# Selective Oxidation of Vinyl Ethers and Silyl Enol Ethers with Hydrogen Peroxide Catalyzed by Peroxotungstophosphate

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The oxidation of vinyl and silyl enol ethers with aqueous hydrogen peroxide was first achieved by the use of peroxotungstophosphate (PCWP) as the catalyst. For example, the oxidation of 1-ethoxy-1-octene with a stoichiometric amount of 35% $H_2O_2$ in the presence of PCWP (0.5 mol %) in a mixed solvent of methanol and dichloromethane at room temperature gave 1-ethoxy-1-methoxy-2-hydroxyoctane, a synthetic equivalent of 2-hydroxyoctanal, in 70% yield. The oxidation of acyclic silyl enol ethers such as 1-[(trimethylsilyl)oxy]-1-octene under these conditions gave 1-hydroxy-2-octanone in 72% yield, while the same oxidation in dichloromethane alone resulted in cleavage of the enol double bond to form heptanal in 71% yield. Cyclic silyl enol ethers were converted into the corresponding α-hydroxy ketones in 48−71% yields under similar reaction conditions.

## Introduction

There are many reports on the transformation of enol ethers such as vinyl and silyl enol ethers to α-hydroxy carbonyl compounds.[1−14] However, little has been published on the oxidation of enol ethers using aqueous hydrogen peroxide as an oxidant, probably because the enol ethers are assumed to be easily hydrolyzed in an aqueous medium. Hydrogen peroxide is one of the most useful oxidants which does not produce any waste except for water; therefore, if aqueous hydrogen peroxide can be applied to such oxidation, this method provides a new facile approach to preparation of α-hydroxy carbonyl compounds which are important precursors for natural product synthesis.[15]

We have shown that a wide variety of organic substrates are smoothly converted into oxygen-containing compounds with aqueous hydrogen peroxide in the presence of a catalytic amount of cetylpyridinium peroxo-tungstophosphate (PCWP), $[C_5H_5N^+(CH_2)_{15}CH_3]_3$-$\{PO_4[W(O)(O_2)_2]_4\}^{3-}$, possessing both a phase-transfer function and strong oxidizing capability (*e.g.,* alkenes to epoxides,[16a,b] alkynes to α,β-unsaturated ketones[16c] or α,β-epoxy ketones,[16d] allenes to α-hydroxy ketones or α-alkoxy ketones,[16c] and diols to α-hydroxy ketones[16e] or α-diketones[16f]). In this paper, we wish to report a new oxidation of enol ethers with aqueous hydrogen peroxide (35% $H_2O_2$) by the use of PCWP under phase-transfer conditions.

## Results and Discussion

**1. Oxidation of Vinyl Ethers to α-Hydroxy Aldehyde Equivalents.** α-Hydroxy carbonyl compounds are structural subunits of natural products including sugars and β-hydroxy-α-amino acids.[15] Hence, the development of synthetic methods for α-hydroxy aldehydes or their synthetic equivalents is an interesting subject from the synthetic point of view. Several methods have so far been reported for this purpose (*e.g.,* masked-formylation of carbonyl compounds using an anion derived from 1,3-dithiane,[17] methyl methathiomethyl sulfoxide,[18] and methylthioformaldine,[19] thallium(I)-catalyzed reaction of ketones with tosylmethyl isocyanide,[20] cobalt-catalyzed reaction of hydrosilane with carbon monoxide,[21] and $SmI_2$-induced formylation of 1,3-dioxane[22]).

There have been some oxidation methods where the primary hydroxy group of diols is oxidized in preference

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to the secondary one.[23] The oxidation of 1,2-diols appears to be a straightforward method to prepare α-hydroxy aldehydes; however, treatment of the 1,2-diols with hydrogen peroxide by PCWP provides α-hydroxy ketones without formation of α-hydroxy aldehydes.[16e] For example, the oxidation of 1,2-octanediol with 35% $H_2O_2$ (6 equiv) by PCWP under biphasic conditions produces 1-hydroxy-2-octanone in 90% yield, but no 2-hydroxyoctanal is formed (eq 1).
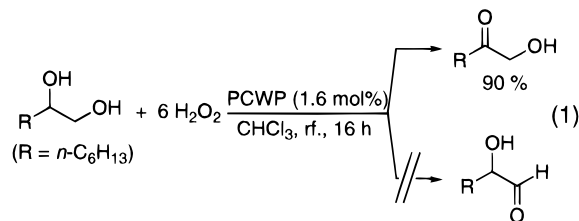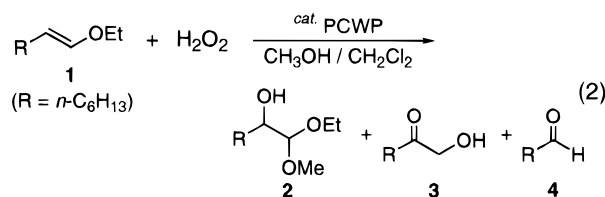


Therefore, our strategy is to use enol ethers as substrates for preparing α-hydroxy aldehydes or their synthetic equivalents. We speculate that the PCWP-catalyzed oxidation of vinyl ether with hydrogen peroxide produces the corresponding epoxy ether **A** as a primary product as shown in Scheme 1. Subsequent reaction of the resulting epoxy ether **A** with water or alcohol probably induces the O−C bond scission of the oxirane ring to lead to α-hydroxy aldehyde or its synthetic equivalent.

**Scheme 1. Working Hypothesis for the Synthesis α-Hydroxy Aldehyde Derivative**
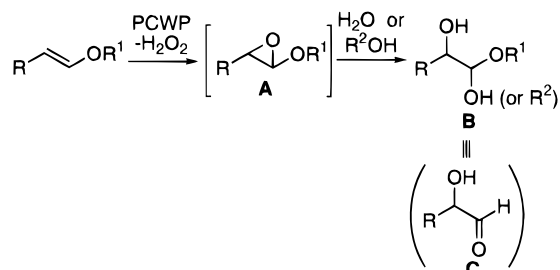


Thus, 1-ethoxy-1-octene (**1**) was chosen as a model substrate and oxidized with 35% $H_2O_2$ in the presence of PCWP under various reaction conditions (eq 2, Table 1). The oxidation of **1** was carried out by adding dropwise 1 equiv of 35% $H_2O_2$ in the presence of a catalytic amount of PCWP (0.5 mol % with respect to **1**) in a mixed solvent of methanol and dichloromethane (1/4 v/v %) at 20 °C for 2 h to give 1-ethoxy-1-methoxy-2-hydroxyoctane (**2**) (76%) together with 1-hydroxy-2-octanone (**3**) (17%) and cleaved product, heptanal (**4**) (6%), in 53% conversion (run 1). In methanol alone, the oxidation of **1** in higher conversion was difficult (run 2). When the oxidation was conducted in a 1:1 mixture of methanol and dichloromethane under these conditions, 67% conversion of **1** was attained, but the selectivity to **2** somewhat decreased (run 3). The oxidation of **1** in methanol/dichloromethane (1/4 v/v %) at refluxing temperature (*ca.* 40 °C) for 16 h produced **2** in satisfactory yield (70%) (run 5). In a mixed solvent of ethanol and dichloromethane, **1** was converted

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**Table 1. Oxidation of 1-Ethoxy-1-octene (1) by the PCWP−$H_2O_2$ System[a]**



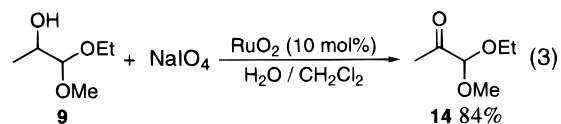| | | temp | conv | selectivity (%) | | |
|---|---|---|---|---|---|---|
| run | solvent (mL) | (°C) | (%) | **2** | **3** | **4** |
| 1 | $CH_3OH/CH_2Cl_2$ (1/4) | 20 | 53 | 76 | 17 | 6 |
| 2 | $CH_3OH$ (5) | 20 | 11 | <1 | <1 | <1 |
| 3 | $CH_3OH/CH_2Cl_2$ (2.5/2.5) | 20 | 67 | 66 | 7 | 2 |
| 4 | $CH_3OH/CH_2Cl_2$ (1/4) | rf | 59 | 76 | 15 | 8 |
| 5[b] | $CH_3OH/CH_2Cl_2$ (1/4) | rf | >98 | 70 | 16 | 8 |
| 6[b] | $C_2H_5OH/CH_2Cl_2$ (1/4) | rf | >98 | (42)[c] | 12 | 12 |
| 7 | $H_2O/CH_2Cl_2$ (1/4) | rf | >98 | − | 39 | 23 |

[a] **1** (1 mmol) was allowed to react with 35% $H_2O_2$ (1 mmol) dropwise over a period of 1 h in the presence of PCWP (0.005 mmol, 0.5 mol %) for 2 h. [b] 16 h. [c] Yield of 2-hydroxyoctanal diethyl acetal (**5**).

into 2-hydroxyoctanal diethyl acetal (**5**) (42%) along with **3** (12%) and **4** (12%) (run 6).

To gain insight into the reaction path for the formation of α-hydroxy ketone **3** by the present oxidation, α-hydroxy acetal **2** prepared independently was allowed to react with 35% $H_2O_2$ under the influence of PCWP in a mixed solvent of methanol/dichloromethane (1/4 v/v %), since **3** is considered to be a further oxidation product of **2**. However, **2** did not react at all under these conditions and was recovered unchanged. α-Hydroxy aldehydes are known to be labile compounds which are easily rearranged to α-hydroxy ketones.[24] Therefore, it is reasonable to assume that **3** is formed through the reaction path shown in Scheme 1. In fact, the PCWP-catalyzed oxidation of **1** with 35% $H_2O_2$ in a solvent of water and dichloromethane (1/4 v/v %) gave **3** and **4** in 39% and 23% yields, respectively (Table 1, run 7).

On the basis of these results, several vinyl ethers were oxidized by 35% $H_2O_2$ in the presence of the PCWP in a mixed solvent of methanol/dichloromethane (1/4 v/v %) (Table 2). 1-Ethoxy-1-heptene (**6**) and 1-ethoxy-1-propene (**8**) were oxidized to the corresponding α-hydroxy acetals, **7** and **9**, in 67% and 69% selectivities, respectively (runs 1 and 2). Similarly, the oxidation of 1-methoxy-2-phenylethene (**12**) afforded 2-hydroxy-2-phenylacetaldehyde dimethyl acetal (**13**) in 61% yield (run 4).

Treatment of α-hydroxy acetal **9** with $NaIO_4$ in the presence of a catalytic amount of $RuO_2$ led to the corresponding α-keto acetal **14**, which is a synthetic equivalent of pyruvic aldehyde, in high yield (84%) (eq 3).



**2. Oxidation of Silyl Enol Ethers.** Oxidation of silyl enol ethers using various oxidants has been investigated for the synthesis of α-hydroxy carbonyl compounds.[4−14] For example, the oxidation of silyl enol

(24) (a) Hurd, C. D.; Saunders, W. H. Jr. *J. Org. Chem.* **1952**, *74*, 5324. (b) Russell, G. A.; Ochrymowycz, L. A. *J. Org. Chem.* **1969**, *34*, 3618. (c) Creavy, X.; Rollin, A. J. *J. Org. Chem.* **1977**, *42*, 4231.
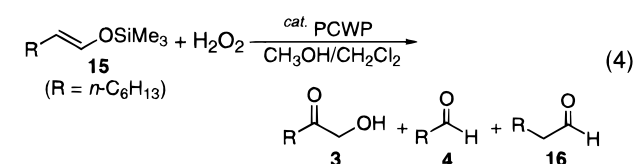
**Table 2. Oxidation of Several Alkyl Enol Ethers by the PCWP–H₂O₂ System[a]**

| Run | Substrate | Conv. (%) | Product / Selectivity (%) |
|---|---|---|---|
| 1 | **6** | 88 | **7** (67) |
| 2[b] | **8** | 91 | **9** (69) |
| 3[c] | **10** | 93 | **11** (55) |
| 4 | **12** | 99 | **13** (61) |

[a] Substrate (1 mmol) was allowed to react with 35% $H_2O_2$ (1 mmol, dropwise over a period of 1 h) in the presence of PCWP (0.005 mmol, 0.5 mol%) in $CH_3OH$ (1 mL) and $CH_2Cl_2$ (4 mL) at 20 °C for 3–6 h. [b] $H_2O_2$ (1 mmol) was added all at once. [c] At refluxing temperature.

ethers with *m*-CPBA followed by treatment with an acid or a base is a general high-yielding method for the specific α-hydroxylation of ketones.[4a]

Table 3 shows the results for the oxidation of 1-[(trimethylsilyl)oxy]-1-octene (**15**) by the PCWP–H₂O₂ system under several reaction conditions. The oxidation of **15** was conducted by adding dropwise a stoichiometric amount of 35% H₂O₂ over a period of 1 h in the presence of PCWP (0.5 mol %) in methanol/dichloromethane (1/4 v/v %) at 20 °C to give 1-hydroxy-2-octanone (**3**) and octanal (**16**) in 54% and 40% yields, respectively, in 99% conversion (run 1). In contrast to the oxidation of vinyl ethers where α-hydroxy acetals were formed as major products, silyl enol ether **15** was converted into α-hydroxy ketone **3** without formation of the corresponding alkyl silyl acetal. This is believed to be attributed to the fact that the alkyl silyl acetal is much more subject to hydrolysis than the dialkyl acetal under the present reaction conditions.

**Table 3. Oxidation of 1-[(Trimethylsilyl)oxy]-1-octene (15) by the PCWP–H₂O₂ System[a]**

$$R\diagup\!\!\diagdown OSiMe_3 + H_2O_2 \xrightarrow[CH_3OH/CH_2Cl_2]{cat.\ PCWP}$$
**15** (R = *n*-C₆H₁₃)

$$\underset{\mathbf{3}}{R\text{-CO-CH}_2\text{OH}} + \underset{\mathbf{4}}{R\text{-CHO}} + \underset{\mathbf{16}}{R\text{-CH}_2\text{-CHO}} \quad (4)$$

| run | solvent (mL) | PCWP (mol%) | conv (%) | 3 | 4 | 16 |
|---|---|---|---|---|---|---|
| 1[b] | CH₃OH/CH₂Cl₂ (1/4) | 0.5 | >99 | 54 | 5 | 40 |
| 2 | CH₃OH/CH₂Cl₂ (1/4) | 1.0 | >99 | 57 | 7 | 25 |
| 3 | CH₃OH/CH₂Cl₂ (1/4) | 2.0 | >99 | 67 | 8 | 23 |
| 4[c] | CH₃OH/CH₂Cl₂ (1/4) | 2.0 | >99 | 72 | 9 | 12 |
| 5 | CH₂Cl₂ (5) | 2.0 | >99 | 34 | 25 | 4 |
| 6[d] | CH₂Cl₂ (2.5) | 2.0 | >99 | 1 | 79 | 4 |

[a] **15** (1 mmol) was allowed to react with 35% H₂O₂ (1 mmol, dropwise over a period of 1 h) catalyzed with PCWP for 2 h. [b] 4 h. [c] At refluxing temperature, 2 h. [d] 35% H₂O₂ (3 mmol) was added all at once, 24 h.

To avoid the hydrolysis of **15** to **16** with water, several reactions were examined. It was found that the hydrolysis of **15** could be suppressed to a considerable extent when slight excess PCWP (2.0 mol %) was used. As a consequence, the selectivity of the oxidation was markedly improved to form 1-hydroxy-2-octanone **3** in 67% yield (run 3). The best selectivity (72%) of **3** was obtained by the oxidation using 2.0 mol % of PCWP at refluxing temperature (*ca.* 40 °C) for 2 h (run 4).

The **3** is considered to be formed *via* α-hydroxy aldehyde in a similar way to the reaction of vinyl ethers. In the oxidation of silyl enol ethers with *m*-CPBA, a similar reaction path through α-hydroxy aldehydes has been proposed for the formation of α-hydroxy ketones.[4b]

The use of dichloromethane as the solvent in the oxidation of **15** led to **3** (34%) and a cleaved product, heptanal **4** (25%), as principal products (run 5). The oxidation of **15** using excess 35% H₂O₂ (3 equiv) for 24 h produced **4** in 79% yield (run 6). This finding provides a new route for preparing one-carbon-less aldehydes than the parent aldehydes, since the silyl enol ethers can be easily prepared by the reaction between aldehydes and trimethylsilyl chloride.[25]

In order to clarify the route to **4** from **15**, α-hydroxy ketone **3** was treated with 35% H₂O₂ (3 equiv) in the presence of PCWP (2 mol %) at room temperature for 9 h to result in the recovery of the starting **3**. This indicates that **4** was not a further oxidation product of **3**. Although the reaction path for the formation of **4** is not clear, **4** may be produced by the further oxidation of epoxy ether **A** by the PCWP–H₂O₂ system as shown in Scheme 2.

**Scheme 2**
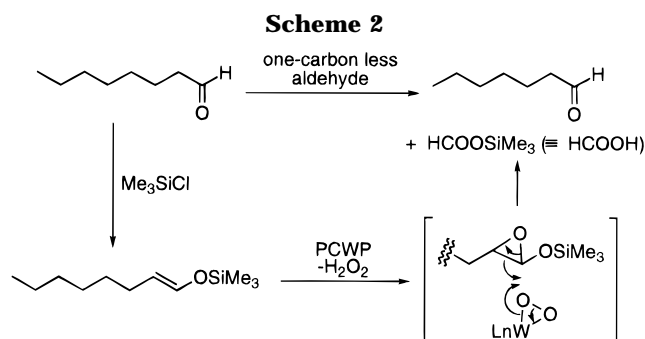


Cyclic silyl enol ethers **17–19a** were also oxidized to the corresponding α-hydroxy ketones **17–19b** in satisfactory yields under phase-transfer conditions (Table 4). Although in a mixed solvent of methanol/dichloromethane (1/4 v/v %) was hydrolyzed 1-[(trimethylsilyl)oxy]-1-cyclohexene (**18a**) to the undesired original ketone **18c** (71%) (run 2), the oxidation of **18c** by the PCWP-H₂O₂ system in dichloromethane at 20 °C for 9 h gave 2-hydroxycyclohexanone (**18b**) and cyclohexanone (**18c**), respectively, in 67% and 12% yields (run 3). However, under these conditions, 1-[(trimethylsilyl)oxy]-1-cyclooctene (**19a**) underwent the hydrolysis to form cyclooctanone (**19c**) as the major product (run 4). It was found that **19a** is converted into 2-hydroxycyclooctanone (**19b**) in 71% yield by the reaction in the presence of excess PCWP (2.0 mol %) in refluxing chloroform for 6 h (run 5).

In conclusion, the first oxidation of enol ethers with aqueous hydrogen peroxide using PCWP as the catalyst has been achieved. Vinyl ethers such as 1-ethoxy-1-

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**Table 4. Oxidation of Several Cyclic Silyl Enol Ethers by the PCWP−H₂O₂ System[a]**

| Run | Substrate | Conv. (%) | Product (Yield / %) | |
|---|---|---|---|---|
| |  | |  |  |
| 1 | **17a** (n = 1) | >99 | **17b** (48) | **17c** (7) |
| 2[b] | **18a** (n = 2) | >99 | **18b** (1) | **18c** (71) |
| 3 | **18a** (n = 2) | >99 | **18b** (67) | **18c** (12) |
| 4[c] | **19a** (n = 4) | >99 | **19b** (13) | **19c** (71) |
| 5[c,d] | **19a** (n = 4) | >99 | **19b** (71) | **19c** (14) |

[a] Substrate (1 mmol) was allowed to react with 35% $H_2O_2$ (1 mmol) in the presence of PCWP (0.005 mmol, 0.5 mol%) in $CH_2Cl_2$ (5 mL) at 20 °C for 9 h. [b] $CH_3OH/CH_2Cl_2$ (1/4 mL) was used as a solvent. [c] 6 h. [d] PCWP (0.020 mmol, 2.0 mol%) in $CHCl_3$ (5 mL) under refluxing temperature.

octene (**1**) were converted into the corresponding α-hydroxy acetal **2**, preparation of which is difficult by conventional methods, in a mixed solvent of alcohol and dichloromethane. The oxidation of acyclic silyl enol ethers such as 1-[(trimethylsilyl)oxy]-1-octene (**15**) gave α-hydroxy ketones such as 1-hydroxy-2-octanone (**3**) in satisfactory yields in a mixed solvent of methanol and dichloromethane. Under phase-transfer conditions using dichloromethane as the solvent, **15** was converted into a cleaved product, heptanal **4**. This provides a facile method for preparing aldehydes with one carbon less than the parent aldehydes.

## Experimental Section

**General Procedures.** Enol ethers **1**, **6**, **10**,[26] **15**, **17a**, and **19a**[25] were synthesized according to the literature procedures and purified by distillation under reduced pressure or by column chromatography on silica gel with hexane. **8**, **12**, and **18a** were commercially available and used without further purification. PCWP was prepared by the method reported previously.[16] GC analysis was performed with a flame ionization detector using a 0.2 mm × 25 m capillary column (OV-1). ¹H- and ¹³C-NMR were measured at 270 or 400 MHz and 67.5 or 100 MHz, respectively, in CDCl₃ with Me₄Si as the internal standard. Infrared (IR) spectra were measured using NaCl plate. GC-MS spectra were obtained at an ionization energy of 70 eV. The product yields were estimated from the peak areas based on the internal standard technique.

**General Procedure for the Oxidation of Vinyl Ethers to α-Hydroxy Acetals.** To a stirred solution of substrate (1 mmol) and PCWP (10 mg, 0.5 mol %) in CH₃OH (1 mL) and CH₂Cl₂ (4 mL) was added dropwise 35% H₂O₂ (1 mmol) over a period of 1 h. The reaction mixture was stirred at 40 °C for 16 h and extracted with dichloromethane. The extract was dried over anhydrous MgSO₄ and evaporated under reduced pressure. The products were purified by column chromatography on silica gel with hexane/ethyl acetate (10−3/1 v/v %).

**1-Ethoxy-1-methoxy-2-hydroxyoctane (2)**: IR (NaCl) 3454, 2927, 1467, 1377, 1279, 1119, 1067 cm⁻¹; ¹H-NMR (CDCl₃, 270 MHz) δ 4.12 (d, J = 6.2 Hz, 1 H), 3.70 −3.62 (m, J = 7.0 Hz, 1 H), 3.56−3.48 (m, J = 7.0 Hz, 2 H), 3.37 (s, 3H), 2.21 (br, 1 H), 1.19−1.16 (m, 13 H), 0.81 (t, J = 7.0 Hz, 3 H);

¹³C-NMR (CDCl₃, 67.8 MHz) δ 106.0, 71.37, 63.5, 54.6, 31.7, 31.7, 29.3, 25.4, 22.5, 15.3, 14.0.

**1,1-Diethoxy-2-hydroxyoctane (5)**: IR (NaCl) 3474, 2927, 1731, 1457, 1375, 1120, 1063, 592 cm⁻¹; ¹H-NMR (CDCl₃, 270 MHz) δ 4.25 (d, J = 5.9 Hz, 1 H), 3.81−3.67 (m, J = 6.9 Hz, 1 H), 3.63−3.52 (m, J = 6.9 Hz, 4 H), 2.41 (br, 1 H), 1.59−1.20 (m, 16 H), 0.88 (t, J = 6.9 Hz, 3 H); ¹³C-NMR (CDCl₃, 67.8 MHz) δ 105.4, 72.0, 63.7, 63.3, 32.1, 29.6, 25.8, 22.9, 15.6, 14.3.

**1-Ethoxy-1-methoxy-2-hydroxyheptane (7)**: IR (NaCl) 3466, 2930, 1066 cm⁻¹; ¹H-NMR (CDCl₃, 270 MHz) δ 4.19 (d, J = 6.3 Hz, 1 H), 3.83−3.68 (m, J = 6.9 Hz, 1 H), 3.65−3.53 (m, 2 H), 3.44 (s, 3 H), 3.41 (s, 3 H), 2.17 (br, 1 H), 1.58−1.21 (m, 11 H), 0.89 (t, J = 6.6 Hz, 3 H); ¹³C-NMR (CDCl₃, 67.5 MHz) δ 106.1, 71.5, 63.9, 63.7, 54.8, 32.0, 31.8, 25.2, 22.7, 15.4, 14.1.

**1-Ethoxy-1-methoxy-2-hydroxypropane (9)**: IR (NaCl) 3443, 2977, 1453, 1372, 1065, 628 cm⁻¹; ¹H-NMR (CDCl₃, 270 MHz) δ 4.15 (d, J = 6.3 Hz, 1 H), 3.80−3.69 (m, 1 H), 3.66−3.57 (m, J = 7.3 Hz, 2 H), 3.43 (d, J = 7.3 Hz, 3 H), 1.28−1.19 (m, J = 6.9 Hz, 3 H); ¹³C-NMR (CDCl₃, 67.8 MHz) δ 106.9, 67.7, 63.7, 54.7, 17.4, 15.3.

**1-Ethoxy-1-methoxy-2-hydroxy-3-cyclohexylpropane (11)**: IR (NaCl) 3462, 2923, 2850, 1720, 1448, 1285, 1128, 1066 cm⁻¹; ¹H-NMR (CDCl₃, 400 MHz) δ 4.16 (d, J = 6.2 Hz, 1 H), 3.76−3.68 (m, J = 6.9 Hz, 2 H), 3.63−3.55 (m, J = 7.0 Hz, 1 H), 3.44 (s, 3 H), 2.15 (s, 1 H), 1.85−0.84 (m, 16 H); ¹³C-NMR (CDCl₃, 100 MHz) δ 106.4, 69.0, 63.5, 54.8, 39.3, 34.5, 33.7, 32.4, 26.6, 26.4, 26.1, 15.3.

**1,1-Dimethoxy-2-hydroxy-2-phenylethane (13)**: IR (NaCl) 3444, 3063, 3032, 2938, 2833, 1688, 1604, 1495, 1454, 1360, 1191, 1068, 976, 915, 835, 763, 701, 578 cm⁻¹; ¹H-NMR (CDCl₃, 270 MHz) δ 7.43−7.26 (m, 5 H), 4.61 (d, J = 6.6 Hz, 1 H), 4.29 (d, J = 6.6 Hz, 1 H), 3.46 (s, 3 H), 3.26 (s, 3 H), 2.62 (br, 1 H); ¹³C-NMR (CDCl₃, 67.5 MHz) δ 139.4, 128.2, 127.9, 127.1, 107.6, 74.0, 55.9, 54.9.

**Procedure for the Oxidation of 9 to 14.**[27] To a stirred solution of **9** (1 mmol) in CHCl₃ (5 mL) and H₂O (5 mL) were added RuO₂ (0.1 mmol), NaIO₄ (6.5 mmol), K₂CO₃ (0.36 mmol), and Et₃NCH₂PhCl (0.01 mmol). The reaction mixture was stirred at 25 °C for 20 h. 2-Propanol (1 mL) was added to consume unreacted NaIO₄ and RuO₄, and the mixture was filtered through Celite. The organic layer was separated and washed with H₂O. The extract was dried over anhydrous MgSO₄ and evaporated under reduced pressure. The product was purified by distillation.

**1-Ethoxy-2-methoxy-2-propanone (14)**: ¹H-NMR (CDCl₃, 270 MHz) δ 4.49 (s, 1 H), 3.62−3.56 (q, J = 6.9 Hz, 2 H), 3.42 (s, 3 H), 1.26 (t, J = 6.9 Hz, 3 H); ¹³C-NMR (CDCl₃, 67.5 MHz) δ 204.1, 103.4, 63.4, 54.6, 24.7, 15.1.

**General Procedure for the Oxidation of Silyl Enol Ethers.** To a stirred solution of substrate (1 mmol) and PCWP (10 mg, 0.5 mol %) in CH₂Cl₂ (5 mL) was added dropwise 35% H₂O₂ (1 mmol) over a period of 1 h under nitrogen atmosphere. The reaction mixture was stirred at room temperature, and the workup was performed by the same method as described above.

**Supporting Information Available:** Copies of ¹³C NMR, ¹H NMR, IR spectra for the compounds **2**, **5**, **7**, **9**, **11**, **13**, **14**, **17b**, **18b**, and **19b** (29 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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