Asymmetric Hydroesterification of Norbornene by Chiral Non-chelate Biphosphine Palladium Complexes

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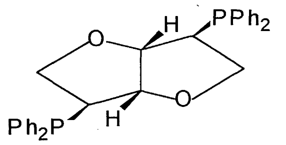
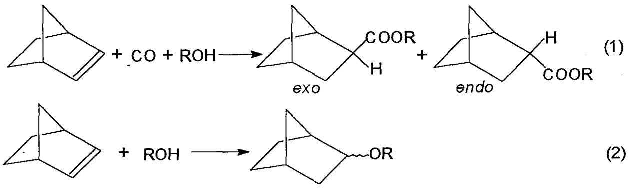
Asymmetric induction up to 92.2% has been obtained in the hydroesterification of norbornene with carbon monoxide and alcohols in the presence of Pd(OAc)$_2$, 1,4:3,6-dianhydro-2,5-dideoxy-2,5-bis(diphenylphosphino)-L-iditol and *p*-toluenesulfonic acid.

Metal complex catalyzed hydroesterification and hydroformylation reactions of olefins are the most extensively investigated in homogeneous catalytic process.[1] Both products of the hydroesterification and hydroformylation of monoolefins are of considerable industrial value. In recent years, asymmetric hydroesterification has attracted a great deal of attention.[2] In 1973, asymmetric hydrocarboxylation of olefins was first reported by Pino et al. using the PdCl$_2$and (-)DIOP at 35 MPa of carbon monoxide at 100 ℃ .[3] Since then attempts have been made to achieve asymmetric hydroesterification, but good enantioselectivity has yet to be realized and reaction conditions used are severe.[4-8] In 1990, Alper et al. reported the synthesis of acids in high optical purity (91%ee), as well as good chemical yield (64.0%) by using an appropriate chiral ligand (BNPPA) for the palladium chloride catalyzed reaction.[9] We first reported the asymmetric hydroesterification of norbornene using the palladium acetate, 1,4:3,6-dianhydro-2,5-dideoxy-2,5-bis(diphenylphosphino)-L-iditol (DDPPI)[10] and *p*-toluenesulfonic acid (*p*-Ts) catalytic system under mild reaction conditions. The high optical purity and good chemical yields are obtained by using the non-chelate biphosphine ligand for palladium acetate catalyzed reaction. The results were listed in Table 1. In this catalytic reaction *p*-toluenesulfonic acid is used as a promoter. The catalytic reaction does not take place without *p*-toluenesulfonic acid.



DDPPI

The asymmetric hydroesterification reaction of norbornene is shown as eqn. (1) , and the side reaction as eqn. (2).



The nature of chiral phosphine ligands plays an important role in asymmertric hydroesterification, hydrogenation and hydroformylation reactions of olefins. Table 1 shows that 1,4:3,6-dianhydro-2,5-dideoxy-2,5-bis(diphenylphosphino) – L – iditol is an effective chiral ligand for hydroesterification of norbornene. The molecular structure of DDPPI shows that this chiral bisphosphine ligand is a good rigid bicycle compound and

Table 1. Palladium-catalyzed asymmetric hydroesterification of norbornene

Run No	L*/Pd(OAc)$_2$ mol/mol	Pressure MPa	Temperature ℃	Conversion %	Yield of ester[a] %	Optical yield[b] %	Configuration[c]
1	3/1	6.0	120	99.6	87.0	45.3	1S, 2S, 4R
2	2/1	6.0	120	99.9	88.6	41.9	1S, 2S, 4R
3	1/1	6.0	120	98.9	86.9	23.2	1S, 2S, 4R
4	0.5/1	6.0	120	99.1	76.8	69.8	1S, 2S, 4R
5	0.5/1	5.0	120	98.9	71.6	92.2	1S, 2S, 4R
6	0.5/1	7.0	120	98.9	77.8	37.6	1S, 2S, 4R
7	0.5/1	6.0	100	97.8	76.4	88.4	1S, 2S, 4R
8	0.5/1	6.0	110	99.3	81.5	81.4	1S, 2S, 4R
9	0.5/1	6.0	130	99.6	75.5	65.6	1S, 2S, 4R
10	0.5/1	6.0	140	99.0	60.7	65.3	1S, 2S, 4R
11[d]	0.5/1	6.0	120	98.2	78.3	53.1	1S, 2S, 4R

Reaction conditions: Pd(OAc)$_2$: 0.021 mmol; norbornene: 10.6 mmol; methanol: 5.0 mL; reaction time: 24 h.

[a] Yields based on the starting olefins. [b] Determined by HPLC analysis with a chiral stationary phase column (Cellulose Tribenzoate) after distillation under reduced pressure. [c] Determined by the signs of optical rotation. [d] Ethanol is used instead of methanol.

it has four chiral carbon atoms, whose configurations are all S. DDPPI can hardly chelate a metal atom or ion. Experimental results showed that higher optical yields were obtained when the phosphorus/Pd ratio was kept at one (Run 1-4). Since DDPPI is a bidentate ligand, this would correspond to coordination of one phosphorus atom of DDPPI per palladium atom, and it suggests that in the catalytic complexes giving predominant formation of methyl *exo*-2-carbomethoxynorbornane, the bisphosphine DDPPI ligand behaves as a monodentate ligand. This conforms to the rules of asymmetric hydroesterification of olefins.[5,6]

The effect of carbon monoxide pressure on the optical yield is shown by the results of Run 5-6. When the pressure of carbon monoxide is 5.0 MPa, an optical yield of 92.2% is obtained. The optical yield decreases with the increase of carbon monoxide pressure.

The results of Run 7-10 show that the highest optical yield is obtained when the reaction temperature is 100 ℃. The optical yield decreases with increase of temperature. In other words, high temperature is unfavourable for the asymemetric hydroesterification of olefins.

The optical yields are also affected to some extent by the nature of solvents (Run 11). Alcohols are used not only as a solvent, but also as a reactant. When ethanol is used instead of methanol, the optical yield decreases rapidly. Another possible explanation is that methanol reacts more easily with norbornene than ethanol does.

The asymmetric induction reaction ocurrs probably before or during the formation of unepimerizable chiral secondary alkyl-metal intermediates. It is possible that the situation is anlogous to the asymmetric hydroformylation.[2]

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