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ASYMMETRIC OXIDATION OF OLEFINS WITH OSMIUM TETROXIDE COORDINATED BY CHIRAL DIAMINES DERIVED FROM L-TARTARIC ACID

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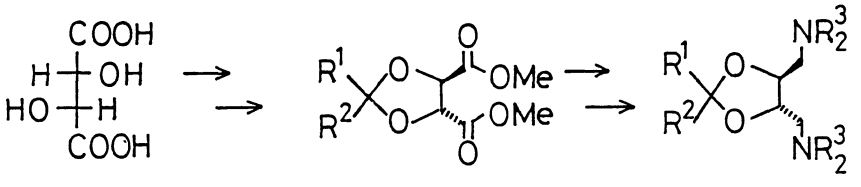
The enantioselective oxidation of olefins with OsO_4 coordinated by chiral diamines derived from L-tartaric acid is described. Phenylketene dimethylacetal and *trans*-stilbene are converted to (R)-methyl mandelate and (1R,2R)-1,2-diphenyl-1,2-ethanediol with moderate and high enantioselectivity, respectively.

Enantioselective oxidation of carbon-carbon double bonds into the corresponding diols or epoxides is one of the most efficient methods for the synthesis of various classes of polyoxygenated natural products such as macrolides and carbohydrates,[1] because this method offers the opportunity to generate two chiral centers with a single reaction. In addition to the effective asymmetric epoxidation of allylic alcohols reported by Katsuki and Sharpless,[2] it has been further desired to develop the enantioselective oxidation of simple olefins.[3]

Among various oxidizing agents, it is known that osmium tetroxide is a reliable reagent for the stereospecific conversion of olefins to the corresponding *cis*-diols. Further, it is reported that tertiary amines or pyridine forms a tight complex with OsO_4[4] and accelerates the oxidation of olefins.[5] It was shown from our laboratory that the chiral diamines derived from L-proline are quite effective ligands for various asymmetric reactions.[6] So it was expected that an enantioselective oxidation of simple olefins would be possible by the combination of OsO_4 with the chiral diamines.

In this communication, we wish to describe the enantioselective oxidation of several substituted olefins with OsO_4 coordinated by chiral diamines. In the first place, we tried the oxidation of *trans*-stilbene using chiral diamine 1, derived from L-proline, as a ligand. Contrary to our expectation, the enantiomeric excess of the produced diol was not so high (Table 1 - entry 1). Then we screened several chiral diamines derived from L-tartaric acid in detail, because the optically pure L-tartaric acid is readily available and has C_2 symmetry which is often used effectively in the enantioselection.[7] Various types of ligands were synthesized from L-tartaric acid in four steps as sketched below.



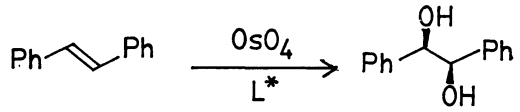
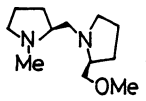
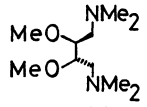
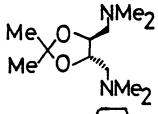
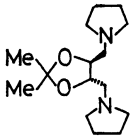
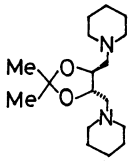
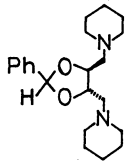
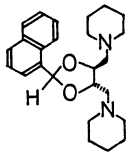


Table 1. Examination of chiral diamines[a)]

Entry	Ligand	Temperature/°C	Yield/%	e.e./%[b)]
1	 1	-78	56	35
2	 2[8)]	-78	quant.	34
3	 3	-78	84	58
4	 4	-78	87	65
5	 5	-78	79	70
6	 6[9)]	-78	76	78
7		-100	61	81
8	 7[10)]	-78	76	78
9		-100	71	90

a) The reaction was carried out in CH_2Cl_2.
b) The enantiomer excess was determined by optical rotation comparison. Ref.11, $[\alpha]_D^{21}$ +91.0°(c 1.1, EtOH).

The results of the oxidation of *trans*-stilbene with OsO_4 and chiral diamines are briefly summarized as follows: a) The chiral diamine in which NR_2^3 is a piperidino group gives better results than that having dimethylamino or pyrrolidino group (entries 3,4,5). b) The bulkiness of R^1 has much influence on the enantioselection. When the diamine which has benzylidene group (R^1=Ph, R^2=H) was employed as a ligand, the oxidation of *trans*-stilbene proceeded in higher e.e. than when diamine 5 (acetonide) was employed. Further, the diamine having more bulky α-naphthyl group as R^1 was found to be the most effective ligand (entry 8), and the oxidation of *trans*-stilbene with OsO_4 and ligand 7 at -100 °C achieved the excellent e.e. (90% e.e.).

In the next place, we tried the application of this reaction system to other olefinic compounds (Table 2). The examination of the oxidation of various olefinic compounds under the above reaction conditions indicates that the oxidation of olefins substituted with phenyl group generally proceeds in higher enantiomeric excess. Among them, the silylketene acetals derived from phenylacetic acid are converted to (R)-mandelate in good enantioselectivity (entries 2,3). Phenylketene dimethylacetal is also oxidized to (R)-methyl mandelate in 66% e.e. (entry 4). These reaction processes are equivalent to the asymmetric α-hydroxylation of esters, and are therefore expected to have a wide applicability as a synthetic tool.

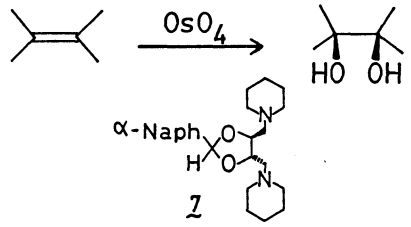


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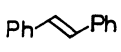
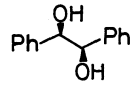
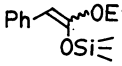
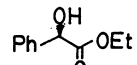
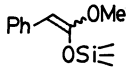
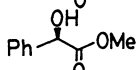
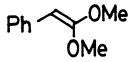
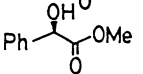
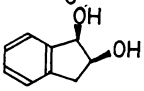
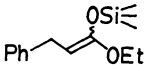
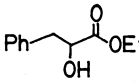
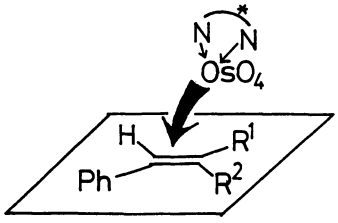
Table 2. Oxidation of various olefins[a)]

Entry	Olefin	Temp /°C	Product[b)]	Yield/%	e.e./%[c)]	Abs.config.
1		-100		71	90[f)]	(1R,2R)
2	 d)	-78		47	60[g)]	(R)
3	 e)	-100		45	55[h)]	(R)
4		-100		95	66[h)]	(R)
5		-78		77	35[i)]	(1R,2S)
6		-78		42	0	

a) The reaction was carried out in CH_2Cl_2.
b) All the products gave satisfactory ^{1}H-NMR and IR spectra.
c) The enantiomer excess was determined by optical rotation comparison.
d) E-Z mixture. Isomer ratio (Z:E) is 2:1.
e) E-Z mixture. Isomer ratio (Z:E) is 3:1.
f) $[\alpha]_D^{19}$ +82.0°(c 0.84,EtOH); Ref.11, (1R,2R)-form $[\alpha]_D^{21}$ +91.0°(c 1.1,EtOH).
g) $[\alpha]_D^{19}$ -61.1°(c 1.0,EtOH); Ref.12, (R)-form $[\alpha]_D^{24}$ -104°(EtOH).
h) $[\alpha]_D^{25}$ -88.0°(c 2.1,EtOH); Ref.13, (S)-form $[\alpha]_D^{26}$ +134.0°(c 1.03,EtOH).
i) $[\alpha]_D^{23}$ +17.7°(c 1.35,$CHCl_3$); Ref.14, (1S,2R)-form $[\alpha]_D^{25}$ -51.0°(c 0.40,$CHCl_3$).

Although detailed considerations on the transition state are not yet clear, the stereochemistry of all the products indicates that OsO_4 coordinated with chiral diamine 7 approaches the carbon-carbon double bond from the pro-R face of the plane consisting of PhCH=C group as shown in the figure.



A typical experimental procedure is described for the oxidation of *trans*-stilbene: To a CH_2Cl_2 solution (6 ml) of OsO_4 (177 mg, 0.69 mmol) was added a CH_2Cl_2 solution (6 ml) of chiral diamine 7 (340 mg, 0.86 mmol) at -78 °C under an argon atmosphere. The color of the solution turned to reddish brown. After being stirred for 1 h at that temperature, the reaction mixture was cooled to -100 °C with a liquid nitrogen-methanol bath. At this temperature, a CH_2Cl_2 solution (6 ml) of *trans*-stilbene (100 mg, 0.55 mmol) was added. After being stirred for 6 h, the reaction mixture was diluted with methanol and the reaction was immediately quenched with bubbling of H_2S. Removal of the resulting black precipitate was followed by the evaporation of the solvent. The product was purified by thin layer chromatography on silica gel (Et_2O-hexane) to yield 1,2-diphenyl-1,2-ethanediol (84 mg, 71% yield) as a white crystal. $[\alpha]_D^{19}$ +82.0° (c 0.84, EtOH).

Thus, chiral diamines 6 and 7, derived from L-tartaric acid, with OsO_4 realized the effective asymmetric oxidation. According to this procedure, (R)-methyl mandelate and (1R,2R)-1,2-diphenyl-1,2-ethanediol are prepared from phenylketene dimethylacetal and *trans*-stilbene with moderate and high enantioselectivity, respectively.

The authors are grateful to Professor Teruaki Mukaiyama for valuable discussion during this work.

References

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3) The oxidation of simple olefins was carried out by the use of OsO_4 and chiral ligands derived from dihydroquinine, and the high e.e. was achieved up to 89.7% e.e. in the oxidation of *trans*-stilbene. S. G. Hentges and K. B. Sharpless, J. Am. Chem. Soc., 102, 4263 (1980).
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9) 6: NMR($CDCl_3$) δ 1.3-1.8 (12H, m), 2.2-2.8 (12H, m), 3.9-4.1 (2H, m), 5.9 (1H, s), 7.2-7.6 (5H, m). IR (neat) 2940, 1460, 1300 cm^{-1}. $[\alpha]_D^{24}$ -12.8°(c 3.0, CH_2Cl_2).
10) 7: NMR($CDCl_3$) δ 1.0-1.7 (12H, m), 2.1-2.8(12H, m), 3.8-4.2 (2H, m), 6.4 (1H, s), 7.1-8.4 (7H, m). IR(neat) 2940, 1450, 1340 cm^{-1}. $[\alpha]_D^{24}$ +12.8°(c 1.14, CH_2Cl_2).
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