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Sodium Chlorite as an Efficient Oxidant and Hydroxy Ion Pump in Osmium-Catalyzed Asymmetric Dihydroxylation

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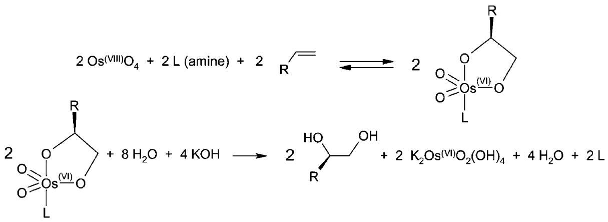
Sodium chlorite is an efficient stoichiometric oxidant in Sharpless asymmetric dihydroxylation. One sodium chlorite provides the reaction with the stoichiometric number of electrons and hydroxide ions needed to dihydroxylate two olefins without the consumption of any additional base. 100% conversion in sodium chlorite asymmetric dihydroxylation of styrene was achieved twice as fast as in the established Sharpless $K_3[Fe(CN)_6]$ dihydroxylation. Even internal olefins were dihydroxylated fast with sodium chlorite without hydrolysis aids. Eight olefins were dihydroxylated to corresponding vicinal diols with yields and ees as good as those reported in the literature for other similar processes.

Introduction

Sodium chlorite ($NaClO_2$) is widely used in water treatment and as a bleaching agent in the paper and pulp industry and in the textile industry. Under acidic conditions, sodium chlorite liberates chlorine dioxide (ClO_2), which is the actual bleaching agent. In organic synthesis, chlorine dioxide has been used for example to oxidize aldehydes to carboxylic acids. In alkaline media, sodium chlorite is relatively stable and the reactive oxidant is the chlorite ion (ClO_2^-). Chlorite ion is a strong oxidant, and as it is reduced to chlorine ion (Cl^-), four electrons are transferred and also four hydroxide ions are formed. Therefore, in principle, chlorite ion should be an ideal oxidant in reactions that both require oxidation and are also hydroxide ion consumers. To elaborate the potentiality of this combined oxidation and hydroxide ion production feature of sodium chlorite in organic synthesis, we chose to investigate osmium tetroxide (OsO_4)-catalyzed Sharpless asymmetric dihydroxylation as a model reaction. Catalytic Sharpless asymmetric dihydroxylation requires both a stoichiometric oxidant to regenerate the catalyst and hydroxide ions to hydrolyze the intermediate cyclic osmate-ester.[1]

Several different reoxidants have been reported for the catalytic Sharpless asymmetric dihydroxylation of olefins. The most widely used reoxidant is $K_3[Fe(CN)_6]$. Another widely used oxidant is *N*-methylmorpholine *N*-oxide. Reports on utilization of oxygen-based reoxidants in asymmetric dihydroxylation such as air,[2] O_2,[3] and H_2O_2[4] have also been published. Bleach (NaOCl) is the most recently reported reoxidant in Sharpless asymmetric dihydroxylation.[5]

Equation 3 shows that a total of four electrons are transferred during the reduction of $NaClO_2$ to sodium chloride (NaCl), which corresponds to the number of electrons needed to oxidize two $K_2Os^{(VI)}O_2(OH)_4$ to two $K_2Os^{(VIII)}O_4(OH)_2$. Four electrons correspond also to the number of electrons needed to oxidize two olefins to two diols (eqs 1 and 2). Hydrolysis of the intermediate cyclic osmate-ester requires hydroxide ions. Two osmate-ester intermediates consume four hydroxide ions (eq 2), which is the same number of hydroxide ions generated after two $K_2Os^{(VIII)}O_4(OH)_2$ are transformed to two $Os^{(VIII)}O_4$ (eq 4).

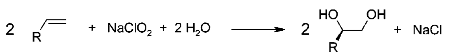


(1)

(2)

$$2\,K_2Os^{(VI)}O_2(OH)_4 + NaClO_2 \longrightarrow 2\,K_2Os^{(VIII)}O_4(OH)_2 + NaCl + 2\,H_2O \qquad (3)$$

$$2\,K_2Os^{(VIII)}O_4(OH)_2 \rightleftharpoons 2\,Os^{(VIII)}O_4 + 4\,KOH \qquad (4)$$



(5)

Results and Discussion

To elaborate the potentiality of the chemistry shown in eqs 1−5, we dihydroxylated styrene with the theoreti-

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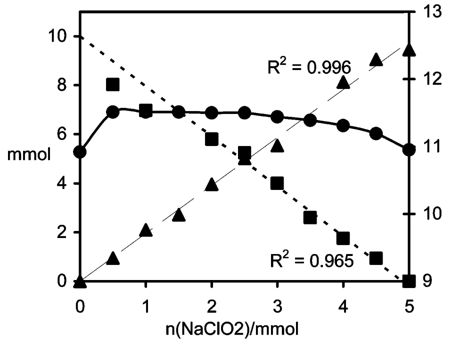

FIGURE 1. Correlation between the amount of added $NaClO_2$ and both the concentration of styrene (■) and the concentration of 1-phenyl-1,2-ethandiol (▲). pH profile of the reaction (●).

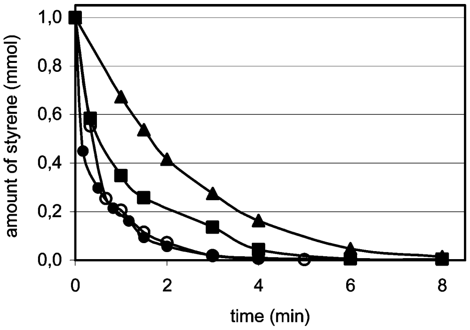

FIGURE 2. Profiles of the reaction rates of $NaClO_2$ (○), K_2CO_3-modified $NaClO_2$ (●), Sharpless (▲), and NaOH-modified Sharpless (■) dihydroxylations of styrene.

cal amount of $NaClO_2$ and monitored the consumption of styrene and the formation of 1-phenyl-1,2-ethandiol during the reaction. The results are presented in Figure 1. Figure 1 shows clearly that there is a linear correlation between the added amount of $NaClO_2$ and both the consumption of styrene and the formation of 1-phenyl-1,2-ethandiol. For example, when 2.5 mmol of $NaClO_2$ was added to the reaction mixture, 5 mmol of styrene was consumed and 5 mmol of 1-phenyl-1,2-ethandiol was formed. Simultaneously, we also monitored pH change during the reaction. The pH profile of dihydroxylation of styrene is also shown in Figure 1. As we could expect from eqs 3 and 4, after 0.1 mL of a 1 M $NaClO_2$ solution was added to the reaction mixture, the pH increased from the starting pH 10.9 to 11.5. By choice of an appropriate addition rate of the oxidant, the pH could be maintained at a level between pH 11.3−11.5. At a conversion of about 75%, the pH started to decrease, and at the end of the reaction, the pH was 10.9, as it was at the beginning of the reaction. The oxidant was added into the reaction mixture over 30 min. In a similar control experiment using $K_3[Fe(CN)_6]$ as the reoxidant and without the addition of a base such as potassium carbonate, the pH dropped from 11.5 to 9.1 during the first minute after styrene was added to the reaction mixture. No consumption of styrene could be detected during the first 30 min, and during this period of time, the pH of the reaction mixture dropped to 7.1.

Our first experiments indicated that the dihydroxylation of styrene is very fast when sodium chlorite is the stoichiometric oxidant. Therefore, we decided to compare the apparent reaction rates of $NaClO_2$ dihydroxylation and established Sharpless asymmetric $K_3[Fe(CN)_6]$ dihydroxylation. Styrene (1 mmol) was dihydroxylated with 1.5 equiv (0.75 mmol) of $NaClO_2$ and by using the original Sharpless AD-process with 1.5 equiv (3 mmol) of $K_3[Fe(CN)_6]$ together with 30 mmol of K_2CO_3, and the consumption of styrene was monitored. The results are presented in Figure 2. At the initial stages of the reactions, the consumption of styrene was much faster in $NaClO_2$ dihydroxylation than in original Sharpless AD-process. A conversion of 50% is achieved in $NaClO_2$ dihydroxylation in 25 s and in Sharpless AD-process in 110 s. After 2 min, the conversion in Sharpless AD-process was 58% and the conversion of the corresponding $NaClO_2$ dihydroxylation was 93%. Mehltretter et. al. have reported that the reaction rate of the Sharpless asymmetric dihydroxylation can be increased by adding hydroxide ions to the reaction mixture.[6] To verify the results of Mehltretter et al., we made a modified Sharpless AD-process of styrene where we added a stoichiometric amount of sodium hydroxide (2 mmol of NaOH/1 mmol of styrene) to the reaction mixture. At the initial stages of the reaction, the rate was three times higher than the reaction rate of the unmodified Sharpless AD-process (Figure 2). After the conversion had reached 50% in the modified Sharpless AD-process, there was no difference in reaction rates between the modified and unmodified Sharpless AD-process. We also made a modified $NaClO_2$ dihydroxylation where we added 30 mmol of K_2CO_3/1 mmol of styrene to the reaction mixture. Coversions of 100% were achieved in both modified and unmodified $NaClO_2$ dihydroxylations in 4 min, in a sodium hydroxide-modified Sharpless AD-process in 6 min, and in a Sharpless AD-process in 8 min. The modified $NaClO_2$ dihydroxylation is faster only at the initial stages of the reaction compared to the unmodified $NaClO_2$ dihydroxylation (Figure 2). Data from experiments for Figure 2 produced a linear graph of $\ln[a_0/a_t]^7x$ time(s). Therefore, reactions were found to follow a first-order rate law. First-order rate constants k_1 were 0.0208 s^{-1} for $NaClO_2$ dihydroxylation, 0.0214 s^{-1} for modified $NaClO_2$ dihydroxylation, 0.0132 s^{-1} for the sodium hydroxide-modified Sharpless AD-process, and 0.0087 s^{-1} for the Sharpless AD-process.

From the results of the styrene dihydroxylations, one can observe a sharp contrast between the hydroxide ion-producing $NaClO_2$ dihydroxylation process and the earlier AD-processes with added bases such as NaOH or K_2CO_3. Double bonds are dihydroxylated extremely fast with $NaClO_2$ as the stoichiometric oxidant even without an added base.

After we had discovered that $NaClO_2$ is an ideal stoichiometric oxidant in catalytic dihydroxylations of olefins, we wanted to elaborate whether it had any effect on the enantioselectivity of the reaction. Eight different olefins were dihydroxylated, and enantioselectivities were compared to the best values of $K_3[Fe(CN)_6]$ dihydroxylations found in the literature. Olefins were selected so that they represented different classes of olefins: terminal aromatic (styrene), terminal aliphatic (1-hexene, 1-hexadecen), 1,2-trans disubstituted (*trans*-stilbene, methyl *trans*-cinnamate), 1,1-disubstituted (α-methyl

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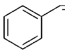
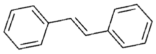
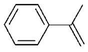
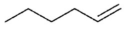
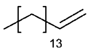
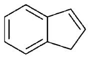
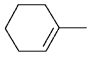
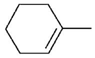
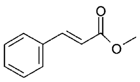
(6) Mehltretter, G. M.; Döbler, C.; Sundermeier, U.; Beller, M. *Tetrahedron Lett.* **2000**, *41*, 8083−8087.

TABLE 1. Results from Asymmetric $NaClO_2$ Dihydroxylations of Various Olefins[a]

entry	olefin	time (h)	yield[b] (%)	ee (%)[c, d]	abs. config.[e]
1		2.5	73	96 (97)[8a]	(R)
2		3	63	>99.5 (99)[8a]	(R,R)
3		1	73	93 (99)[4a]	(R)
4		5	80	78 (80)[8b]	(R)
5		6	77	87	(R)
6		2	65	41 (42)[8c]	(1R,2S)
7		3.5	75	52 (52)[8b]	(1S,2R)
8		2.5	63	70 (52)[8b]	(1S,2R)
9		2	72	>99.5 (99)[8d]	(2S,3R)

[a] All reactions were performed essentially as described in Experimental Section general procedure for asymmetric dihydroxylation with some variations: (8) methyl ethyl ketone as the organic solvent; (9) room temperature, amount of catalyst 0.8 mol %, pH 8.7−9.5. [b] Isolated yields. [c] Ees were determined by integrating appropriate ^1H NMR peaks of (Mosher's) esters of diols. [d] Best literature values are in parentheses. [e] Absolute configurations were determined by comparing the optical rotatory powers to literature values.[9]

styrene), 1,2-cis disubstituted (indene), and trisubstituted (1-methyl cyclohexene). Results from the $NaClO_2$ dihydroxylations are presented in Table 1. Results show clearly that enantioselectivities were not affected by changing $K_3[Fe(CN)_6]$ to $NaClO_2$. Ees of the dihydroxylations of olefins in the presence of $(DHQD)_2PHAL$ ligand were comparable with the best values found in the literature. Yields were good, varying from 63 to 80%.

A final observation of the experimental details in our $NaClO_2$ AD-process is that we control the addition rate of the oxidant by monitoring the pH and/or the color of the reaction mixture. The reduced form of the catalyst gives a pale violet color to the water layer. After adding a small portion of the oxidant, the color disappears as the catalyst is oxidized (eq 3). Simultaneously, the pH of the reaction mixture rises as oxidized catalyst enters the organic layer and hydroxide ions are liberated (eq 4). The pale violet color reappears in the water layer after that all the oxidant has been consumed and the catalyst returns to the reduced form (eq 2). Also, the pH of the reaction mixture returns to the same level as before the addition of the oxidant because all the hydroxide ions that are formed as the catalyst enters the organic layer (eq 4) are consumed during the hydrolysis of the osmate-ester (eq 2). Control of the addition rate may be important especially in future large-scale dihydroxylations because it prevents the accumulation of an excess of potentially hazardous and explosive oxidants in the reaction mixture.

Conclusion

Our experiments have shown that $NaClO_2$ can be used as the stoichiometric reoxidant in Sharpless asymmetric dihydroxylation. Use of 1 mmol of $NaClO_2$ can oxidize 2 mmols of olefins to corresponding diols. $NaClO_2$ AD-process is also hydroxide ion efficient because it provides the dihydroxylation with the stoichiometric number of hydroxide ions. The consumption of styrene in a $NaClO_2$ reaction is extremely fast compared with the corresponding unmodified and NaOH-modified $K_3[Fe(CN)_6]$ processes. The dihydroxylation reaction can be controlled by the addition rate of $NaClO_2$. Enantioselectivities of the $NaClO_2$ AD-process are comparable with the enantioselectivities of other AD-processes. The method described here opens up new perspectives for preparation of chiral diols on a large scale.

Experimental Section

Dihydroxylation of Styrene in the Presence of $NaClO_2$ and GC Standard: pH Profile of the Dihydroxylation (Figure 1). A 250 mL three-necked flask equipped with a magnetic stirring bar and a pH electrode was charged with 10 mmol of styrene, 5.5 g of NaCl, 78 mg (0.1 mmol) of ligand ($(DHQD)_2PHAL$), 14.7 mg (0.04 mmol) of $K_2OsO_4{\cdot}2H_2O$, 0.78 g of menthol (5.0 mmol, internal GC standard), and 100 mL of $H_2O/^tBuOH$ (1:1) solution. pH was adjusted to 10.9 with 0.5 M NaOH. A 0.1 mL portion of the 1 M $NaClO_2$ solution was added to the reaction mixture, and the characteristic violet color of Os^{VI} disappeared from the water phase. The residual $NaClO_2$ was then added in portions of 0.1 mL to the reaction mixture immediately after that the violet color appeared again in the water layer. In total, 5.0 mL (5 mmol) of the 1 M $NaClO_2$ solution was added. A 0.1 mL aliquot was withdrawn from the reaction mixture after every addition of 0.5 mL of the $NaClO_2$ solution. The sample was then diluted with 0.5 mL of EtOAc, and the resulting organic layer was analyzed using GC. In total, 11 samples were analyzed with GC. The pH of the reaction mixture was determined simultaneously with the withdrawal of the aliquot. The total reaction time was 30 min.

Dihydroxylation of Styrene in the Presence of $K_3[Fe(CN)_6]$ and GC Standard in Nonbuffered Conditions. A 250 mL three-necked flask equipped with a magnetic stirring bar and a pH electrode was charged with 9.88 g (30 mmol) of $K_3[Fe(CN)_6]$, 78 mg (0.1 mmol) of ligand ($(DHQD)_2PHAL$), 14.7 mg (0.04 mmol) of $K_2OsO_4\cdot 2H_2O$, 0.78 g of menthol (5.0 mmol, internal GC standard), and 100 mL of $H_2O/^tBuOH$ (1:1) solution. pH was adjusted to 11.5 with 0.5 M NaOH. Reaction was initiated by adding 10 mmol of styrene to the reaction mixture in one portion. A 0.1 mL aliquot was withdrawn from the reaction mixture after 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, and 30 min. Samples were diluted with 0.5 mL of EtOAc, and the resulting organic layer was analyzed using GC. The pH of the reaction mixture was determined simultaneously with the withdrawal of the aliquot.

Dihydroxylation of Styrene: Reaction Rate Profile of the $NaClO_2$ Dihydroxylation (Figure 2). A 250 mL three-necked flask equipped with a magnetic stirring bar and a pH electrode was charged with 5.5 g of NaCl, 78 mg (0.1 mmol) of ligand ($(DHQD)_2PHAL$), 14.7 mg (0.04 mmol) of $K_2OsO_4\cdot 2H_2O$, 85 mg (0.75 mmol) of $NaClO_2$, and 100 mL of $H_2O/^tBuOH$ (1:1) solution. pH was adjusted to 11.8 with 0.5 M NaOH. The biphasic mixture was cooled in an ice/water bath to 0−1 °C. Reaction was initiated by adding 1 mmol of styrene to the reaction mixture in one portion. A 100 μL aliquot was withdrawn from the reaction mixture after 20, 40, 60, 90, 120, 180, 240, 300, 360, and 480 s. The samples were then diluted with 2 mL of 0.5 mM diphenyl ether acetonitrile/water (7:3) solution. Samples were analyzed with HPLC.

Dihydroxylation of Styrene: Reaction Rate Profile of the K_2CO_3-Modified $NaClO_2$ Dihydroxylation (Figure 2). A 250 mL three-necked flask equipped with a magnetic stirring bar and a pH electrode was charged with 4.14 g of K_2CO_3 (17% water), 78 mg (0.1 mmol) of ligand ($(DHQD)_2PHAL$), 14.7 mg (0.04 mmol) of $K_2OsO_4\cdot 2H_2O$, 85 mg (0.75 mmol) of $NaClO_2$, and 100 mL of $H_2O/^tBuOH$ (1:1) solution. The biphasic mixture was cooled in an ice/water bath to 0−1 °C. Reaction was initiated by adding 1 mmol of styrene to the reaction mixture in one portion. A 100 μL aliquot was withdrawn from the reaction mixture after 10, 20, 30, 50, 70, 90, 120, 180, 240, and 360 s. The samples were then diluted with 2 mL of 0.5 mM diphenyl ether acetonitrile/water (7:3) solution. Samples were analyzed with HPLC.

Dihydroxylation of Styrene: Reaction Rate Profile of the Sharpless Asymmetric Dihydroxylation (Figure 2). A 250 mL three-necked flask equipped with a magnetic stirring bar and a pH electrode was charged with 0.988 g (3 mmol) of $K_3[Fe(CN)_6]$, 4.14 g (30 mmol) of K_2CO_3 (17% water), 78 mg (0.1 mmol) of ligand ($(DHQD)_2PHAL$), 14.7 mg (0.04 mmol) of $K_2OsO_4\cdot 2H_2O$, and 100 mL of $H_2O/^tBuOH$ (1:1) solution. The biphasic mixture was cooled in an ice/water bath to 0−1 °C. Reaction was initiated by adding 1 mmol of styrene to the reaction mixture in one portion. A 100 μL aliquot was withdrawn from the reaction mixture after 20, 40, 60, 90, 120, 180, 240, 360, 480, and 600 s. The samples were then diluted with 2 mL of 0.5 mM diphenyl ether acetonitrile/water (7:3) solution. Samples were analyzed with HPLC.

Dihydroxylation of Styrene: Reaction Rate Profile of the NaOH-Modified Sharpless Asymmetric Dihydroxylation (Figure 2). A 250 mL three-necked flask equipped with a magnetic stirring bar and a pH electrode was charged with 0.988 g (3 mmol) of $K_3[Fe(CN)_6]$, 4.14 g (30 mmol) of K_2CO_3 (17% water), 2 mL of 1 M NaOH (2 mmol), 78 mg (0.1 mmol) of ligand ($(DHQD)_2PHAL$), 14.7 mg (0.04 mmol) of $K_2OsO_4\cdot 2H_2O$, and 100 mL of $H_2O/^tBuOH$ (1:1) solution. The biphasic mixture was cooled in an ice/water bath to 0−1 °C. Reaction was initiated by adding 1 mmol of styrene to the reaction mixture in one portion. A 100 μL aliquot was withdrawn from the reaction mixture after 20, 40, 60, 90, 120, 180, 240, 360, 480, 600 s. The samples were then diluted with 2 mL of 0.5 mM diphenyl ether acetonitrile/water (7:3) solution. Samples were analyzed with HPLC.

General Procedure for Asymmetric Dihydroxylation. A 250 mL three-necked flask equipped with a magnetic stirring bar and a pH electrode was charged with 10 mmol of olefin, 5.5 g of NaCl, 78 mg (0.1 mmol) of ligand ($(DHQD)_2PHAL$), 14.7 mg (0.04 mmol) of $K_2OsO_4\cdot 2H_2O$, and 100 mL of $H_2O/^tBuOH$ (1:1) solution (or 100 mL of H_2O/methyl ethyl ketone (1:1) solution, Table 1, entry 8). The biphasic mixture was cooled in an ice/water bath to 0−1 °C. To the mixture was added 0.1 mL of 1 M $NaClO_2$ solution via syringe. pH was adjusted to about 11.8 with 0.5 M NaOH. In total, 5.0 mL (5 mmol) of 1 M $NaClO_2$ solution was added portionwise after the pale violet color of Os^{VI} appeared in the water layer or the pH dropped to the same level as before the addition of the oxidant. The reaction mixture was transferred to a separatory funnel, and 100 mL of EtOAc was added. The organic layer was extracted with 50 mL of 1 M HCl, 50 mL of saturated Na_2CO_3, and 50 mL of brine. The organic layer was dried with Na_2SO_4, filtered, and evaporated in a rotary evaporator.

1-Phenylethane-1,2-diol. The crude product was purified by flash chromatography using a 2:1 solution of EtOAc/*n*-hexane as the eluent: yield 1.01 g (73%); mp 64−65 °C (lit.[10a] 66−67 °C); ^1H NMR (200 MHz, *d*-acetone) δ 7.30 (m, 5H), 4.72 (ddd, J = 4, 4, 4 Hz, 1H), 4.32 (d, J = 4 Hz, 1H), 3.82 (dd, J = 7, 6 Hz, 1H), 3.57 (m, 2H); HRMS m/z (M +Na) found 161.0570, calcd 161.0578 ($C_8H_{10}O_2Na$).

1,2-Diphenylethane-1,2-diol. The crude product was purified by recrystallization from toluene: yield 1.35 g (63%); mp 139−140 °C (lit.[10b] 139−140 °C); ^1H NMR (200 MHz, *d*-acetone) δ 7.17 (br, 10H), 4.62 (br, 4H); HRMS m/z (M + Na) found 237.0869, calcd 237.0891 ($C_{14}H_{14}O_2Na$).

2-Phenylpropane-1,2-diol. The crude product was purified by flash chromatography using a 2:1 solution of EtOAc/*n*-hexane as the eluent. The yield was 1.11 g (73%). An analytical sample of the product was obtained crystallization from EtOAc: mp 43−45 °C (EtOAc) (lit.[10c] 44−45 °C); ^1H NMR (200 MHz, *d*-acetone) δ 7.50 (br, 2H), 7.25 (br, 3H), 3.99 (s, 1H), 3.81 (t, J = 6 Hz, 1H), 3.58 (d, J = 6 Hz, 2H), 1.48 (s, 3H); HRMS m/z (M + Na) found 175.0728, calcd 175.0735 ($C_9H_{12}O_2Na$).

Hexane-1,2-diol. The crude product was purified by flash chromatography using a 2:1 solution of EtOAc/*n*-hexane as the

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(7) a_0 = initial concentration of styrene, a_t = concentration of styrene at a given time.

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eluent, affording a colorless oily residue: yield 0.95 g (80%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.68 (br, 2H), 3.43 (m, 1H), 2.11 (d, $J = 4$ Hz, 1H), 2.01 (dd, $J = 12$, 6 Hz, 1H), 1.4 (br, 6H), 0.92 (t, $J = 7$ Hz, 3H); HRMS m/z (M + Na) found 141.0903, calcd 141.0891 ($C_6H_{14}O_2Na$).

Indane-1,2-diol. The crude product was purified by flash chromatography using a 2:1 solution of EtOAc/*n*-hexane as the eluent: yield 0.98 g (65%); mp 92−93 °C (lit.[10d] 92−93 °C); ^{1}H NMR (200 MHz, *d*-acetone) δ 7.28 (m, 4H), 4.92 (dd, $J = 6$, 6 Hz, 1H), 4.42 (m, 1H), 4.21 (d, $J = 7$ Hz, 1H), 3.85 (d, $J = 5$ Hz), 3.20 (dd, $J = 16$, 5 Hz, 1H), 2.85 (dd, $J = 16$, 4 Hz, 1H); HRMS m/z (M + Na) found 173.0597, calcd 173.0578 ($C_9H_{10}O_2$-Na).

Hexadecan-1,2-diol. The crude product was purified by recrystallization from $CHCl_3$: yield 1.9 g (77%); mp 75−78 °C (lit.[10e] 80 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.70 (br, 2H), 3.43 (br, 1H), 2.00 (d, $J = 4$ Hz, 1H), 1.86 (t, $J = 5$ Hz, 1H), 1.45 (br, 2H), 1.28 (br, 24H), 0.89 (t, $J = 6$ Hz, 3H); HRMS m/z (M + Na) found 281.2463, calcd 281.2457 ($C_{16}H_{34}O_2Na$).

1-Methyl Cyclohexane-1,2-diol. The crude product was purified by flash chromatography using a 2:1 solution of EtOAc/*n*-hexane as the eluent. The yield was 0.98 g (75%). An analytical sample of the product was obtained crystallization from EtOAc: mp. 66−67 °C (EtOAc) (lit.[10f] 67−68 °C); ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.41 (m, 1H), 1.90−1.28 (br, 11H), 1.25 (s, 3H); HRMS m/z (M + Na) found 153.0918, calcd 153.0891 ($C_7H_{14}O_2Na$).

Methyl 2,3-Dihydroxy-3-phenylpropanoate. The crude product was purified by recrystallization from solution of EtOAc/*n*-hexane: yield 1.41 g (72%); mp 83−85 °C (lit.[10g] 85−85.5 °C); ^{1}H NMR (200 MHz, *d*-acetone) δ 7.35 (m, 5H), 5.00 (dd, $J = 6$, 3 Hz, 1H), 4.59 (d, $J = 6$ Hz, 1H), 4.28 (dd, $J = 8$, 3 Hz), 4.15 (d, $J = 8$ Hz, 1H), 3.69 (s, 3H); HRMS m/z (M + Na) found 219.0628, calcd 219.0633 ($C_{10}H_{12}O_4Na$).

Supporting Information Available: Kinetics of different dihydroxylations of styrene and ^{1}H NMR spectra of the products and ^{1}H NMR spectra of the (Mosher's) esters of the products. This material is available free of charge via the Internet at http://pubs.acs.org.

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