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ASYMMETRIC HYDROGENATION BY CHIRAL AMINOPHOSPHINE-PHOSPHINITE RHODIUM COMPLEXES

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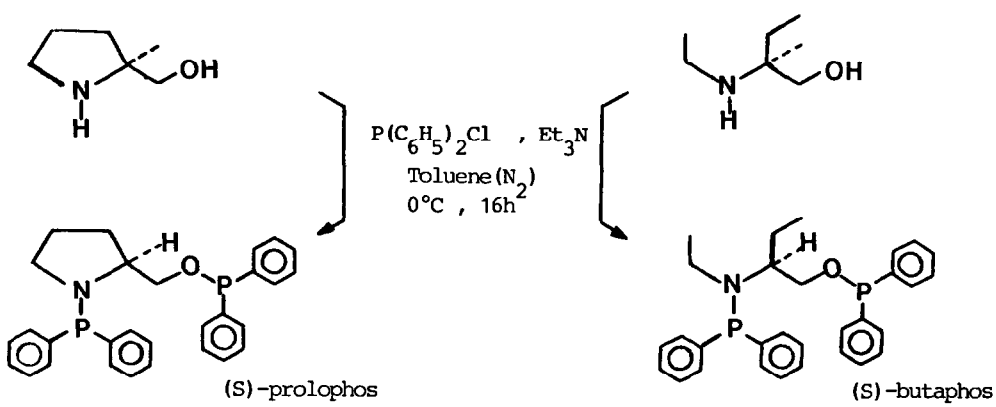
The ligands (S)-N-(diphenylphosphino)-2-diphenylphosphinoxymethylpyrrolidine,(S)-prolophos,and (S)-1-diphenylphosphinoxy-2-N-ethyl-N-diphenylphosphinoaminobutane,(S)-butaphos, have been prepared.The Rh(I) complexes of these phosphines act as efficient homogeneous hydrogenation catalysts at ambient temperature and pressure for α-N-acetaminoacrylic acid and itaconic acid.

Asymmetric reduction of prochiral substrates,mainly (Z) α-N-acylaminoacrylic acids,has assumed a steadily increasing interest during the last years,the best results being achieved with the Wilkinson's type catalyst,asymmetrically modified by means of P or C chiral tertiary mono or bidentate phosphines[1,2].In the class of the bidentate ligands,aminophosphines[3,4]and phosphinites[5]have proved to be efficient in asymmetric hydrogenation.We report here the first results concerning the asymmetric hydrogenation of some prochiral olefinic substrates catalyzed by Rh(I) bound to (S)-N-(diphenylphosphino)-2-diphenylphosphinoxymethylpyrrolidine,(S)-prolophos and (S)-1-diphenylphosphinoxy-2-N-ethyl-N-diphenylphosphinoaminobutane,(S)-butaphos.These ligands, whose starting material,(L)-2prolinol and α-N(ethyl)aminobutanol are cheap and easily available, are of interest because they can be synthesized in one step and in almost quantitative yield according to the scheme:



(S)-prolophos and (S)-butaphos are viscous transparent oils and have been identified by elemental analysis,MS,IR and 80 MHz ^{1}H and ^{31}P NMR spectroscopy; (S)-prolophos :$[\alpha]_D^{25}$ = - 15.4 (c = 1,$CHCl_3$) ; (S)-butaphos :$[\alpha]_D^{25}$ = - 3.0 (c = 1,$CHCl_3$).

The cationic Rh(I) complexes [Rh(COD)(S)-prolophos]ClO_4 and [Rh(COD)(S)-butaphos]ClO_4 are prepared according to the method of Schrock and Osborn [6] .All catalytic hydrogenations are carried out under ambient conditions in EtOH ; the working up of the reaction mixtures follows

the literature methods in order to avoid undue optical enrichment [7].

In table 1 are reported the results in asymmetric hydrogenation of α-N-acetaminocinnamic acid, α-N-acetaminoacrylic acid and itaconic acid.

TABLE 1

Catalyst	substrate	hydrogen absorbed %	optical yield(*)	absolute configuration
[Rh(COD)(S)-prolophos]ClO_4	$CH_2=C(NHCOCH_3)COOH$	95	80	S
" " " "	$C_6H_5CH=C(NHCOCH_3)COOH$	95	50	S
" " " "	$CH_2=C(COOH)CH_2COOH$	100	20	R
[Rh(COD)(S)-butaphos]ClO_4	$CH_2=C(NHCOCH_3)COOH$	95	55	S
" " " "	$C_6H_5CH=C(NHCOCH_3)COOH$	95	23	S
" " " "	$CH_2=C(COOH)CH_2COOH$	100	10	R

[Rh]= 1.2 mM ; T = 20°C ; $P(H_2)$ = 1 atm. (*) Optical yields are calculated with respect to the following values for the optically pure compounds: N-acetyl-(S)-alanine $[\alpha]_D$ = -66.2 (c 2, H_2O) N-acetyl-(S)-phenylalanine $[\alpha]_D$ = +46.0 (c 1, EtOH), ref. [7] ; (R)-methylsuccinic acid $[\alpha]_D$ = +16.9 (c 2.16, EtOH) , ref. [8] .

The $[Rh(S)\text{-prolophos}]^+$ gives better results than the $[Rh(S)\text{-butaphos}]^+$ complex. This is not unexpected and may confirm the role of a rigid backbone in dictating the conformation of the chelating ring and the chiral array of the phenyl groups of the phosphines. The absence of the fused five membered ring in the (S)-butaphos should give to the chelating ligand a higher conformational freedom, causing a lower otical yield of the products, even if the two ligands maintain the same trend in the stereodiscrimination of the prochiral substrates.

These aminophosphine-phosphinite ligands have given encouraging results, enhanced by their really easy availability. We are currently investigating the use of other asymmetric aminophosphine-phosphinite ligands and their effectiveness in asymmetric reactions other than hydrogenation.

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