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ASYMMETRIC HYDROGENATION OF α-ACYLAMINOACRYLIC ACIDS AND ESTERS WITH AXIALLY DISSYMMETRIC BISAMINOPHOSPHINE-RHODIUM COMPLEXES

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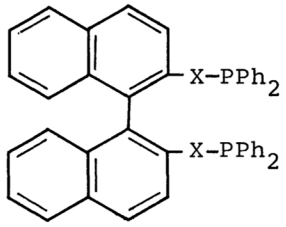
From easily resolved 2,2'-diamino-1,1'-binaphthyl were prepared axially dissymmetric bisphosphine ligands, (R)- and (S)-2,2'-bis-(diphenylphosphinamino)-1,1'-binaphthyl; the rhodium-catalyzed asymmetric hydrogenation of α-acylaminoacrylic acids and esters gave the corresponding amino acids of up to 95% optical purity.

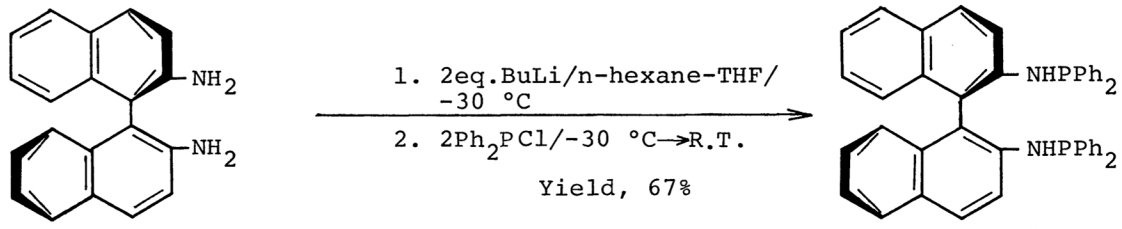
Axially dissymmetric 1,1'-binaphthyl moiety has proved to be a desirable asymmetry-inducing unit because of its structural rigidity and simplicity, resistance to racemization, and inter alia, effectiveness of chiral recognition.[1] There have been reported two chiral bisphosphine ligands, (S)-1a[2] and (S)-1b,[3] which contain the atropisomeric 1,1'-binaphthyl structure as the chiral element for use in the transition-metal catalyzed asymmetric reactions. However, tedious manipulations required for the preparation of these chiral phosphines impose some restrictions to their wide use.



1a; -X- = $-CH_2-$
1b; -X- = -O-
1c; -X- = -NH-

It has long been known that 2,2'-diamino-1,1'-binaphthyl can easily be resolved into its antipodes.[4] We wish to report here a facile preparation of third members of the atropisomeric binaphthylphosphines, (R)- and (S)-2,2'-bis(diphenylphosphinamino)-1,1'-binaphthyl ((R)- and (S)-1c)[5] (Scheme), and their utilization for the rhodium-catalyzed asymmetric hydrogenation of α-acylaminoacrylic acids and esters (Table).

In a typical run, the catalyst was formed by mixing a calculated amount of $[Rh(cyclooctene)_2Cl]_2$ with either of the aminophosphines in benzene under nitrogen, and then transferred into a hydrogenation vessel by syringe. Unless otherwise



(R)-2; $[\alpha]_D^{23}$ +157 (c 1.1, pyridine)

(R)-1c; $[\alpha]_D^{23}$ +27.2 (c 1.14,PhH)

Scheme.

Table. Asymmetric hydrogenation[a] of $\begin{matrix} R^1 \\ H \end{matrix}\!\!>\!C\!=\!C\!<\!\!\begin{matrix} NHCOR^2 \\ COOR^3 \end{matrix}$

R^1	R^2	R^3	Ligand	Solvent	O.P.(%)[b]	Config.
H	Me	H	(R)-1c	EtOH-PhH(2:1)	86	R
			(S)-1c	EtOH-PhH(2:1)	88	S
Ph	Me	H	(R)-1c	EtOH-PhH(2:1)	85	R
			(R)-1c	EtOH-PhH(2:1)[c]	29	R
			(R)-1c	MeOH-PhH(2:1)	89	R
			(R)-1c	i-PrOH-PhH(2:1)	15	R
			(R)-1c	PhMe-Me_2CO(1:1)[d]	7.0[e]	R
			(S)-1c	THF	8.7[f]	S
Ph	Ph	H	(R)-1c	EtOH-PhH(2:1)	95	R
			(R)-1c	EtOH-PhH(2:1)[c]	65	R
Ph	Me	Me	(R)-1c	MeOH-PhH(2:1)	69	R
Ph	Ph	Me	(R)-1c	MeOH-PhH(2:1)	89	R

a) Solvent = 12 - 15 ml; $P(H_2)$ = 30 atm; $[Rh(cyclooctene)_2Cl]_2 = 2.5 \times 10^{-5}$ mol; ligand = 5.5×10^{-5} mol; substrate = 5.0×10^{-3} mol; room temperature, 24 h. b) Calculated on the basis of reported values for the optically pure enantiomers, ref. 6) and 7); values for the (S)-1c were corrected for the 95% o.p. of the ligand. c) Et_3N was added (Et_3N/Rh molar ratio = 4 - 4.7). d) Solvent = 24 ml. e) - f) Conversion = 20% (e), 32% (f).

noted, the hydrogenation was completed under the reaction conditions specified in Table. It can be seen that these aminophosphines compare advantageously with precedent binaphthyl phosphines mentioned above in regard to the catalyst activity and efficiency in asymmetric induction. It should be noted that choice of the solvent (MeOH- or EtOH-PhH) is critical for attaining high optical yield, and addition of triethylamine to the (R)-1c-Rh catalyst system in EtOH-PhH gave reverse effect. The acrylic acids tended to give higher optical yields than the corresponding esters; this is sharp contrast to the results obtained by (S)-1b.[3]

References and Note

1. See, for example, R. Noyori, I. Tomino, and Y. Tanimoto, J. Am. Chem. Soc., 101, 3129 (1979).
2. K. Tamao, H. Yamamoto, H. Matsumoto, N. Miyake, T. Hayashi, and M. Kumada, Tetrahedron Lett., 1977, 1389.
3. R. H. Grubbs and R. A. DeVries, Tetrahedron Lett., 1977, 1879.
4. R. Kuhn and P. Goldfinger, Liebigs Ann. Chem., 470, 183 (1929).
5. (R)-1c: mp 150-151 °C (Cf. racemate; mp 163-165 °C). Found: C, 80.66; H, 5.19; N, 4.42. Calcd for $C_{44}H_{34}N_2P_2$: C, 80.96; H, 5.25; N, 4.29; P, 9.49. m/e 654 (M+2, 0.9), 653(M+1, 3.9), 652(M, 6.9), 466(M-Ph_2PH, 100).
(S)-1c: $[\alpha]_D^{23}$ -25.8 (c 0.776, PhH); mp 149-150 °C.
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7. H. B. Kagan and T.-P. Dang, J. Am. Chem. Soc., 94, 6429 (1972).

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