solution containing quinine hydrochloride (0.397 g, 0.001 mol) which was previously deaerated by nitrogen, followed by stirring for 5 min. To this solution was added 30 ml of deaerated aqueous solution containing sodium hydroxide (0.004 mol) and base (0.001 mol)

TABLE 1. ASYMMETRIC INDUCTION BY OPTICALLY ACTIVE COMPOUNDS IN THE HYDROGENATION OF BENZIL TO BENZOIN[a)]

Run	Optically active compound	Amine	$[\alpha]_D$	Optical yield (%)	Conf[b)]
1	Quinine	Ammonia	+42.8	36.1	*S*
2	Quinine	Glycine	+20.7	17.5	*S*
3	L-Ascorbic acid	Ammonia	−5.81	4.9	*R*
4	L-Ascorbic acid	Glycine	−3.74	3.2	*R*
5	L-Tyrosine	L-Tyrosine	−1.64	1.4	*R*
6	L-Lysine	L-Lysine	−0.89	0.8	*R*
7	L-Glutamic acid	L-Glutamic acid	−0.62	0.5	*R*
8	L-Aspartic acid	L-Aspartic acid	−0.37	0.3	*R*

a) In every case, chemicaly yield was almost quantitative.
b) Configuration of predominant isomer.

TABLE 2. EFFECT OF THE PRE-ABSORPTION OF HYDROGEN BY $Co(DMG)_2$–NH_3 COMPLEX ON THE ASYMMETRIC HYDROGENATION OF BENZIL[a)]

Run	A[b)] (ml)	Optical yield (%)	Conf[c)]	IH[d)] (10^{-3} s^{-1})	Time[e)] (min)
1	0.00	36.1	*S*	2.27	240
2	6.90	44.2	*S*	2.06	310
3	12.90	46.2	*S*	1.46	330
4	18.80	47.7	*S*	1.03	370
5	25.30	50.4	*S*	0.94	390
6	30.05	51.4	*S*	0.54	480

a) In every case, quinine was used as an optically active compound and chemical yield was almost quantitative. Initial pH was approximately 7.3—7.9. b) Amount of the hydrogen pre-absorbed by $Co(DMG)_2$–NH_3 complex at 20 °C. c) Configuration of predominant isomer. d) Initial rate of hydrogen absorption in the presence of benzil (H_2-mol consumed/s/mol of catalyst). e) Time necessary for the completion of hydrogenation.

TABLE 3. EFFECT OF THE AMOUNT OF ADDED NaOH ON THE ASYMMETRIC HYDROGENATION OF BENZIL CATALYZED BY $Co(DMG)_2$–AMINE[a)]

Run	Optically active compound (mmol)	Amine	Amount of added NaOH (mmol)	pH[b)]	Optcal yield (%)	Time[c)] (min)
1	Quinine	Ammonia	3.00	6.6	54.5	540
2	(0.25)		3.25	7.9	43.5	340
3			3.50	8.7	33.5	510
4			3.75	9.5	25.4	720
5	L-Ascorbic acid	Ammonia	3.00	5.3	1.5	550
6	(1.0)		3.50	6.5	2.8	520
7			4.00	7.4	4.9	370
8			4.50	8.3	4.3	450

a) In every case, chemical yield was almost quantitative. b) Initial pH of an aqueous phase.
c) Time necessary for the completion of hydrogenation.

Table 4. Relationship between optical yield of benzoin and mole ratio of quinine or L-ascorbic acid to the cobalt complex[a)]

Run	Amine	Optically active compound	A/Co[b)]	Optical yield (%)	Conf[c)]	Time[d)] (min)
1	Ammonia	Quinine	0	0.0	—	220
2			1/16	46.3	*S*	320
3			1/8	42.7	*S*	300
4			1/4	43.5	*S*	340
5			1/2	39.1	*S*	360
6			1	36.1	*S*	240
7			2	26.6	*S*	380
8	Ammonia	L-Ascorbic acid	0	0.0	—	220
9			1/8	0.9	*R*	480
10			1/4	2.5	*R*	470
11			1/2	3.7	*R*	480
12			1	4.9	*R*	370
13			2	6.2	*R*	270

a) In every case, chemical yield was almost quantitative, and initial pH was approximately 7.3—7.9. b) Mole ratio of quinine or L-ascorbic acid to the cobalt. c) Configuration of predominant isomer. d) Time necessary for the completion of hydrogenation.

such as ammonia and amino acid, and then 30 ml of deaerated benzene solution containing benzil (0.420 g, 0.002 mol). The vessel was replaced by hydrogen and the solution was stirred under atmospheric pressure of hydrogen at room temperature. The amount of hydrogen absorbed was measured by a gas burette every definite interval. The amount of sodium hydroxide added was controlled, if necessary, so as to give a desired pH.

After absorption of the theoretical amount of hydrogen, the reaction mixture was transferred into a 100-ml separatory funnel and shaken with 30 ml of benzene, followed by separating the aqueous layer. The residual benzene layer was washed with each 50 ml of water, 2M-HCl and water in that order, one, three and four times, respectively. The benzene layer was concentrated *in vacuo*. The resulting product was dried overnight in a desiccator and obtained as white needles, followed by measuring the optical rotation of its acetone solution (c=0.8—1.2). The optical yield was calculated from the specific rotation of the product and that of the optically pure benzoin.[4)] Based on the additional data of melting point and mass spectrum, the above product was identified as (S)-benzoin.

As seen from Table 1, the asymmetric hydrogenation of benzil proceeded more or less only if an optically active compound was present in either a benzene phase or aqueous phase. The optical yield depended on the amount of the hydrogen pre-absorbed by $Co(DMG)_2$–NH_3 (Table 2), pH of the aqueous phase (Table 3) and the mole ratio of quinine or L-ascorbic acid to the cobalt complex (Table 4). Though the relationships between the optical yield and the above mentioned factors are interesting, their reasons still remain unknown.

References

1) Y. Ohashi, Y. Sasada, Y. Tashiro, Y. Ohgo, S. Takeuchi, and J. Yoshimura, This Bulletin, **44**, 583 (1971); *ibid.*, **46**, 2589 (1973); *Chem. Lett.*, **1973**, 265; *ibid.*, **1974**, 33, 709, 1327.

2) For example, T. Ozawa and Y. Nakamura, *Yakugaku Zasshi*, **90**, 933 (1970). This was also confirmed experimentally.

3) T. Takaya, T. Koga, and T. Hara, This Bulletin, **39**, 654 (1966).

4) I. V. Hopper and F. J. Wilson, *J. Chem. Soc.*, **1928**, 2483.