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ASYMMETRIC HYDROGENATION OF SILYL ENOL ETHERS. AN ALTERNATIVE ROUTE TO OPTICALLY ACTIVE ALCOHOLS

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Asymmetric synthesis of alcohols has been achieved via hydrogenation of silyl enol ethers catalyzed by rhodium complexes with a variety of optically active phosphine ligands.

Silyl enol ethers have been recongnized to have elegant and broad utility in organic syntheses.$^{1)}$ However, little attention has been paid to the reactions of silyl enol ethers with transition metal complexes. On the other hand, asymmetric syntheses catalyzed by chiral phosphine-transition metal complexes have attracted special interests recently. The authors have reported the asymmetric hydroformylation$^{2)}$ and reduction of simple ketones.$^{3)}$ In this communication, we wish to describe an asymmetric reduction of ketones via hydrogenation of silyl enol ethers.

A typical reaction procedure is as follows. To a benzene solution (10 ml) of $[Rh(1,5\text{-hexadiene})Cl]_2$ (33 mg, 7.5×10^{-5} mol) and (-)-2,3-O-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane ((-)-diop, 75 mg, 1.5×10^{-4} mol) was added 2-(1-trimethylsiloxyvinyl)naphthalene (3 ml), and the reaction solution was agitated at 30°C under hydrogen of atmospheric pressure over a period of 24 hr. Distillation of the reaction mixture gave 1-(2-naphthyl)ethyl trimethylsilyl ether, b.p. 102 - 104°C/0.7 mmHg, $[\alpha]_D$ + 2.78° (neat), which was then transformed into 1-(2-naphthyl)ethanol (1), m.p. 73.9 - 75.1°C, $[\alpha]_D$ + 3.99° (chloroform, c = 6.16), by hydrolysis with 1N-HCl. This optical rotation indicates a 7.2% optical purity for (1). The results of hydrogenation of

$$\mathrm{R(Me_3SiO)C{=}CH_2 + H_2 \longrightarrow R(Me_3SiO)\overset{*}{C}HCH_3 \xrightarrow{H^+} R\overset{*}{C}H(OH)CH_3}$$

(R = 2-Naph, Ph, and $\mathrm{Bu^t}$)

other silyl enol ethers catalyzed by the (-)-diop-rhodium complex are summarized in Table 1. Hydrogenation of the enol ethers proceeds smoothly and the optical yield is comparable with or better than that achieved by the other methods developed so far.[3,4] 2-(1-Trimethylsiloxyvinyl)naphthalene and α-trimethylsiloxystyrene gave (R)-alcohols in enantiomeric excess, while 2-trimethylsiloxy-3,3-dimethyl-1-butene gave (S)-alcohol. These results seem to indicate the difference of the mode of the stereochemical control in aromatic and aliphatic silyl enol ethers. Analogous difference in the enantioselectivity is also noted in the reduction of simple ketones.[3)]

Table 1. Asymmetric Hydrogenation of Silyl Enol Ethers Catalyzed by the (-)-Diop-Rhodium Complex at 30°C for 24 hr

Silyl enol ether	Silyl ether $[\alpha]_D$ (neat)	Yield (%)	Alcohol $[\alpha]_D$ (neat)	Configuration	Optical Yield (%)
$\mathrm{2\text{-}Naph\text{-}\underset{\mathrm{OSiMe_3}}{\underset{\mid}{C}}{=}CH_2}$	+2.78	83	+3.99	R	7.2[a)]
$\mathrm{Ph\text{-}\underset{\mathrm{OSiMe_3}}{\underset{\mid}{C}}{=}CH_2}$	+4.09	82	+2.82[b)]	R	6.5[c)]
$\mathrm{Bu^t\text{-}\underset{\mathrm{OSiMe_3}}{\underset{\mid}{C}}{=}CH_2}$ [d)]	+1.63	100	+0.58	S	7.5[e)]

a) In chloroform, c = 6.16, maximum rotation; $[\alpha]_D$ + 55.8° (ref. 5).

b) Calculated according to the result noted in the ref. 4.

c) Maximum rotation; $[\alpha]_D$ + 43.6° (ref.6).

d) Heated at 60°C for 8 days.

e) Maximum rotation; $[\alpha]_D$ + 7.71° (ref.7).

Hydrogenation of α-trimethylsiloxystyrene has been examined with a variety of optically active phosphine-rhodium complexes, and the results are shown in Table 2. In general, it is expected that the nearer the chiral center is to the reaction center, the more effective stereochemical control will be achieved, and therefore P-chiral (chiral center on phosphorus) phosphines are believed to be more effective than C-chiral (chiral center on carbon) ones. However in the hydrogenation of α-trimethylsiloxystyrene, the optical yield of 1-phenylethyl trimethylsilyl ether was not so high in the case of every P-chiral phosphine, while neo-menthyldiphenylphosphine (nmdpp) gave a better result though it is a non-chelating C-chiral phosphine. Of all phosphines examined, (-)-diop gave the best results, which may be attributable to the rigidity of the conformation of the diastereomeric intermediate brought about by the chelation of (-)-diop to rhodium. In order to improve the optical yield, the reaction at 0°C was examined using (-)-diop as a chiral ligand, however the result was unexpectedly poorer than that at 30°C.

Further developments are now in progress, and the results will be published in the near future.

Table 2. Asymmetric Hydrogenation of α-Trimethylsiloxystyrene Catalyzed by Various Chiral Phosphine-Rhodium Complexes at 30°C [a]

Phosphine	Reaction time (hr)	Yield (%)	Silyl ether $[\alpha]_D$ (neat)	Configuration	Optical Yield[b] (%)
(R)-PEtMePh	24	100	-0.72	S	1.1
(R)-PEtMePh[c]	24	100	-0.70	S	1.1
(R)-$P(CH_2Ph)MePh$	24	74	-0.59	S	1.2
(R)-$PMePhPr^n$	24	100	-0.61	S	1.3
Nmdpp	120	91	-2.33	S	3.7
(-)-Diop	24	82	+4.09	R	6.5
(-)-Diop[d]	168	94	+2.93	R	4.6

a) $[Rh(1,5\text{-hexadiene})Cl]_2$ 33mg, phosphine : Rh = 2.

b) Optical yield was calibrated for the optical purities of the phosphines in the case of (R)-$P(CH_2Ph)MePh$ (76.6%) and (R)-$PMePhPr^n$ (85.6%).

c) Phosphine : Rh = 3

d) The reaction at 0°C.

REFERENCES

1) YU. L. Baukov and I.F.Lutsenko, Organometal. Chem. Rev. A, 6, 355 (1970).

2) M.Tanaka, Y. Watanabe, T. Mitsudo, and Y. Takegami, Chem. Lett., 483 (1972).

3) M. Tanaka, Y. Watanabe, T. Mitsudo, H. Iwane, and Y. Takegami, ibid., 239 (1973). An analogous report has been independently published; P. Bonvinici, A. Levi, G. Modena, and G. Scorrano, Chem. Commun., 1188 (1972).

4) K. Yamamoto, Y. Hayashi, and M. Kumaka, J. Organometal. Chem., 54, C45 (1973).

5) T. A. Collyer and J. Kenjon, J. Chem. Soc., 676 (1940).

6) E. L. Eliel, J. Amer. Chem. Soc., 71, 3970 (1949).

7) R. H. Pickard and J. Kenjon, J. Chem. Soc., 105, 1115 (1914).

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