$[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)]^{2-}$-Catalyzed Epoxidation of Allylic Alcohols in Water with High Selectivity and Utilization of Hydrogen Peroxide

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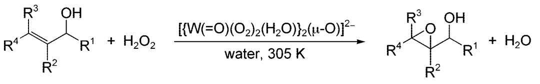
Abstract: A dinuclear peroxotungstate, $K_2[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)] \cdot 2\,H_2O$, exhibits high catalytic performance for the epoxidation of various allylic alcohols with only one equivalent of hydrogen peroxide at 305 K in water solvent. The effectiveness of this system is evidenced by high chemo-, regio-, and diastereoselectivity, and stereospecificity for the epoxidation of allylic alcohols. Furthermore, products/catalyst separation can be easily carried out by simple extraction and the catalyst recovered can be reused with the maintenance of the catalytic performance.

Keywords: allylic alcohols; dinuclear peroxotungstate; epoxidation; hydrogen peroxide

Epoxidation of allylic alcohols is of great importance[1–5] because epoxides have been used as raw materials for epoxy resins and building blocks for the synthesis of biologically important compounds including natural products,[6,7] and chiral carbons are formed by the epoxidation.[1–5] Although many methods for the epoxidation of allylic alcohols have been developed, catalytic processes with expensive and environmentally-unacceptable oxidants such as peracids and hydroperoxides in explosive, hazardous, and carcinogenic organic solvents are still widely used.[8] In this context, the development of efficient catalytic processes using hydrogen peroxide or molecular oxygen as a green oxidant in non-explosive solvent, *especially water*, achieves economical and environmental benefits, and is challenging.[9–15]

We reported very recently an efficient and simple route for epoxidation of both internal and terminal olefins with hydrogen peroxide catalyzed by the divacant lacunary silicotungstate, $[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$.[16] During the course of our investigation of tungsten-catalyzed oxidation, we found that the simple dinuclear peroxotungstate, $K_2[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)] \cdot 2\,H_2O$ (**I**), could act as an effective catalyst for the epoxidation of allylic alcohols using hydrogen peroxide *in water* under mild reaction conditions [Eq. (1)]. To our knowledge, the isolated **I** itself has never been used for the catalytic epoxidation of allylic alcohols using hydrogen peroxide in water without additives although **I** is a previously known compound.[17]

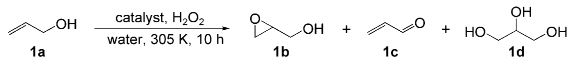


(1)

Epoxidation of 2-propen-1-ol as a model substrate using 30% aqueous hydrogen peroxide in various solvents was carried out in the presence of **I**. The results are summarized in Table 1. The oxidation did not proceed in the absence of **I** (entry 2). Water was the most effective solvent for the present epoxidation: 96% conversion, 99% selectivity to 2,3-epoxy-1-propanol, and 97% efficiency of hydrogen peroxide utilization for the epoxidation of 2-propen-1-ol (entry 1). The use of non-polar toluene, benzene, and dichloromethane solvents (organic/aqueous biphasic system) gave 2,3-epoxy-1-propanol yields of 90, 80, and 63%, respectively (entries 3–5). On the other hand, water-miscible polar acetonitrile (5% yield) and methanol (< 1% yield) were poor solvents probably because of the strong coordination to the tungsten center (entries 6 and 7).

Table 2 shows the results of epoxidation of various allylic alcohols with only one equivalent of hydrogen peroxide catalyzed by **I** in water solvent. The pH value of the reaction media was in the range of 4–5 under the present conditions. The catalyst **I** was intrinsically stable in the pH range of 2.5–7 as was confirmed by ^{183}W NMR and IR spectra. The efficiency of the hydrogen peroxide utilization was more than 90% in each case. Oxidation of simple primary allylic alcohols proceeded almost quantitatively and chemoselectively to afford the epoxy alcohols without formation of the corresponding aldehydes and carboxylic acids (entries 1–5). A 100-mmol scale epoxidation of the internal allylic alcohol of

Table 1. Oxidation of 2-propen-1-ol with hydrogen peroxide in various solvents.[a]



Entry	Solvent	Yield [%]			H_2O_2 efficiency [%]
		1b	**1c**	**1d**	
1	water	95	1	< 1	97
2[b]	water (no catalyst)	no reaction			–
3	toluene	90	2	< 1	91
4	benzene	80	< 1	< 1	90
5	dichloromethane	63	< 1	1	79
6	acetonitrile	5	< 1	< 1	95
7	methanol	no reaction			–

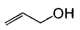
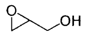
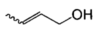
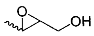
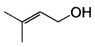
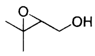
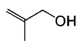
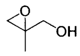
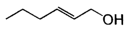
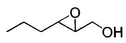
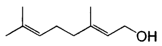
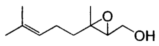
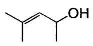
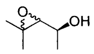
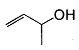
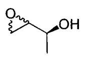
[a] Reaction conditions: 2-propen-1-ol (5 mmol), **I** (100 μmol, 2 mol %), 30% aqueous H_2O_2 (5 mmol), solvent (6 mL), 305 K, 10 h. Yields were determined by gas chromatography and ^{1}H NMR with an internal standard technique, and based on allyl alcohol. Remaining H_2O_2 after reaction was estimated by potential difference titration of Ce^{3+}/Ce^{4+} (0.1 M of aqueous $Ce(NH_4)_4(SO_4)_4 \cdot 2H_2O$). H_2O_2 efficiency (%) = products (mol)/consumed H_2O_2 (mol) × 100.

[b] Reaction was carried out in the absence of catalyst.

2-buten-1-ol (**I**:H_2O_2:substrate = 1:5000:5000) showed a turnover frequency (TOF) of 594 h^{-1} and a turnover number (TON) of 4200. *These values are higher than those reported to be active for the tungsten-catalyzed epoxidation of internal allylic alcohols with hydrogen peroxide*: Na_2WO_4-$NH_2CH_2PO_3H_2$-[$CH_3(n\text{-}C_8H_{17})_3N$]-$HSO_4$ in toluene, 86 h^{-1} (TOF) and 43 (TON);[18] [$C_5H_5N(n\text{-}C_{16}H_{33})$]$_3PW_{12}O_{40}$ in 1,2-dichloroethane, 5 h^{-1}, 20;[19] [$(n\text{-}C_4H_9)_4N$]$_2$[$PhPO_3\{WO(O_2)_2\}$] in 1,2-dichloroethane, 80 h^{-1}, 40;[20] $\{WZn[M(H_2O)]_2(ZnW_9O_{34})_2\}^{q-}$ (M: Zn^{2+}, Mn^{2+}, Ru^{3+}, Fe^{3+}, etc.) in 1,2-dichloroethane, 167 h^{-1}, 1000;[21] Na_2WO_4-phosphate buffer-β-D-fructopyranoside in water, 0.4 h^{-1}, 10.[22]

For the epoxidation of *cis*- and *trans*-allylic alcohols, the configurations around the C=C moieties were retained in the corresponding epoxy alcohols (entries 2, 5, and 6). Such a stereospecific epoxidation suggests that the free-radical intermediates are not involved in the epoxidation. Furthermore, regioselective epoxidation of 3,7-dimethyl-2,6-octadien-1-ol took place at the electron-deficient allylic 2,3-double bond to afford only the 2,3-epoxy alcohol in high yield (entry 6). The epoxidation of secondary β,β-disubstituted allylic alcohol (1,3-allylic strained alcohol), 4-methyl-3-penten-2-ol, proceeded diastereoselectively to form mainly the *threo*-epoxy alcohol (entry 7). An allylic alcohol without 1,3-allylic strain, 3-penten-2-ol, gave the *erythro*-rich epoxy alcohol (entry 8). These selectivities for the epoxidations of secondary allylic alcohols are similar to those for $VO(acac)_2$/TBHP systems,[5,23–25] and different from those with dimethyldioxirane[5,25] and TS-1/urea-hydrogen peroxide.[5,25]

Table 2. Epoxidation of various allylic alcohols with hydrogen peroxide in water catalyzed by **I**.[a]

Entry	Substrate	Time [h]	Product	Yield [%]
1[b]		10		95
2[c]		2		96
3		2		97
4		4		90
5		5		98[d]
6[e]		12		85[d]
7		6		85 *erythro/threo* (6/94)
8[b]		10		83[f] *erythro/threo* (76/24)

[a] Reaction conditions: allylic alcohol (5 mmol), **I** (20 μmol, 0.4 mol %), 30% aqueous H_2O_2 (5 mmol), water (6 mL), 305 K. Yields were based on allylic alcohol which were determined by GC and ^{1}H NMR using an internal standard technique.

[b] **I** (100 μmol, 2 mol %).

[c] Substrate: *cis*/*trans* = 13/87, epoxy alcohol: *cis*/*trans* = 13/87.

[d] Isolated yield.

[e] [$n\text{-}(C_{12}H_{25}N(CH_3)_3)_2[W_2O_3(O_2)_4(H_2O)]$] (20 μmol) was used as a catalyst.

[f] 3-Buten-2-one was produced as a by-product (7% yield).

The structural stability of catalyst **I** was confirmed by direct observation of the reaction solution with *in-situ* IR and UV-vis spectroscopy. No changes in the spectra were observed during the oxidation. The concentrated solution of **I** (0.3 M) was prepared for ^{183}W NMR measurements and the spectrum showed one signal at – 704.5 ppm. No spectral changes were observed during the reaction. These facts show that **I** is stable under the reaction conditions. Oxidation products could easily be isolated by simple extraction using dichloromethane (or pentane) after the oxidation since catalyst **I** was completely insoluble in these solvents. Actually, no leaching of tungsten into the organic phase was confirmed by inductively coupled plasma atomic emission analysis. Therefore, the aqueous phase including the catalyst could be recovered without loss of the tungsten species. It is notable that **I** could be reused for the epoxidation of 2-buten-1-ol without loss of the high catalytic performance.

In summary, the dinuclear peroxotungstate **I** is found to be an effective homogeneous catalyst for the highly chemo-, regio-, and diastereoselectivity, and stereospecific epoxidation of allylic alcohols in water with high efficiency of hydrogen peroxide utilization. The mechanistic work is in progress.

Experimental Section

Materials

The compound **I** was synthesized by a modification of the procedure reported in ref.[17] and characterized by elemental analysis, IR, UV-vis, ^{183}W NMR spectroscopy, and X-ray crystallographic structural analysis. The characterization results are as follows: anal. calcd. for $K_2[\{W(=O)(O_2)_2(H_2O)\}_2(\mu\text{-}O)] \cdot 2\,H_2O$: H 1.16, O 34.6, K, 11.27 W 52.99%; found: H 1.12, K 11.98, W 53.19%. IR (400–4000 cm^{-1}: KBr disk; below 600 cm^{-1}: polyethylene disk): $\nu = 966\ \nu(W{=}O)$, $854\ \nu(O\text{-}O)$, $764\ \nu_{asym}(W\text{-}O\text{-}W)$, $615\ \nu_{sym}(W(O_2))$, $566\ \nu_{asym}(W(O_2)$, $332\ \nu(W(OH_2))$ cm^{-1}; UV-vis (H_2O): λ (ε/M^{-1} cm^{-1}) = 243 nm (608); ^{183}W NMR (11.2 MHz, D_2O, Na_2WO_4, 0.3 M, pH = 2.5): $\delta = -704.5$. 4-Methyl-3-penten-2-ol was synthesized and confirmed by GC analysis in combination with mass and ^{1}H and ^{13}C NMR spectroscopy as reported previously.[26,27] All epoxy alcohols are known and have been identified by comparison of their ^{1}H and ^{13}C NMR signals with the literature data.[28–35]

Procedure for the Oxidation of Allylic Alcohols

The epoxidation was carried out in a glass vial containing a magnetic stirring bar. A typical procedure for the epoxidation of allylic alcohol is as follows. Into a glass vial were successively placed **I** (20 μmol), 2-buten-1-ol (5 mmol), hydrogen peroxide (30% aqueous solution, 5 mmol), and water (6 mL). The reaction mixture was stirred at 305 K for 2 h. After the reaction was finished, the products were extracted by using dichloromethane or pentane, and the yield and product selectivity were determined by GC or ^{1}H NMR analysis. The recovered aqueous phase was subjected to recycling.

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