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Preliminary communication

ENANTIOSELECTIVE TRANSFER HYDROGENATION OF KETONES CATALYZED BY RHODIUM(I) COMPLEXES OF CHIRAL SCHIFF BASES

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Summary

The system formed in situ from $[RhEDCl]_2$ + PPEI* catalyses the asymmetric hydrogen transfer from propan-2-ol to some ketones and gives enantioselectivities of up to 23%.

Transfer hydrogenation from a donor to a prochiral ketone catalyzed by optically active complexes of transition metals provides a method for asymmetric synthesis of alcohols. Only a few examples of this reaction have been described, and all involve the use of iridium(I) [1,2] or ruthenium(II) [3,4] complexes as catalysts.

We describe here initial results obtained in the hydrogen transfer from propan-2-ol to various ketones using the system formed in situ from $[RhECDl]_2$ and (−)-2-pyridinalphenylethylimine (PPEI) as catalyst in the presence of small amounts of KOH as cocatalyst. The initially formed system needs an activation to give the catalytically active species; this can be carried out by air oxidation of the isopropanol solutions of $[RhEDCl]_2$ + PPEI, as in the case of the compound $[Ir(COD)PPEI]^+ClO_4^-$ [1], or by refluxing the solutions in an argon stream.

In Table 1 are shown the results obtained in the reduction of acetophenone. It will be seen that the system shows a good catalytic activity and a moderately good enantioselectivity.

The reaction rate increases with increase in the [KOH]/[Rh] ratio, and correspondingly the optical yield remains almost constant. Furthermore both the activity and the optical induction depend on the [PPEI]/[Rh] ratio, showing a maximum when the [PPEI]/[Rh] ratio is 10. The activation method also affects the rate and the selectivity; both are lowered in the case of thermal activation.

*ED = 1,5-hexadiene; PPEI = (—)-2-pyridinalphenylethylimine.

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TABLE 1

REDUCTION OF ACETOPHENONE WITH PROPAN-2-OL CATALYZED BY $[RhEDCl]_2$ [a] + (—)PPEI [b]

(Reaction conditions: [Rh] 3.2×10^{-4} *M*; [sub]/[Rh] = 500; solvent = propan-2-ol (250 ml); *T* 83°C.)

[KOH]/[Rh]	[PPEI]/[Rh]	Time (min)	Conversion (%)	Optical yield (%) [c] (configuration)
1.5	10	150	82	22 (*R*)
3	10	50	81	23 (*R*)
6	10	30	82	23 (*R*)
6 [d]	10	60	82	13 (*R*)
6	5	60	81	16 (*R*)
6	15	130	82	20 (*R*)

[a] Activation by oxidation. [b] Derived from condensation of pyridine-2-aldehyde and (*R*)(+)-1-phenylethylamine. [c] Optical yields are calculated from the specific rotation of pure enantiomer: 1-phenylethanol $[\alpha]_D^{25} = 44.2$ (neat) [5]. [d] Thermal activation.

The structure of the substrate employed has a significant influence on the rate and on the optical purity of the alcohol obtained. As can be seen from Table 2, increase in steric hindrance causes a decrease in the rate and in the enantiomeric excess.

TABLE 2

REDUCTION OF SOME PROCHIRAL KETONES WITH PROPAN-2-OL CATALYZED BY $[RhEDCl]_2$ [a] + (—)PPEI

(Reaction conditions: [Rh] 3.2×10^{-4} *M*; [KOH]/[Rh] 6; [PPEI]/[Rh] = 10; [sub]/[Rh] = 500; solvent = propan-2-ol (250 ml); *T* 83°C.)

Substrate	Time (min)	Conversion (%)	Optical yield (%) [b] (configuration)
$C_6H_5COCH_3$	30	82	23 (*R*)
$C_6H_5COCH_2CH_3$	75	79	20 (*R*)
$C_6H_5CO(CH_2)_2CH_3$	180	79	19 (*R*)
$C_6H_5COCH(CH_3)_2$	460	78	9 (*R*)

[a] Activation by oxidation. [b] Optical yields are calculated from the specific rotation of pure enantiomers: 1-phenylpropanol $[\alpha]_D^{22} = 28.1$ (neat) [6], 1-phenylbutanol $[\alpha]_{546}^{40} = 36.6$ (neat) [7], 2-methyl-1-phenyl-1-propanol $[\alpha]_D^{20} = 47.7$ (*c* 6.8 diethyl ether) [8].

The results indicate that it would be of interest to make a more detailed investigation involving variation of the nature of the hydrogen donor, the chelating ligand and the substrate with special attention being given to the α-(*N*,*N*-dialkylamino)alkyl aryl ketones [9].

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