

Priority communication

Asymmetric hydroesterification of styrene by PdCl₂–CuCl₂-chiral phosphine catalyst systems

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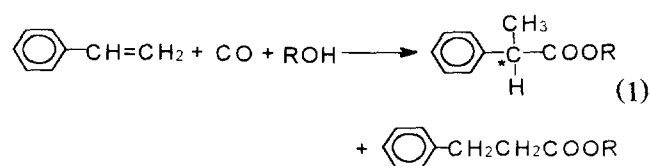
Received 26 February 1997; revised 2 April 1997

Abstract

Asymmetric induction up to 99.0% and good regioselectivities have been obtained in the hydroesterification of styrene with carbon monoxide and alcohol in the presence of PdCl₂–CuCl₂-chiral phosphines. © 1997 Elsevier Science S.A.

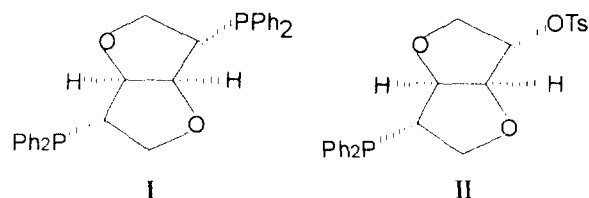
Keywords: Asymmetric; Hydroesterification; Styrene; PdCl₂–CuCl₂-chiral phosphine catalyst systems

Metal complex catalyzed hydroesterification and related hydrocarboxylation reactions of olefins are, together with hydroformylation, among the most extensively investigated reactions in homogeneous catalytic processes [1]. This methodology is of use in synthesis of linear fatty acid esters. Valuable representatives of branch-chain acids are 2-aryl propionic acids, which are the most important class of nonsteroidal antiinflammatory agents. A mild and regiospecific route to branch-chain acids was described in 1994 [2], using PdCl₂–CuCl₂–PPh₃ catalyst system.



While attempts have been made to achieve asymmetric hydroesterification and hydrocarboxylation, good enantioselectivity has yet to be realized [3–9]. In 1990, Alper et al. reported the synthesis of 2-aryl propionic 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 [10]. Recently, asymmetric induction up to 92.2% has been obtained by us using Pd(OAc)₂-chiral phosphine [11]. In this work we first reported the asym-

metric hydroesterification of styrene using the PdCl₂–CuCl₂-chiral phosphine catalyst systems under mild reaction conditions. The asymmetric hydroesterification reaction of styrene is shown as Eq. (1). Three kinds of ligands, 1,4:3,6-dianhydro-2,5-dideoxy-2,5-bis(diphenylphosphino)-L-iditol (I) [12], 1,4:3,6-dianhydro-2-O-(*p*-toluenesulfonyl)-5-(diphenylphosphino)-L-iditol (II) [13] and BINAP were used in the hydroesterification reaction. High optical purity and good regiochemical yields are obtained by using the biphosphine ligand I for PdCl₂–CuCl₂ catalyzed reaction. The results were listed in Table 1.



The nature of chiral phosphine ligands plays an important role in asymmetric hydroesterification, hydrogenation and hydroformylation reactions of olefins. The results in Table 1 show that ligand I is an effective chiral ligand for hydroesterification of styrene. The molecular structure of ligand I shows that this biphosphine is a bicycle compound with high rigidity and it contains four chiral carbon atoms whose configurations are all S. Highest optical yields and best regiochemical yields are obtained when the phosphorous/Pd is kept at

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Table 1
Asymmetric hydroesterification of styrene catalyzed by PdCl₂–CuCl₂–ligand I

Run No.	P/Pd mol/mol	Press. MPa	Conversion %	Yields of esters (%) ^a		<i>b</i> / <i>n</i>	Optical yield % ^b
				<i>b</i>	<i>n</i>		
1	4/1	5.0	59.4	51.3	8.1	6.3	99.2 (<i>S</i>)
2	3/1	5.0	~ 100	92.8	7.2	12.9	99.3 (<i>S</i>)
3	2/1	5.0	40.5	37.9	2.4	15.8	99.0 (<i>S</i>)
4	1/1	5.0	10.5	10.5	trace	—	75.0 (<i>S</i>)
5	3/1	4.0	58.7	52.2	6.5	8.0	99.0 (<i>S</i>)
6	3/1	6.0	99.4	94.0	5.4	17.4	97.0 (<i>S</i>)
7	3/1	7.0	84.7	78.9	5.8	13.6	99.0 (<i>S</i>)
8 ^c	3/1	5.0	96.7	93.2	3.5	26.6	99.1 (<i>S</i>)
9 ^d	3/1	5.0	99.2	99.2	trace	—	98.1 (<i>S</i>)

Reaction conditions: PdCl₂, 0.08 mmol; CuCl₂, 0.185 mmol; temperature, 80°C; time, 24 h; styrene, 0.5 ml; methanol, 0.5 ml; methyl ethyl ketone, 5.0 ml.

^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. Configuration was determined by the signs of optical rotation.

^c 1,2-Dimethoxyethane was used as solvent.

^d 1,4-Dioxane was used as solvent.

Table 2
Asymmetric hydroesterification of styrene catalyzed by PdCl₂–CuCl₂–chiral phosphine complexes

Ligands	P/Pd mol/mol	Press. MPa	Conversion %	Yields of esters (%) ^a		<i>b</i> / <i>n</i>	Optical yield % ^b
				<i>b</i>	<i>n</i>		
I	3/1	5.0	~ 100	92.8	7.2	12.9	99.3 (<i>S</i>)
II	3/1	5.0	~ 100	~ 100	trace	—	38.5 (—)
BINAP	3/1	5.0	14.9	3.6	11.3	0.3	—

Reaction conditions: PdCl₂, 0.08 mmol; CuCl₂, 0.185 mmol; temperature, 80°C; time, 24 h. styrene, 0.5 ml; methanol, 0.5 ml; methyl ethyl ketone 5.0 ml.

Notes ^a and ^b are the same as in Table 1.

3. (Run 2). The effect of carbon monoxide pressure on the optical yields is revealed by the results of Run 5–7. When the pressure of carbon monoxide is 6.0 MPa, the chemical yield of methyl 2-phenyl propionate is 94.0%, and the optical yield is 97.0%. When 1,2-dimethoxyethane and 1,4-dioxane are used as solvents, the optical yields are maintained almost unchanged (Run 8–9).

The other ligands, II and BINAP, are also investigated (see Table 2). When BINAP is used as ligand under the same reaction conditions, only methyl 2-phenyl propionate was obtained in very poor chemical yield. The highest regioselectivity, but lower enantioselectivity were obtained by using ligand II. It is believed that the reason of low enantioselectivity obtained by using ligand II is that ligand II is a monophosphine.

Acknowledgements

We are grateful to the Chinese National Natural Sciences Fund Council for supporting this research.

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