Anti-Markovnikov Oxidation of β-Alkyl Styrenes with H₂O as the Terminal Oxidant

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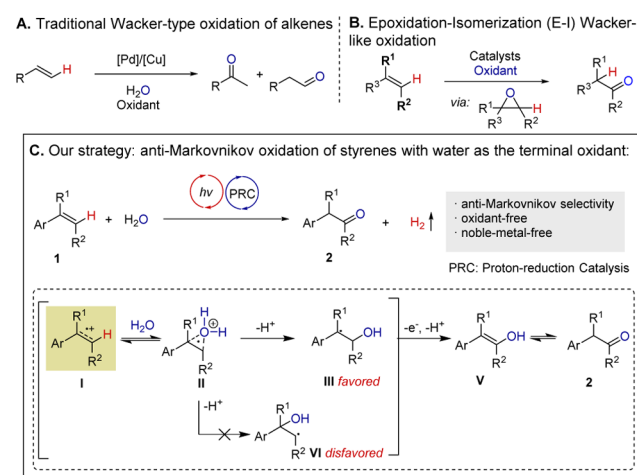
Ⓢ Supporting Information

ABSTRACT: Oxygenation of alkenes is one of the most straightforward routes for the construction of carbonyl compounds. Wacker oxidation provides a broadly useful strategy to convert the mineral oil into higher value-added carbonyl chemicals. However, the conventional Wacker chemistry remains problematic, such as the poor activity for internal alkenes, the lack of anti-Markovnikov regioselectivity, and the high cost and chemical waste resulted from noble metal catalysts and stoichiometric oxidant. Here, we describe an unprecedented dehydrogenative oxygenation of β-alkyl styrenes and their derivatives with water under external-oxidant-free conditions by utilizing the synergistic effect of photocatalysis and proton-reduction catalysis that can address these challenges. This dual catalytic system possesses the single anti-Markovnikov selectivity due to the property of the visible-light-induced alkene radical cation intermediate.

Scheme 1. Regiocontrol Strategies on the Anti-Markovnikov Wacker-Oxidation[a]

[a](A) Palladium mediated Wacke- oxidation. (B) Epoxidation–isomerization (E−I) strategy for the anti-Markovnikov olefins oxidation. (C) Radical cation mediated anti-Markovnikov oxidation of styrenes.

The oxidation of olefins represents a powerful synthetic tool for converting the mineral oil into high value-added chemicals, such as epoxides, carbonyl compounds, etc.[1] For more than a half century, Wacker oxidation has been proven as an industrially viable and synthetically useful transformation for the construction of carbonyls due to its high functional group tolerance, efficiency, and reliability.[2] In contrast to the Wacker-oxidation of terminal olefins that is well-established, the efficient catalytic systems for the selective oxidation of internal alkenes have been sparsely reported. It has been highly desirable and historically challenging to achieve the Wacker-type oxidation of internal alkenes with high activity.[3]

The regioselectivity issue of oxygenation of olefins represents another longstanding challenge in traditional Wacker chemistry.[2g] Especially, the anti-Markovnikov oxidation of internal alkenes remains very problematic. In most cases of conventional Wacker-oxidation, the selectivity outcome is generally controlled by the substrate obeying Markovnikov's rule (Scheme 1A).[4] Only for some certain substrates, which are bearing a chelating group located at a suitable position, anti-Markovnikov selectivity can be observed.[2e,5] Apart from this, significant breakthroughs have been achieved toward the catalyst-dependent anti-Markovnikov selective Wacker-oxidation by Grubbs,[6] Spencer,[7] and others[8] through the modification of catalytic factors, albeit restricted to terminal olefins. Recently, the achievement of a tandem

epoxidation−isomerization (E−I) strategy resulting in net anti-Markovnikov alkene oxygenation significantly complements the classical Wacker-oxidation (Scheme 1B).[9] However, the employment of noble-metal catalysts, stoichiometric copper, and oxidant would bring high costs and chemical waste, which is also a serious problem we are facing. Therefore, less hazardous, cost-effective, and noble-metal-free anti-Markovnikov oxygenation of internal alkenes is an attractive and worthwhile pursuit. Here, we present a direct anti-Markovnikov dehydrogenative oxygenation of β-alkyl styrenes and its derivatives with water under external-oxidant-free conditions by using a photoredox-metal dual catalytic system,[10] as an ideal catalytic system to rapidly access the carbonyl compounds.

Our strategy for the regioselectivity control is based on an alkene radical cation intermediate I (Scheme 1C). Followed by the nucleophilic attack of water, the attained distonic radical cation II tends to deprotonate to produce the anti-Markovnikov

intermediate **III** rather than Markovnikov selective adduct **VI** because of the better stability of **III**.[11] The subsequent single-electron-oxidation, elimination, and keto−enol tautomerism would generate the corresponding carbonyls directly. However, the severe oxidative conditions, such as strong oxidants, for the further oxidation of **III** easily leads to the cleavage of C−C double bond,[12] which restricts the further use of this alternative Wacker-like oxidation strategy. Therefore, to overcome this difficulty, we suggest to merge an in situ generated "alkene radical cation" with a proton-reduction catalysis to improve the catalytic reaction under oxidant-free conditions. Alkene radical cation, generated by the photoinduced system, has been established as an attractive strategy for the anti-Markovnikov hydrofunctionalization of alkenes.[13] Although the photocatalytic production of hydrogen from water is a well-known chemistry,[14] no dual catalytic system of photoredox/proton reduction[15] for the alkene C−H bond functionalization with water was reported. Herein, we envisioned that a proper catalytic system via the synergistic effect of this dual catalytic system should be achievable to proceed the direct anti-Markovnikov oxidation of olefins with H_2 liberation.

To examine the feasibility of the propose strategy, 1,2-dihydronaphthalene **1a** was chosen as the model substrate for the investigation of a suitable catalytic system to produce the 2-tetralone derivatives, which are valuable intermediates in the synthesis of natural products and pharmaceuticals. In order to proceed with this transformation, 9-mesityl-10-methylacridinium perchlorate **3**, which can gain an electron from alkenes to generate the radical cation under its excited-state,[16] and Co(dmgH)₂pyCl (dmgH = dimethylglyoximate monoanion; py = pyridine), a well-known proton-reducing catalyst in the context of hydrogen evolution,[14c] were chosen and combined as the photosensitizer and synergistic catalyst, respectively. Encouragingly, in the presence of 5 mol % of photosensitizer **3** and 3 mol % of cobalt complex **4**, desired 2-tetralone **2a** can be isolated in 83% yield, after the irradiation of blue LEDs light for 24 h (Scheme 2, **2a**). Meanwhile, 90% yield of H_2 was detected by GC, supporting our mechanistic hypothesis. Control experiments indicated no desired reaction would be observed when light, photosensitizer **3**, or catalyst **4** was omitted (Figure S1).

To probe the versatility of this catalytic system, the scope of alkenes was successfully evaluated. As shown in Scheme 2, the synergetic catalysis could be employed on a variety of styrene derivatives to achieve the production of carbonyl compounds in good to excellent yields and single anti-Markovnikov selectivity (regioisomeric ratios were determined by GC−MS and ¹H NMR). 1,2-Dihydronaphthlene **1a**, indene **1b**, 6,7-dihydro-5H-benzoannulene **1c**, and their derivatives can be used to enable facile access to corresponding cycloketones (**2a**−**2g**). Moreover, tetralones **2f** and **2g** have been used as medicinal intermediate in the synthesis of an antitussive drug nepinalone[17] and an anti-Parkinson drug rotigotine.[18] Additionally, under the radical-cation pathway, β-methyl-styrene afforded full anti-Markovnikov regioselectivity (**1h**, 64%), which is drastically different from the previous Pd-mediated system.[3a] Then the functional group tolerance of this transformation was explored by using various β-methyl-substituted styrenes (cis- and trans-mixture) bearing either electron-donating (**1i**, **1j**) or electron-withdrawing groups (**1k**−**1p**), which produced the corresponding ketones up to 95% yield. The procedure can tolerate several functional groups such as alkyl (**1i**, **1j**), cyano (**1l**), ester (**1m**), and halogen (**1n**−**1p**), which is particularly important for the subsequent functionalization. Moreover, other acyclic β-alkyl styrenes (**1q**−**1s**) are also suitable substrates for the ketone formations (**2q**−**2s**). The

**Scheme 2. Substrate Scope for the Selective Oxidation of Styrenes**[a]
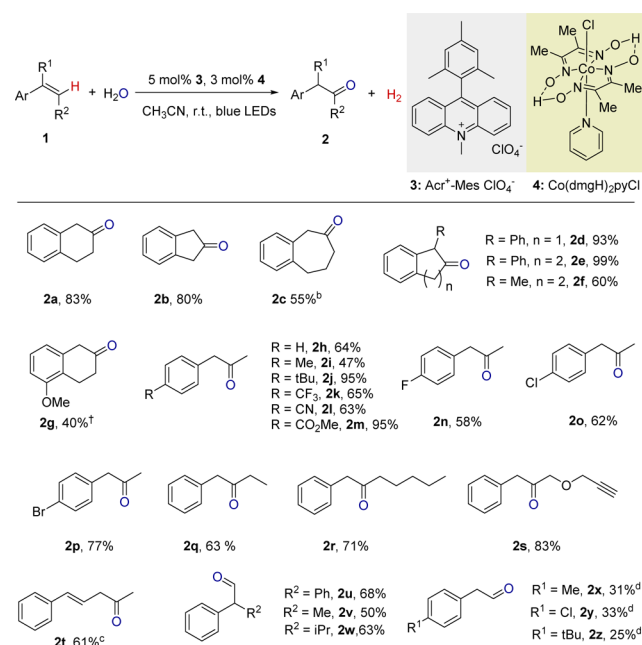
ᵃOlefin **1** (0.2 mmol), **3** (5 mol %), **4** (3 mol %), water (200 μL), CH₃CN (2 mL), 12 W blue LEDs, 24 h; isolated yields are shown and regioisomeric ratios were determined by GC−MS and ¹H NMR. ᵇ48 h. ᶜ**3** (10 mol %), **4** (6 mol %). ᵈThe yields were determined by ¹H NMR analysis.

alkynyl functional group (**2s**, 83%) can be well tolerated and provide an excellent handle for subsequent synthetic derivatization. Notably, the diene **1t** was oxidized to afford the β,γ-unsaturated ketone **2t** in 61% yield by using higher catalyst loading. When we prolong reaction time, the further oxidation of **2t** to diketone can also be observed.

Furthermore, the anti-Markovnikov oxygenation of mono- and disubstituted terminal alkenes into corresponding aldehydes (**2u**−**2z**) can also be reached as well. Styrene derivatives (**1x**−**1z**) bearing electron-donating groups permit access to the substituted 2-phenylacetaldehyde in relatively low yields. Unexpectedly, 1-phenylcyclohexene **1aa** would afford a mixture of 2-phenyl-cyclohexanone **2aa** and 2,3,4,5-tetrahydro-[1,1′-biphenyl]-2-ol **2ab** (Scheme 3). This isomerization might be generated from the

**Scheme 3. Photocatalytic Oxygenation of 1-Substituted Cyclohexene**
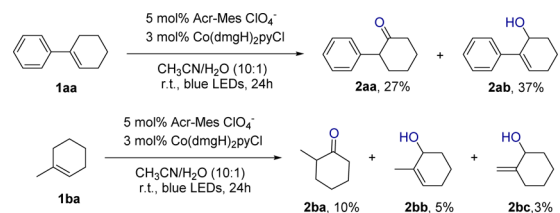
different elimination pathway of the cation intermediate. In sharp contrast, the epoxide of 1-pheylcylohexene preferably undergoes rapid alkyl migration during the isomerization to give the ring contract product (1-phenyl-1-cyclopentane carboxaldehyde)[9c] in previous epoxidation−isomerization (E−I) process. This obvious discrepancy could eliminate an epoxide intermediate in the

conversion. A trisubstituted aliphatic alkene, 1-methylcyclohexene **1ba**, can provide the anti-Markovnikov oxygenation product in relatively lower yield (Scheme 3, the yields were determined by GC), while no photocatalytic oxygenation of the chain aliphatic olefin, 1-hexene, occurs under the present experimental conditions due to its much higher oxidation potential ($E_{1/2 \, ox}$ = 2.85 V vs SCE).[19]

A number of isotope labeling experiments were conducted to examine the mechanistic hypothesis (Scheme 4). When D_2O was

Scheme 4. Isotope Labelling Experiments
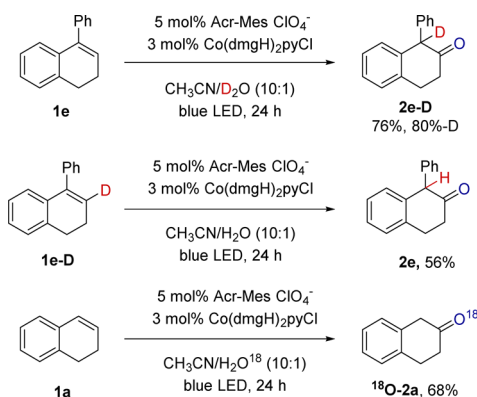
used instead of water in the anti-Markovnikov oxidation of **1e**, the deuterization at the α-position of carbonyl **2e-D** can be observed. However, the direct oxidation of deuterium olefin **1e-D** hardly afforded the same deuterium ketone. These results indicated the epoxidation—isomerization pathway can be ruled out. To investigate the O-source of the carbonyl compounds, the oxygenation of **1a** was performed in an acetonitrile/$H_2^{18}O$ mixture, which gave almost completely ^{18}O labeled 2-tetralone. Therefore, the O atom of carbonyl compounds originates from water, and the proposed ketone-enol tautomerization mechanism is reasonable.

Additionally, the kinetic isotope effect experiments were conducted by using *in situ* IR (Scheme 5). A new peak at 1720

Scheme 5. Kinetic Isotope Effect Experiments[a]
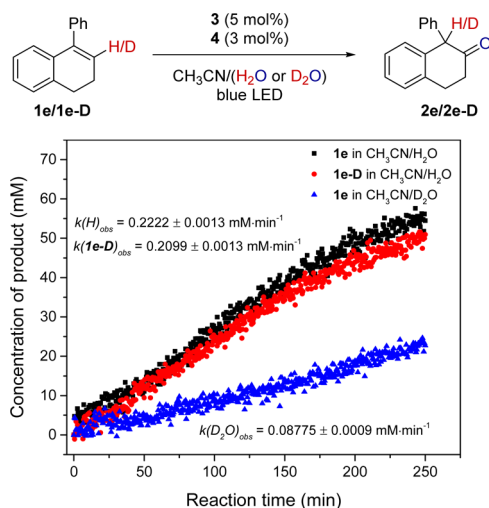
[a]Black curve: kinetic plots of anti-Markovnikov oxidation of **1e**. Red curve: kinetic plots of oxidation of **1e-D** with H_2O. Blue curve: kinetic plots of oxidation of **1e** with D_2O.

cm^{-1} belonging to carbonyl group of **2e** can be observed accompanied with the consumption of olefin. As shown in Scheme 5, the initial rate of this anti-Markovnikov oxygenation for **1e** was determined as 0.2222 mM•min^{-1}. Then, the comparison of the initial rates of oxidation of substrate **1e** versus its deuterated analogue **1e-D** provided a $(k_H/k_{1e-D})_{obs}$ value of 1.1, which suggests that C—H bond breaking of the olefin is not involved in the rate-determining step of the reaction. In contrast, the water-mediated olefin oxygenation reaction proceeds more slowly in D_2O than in H_2O (Scheme 5). A $(k_{H_2O}/k_{D_2O})_{obs}$ of 2.5 is observed, indicating that the rate-determining step of the transformation might involve the O—H bond cleavage of water.

Consequently, a detailed description of the proposed mechanism can be revealed in Figure 1. Alkene **1**, first, can be
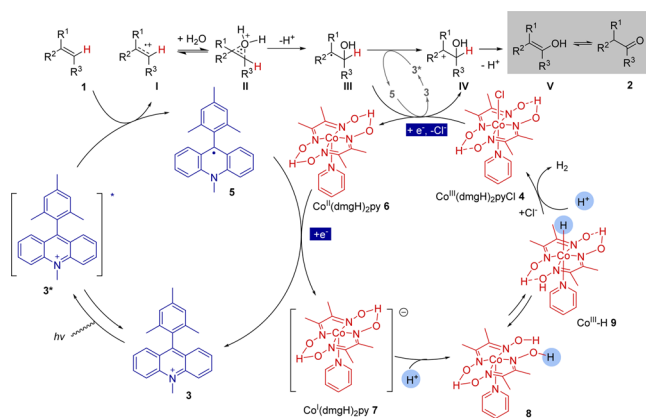

Figure 1. Proposed mechanism for photocatalytic Wacker-like oxidation of alkenes.

oxidized by the excited-state of photosensitizer (3^*, $E_{1/2red}[\text{Acr}^\bullet-\text{Mes}^{\bullet+}/\text{Acr}^\bullet-\text{Mes}]$ = +2.06 V vs SCE)[16a,e,20] to generate the radical cation intermediate **I**. Subsequently, the anti-Markovnikov addition of water and deprotonation would furnish a C-radical intermediate **III**, which is further oxidized by **4** ($E_{1/2red}[\text{Co(III)}/\text{Co(II)}]$ = −0.67 V vs SCE)[21] to form a cation intermediate **IV** and Co(II) species **6**, respectively. Because of the relatively high oxidation potential of **III**,[22] 3^* might also be used to assist the oxidation of **III**, then **5** reacts with Co(III) species **4** to regenerate catalyst **3** and Co(II) species **6**. Afterward, the elimination and keto—enol tautomerism would produce the corresponding carbonyl compounds **2**. However, in the cobalt side, a single-electron reduction of Co(II) species **6** ($E_{1/2red}[\text{Co(II)}/\text{Co(I)}]$ = −1.12 V vs SCE)[21] can be provided by **5** to obtain a Co(I) species **7**. The protonation of **7** gained **8**, which sequentially produced Co(III)—H **9** through possible intramolecular proton transfer.[23] As a result, the protonation of cobalt hydride released H_2 and completed the catalytic cycle. The alternative homolytic mechanism involving two Co(III)—H hydrides to form H_2 could not be ignored.[14a] Another reaction pathway involving the insertion of benzylic radical **III** to Co(II) species **7** and β—H elimination[24] might be also possible and cannot be completely ruled out at the current stage (Figure S7). However, the formation of the Co(I) species can be observed by using UV—vis absorption spectra, making cation intermediate more favorable.[25]

In conclusion, we have demonstrated that the combination of Fukuzumi's catalyst and cobaloxime enables the anti-Markovnikov oxidation of styrenes with water, which provides an unprecedented method for the construction of carbonyl compounds to form alkenes under external-oxidant-free con-

ditions. Through the visible-light-induced alkene radical cation, the high anti-Markovnikov regioselectivity of oxidation process can be achieved. The mechanistic experiments suggest that the oxygen atom of carbonyl group is originated from water. Moreover, the mildness and high atomic economy of this approach makes it appealing for the further application into the anti-Markovnikov C−H functionalization of olefins.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b07411.

> Experimental procedure, characterization data, and copies of ^{1}H and ^{13}C NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

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