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ASYMMETRIC REDUCTION OF KETONES WITH A CATIONIC CHIRAL PHOSPHINE RHODIUM COMPLEX CATALYST

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Methyl ethyl ketone, pinacoline and acetophenone are reduced asymmetrically to the corresponding alcohols with a chiral phosphine rhodium complex catalyst, $[Rh(NBD)\{(R)\text{-}PEtMePh\}_2]^+ PF_6^-$ (NBD = 2,5-norbornadiene).

Catalytic asymmetric reactions with chiral phosphine transition metal complexes have attracted special interests recently, and papers on asymmetric hydrogenation,[1] hydrosilylation[2] and hydroformylation[3] of olefins have been published so far. Very recently, Yamamoto et al.[4] reported the two-step pathway of asymmetric reduction of ketones, that is asymmetric hydrosilylation of ketones with chiral phosphine platinum complexes as catalysts, and then hydrolysis of the resultant alkyl silyl ethers to the alcohols. We wish to describe here the first example of asymmetric reduction of simple ketones with a homogeneous rhodium phosphine complex.

In 1970, Osborn et al.[5] briefly reported catalytic reduction of ketones with the cationic rhodium complexes, $[H_2RhP_2S_2]^+$ (P = phosphine, S = solvent). We synthesized $[Rh(NBD)\{(R)\text{-}PEtMePh\}_2]^+PF_6^-$ which is believed to be the precursor of $[H_2Rh\{(R)\text{-}PEtMePh\}_2S_2]^+$ as follows. To the suspension of 224 mg of $[Rh(NBD)Cl]_2$ and 253 mg of $AgPF_6$ in 3 ml of tetrahydrofuran was slowly added 0.35 ml of (R)-PEtMePh ($[\alpha]_D^{24}$ -4.98°, toluene, c = 9.36), and stirring was continued for thirty minutes. After filtration, tetrahydrofuran was added to the orange red filtrate until the total volume became 5 ml, which was used as catalyst solution.

Reduction of ketones was performed at 50°C under atmospheric hydrogen over a period of 3 days employing 5 ml of ketone, 0.5 ml of the catalyst

solution and 0.1 ml of water. Optical active alcohols produced were isolated by distillation. If necessary, the reaction mixture was treated with semicarbazide hydrochloride to remove unreacted ketone before distillation. Examples of the results are shown in Table I. Ketones are smoothly reduced under mild conditions by $[Rh(NBD)\{(R)\text{-}PEtMePh\}_2]^+PF_6^-$, and no side reactions take place. Though the stereochemical control by (R)-PEtMePh is not so effective as (R)-$P(CH_2Ph)MePh$ and (R)-$PMePhPr^n$ in the hydrosilylation method,[4] the result shows that one mole of the rhodium complex produces more than one mole of the chiral alcohol.

We are currently investigating the possibility of using other phosphines, and amines as optically active ligands.

Table I. Reduction of Ketones by $[Rh(NBD)\{(R)\text{-}PEtMePh\}_2]^+PF_6^-$

Ketone	Yield (%)	$[\alpha]_D$ [a]	Configuration	Optical purity (%)
Methyl ethyl ketone	80	+0.082°	S	0.59[b]
Pinacoline	41	+0.054°	S	0.69[c]
Acetophenone	77	+0.106°	R	0.24[d]

a) The optical rotation of the alcohol was measured neat. b) Maximum rotation, $[\alpha]_D^{20}$ +13.83° (ref. 6). c) Maximum rotation, $[\alpha]_D^{20}$ +7.71° (ref. 7). d) Maximum rotation, $[\alpha]_D$ +43.6° (ref. 8).

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