

ASYMMETRIC HYDROGENATION BY A RHODIUM CATALYST  
COMPLEXED WITH A PHOSPHINITE DERIVED FROM CELLULOSE

Yasuziro KAWABATA, Masato TANAKA, and Ikuei OGATA  
National Chemical laboratory for Industry,  
Honmachi, Shibuya-ku, Tokyo 151

High optical yields up to ca. 77% were obtained in the hydrogenation of 2-phenyl-1-butene by use of a rhodium catalyst complexed with an insoluble phosphinite derived from 6-*O*-triphenylmethylcellulose. Recycling of the catalyst was also investigated.

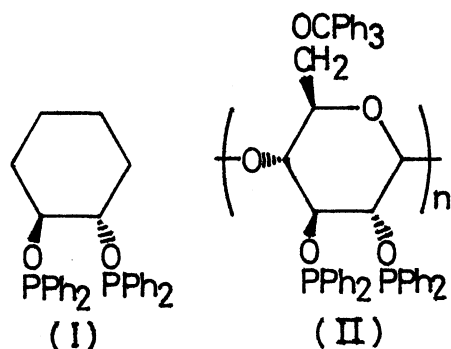
Immobilized complex catalysts have received considerable recent attention in the field of organometallic catalysts,<sup>1)</sup> and highly enantioselective hydrogenation has been accomplished in the presence of various types of chiral ligands. However, there are only a few reports<sup>2)</sup> of immobilized chiral complex catalysts, where the optical yields attained are much poorer in comparison with those by homogeneous ones.

Previously, we reported that the chiral diphosphinite (I) is an excellent ligand for rhodium catalyzed asymmetric hydrogenation.<sup>3)</sup> This result has stimulated the preparation of a chiral phosphinite linked to cellulose which is readily available in optically pure state, because the oxacyclohexane ring is conformationally more rigid than the cyclohexane ring of I.

We attempted the preparation of a chiral ligand, i.e. 2,3-*O*-bis(diphenylphosphino)-6-*O*-triphenylmethylcellulose (II) as follows. 6-*O*-Triphenylmethylcellulose was prepared by addition of pyridine solution of chlorotriphenylmethane to regenerated cellulose, obtained by hydrolysis of cellulose acetate according to the literature<sup>4)</sup> [ Anal. Found : C, 73.34; H, 5.93%. Calcd for C<sub>25</sub>H<sub>24</sub>O<sub>5</sub> : C, 74.24; H, 5.98%. ]. The 6-*O*-triphenylmethylcellulose (5 g) was treated by diphenylphosphinous chloride (10 g) in pyridine (150 ml) at room temperature for five days. Three times reprecipitation from pyridine solution with methanol yielded white powder (III, 7.2 g) [ Anal. Found : C, 73.82; H, 5.68; P, 3.66%. Calcd for C<sub>49</sub>H<sub>42</sub>O<sub>5</sub>P<sub>2</sub> : C, 76.16; H, 5.48; P, 8.02%. ]. This analysis shows that the phosphinite

formation was incomplete. However, all attempts to prepare a phosphinite of higher phosphorus content were unsuccessful. Nevertheless, the phosphinite III with low phosphorus content brought about higher stereoselectivity than I when used in rhodium catalyzed hydrogenation of 2-phenyl-1-butene, as described below.

The catalyst was prepared by mixing a calcd. amount of [Rh(1,5-hexadiene)Cl]<sub>2</sub> and III in benzene in a 50 ml stainless steel reactor with a TEFLON-



coated magnetic rotor. After stirring the mixture under nitrogen to promote the rhodium-III complexation, 2-phenyl-1-butene, hydrogen, and also ethanol in some cases were introduced into the reactor, which was then heated at the temperatures shown in the table. After a given period, the reaction

Table. Hydrogenation of 2-phenyl-1-butene with Rh-III complex catalyst<sup>a)</sup>

Run	P/Rh <sup>b)</sup>	Complexation		Reaction		Conversion (%)	Optical yield(%) <sup>c)</sup>
		Temp.(°C)	Time(day)	Temp.(°C)	Time(day)		
1	2.3	50	5	50	4	67.9	4.3 ± 0.1
2	11.5	50	5	50	8	10.7	57.6 ± 1.1
3	23	50	5	50	20	16.8	51.8 ± 2.6
4	d)	-	-	50	13	36.0	40.8 ± 0.3
5	d)	-	-	50	10	41.7	35.6 ± 0.2
6	11.5	50	5	50	8	1.2	77.3 ± 8.3
7	11.5	r.t.	3	r.t.	28	12.6	20.2 ± 0.9
8	11.5	80	1.7	80	6	71.4	49.2 ± 0.2
9	11.5	80	1.7	120	2	100.0	40.3 ± 0.1
10	11.5	120	1.7	120	2	100.0	48.8 ± 0.2

a) 2-Phenyl-1-butene: 1.5 ml,  $P_{H_2}$ : 50 atm,  $[Rh(1,5\text{-hexadiene})Cl]_2$ :  $7.5 \times 10^{-6}$  mol, Solvent: benzene 10 ml (run 1~5) or benzene 5 ml + ethanol 5 ml (run 6~10).

b) Atomic ratio of phosphorus to rhodium. c) Optically pure (R)-2-phenylbutane shows  $[\alpha]_D^{20} = -27.31^\circ$ .<sup>5)</sup> d) Run 4 and 5 were carried out using the catalyst recovered from run 3 and 4, respectively.

mixture containing suspended gelatinous catalyst was poured into methanol (100 ml), the catalyst precipitated was removed by filtration, and the product, 2-phenylbutane, was distilled.

The results of hydrogenation are listed in Table. In all cases the prevailing configuration of the product was R. When the value of P/Rh was enough high, high optical yields were obtained in the hydrogenation of 2-phenyl-1-butene in benzene. In a benzene-ethanol (1:1) mixed solvent, the optical yield observed was as high as 77%, though the hydrogenation proceeded very slowly probably because of the insolubility of the catalyst. Elevation of the complexation temperature or lowering of the reaction temperature tended to give a higher optical yield. Experiments for comparison by use of I, or (-)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane (DIOP) under the same reaction conditions gave (R)-2-phenylbutane in 33.0 or 24.5% enantiomeric excess, respectively.

The results of the reaction using the recovered catalyst (run 4 and 5) show that the stereoselectivity was lost to some extent even if all operations of the recovery were carried out under nitrogen atmosphere.

Asymmetric hydrogenation of  $\alpha$ -acetoamidocinnamic acid by use of the catalyst system (P/Rh=11.5) at 50°C in benzene-ethanol (1:1) mixed solvent gave after seven days N-acetylphenylalanine in 52 and 17.5% optical and chemical yield, respectively.

#### References

- 1) Z. M. Michalska and D. E. Webster, Chem. Technol., 1975, 117.
- 2a) W. Dumont, J. Poulin, T. Dang, and H. B. Kagan, J. Am. Chem. Soc., 95, 8295 (1973).
- 2b) H. Pracejus and M. Bursian, German (East) Patent 92031 (1972); Chem. Abstr., 78, 72591b (1973).
- 3) M. Tanaka and I. Ogata, J. Chem. Soc., Chem. Commun. 1975, 735.
- 4) J. W. Green, "Methods in Carbohydrate Chemistry", Vol. 3, ed. by R. L. Whistler, Academic Press, New York-London (1963), pp. 327-331.
- 5) P. W. B. Harrison, J. Kenyon, and J. R. Shepherd, J. Chem. Soc., 1926, 658.

(Received September 7, 1976)