Hydrogen-Bond-Assisted Epoxidation of Homoallylic and Allylic Alcohols with Hydrogen Peroxide Catalyzed by Selenium-Containing Dinuclear Peroxotungstate

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Abstract: The reaction of peroxotungstates (H_2WO_4 + H_2O_2) with H_2SeO_4 gave the novel selenium-containing dinuclear tungsten species, $(TBA)_2[SeO_4\{WO(O_2)_2\}_2]$ (**I**, TBA = $[(n\text{-}C_4H_9)_4N]^+$), which was characterized by elemental analysis, IR, Raman, UV–vis, ^{77}Se NMR, ^{183}W NMR, and CSI-MS. Various kinds of homoallylic and allylic alcohols were efficiently epoxidized to the corresponding epoxy alcohols in high yields with 1 equiv. H_2O_2 with respect to the substrates. Compound **I** showed the highest catalytic activity for H_2O_2-based epoxidation of homoallylic and allylic alcohols among selenium and tungsten complexes. The turnover frequency reached up to 150 h^{-1} in a 10 mmol-scale epoxidation of *cis*-3-hexen-1-ol and this value was the highest among those reported for the transition-metal catalyzed epoxidation of homoallylic alcohols with H_2O_2. The kinetic, mechanistic, computational studies showed that the stabilization of the transition-state by the hydrogen bonding between **I** and the substrates results in the high reactivity for the **I**-catalyzed epoxidation of homoallylic and allylic alcohols. The nature of the hetero atoms in the di- and tetranuclear peroxotungstates with XO_4^{n-} ligands (X = As(V), P(V), S(VI), Si(IV), etc.) was crucial in controlling the Lewis acidity of the peroxotungstates, which significantly affects their electrophilic oxygen transfer reactivity. All the data of the structural, kinetic, spectroscopic, and computational comparison show that the dimeric peroxotungstate unit, $\{WO(O_2)_2\}_2$, in **I** is activated by the SeO_4^{2-} ligand.

Introduction

Oxidation reaction is an industrial core technology for converting bulk chemicals to useful products.[1] Epoxy alcohols are versatile building blocks in organic synthesis because a wide variety of structural moieties can be constructed by the subsequent regio- and stereoselective attack of various nucleophiles.[2] The 3,4-epoxy alcohols have widely been used in organic syntheses, particularly in the preparation of 1,3-diols and *O*- and *N*-heterocyclic compounds.[2,3] The iodocyclization-based method is frequently used for the synthesis of the 3,4-epoxy alcohols.[4] However, the iodocyclization requires stoichiometric reagents of a strong base and gaseous carbon dioxide and the atom efficiency is low. In this context, the transition metal-catalyzed epoxidation of homoallylic alcohols is a reliable solution, which replaces synthetic process with low atom efficiency using stoichiometric reagents.

While the chemo-, regio-, diastereo-, and stereoselective epoxidation of allylic alcohols with a wide variety of oxidants and/or catalysts have been developed,[5] the effective catalytic systems for the epoxidation of homoallylic alcohols have been limited. Although titanium, molybdenum, vanadium, and zirconium complexes catalyze the selective epoxidation of homoallylic alcohols, the use of organic hydroperoxides such as *tert*-butyl hydroperoxide (TBHP) and cumene hydroperoxide is required.[6] The use of H_2O_2 as an oxidant is much more desirable from economic and environmental points of view. However, most metal-catalyzed H_2O_2-based systems have disadvantages,[7] especially their low reactivities (5–46% H_2O_2-

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based yields to epoxy alcohols), low selectivities due to the rearrangement of epoxy alcohols to triols or five-membered cyclic byproduct, use of an excess H_2O_2 (1.5−4.0 equiv) with respect to substrates, narrow applicability to a limited number of substrates, and/or the need of additives. Thus, the truly efficient catalytic systems for the epoxidation of homoallylic alcohols with H_2O_2 have scarcely been known.

Over the past few decades, homogeneous and heterogeneous transition metal catalysts such as Ti, V, Mn, Fe, W, Re, and Pt for the H_2O_2-based epoxidation have been developed.[5,8,9] The tungstate-based epoxidation systems with H_2O_2 have attracted much attention because of their high reactivities and inherent poor activity for the decomposition of H_2O_2.[5,9] Among them, $[PO_4\{WO(O_2)_2\}_4]^{3-}$ can catalyze the epoxidation of various organic substrates[10] and the peroxo species has been postulated to be a catalytically active under both Ishii's conditions ($H_3PW_{12}O_{40}/H_2O_2$) and Venturello's conditions ($H_2WO_4/H_3PO_4/H_2O_2$).[10,11] Much effort has also been made to synthesize mono-, di-, and tetranuclear peroxotungstate analogues containing other hetero atoms such as As, S, and Si. While some hetero atoms can enhance the activity of peroxotungstates,[12,13] the effect of hetero atoms of peroxotungstates on the epoxidation activities has not yet been clarified. It is important to reveal the relationship between the structures of the peroxotungstates and their oxidation activity in order to develop the novel tungstate catalysts. In this context, computational approaches are very useful not only to understand the roles of hetero atoms but also to predict the superior catalysts.[14] Although there are many computational reports on the epoxidation by mononuclear species such as Mo,
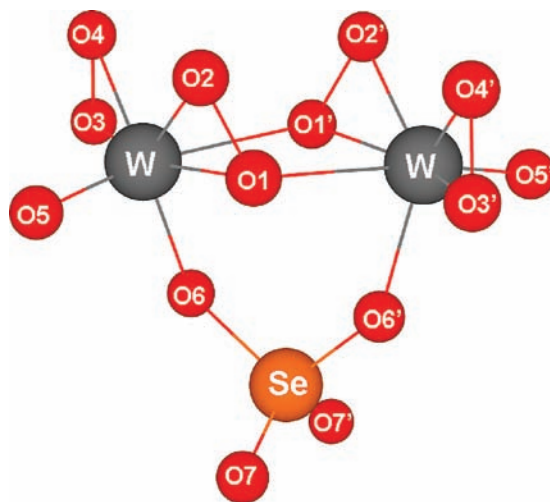

Figure 1. Proposed structure of the anion part of **I**. The structure of $[SeO_4\{WO(O_2)_2\}_2]^{2-}$ was calculated with DFT using the Gaussian 03 program package. Theory: B3LYP; basis sets: 6-31+G(d,p) (O atoms) and LanL2DZ (Se and W atoms). Orange, gray, and red balls represent selenium, tungsten, and oxygen atoms, respectively.

Ti, W, and Re,[15] the computational approaches of the polynuclear peroxotungstates containing hetero atoms are scarcely known.[16]

In this paper, we report the efficient hydrogen-bond-assisted epoxidation of homoallylic and allylic alcohols with H_2O_2 catalyzed by a novel selenium-containing dinuclear peroxotungstate, $(TBA)_2[SeO_4\{WO(O_2)_2\}_2]$ (**I**, TBA=(n-$C_4H_9)_4N^+$, Figure 1; eq 1). To the best of our knowledge, the selenium-containing peroxotungstate and its use in catalytic oxidation with H_2O_2 have never been reported. The present system has the following significant advantages: (i) high yields, selectivities to epoxy alcohols, and efficiencies of H_2O_2 utilization; (ii) use of 1 equiv. H_2O_2 with respect to a substrate instead of excess H_2O_2 or organic hydroperoxides; and (iii) mild reaction conditions. The catalyst effect, kinetic, mechanistic, and computational studies on the **I**-catalyzed epoxidation suggest that a strongly hydrogen-bonded transition state results in the specific reactivity of **I** and that the SeO_4^{2-} ligand enhances the reactivity of a dimeric peroxotungstate unit.
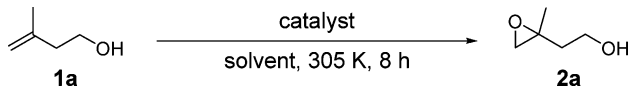

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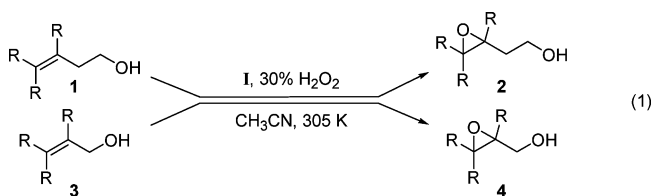
Results and Discussion

Epoxidation of Homoallylic and Allylic Alcohols. The catalytic activity of **I** was compared with those of selenium and tungsten catalysts for the epoxidation of 3-methyl-3-buten-1-ol (**1a**)

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Table 1. Effect of Catalysts on Epoxidation of **1a** with H_2O_2[a]

entry	catalyst	yield (%)	E_{ox} (%)	R_0 (mM min^{-1})
1	**I**	84	99	0.54
2	without	<1		
3[b]	H_2SeO_4	<1		
4[c]	SeO_2	<1		
5[d]	H_2WO_4	17		
6[b]	H_2SeO_4 + H_2WO_4	<1		
7[e]	H_2WO_4 + Me_3NO	<1		
8[f,g]	H_2WO_4 + Na_2WO_4 + chloroacetic acid + [(n-C_8H_{17})$_3$MeN]Cl	<1		
9[g]	$K_2[\{WO(O_2)_2(H_2O)\}_2(\mu\text{-}O)]\cdot 2H_2O$	23	39	0.09
10	$(TBA)_2[\{WO(O_2)_2\}_2(\mu\text{-}O)]$	16	23	0.09
11	$(TBA)_2[SO_4\{WO(O_2)_2\}_2]$	69	89	0.48
12[h]	$(THA)_3[AsO_4\{WO(O_2)_2\}_4]$	62	89	0.18
13[h]	$(THA)_3[PO_4\{WO(O_2)_2\}_4]$	28	30	0.15
14	$(TBA)_2[HAsO_4\{WO(O_2)_2\}_2]$	12	35	0.04
15	$(TBA)_2[HPO_4\{WO(O_2)_2\}_2]$	6	99	0.01
16	$(TBA)_2[Ph_2SiO_2\{WO(O_2)_2\}_2]$	<1	<1	
17	$(TBA)_4[\gamma\text{-}SiW_{10}O_{34}(H_2O)_2]$	34	95	0.15
18[i]	$(TBA)_4[\gamma\text{-}SiW_{10}O_{38}V_2(\mu\text{-}OH)_2]$	33	35	0.31

[a] Reaction conditions: Catalyst (W: 6 mol % relative to **1a** and H_2O_2), **1a** (1 mmol), 30% aqueous H_2O_2 (1 mmol), CD_3CN (6 mL), 305 K, 8 h. Yields of **2a** were determined by ^1H NMR. Remaining H_2O_2 after the reaction was estimated by potential difference titration of Ce^{3+}/Ce^{4+} (0.02 M of aqueous $Ce(NH_4)_4(SO_4)_4\cdot 2H_2O$). E_{ox} (H_2O_2 efficiency) (%) = products (mol)/consumed H_2O_2 (mol) × 100. R_0 values were determined from the reaction profiles at low conversions (≤10%) of both **1a** and H_2O_2. [b] H_2SeO_4 (3 mol %). [c] SeO_2 (3 mol %). [d] R_0 value and H_2O_2 efficiency could not be estimated because of the production of large amounts of unknown byproduct. [e] Me_3NO (9 mol %). [f] H_2WO_4 (3 mol %), Na_2WO_4 (3 mol %), chloroacetic acid (3 mol %), [(n-C_8H_{17})$_3$MeN]Cl (24 mol %). [g] D_2O (6 mL). [h] THA = [(n-C_6H_{13})$_4$N]$^+$. [i] CD_3CN/t-BuOH (3/3 mL).

(Table 1). Among the catalysts tested, **I** showed the highest yield (84%) of the corresponding epoxy alcohol (**2a**) (entry 1). The epoxidation did not proceed in the absence of **I** (entry 2). The SeO_2 catalyst, which has been applied to various oxidations with H_2O_2, was inactive (entry 4).[17] The catalyst precursor of H_2WO_4 was also inactive under the present conditions even in the presence of additives such as H_2SeO_4, trimethylamine N-oxide,[7b] and chloroacetic acid (entries 5–8).[7c] The catalytic activities of other peroxotungstates and polyoxotungstates were much lower than that of **I** (entries 9–18).[10–13,18] The yields of **2a** and efficiencies of H_2O_2 utilization of the dinuclear peroxotungstates with XO_4^{n-} ligands (X = Se, S, P, As, and Si) decreased in the order of Se (84%, 99%) > S (69%, 89%) > As (12%, 35%) > P (6%, 99%) > Si (<1%, <1%).[12,13] The activity (yield) order was the same as that of pK_a values of H_nXO_4, suggesting that the strongest Lewis acidity of W atoms in **I** has an important role for the epoxidation.[19–21]

Various homoallylic alcohols **1a**–**1j** could efficiently be epoxidized under the stoichiometric conditions (substrate:H_2O_2

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Table 2. Epoxidation of Homoallylic Alcohols with 30% Aqueous H_2O_2 Catalyzed by **I**[a]

entry	substrate	time (h)	product	yield (%)
1[b]	**1a**	8	**2a**	84 (76)
2[c]	**1b** (R=C_2H_5)	8	**2b**	84 (79)
3[c]	**1b**	6	**2b**	81
4	**1c** (R=C_4H_9)	7	**2c**	81 (80)
5	**1d** (R=C_5H_{11})	7	**2d**	89 (75)
6[d]	**1e**	10	**2e**	76 (66)
7	**1f**	10	**2f**	34
8[b]	**1g**	6	**2g**	40
9	**1h**	9	**2h** cis/trans = 54/46	84 (76)
10[e]	**1i**	4	**2i** cis/trans = 58/42	68
11[e]	**1j**	6	**2j** cis/trans = 54/46	86

[a] Reaction conditions: **I** (1 mol % relative to substrate and H_2O_2), substrate (1 mmol), 30% aqueous H_2O_2 (1 mmol), CD_3CN (6 mL), 305 K. Yield and selectivity were determined by ^1H NMR and GC-MS. The values in the parentheses were the isolated yields for the large-scale (10 mmol scale) epoxidation (see the Supporting Information). Yield (%) = product (mol)/H_2O_2 (mol) × 100. [b] **I** (3 mol %). [c] **I** (3 mol %), 10% aqueous H_2O_2 (1 mmol). [d] **I** (5 mol %). [e] **I** (2 mol %).
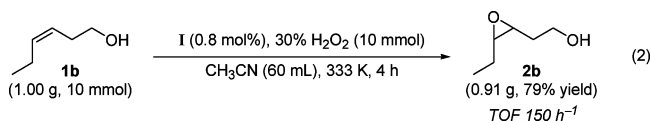
= 1:1), and the corresponding epoxy alcohols were obtained with high yields and selectivities (Table 2). The efficiency of H_2O_2 utilization was more than 95% in each case. The epoxidation of primary disubstituted homoallylic alcohols **1a**–**1e** proceeded chemoselectively to afford the corresponding epoxy alcohols without significant formation of aldehydes, five-membered cyclic byproduct, and triols (entries 1–5).[7] For example, the turnover frequency (TOF) was as high as 150 h^{-1} in a 10 mmol-scale epoxidation of **1b** (eq 2). This value was the highest among those (0.5–77 h^{-1}) reported for the transition-metal catalyzed epoxidation of homoallylic alcohols with H_2O_2.[7] In addition, 0.91 g of **2b** (79% yield, 99% purity by ^1H NMR spectroscopy) could be isolated. For the epoxidation of *cis*- and *trans*-homoallylic alcohols, the configurations around the C=C moieties were retained in the corresponding epoxy alcohols (entries 2–6), suggesting that the free-radical intermediates are not involved in the present epoxidation. The epoxidation of **1b** with more diluted H_2O_2 (10% aqueous solution) also proceeded to afford **2b** in 81% yield (entry 3). The epoxidation of the primary trisubstituted homoallylic alcohols **1f** and **1g** gave the corresponding epoxy alcohols in moderate yields (entries 7 and 8). After the epoxidation of **1b** was completed, **1b** and 30% aqueous H_2O_2 were added to the reaction solution (see the Supporting Information). The epoxidation again proceeded with almost the same yield and selectivity as those observed for the first run (Figure S1). Thus, **I** is intrinsically recyclable. In addition, **I** could easily be recovered in almost quantitative yield by addition of an excess amount of diethyl ether (precipitation method, see the Supporting Information) to the reaction solution. The recovered **I** could be reused without loss of its catalytic activity and selectivity. The ^{77}Se NMR spectrum of **I** after the epoxidation showed a signal at 1046 ppm, which was observed

for the as-synthesized **I**. These facts show that **I** is stable under the catalytic conditions.

(2)

Secondary acyclic and cyclic homoallylic alcohols **1h**, **1i**, and **1j** were converted to the corresponding *cis*- and *trans*-epoxide mixtures of **2h** (54:46), **2i** (58:42), and **2j** (54:46), respectively (entries 9–11). Similar diastereoselectivities are observed for the stoichiometric epoxidation with *m*-chloroperbenzoic acid (*m*-CPBA)[6a] (60:40) and dimethyl dioxirane (DMD)[22] (53:47) while the VO(acac)$_2$/TBHP system shows high diastereoselectivities to *cis*-epoxy alcohols (>92:<8).[6a,b]

Complex **I** also catalyzed the epoxidation of various kinds of allylic alcohols with 30% aqueous H$_2$O$_2$ under the stoichiometric conditions (substrate:H$_2$O$_2$ = 1:1) (Table 3). The corresponding epoxy alcohols were obtained with high yields and selectivities. The efficiency of H$_2$O$_2$ utilization was more than 85% in each case. The epoxidation of primary allylic alcohols **3a**–**3e** proceeded chemoselectively to afford the epoxy alcohols without formation of α,β-unsaturated aldehydes and carboxylic acids (entries 1–5). For the epoxidation of *cis*- and *trans*-allylic alcohols, the configurations around the C=C moieties were retained in the corresponding epoxy alcohols (entries 1, 2, 4, 5, 7, and 9–11).

For the competitive epoxidation of homoallylic and allylic alcohols (**1a** vs **3c**) catalyzed by **I**, the ratio of the formation rate of 2,3-epoxy-2-methyl-1-propanol (**4c**) to that of **2a** was 57:43 (Figure S2(a)). This value was comparable to those of the methyltrioxorhenium (MTO)/urea-hydrogen peroxide adduct (UHP) system (42:58)[23f] and the *m*-CPBA system (57:43).[6a] On the other hand, **3c** was epoxidized much more preferentially than **1a** in the K$_2$[{WO(O$_2$)$_2$(H$_2$O)}$_2$(μ-O)]·2H$_2$O/H$_2$O$_2$ system (>99:<1, Figure S2(b)). These results suggest that the metal-

Table 3. Epoxidation of Allylic Alcohols with 30% Aqueous H$_2$O$_2$ Catalyzed by **I**[a]

entry	substrate	time (h)	product (yield (%))
1[b]	3a	6	4a (93)
2	3b	2	4b (94)
3[c]	3c	3	4c (76)
4[d]	3d	3	4d (89)
5	3e	2.5	2,3-4e (76) / 6,7-4e (17)
6	3f	13	4f (61) *threo/erythro* = 60/40
7	3g	4	4g (93) *threo/erythro* = 74/26
8[c]	3h	5	4h (71) *threo/erythro* = 42/58
9	3i	3	4i (88) *threo/erythro* = 47/53
10	3j	2	4j (91) *threo/erythro* = 94/6
11	3k	1.5	4k (89) *threo/erythro* = 94/6
12	3l	5	4l (85) *threo/erythro* = 96/4
13	3m	5	4m (72) *threo/erythro* = 23/77
14	3n	7	4n (68) *cis/trans* = 83/17

[a] Reaction conditions: **I** (1 mol % relative to substrate and H$_2$O$_2$), substrate (1 mmol), 30% aqueous H$_2$O$_2$ (1 mmol), CD$_3$CN (6 mL), 305 K. Yield and selectivity were determined by ^{1}H NMR. Yield (%) = product (mol)/H$_2$O$_2$ (mol) × 100. [b] **I** (3 mol %). [c] **I** (5 mol %). [d] **I** (2 mol %).

alcoholate species is not formed in the transition state for the present **I**-catalyzed epoxidation of homoallylic alcohols.[24,25]

In addition, the chemo-, regio-, and diastereoselectivities observed for the **I**-catalyzed epoxidation of primary cyclic allylic and secondary allylic alcohols were different from those for H$_2$O$_2$-based typical tungsten systems such as H$_2$WO$_4$, K$_2$[{WO(O$_2$)$_2$-(H$_2$O)}$_2$(μ-O)]·2H$_2$O, [WZnM$_2$(ZnW$_9$O$_{34}$)$_2$]$^{12-}$ (M = Zn(II) and Mn(II)), and [PW$_{11}$O$_{39}$]$^{7-}$.[5,7,9,18,23g] The present epoxidation of geraniol **3e** gave a mixture of the 2,3-**4e** and 6,7-**4e** in a ratio of 82:18, while no formation of 6,7-**4e** was observed for the K$_2$[{WO(O$_2$)$_2$(H$_2$O)}$_2$(μ-O)]·2H$_2$O/H$_2$O$_2$ system.[18c] The secondary allylic alcohols **3f** and **3g** without allylic strain were epoxidized in low *threo* diastereoselectivities (entries 6 (60%) and 7 (74%)). The substrate **3j** with the 1,3-allylic strain showed high *threo* selectivity (94%) while **3h** and **3i** with the 1,2-allylic strain were epoxidized to the *threo*- and *erythro*-epoxide mixtures of **4h** (*threo/erythro* = 42/58) and **4i** (*threo/erythro* = 47/53), suggesting the weak influence of the 1,2-allylic strain (entries 8–10). The *threo*-epoxy alcohol was dominantly

(20) For the catalytic epoxidation by the d_0-transition metal catalysts, the oxidation states of the metal centers are not changed during the catalysis. The metal centers function as Lewis acids by withdrawing electrons from the O–O bond and thus increasing the electrophilic character of the coordinated peroxide. Active catalysts are the metal centers with strong Lewis acidity. (a) Thiel, W. R.; Eppinger, J *Chem.–Eur. J.* **1997**, *3*, 696. (b) Arends, I. W. C. E.; Sheldon, R. A. *Top. Catal.* **2002**, *19*, 133. (c) Oyama, S. T. In *Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis*; Oyama, S. T., Ed.; Elsevier: Amsterdam, 2008; pp 1–99.

(21) The pK_a values of the ligands can be recognized as an index of the Lewis acidity of transition metal complexes: Nabavizadeh, S. M.; Rashidi, M. *J. Am. Chem. Soc.* **2006**, *128*, 351.

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(24) The formation of tungsten-alcoholate species is not possible in the present epoxidation because the W atoms in **I** are coordinatively saturated. In contrast, the aquo ligands of K$_2$[{WO(O$_2$)$_2$(H$_2$O)}$_2$(μ-O)]·2H$_2$O could be exchanged with alcohols to form metal-alcoholate species.[18c] Therefore, the present diastereoselectivity (*threo/erythro* = 94/6) for **3k** was quite different from those (34/66–56/44) for typical H$_2$O$_2$-based tungsten systems, for which the formation of tungsten-alcoholate species has been proposed.[18c,23g]

(25) The epoxidation of 3-methyl-3-butenyl acetate gave the corresponding epoxide in 13% yield under the same reaction conditions as those in Table 1. The yield for the acetate derivative was much lower than that (84%) for the homoallylic alcohol **1a**, suggesting that the hydroxyl functionality plays an important role in the present epoxidation.
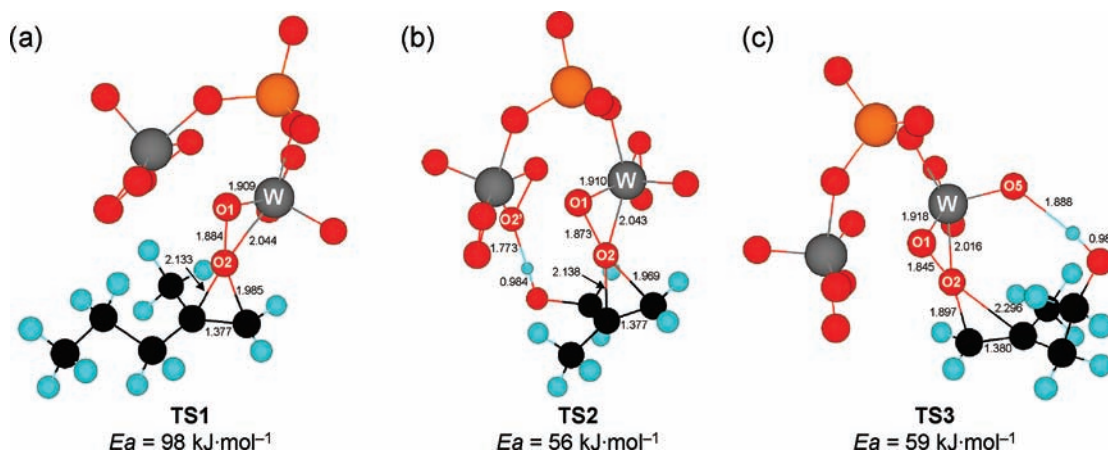
Figure 2. Transition-state structures and the corresponding activation barriers for the epoxidation of (a) 2-methyl-1-pentene, (b) 2-methyl-2-propen-1-ol (**3c**), and (c) 3-methyl-3-buten-1-ol (**1a**) with **I** (bond lengths in Å). Orange, gray, red, black, and light blue balls represent selenium, tungsten, oxygen, carbon, and hydrogen atoms, respectively.

produced (94% selectivity) for the epoxidation of the stereo-chemical probe (Z)-3-methyl-3-penten-2-ol (**3k**) with both 1,2- and 1,3-allylic strains (entry 11). The high *threo* diastereo-selectivities for **3j** and **3k** indicate the large 1,3-allylic strains. The present diastereoselectivities for the epoxidation of the methyl-substituted secondary allylic alcohols are similar to those of Ti-β/H$_2$O$_2$, MTO/UHP, *m*-CPBA, and DMD systems, for which hydrogen-bonded transition states have been proposed.[23] In the case of 2-cyclohexen-1-ol **3n**, the *cis*-epoxy alcohol **4n** was obtained in high chemo- and diastereoselectivities (*cis/trans* = 83/17) without the significant formation of the α,β-unsatu-rated ketone (80% selectivity to **4n**) (entry 14), while 2-cyclo-hexen-1-one was formed as a major product in the K$_2$[{WO(O$_2$)$_2$-(H$_2$O)}$_2$(μ-O)]·2H$_2$O/H$_2$O$_2$ (45% selectivity to **4n**)[18c] and [WZnM$_2$(ZnW$_9$O$_{34}$)$_2$]$^{12-}$ (M = Zn(II) and Mn(II))/H$_2$O$_2$ (42−45% selectivity to **4n**) systems,[23g] for which the metal-alcoholate binding with allylic alcohols has been postulated. All these results for the chemo-, regio-, and diastereoselectivities support that the present epoxidation of allylic alcohols proceeds via a hydrogen-bonded transition state between **I** and the substrates.[26,27] The *tert*-butyl-substituted allylic alcohols **3l** and **3m** (entries 12 and 13) allow a differentiation between the two dihedral arrangements (ca. 120° for *m*-CPBA, Ti-β, and MTO vs ≥ 130° for DMD).[23] The high *threo* selectivity of **4l** (*threo/erythro* = 96/4) and *erythro* selectivity of **4m** (*threo/erythro* = 23/77) were observed, showing that the dihedral angles (C=C−C−O) of the present epoxidation system is ca. 120°.

Reaction Mechanism. On the basis of these results, the present epoxidation would proceed via a hydrogen-bonded transition state. For the competitive epoxidation of the homoallylic alcohol (**1a**), allylic alcohol (**3c**), and simple olefin (2-methyl-1-pentene) catalyzed by **I**, the reactivity decreased in the order of **3c** (4.8) > **1a** (3.4) > 2-methyl-1-pentene (1.0) (Table S1). This order was not consistent with that of π(C=C) HOMO energies (2-methyl-1-pentene (−9.44 eV) > **1a** (−9.61 eV) > **3c** (−9.67 eV)),[28] showing that the template effect reflects the reactivity of these olefins. While the hydrogen-bonded transition state has been proposed for the *m*-CPBA system, the reaction rates of the allylic and homoallylic alcohols were lower than that of the simple olefin (Table S1) and the template effect was not observed.[6a] Similar lower reaction rates of the allylic and

homoallylic alcohols than those of the simple olefins have been reported for the DMD and MTO/H$_2$O$_2$ systems.[29]

In order to investigate the possible hydrogen-bond-mediated activation of homoallylic and allylic alcohols for the present epoxidation, the density functional theory calculations were carried out. The transition-state structures and activation barriers for the epoxidation of **1a**, **3c**, and 2-methyl-1-pentene with **I** were calculated on the assumption that the olefin double bond directly attacks the peroxo oxygen groups in a spiro fashion (i.e., the CCO plane is almost orthogonal to the WOO plane).[15] The transition-state structures with the lowest activation barriers for the substrates are shown in Figure 2.[30] For the epoxidation of **1a** and **3c**, the intermolecular oxygen transfer was assisted by the hydrogen bonding, where the oxo and/or peroxo species act as hydrogen bond acceptors and HOR (R = 2-methyl-2-propenyl and 3-methyl-3-butenyl) as hydrogen bond donors. The activation barriers of **3c** (**TS2**, 56 kJ·mol^{-1}) and **1a** (**TS3**, 59 kJ·mol^{-1}) were much lower than that of 2-methyl-1-pentene (**TS1**, 98 kJ·mol^{-1}). The hydrogen bond lengths (OH···OW) in **TS2** and **TS3** were 1.773 and 1.888 Å, respectively.[31] These values were much smaller than those calculated for *m*-CPBA/propenol (2.056−2.973 Å),[29b] DMD/propenol (2.097−2.703

(26) The ^{1}H NMR spectrum of **1a** (33 mM) in CD$_2$Cl$_2$ at 233 K showed a broad signal of the OH hydrogen at 1.91 ppm. Upon addition of one equivalent **I** (33 mM) with respect to **1a** at 233 K, the broad signal was observed at 2.03 ppm. The downfield shift of **1a** in the presence of **I** indicates the hydrogen bonding between **I** and **1a** since the downfield shift of the OH hydrogen by the presence of the hydrogen bonding has been reported.[27]

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(28) The electron-withdrawing substituents decrease the electron density of the C=C double bond and reduce the π(C=C) HOMO energy, resulting in the decrease of the reactivity of the olefin with electrophilic oxidants.

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(30) While the activation barriers were dependent on the olefin attack directions, hydrogen-bonding sites, and conformations of the substrates, the activation barriers decreased in the order of **3c** (56−86 kJ·mol^{-1}) > **1a** (59−98 kJ·mol^{-1}) > 2-methyl-1-pentene (98−111 kJ·mol^{-1}) (Figures S3−S5 and Tables S2−S5).

Å),[29c] and $CH_3ReO(O_2)_2$/propenol (1.937−3.220 Å) systems,[29e] suggesting the strong hydrogen bonding interaction of **I**. Such stabilization of the transition-state by the hydrogen bonding between **I** and the substrates without the formation of tungsten-alcoholate species probably results in the high reactivity for the **I**-catalyzed epoxidation of homoallylic alcohols. The computational thermodynamic activation parameters of **TS1** ($\Delta H^{\ddagger}_{298K}$ = 101.4 kJ·mol^{-1}, $\Delta S^{\ddagger}_{298K}$ = −153.9 J·mol^{-1}·K^{-1}, and $\Delta G^{\ddagger}_{298K}$ = 147.3 kJ·mol^{-1}), **TS2** ($\Delta H^{\ddagger}_{298K}$ = 60.4 kJ·mol^{-1}, $\Delta S^{\ddagger}_{298K}$ = −160.7 J·mol^{-1}·K^{-1}, and $\Delta G^{\ddagger}_{298K}$ = 108.3 kJ·mol^{-1}), and **TS3** ($\Delta H^{\ddagger}_{298K}$ = 61.6 kJ·mol^{-1}, $\Delta S^{\ddagger}_{298K}$ = −170.6 J·mol^{-1}·K^{-1}, and $\Delta G^{\ddagger}_{298K}$ = 112.5 kJ·mol^{-1}) suggest that the formation of hydrogen bonds in the transition states gives rise to more a negative activation entropy.[29b,32]

Role of Hetero Atom. In order to clarify the effect of hetero atoms of the di- and tetranuclear peroxotungstates with the XO_4^{n-} ligands (X = Se(VI), As(V), P(V), S(VI), and Si(IV)) on the oxidation activity, the structures of various peroxotungstates were optimized by the DFT calculations and the relationship between the reactivities and the structures of peroxotungstates was investigated. The calculated geometries well agreed with experimental ones; the bond length deviations are within 0.15 Å (Table S5 and Figure S6). Among various plots of the bond lengths against the reaction rates of the catalytic epoxidation of cyclooctene,[33] the reaction rates increased with an increase in the bond lengths between the W atom and the O atom of the XO_4^{n-} ligand, XO−W (X = Se, As, P, S, and Si) (Figure 3a). These trends were also observed in the experimental X-ray crystallographic data. The decrease in the XO−W bond lengths results in the strong interaction between the XO_4^{n-} ligand and dimeric peroxotungstate unit and the low Lewis acidity of W atoms.

The ^{183}W NMR spectra of various peroxotungstates in CD_3CN showed sharp resonances ($\Delta\nu_{1/2}$ = 2.6−7.3 Hz) in the region of −560∼−670 ppm (Figure S7), showing the formation of the single peroxotungstates with O_2^{2-}/W=2.[34] The ^{183}W NMR chemical shifts of the peroxotungstates also had a good correlation with the reaction rates for the catalytic epoxidation (Figure 3b). The reaction rates also increased with an increase in the ^{183}W NMR chemical shifts. The chemical shift reflects the difference in shielding constant (σ) between the reference compound and observed nucleus, and σ is a sum of the

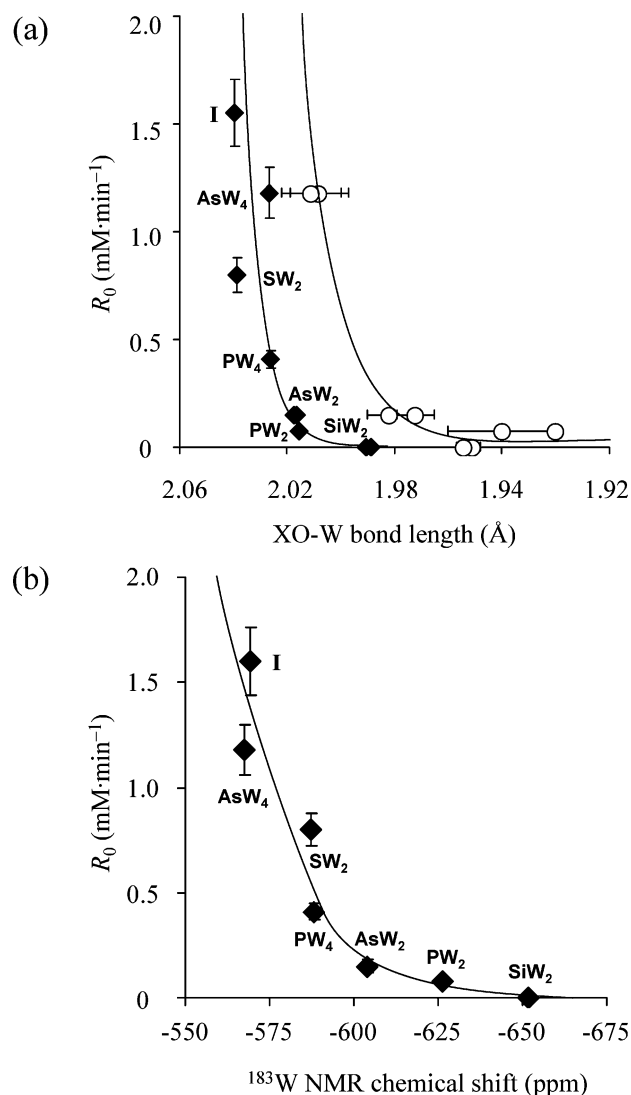**Figure 3.** Correlation between the catalytic epoxidation rates and (a) the theoretical (♦) and experimental (○) XO-W bond lengths and (b) the ^{183}W NMR chemical shift of peroxotungstates. Reaction conditions: Peroxotungstate (W: 10 μmol), cyclooctene (5 mmol), 30% aqueous H_2O_2 (1 mmol), CH_3CN (6 mL), 305 K. R_0 values were determined from the reaction profiles at low conversions (≤10%) of both cyclooctene and H_2O_2. Peroxotungstates were abbreviated as follows: (THA)$_3$[AsO$_4${WO(O$_2$)$_2$}$_4$] (**AsW4**), (TBA)$_2$[SO$_4${WO(O$_2$)$_2$}$_2$] (**SW2**), (THA)$_3$[PO$_4${WO(O$_2$)$_2$}$_4$] (**PW4**), (TBA)$_2$[HAsO$_4${WO(O$_2$)$_2$}$_2$] (**AsW2**), (TBA)$_2$[HPO$_4${WO(O$_2$)$_2$}$_2$] (**PW2**), and (TBA)$_2$[Ph$_2$SiO$_2${WO(O$_2$)$_2$}$_2$] (**SiW2**).

diamagnetic and paramagnetic terms ($\sigma = \sigma_d + \sigma_p$).[35] In the case of the transition metals, σ_d can be ignored and the shielding of transition metals is determined by the paramagnetic term σ_p, which depends on the mixing of excited states of appropriate energy and symmetry with the ground state in the presence of a magnetic field.[36,37] The ΔE values in the equation were estimated from the ligand-to-metal charge transfer (LMCT)

(31) Only a signal at 1046 ppm was observed and the chemical shift was the same as that of the as-synthesized **I**. In addition, the transition-state structures and activation barriers for the epoxidation of **1a** with **I** were calculated on the assumption that the oxo species of the SeO$_4^{2-}$ ligand act as hydrogen bond acceptors (**TS3−13**, **TS3−14**, **TS3−17**, and **TS3−20** in Figure S5). The activation barriers of **TS3−13** (75 kJ mol^{-1}), **TS3−14** (71 kJ mol^{-1}), **TS3−17** (67 kJ mol^{-1}), and **TS3−20** (66 kJ mol^{-1}) were higher than that of **TS3** (59 kJ mol^{-1}). Therefore, the interaction between a homoallylic alcohol and an oxo species of the SeO$_4^{2-}$ ligand would not be strong in comparison with those between a homoallylic alcohol and oxo and/or peroxo species of the WO(O$_2$)$_2$.

(32) The computed enthalpy, entropy, and free enthalpy were converted from the 1 atm standard state into the standard state of molar concentration (ideal mixture at 1 mol/L and 1 atm). Rastelli, A.; Bagatti, M.; Gandolfi, R. *J. Am. Chem. Soc.* **1995**, *117*, 4965.

(33) Cyclooctene was used as a model substrate to estimate the true oxygen transfer ability of the peroxotungstates without the hydrogen-bonding interaction between substrate and catalyst.

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(37) The paramagnetic term σ_p can be estimated from the Jameson and Gutowsky equation: $\sigma_p = (2e^2h^2)/(3m^2c^2\Delta E)[\langle r^{-3}\rangle_p P_u + \langle r^{-3}\rangle_d D_u]$ where P_u and D_u represent respectively the unbalance of valence electrons in p and d orbitals centered on the atom, ΔE is the average energy of excitation to a state of the correct symmetry to be mixed with the ground state, and $\langle r^{-3}\rangle_{p,d}$ represents the average value of r^{-3} over the p and d wave functions.[35,36]
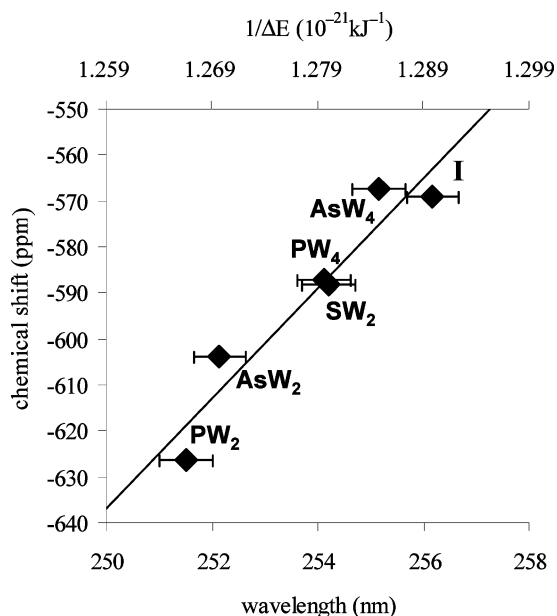
Figure 4. Plots of ^{183}W NMR chemical shifts against wavelengths (lower *x* axis) and the reciprocal of the LMCT energies (upper *x* axis). The abbreviations of peroxotungstates are shown in Figure 3.

transitions in the UV−vis spectra.[38] The approximately linear relationship between the ΔE values and ^{183}W NMR chemical shifts for the peroxotungstates was observed as shown in Figure 4. Such linear correlations were also observed for the transition metal peroxo complexes, polyoxometalates, and cobalt(III) porphyrin complexes.[39] The electronic character of the ligands for vanadium peroxo complexes was also quantitatively correlated with the ^{51}V NMR chemical shift values: The shielding increases with the electron donating ability of the ligand. A good Ramsey-type correlation as shown in Figure 4 suggests that the energy of the LMCT transitions is influenced by the electron density in the peroxo-metal bonding interaction.[39e,40] All these observations indicate that peroxotungstates containing strongly electron donating ligands (i.e., with short XO-W bond lengths) are weak electrophilic oxidants.

Conclusion

In conclusion, the novel selenium-containing dinuclear peroxotungstate of **I** was synthesized and characterized. Complex **I** showed high catalytic activities for epoxidation of homoallylic and allylic alcohols with one equivalent H_2O_2 with respect to the substrate. The kinetic, mechanistic, computational studies showed that the stabilization of the transition-state by hydrogen bonding between **I** and the substrates without the

formation of tungsten-alcoholate species results in the high reactivity for the **I**-catalyzed epoxidation of homoallylic and allylic alcohols. On the basis of the DFT calculations and ^{183}W NMR results, the XO-W bonds play an important role in the oxygen-transfer ability of peroxotungstates. This reflects the fact that the oxygen transfer to C=C double bond of olefin is hardly available when the XO_4^{n-} ligands are coordinated to the tungsten strongly (i.e., short XO-W bond lengths). Such push−pull ligand effect would modify the Lewis acidic properties of tungsten atoms and the activity of peroxo ligands.

Experimental Section

Materials. Acetonitrile (Kanto Chemical) and dichloromethane (Kanto Chemical) were purified by The Ultimate Solvent System (GlassContour Company) prior to use.[41] Substrates were purified according to the reported procedure.[42] Deutrated solvents (CD$_3$CN, CDCl$_3$, and D$_2$O) were purchased from Aldrich and used as received. Tungstic acid (Wako Chemical), H$_2$SeO$_4$ (Kanto Chemical, 80% aqueous solution), tetra-*n*-butylammonium nitrate (Wako Chemical), H$_2$O$_2$ (Kanto Chemical, 30% aqueous solution) were purchased and used as received. Homoallylic alcohols (**1g**, **1h**, **1i** and **1j**)[43] and secondary allylic alcohols (**3h**, **3i**, **3j**, **3k**, **3l**, and **3m**)[44] were synthesized and confirmed by ^{1}H and ^{13}C NMR spectroscopy and GC/MS as reported previously.

Instruments. IR spectra were measured on a Jasco FT/IR-460 spectrometer Plus using KCl disks. Raman spectra were recorded on a Jasco NR-1000 spectrometer with excitation at 532.36 nm using JUNO 100 green laser (Showa Optronics Co., Ltd.). UV−vis spectra were recorded on a JASCO V-570 spectrometer. NMR spectra were recorded on a JEOL JNM-EX-270 spectrometer (^{1}H, 270.0 MHz; ^{13}C, 67.80 MHz; ^{29}Si, 53.45 MHz; ^{31}P, 109.25 MHz; ^{51}V, 70.90 MHz; ^{77}Se, 51.30 MHz; ^{183}W, 11.20 MHz) by using 5 mm tubes (for ^{1}H, ^{13}C, and ^{31}P) or 10 mm tubes (for ^{29}Si, ^{51}V, ^{77}Se, and ^{183}W). Chemical shifts (δ) were reported in ppm downfield from SiMe$_4$ (solvent, CDCl$_3$) for ^{1}H, ^{13}C, and ^{29}Si NMR spectra, 85% H$_3$PO$_4$ for ^{31}P NMR spectra, VOCl$_3$ for ^{51}V NMR spectra, Me$_2$Se for ^{77}Se NMR spectra, and 2 M Na$_2$WO$_4$ (solvent, D$_2$O) for ^{183}W NMR spectra, respectively. GC analyses were performed on Shimadzu GC-2014 with a flame ionization detector equipped with a InertCap 5 capillary column (internal diameter = 0.25 mm, length = 60 m) and Shimadzu GC-17A with a flame ionization detector equipped with a InertCap Pure-WAX capillary column (internal diameter = 0.25 mm, length = 30 m).

Synthesis and Characterization of [(*n*-C$_4$H$_9$)$_4$N]$_2$[SeO$_4$-{WO(O$_2$)$_2$}$_2$] (I). The TBA salt derivative of [SeO$_4${WO(O$_2$)$_2$}$_2$]$^{2-}$ was prepared as follows: H$_2$WO$_4$ (1.75 g, 7 mmol) was suspended in 15% aqueous H$_2$O$_2$ (9.25 mL, 42 mmol) and the resulting suspension was stirred at 305 K for 30 min until a pale yellow solution was obtained. The solution was filtered to remove insoluble materials followed by addition of 80% H$_2$SeO$_4$ (2.1 mL, 28 mmol). After stirring the solution for 60 min at 273 K, an excess amount of TBA·NO$_3$ (3.05 g, 10 mmol) was added in a single step. After stirring the solution for 30 min at 273 K, the resulting white precipitate was collected by the filtration and then washed with an

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excess amount of H$_2$O and diethyl ether. After the dryness, acetonitrile solution (1 mL) containing the crude product (0.2 g) and a drop of H$_2$O$_2$ was cooled to 277 K. The colorless plate-like crystalline solid was obtained by vapor diffusion of diethyl ether into the acetonitrile solution. Yield: 0.11 g (55% based on the crude product). The ^{77}Se NMR spectrum of **I** in CD$_3$CN showed one signal at 1046 ppm and the chemical shift was different from that of free H$_2$SeO$_4$ (1001 ppm).[45] The ^{183}W NMR spectrum of **I** in CD$_3$CN showed one signal at −570 ppm, showing the formation of the single peroxotungstate with O$_2$$^{2−}$/W=2.[34] The elemental analysis of **I** indicated that the TBA:Se:W molar ratio is 2:1:2. The stoichiometric oxidation of triphenylphosphine with **I** produced triphenylphosphine oxide with 400% yield, suggesting that **I** has 4 equiv of the active oxygen species. The UV−vis spectrum of **I** in CH$_3$CN showed an absorption band at 256.2 nm characteristic of the peroxotungstates.[34] The IR and Raman bands in the range of 520−590, 840−850, and 970−980 cm^{-1} can be assigned to ν(W(O$_2$)), ν(O−O), and ν(W=O), respectively, and the peak positions were close to those of peroxotungstates.[34] The positive ion CSI-MS (cold spray ionization mass spectrometry) of the CH$_3$CN solution of **I** showed a +1-charged ion peak at $m/z = 1398$ attributed to [(TBA)$_3$SeO$_4${WO(O$_2$)$_2$}$_2$]$^+$. All these results suggest that **I** is (TBA)$_2$[SeO$_4${WO(O$_2$)$_2$}$_2$] (Figure 1). Our attempts to obtain crystallographic quality single crystals of **I** in acetonitrile with the vapor diffusion of diethyl ether have been unsuccessful because the poor quality of the crystal did not allow structure refinement. However, the cell parameters and space group of **I** (Orthorhombic, *Pbcn* (no. 60), $a = 14.974(13)$, $b = 15.983(15)$, $c = 18.371(18)$ Å, $V = 4384(7)$ Å^3) were similar to those of TBA$_2$[SO$_4${MoO(O$_2$)$_2$}$_2$]. Therefore, the molecular structure of **I** would be isostructural to [SO$_4${MoO(O$_2$)$_2$}$_2$]$^{2−}$.[46] ^{183}W NMR (11.20 MHz, CD$_3$CN, 298 K, Na$_2$WO$_4$): $\delta = -569.2$ ($\Delta\nu_{1/2} = 3.9$ Hz); ^{77}Se NMR (51.30 MHz, CD$_3$CN, 298 K, (CH$_3$)$_2$Se): $\delta = 1046.4$ ($\Delta\nu_{1/2} = 5.1$ Hz); UV/vis (CH$_3$CN) λ_{max} (ϵ) 256.2 nm (1258 (mol of W)$^{-1}$dm^{3}cm^{-1}); IR (KCl): 972, 915, 884, 864, 847, 831, 779, 739, 698, 654, 593, 576, 520, 463, 393, 371 cm^{-1}; Raman: $\nu = $ 987, 974, 922, 884, 868, 838, 783, 599, 583, 542, 398, 336, 306, 264 cm^{-1}; positive ion MS (CSI, CH$_3$CN): m/z: 1398 [(TBA)$_3$SeO$_4${WO(O$_2$)$_2$}$_2$]$^+$, 2554 [(TBA)$_5${SeO$_4${WO(O$_2$)$_2$}$_2$}$_2$]$^+$, 3709 [(TBA)$_7${SeO$_4${WO(O$_2$)$_2$}$_2$}$_3$]$^+$; elemental analysis calcd (%) for C$_{32}$H$_{72}$N$_2$O$_{14}$SeW$_2$ ((TBA)$_2$[SeO$_4${WO(O$_2$)$_2$}$_2$]): C 33.26, H 6.28, N 2.42, Se 6.83, W 31.82; found: C 33.21, H 6.30, N 2.48, Se 6.53, W 31.21.

Procedure for Catalytic Epoxidation. The catalytic epoxidation of various organic substrates was carried out in a 30-mL glass vessel containing a magnetic stir bar. All products were identified by the comparison of GC retention time, mass spectra, and NMR spectra with those of the authentic samples. A typical procedure for the catalytic oxidation was as follows: **1b** (1 mmol), acetonitrile (6 mL), and 30% aqueous H$_2$O$_2$ (1 mmol) were charged in the reaction vessel. The reaction was initiated by the addition of **I** (10 μmol) and the reaction solution was periodically analyzed. The substrates (**1g**,[43b] **1h**,[48a] **1i**,[43a] **1j**,[43a] **1k**,[48b] **3h**,[44a] **3i**,[48a] **3j**,[48b] and **3k**,[48c]) and epoxy alcohols (**2a**,[49a] **2b**,[49b] **2c**,[49c] **2d**,[49c] **2e**,[49b] **2f**,[49b] **2g**,[49d] **2j**,[49e] **2k**,[49f] **4a**,[50a] **4b**,[50b] **4c**,[50c] **4d**,[50d] 2,3-**4e**,[50e] 6,7-**4e**,[50a] **4f**,[50f] **4g**,[50g] **4h**,[50h] **4i**,[50i] **4j**,[50i] **4k**,[50j] **4l**,[50k,l] **4m**,[23d] and **4n**[50d]) are known and identified by comparison of their ^{1}H and ^{13}C NMR signals with the literature data.

Quantum Chemical Calculations. The calculations were carried out at the B3LYP level theory[51] with 6-31+G(d,p) basis sets for

H, C, O, Si, P, and S atoms and the double-ξ quality basis sets with effective core potentials proposed by Hay and Wadt[52] for As, Se, and W atoms. The entire structure of peroxotungstates was used as a model in the calculations and the overall charge of the system was −3 ([AsO$_4${WO(O$_2$)$_2$}$_4$]$^{3−}$ and [PO$_4${WO(O$_2$)$_2$}$_4$]$^{3−}$) and −2 ([SeO$_4${WO(O$_2$)$_2$}$_2$]$^{2−}$, [SO$_4${WO(O$_2$)$_2$}$_2$]$^{2−}$, [HAsO$_4${WO(O$_2$)$_2$}$_2$]$^{2−}$, [HPO$_4${WO(O$_2$)$_2$}$_2$]$^{2−}$, and [Ph$_2$SiO$_2${WO(O$_2$)$_2$}$_2$]$^{2−}$), respectively. 2-Methyl-1-pentene, 3-methyl-3-buten-1-ol (**1a**), and 2-methyl-2-propen-1-ol (**3c**) were used as model substrates. The all geometries were optimized without the symmetry restrictions. Transition-state structures were searched by numerically estimating the matrix of second-order energy derivatives at every optimization step and by requiring exactly one eigenvalue of this matrix to be negative. The optimized geometries were shown in Tables S2−S5 and Figures 2 and S3−S6. The zero-point vibrational energies were not included. All calculations were performed with the Gaussian 03 program package.[53] The computed enthalpy, entropy, and free enthalpy were converted from the 1 atm standard state into the standard state of molar concentration (ideal mixture at 1 mol/L and 1 atm).[32]

Supporting Information Available: Experimental details, data of substrates and products, Tables S1−S5, and Figures S1−S7. This material is available free of charge via the Internet at http://pubs.acs.org.

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