



Visible-light- induced aerobic dioxygenation of styrenes under metal- and additive-free ambient conditions



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ARTICLE INFO

Article history:

Received 25 November 2016
Revised 22 December 2016
Accepted 23 December 2016
Available online 30 December 2016

Keywords:

Visible light
Hydroperoxidation
Styrenes
Metal-free
Additive-free

ABSTRACT

Visible light promoted hydroperoxidation of styrenes using hydroxylamine and molecular oxygen from air under metal-free and additive-free conditions at room temperature is described. Hydroperoxides were further converted into corresponding hydroxy compounds and α -oxygenated ketones in high yields under ambient conditions.

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Oxygen is a highly atom-economical, environmentally benign and abundant oxidant, which makes it ideal in many ways. The construction of various types of oxygen-containing compounds using molecular oxygen considered to be a vital and essential subject in synthetic chemistry.¹ As a result, significant progress has been achieved by various groups during the past decade in the area of molecular oxygen activation.² Alkenes are the simplest and most highly valuable starting materials and they can be transformed into different oxygenated molecules such as 1,2-diols,³ α -hydroxyketones⁴ and 1,2-dicarbonyl compounds.⁵ Recently, visible-light promoted chemical transformations have received much attention in organic synthesis.⁶ Considering the importance of photoredox catalysis, many groups have demonstrated photo catalyzed organic transformations under visible-light irradiation.⁷ Therefore, the exploitation of new strategies and reagents to develop direct and greener methodologies to avoid the use of expensive transition-metal catalysts, toxic reagents, as well as explosive oxidants is highly desirable.⁸

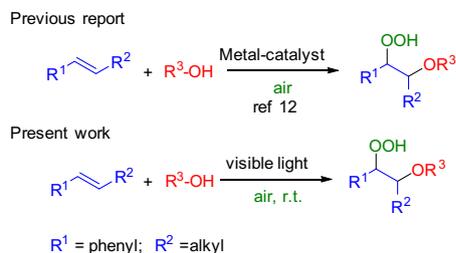
Transition metal-catalyzed oxygenation of hydrocarbons by the activation of molecular oxygen has been well established.⁹ Among them, the dioxygenation of alkenes is an attractive strategy due to the wide utility of oxygenated molecules in synthetic chemistry.¹⁰ Therefore, substantial efforts have been made by various groups for the dioxygenation of alkenes with molecular oxygen to obtain β -keto/ β -hydroxy-N-alkoxyamines systems.¹¹ Recently,

Punniyamurthy's group developed an iron catalyzed aerobic dioxygenation of styrenes for the synthesis of β -hydroperoxy-N-alkoxyamines.¹² In continuation of our interest on functionalization of olefins,¹³ in particular oxygenation of styrenes,¹⁴ we report herein, a novel strategy on hydroperoxidation of styrenes using hydroxylamine and molecular oxygen from air under metal-free conditions at room temperature (Scheme 1). Further, the hydroperoxides were transformed into corresponding hydroxy compounds and α -oxygenated ketones in high yields using Me₂S and phenyliodoniumdiacetate respectively at ambient temperature. These compounds generate variety of useful intermediates such as vicinal 1,2-diols, β -hydroxy-N-alkoxyamines, α -haloketones, α -azido ketones, β -ketoalkoxyamines and vinylphosphates upon chemical modification.^{14,11b} To the best of our knowledge, no prior reports available for the visible-light-promoted dioxygenation of styrenes under metal-free and additive-free conditions.

We began our investigation with 4-methylstyrene **1a** and N-hydroxyphthalimide (NHPI) **2** as the model substrates and subjected for oxidative dioxygenation at room temperature using 3 W blue LED bulb in open atmosphere and the results are summarized in Table 1. Initially, the reaction was performed using 0.50 mmol of **1a**, 0.50 mmol of **2** in CH₃CN at room temperature under 3 W blue LED, after 18 h **3a** was isolated in 82% yield (Table 1, entry 1). Increasing the amount of **2** to 0.55 mmol (1.1 equiv) and 0.60 mmol (1.2 equiv) led to increase in the yield of **3a** to 87% and 96% respectively (Table 1, entries 2 and 3). By decreasing the reaction time from 18 h, the yield of the product was dropped (Table 1, entries 4 and 5). When the same reaction

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Scheme 1. Aerobic dioxygenation of alkenes.

was performed under O_2 atmosphere the desired product **3a** was obtained in 95% yield (Table 1, entry 6). Further we screened the effect of other solvents on oxidative dioxygenation of **1a**, but no improvement was observed (Table 1, entries 7–14). A control experiment showed that only a small amount of product **3a** was obtained in the absence of light (entry 15). When the same reaction was performed under sunlight for 9 h the desired product **3a** was obtained in 55% yield (entry 16).

With the optimized conditions in hand, we explored the substrate scope and limitations of the visible-light-mediated hydroperoxidation of various styrenes and the results are compiled in Table 2. As evident from Table 2, dioxygenation of a variety of styrenes with NHPI were smoothly reacted and afford the desired products in moderate to excellent yields. The reaction of styrene **1b** gave the corresponding compound **3b** in 67% yield. As expected, a variety of styrenes bearing both electron-donating and/or electron withdrawing groups (R = Me, OMe, OAc, Ph, *tert*-butyl, F, Cl and Br) at either (para/ortho/meta) position were tolerated under the present reaction conditions and furnished the expected products **3c–3k** in 62–88% yields. The reaction of 1-vinylnaphthalene also proceeded well, giving the product **3l** in 71% yield. It is noteworthy to mention that, α -methyl and phenyl styrenes performed well and afforded the corresponding products **3m** and **3n** in

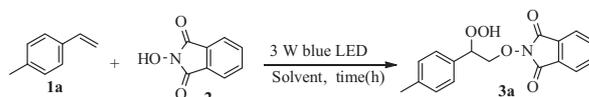
moderate (60%) to excellent (98%) yields. Further, *trans*- β -methyl styrene was also compatible under the present reaction conditions, and the desired product **3o** was obtained in 84% yield. Notably, cinnamyl alcohol was tolerable to these conditions and delivered the product **3p** in 51% yield. To explore the present protocol, we performed the oxidation of the alkenes **1a**, **1c**, **1n** and **1o** having substituents on the aryl ring as well as alkenes with *N*-hydroxybenzotriazole (HOBt) furnished the corresponding peroxy products **3r–3v** in 62–91% yields. Unfortunately, the present protocol is not applicable for vinyl pyridine and non-conjugated alkenes (**3w–3z**). More over to validate the methodology, few examples were performed at 5 mmol scale and the results revealed that our strategy was effective at gram scale preparation of products **3a**, **3n**, and **3r**.

Encouraged by the results obtained (products in Table 2), we further sought to explore other hydroxylamines 5 (*N*-hydroxysuccinimide (NHS) and methyl-*N*-hydroxy-*N*-phenylcarbamate) for dioxygenation of styrenes. Reaction of representative styrene derivatives under air with 25 W CFL bulb in open air at room temperature gave the desired dioxygenated products **6a–d** in 31–57% yields (Scheme 2).

The structural motifs of **7**, are commonly found in many natural products and are versatile intermediates in organic synthesis. Due to the biological importance of these molecules, we studied the transformation of **3** into alcohols **7** under unoptimized conditions. The reaction of β -hydroperoxy-*N*-alkoxyamines **3a**, **3b**, **3d**, **3n** and **3r** with Me_2S provided the corresponding hydroxy compounds **7a–e** in 91–96% yields at room temperature (Scheme 3).

Finally, the reaction of β -hydroperoxy-*N*-alkoxyamines **3** were extended with phenyliodonium diacetate (PIDA) to get α -oxygenated ketones (Scheme 4). α -Oxygenated ketones are extensively useful intermediates in both medicinal and biological sciences.¹⁵ Considering the importance of these α -oxygenated ketones, we further carried out the conversion of **3–8** under unoptimized conditions. The reactions readily proceeded with good to

Table 1
Optimization of the reaction conditions for **3a**.^a



Entry	1a : 2	Oxidant (eq)	Solvent	Time (h)	Yields (%) ^b
1	1:1	Air	CH ₃ CN	18	82
2	1:1.1	Air	CH ₃ CN	18	87
3	1:1.2	Air	CH ₃ CN	18	96
4	1:1.2	Air	CH ₃ CN	6	65
5	1:1.2	Air	CH ₃ CN	12	78
6	1:1.2	O ₂	CH ₃ CN	18	95
7	1:1.2	Air	Toluene	36	81
8	1:1.2	Air	DCE	36	84
9	1:1.2	Air	THF	36	23
10	1:1.2	Air	DMF	36	28
11	1:1.2	Air	DMSO	36	13
12	1:1.2	Air	H ₂ O	36	10
13	1:1.2	Air	EtOH	36	0
14	1:1.2	Air	Acetone	36	34
15 ^c	1:1.2	Air	CH ₃ CN	36	Trace
16 ^d	1:1.2	Air	CH ₃ CN	9	55

^a Reaction conditions otherwise stated: **1a** (0.50 mmol), **2** (0.60) mmol and solvent (1.5 mL), at room temperature.

^b Isolated yields.

^c Reaction performed under dark condition.

^d Reaction performed under sunlight for 9 h.

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