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Visible Light-Promoted Dihydroxylation of Styrenes with Water and Dioxygen

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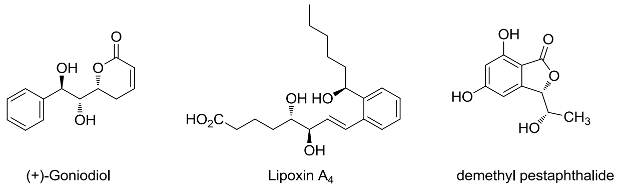
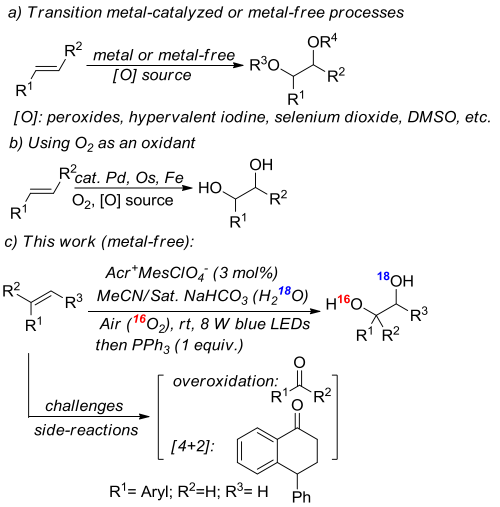
An efficient visible light promoted metal-free dihydroxylation of styrenes with water and dioxygen has been developed for the construction of vicinal alcohols. The protocol was operationally simple with broad substrate scope. The mechanistic studies demonstrated that one of the hydroxyl group came from water and the other one came from molecular oxygen. Additionally, the ß-alkyoxy alcohols could also be obtained using a similar strategy.

The vicinal alcohols motifs are vastly existed in natural and artificial products that have emerged biologically active properties (Scheme 1).[1] Dihydroxylation of alkenes to achieve 1,2-diols derivatives is one of the most powerful and straightforward methods.[2] There are tremendous metal-catalyzed or metal-free or enzyme-catalyzed processes capable of making 1,2-dioxylation products.[3] However, the directly construction of free 1,2-diols is still limited. Among these cases, peroxides, hypervalent iodines, periodate salt and selenium dioxide are usually used as stoichiometric oxidants which have explosive characteristic or produce stoichiometric wastes (Scheme 2a).



Scheme 1. 1,2-Diol motif in natural and artificial products.

Dioxygen is generally considered as an ideal oxidant, and also a clean and cheap oxygen source (Scheme 2b).[4] Beller group[5] developed an osmium-catalyzed dihydroxylation of olefins using 1 bar of dioxygen which was used as the terminal oxidant to regenerate the osmium species and the water afforded the oxygen sources. Jiang and co-workers[6] reported a facile palladium-catalyzed dihydroxylation of alkenes under 8 atm of dioxygen at 100 °C, in which dioxygen played a role of oxidant. The oxygen atom in products came from acetic acid or water. Paine and co-workers[7,8] developed an iron-oxygen oxidant generated from dioxygen and an Fe^{II}-benzilate complex of a facile N_3 ligand which could be used to conduct olefin dihydroxylation. It should be noted that the oxygen atom of water could be partially incorporated into the alcohols in the presence of Lewis acid. However, these approaches require the utilization of transition metal complexes and/or harsh conditions. Furthermore, the intrinsic limitations of transition metal catalyzed processes are associated with the limited functional group tolerances. Additionally, it is difficult to selectively oxidize the aryl alkenes and aliphatic alkenes in transition metal catalyzed processes. The development of efficient, mild and green approaches to address these issues is highly desirable. To the best of our knowledge, the selective use of readily available dioxygen and water as oxygen sources for direct dihydroxylation of alkenes under mild conditions has not been well explored.



Scheme 2. Dihydroxylation of alkenes

Visible light, as a safe and abundant energy source, has emerged as a powerful tool to construct organic molecules under mild conditions.[9] We are particularly interested in visible light-promoted alkene difunctionalization and dioxygen oxidation.[10] Here, our strategy is aimed to use the abundant and environmentally friendly molecular oxygen and water as oxygen sources to directly achieve the dihydroxylation of alkenes utilizing visible light (Scheme 2c).

Based on the previously reported literatures[11], the excited state of Acr^+Mes generated by absorbing visible light could oxidize the aryl alkene to its radical cation. We envisioned whether the radical cation could be trapped by water and dioxygen directly to achieve the dihydroxylation of alkenes. However, a number of challenges

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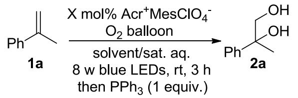
Table 1. Optimization of reaction conditions[a]



Entry	X (mol%)	Sat. aq	Solvent	Yield of 2a (%)
1	5	H_2O	Acetone	27-57
2	5	KH_2PO_4	Acetone	75
3	5	K_2HPO_4	Acetone	40
4	5	K_3PO_4	Acetone	19
5	5	K_2CO_3	Acetone	24
6	5	NaOH	Acetone	0
7	5	$NaHCO_3$	Acetone	40
8	5	K_2HPO_4	MeCN	63
9	5	$NaHCO_3$	MeCN	87
10[b]	3	$NaHCO_3$	MeCN	92
11[b,c]	3	$NaHCO_3$	MeCN	0
12[b]	/	$NaHCO_3$	MeCN	0
13[b,d]	3	$NaHCO_3$	MeCN	0
14[b,e]	3	$NaHCO_3$	MeCN	93
15[b,e,f]	3	$NaHCO_3$	MeCN	94(87[g])

[a] Reaction conditions: **1a** (0.3 mmol), Acr$^+$MesClO$_4^-$ (5 mol%), and solvent/saturated aqueous (v/v, 11/1, 6 mL) were stirred for 3 h under O_2 balloon. Yields determined by ^{1}H NMR spectra with mesitylene as an internal standard after treated with PPh_3 (1 equiv.) in one pot. [b] 6 h. [c] Without light. [d] Under N_2. [e] Under air. [f] 0.1 M. [g] Isolated yield.

Table 2. Substrate scope of alkenes[a]

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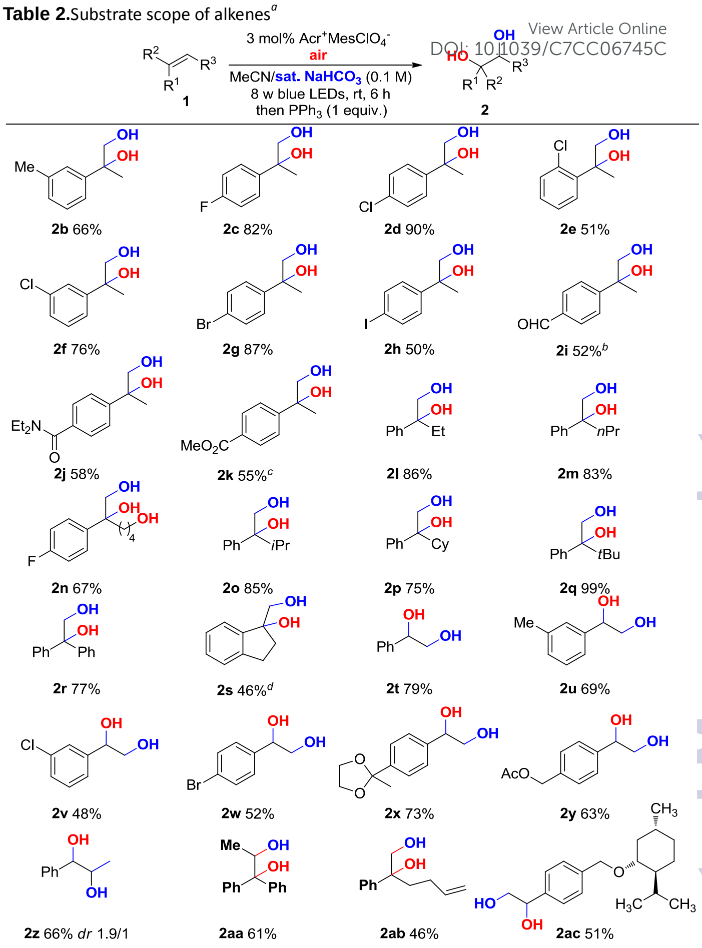

[a] Standard conditions: alkenes (0.3 mmol), Acr$^+$MesClO$_4^-$ (3 mol%), saturated $NaHCO_3$ (0.25 mL) in a solution of MeCN (2.75 mL) under the irradiation of 8 W blue LEDs under air for 6 h. Isolated yield after reduction workup with PPh_3 (1 equiv.). [b] 12 h. [c] 14 h. [d] Saturated aqueous KH_2PO_4 was used.

had to be addressed in developing such a transformation. For instance, the aryl alkenes are easily oxidized to ketones or aldehydes under dioxygen atmosphere employing visible light.[12] Furthermore, the radical cations of simple alkenes are prone to react with itself to afford [4+2] cycloaddition products (**Scheme 2c**).[13]

Initially, we chose α-methyl styrene **1a** as a model substrate to explore the dihydroxylation of alkenes using dioxygen and pure water. To our disappointed, various solvents, photosensitizers and additives were examed, only a small amount of desired product **2a** was obtained accompanied by the formation of acetophenone and [4+2] oxidative cycloaddition reaction. The reproducibility of these reactions was also disastrous (Table 1, entry 1). We speculated that the intermediate might be unstable under the reaction conditions. Given the fact that photocatalyst Acr$^+$Mes was easily decomposed under the moderate to strong basic conditions in the presence of dioxygen. As a result, we used the weak basic and acidic solutions as alternatives to pure water to test the model reaction.

To investigate our proposal, we first used the saturated aqueous KH_2PO_4 solutions as nucleophiles in the presence of 5 mol% Acr$^+$MesClO$_4$ and O_2 with acetone as solvent to examine the dihydroxylations of alkenes (Table 1). To our delight, 75% yield of **2a** was obtained with 100% conversion of alkene after reduction workup with triphenyl phosphine in one pot (entry 2). Various saturated aqueous solutions were screened, the yields were lower (entries3-7). It was worth to note that although only 40% yield of **2a** was obtained in the presence of saturated aqueous $NaHCO_3$solution (entry 7), the side-products were rare. The yield of **2a** was significantly improved to 87% yield in acetonitrile using a saturated aqueous $NaHCO_3$ solution as nucleophiles (entries 8 and 9). The reaction using 3 mol% of catalyst was carried out for 6 h to afford **2a** in 92% yield (entry 10). No desired product **2a** was obtained without light, photocatalyst or dioxygen which demonstrated that the light, photocatalyst and dioxygen were all essential to the reactions (entries 11-13). The **2a** could also be obtained under air in 93% yield (entry 14). The reaction was also performed smoothly in0.1 M, yielding **2a** in 87% isolated yield (entry 15). The standard conditions were established as following: 3 mol% of Acr$^+$MesClO$_4^-$, MeCN/sat. $NaHCO_3$ (*v*/*v*, 11/1) (0.1 M) under air irradiated by 8 W blue LEDs for 6 h and then reduction workup with triphenylphosphine (1 equiv.).

With the optimized reaction conditions in hand, a range of alkenes were subjected to yield the corresponding vicinal alcohols (Table 2). When aryl alkenes bearing both electron-donating and electron-withdrawing groups were used as substrates, the corresponding diols were obtained in moderate to excellent yield (**2a**-**2k**). The *ortho*-, *meta*- and *para*-substituted chloro styrenes with different steric hindrance furnished the transformations producing the desired products in 51%, 76%, and 90% yields, respectively (**2d-2f**). It was noteworthy that a number of styrenes bearing functional groups, such as aldehyde, amide, ester and alcohols, performed well under the standard conditions to afford the corresponding vicinal alcohols in moderate yields (**2i-2k, 2n**). Importantly, no obvious side-products were formed with the recoveries of the alkenes.

The α-substituents on styrenes could be not only 1°- alkyl group but also more sterically hindered 2°- and 3°- alkyl groups (**2l**-**2q**). The 1,1-diaryl alkene was allowed for the transformations delivering the vicinal alcohol in 77% yield (**2r**). The 1-methyleneindanecould be transformed into corresponding alcohol (**2s**) in 46% yield using saturated aqueous KH_2PO_4 solutions instead of saturated aqueous $NaHCO_3$ solutions. A majority of mono-substituted aryl alkenes

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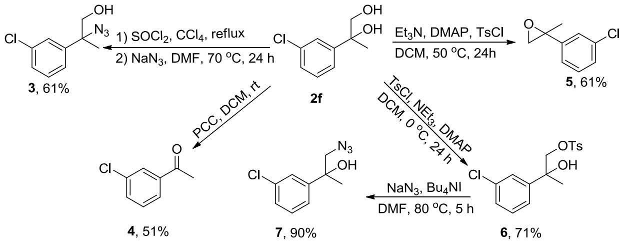
performed well under the standard conditions to afford the corresponding alcohols in 48-79% yields (**2t**-**2y**). Notably, the 1,2-disubstituted alkenes could also be transformed into the desired products in 66% yield with 1.9/1 *dr*. Moreover, the trisubstituted alkene was also a suitable partner to producing 61% yield of **2aa**. It should be noted that **2ab** could be isolated in 46% yield through selective oxidation of aryl alkene. The relatively complex molecules derived from DL-Menthol could be converted to **2ac** in 51% yield.

Gram-scale reaction could be conducted in 71% yield (eq. 1).

$$\underset{\text{8 mmol}}{\mathbf{1r}} \xrightarrow[\text{12 h}]{\textit{standard conditions}} \underset{\text{71\% yield}}{\underset{\mathbf{1.2174\ g}}{\mathbf{2r}}} \qquad (1)$$

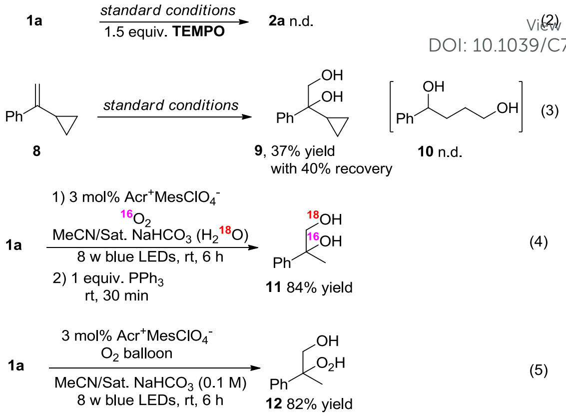
The further derivatizations were shown in **Scheme 3**. The high-value-added ß-hydroxyazide **3** could be obtained by nucleophilic attack the cyclic sulfites which was generated from the reaction ofthionyl chloride and **2f**. The **2f** could also be transformed into **4** by simple oxidation of pyridinium chlorochromate. The oxirane **5** could be prepared in 61% yield. Additionally, the protection of ß-hydroxy group in **2f** by TsCl could deliver **6** in 71% yield, followed by NaN_3 nucleophile-attacking to afford the ß-azido alcohol **7** in 90% yield.



Scheme 3. The transformations of vicinal alcohols

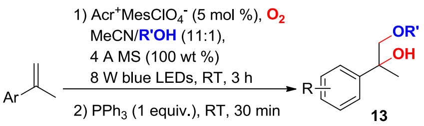
To gain further insight into the mechanism of the dihydroxylation of alkenes, control experiments were conducted as illustrated in **Scheme 4**. No vicinal alcohol **2a** was detected when 1.5 equiv. TEMPO was added under standard conditions using **1a** as substrate (eq. 2). The results indicated that a radical pathway maybe involved in the transformations. To further demonstrate the existence of radical intermediate, **8** was used as a substrate to be performed under standard conditions (eq. 3). Interestingly, 37% yield of **9** was isolated with 40% recovery of **8**. No ring-opening dihydroxylation of **8** was observed by ^1H NMR analysis. This phenomenon maybe attributed to the fact that the radical cation generated from alkene was quickly oxygenated by dioxygen resulting in no **10** was detected. To elucidate where are the two oxygen atoms come from, a $H_2{}^{18}O$ isotopic labeling experiment was conducted (eq. 4). The alkene **1a** was conducted under dry O_2 atmosphere using the saturated $NaHCO_3$ solution freshly prepared from $H_2{}^{18}O$ and $NaHCO_3$. **11** was confirmed by HRMS (ESI) ([M+Na$^+$] 177.0772). As expected, one of the oxygen atom of vicinal alcohol **11** originated from the water and another oxygen atom derived from molecular oxygen. In addition, to clearly demonstrate one of which oxygen atom of vicinal alcohol **11** come from H_2O and which one come from dioxygen, **1a** was performed under the standard conditions without reduction workup to afford **12** which was in accordance with the previously reported literature (eq. 5).[14] The result clearly shows that the oxygen atom of α-hydroxyl of **11** originated from air, the other oxygen atom come from H_2O.

To probe the H_2O-nuclephilic attack to radial cation, alcohols were used instead of H_2O. Under the slightly optimization conditions, the reaction of α-methyl styrene with methanol under the atmosphere O_2 afforded the hydroxyetherification product **13a** in 63% yield. Various styrenes such as *ortho*-, *meta*-, and *para*-methyl styrenes could be transformed into corresponding products in moderate to good yields. Moreover, a variety of alcohols, such as 1°-, 2°-, 3°-alkyl alcohols were suitable partners delivering the hydroxyetherfication products (**13b**-**13h**, in **Table 3**).



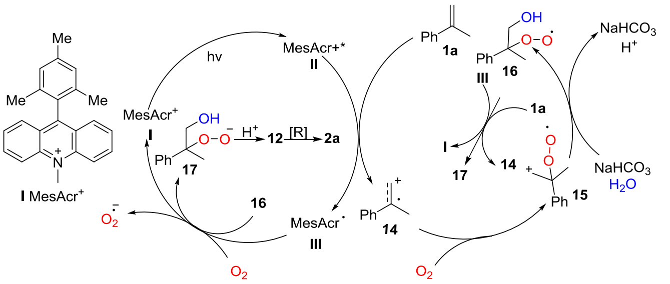
Scheme 4. Mechanistic studies

Table 3. Dioxygenation of alkenes



13a: R = H, R' = Me, 63%
13b: R = 2-Me, R' = Me, 47%
13c: R = 3-Me, R' = Me, 75%
13d: R = 4-Me, R' = Me, 60%
13e: R = 4-Cl, R' = Me, 76%
13f: R = H, R' = Et, 63%
13g: R = H, R' = *i*Pr, 51%
13h: R = H, R' = *t*Bu, 33%

A plausible mechanism is proposed in **Scheme 5**. The styrene **1a** (E_{ox} = 1.91 V vs SCE)[15] could be oxidized to its radical cation **14** by the excited state of photosensitizer (**II**, E_{red*} = 2.06 V vs SCE)[16]generated through absorbing visible light under the irradiation of 8 w blue LEDs. The radical cation **14** was quickly oxygenated by molecule oxygen under air to afford **15** which was nucleophilic attacked by water to generate peroxy radical species **16**.[17] The **16** was reduced by **III** (Mes-Acr•) to form **17** and regenerated the photocatalyst **I** through SET process, respectively. The another possible pathway which could not be exclusively ruled out is that **16** also could be reduced by **1a** to provide **17** which got a proton to deliver **12**. Moreover, **12** had been isolated before reduction workup, which is another proof that the ß-oxygen atom originated from dioxygen. Additionally, the photocatalyst could also be regenerated by dioxygen. It was noteworthy that the product **12** could exist stably under the standard conditions.



Scheme 5. A proposed mechanism for dihydroxylation of alkenes

In conclusion, we have developed a mild condition to achieve the dihydroxylation of aryl alkenes with water and dioxygen from air. The operationally simple protocol features a broad substrate scope, mild conditions and great functional group tolerance. The mechanistic experiments suggest that the α-oxygenatom and the ß-oxygen atom are originated from the molecular oxygen and water, respectively. Additionally, the ß-alkyoxy alcohols could also be obtained using a similar strategy. The new difunctionalizations of alkenes will be explored in our laboratory.

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