Oxidative Functional Group Transformations with Hydrogen Peroxide Catalyzed by Divanadium-Substituted Polyoxometalates

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Introduction

Polyoxometalates are a large family of anionic metal–oxygen clusters of early transition metals and stimulated many current research activities in broad fields of science such as catalysis, material, and medicine, because their chemical properties such as redox potentials, acidities, and solubilities in various media can finely be tuned by choosing constituent elements and counter cations. Herein, we report various kinds of oxidative functional group transformations with H_2O_2 catalyzed by divanadium-substituted polyoxotungstates (Fig. 1): (i) Efficient, stereospecific, diastereoselective, and regioselective epoxidation of alkenes catalyzed by $[\gamma\text{-}H_2SiV_2W_{10}O_{40}]^{4-}$ (**I**) [1,2], (ii) regioselective hydroxylation of alkanes catalyzed by $[\gamma\text{-}H_2PV_2W_{10}O_{40}]^{3-}$ (**II**) [3], and (iii) oxidative bromination (chlorination) of alkenes, alkynes, and aromatics [4].

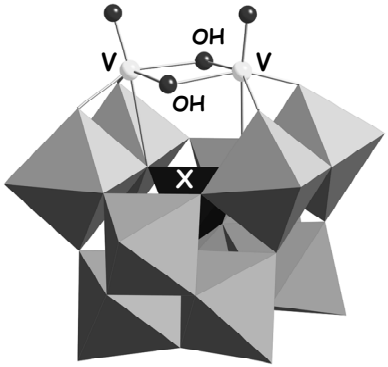


Figure 1. Molecular structures of the anion parts of **I** (X=Si) and **II** (X=P).

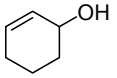
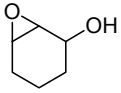
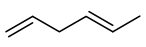
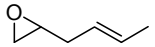
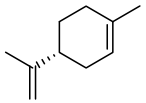
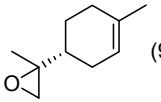
Experimental

The tetra-*n*-butylammonium salts of **I** and **II** were synthesized according to the literature procedures [1,3]. The catalytic reactions were carried out with a glass tube (30 mL) containing a magnetic stir bar. The catalyst, solvent, and substrate were charged in the reaction vessel. The reaction was initiated by the addition of 30% aqueous H_2O_2. The reaction solution was periodically analyzed by GC, GC-MS, and NMR. The $Ce^{3+/4+}$ titration showed that no H_2O_2 remained after the reaction.

Results/Discussion

Compound **I** could catalyze the epoxidation of various kinds of alkenes with H_2O_2 with high epoxide yields and high efficiencies of H_2O_2 utilization under very mild reaction conditions (Table 1). Non-activated aliphatic terminal C3–C10 alkenes including propylene could be transformed to the corresponding epoxide with ≥99% selectivities and ≥87% efficiencies of H_2O_2 utilization. The epoxidation of 3-substituted cyclohexenes diastereoselectively gave the corresponding epoxides with oxirane ring *trans* to the substituents (i.e., *anti* configuration). Further, it is noted that more accessible, but less nucleophilic double bonds in non-conjugated dienes were highly regioselectively epoxidized in high yields [1,2]. While the hydroxylation of alkanes catalyzed by **I** also proceeded, the reaction rate was very low.

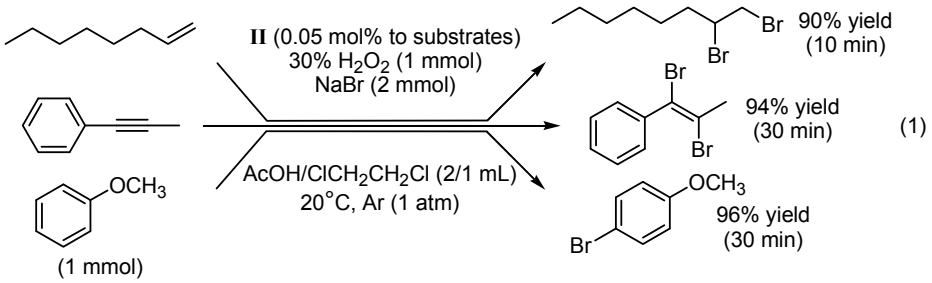
Table 1. Epoxidation of various alkenes with H_2O_2 catalyzed by **I**.[a]

Entry	Substrate	Yield (%)	Product (Selectivity (%))	H_2O_2 efficiency (%)
1[b]	R = CH_3	87	R = CH_3 (99)	87
2	R = *n*-C_4H_9	92	R = *n*-C_4H_9 (99)	92
3	R = *n*-C_6H_{13}	93	R = *n*-C_6H_{13} (99)	93
4	R = *n*-C_8H_{17}	93	R = *n*-C_8H_{17} (99)	93
5		91	 (97) *syn*/*anti* = 5/95	91
6		87	 (95) *syn*/*anti* = 12/88	91
7		91	 (>99)	91
8		90	 (99)	91

[a] Reaction conditions: **I** (5 mol% with respect to substrate and H_2O_2), alkene (0.1 mmol), 30% aqueous H_2O_2 (0.1 mmol), CH_3CN/*t*-BuOH (1.5/1.5 mL), 20°C, 24 h. Yield (%) = products (mol)/initial H_2O_2 (mol) × 100. H_2O_2 efficiency (%) = products (mol)/H_2O_2 consumed (mol) × 100. [b] Propylene (6 atm).

In order to improve the catalytic activity of **I**, we changed the central heteroatom from Si(IV) to P(V). Compound **II** could catalyze the oxidation of various kinds of cyclic alkanes with H_2O_2. The oxidation of cyclic alkanes proceeded selectively to afford the corresponding alcohols (≥98% selectivity). Acyclic *n*-hexane was also hydroxylated to the corresponding alcohols with ≥96% selectivity. Notably, the present system also showed the unusual regioselectivity to the secondary alcohols for the oxidation of some cycloalkanes with both secondary and tertiary C−H bonds (Table 2). The oxidation of *trans*-1,2-dimethylcyclohexane with two adjacent tertiary C−H groups, the selectivities to *trans*-3,4-dimethylcyclohexanol was 86%. Such a high regioselectivity to the only one secondary alcohol even in the presence of the more electron-rich tertiary C−H bonds has never been reported [3].

Compound **II** showed the high catalytic performance for the H_2O_2-based oxidative bromination of various alkenes, alkynes, and aromatics in a mixed solvent of acetic acid and 1,2-dichloroethane under very mild reaction conditions (eq 1) [4]. When the bromination of 1-octene was carried out with **II** (0.05 mol%) using stoichiometric amounts of H_2O_2 and NaBr, 90% yield of 1,2-dibromooctane was obtained within only 10 min, showing the high efficiencies of H_2O_2 and Br^- utilizations (≥90%). Various kinds of structurally diverse alkenes, alkynes, and aromatics could be converted into the brominated compounds in high yields.



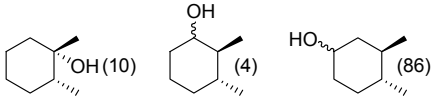
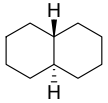
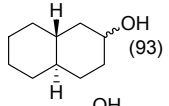
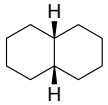
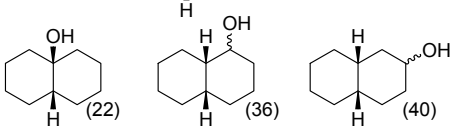
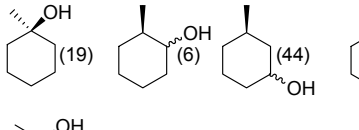
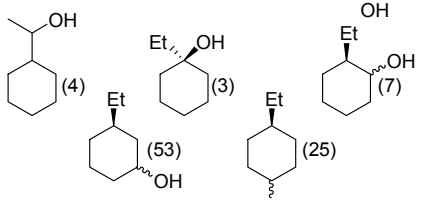
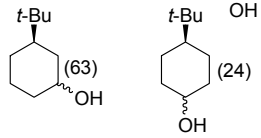
(1)

In conclusion, **I** and **II** showed the high catalytic activities for the H_2O_2-based oxidative functional group transformations including epoxidation, hydroxylation, and bromination.

References.

1. Y. Nakagawa, K. Kamata, M. Kotani, K. Yamaguchi, N. Mizuno. *Angew. Chem. Int. Ed.*, **44**, 5136 (2005)
2. Y. Nakagawa, N. Mizuno, *Inorg. Chem.*, **46**, 1727 (2007)
3. K. Kamata, K. Yonehara, Y. Nakagawa, K. Uehara, N. Mizuno. *Nature Chem.*, **2**, 478 (2010)
4. K. Yonehara, K. Kamata, K. Yamaguchi, N. Mizuno, *Chem. Commun.*, **47**, 1692 (2011)

Table 2. Regioselective hydroxylation of various cycloalkanes with H_2O_2 catalyzed by **II**.[a]

Entry	Substrate	Yield (%)	Product (Selectivity (%))	[2° alcohols] /[3°alcohols]
1		59		90/10
2[b]		51		>99/<1
3[c]		72		78/22
4[d]		75		81/19
5[e]		64		97/3
6[f]		67		>99/<1

[a] Reaction conditions: $[(n\text{-}C_4H_9)_4N]_4[\gamma\text{-}HPV_2W_{10}O_{40}]$ (1.3 mM), $HClO_4$ (1.3 mM), alkane (2.5 M), 30% aqueous H_2O_2 (50 mM), CH_3CN/*t*-BuOH (0.67/1.33 mL), 60°C, reaction time (1 h (entries 1–4), 2 h (entries 5 and 6)). Yield (%) = products (mol)/initial H_2O_2 (mol) × 100. The values in the parentheses are isolated yields. [b] *trans*-2-Decalone (7% selectivity). [c] *cis*-2-Decalone (1% selectivity). [d] 3-Methylcyclohexanone (4% selectivity) and 4-Methylcyclohexanone (2% selectivity). [e] 3-Ethylcyclohexanone (6% selectivity)vand 4-Ethylcyclohexanone (2% selectivity). [f] 3-*tert*-Butylcyclohexanone (10% selectivity)vand 3-*tert*-Butyl cyclohexanone (3% selectivity).