

Research Note

# Efficient, regioselective epoxidation of dienes with hydrogen peroxide catalyzed by $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$ <sup>☆</sup>

Keigo Kamata,<sup>a</sup> Yoshinao Nakagawa,<sup>b</sup> Kazuya Yamaguchi,<sup>a,b</sup> and Noritaka Mizuno<sup>a,b,\*</sup>

<sup>a</sup> Core Research for Evolutional Science and Technology (CREST), Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama, 332-0012, Japan

<sup>b</sup> Department of Applied Chemistry, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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## Abstract

A divacant, lacunary, Keggin-type silicotungstate,  $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$ , exhibits high catalytic performance for the epoxidation of various nonconjugated dienes using hydrogen peroxide under mild conditions, high regioselectivity to the more accessible double bonds, and high efficiency of hydrogen peroxide utilization. The high regioselectivity for the  $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$ -catalyzed epoxidation would be caused by the steric hindrance of the active site.

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## 1. Introduction

Epoxidation of olefins is an important reaction in the laboratory as well as the chemical industry, because epoxides are widely used as intermediates in organic syntheses [1,2]. Generally, more electron-rich double bonds of dienes are preferably epoxidized when stoichiometric oxidants such as peroxyacids [3] and peroxides [4] or hydroperoxides in the presence of molybdenum compounds [5–7] are used. The effects of steric protection of catalysts for the regioselective epoxidation of nonconjugated dienes have been examined. For example, the highly regioselective epoxidation of more accessible, but less nucleophilic, double bonds using sterically hindered metalloporphyrins with NaOCl and PhIO has been developed [8–11]. In contrast to these expensive oxidants, hydrogen peroxide is an attractive oxidant from economical and environmental viewpoints because it generates only water as a by-product and has a high content of active oxygen species. Although various catalysts for the regioselective epoxidation of nonconjugated dienes with hydrogen peroxide have been studied [12–26], the efficiency of hydrogen peroxide utilization and/or the regioselectivity

is still low. Therefore, efficient systems for the regioselective epoxidation of dienes with hydrogen peroxide are previously unknown.

Very recently, we have reported an efficient, simple route for the epoxidation of various olefins including nonactivated terminal olefins such as propylene with hydrogen peroxide catalyzed by a divacant lacunary silicotungstate,  $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$  (**I**) [27]. In this paper, we report the efficient, regioselective epoxidation of various nonconjugated dienes with hydrogen peroxide catalyzed by **I**.

## 2. Experimental

### 2.1. Instruments

IR measurements were carried out with KBr pellets using a Perkin-Elmer Paragon 1000PC spectrometer. NMR spectra were recorded at 298 K on a JEOL JNM-EX-270 (<sup>1</sup>H, 270 MHz; <sup>13</sup>C, 67.5 MHz; <sup>29</sup>Si, 53.45 MHz; <sup>183</sup>W, 11.20 MHz) spectrometer. Chemical shifts ( $\delta$ ) were reported using SiMe<sub>4</sub> (<sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si) and Na<sub>2</sub>WO<sub>4</sub> (<sup>183</sup>W) as external standards. UV–vis spectra were recorded on a Perkin-Elmer Lambda 12 spectrometer. GC analyses were performed on Shimadzu GC-14B with a flame ionization detector equipped with a TC-WAX capillary or SE-30 packed

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\* Corresponding author. Fax: +81-35841-7220.

E-mail address: [tmizuno@mail.ecc.u-tokyo.ac.jp](mailto:tmizuno@mail.ecc.u-tokyo.ac.jp) (N. Mizuno).

column. Mass spectra were recorded with a Perkin-Elmer TurboMass spectrometer at an ionization voltage of 70 eV.

## 2.2. Procedure for the oxidation of dienes

The epoxidation of nonconjugated dienes was carried out with a 30-mL glass vessel containing a magnetic stir bar. Nonconjugated dienes and solvents were obtained from Aldrich and Tokyo Kasei, and purified by the standard procedure [28]. 1,2-Epoxy limonene and 1,2-epoxy-4-vinylcyclohexene were obtained from Aldrich and used as authentic samples. The other epoxides were synthesized via Payne oxidation [29] and/or *m*-CPBA oxidation, and used as authentic samples. The products were identified by the comparison of GC retention time, mass spectra, and NMR spectra with those of the authentic samples. The quantifications were carried out by calibrated GC analyses. The reaction conditions (i.e., concentration of diene, diene to oxidant ratio, reaction temperature, etc.) were controlled to avoid double epoxidation. It was confirmed that the internal standard was not oxidized at all under the reaction conditions. The diene to oxidant ratio was 5/1 (diene, 5 mmol; H<sub>2</sub>O<sub>2</sub>, 1 mmol). Under the present reaction conditions, diepoxides and glycols were hardly produced in all cases. The carbon balance in each experiment was in the range of 95–100%. The H<sub>2</sub>O<sub>2</sub> remaining after the reaction was analyzed by Ce<sup>4+/3+</sup> titration [30]. A typical procedure for the catalytic epoxidation of nonconjugated dienes was as follows: catalysts containing 80 μmol of tungsten (i.e., [γ-SiW<sub>10</sub>O<sub>34</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>4-</sup>, 8 μmol; [PO<sub>4</sub>{WO(O<sub>2</sub>)<sub>2</sub>}<sub>4</sub>]<sup>3-</sup>, 20 μmol; [W<sub>2</sub>O<sub>3</sub>(O<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup>,

40 μmol), solvent (CH<sub>3</sub>CN, 6 mL), diene (5 mmol), and an internal standard (*n*-decane or naphthalene) were charged in the reaction vessel. The reaction was initiated by the addition of 30% aqueous H<sub>2</sub>O<sub>2</sub> (1 mmol). The reaction solution was periodically sampled and analyzed by NMR and GC in combination with mass spectroscopy. A detailed presentation of physical data of dienes and epoxides is given in Supporting Information. The stoichiometric epoxidation of dienes with *m*-CPBA was carried out under the following conditions: *m*-CPBA (850 μmol), CHCl<sub>3</sub> (6 mL), nonconjugated diene (5 mmol), reaction temperature (305 K), reaction time (0.5 h).

## 3. Results and discussion

Table 1 shows the epoxidation of various dienes with hydrogen peroxide in acetonitrile at 305 K catalyzed by the tetrabutylammonium salt derivative of **I** (TBA-I). Under the present reaction conditions, the amounts of diepoxides and glycols produced through the hydrolysis were negligible in all cases. Under the stoichiometric conditions (1-methyl-1,4-cyclohexadiene (**1a**)/H<sub>2</sub>O<sub>2</sub> molar ratio = 1/1), the total product yield was 61% and the diepoxide was formed. Therefore, we used the reaction conditions in the high ratio of substrate to H<sub>2</sub>O<sub>2</sub>. For the epoxidation of **1a** (entry 1), the [**1b**]/[total epoxide] ratio was 0.89 and the more accessible double bond was much more selectively epoxidized. The value was higher than or comparable to those reported for sterically hindered porphyrin systems with NaOCl or PhIO (0.11–0.95) [3,9,11] and

Table 1  
Epoxidation of dienes catalyzed by TBA-I with hydrogen peroxide<sup>a</sup>

Entry	Diene	Time (h)	Product (yield (%))		<b>b</b> /( <b>b</b> + <b>c</b> )	H <sub>2</sub> O <sub>2</sub> efficiency (%)
1		4	(83)	(10)	0.89	> 99
2 <sup>b</sup>		7	(43)	(27)	0.61	81
3 <sup>c</sup>		7	(34)	(55)	0.38	93
4		6	(16)	(78)	0.17	> 99
5		4	(4)	(94)	0.04	98

<sup>a</sup> Reaction conditions: TBA-I (8 μmol), diene (5 mmol), 30% aq hydrogen peroxide (1 mmol), acetonitrile (6 mL), reaction temperature (305 K). The reaction conditions were controlled to inhibit the double epoxidation. Yields were determined by gas chromatographic analysis with an internal standard technique. Yield (%) = product (mol)/H<sub>2</sub>O<sub>2</sub> used (mol) × 100. Remaining H<sub>2</sub>O<sub>2</sub> after the reaction was estimated by potential difference titration of Ce<sup>3+</sup>/Ce<sup>4+</sup>. H<sub>2</sub>O<sub>2</sub> efficiency = products (mol)/H<sub>2</sub>O<sub>2</sub> consumed × 100.

<sup>b</sup> Toluene was produced as a by-product (7% yield).

<sup>c</sup> Acetonitrile (9 mL).

the mono-cobalt-substituted heteropolytungstate system with O<sub>2</sub> in the presence of aldehydes (0.69) [31] (Table S1). For the epoxidation of *trans*-1,4-hexadiene (**2a**, entry 2), the terminal double bond was preferably epoxidized. The [**2b**]/[total epoxide] ratio was 0.61 and the value was much higher than those reported for Mo(CO)<sub>6</sub>/CHP (0.14) [5] and sterically hindered porphyrin systems with NaOCl or PhIO; Mn(TTPPP)(OAc)/NaOCl (0.35) [9], Mn(T(2', 6'-G1Aph)P)Cl/PhIO (0.20) [3], Mn(TPP)(OAc)/NaOCl (0.03) [9], and Mn(T(3', 5'-G2Ph)P)Cl/PhIO (0.03) [3] (Table S2).

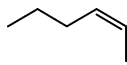
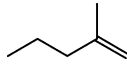
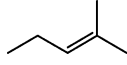
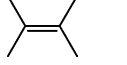
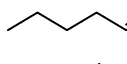
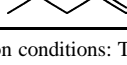
The epoxidation of *R*-(+)-limonene (**3a**, entry 3) easily proceeded to afford a mixture of diastereoisomeric epoxides and the [**3b**]/[total epoxide] ratio was 0.38. The value was higher than or comparable to those reported for H<sub>2</sub>O<sub>2</sub>-based epoxidation; peroxotungstates (<0.03) [20–23], polyoxometalates (<0.01) [15,16], Fe(TDCPN<sub>5</sub>P)Cl (0.27) [13], MTO/UHP (<0.01) [18], manganese complexes (0.17) [19], stoichiometric reactions such as dimethyldioxirane (<0.01) [4], *m*-CPBA (0.09) [3], benzonitrile/K<sub>2</sub>CO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (0.37) [24], and diisopropylcarbodiimide/K<sub>2</sub>CO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (0.18–0.40) [25,26]. Although the regioselectivity for TBA-I is lower than the values reported for sterically hindered porphyrin systems with NaOCl or PhIO (0.62–0.75) [3,11] and various H<sub>2</sub>O<sub>2</sub>-based systems of Mn(TDCPP)Cl/imidazole (0.59–0.67) [12], [WZnMn<sub>2</sub>(ZnW<sub>9</sub>O<sub>34</sub>)<sub>2</sub>]<sup>12-</sup> (0.50) [14], and Ti-β (0.55) [17], these systems have disadvantages: the use of rather expensive, nongreen oxidants such as NaOCl and PhIO; the necessity of excess amounts of oxidant; a long reaction time; and a high reaction temperature (Table S3).

Similarly, the high selectivity to the epoxidation of the electron-poor terminal double bond for the epoxidation of 7-methyl-1,6-octadiene (**4a**, entry 4) was observed. The [**4b**]/[total epoxide] ratio was 0.17 and the value was much higher than those for the H<sub>2</sub>O<sub>2</sub>-based epoxidation systems of Al<sub>2</sub>O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (<0.01) [32], CF<sub>3</sub>CH<sub>2</sub>OH/Na<sub>2</sub>HPO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (<0.01) [33], and (CF<sub>3</sub>)<sub>2</sub>CO/C<sub>2</sub>F<sub>5</sub>OH/NaHPO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub> (<0.01) [34] (Table S4). The epoxidation of 4-vinyl-1-cyclohexene (**5a**, entry 5) proceeded exclusively at the ring position rather than the external position, and the [**5b**]/[total epoxide] ratio of 0.04 was lower than those reported for sterically hindered porphyrin systems with NaOCl or PhIO (0.20–0.73) [9,10] and comparable to dendrimer-metalloporphyrins (0.04–0.11) [3] (Table S5). The results of competitive epoxidation of C<sub>6</sub>-olefins which have similar alkyl substituents to the corresponding dienes (**1a**–**5a**) are in good agreement with the trends of regioselectivity for **I** (Table S6).

The regioselectivity for the epoxidation of various non-conjugated dienes in the present system was compared with those using *m*-CPBA as a stoichiometric oxidant or H<sub>2</sub>O<sub>2</sub> in the presence of peroxotungstates of [PO<sub>4</sub>{WO(O<sub>2</sub>)<sub>2</sub>}<sub>4</sub>]<sup>3-</sup> and [W<sub>2</sub>O<sub>3</sub>(O<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup>, which have been reported to be effective catalysts for the H<sub>2</sub>O<sub>2</sub>-based epoxidation [20–23]. The results are shown in Fig. 1A. In the case of *m*-CPBA, more electron-rich double bonds are preferably oxidized in all cases. Among the tungsten catalysts tested, TBA-I

Table 2

Initial and relative rates for the epoxidation of a series of C<sub>6</sub>-olefins catalyzed by TBA-I with hydrogen peroxide<sup>a</sup>

Entry	Olefin	R <sub>0</sub> (mM min <sup>-1</sup> )	Relative rate <sup>b</sup>
1		3.08	13.9
2		0.68	3.1
3		0.68	3.0
4		0.47	2.1
5		0.30	1.4
6		0.22	1.0

<sup>a</sup> Reaction conditions: TBA-I (8 μmol), olefin (5 mmol), 30% aq hydrogen peroxide (1 mmol), acetonitrile (6 mL), reaction temperature (305 K). R<sub>0</sub> values were determined from the reaction profiles at low conversion (≤10%) of hydrogen peroxide.

<sup>b</sup> The values are ratios of R<sub>0</sub>/R<sub>0</sub> (*trans*-2-hexene).

showed the highest regioselectivity to the more accessible, but less nucleophilic, double bond. In addition, TBA-I showed higher TONs than those for [PO<sub>4</sub>{WO(O<sub>2</sub>)<sub>2</sub>}<sub>4</sub>]<sup>3-</sup> and [W<sub>2</sub>O<sub>3</sub>(O<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup> as shown in Fig. 1B. It was confirmed that the other tungstate fragments such as [W<sub>2</sub>O<sub>3</sub>(O<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup> and [SiO<sub>4</sub>{WO(O<sub>2</sub>)<sub>2</sub>}<sub>4</sub>]<sup>4-</sup> were not formed during the catalysis by **I**, suggesting the stability of **I**. Further, the fact that a fully occupied silicododecatungstate, [γ-SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup>, was inactive for epoxidation suggests the generation of an active oxidant on a divacant lacunary site.

Table 2 shows the order of reactivity for epoxidation of a series of C<sub>6</sub>-olefins catalyzed by **I**. The reactivity was decreased in the order of *cis*-2-hexene (13.9) > 2-methyl-1-pentene (3.1) ~ 2-methyl-2-pentene (3.0) > 2,3-dimethyl-2-butene (2.1) > 1-hexene (1.4) > *trans*-2-hexene (1.0). This order is not consistent with that of the π(C=C) HOMO energies of C<sub>6</sub>-olefins,<sup>1</sup> but that observed for the epoxidation catalyzed by TS-1, where restricted transition-state shape selectivity and diffusion effects were observed [43]. Therefore, the inconsistency of the orders between the π(C=C) HOMO energy and the reactivity would be caused by the steric constraints of the active site of **I**.

<sup>1</sup> The π(C=C) HOMO energies of C<sub>6</sub>-olefins were calculated at the HF/6-311G(d,p) level and decreased in the order of 2,3-dimethyl-2-butene (-8.67 eV) > 2-methyl-2-pentene (-8.97 eV) > *trans*-2-hexene (-9.30 eV) ~ *cis*-2-hexene (-9.32 eV) > 2-methyl-1-pentene (-9.44 eV) > 1-hexene (-9.72 eV). The alkyl substitution increases electron density of the C=C double bond and raises the π(C=C) HOMO energy, resulting in an increase of the reactivity of the olefin with electrophilic oxidants without steric hindrance such as peroxyacids, peroxides, and peroxy complexes (see Refs. [35–42]).

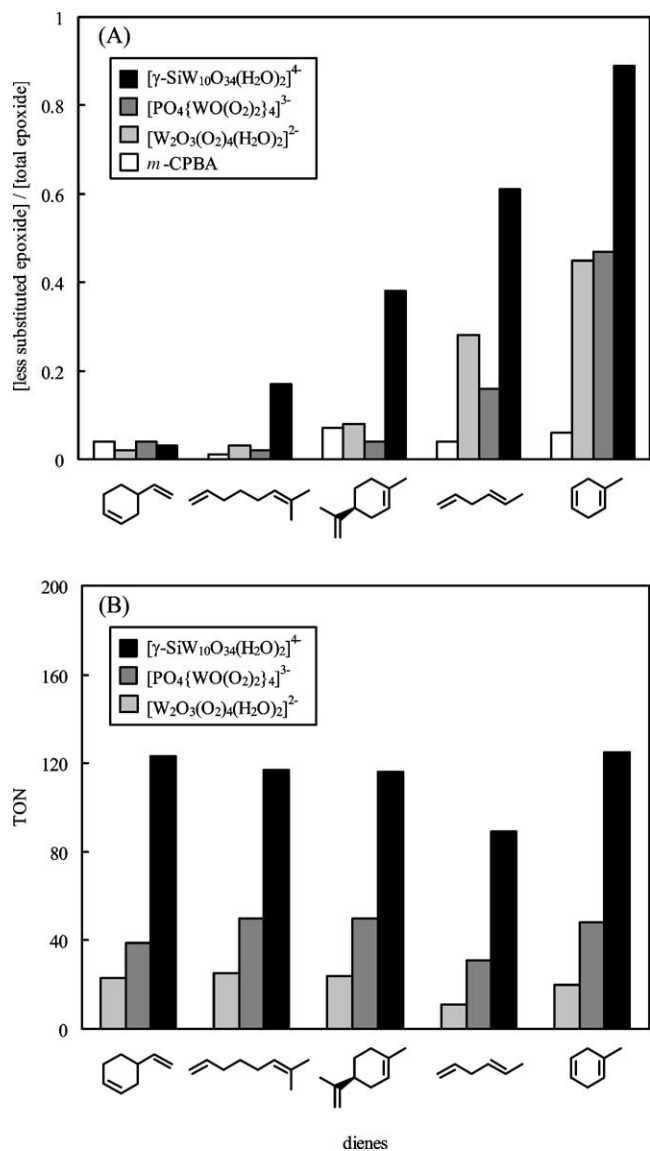


Fig. 1. (A) Ratio of less substituted epoxides to total epoxides formed by the epoxidation of various dienes. (B) Comparison of the TONs of TBA-I with those of [PO<sub>4</sub>{WO(O<sub>2</sub>)<sub>2</sub>]<sub>4</sub>]<sup>3-</sup> and [W<sub>2</sub>O<sub>3</sub>(O<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sup>2-</sup>. Reaction conditions are the same as those in Table 1. TON = products (mol)/catalyst used (mol).

In conclusion, TBA-I exhibits high regioselectivity for epoxidation of nonconjugated dienes which is quite different from those of various classical reagents. The specific regioselectivity and the order of reactivity for epoxidation of a series of C<sub>6</sub>-olefins suggest the contribution of active species on the divacant site of the rigid structure of I.

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