Allylic CH Oxidation versus Epoxidation of 2-Cyclohexenols, Catalyzed by Chromium- and Manganese-Substituted Polyoxometalates and Salen Complexes

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2-Cyclohexenol (**1**) is oxidized chemoselectively to 2-cyclohexenone (**2a**) by the α-Keggin chromium-substituted polyoxometalate (POM) **Ia** as the catalyst and iodosobenzene as the oxygen source. For the chromium(salen) catalyst **IIa** the same chemoselectivity in favor of allylic CH oxidation is observed. The manganese-substituted POM **Ib** and the manganese(salen) complex **IIb**, however, afford appreciable amounts of the epoxy alcohol **2b**. For the stereolabeled 5-*tert*-butyl-2-cyclohexenols **5**, the diastereoselectivity of the epoxidation was appreciable (*syn:anti* 82:18) in the case of the manganese(salen) complex **IIb** with the *cis* isomer, while the manganese-substituted POM **Ib** exhibited no *syn* versus *anti* π-facial differentiation for the *cis* or *trans* diastereomer of the cyclohexenol **5**. The observed *syn* hydroxy directivity for the manganese(salen) complex **IIb** is rationalized in terms of optimal hydrogen bonding between the Mn^V oxo complex **IIb** and the *trans* diastereomer of the allylic alcohol substrate **5**.

Introduction

The selective and catalytic oxyfunctionalization is a pivotal reaction in organic chemistry that has received much attention over the years.[1] Thus, there has been an intensive search for versatile and selective reagents with catalytic activity. To assess the general scope and efficacy of a catalytic oxidation system, the catalyst, the substrate and the oxygen source need to be optimized.

Transition metal complexes can serve as excellent catalysts for oxidation provided they are equipped with an appropriate organic ligand. A prominent example is the Jacobsen[2]−Katsuki[3] chiral manganese(salen) complex, which catalyzes the asymmetric epoxidation of a great variety of unfunctionalized olefins. In this context, we have shown previously that manganese(salen) complexes epoxidize acyclic allylic alcohols chemo-, regio-, and diastereoselectively.[4] Chromium(salen) complexes, however, catalyze chemoselectively the CH oxidation of allylic alcohols to carbonyl products.[5]

Alternatively, polyoxometalates (POMs) have received much attention in oxidation chemistry. These materials are made up of an oxidatively resistant inorganic framework of transition-metal oxides, primarily those of molybdenum and tungsten; for oxidation purposes some of the framework metals are substituted by an oxidatively active metal.[6] In 1986, it was demonstrated for the first time that such transition-metal-substituted polyoxometalates (TMSP) efficiently catalyze the oxyfunctionalization of organic substrates.[7] Since then, numerous catalytic oxidations by POMs have been discovered, although mostly with alkenes as substrates.[6]

We report herein on the catalytic oxidation of 2-cyclohexenol (**1**) by chromium- and manganese-substituted α-Keggin-type polyoxometalates **I** and by their respective salen complexes **II** (Scheme 1), with iodosobenzene and hydrogen peroxide as oxygen sources. 4-Phenylpyridine *N*-oxide (PPNO) was added for the salen complexes as it has been reported that this donor ligand enhances the rate of the Cr(salen)-catalyzed oxidation,[8] while for the Mn(salen) complex cleaner oxygen-transfer reactions are observed by suppressing the radical-type redox chemistry.[9] It was of interest to assess the chemoselectivity of these metal catalysts, i.e., allylic CH oxidation versus epoxidation. The conformationally fixed *cis* and *trans* diastereomers of the allylic alcohol 5-*tert*-butyl-2-cyclohexenol (**5**) were chosen to acquire mechanistic information on the oxygen-transfer process. Comparison of the *syn* versus *anti* diastereoselectivity with that of the established oxidants MTO/UHP,[10] *m*-CPBA[11] and DMD,[12] provides valuable data on the transition-state geometry of this oxidation process.

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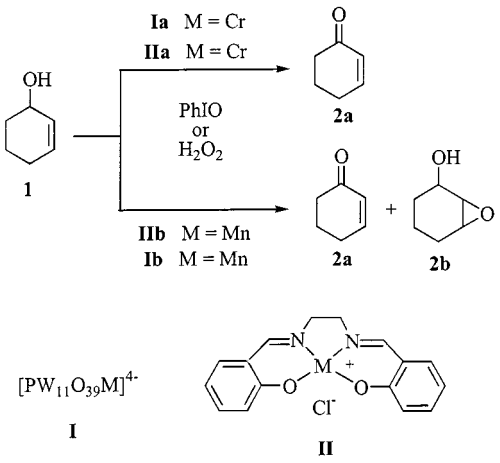
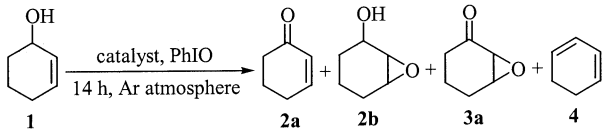


Scheme 1

Results

The oxidations were conducted under an argon atmosphere for 14 h with a catalyst **I**/substrate/PhIO ratio of 0.04:1.00:1.50 in CH_3CN and a catalyst **II**/PPNO/substrate/PhIO ratio of 0.14:0.30:1.00:1.50 in CH_2Cl_2. General procedures are given in the Exp. Sect. (see also Supporting Information); the quantitative results for both catalysts, the POMs **I** and the metal(salen) complexes **II,** are summarized in Table 1. The chromium-substituted polyoxometalate **Ia** and the chromium(salen) complex **IIa** (Table 1, entries 1, 2, 4 and 5) afforded the enone **2a** with excellent chemoselectivities (> 95%). The manganese complexes, however, gave the enone **2a** (major oxidation product), the epoxy alcohol **2b** and the epoxy ketone **3a** (entries 3 and 6).

Table 1. Catalytic oxidation of 2-cyclohexenol (**1**) by chromium- and manganese-substituted polyoxometalates **I** and their salen complexes **II** with iodosobenzene as the oxygen source



Entry	Catalyst		Convn. (%)[a]	TON[a] [b]	Product distribution (%)[a] [c] 2a	2b	3a	4
1[d]	Cr-POM	**Ia**	95	21	> 95	–	–	–
2[e]	Cr-POM	**Ia**	91	29	> 95	–	–	–
3[f]	Mn-POM	**Ib**	94	19	52	25	21	2
4[g]	Cr-salen	**IIa**	95	6	> 95	–	–	–
5[h]	Cr-salen	**IIa**	90	13	> 95	–	–	–
6[g]	Mn-salen	**IIb**	93	5	60	36	4	–

[a] Determined by GC analysis with an internal standard (cyclopentanone); error ± 5% of the given values; mass balances were > 85%. [b] Turnover numbers = mol of oxidation products/mol of catalyst. [c] Product distribution normalized to 100%. [d] Reaction conditions: 0.04 equiv. of the catalyst, 2 equiv. of PhIO, in CH_3CN at 50 °C. [e] Reaction conditions: 0.03 equiv. of the catalyst, 2 equiv. of PhIO, in CH_3CN at 50 °C. [f] Reaction conditions: 0.04 equiv. of the catalyst, 2 equiv. of PhIO, in CH_3CN at 24 °C. [g] Reaction conditions: 0.3 equiv. of 4-phenylpyridine *N*-oxide (PPNO), 0.14 equiv. of the catalyst, 1.5 equiv. of PhIO, in CH_2Cl_2 at 24 °C. [h] Reaction conditions: 0.3 equiv. of 4-phenylpyridine *N*-oxide (PPNO), 0.07 equiv. of the catalyst, 1.5 equiv. of PhIO, in CH_2Cl_2 at 24 °C.

The turnover numbers (TON) were determined for the catalytic efficiency of the polyoxometalate **I** and the metal(salen) complex **II**. The TON could be increased to 29 for the chromium polyoxometalate **Ia** (Table 1, entry 2) and to 13 for the chromium(salen) complex **IIa** (entry 5) by lowering the amount of catalyst used.

To acquire structural information on the transition state of the oxygen transfer in the epoxidation by the manganese(salen) complex (**IIb**) and manganese POM (**Ib**), the two conformationally rigid allylic alcohols *trans*- and *cis*-5-*tert*-butyl-2-cyclohexenol (**5**) were employed as substrates (Figure 1).[13]

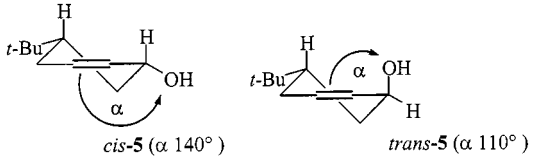
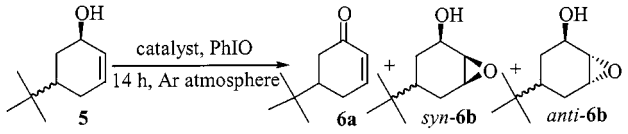


Figure 1. Structures *cis*-**5** and *trans*-**5**

The *cis* and *trans* diastereomers of these cyclic allylic alcohols gave similar chemoselectivities in their oxidation; in both cases slightly more epoxy alcohol **6b** than enone **6a** was formed (Table 2). The diastereoselectivities, however, differed significantly for the *cis* and *trans* substrates (Table 2, entry 1 and 2). Thus, the manganese(salen)-catalyzed epoxidation was more *syn*-selective for the *trans*-con-

Table 2. Diastereoselectivity in the catalytic oxidation of *cis*- and *trans*-5-*tert*-butyl-2-cyclohexenol (**5**) by the manganese-substituted POM **Ib** and the manganese(salen) complex **IIb** with iodosobenzene as the oxygen source

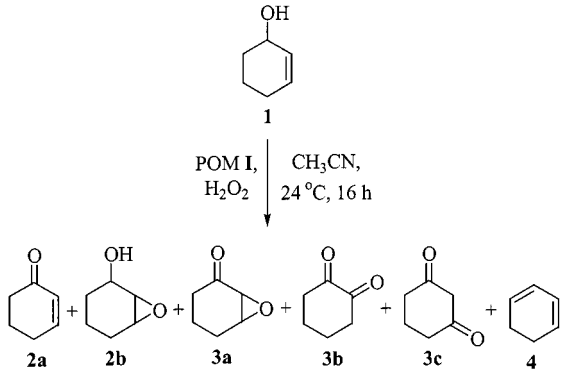


Entry	Catalyst		Substrate	Selectivity[a] chemo **6a**:**6b**	diastereo of **6b** *syn*:*anti*
1[b]	Mn-salen	IIb	*trans*-**5**	41:59	82:18
2[b]	Mn-salen	IIb	*cis*-**5**	42:58	68:32
3[c]	Mn-POM	Ib	*trans*-**5**	42:58	51:49
4[c]	Mn-POM	Ib	*cis*-**5**	49:51	40:60

[a] Determined by ^1H NMR analysis; error ± 5% of the given values; mass balances and conversions were >85%. [b] Reaction conditions: 0.3 equiv. of 4-phenylpyridine *N*-oxide (PPNO), 0.07 equiv. of the catalyst, 1.5 equiv. of PhIO, in CH_2Cl_2 at 24 °C. [c] Reaction conditions: 0.03 equiv. of the catalyst, 2 equiv. of PhIO, in CH_3CN at 50 °C.

figured allylic alcohol (82:18) than for the *cis* one (68:32). In the POM-catalyzed reactions, the diastereoselectivities were very low (entries 3 and 4). Experiments with the respective chromium catalysts (not shown in Table 2) revealed that, analogous to the substrate 2-cyclohexenol (**1**), both diastereomers of the allylic alcohols **5** were oxidized only to the enone **6a**.

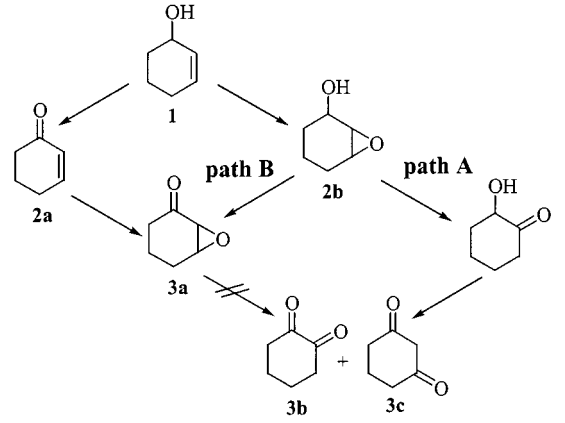
When hydrogen peroxide was used as the oxygen source instead of iodosobenzene in the POM-catalyzed oxidation of alcohol **1**, a more complex product mixture was obtained. Thus, besides the oxidation products **2a,b** and **3a** obtained with iodosobenzene, the diones **3b** and **3c** were also observed for hydrogen peroxide (Scheme 2).



Scheme 2

Discussion

The product data show that while the chromium-catalyzed oxidation of 2-cyclohexenol (**1**) gives exclusively 2-cyclohexenone (**2a**) by CH insertion, a more complex product mixture is observed for the manganese-catalyzed process (Table 1, entry 3 and 6). Thus, besides allylic oxidation to the enone **2a**, significant amounts of the epoxide **2b** are also formed, as well as the epoxy enone **3a** and traces of the diene **4**. The formation of the enone **2a** may be explained in terms of further oxidation of the primary oxidation products, as summarized in Scheme 3. The epoxy ketone **3a** derives from further oxidation of enone **2a** (epoxidation) and



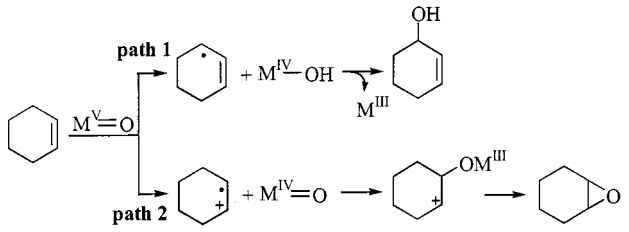
Scheme 3

of epoxy alcohol **2b** (allylic oxidation), as confirmed by control experiments (see Supporting Information). The diene **4** is the result of dehydration of the allylic alcohol **1** due to the acidity of the metal catalyst.

The traces of diones **3b,c** (Scheme 3) when hydrogen peroxide is used as the oxygen source instead of iodosobenzene, may arise from two alternative routes: either acid-catalyzed opening of the epoxide ring in the epoxy alcohol **2b** and rearrangement, followed by oxidation at the hydroxy group (path A), or the reverse, i.e. the oxidation of the hydroxy epoxide **2b** to the keto epoxide **3a** takes place first, followed by the ring-opening of the latter to the diones **3b,c** (path B). Path B, however, can be excluded because the keto epoxide **3a** does not undergo ring opening under the present conditions.

A comparison of the chromium and manganese catalysts reveals that the ligand environment of the transition metal, i.e. the salen ligand (Table 1, entries 4 and 6) versus the lacunary Keggin POM (entries 1 and 3), does not markedly affect the chemoselectivity of the metal catalyst. In contrast, the choice of the transition metal has a substantial effect on the product selectivity of the oxidation (Table 1). This chemoselectivity may be understood in terms of the hydrogen-abstraction versus electron-transfer mechanisms proposed for the oxidation of cyclohexene by porphyrin complexes (Scheme 4),[14] since these also display a preference of chromium for allylic oxidations versus epoxidation by manganese.[14] For cyclohexenol, in the first step of Scheme 4, the direct hydrogen abstraction for the allylic oxidation (path 1) competes with the electron transfer for the epoxidation (path 2). A means of differentiating between these two mechanisms would be in terms of the reduction potentials, but these are not known for the present chromium- and manganese(salen) catalysts. Nevertheless, the reduction potential of the manganese(porphyrin) complex (E_{red} = 1.05 V) is known to be higher than that of the chromium(porphyrin) one (E_{red} = 0.63 V), and this fact may serve as a guide for the respective salen complexes.[15] Such a comparison of the porphyrin and salen ligands is appropriate as these are electronically very similar. Thus, we may assume that the manganese complex is more readily reduced than the chromium one. Presumably, the reduction potential of the manganese complex is sufficiently higher than that of the chromium one to allow electron transfer from the cyclohexene substrate to the metal catalyst and thus allow competitive epoxide formation to take place. Conversely, for the more difficult to reduce chromium complex, allylic oxidation by hydrogen abstraction (path 1) dominates. However, for the chromium catalyst it has been shown that the chromate ester mechanism operates for such allylic alcohol oxidation to enones.[5]

We suggest that the higher catalytic activity of the POM **Ia** than the salen complex **IIa** (Table 1, entry 2 and 5) derives from the higher oxidative persistence of the POM. The tungsten(VI) and phosphate(V) atoms of the POM **I** are in their highest oxidation states and thus the $(W-O-W)_n$ and W−O−P frameworks are not susceptible to oxidative degradation.



Scheme 4

The *syn* diastereoselectivity for the epoxidation of the allylic alcohols **5** by the manganese(salen) complex **IIb** (Table 2, entries 1 and 2) implies hydrogen bonding between the allylic hydroxy group and the catalytically active species. This hydroxy-directing effect in the manganese(salen)-catalyzed epoxidation has previously been established for acyclic allylic alcohols.[4] Since the diastereoselectivity of the manganese-POM **Ib** is very low for both the *cis* and the *trans* isomers (Table 2, entries 3 and 4), a hydroxy-directing effect may be excluded for this catalytic system.

The absence of the hydroxy-directing effect may be due to ineffective hydrogen bonding between the allylic alcohol and manganese-oxo site in the POM catalyst; alternatively, neighboring oxygen atoms of the POM may compete in the hydrogen bonding with the allylic alcohol and thereby cause a low diastereoselectivity.

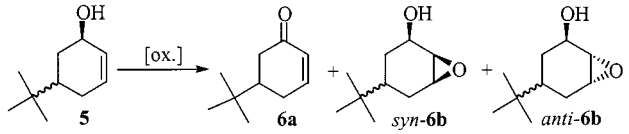
From the diastereoselectivity of the manganese(salen)-catalyzed epoxidations, valuable structural information may be acquired on the transition state of the oxygen transfer. Notably, the higher *syn* diastereoselectivity for the *trans*-configured cyclohexenol **5** than for the *cis* one (Table 3, entries 1 and 2) suggests that the dihedral angle α is closer to 110° than to 140° (see Figure 1) for beneficial hydrogen bonding.[13] A comparison with established oxidants (Table 3) allows a more precise assignment of the dihedral angle α.

For the methylrhenium trioxide/urea-hydrogen-peroxide adduct (MTO/UHP)[10] an optimal dihedral angle α of 130° has been estimated (entries 3 and 4), for dimethyldioxirane (DMD)[13] 130−140° (entries 5 and 6), and for *meta*-chloroperbenzoic acid (*m*-CPBA)[11] 130−140° (entries 7 and 8). Inspection of the composite diastereoselectivity data in Table 3 reveals that only for the manganese(salen)/PhIO oxidant (entries 1 and 2) does the *trans*-configured substrate exhibit a higher *syn* attack than the *cis* substrate. From this data we infer that for effective hydrogen bonding in the transition structure, the dihedral angle α for the manganese(salen) complex should be between 90° and 120°.

This estimate is in good agreement with the literature values of the dihedral angle α estimated for the epoxidation of chiral, acyclic allylic alcohols **7** by manganese(salen) complexes (Table 4).[4]

For the latter, a high preference (89:11) of the *threo* diastereomer was observed in the epoxidation of the substrate **7a** with 1,3-allylic strain (Table 4, entry 1). In contrast, for the substrate **7b** with only 1,2-allylic strain (entry 2), a negligible diastereoselectivity (48:52) was found. When 1,2- and 1,3-allylic strain are both competing in the same molecule, as in the stereochemical probe **7c**,[16] the epoxidation is still

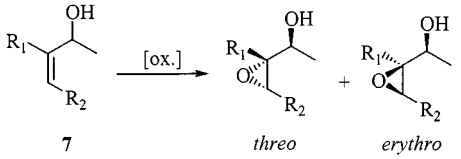
Table 3. Diastereoselectivity in the catalytic oxidation of *cis*- and *trans*-5-*tert*-butyl-2-cyclohexenol (**5**) by the manganese(salen) complex **IIb**, MTO/UHP, DMD and *m*-CPBA



Entry	Oxidant	Substrate	Selectivity[a] chemo **6a**:**6b**	diastereo of **6b** *syn*:*anti*	optimal dihedral angle (°)
1	Mn-salen/PhIO	*trans*-**5**	41:59	82:18	90−120
2	Mn-salen/PhIO	*cis*-**5**	42:58	68:32	
3[b]	MTO/UHP	*trans*-**5**	05:95	72:28	130
4[b]	MTO/UHP	*cis*-**5**	05:95	84:16	
5[c]	DMD	*trans*-**5**	33:67	58:42	130−140
6[c]	DMD	*cis*-**5**	43:57	82:18	
7[d]	*m*-CPBA	*trans*-**5**	03:97	90:10	130−140
8[d]	*m*-CPBA	*cis*-**5**	01:99	98:02	

[a] Determined by ^{1}H NMR analysis; error ± 5% of the given values; mass balances were > 85%. [b] $CDCl_3$ (ref.[10]). [c] CCl_4/acetone (ref.[13]). [d] CH_2Cl_2 (ref.[11]).

Table 4. Diastereoselectivity for the epoxidation of chiral allylic alcohols **7** by the manganese(salen) complex **IIb**



Entry		Substrate R^1	R^2	*threo*:*erythro* Diastereoselectivity Mn(salen)/PhIO[a]	Ti(O*i*-Pr)$_4$/TBHP[b]	*m*-CPBA[c]
1	**7a**	H	Me	89:11	91:09	95:05
2	**7b**	Me	H	48:52	22:78	45:55
3	**7c**	Me	Me	81:19	83:17	90:10

[a] CH_2Cl_2 (ref.[4]). [b] $CDCl_3$ (ref.[17]). [c] CH_2Cl_2 (ref.[18]).

highly (81:19) *threo*-selective. A comparison of these *threo*:*erythro* diastereoselectivities with those of established oxidants (Table 4) suggests that the dihedral angle α in the transition structure with the manganese(salen) oxidant lies between that for Ti(O*i*Pr)$_4$/TBHP (70−90°)[17] and *m*-CPBA (120°).[18] An α value of 110−115° was assigned, which matches well the value of 90−120° estimated here for the *cis*- and *trans*-cyclohexenols **5**.

Conclusion

In conclusion, an oxidation system (cat Ia/PhIO) with good catalytic activity and excellent product selectivity has been developed for the allylic oxidation of 2-cyclohexenol (**1**). The present data of the chromium and manganese POMs and the respective salen complexes show that the choice of the transition metal (chromium versus manganese) has a substantial effect on the product selectivity (CH oxidation versus epoxidation). In contrast, the ligand environment of the transition metal, i.e. the salen ligand versus the lacunary α-Keggin POM, does not markedly affect the product selectivity.

Experimental Section

General Remarks: For GC analysis, a Hewlett−Packard 6890 Series instrument was employed, equipped with a FID detector and a nonpolar column (5% PH ME Siloxane). Cyclopentanone was used as an internal standard for the quantification of the conversion of the starting material and the mass balance. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker AC 200 (^{1}H at 200 MHz, ^{13}C at 50 MHz) against $CDCl_3$ as reference standard on the δ scale (ppm). TLC analysis was conducted on precoated silica-gel foils 60 F_{254} (20 × 20) from Merck, Darmstadt. Spots were visualized either by UV irradiation (254 nm) or by a 5% polymolybdic acid solution in ethanol. Silica gel (32−63 μm) from Woelm, Erlangen was used for flash chromatography. The solvents were dried and purified by standard methods.[19]

The parent 2-cyclohexenol (**1**) is commercially available (Aldrich), whereas the *tert*-butyl-substituted derivatives *cis*-**5** and *trans*-**5** were synthesized following the known methods.[20] Iodosobenzene (95% by iodometry[21]) was prepared by hydrolysis of the corresponding diacetate according to the literature method.[22] The catalysts **Ia**,[23] **Ib**,[24] **IIa**,[5] **IIb**[25] were obtained analogously to the reported methods.

General Procedure for the Oxidation of 2-Cyclohexenol (1) Catalyzed by Metal(salen) Complexes II: At room temperature (ca. 24 °C) and under an argon atmosphere, 0.30 equiv. of PPNO, 0.14 equiv. of the catalyst **II** and 1.50 equiv. of PhIO were added to a solution of 2-cyclohexenol (**1**) (20.8 μL, 213 μmol) in 0.40 mL of dichloromethane. After 14 h, the reaction mixture was centrifuged and an aliquot was analyzed by gas chromatography. The quantitative results are given in Table 1 (see main text).

General Procedure for the Oxidation of 2-Cyclohexenol (1) Catalyzed by POMS I: Under an argon atmosphere, 2.00 equiv. of the iodosobenzene was added to a solution of 2-cyclohexenol (**1**) (10.4 μL, 106 μmol) and 0.04 equiv. of the POM catalyst **I** in 0.20 mL of acetonitrile. The reaction mixture was stirred for 14 h at the temperature specified in Table 1. The mixture was centrifuged, aliquots were taken and analyzed by gas chromatography. The quantitative results are given in Table 1 (see main text).

General Procedure for the Catalytic Oxidation of 5-*tert*-Butyl-2-cyclohexenol *cis*- and *trans*-5: The same general procedure outlined above for the parent 2-cyclohexenol **1** was followed for the *tert*-butyl derivative **5**. After completion of the reaction, the solvent was evaporated carefully (25 °C, 600 Torr) and the brown residue was prepurified by passing through a short (10 g) silica-gel column. First petroleum ether (50 mL) was employed as eluent to separate the iodobenzene, then diethyl ether (200 mL) was used to obtain the oxidation products and the starting material. The solvent was removed as above (25 °C, 600 Torr), and the conversion, mass balance, chemo- and diastereoselectivities were determined by ^{1}H and ^{13}C NMR spectroscopy. The quantitative results are given in Table 2 (see main text).

Acknowledgments

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