Asymmetric Hydrogenation by a Chiral Diphosphinite Rhodium Complex

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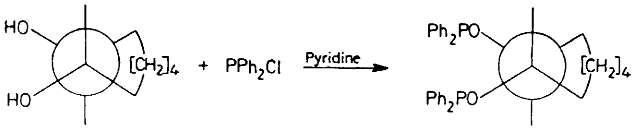
Summary Asymmetric hydrogenation has been successfully carried out using a rhodium complex with a chiral diphosphinite prepared from (+)-cyclohexane-(1*S*,2*S*)-diol.

ASYMMETRIC syntheses have been successfully performed using optically active phosphine–transition metal complex catalysts. Most of the studies, however, have concentrated on the application of *P*-chiral phosphines or the *C*-chiral phosphine (−)-diop {[(2,2-dimethyl-1,3-dioxolan-4,5-diyl)-bis(methylene)]bis(diphenylphosphine)}, as chiral ligands,[1] and no systematic search for new *C*-chiral ligands which bring about high degree of stereoselectivity has been reported. We now report the preparation of a new chiral diphosphinite, and its application to asymmetric hydrogenation of olefins.

The new chiral diphosphinite, (+)-*trans*-BDPCH [(+)-*trans*-1,2-bis(diphenylphosphinoxy)cyclohexane, $C_6H_{10}(OPPh_2)_2$], was prepared[2] from (+)-*trans*-cyclohexane-(1*S*,2*S*)-diol (85·5% optical purity) as a viscous liquid, b.p. 175—190 °C (bath temperature) at $1{\cdot}0 \times 10^{-4}$ Torr, $[\alpha]_D$ + 43·3° (toluene, *c* 2·61).



Hydrogenation was carried out with the rhodium complex $[Rh(1,5\text{-hexadiene})Cl]_2$ in the presence of (+)-*trans*-BDPCH. The results in the Table show that fairly effective stereochemical control was achieved. For example, the optical yield in the hydrogenation of α-ethylstyrene is higher than that obtained using (−)-diop (24·5% at 50 °C) or (*S*)-methylphenyl-n-propylphosphine (7% at room temperature).[3] In the case of *N*-acetamidoacrylic acid derivatives, a much higher optical yield was observed, and the optical purity of the *N*-acetylamino acids formed could be increased to nearly 100% by recrystallization from ethanol–hexane. The fairly good stereoselectivity may be attributable to the chelating power and to the greater distortion of the diphenylphosphino group of the diphosphinite than that of (−)-diop brought about by the configuration of the asymmetric carbons and the conformation of the six-membered ring.

The optical yield was very low (0·4—2·6%) in the case of hydroformylation with $[Rh(CO)_2Cl]_2$, perhaps because of the poor co-ordination ability of the diphosphinite, and, under high CO pressure, (+)-*trans*-BDPCH cannot behave as a bidentate chelating ligand but as only a monodentate one.

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TABLE. Hydrogenation by the (+)-*trans*-BDPCH–rhodium complex catalyst[a]

Substrate	Reaction temp. (°C)	Product Configuration	Product Optical yield (%)
α-Ethylstyrene	50	*R*	33·0
cis-2-Phenyl-2-butene[b]	50	*S*	14·4
α-Acetamidoacrylic acid	−20	*S*	78·9
α-Acetamidocinnamic acid	0	*S*	68·5
α-Acetamido-*p*-hydroxycinnamic acid ..	15	*S*	48·5

[a] $P(H_2)$ = 50 atm; (+)-*trans*-BDPCH/Rh = 1·1; reaction time, 24 h. [b] Reaction time, 288 h.

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[2] G. M. Kosolapoff and L. Maier, 'Organic Phosphorus Compounds,' Vol. 4, Wiley-Interscience, New York, 1972, pp. 473—475.

[3] L. Horner, H. Siegel, and H. Buthe, *Angew. Chem.*, 1968, **80**, 1034.