Chemical and Electrochemical Asymmetric Dihydroxylation of Olefins in $I_2-K_2CO_3-K_2OsO_2(OH)_4$ and $I_2-K_3PO_4/K_2HPO_4-K_2OsO_2(OH)_4$ Systems with Sharpless' Ligand

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Iodine-assisted chemical and electrochemical asymmetric dihydroxylation of various olefins in $I_2-K_2CO_3-K_2OsO_2(OH)_4$ and $I_2-K_3PO_4/K_2HPO_4-K_2OsO_2(OH)_4$ systems with Sharpless' ligand provided the optically active glycols in excellent isolated yields and high enantiomeric excesses. Iodine (I_2) was used stoichiometrically for the chemical dihydroxylation, and good results were obtained with nonconjugated olefins in contrast to the case of potassium ferricyanide as a co-oxidant. The potentiality of I_2 as a co-oxidant under stoichiometric conditions has been proven to be effective as an oxidizing mediator in electrolysis systems. Iodine-assisted asymmetric electro-dihydroxylation of olefins in either a *t*-BuOH/H_2O(1/1)−K_2CO_3/(DHQD)$_2$PHAL−(Pt) or *t*-BuOH/H_2O(1/1)−K_3PO_4/K_2HPO_4/(DHQD)$_2$PHAL−(Pt) system in the presence of potassium osmate in an undivided cell was investigated in detail. Irrespective of the substitution pattern, all the olefins afforded the diols in high yields and excellent enantiomeric excesses. A plausible mechanism is discussed on the basis of cyclic voltammograms as well as experimental observations.

Introduction

Asymmetric induction has been frequently used in syntheses of optically active natural products and biologically active compounds since the asymmetric centers present in these compounds may be provided by chiral transfer to readily available prochiral moieties.[1] The synthetic strategy is mostly left to the imagination of chemists and not restricted by the availability of certain starting materials. Among the most prominent examples of asymmetric reactions, the "Sharpless process" for the asymmetric dihydroxylation of olefinic compounds is widely recognized in recent years.[2] Our efforts in this field have led to the establishment of chemical and electrocatalytic asymmetric dihydroxylation of olefins featured by (1) novel co-oxidant systems for conjugated olefins as well as nonconjugated terminal olefins, (2) the use of less amount of the co-oxidant, and (3) performing the electrolysis in an undivided cell.

Criegee's pioneering work[3] showed that osmium tetraoxide in a stoichiometric amount could be used for effective *cis*-dihydroxylation of olefins and that this method is more reliable than other diol syntheses despite its high cost and toxicity. Catalytic hydroxylation[4] emerged in the field due to the growing economical requirement. Inorganic co-oxidants such as sodium or potassium chlorate[5a] and hydrogen peroxide[5b] were the first to be introduced, but in some cases these reagents led to diminished yields of diols due to overoxidation. Subsequently, some organic co-oxidants such as alkaline *tert*-butyl hydroperoxide[6] and *N*-ethylmorpholine *N*-oxide[7] were introduced, which afforded comparatively better results. Recently, potassium ferricyanide in combination with potassium carbonate has been demonstrated to be a powerful system for osmium-catalyzed asymmetric dihydroxylation of olefins.[8−10] The effective chiral ligands for enantioselective dioxyosmylation of olefins have been investigated in detail.[11] Among the reported asymmetric dihydroxylation systems, an H_2O/*t*-BuOH−$K_3Fe(CN)_6$/

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(1) For a review, see: (a) *Asymmetric Catalysis in Organic Synthesis*; Noyori, R.; Wiley-Interscience Publications: New York, 1993. (b) *Catalytic Asymmetric Synthesis*; Ojima, I., Ed.; VCH Publications: New York, 1993. (c) Berrisford, D. J.; Bolm, C.; Sharpless, K. B. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1059.

(2) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483.

(3) (a) Criegee, R. *Justus Liebigs Ann. Chem.* **1936**, *522*, 75. (b) Criegee, R. *Angew. Chem.* **1937**, *50*, 153. (c) Criegee, R. *Angew. Chem.* **1938**, *51*, 519. (d) Criegee, R.; Marchand, B.; Wannowis, H. *Justus Liebigs Ann. Chem.* **1942**, *550*, 99.

(4) Schroder, M. *Chem. Rev.* **1980**, *80*, 187.

(5) (a) Hofmann, K. A. *Chem. Ber.* **1912**, *45*, 3329. (b) Milas, N. A.; Trepagnier, J. H.; Nolan, J. T., Jr.; Iliopulos, M. I. *J. Am. Chem. Soc.* **1959**, *81*, 4730.

(6) Sharpless, K. B.; Akashi, K. *J. Am. Chem. Soc.* **1976**, *98*, 1986.

(7) (a) Schneider, W. P.; McIntosh, A. V. U.S. Patent 2,769,824, Nov 6, 1956; *Chem. Abstr.* **1956**, *51*, 8822e. (b) Van Rheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973.

(8) Minato, M.; Yamamoto, K.; Tsuji, J. *J. Org. Chem.* **1990**, *55*, 766.

(9) (a) Gao, Y.; Charles, M. Z. U.S. Patent 5,302,257, Apr 12, 1994; *Chem. Abstr.* **1994**, *120*, 119437j. (b) Amundsen, A. R.; Balko, E. N. *J. Appl. Electrochem.* **1992**, *22*, 810.

(10) Torii, S.; Liu, P.; Tanaka, H. *Chem. Lett.* **1995**, 319.

(11) (a) Hentges, S. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102*, 4263. (b) Sharpless, K. B.; Amberg, W.; Beller, M.; Chen, H.; Harturg, J.; Kawanami, Y.; Lübben, D.; Manoung, E.; Ogino, Y.; Shibata, T.; Ukita, T. *J. Org. Chem.* **1991**, *56*, 4585. (c) Sharpless, K. B.; Amberg, W.; Bennani, Y. L.; Crispino, G. A.; Hartung, J.; Jeong, K.-S.; Kwong, H.-L.; Morikawa, K.; Wang, Z.-M.; Xu, D.; Zhang, X.-L. *J. Org. Chem.* **1992**, *57*, 2768. (d) Andersson, P. G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1993**, *115*, 7047. (e) Wang, S.-M.; Kakiuchi, K.; Sharpless, K. B. *J. Org. Chem.* **1994**, *59*, 6895. (f) Becker, H.; King, S. B.; Taniguchi, M.; Vanhessche, K. P. M.; Sharpless, K. B. *J. Org. Chem.* **1995**, *60*, 3940. (g) Tomioka, K.; Nakajima, M.; Koga, K. *J. Am. Chem. Soc.* **1987**, *109*, 6213. (h) Tomioka, K.; Nakajima, M.; Iitaka, Y.; Koga, K. *Tetrahedron Lett.* **1988**, *29*, 573. (i) Yamada, T.; Narasaka, K. *Chem. Lett.* **1986**, 131. (j) Tokles, M.; Snyder, J. K. *Tetrahedron Lett.* **1986**, *27*, 3951. (k) Hirama, M.; Oishi, T.; Ito, S. *J. Chem. Soc., Chem. Commun.* **1989**, 665. (l) Annunziata, R.; Cinquini, M.; Cozzi, F.; Raimondi, L.; Stefanelli, S. *Tetrahedron Lett.* **1987**, *28*, 3139. (m) Corey, E. J.; Jardine, P. D.; Virgil, S.; Yuen, P.-W.; Connell, R. D. *J. Am. Chem. Soc.* **1989**, *111*, 9243. (n) King, S. B.; Sharpless, K. B. *Tetrahedron Lett.* **1994**, *35*, 5611.

(12) Mukaiyama, T.; Imagawa, K.; Yamada, T.; Takai, T. *Chem. Lett.* **1992**, 231.

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Table 1. Electro-dihydroxylation[a] of Styrene with Various Co-Oxidants

entry	co-oxidant	amount/ mmol	conversion yield/%	enantiomeric excess/% ee
1	$K_3Fe(CN)_6$	0.1	95.0	97.3
2	KCl	1.0	48.0	92.0
3	KBr	1.0	65.3	92.8
4	KI	4.0	41.4	86.8
5	KI/I_2	2/1	87.6	96.5
6	KI/I_2	2/0.5	91.6	95.0
7	I_2	0.5	93.7	97.9

[a] Carried out in a mixed solution of *t*-BuOH (5 mL) and H_2O (5 mL) in the presence of $(DHQD)_2PHAL$ (0.01 mmol), $K_2OsO_2(OH)_4$ (0.002 mmol), and K_2CO_3 (3.0 mmol) under passage of 2.5−5.0 F/mol of electricity for 25−30 h.

K_2CO_3 system with chiral ligands such as dihydroquinidine (DHQD) and/or dihydroquinine (DHQ) derivatives has been found to be superior.[11c]

In the preceding paper,[10] we reported the electrochemical asymmetric dihydroxylation of olefins using Sharpless' ligand in the presence of potassium osmate by recycling a catalytic amount of potassium ferricyanide by electrochemical oxidation. We also mentioned a possibility of the choice of other co-oxidants as well as bases in the electrolytic conversion.

In continuation of our research in chemical and electrocatalytic asymmetric dihydroxylation reactions, now, we found that I_2 and iodine−iodide combinations are efficient co-oxidants for the osmate recycling. Namely, the novel co-oxidant−base systems involving an $I_2-K_2CO_3-K_2Os_2(OH)_4$ and $I_2-K_3PO_4/K_2HPO_4-K_2Os_2(OH)_4$ combination, which can realize efficient enantioselective dioxyosmylation of olefins, were proved to be more effective both under chemical and electrochemical conditions.

Results and Discussion

Initially, we studied the potentiality of I_2 as an alternative co-oxidant in the $K_2CO_3-K_2OsO_2(OH)_4-(DHQD)_2PHAL$ system for asymmetric dihydroxylation of styrene. Halides have been found to be an efficient catalyst in mediatory systems, which spured us to gather precise data in the isolated and enantiomeric excess yields taking advantage of the halide-assisted electrodihydroxylation of styrene (Table 1, entries 2−7). Apparently, most co-oxidant systems provided the diols in high yields of % ee. However, different efficiencies were noticed in conversion yields. In comparison with the case of potassium ferricyanide (Table 1, entry 1), the potassium halides (entries 2, 3, and 4) were less effective even when they were used in excesses more than 10 times larger than that of potassium ferricyanide. This situation, however, seems to be improved by addition of I_2 (entries 5 and 6). The most exciting results were obtained when I_2 alone was used in an $I_2-K_2CO_3-K_2OsO_2(OH)_4$ system as a co-oxidant (entry 7) under electrochemical conditions. The correlation of the isolated and enantiomeric excess yields in respect to the amount of I_2 is demonstrated in Figure 1. Apparently, the use of 0.3 equiv of I_2 still afforded sufficiently high yield of the chiral diol from styrene. Without passing electricity, the isolated yield sharply decreased in proportion to the amount of I_2, being less than 1.5 equiv. These trends were not changed with different systems.

The chemical asymmetric dihydroxylation with I_2 smoothly proceeded in 96.6% isolated yield together with 96.2% ee when the molar ratio of styrene and I_2 was 1.5. However, the isolated yield diminished in proportion with the amount of I_2. Interestingly, under these circumstances, the value of enantiomeric excess was always around 96%. Next, we investigared electrochemical osmium-catalyzed asymmetric dihydroxylation in the same system by recycling use of a catalytic amount of I_2 (electrochemical procedure I). As shown in Figure 1, it is clear that the $I_2-K_2CO_3-K_2OsO_2(OH)_4-(DHQD)_2$-PHAL system operated well under electrolysis conditions and that the I_2 played the expected role as a recyclable co-oxidant for potassium osmate. Actually, more than 90% of isolated yields (96% ee) could be attained in the presence of 0.3 equiv of I_2. Under a similar electrolysis condition, a large amount of styrene (5 equiv) can be oxidized by changing the electrolysis time and current density to afford **3** in 89% yield (91.9% ee).

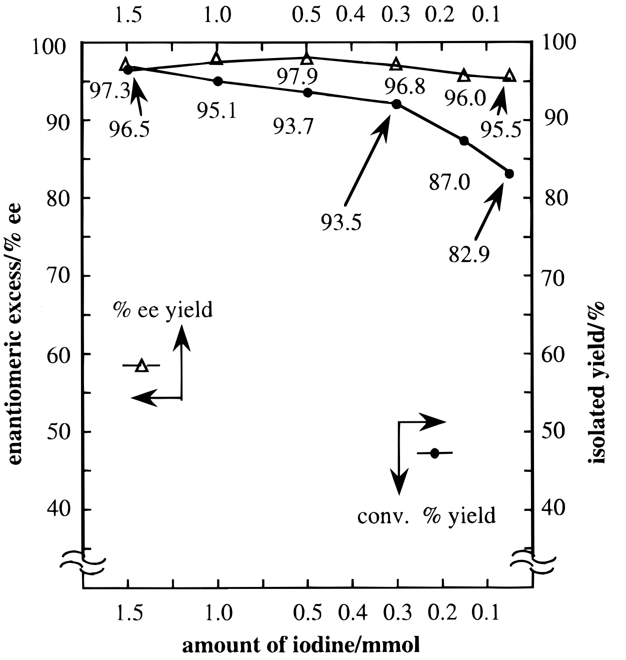
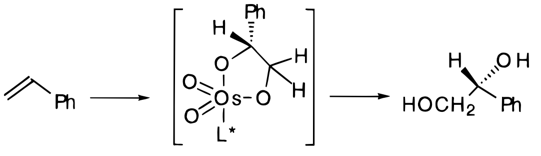


Figure 1. Electrochemical asymmetric dihydroxylation of styrene in an $I_2-K_2CO_3-K_2OsO_2(OH)_4$ system in the presence of $(DHQD)_2PHAL$. Isolated yield, % (●), obtained by changing the amount of iodine under the following conditions: styrene (1.0 mmol), $(DHQD)_2PHAL$ (0.01 mmol), $K_2OsO_2(OH)_4$ (0.002 mmol), K_2CO_3 (3.0 mmol) in *t*-BuOH (5 mL)−H_2O (5mL) at 0 °C in an undivided cell with 5.11 F/mol electricity (1.5−3.0 V, 5 mA/cm^2). Enantiomeric excess, % ee (△), determined by HPLC analysis of the diol (CHIRALCEL OB-H column, 10% *i*-PrOH in hexane, 0.5 mL/min).



1 **2** **3**

Encouraged by our initial results, we sought an alternative co-oxidant−base combination for the $K_2OsO_2(OH)_4-(DHQD)_2PHAL$ system active at pH values around 11.0−11.5 which is required for the hydrolysis of the chiral monoglycolate intermediate **2**. The $I_2-K_3PO_4/K_2HPO_4$ combination was proven to be ideal for the present purpose, and the results are indicated in Figure 2. Electrolysis of **1** in a I_2(0.5 equiv)−K_3PO_4/K_2HPO_4(1.88/

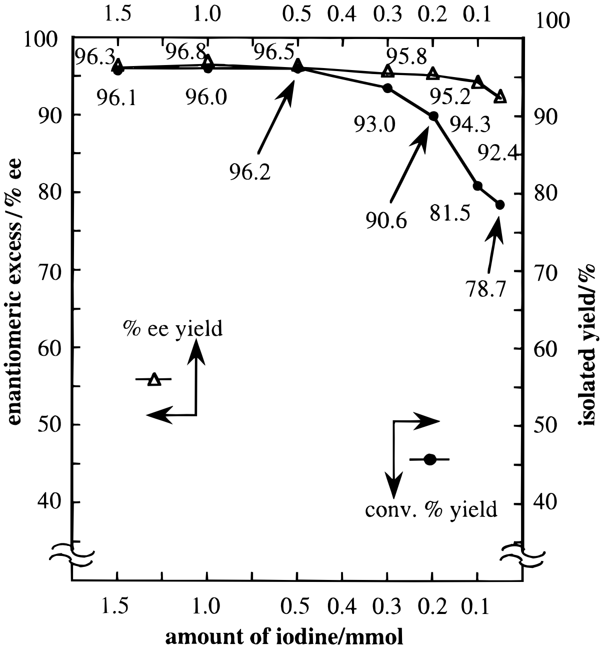


Figure 2. Electrochemical asymmetric dihydroxylation of styrene in an I_2–K_3PO_4/K_2HPO_4–$K_2OsO_2(OH)_4$ system in the presence of $(DHQD)_2PHAL$. Isolated yield, % (●), obtained by changing the amount of iodine under the following conditions: styrene (1.0 mmol), $(DHQD)_2PHAL$ (0.01 mmol), $K_2OsO_2(OH)_4$ (0.002 mmol), K_3PO_4/K_2HPO_4 (1.88/1.12 mmol) in *t*-BuOH (5 mL)–H_2O (5mL) at 0 °C in an undivided cell with 5.11 F/mol electricity (1.5–3.0 V, 5 mA/cm^2). Enantiomeric excess, % ee (△), determined by HPLC analysis of the diol (CHIRALCEL OB-H column, 10% *i*-PrOH in hexane, 0.5 mL/min).

1.12 equiv)–$K_2OsO_2(OH)_4$–$(DHQD)_2PHAL$ system afforded the diol **3** in 96.2% yield (96.5% ee) (see electrochemical procedure II). As shown in Figure 2, the presence of 0.2 equiv of I_2 could afford the diol in more than 81.8% yields in isolated yield with 95.2% enantiomeric excess.

Table 2 further illustrates the results obtained from the asymmetric dihydroxylation of a variety of olefins using iodine–base combination systems under both chemical and electrochemical conditions in comparison with the previous results.[11] It is obvious that both the I_2–K_2CO_3 and I_2–K_3PO_4/K_2HPO_4 systems are well suited for various olefins under the above conditions. Especially, terminal as well as di- and trisubstituted olefins bearing alkyl and aryl groups were good candidates for the asymmetric dihydroxylation. Some exceptions were encountered when the present I_2–K_2CO_3 system was extended to the asymmetric dihydroxylation of α,β-unsaturated esters (entries 4, 11, and 12), which exhibited relatively lower conversion yields probably due to hydrolysis of the ester groups under the employed conditions. However, the use of $K_2CO_3/KHCO_3$ (2.5/0.5 mmol) in place of K_2CO_3 (3 mmol) was proven to be effective for the improvement of the conversion yields. The scale-up electrolysis performed in a microflow cell (ElectroCell AB, Sweden) provided the same results obtained in a glass apparatus (EOS-22, Japan). The diols obtained from olefins (entries 5, 13, and 14) are well-known as chiral synthons for the synthesis of chiral β-blockers,[13] chiral auxiliaries,[11n] and a variety of optically active natural products.[14] A successful application of the present procedures for the synthesis of chiral *l*-shikonin has been carried out which will be published soon elsewhere.[15]

Electrochemical Measurement of the Redox System $K_2Os(VI)O_2(OH)_4/I_2$ in Water. The cyclic voltammogram of a solution of $K_2OsO_2(OH)_4$ (2 mM) in water containing K_2CO_3 (0.3 M) as supporting electrolyte exhibits two oxidation peaks (Figure 3). The first electron transfer is controlled by the diffusion and takes place at $E_{pa}(O_1) = -0.115$ V (eq 1, at a platinum electrode at the scan rate of 0.2 V s^{-1}). The first oxidation produces a species that is adsorbed at the electrode surface, and therefore the second electron transfer at $E_{pa}(O_2) = +0.225$ V (eq 3) is not controlled by the diffusion. The species resulting from the first electron transfer is also reduced at $E_{pc}(R_1) = -0.225$ V (eq 2), and the shape of the reduction peak is also characteristic of a species adsorbed on the electrode surface.

$$\mathrm{Os(VI)O_2(OH)_4}^{2-} \xrightarrow{-e} \mathrm{Os(VII)O_3(OH)_3}^{2-} + \mathrm{H}^+ \qquad \mathrm{O_1} \quad (1)$$

$$\mathrm{Os(VII)O_3(OH)_3}^{2-} \xrightarrow{\mathrm{H}^+,e} \mathrm{Os(VI)O_2(OH)_4}^{2-} \qquad \mathrm{R_1} \quad (2)$$

$$\mathrm{Os(VII)O_3(OH)_3}^{2-} \xrightarrow{-e} \mathrm{Os(VIII)O_4(OH)_2}^{2-} + \mathrm{H}^+ \qquad \mathrm{O_2} \quad (3)$$

Addition of 1 equiv of I_2 results in a decay of the oxidation peak O_1 while two new oxidation peaks appear at more positive potential at $E_{pa}(O_3) = +0.295$ V and $E_{pa}(O_4) = +0.506$ V (eqs 4 and 5; Figure 3). These oxidation peaks are characteristic of the oxidation of iodide anions (I^-) as evidenced by the increase in their respective magnitude when potassium iodide is added to the solution. Therefore we assume that I_2 oxidizes the osmium(VI) salt in water and itself is reduced to I^-.

$$\mathrm{I_2} + \mathrm{K_2Os(VI)O_2(OH)_4} \rightarrow 2\mathrm{I}^- + \mathrm{K_2Os(VIII)O_4(OH)_2} + 2\mathrm{H}^+ \quad (4)$$

$$\text{or } 2\mathrm{KI} + \mathrm{Os(VIII)O_4} + 2\mathrm{H_2O} \quad (5)$$

Electrochemical Measurement of the Redox System $K_2Os_2(OH)_4/I_2$ in a Mixture (1/1) of Water and *tert*-Butyl Alcohol. A mixture of water and *tert*-butyl alcohol (1/1) containing K_2CO_3 (0.3 M) as a supporting electrolyte results in the formation of two phases. $K_2Os(VI)O_2(OH)_4$ (2 mM) is only soluble in the aqueous phase as attested by its pale violet color. No oxidation peak is detected when voltametry is performed in the organic phase. In the aqueous phase, the two oxidation peaks of $K_2Os(VI)O_2(OH)_4$ are detected at $E_{pa}(O_1) = +0.040$ V and $E_{pa}(O_2) = +0.205$ V, *i.e.*, at potentials similar to that mentioned above in pure water. When I_2 is added to this solution, the pale violet color characteristic of $K_2Os(VI)O_2(OH)_4$ disappears and a yellow color characteristic of $Os(VIII)O_4$ appears in the organic phase. However, no reduction peak that could characterize $Os(VIII)O_4$ is observed (carried out with an authentic sample of $Os(VIII)O_4$ alone). In the presence of 5 equiv of the ligand, the oxidation peaks of $K_2Os(VI)O_2(OH)_4$ are

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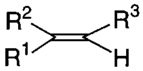
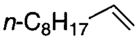
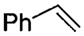
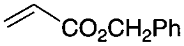
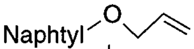
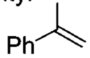
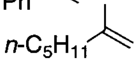
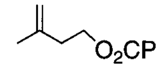
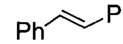
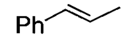
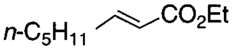
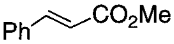
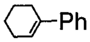
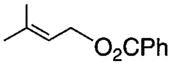
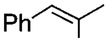
(13) Rama Rao, A. V.; Gurjar, M. K.; Joshi, S. V. *Tetrahedron: Asymmetry* **1990**, *1*, 697.

(14) Dumount, V. R.; Phander, H. *Helv. Chim. Acta* **1983**, *66*, 814.

(15) Torii, S.; Akiyama, K., *Chem. Lett.* **1996**, in press.

Table 2. Asymmetric Dihydroxylation of Olefins Using a Variety of Iodine−Base Systems

			chemical method[a]				eletrolytic method[b]					
			I_2-K_2CO_3		I_2-K_3PO_4/K_2HPO_4		I_2-K_2CO_3		I_2-K_3PO_4/K_2HPO_4			
entry	 olefin	reported[c] % ee	% ee[d]	yield, %[e]	% ee[d]	yield, %[e]	% ee[d]	yield, %[e]	% ee[d]	yield, %[e]	confign[f]	ref.
1		84	>99	95.8	>99	89.0	>99	86.3	>99	82.9	R	11c
2		97	96.5[g]	96.0	96.2[g]	96.5	97.9[f]	93.7	97.1[f]	96.0	R	11c
3		-	>99	92.2	>99	87.0	>99	92.0	>99	87.6	R	11b
4		77	62.3	51.2[h]	63.4	77.5	-	-	-	-	S	11c
5		91	>99	94.4	>99	86.3	>99	85.0	>99	89.3	S	11c
6		94	95.0	98.4	95.0	93.5	96.3	98.8	94.0	92.9	R	11c
7		78	90.0	95.8	90.1	85.9	95.6	88.5	95.8	92.4	R	11c
8		-	>99	91.6	>99	91.8	>99	92.8	>99	91.9	-	12
9		99.5	>99[g]	93.0	>99[g]	97.1	>99	88.8	>99	88.2	RR	11c
10		-	>99	92.2	>99	91.3	98.6	83.9	97.3	92.9	RR	11m
11		99	>99	76.4[h]	>99	72.8	-	-	-	-	SR	11c
12		97	>99	72.3[h]	>99	74.0	-	-	-	-	SR	11c
13		99	92.0	97.6	92.3	92.1	>99	89.5	98.3	90.4	RR	11c
14		-	>99	98.8	>99	97.4	97.0	94.5	97.0	87.8	R	14
15		-	95.0	90.3	94.5	95.4	89.5	88.9	87.0	86.0	R	11b

[a] Carried out in a mixture of *t*-BuOH (5 mL) and H_2O (5 mL) in the presence of K_2CO_3 (3.0 mmol) or K_3PO_4/K_2HPO_4 (1.88/1.12 mmol), $(DHQD)_2PHAL$ (0.01 mmol), I_2 (1.5 mmol) and $K_2OsO_2(OH)_4$ (0.002 mmol) based on 1 mmol of olefin at 0 °C or rt for 30 h. [b] Performed by use of substrate (1 mmol), *t*-BuOH (5 mL), H_2O (5 mL), K_2CO_3 (3.0 mmol) or K_3PO_4/K_2HPO_4 (1.88/1.12 mmol), $(DHQD)_2PHAL$ (0.01 mmol), I_2 (0.5 mmol), $K_2OsO_2(OH)_4$ (0.002 mmol) in an undivided cell at 0 °C or rt for 5.11 F/mol of electricity (1.5−3.0 V). [c] Reported by Sharpless *et al.*, with $(DHQD)_2PHAL$.[11c] [d] Enantiomeric excess, ee %, determined by ^{19}F-NMR and ^{1}H-NMR analyses of mono- and bis-MTPA esters of the corresponding diols. [e] The yields reported here are isolated yields. [f] Determined by comparison of optical rotation values with reported ones. [g] Ee % determined by HPLC analysis of the diols (CHIRALCEL OB-H column, 10% *i*-PrOH in hexane). [h] Instead of K_2CO_3, a mixed base of K_2CO_3/$KHCO_3$ (2.5/0.5 mmol) was used.

detected in the aqueous phase. Addition of I_2 results in the oxidation of $K_2Os(VI)O_2(OH)_4$ as attested by the decay of the oxidation peaks of $K_2Os(VI)O_2(OH)_4$ and the appearance of oxidation peaks of I^- ($E_{pa}(O_3) = +0.325$ V and $E_{oa}(O_4) = +0.535$ V). But no reduction peaks characteristic of the new complex $Os(VIII)O_4L^*$ can be detected in the organic phase. The reduction of the ligand alone can be observed in THF. Its cyclic voltammogram exhibits two irreversible reduction peaks at −2.00 and −2.03 V and a third reversible one at −2.275 V. The reduction of the ligand cannot be observed in the mixture of water/*tert*-butyl alcohol since in this system the reduction of the solvent takes place at around −0.9 V (carried out with an authentic sample of $Os(VIII)O_4$ + ligand (5 equiv) in water/*tert*-butyl alcohol). Therefore, the oxidation of the osmium(VI) salt by I_2 and the recycling of I^- to I_2 by oxidation at the anode proceed in the aqueous phase whereas the osmium(VIII) complex produced by oxidation of the osmium(VI) salts is transferred to the organic phase.

Optimal Experimental Conditions for the Electrochemical Process. Although $K_2Os(VI)O_2(OH)_4$ can be oxidized at the anode, its direct electrochemical oxidation leads to adsorption on the electrode that may stop the process. It is why a mediator is necessary to perform the oxidation of $K_2Os(VI)O_2(OH)_4$ in the solution. Iodine plays this role, and the resulting iodide anions (I^-) are oxidized at the anode back to I_2. Since $K_2Os(VI)O_2(OH)_4$ is more easily oxidized than I^-, it is not possible to oxidize I^- to I_2 in the presence of $K_2Os(VI)(OH)_4$. This can explain why performing the reaction using a mixture of $K_2Os(VI)O_2(OH)_4$ and potassium iodide leads to lower yield than starting from the mixture of $K_2Os(VI)O_2(OH)_4$ and I_2. Indeed, it is necessary to start the electrolysis with a mixture of $K_2Os(VI)O_2(OH)_4$ and an excess of I_2. Thus, I_2 is able to convert quantitatively the $K_2Os(VI)O_2(OH)_4$ to Os(VIII). This depletes the Os(VI) concentration in the diffusion layer and replenishes it with a concentration of iodide ions which can then be freely oxidized to regenerate I_2. The process could only work if I^- is alone in the diffusion layer (or with Os(VIII) but without the Os(VI)). This implies that I_2 should oxidize the Os(VI) by a very fast reaction compared to the electrolysis.

In the aqueous electrolysis, the osmate $Os(VI)O_2(OH)_4^{2-}$ unambiguously undergoes a two-electron oxidation with

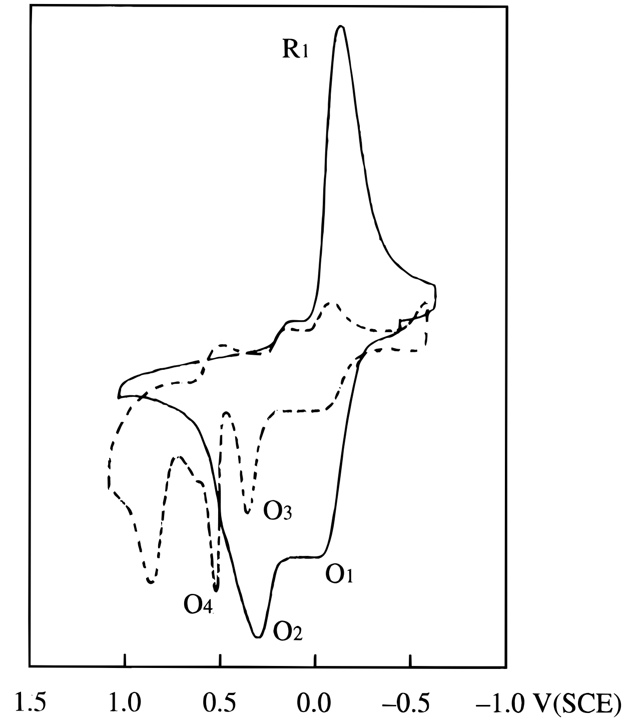


Figure 3. (—) Cyclic voltammetry of $K_2Os(VI)O_2(OH)_4$ (2 mM) in water containing K_2CO_3 (0.3M) at a stationary platinum disk electrode ($d = 0.5$ mm) with a scan rate of 0.2 V s^{-1} at 20 °C. (- - -) Cyclic voltammetry of $K_2Os(VI)O_2(OH)^4$ (2 mM) in the presence of I_2 (2 mM) performed under the same conditions as above.

electrochemically produced active iodine-oxidizing species to form $Os(VIII)O_6(OH)_2^{2-}$ in a basic buffering conditions (eq 6). The octavalent Os species would change into OsO_4 by eliminating hydroxy anions (eq 7). This process seems to be reversible; osmium tetraoxide, however, is more soluble in an organic phase. The combination of OsO_4 with nitrogen-containing chiral ligands L* proceeds promptly to provide a rather tight complex which may provide a binding pocket for olefin (eq 8). Subsequently, olefin would be trapped by the binding pocket to afford the olefin−Os−L* complexes as a precursor of the chiral diol (eq 9). The hydrolysis of the complexes may give chiral diols, chiral ligands, and osmate(VI) (eq 10).

$$Os(VI)O_2(OH)_4^{2-} \rightarrow Os(VIII)O_4(OH)_2^{2-} + 2e^- + 2H^+ \qquad (6)$$

$$Os(VIII)O_4(OH)_2^{2-} \rightarrow Os(VIII)O_4 + 2OH^- \qquad (7)$$

$$Os(VIII)O_4 + L^* \rightarrow Os(VIII)O_4L^* \qquad (8)$$

$$Os(VIII)O_4L^* + \text{olefin} \rightarrow \text{olefin}-Os(VIII)O_4L^* \qquad (9)$$

$$\text{olefin}-Os(VIII)O_4L^* + OH^- \rightarrow \\ \text{diol}^* + L^* + Os(VI)O_2(OH)_4^{2-} \qquad (10)$$

Experimental Section

General. Starting olefinic substrates, unless specially stated, were purchased from commercial sources and not further purified prior to use. All reactions were monitored by thin layer chromatography (TLC) and judged complete when starting material was no longer detected in TLC. The enantiomeric excesses of the chiral diols were determined by HPLC analysis of diols on a CHIRALCEL OB-H column (Daicel) or NMR analysis *via* Mosher derivatives (mono-, or bis-MTPA esters) prepared by standard procedures.[16] ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded in deuteriochloroform ($CDCl_3$) at 200 and 500 MHz. Optical rotations were taken at 25 °C at the sodium line.

Electrolysis Apparatus. Unless otherwise noted, an undivided cell (EOS-V22, TECHNOSIGMA, Japan, 2.2 cm in diameter and 6 cm in height (*ca.* 20 mL)) fitted with a stirring bar and a gas outlet pipe or a flow cell (MICRO FLOW CELL, ElectroCell AB, Sweden) was used. In the EOS-V22, two platinum foil electrodes were placed parallel to each other 10 mm apart. The vessel was immersed in a ice−water bath or kept at room temperature.

Electrochemical Setup and Electrochemical Procedure for Cyclic Voltammetry. Cyclic voltammetry was performed with a homemade potentiostat and a waveform generator, PAR Model 175. Cyclic voltammograms were recorded with a Nicolet 3091 digital oscilloscope. Experiments were carried out in a three-electrode cell connected to a Schlenk line. The counterelectrode was a platinum wire of *ca.* 1 cm^2 apparent surface area; the reference was a saturated calomel electrode (Tacussel) separated from the solution by a bridge (3 mL) filled with a 0.3 M K_2CO_3 solution in a mixture of water and *tert*-butyl alcohol (1/1). A 12 mL volume of a mixture of water and *tert*-butyl alcohol (1/1) containing 0.3 M K_2CO_3 was poured into the cell. A 8.84 mg amount (2×10^{-3} M) of $K_2Os(VI)O_2(OH)_4$ (commercial from Aldrich) was then added. Cyclic voltammetry was performed in the aqueous phase at a stationary disc electrode (a platinum disc made from a cross section of wire, 0.5 mm in diameter, sealed into glass) at a scan rate of 0.2 V s^{-1}. Suitable amounts of required reagents (*e.g.*, 5.6 mg amount (2×10^{-3} M) of I_2 and/or 93.4 mg amount (10^{-2} M) of the ligand $(DHQD)_2PHAL$) were then added to the cell, and the cyclic voltammetry was performed again.

Electrochemical Procedure I with the I_2−K_2CO_3−$K_2OsO_2(OH)_4$ System. To a stirred solution of *tert*-butyl alcohol (5 mL), I_2 (127 mg, 0.5 mmol), K_2CO_3(410 mg, 3.0 mmol), $(DHQD)_2PHAL$ (7.8 mg, 0.01 mmol), and $K_2OsO_2(OH)_4$ (0.74 mg, 0.002 mmol) at 0 °C in an undivided cell (EOS-V22) was added styrene (1 mmol) at once. The mixture was electrolyzed under a constant current of 5 mA/cm^2 under vigorous stirring (applied voltage 1.0−3.0 V). After passage of 5.11 F/mol of electricity for *ca.* 27 h, the reaction (monitored by TLC) was quenched with a saturated sodium thiosulfate solution. Usual workup followed by column chromatography gave (−)-(*R*)-1-phenyl-1,2-ethanediol (**3**, 129.3 mg; 93.7%); $[\alpha]^{25}_D = -62.03°$ ($c = 1.98$ ($CDCl_3$)). The enantiomeric excess of the *R*-diol was determined by HPLC analysis (CHIRALCEL OB-H; Daicel) to be 97.9%.

Electrochemical Procedure II with the I_2−K_3PO_4/K_2HPO_4−$K_2OsO_2(OH)_4$ System. To a stirred solution of *tert*-butyl alcohol (5 mL), water (5 mL), I_2 (127 mg, 0.5 mmol), K_3PO_4 (398 mg, 1.88 mmol), K_2HPO_4 (196 mg, 1.12 mmol), $(DHQD)_2PHAL$ (7.8 mg, 0.01 mmol), and $K_2OsO_2(OH)_4$ (0.74 mg, 0.002 mmol) at 0 °C in an undivided cell (EOS-V22) was added styrene (1 mmol) at once. The mixture was electrolyzed (5.0 mA/cm^2) under vigorous stirring (applied voltage 1.0−3.0 V). After passage of 5.11 F/mol of electricity for *ca.* 27 h, the mixture (monitored by TLC) was worked up in a usual manner and chromatographed to give (−)-(*R*)-1-phenyl-1,2-ethanediol (**3**, 130 mg; 96%); $[\alpha]^{25}_D = -61.8°$ ($c = 2.46$ ($CDCl_3$)). The enantiomeric excess of the *R*-diol was determined by HPLC analysis (CHIRALCEL OB-H, Daicel) to be 97.1%.

Electrochemical Procedure III in a Flow Cell System. A mixture of *tert*-butyl alcohol−water (25/25 mL), methanesulfonamide (5 mmol), K_2CO_3 (15 mmol), I_2 (2.0 mmol), $K_2OsO_2(OH)_4$ (0.01 mmol), $(DHQD)_2PHAL$ (0.05 mmol), and *trans*-stilbene (5 mmol) was electrolyzed in an undivided flow cell (MICRO FLOW CELL) equipped with two platinum electrodes (3×4 cm^2). After passage of 2.33 F/mol of electricity at room temperature (progress was monitored by TLC), 5 g of

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[16] Dale, J. A.; Dull, D. L.; Mosher, H. S. *J. Org. Chem.* **1969**, *34*, 2543.

solid sodium sulfite was added and the solution was stirred for 40 min. The two phases were separated, and the aqueous phase was then extracted (3 × 25 mL) with EtOAc. The combined organic phases were washed with 2 M NaOH and dried over $MgSO_4$. Concentration and flash chromatography afforded the (+)-(1*R*,2*R*)-1,2-phenyl-1,2-ethanediol in 82.4% yield, $[\alpha]^{25}_{D} = +91°$ ($CDCl_3$). The enantiomric excess of the *RR*-diol was determined by HPLC analysis [CHIRALCEL OB-H column (Daicel), 10% *i*-PrOH in hexane, 0.5 mL/min] to be 99.5%. The alkaliod ligand was recovered in 84.0% yield.

Chemical Procedure I with the I_2–K_2CO_3–$K_2OsO_2(OH)_4$ System. To a stirred solution of *tert*-butyl alcohol/water (50/50 mL), K_2CO_3 (30 mmol), I_2 (15 mmol), methanesulfonamide (10 mmol), $K_2OsO_2(OH)_4$ (0.02 mmol), and $(DHQD)_2$-PHAL (0.1 mmol) was added *trans*-stilbene (10 mmol) at once at 0 °C, the mixture was stirred vigorously for more than 30 h (monitored by TLC), and the reaction was quenched with 10 g of solid sodium sulfite. The two phases were separated, and the aqueous phase was then extracted (3 × 50 mL) with EtOAc. The combined organic phases were washed with 2 M NaOH and dried over $MgSO_4$. Concentration and flash chromatography afforded the (+)-(1*R*,2*R*)-1,2-phenyl-1,2-ethanediol in 98.4% yield, $[\alpha]^{25}_{D} = +91°$ ($CDCl_3$). The enantiomeric excess of the *RR*-diol was determined by HPLC analysis [CHIRALCEL OB-H column (Daicel), 10% *i*-PrOH in hexane, 0.5 mL/min] to be 99.5%. The alkaloid ligand was recovered in 88.0% yield.

Chemical Procedure II with the I_2–K_3PO_4/K_2HPO_4–$K_2OsO_2(OH)_4$ System. To a stirred solution of *tert*-butyl alcohol (5 mL), I_2 (382 mg, 1.5 mmol), K_3PO_4 (1.88 mmol), K_2HPO_4(mg, 1.12 mmol), $(DHQD)_2$PHAL (7.8 mg, 0.01 mmol), and $K_2OsO_2(OH)_4$ (0.74 mg, 0.002 mmol) at 0 °C was added styrene (1 mmol) at once. The mixture was stirred vigorously for *ca*. 30 h (progress was monitored by TLC and GLC), and the reaction was quenched with a saturated sodium thiosulfate solution (5 mL). Usual workup followed by column chromatography gave (−)-(*R*)-1-phenyl-1,2-ethanediol (**3**) in 96.5% yield, $[\alpha]^{25}_{D} = -61.5°$ ($c = 1.98$ ($CDCl_3$)). The enantiomeric excess of the *R*-diol was determined by HPLC analysis (CHIRALCEL OB-H; Daicel) to be 96.2%.

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