# Electrochemical Os-Catalyzed Asymmetric Dihydroxylation of Olefins with Sharpless' Ligand

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(Received January 13, 1995)

Asymmetric dihydroxylation of olefins using Sharpless' ligand in the presence of potassium osmate [$K_2OsO_2(OH)_4$] has been attained by recycling use of a catalytic amount of potassium ferricyanide [$K_3Fe(CN)_6$] in electrolysis media. The prominent advantage of the electrooxidation method is that minimum use of reoxidizing agent as well as $K_2OsO_2(OH)_4$ may cause to improve enantioselectivities in comparison with the case of stoichiometric oxidant systems.

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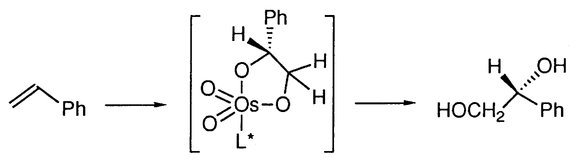
Notable success of chiral ligands[1] for Os-catalyzed asymmetric dihydroxylation of olefins[2] stimulates further development as an electrochemical process, which could be encountered: (1) minimum use of co-oxidant [$K_3Fe(CN)_6$] for potassium osmate[2e-o,3]; (2) decrease of the amount of $K_2OsO_2(OH)_4$,[2e-o] (3) possible choice of other co-oxidants in place of $K_3Fe(CN)_6$. This paper especially communicates the above two beginning items together with use of other co-oxidants. Recently, the effective chiral ligands for enantioselective dihydroxylation of olefins have intensively been investigated.[2-9] Among the reported asymmetric dihydroxylation systems, the superiority of a $H_2O$/*t*-BuOH-$K_3Fe(CN)_6$/$K_2CO_3$ system with chiral ligands, *i.e.*, dihydroquinidine (DHQD) and/or dihydroquinine (DHQ) derivatives, has been mentioned.[2e-o] We wish now to communicate the electrochemical Os-catalyzed asymmetric dihyroxylation of olefins with Sharpless' ligands.

As shown in Table 1, the reconfirmative attempt for Sharpless' chiral diol synthesis on styrene was fully successful by obtaining 97.2% ee in 88% conversion yield (Scheme 1).[2g] Our initial efforts were focused on the chiral Os-complex assisted electrosynthesis to examine mediator activity by employing 0.3 equivalent (10 weight %) of potassium ferricyanide as a co-oxidant. Happily enough, we could obtain the desired diol 3 in very high values both on % ee and conversion yield (Table1, Run A), clearly demonstrating that the chiral induction system together with the co-oxidant does work under the employed electrolysis conditions. Further reducing the amount of the co-oxidant [$K_3Fe(CN)_6$] to 0.1 equivalent did not give any change on the asymmetric induction as well as the conversion yields (Table 1, Run B). Under a similar electrolysis conditions, small change in the yields has been found when the amount of the co-oxidant was diminished to 0.05 mmol. We obtained the diol 3 in 95.3% ee and 82% conversion yield. It is worthy to note that both potassium chloride and potassium bromide are also effective as co-oxidants in the absence of $K_3Fe(CN)_6$. The electrolysis systems of $K_2OsO_2(OH)_4$/KCl and/or $K_2OsO_2(OH)_4$/KBr afforded ca. 92 ~ 93% ee at room temperature in spite of their inferior conversion yields (ca. 48 ~ 65%).

Next attempt was to clarify the limitation of reducing the amount of potassium osmate in the electrolytic recycling system. The result obtained by use of one-fourth amount of the Os-catalyst (Table 1, Run C) demonstrates that asymmetric dihydroxylation of styrene proceeded still in high yield of enantiomeric excess (ca. 99% ee). However, the decrease of the conversion yield down to 72% should be improved. It is likely that the efficient formation of chiral osmate ester 2 [2f] in an electrolytic bulk solution may reflect high values of enantiomeric excess in every electrolysis conditions (Runs A, B, and C). Enantiomeric excesses obtained in the electrolytic asymmetric dihydroxylation of various olefins under the typical experimental



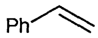
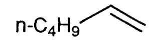
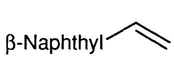
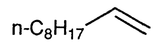
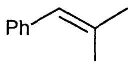
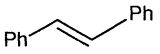
Scheme 1.

**Table 1.** Chiral Os-complex assisted electrosynthesis of chiral diol from styrene

| Conditions | Reexam. Sharpless' conditions[a] | Electrolysis run A | B | C |
|---|---|---|---|---|
| Styrene [b] | 1 | 1 | 1 | 1 |
| *t*-BuOH [c] | 5 | 5 | 5 | 5 |
| $H_2O$ [c] | 5 | 5 | 5 | 5 |
| $K_2CO_3$ [b] | 3 | 3 | 3 | 3 |
| $(DHQD)_2PHAL$ [b] | 0.01 | 0.01 | 0.01 | 0.01 |
| $K_3Fe(CN)_6$ [b] | 3 | 0.3 | 0.1 | 0.1 |
| $K_2OsO_2(OH)_4$ [b] | 0.002 | 0.002 | 0.002 | 0.0005 |
| Electricity (F/mol) | - | 2.33 | 2.33 | 2.33 |
| Time (h) | | 31.2 | 31.2 | 31.2 |
| Temp (°C) | 0 | 0 | 0 | 0 |
| Conv. Yield, (%) | 88 | 95 | 95 | 72 |
| % ee [c] | 97.2 | 97.2 | 97.3 | 99.0 |
| $[\alpha]_D^{25}$ [d] | -62.1 | -62.3 | -63.4 | -63.4 |
| ($CHCl_3$) | (c 2.63) | (c 1.78) | (c 2.48) | (c 1.87) |

[a]Ref. 2g; [b]mmol; [c]mL; [d]Percent ee determined by HPLC with CHIRALCEL OB-H (Daicel); [e]Reported value: $[\alpha]_D^{25}$ -63.7 ( c 5.45, $CHCl_3$ )[10]

**Table 2.** Chiral Os-complex assisted electrosynthesis of chiral diols[a]

| Olefin | Conv. Yield, % | Ee, %[b] | Config. | Obs[α] D |
|---|---|---|---|---|
|  | 95 | 97.3 | R(−) | -63.4 [d] |
|  | 71.2 | 84.1 | R(+) | +14.1 [e] |
|  | 75 | 86.4 | R(−) | -29.1 [f] |
| | 87.0 [c] | 86.3 | R(−) | -29.1 [f] |
|  | 69<br>(93, GC) | 91.8 | R(+) | +10.9 [g] |
|  | 92.8 | 90.3 | R(−) | -13.1 [f] |
|  | 97.0 | 100 | RR(+) | +91.0 [i] |

[a]Carried out at 0 °C; [b]Percent ee determined by HPLC with CHIRALCEL OB-H (Daicel) ; [c]Obtained by the reaction at room temp; [d]Reported value: -63.7 [10]; [e]Reported value: +16.81 [6]; [f]Reported value: -33.7 [11]; [g]Reported value: -11.9 (antipode) [12]; [h]Reported value: -11.3 [2e]; [i]Reported value: +91.0 [13].

conditions are summarized in Table 2. The relatively better % ee and conversion yield are obtained in respects to the figures reported in the literatures.[2e, 10-13]

Typical procedure of electrochemical Os-catalyzed asymmetric dihydroxylation of styrene: To a stirred solution of *t*-butyl alcohol (5 mL), water (5 mL), $K_3Fe(CN)_6$ (32 mg, 0.1 mmol), $K_2CO_3$(410 mg, 3.0 mmol), $(DHQD)_2PHAL$[14] (7.8 mg, 0.01 mmol), and $K_2OsO_2(OH)_4$ (0.74 mg, 0.002 mmol) in an undivided cell equipped with two Pt-electrodes was added styrene (1 mmol) at once. The mixture was electrolyzed under a constant current of 2 mA/cm$^2$ under vigorous stirring (applied voltage: 1.0~3.0 V). After passage of 2.33 F/mol of electricity for ca. 31 h (monitored by TLC and GLC), the mixture was treated with a saturated sodium thiosulfate solution under stirring for 30~60 min. Usual workup followed by column chromatography gave (-)-(R)-1-phenyl-1,2-ethanediol (131.1 mg, 95%), $[\alpha]_D^{25} = -63.38$ (c 2.482, $CHCl_3$). The enantiomeric excess of the (R)-diol was determined by HPLC analysis (Chiralcel OB-H, Daicel) to be 97.3%.

The present work was supported by The Grant-in-Aid for Scientific Research Nos. 05235107 and 05403025 from the Ministry of Education, Science and Culture. We are grateful to the 500 MHz SC-NMR laboratory of Okayama University for experiments.

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14 $(DHQD)_2PHAL$: dihydroquinidine phthalazine, see Ref. 2k.