CHEMISTRY LETTERS, pp. 1921-1922, 1987.

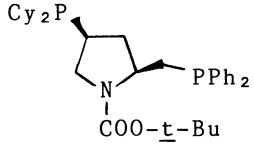
Dramatic Hydrogen Pressure and Triethylamine Effects on the Asymmetric Hydrogenation of Itaconic Acid Which Give a New Mechanistic Aspect on Asymmetric Induction[1)]

Hisashi TAKAHASHI and Kazuo ACHIWA*
School of Pharmaceutical Sciences, University of Shizuoka,
2-2-1 Oshika, Shizuoka 422

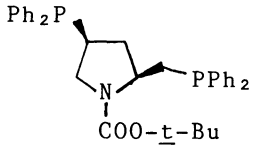
Dramatic hydrogen pressure and triethylamine effects on the asymmetric hydrogenation of itaconic acid catalyzed by BCPM-Rh^+ and an explanation for these effects were described.

(2S,4S)-N-(t-Butoxycarbonyl)-4-(dicyclohexylphosphino)-2-[(diphenylphosphino)methyl]pyrrolidine (BCPM, **1**) was found to be the most effective chiral ligand for asymmetric hydrogenations of ketopantolactone, α-keto esters, α-keto aldehyde derivatives and phenacylamine hydrochlorides.[2)]

Here, we wish to describe the asymmetric hydrogenation of itaconic acid (**2**), a typical prochiral olefin, catalyzed by BCPM-Rh^+ complex, where contrary to the constant behaviors of BPPM(**3**)-Rh^+ complexes on the optical yields of asymmetric hydrogenation of itaconic acid,[3)] both hydrogen pressure and triethylamine addition were critical factors for the effective asymmetric induction catalyzed by BCPM-Rh^+ complexes. These data were listed in Table 1.



BCPM (**1**)

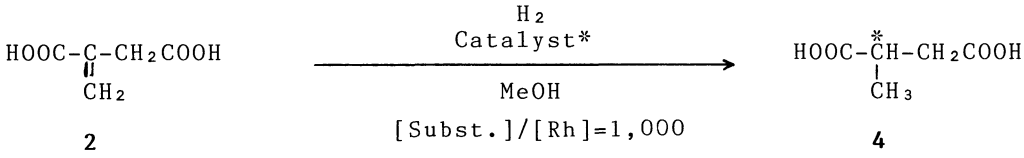


BPPM (**3**)

The table clearly indicated that the dicyclohexylphosphino group of BCPM caused the dramatic hydrogen pressure and triethylamine effects on the optical yields and also played an important role in accelerating the reaction rate. This and the other facts[4-7)] may suggest that **A** → **B** is an intermediary rate-determining step where the $\sigma^*(H_2)$-d(Rh) orbital overlapping is more enhanced by the dicyclohexylphosphino group of BCPM as a better electron donor than that of the diphenylphosphino group of BPPM, and under higher hydrogen pressures, formation of $Rh^{(I)}$-BCPM-substrate complex (**A**) decreases more dramatically in competition with that of $Rh^{(III)}$-BCPM-hydrogen complexes leading to the product of lower optical yield, because that BCPM-Rh^+ complex is also susceptible to oxidative addition of molecular hydrogen as reasoned for **A** → **B**.

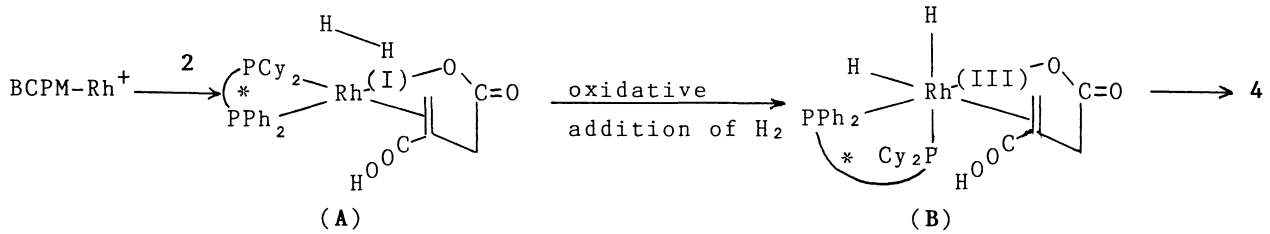
Further investigations along this line are actively under way.

Table 1. Asymmetric Hydrogenation of Itaconic Acid[a)]



Catalyst*	Triethylamine (equiv./[Subst.])	Conditions (H_2 Press./atm; Temp /°C; Time/h)	Convn./%[b)]	Opt. yield/%[c)] (Confign.)
[Rh(COD)BCPM]ClO$_4$	1	50; 20; 20	100	58 (S)
	-	50; 20; 20	100	3 (S)
	1	5; 20; 20	100	79 (S)
	1	1; rt; 20	100	92 (S)
	-	1; rt; 20	100	26 (S)
[Rh(COD)BPPM]ClO$_4$	1	1; rt; 20	<10	≈92 (S)

a) All hydrogenations of **2** (10 mmol) were carried out with 0.01 mmol of catalyst in 20 ml of MeOH. *b*) Determined by ^{1}H-NMR spectra. *c*) Calculated on the basis of the reported value for optically pure (R)-**4**; $[\alpha]_D^{20}$ +16.88° (c2.16, EtOH).[8)]



References

1) Asymmetric Reactions Catalyzed by Chiral Metal Complexes XXVI.
2) H. Takahashi, M. Hattori, M. Chiba, T. Morimoto, and K. Achiwa, Tetrahedron Lett., 27, 4477 (1986); T. Morimoto, H. Takahashi, K. Fujii, M. Chiba, and K. Achiwa, Chem. Lett., 1986, 2061; H. Takahashi, T. Morimoto, and K. Achiwa, Chem. Lett., 1987, 855; H. Takeda, M. Aburatani, T. Tachinami, H. Takahashi, and K. Achiwa, in preparation.
3) K. Achiwa, Chem. Lett., 1978, 561; I. Ojima, T. Kogure, and N. Yoda, J. Org. Chem., 45, 4728 (1980).
4) C. R. Landis and J. Halpern, J. Am. Chem. Soc., 109, 1746 (1987).
5) C. E. Johnson and R. Eisenberg, J. Am. Chem. Soc., 107, 3148 (1985).
6) R. H. Crabtree and R. J. Uriarte, Inorg. Chem., 22, 4152 (1983).
7) A. Dedieu and A. Strich, Inorg. Chem., 18, 2940 (1979).
8) E. Berner and R. Leonardsen, Justus Liebigs Ann. Chem., 538, 1 (1939).

(Received July 3, 1987)