In Situ Generation of NMO in the Osmium-Catalyzed Dihydroxylation of Olefins. Stereoselective Oxidation of Olefins to Cis Diols by *m*-CPBA

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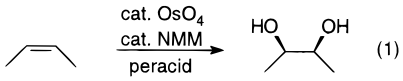
Introduction

There are numerous examples of mild transition metal-catalyzed oxidations of organic substrates, the osmium-catalyzed dihydroxylation of olefins being an excellent example of a stereospecific catalytic reaction.[1] The catalytic cis-selective oxidation of olefins to vicinal diols has been known since 1912 when osmium tetroxide was used in combination with stoichiometric amounts of metal chlorates.[2,3] In 1936 Milas found that hydrogen peroxide can be employed as the terminal oxidant in combination with catalytic amounts of osmium tetroxide.[4−6] The stoichiometric reaction was studied by Criegee who showed that an intermediate osmate ester is formed, which gives the diol on hydrolysis.[7,8]

In the presence of metal chlorates or hydrogen peroxide, overoxidation is a commonly encountered problem resulting in nonselective reactions. Due to these problems associated with the catalytic procedures, the stoichiometric method was for a long time the most reliable way of transforming olefins to *cis*-1,2-diols. However, since the use of large amounts of the osmium reagent is associated with drawbacks such as high toxicity and cost of the metal, the search for more efficient catalytic procedures was continued. Some improvement was obtained with the use of *tert*-butyl hydroperoxide (TBHP) as the terminal oxidizing agent under alkaline conditions.[9,10] A major breakthrough was realized in 1976 when VanRheenen demonstrated that *N*-methylmorpholine *N*-oxide (NMO) is a mild and efficient oxidant, which can be used in the osmium-catalyzed dihydroxylation of olefins without giving rise to overoxidation of sensitive substrates (the Upjohn procedure).[11,12] This catalytic stereoselective oxidation has been further developed by Sharpless into a highly efficient enantioselective process for transformation of olefins into cis diols.[13−15] In reactions employing NMO as the stoichiometric oxidant, the corresponding amine, *N*-methylmorpholine (NMM), is formed.

We have for a long time been interested in the in situ generation of oxidants in transition metal-catalyzed reactions.[16−23] One objective has been to develop mild procedures where the in situ generation is carried out with the aid of a simple oxidant such as molecular oxygen or hydrogen peroxide. It seemed highly attractive to regenerate NMO in the osmium-catalyzed dihydroxylation instead of using the amine *N*-oxide as a stoichiometric reagent. This would be possible if one could find a way for selective oxidation of the amine NMM in the presence of other components present in the reaction media.

Since amines are known to be oxidized easily to their corresponding *N*-oxides by *m*-CPBA,[24] we decided to use the latter in model studies of in situ generation of NMO (Scheme 1). We now report on an osmium- and NMM-catalyzed dihydroxylation in which NMM is reoxidized by *m*-CPBA (eq 1). To the best of our knowledge, this is the first example of in situ generation of NMO in the osmium-catalyzed dihydroxylation of olefins.



(1)

Results and Discussion

It is known from previous studies that the use of certain oxidants such as hydrogen peroxide and *tert*-butyl hydroperoxide often results in overoxidized products, e.g. α-hydroxyketones or compounds derived from C−C bond cleavage (vide supra).[4,6,9,10] The reported systems all employ the peroxides as direct oxidants for osmium(VI), which means that they interact with the intermediate osmate esters. The use of peracids as direct oxidizing agents would most likely result in similar problems.

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(1) Schröder, M. *Chem. Rev.* **1980**, *80*, 187.
(2) Hofmann, K. A. *Chem. Ber.* **1912**, *45*, 3329.
(3) Hofmann, K. A.; Ehrhart, O.; Schneider, O. *Chem. Ber.* **1913**, *46*, 1657.
(4) Milas, N. A.; Sussman, S. *J. Am. Chem. Soc.* **1936**, *58*, 1302.
(5) Milas, N. A.; Sussman, S. *J. Am. Chem. Soc.* **1937**, *59*, 2345.
(6) Milas, N. A.; Trepagnier, J. H.; Nolan, J. T.; Iliopulos, M. I. *J. Am. Chem. Soc.* **1959**, *81*, 4730.
(7) Criegee, R. *Justus Liebigs Ann. Chem.* **1936**, *522*, 75.
(8) Criegee, R.; Marchand, B.; Wannowius, H. *Justus Liebigs Ann. Chem.* **1942**, *550*, 99.
(9) Sharpless, K. B.; Akashi, K. *J. Am. Chem. Soc.* **1976**, *98*, 1986.
(10) Akashi, K.; Palermo, R. E.; Sharpless, K. B. *J. Org. Chem.* **1978**, *43*, 2063.
(11) VanRheenen, V.; Kelly, R. C.; Cha, D. Y. *Tetrahedron Lett.* **1976**, 1973.
(12) VanRheenen, V.; Cha, D. Y.; Hartley, W. M. *Organic Synthethes*; Wiley: New York, 1988; Collect. Vol. VI, p 342.
(13) Jacobsen, E. N.; Markó, I.; Mungall, W. S.; Schröder, G.; Sharpless, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 1968.
(14) Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483.
(15) In 1990, it was discovered that potassium ferricyanide could be used as a reoxidant for osmium(VI) (see ref 29). Furthermore, it was realized that this salt was superior to NMO in the asymmetric dihydroxylation of olefins giving diols with higher ee's: Kwong, H.-L.; Sorato, C.; Ogino, Y.; Chen, H.; Sharpless, K. B. *Tetrahedron Lett.* **1990**, *31*, 2999.
(16) Bäckvall, J.-E.; Hopkins, R. B.; Grennberg, H.; Mader, M. M.; Awasthi, A. K. *J. Am. Chem. Soc.* **1990**, *112*, 5160.
(17) Grennberg, H.; Gogoll, A.; Bäckvall, J.-E. *J. Org. Chem.* **1991**, *56*, 588.
(18) Bäckvall, J.-E.; Chowdhury, R. L.; Karlsson, U. *J. Chem. Soc., Chem. Commun.* **1991**, 473.
(19) Grennberg, H.; Bäckvall, J.-E. *J. Chem. Soc., Chem. Commun.* **1993**, 1331.
(20) Grennberg, H.; Faizon, S.; Bäckvall, J.-E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 263.
(21) Wang, G.-Z.; Andreasson, U.; Bäckvall, J.-E. *J. Chem. Soc., Chem. Commun.* **1994**, 1037.
(22) Grennberg, H.; Bergstad, K.; Bäckvall, J.-E. *J. Mol. Catal. A* **1996**, *113*, 355.
(23) Bergstad, K.; Grennberg, H.; Bäckvall, J.-E. *Organometallics* **1998**, *17*, 45.
(24) Craig, J. C.; Purushothaman, K. K. *J. Org. Chem.* **1970**, *35*, 1721.

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Scheme 1. In Situ Generation of NMO in the Osmium-Catalyzed Dihydroxylation of Olefins

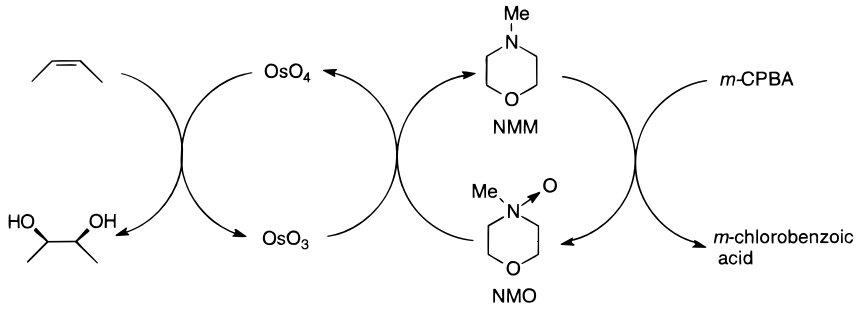


Table 1. Cis-Selective Dihydroxylation of *trans*-5-Decene Using *m*-CPBA as Oxidant[a]

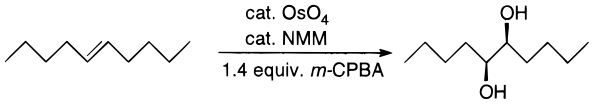
entry	oxidant[b]	NMM (equiv)	additives[c]	reacn time, h[d]	yield, %[e]
1	1.2 equiv of NMO			8	95
2	1.4 equiv of *m*-CPBA			23	13
3	1.1 equiv of *m*-CPBA	1.0		28	75
4	1.4 equiv of *m*-CPBA	0.5		22	67
5	1.4 equiv of *m*-CPBA	0.25		7.5	37
6	1.4 equiv of *m*-CPBA	0.5	1.3 equiv of TEAA	7	95
7	1.4 equiv of *m*-CPBA	0.25	1.3 equiv of TEAA	7	90[f]
8	1.4 equiv of *m*-CPBA	0.20	1.3 equiv of TEAA	24	80
9	1.4 equiv of *m*-CPBA	0.10	1.3 equiv of TEAA	24	71
10	1.4 equiv of *m*-CPBA	0.05	1.3 equiv of TEAA	24	63[f]
11	1.4 equiv of *m*-CPBA		1.3 equiv of TEAA	24	47[f]

[a] *trans*-5-Decene (1 mmol) was oxidized at room temperature employing 1 mol % OsO_4 as catalyst in combination with an oxidant in stoichiometric amounts. A 3:1 mixture of acetone/ H_2O was used as solvent. [b] The *m*-CPBA oxidant was added over 4−5 h, except in entry 3 where NMM is present in equimolar amounts to the peracid. [c] Tetraethylammonium acetate (TEAA). [d] The reactions were followed by GC using *n*-dodecane as internal standard. Reactions which had reached >90% conversion after a 7 h reaction time were quenched at this point. Reactions showing 75−90% conversion after 7 h were stirred for an additional 17 h to ensure complete oxidation (except for the reaction reported in entry 5, which was quenched after 7.5 h to make a direct comparison with entry 7 possible). [e] Isolated yields of cis diol after flash chromatography. The cis stereochemistry of the product was verified by ^{1}H NMR. [f] GC analysis showed ≥ 99% of the cis isomer.

However, trapping of the reactive nonselective oxidant by NMM under the formation of NMO could possibly be a way of achieving a selective osmium-catalyzed dihydroxylation of olefins (Scheme 1).

The oxidation of amines to amine *N*-oxides by peracids is known to occur readily.[24] However, in the presence of an olefinic substrate, epoxidation could be a competing reaction, which would result in contamination of the desired syn products by either epoxides or anti 1,2-diols. It was therefore of primary interest to investigate the kinetics of these two competing oxidations. The rates of the two reactions were studied by ^{1}H NMR spectroscopy. NMM was found to be completely oxidized within less than 5 min,[25] whereas epoxidation of *trans*-5-decene required almost 3 h to reach 80% conversion. Product contamination due to epoxidation of the substrate therefore seemed to be a minor problem. These results encouraged us to further study the in situ formation of NMO in the osmium-catalyzed dihydroxylation of olefins using a peracid as the terminal oxidant.

The cis dihydroxylation of *trans*-5-decene was studied as a model reaction employing *m*-CPBA as the stoichiometric oxidant in combination with 1 mol % of OsO_4 and varying amounts of NMM (eq 2, Table 1). In a control experiment where the standard conditions for cis-selective dihydroxylation of olefins were used (i.e., stoichiometric NMO), it was demonstrated that *trans*-5-decene is a suitable substrate in this model study (entry 1).[11,12] Another control reaction showed that *m*-CPBA is not a suitable oxidant for direct oxidation of osmium(VI) formed in the reaction, since diol **1** was only formed in 13% yield (entry 2).[26]



(2)

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Since oxidation of the amine NMM to NMO by *m*-CPBA is a fast reaction (vide supra), we expected that when NMO was replaced by 1 equiv of NMM together with an excess of the peracid the reaction would become almost comparable to that reported in entry 1. The cis diol was formed as expected but somewhat surprisingly there was a substantial drop in yield (75% vs 95%; entries 3 and 1). A possible explanation for this result can be the difference in pH between the two reactions, since in the reaction reported in entry 3 there is 1 equiv of acid present in addition to the stoichiometric amount of NMM (vide infra).[1,9,10,27]

A procedure for in situ generation of NMO in the osmium-catalyzed oxidation would be much more attractive if the amine could be used in catalytic amounts. However, when the amount of NMM was decreased to 50 or 25 mol %, even lower yields were observed (67% and 37%, entries 4 and 5, respectively).[28]

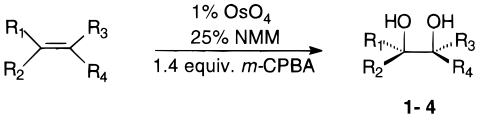
(25) The first ^{1}H NMR spectra was taken after 5 min due to practical reasons such as the time required for locking and shimming.

(26) A control experiment showed that a diol, the (1*RS*,2*RS*)-1,2-diphenyl-1,2-ethanediol (**2**), was stable under these reaction conditions. The overoxidation products can thus be considered to be formed during the reactions, and not in subsequent oxidations of the diols.

(27) Lohray, B. B.; Bhushan, V.; Kumar, R. K. *J. Org. Chem.* **1994**, *59*, 1375.

(28) The peracid was added slowly in order to avoid overoxidation.

Scheme 2. Peracid-Mediated Cis Dihydroxylation of Olefins



	R_1	R_2	R_3	R_4	
trans	H	C_4H_9	C_4H_9	H	**1**; 90 %; ≥ 99 % cis addition
	H	Ph	Ph	H	**2**; 83 %; ≥ 99 % cis addition
	H	Ph	Me	H	**3**; 76 %; ≥ 99 % cis addition
cis	Ph	H	Ph	H	**4**; 76 %; ≥ 99 % cis addition

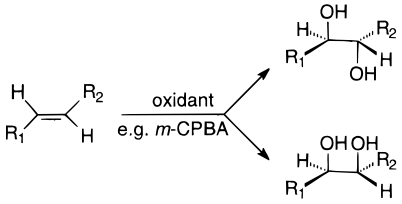
The slow step in the osmium cycle is most likely hydrolysis of the intermediate osmate ester.[9,10,29] The lower pH in the reactions involving the in situ generation of NMO may lead to slower cleavage of this ester, resulting in less efficient reactions. The hydrolysis step is described in the literature to be facilitated by addition of salts such as tetraethylammonium acetate (TEAA).[9,10,27,30] We therefore decided to study the influence of this salt on the NMM-catalyzed dihydroxylation of *trans*-5-decene based on *m*-CPBA as the terminal oxidant. Addition of TEAA to the reaction mixture did indeed result in a major improvement of the reaction with 50 mol % of NMM, giving cis diol **1** in an excellent yield (95%, entry 6).[31] Having found conditions for an efficient cis-selective dihydroxylation via in situ generation of NMO from catalytic amounts of NMM, the apparent next step was to lower the amount of amine. With 25 mol % of NMM there was still a high yield (90%, entry 7). With less than 25 mol % of NMM, the yields dropped (entries 8−10).

Interestingly, a control experiment showed that in the presence of TEAA the use of *m*-CPBA as a direct oxidant for osmium(VI) (without NMM) gave the diol in 47% yield (entry 11). This should be compared to the 13% obtained in the absence of TEAA (entry 2).

The conditions for the osmium-catalyzed cis-selective dihydroxylation employing a peracid as the terminal oxidant were used for oxidation of several other olefins. All acyclic substrates, including both trans and cis olefins, gave the 1,2-diols in good yields in highly stereospecific cis additions (Scheme 2).

The oxidation of cyclic olefins turned out to be somewhat more troublesome, giving the desired vicinal diols in only moderate yields. A possible reason for this is that the cyclic osmate esters of these diols may be more stable toward hydrolysis than those of the other diols.[32] Thus,

Scheme 3. Stereoselective Preparation of Cis and Trans Diols Using *m*-CPBA as Oxidant



oxidation of 1-methyl-1-cyclohexene and 1,2-dihydronaphthalene gave cis diols **5** and **6** in 51% and 46% isolated yields, respectively. In the latter case, 34% of the corresponding α-hydroxyketone was formed as the major byproduct.[33,34]

5; 51 %; ≥ 99 % cis addition **6**; 46 %; ≥ 98 % cis addition

It is interesting to note that a given olefin can now be converted to either a cis or trans diol in reactions employing the same oxidant (*m*-CPBA). Noncatalyzed oxidation of the substrate followed by aqueous ring opening of an intermediate epoxide[35−39] gives the trans diol, whereas the catalytic oxidation (catalytic OsO_4, catalytic NMM) produces the cis diol (Scheme 3).[40]

To demonstrate that *m*-CPBA can be used as an efficient oxidant in stereoselective formation of both cis and trans diols from olefins, the trans diol **7** was synthesized from *trans*-5-decene via epoxidation of the olefin by *m*-CPBA followed by acid-catalyzed ring opening[41] of the isolated epoxide (eq 3). The diastereomeric syn diol **1** was obtained in excellent yields via cis-selective oxidation of the same substrate by *m*-CPBA according to the procedure employing catalytic amounts of OsO_4 and NMM (Table 1, entry 7).

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

(30) The rate increase observed in the presence of this salt is sometimes referred to as an effect of an added base, and sometimes as a result of addition of an extra nucleophile. See refs 9, 10, and 27.

(31) In a control experiment TEAA was replaced by K_2CO_3 (1.3 equiv). Since the diol **1** was formed in 72% isolated yield, compared to the 37% in the reaction reported in Table 1, entry 5, it can be concluded that the presence of base is necessary for efficient reactions. Somewhat surprisingly the addition of $MeSO_2NH_2$, which is commonly used for similar purposes, did not have any effect under the reaction conditions employed in this work.

(32) Tri- and tetrasubstituted olefins are known to react only slowly in the osmium-catalyzed dihydroxylation due to a slow hydrolysis of the osmate ester. Moreover, the osmate ester from cholesterol is extremely unreactive toward hydrolysis due to steric reasons and has been used as a model substrate to test the efficiency when modified procedures for the osmium-catalyzed dihydroxylation have been developed. See refs 1, 9, and 10.

(33) The spectroscopic data of the α-hydroxyketone are in accordance with previously reported data. See: Guertin, K. R.; Chan, T.-H. *Tetrahedron Lett.* **1991**, *32*, 715.

(34) Sharpless has proposed that there may be two major pathways operating in the dihydroxylation of olefins, a fast primary cycle and a slow secondary cycle. One way of avoiding the secondary cycle is via slow addition of the olefin (see: Wai, J. S. M.; Marko, I.; Svendsen, J. S. Finn, M. G. Jacobsen, E. N. Sharpless, K B. *J. Am. Chem. Soc.* **1989**, *111*, 1123). Lohray describes the second cycle as the one giving rise to overoxidation problems in the presence of peroxides as terminal oxidants (see ref 27). In an attempt to increase the ratio of diol/α-hydoxyketone formed in the oxidation of 1,2-dihydronaphthalene, the olefin was added slowly. However, no improvement was observed in the oxidation of this seemingly sensitive substrate.

(35) Swern, D. *Org. React.* **1953**, *7*, 378.

(36) Gorzynski Smith, J. *Synthesis* **1984**, 629.

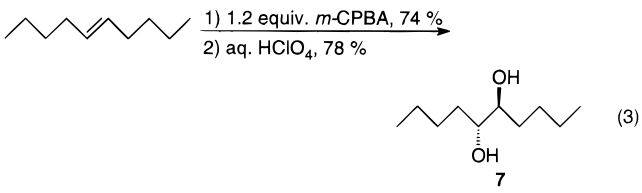
(37) Rao, A. S. *Tetrahedron* **1983**, *39*, 2323.

(38) Fringuelli, F.; Germani, R.; Pizzo, F.; Savelli, G. *Synth. Commun.* **1989**, *19*, 1939.

(39) Trans diols can also be formed in base-catalyzed ring opening of epoxides. However, these reactions often require harsher conditions compared to the mild acid-catalyzed epoxide opening. See ref 38.

(40) There are some procedures reported in the literature for stereoselective formation of either cis or trans diols from olefins by the use of the same reagents. In the Prévost reaction (dry conditions) a trans diol will be formed, whereas in the Woodward reaction (wet conditions) the product is a diol with cis stereochemistry. See the following references. Wilson, C. V. *Org. React.* **1957**, *9*, 332. Haines, A. H. Addition Reactions with Formation of Carbon−Oxygen Bonds: (iii) Glycol Forming Reactions in *Comprehensive Organic Chemistry*, Vol. 7; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, U.K., 1991;, pp 437−448.

(41) Fieser, L. F.; Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1967, Vol. 1, p 796.



(3)

Conclusion

From an economical and environmental point of view, *m*-CPBA may not be of any major advantage over stoichiometric amounts of NMO. However, the main purpose with this paper has been to demonstrate the principle that NMO can be regenerated in situ in the osmium-catalyzed dihydroxylation rather than to develop a new synthetic procedure for dihydroxylation. A major problem in realizing such a process has been that the rate of the cleavage of the osmate ester decreases when catalytic amounts of NMM/NMO are employed. This problem was solved by addition of tetraethylammonium acetate. One advantage with the in situ generation of NMO is that specifically designed *N*-oxides can be used, which should be synthetically useful. We will now try to extend the in situ generation of NMO in the osmium-catalyzed dihydroxylation of olefins to other oxidants such as hydrogen peroxide and molecular oxygen.

Experimental Section

General Procedures. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100.6 MHz, or 200 and 50.3 MHz, respectively. Chemical shifts (δ) are reported in ppm, using residual solvent as internal standard. Most reagents were purchased from Lancaster except for *N*-methylmorpholine (Fluka), *N*-methylmorpholine *N*-oxide (Aldrich), *trans*-β-methylstyrene (Aldrich), *m*-CBPA (50−60%, Aldrich), and 1-methyl-1-cyclohexene (TCI Kasei). OsO_4 was purchased as a 2.5 wt % solution in ^{t}BuOH (Aldrich). Tetraethylammonium acetate (TEAA) was acquired from Aldrich (99%) or Lancaster (50% aqueous solution). Commercial chemicals were used as received without further purification. The products were purified by chromatography on silica gel (Merck silica gel 60, 230−400 mesh). Progress of the reaction was followed by TLC on Merck silica gel 60 F_{254} plates, or by GC using a SE 54 column (25m, 250 μm) with *n*-dodecane as internal standard. A syringe pump Sage model 355 was used for slow additions. For all substrates used, cis diols were prepared as reference compounds by the osmium-catalyzed dihydroxylation using NMO as stoichiometric oxidant (see Supporting Information for details). Trans diols were synthesized via epoxidation of the olefins followed by acid- or base-catalyzed opening of the epoxides (see Supporting Information for details). All the trans and cis diols separated on either ^{1}H NMR (all prepared diols) or GC (DBWAX-5 column, 30 m, 320 μm; 5,6-decanediol and 1-methyl-1,2-cyclohexanediol).

General Procedure for Preparation of Cis Diols from Olefins with In Situ Formation of NMO. (5*RS*,6*RS*)-5,6-Decanediol (1). *trans*-5-Decene (190 μL, 1.00 mmol) was dissolved in acetone (2.3 mL). To this mixture were added tetraethylammonium acetate (0.7 g, 50% aqueous solution, 1.3 mmol), *N*-methylmorpholine (28 μL, 0.25 mmol), and OsO_4 (120 μL, 2.5 wt % in ^{t}BuOH, 0.01 mmol). A solution of *m*-CPBA (480 mg, 50−60%, ca. 1.4 mmol) in acetone (1.5 mL) and H_2O (0.5 mL) was added slowly over 4 h. The mixture was stirred for an additional 3 h and then quenched by addition of $Na_2S_2O_4$ (0.8 g) and magnesium silicate (0.5 g) in H_2O (0.8 mL). After 2 h of stirring at room temperature, the mixture was filtered over Celite, and the Celite was subsequently rinsed with EtOAc (75 mL). The aqueous phase was extracted with EtOAc (4 × 12 mL), and the combined organic phases were washed with 2 M NaOH (2 × 10 mL). The organic phase was dried ($MgSO_4$) and concentrated in a vacuum to give the crude diol **1**. The crude product was purified by column chromatography (50:50 pentane/ Et_2O) to yield **1** as a white solid (157 mg, 90%, ≥99% cis). NMR data were in accordance with previously reported data.[42]

(*1RS,2RS*)-1,2-Diphenyl-1,2-Ethanediol (2). The same procedure as above afforded **2** as a white solid (177 mg, 83%, ≥ 99% cis). NMR data were in accordance with previously reported data.[43,44]

(1*RS*,2*RS*)-1-Phenyl-1,2-propanediol (3). The same procedure as above, except for the use of solid tetraethylammonium acetate (0.53 g, 2.03 mmol), afforded **3** as a white solid (116 mg, 76%, ≥ 99% cis). NMR data were in accordance with previously reported data.[45]

(1*RS*,2*SR*)-1,2-Diphenyl-1,2-ethanediol (*meso*) (4). The same procedure as above afforded **4** as a white solid (162 mg, 76%, ≥ 99% cis). NMR data were in accordance with previously reported data.[46]

***cis*-1-Methyl-1,2-cyclohexanediol (5).** The same procedure as above, except for a 15 h reaction time after complete addition of the oxidant and saturation of the aqueous phase with NaCl (s) before extraction with EtOAc, afforded **5** as a white solid (66 mg, 51%, ≥99% cis). NMR data were in accordance with previously reported data.[47]

***cis*-1,2,3,4-Tetrahydro-1,2-naphthalenediol (6).** A solution of *m*-CPBA (480 mg, 50−60%, ca. 1.4 mmol) in acetone (1.5 mL) and H_2O (0.5 mL) was added slowly over 12 h to a mixture of 1,2-dihydronaphthalene (130 μL, 1.00 mmol), tetraethylammonium acetate (0.53 g, 2.03 mmol), *N*-methylmorpholine (28 μL, 0.25 mmol), OsO_4 (120 μL, 2.5 wt % in ^{t}BuOH, 0.01 mmol), acetone (2.3 mL), and H_2O (0.7 mL). The mixture was stirred for an additional 12 h. Purification of the crude product (gradient 50:50 pentane/ Et_2O to 100% Et_2O) gave **6** as a white solid (75 mg, 46%, ≥98% cis). NMR data were in accordance with previously reported data.[48]

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Supporting Information Available: Experimental details for synthesis of cis diols **1**−**6** via a general procedure employing NMO as stoichiometric oxidant, synthesis of *trans*-5-decene oxide, *trans*-stilbene oxide, and 1,2-dihydronaphthalene oxide via epoxidation of the corresponding olefins, and synthesis of *trans*-1,2-diols from *trans*-5-decene (i.e. **7**), *trans*-stilbene (i.e. **4**), 1,2-dihydronaphthalene, 1-methyl-1-cyclohexene, and *trans*-β-methylstyrene via acid- or base-catalyzed opening of the corresponding epoxides. This material is available free of charge via the Internet at http://pubs.acs.org.

JO981945Q

(42) Tanner, D.; Birgersson, C.; Gogoll, A.; Luthman, K. *Tetrahedron* **1994**, *50*, 9797.
(43) Wang, Z.-M.; Sharpless, K. B. *J. Org. Chem.* **1994**, *59*, 8302.
(44) Nymann, K.; Jensen, L.; Svendsen, J. S. *Acta Chem. Scand.* **1996**, *50*, 832.
(45) Pedragosa-Moreau, S.; Archelas, A.; Furstoss, R. *Tetrahedron* **1996**, *52*, 4593.
(46) Corriu, R. J. P.; Lanneau, G. F.; Yu, Z. *Tetrahedron* **1993**, *49*, 9019.
(47) Tamura, Y.; Annoura, H.; Kondo, H.; Fuji, M.; Yoshida, T.; Fujioka, H. *Chem. Pharm. Bull.* **1997**, *35*, 22305.
(48) Naemura, K.; Wakebe, T.; Hirose, K.; Tobe, Y. *Tetrahedron: Asymmetry* **1997**, *8*, 2585.