Asymmetric Reduction of Carbon–Nitrogen, Carbon–Oxygen, and Carbon–Carbon Double Bonds by Homogeneous Catalytic Hydrogenation

By Arrigo Levi, Giorgio Modena, and Gianfranco Scorrano*

(*Centro CNR Meccanismi di Reazioni Organiche, Istituto di Chimica Organica, via Marzolo,* 1-35100 *Padova, Italy*)

Summary Asymmetric homogeneous hydrogenations of carbon–nitrogen, carbon–oxygen, and carbon–carbon double bonds have been achieved with the same $\mathrm{Rh^{I}}$–chiral diphosphine [(−)-diop] catalyst; all the products have the *R* configuration and a small increase in optical yields is obtained by changing the solvent from methanol to propan-2-ol.

We have recently reported[1] that $[\mathrm{Rh(nbd)L_2}]^+\mathrm{ClO_4}^-$ [nbd = norborna-2,5-diene, L = *R*-(+)-benzylmethylphenylphosphine] asymmetrically reduces, in ethanol, phenyl methyl ketone and butan-2-one to the corresponding *R* alcohols with low but significant stereospecificity ($p = 8{\cdot}6$ and 1·9, respectively).

We now report results obtained with a chiral diphosphine, [(2,2-dimethyl-1,3-dioxolan-4,5-diyl)bis(methylene)]bis-[diphenylphosphine] (diop) {m.p. 88—90°; $[\alpha]_{\mathrm{D}}^{25}$ − 12·3 (*c* 0·06, $\mathrm{C_6H_6}$)} as ligand. This ligand, which can be prepared easily from tartaric acid,[2] is effective in the asymmetric hydrogenation of carbon–carbon double bonds in a Wilkinson-type catalyst.[2]

$[\mathrm{Rh(nbd)(diop)}]^+\mathrm{ClO_4}^-$ (I) was prepared from [Rh(nbd)(acac)] and diop by a procedure similar to that described by Schrock and Osborn[3] for analogous compounds.

The complex (I) is an effective catalyst not only for the reduction of ketones and alkenes, but also for Schiff bases.

Table. Optical yields in the catalytic asymmetric hydrogenation of alkenes, ketones, and imines with $[\mathrm{Rh(nbd)(diop)}]^+\ \mathrm{ClO_4}^-$

Substrate	Solvent	$[\alpha]_{\mathrm{D}}$/deg.		Optical yield[a] (%)
PhMeC=N-$\mathrm{CH_2Ph}$	MeOH	+ 9·89	(*c* 0·42)[b]	17·6
	EtOH	+ 8·99	(*c* 0·171)[b]	16·0
	$\mathrm{Pr^iOH}$	+12·36	(*c* 0·176)[b]	22·0
PhMeC=O	MeOH	+ 1·68	(*c* 0·341)[c]	3·2
	EtOH	+ 1·56	(*c* 0·262)[c]	3·0
	$\mathrm{Pr^iOH}$	+ 4·26	(*c* 0·190)[c]	8·1
(*Z*)-PhHC=C-(NHAc)$\mathrm{CO_2H}$	MeOH	−40·5	(*c* 0·033)[b]	78
	EtOH	−43·6	(*c* 0·032)[b]	84
	$\mathrm{Pr^iOH}$	−44·1	(*c* 0·069)[b]	85

[a] Optical yields were calculated on the basis of literature values for the optically pure compounds; *N*-acetyl-(*R*)-phenylalanine; $[\alpha]_{\mathrm{D}}^{26}$ −51·8° (*c* 1, EtOH) (F. Knoop and J. G. Blanco, *Z. Phys. Chem.*, 1925, **146**, 272); (*S*)-1-phenylethanol, $[\alpha]_{\mathrm{D}}^{23}$ −52·5°, (*c* 2·27, $\mathrm{CH_2Cl_2}$) (U. Nagai, T. Shishido, R. Chiba, and H. Mitsuhashi, *Tetrahedron*, 1965, **21**, 1701); (*R*)-1-phenylethyl-*N*-benzylamine, $[\alpha]_{\mathrm{D}}^{20}$ + 56·2° (*c* 1·071, EtOH) (K. Parck, *J. Prakt. Chem.*, 1912, **86**, 287). [b] In EtOH. [c] In $\mathrm{CH_2Cl_2}$.

In a typical experiment a solution of *N*-(α-methylbenzylidene)benzylamine (1·5 g) in ethanol (5 ml), was added to the catalyst (0·1 g) in anhydrous ethanol (20 ml) at 30 °C under hydrogen (1 atmos). *N*-Benzyl-1-phenylethylamine is isolated in good yields (67—80%) after the absorption of the theoretical amount of hydrogen. The reaction is fairly slow (about a day to completion; the rates are not reproducible[1,4]) and strongly dependent on the age of the catalyst. Optical yields lower than those in the Table have been observed with aged catalysts.

A small increase in optical yields was observed in the cases studied by changing the solvent from methanol to propan-2-ol. This suggests that solvent is present in the co-ordination sphere of the rhodium in such a position to affect the geometry of the transition state.

Hydrogenation of carbon–nitrogen double bonds *via* homogeneous catalysis has been reported only in a few cases[5] and, to our knowledge, this is the first case where the behaviour of three typical double bonds toward reduction can be compared under the same set of conditions. Schiff bases, ketones, and alkenes are reduced to the *R* enantiomers. It is also noteworthy that the asymmetric hydroformylation of alkenes with similar catalysts[6] always yields the *R* enantiomer. The hydrogen, or CO and hydrogen, must enter the same prochiral face of the double bonds. The geometries of the activated complexes should be very similar for these four reactions and this finding may serve as a guide to a better understanding of the reaction mechanisms.

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