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PII: S0040-4039(16)31729-4
DOI: http://dx.doi.org/10.1016/j.tetlet.2016.12.073
Reference: TETL 48485

To appear in: *Tetrahedron Letters*

Received Date: 25 November 2016
Revised Date: 22 December 2016
Accepted Date: 23 December 2016

Please cite this article as: Samanta, S., Ravi, C., Joshi, A., Pappula, V., Adimurthy, S., Visible-light- induced aerobic dioxygenation of styrenes under metal- and additive-free ambient conditions, *Tetrahedron Letters* (2016), doi: http://dx.doi.org/10.1016/j.tetlet.2016.12.073

Graphical Abstract

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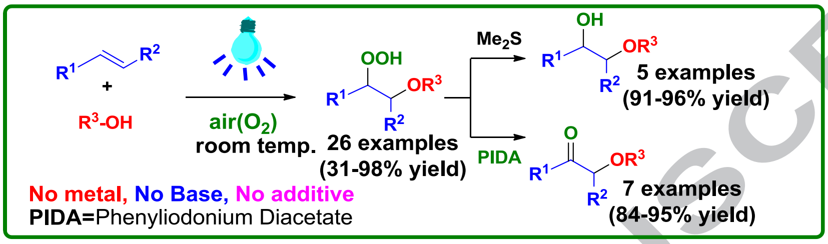

Tetrahedron Letters
journal homepage: www.elsevier.com

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ARTICLE INFO

Article history:
Received
Received in revised form
Accepted
Available online

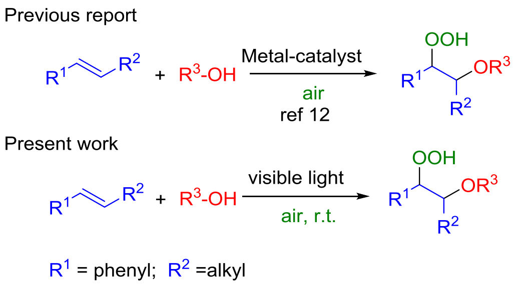
Keywords:
Visible light
Hydroperoxidation
Styrenes
Metal-free
Additive-free

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.

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-hydroxyketones[4] 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]

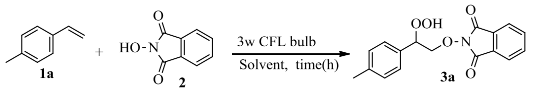
Transition metal-catalyzed oxygenation of hydrocarbons by the activation of molecular oxygen has been well established.[9] Among them, the dioxygenation of alkenes is an attractive strategy due to the wide utility of oxygenated molecules in synthetic chemistry.[10] Therefore, substantial efforts have 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 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 Me_2S 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.



Scheme 1. Aerobic dioxygenation of alkenes

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 3W 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 CH_3CN at room temperature under 3W blue LED, after 18 hours **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 was performed under O_2 atmosphere the desired product **3a** was obtained in 95% yield (Table 1, entries 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 9h the desired product **3a** was obtained in 55% yield (entry 16).

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

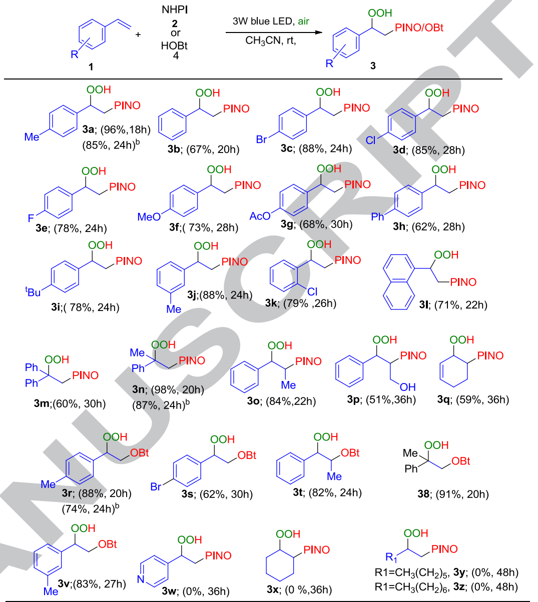


entry	1a : 2	oxidant (eq)	solvent	time (h)	yields (%)[b]
1	1:1	air	CH_3CN	18	82
2	1:1.1	air	CH_3CN	18	87
3	1:1.2	air	CH_3CN	18	96
4	1:1.2	air	CH_3CN	6	65
5	1:1.2	air	CH_3CN	12	78
6	1:1.2	O_2	CH_3CN	18	95
7	1:1.2	air	Toluene	36	81
8	1:1.2	air	DCE	36	84
9	1:1.2	air	THF	36	23
10	1:1.2	air	DMF	36	28
11	1:1.2	air	DMSO	36	13
12	1:1.2	air	H_2O	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_3CN	36	trace
16[d]	1:1.2	air	CH_3CN	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 9h.

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-vinylnapthalene 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%. Unfortunately, the present protocol is not applicable for vinyl pyridine and non-conjugated alkenes (**3w-3z**). More over to validate the methodology, few example 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**.

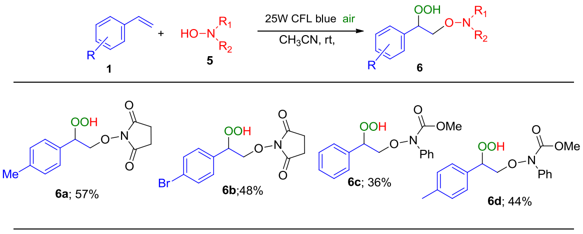
Table 2. Substrate scope for the visible-light-mediated of dioxygenation of alkene with NHPI and HOBt[a].



[a]Reaction conditions otherwise stated: **1** 0.50 mmol, **2** or **4** 0.60 mmol, under air and 3W blue LED, CH_3CN (2.0 mL) at rt , for 18 h, isolated yields. [b]Reactions performed at 5.0 mmol of **1a**, 6.0 mmol of **2** or **4**.

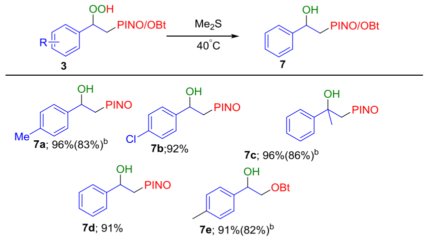
Encouraged by the results obtained (products in Table 2), we further sought to explore other hydroxylamines 5 (N-hydroxysuccinimide (NHS) and methyl-N-hydroxy-N-phenylcarbamate) for deoxygenation of styrenes. Reaction of representative styrene derivatives under air with 25W CFL bulb in open air at room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

Scheme 2. Oxidations with *N*-hydroxysuccinimide and methyl-*N*-hydroxy-*N*-phenylcarbamate[a]



[a]Reaction conditions otherwise stated: 0.50 mmol of **1a**, 0.60 mmol of **2** or **4** in air under 25W CFL bulb, in 2.0 mL of CH_3CN at r.t. for 48h, isolated yields.

Scheme 3. Transformation of **3** to **7** hydroxy compounds[a]



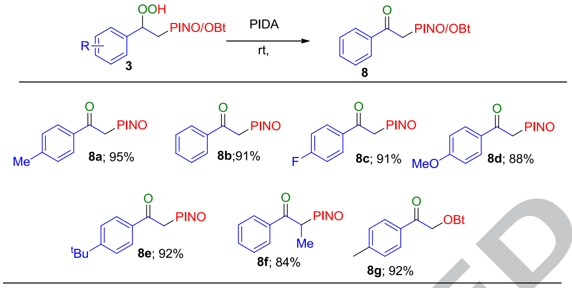
[a]Reaction conditions unless stated: **3** (0.2 mmol), Me_2S (1.2 mmol), CH_2Cl_2 (2.0 mL), 40˚C, 1.0h, isolated yields. [b]Yields obtained from **1** (0.20 mmol), **2**

or **4** (0.25 mmol) under air and 3W blue LED, CH$_3$CN (1.0 mL), 18 h at room temperature, then Me$_2$S was added and reaction continued for another 1.0 h, at 40˚C.

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$_2$S 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 phenyliodoniumdiacetate (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** to **8** under unoptimized conditions. The reactions readily proceeded with good to excellent yields. The reaction of **3a** with PIDA proceeded readily to yield **8a** in 95% yield. Similarly the reaction of PIDA with other substrates **3b, 3e, 3f, 3i, 3o** and **3r**, reacted smoothly and furnished the corresponding α-oxygenated ketones **8b−g** in 84−92% yields (Scheme 4).

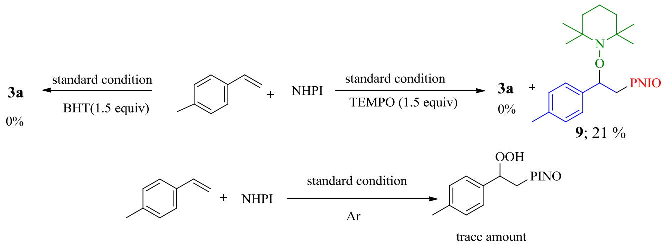
Scheme 4. Transformation of **3** to α-oxygenated ketones (**8**)[a]



[a]Reaction conditions: **3** (0.3 mmol), PIDA (0.3 mmol), CH$_2$Cl$_2$ (2.0 mL), rt, 18h, isolated yields.

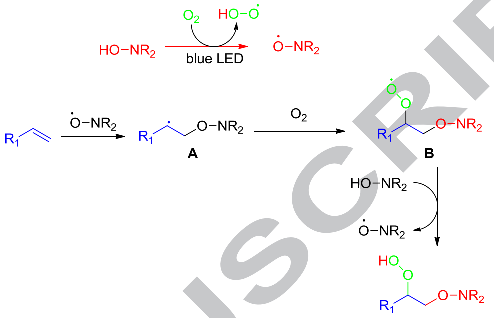
To propose a probable mechanism for the present transformation, some experiments were performed (Scheme-5). First, the reaction of **1a** was conducted in presence of radical scavenger, TEMPO under optimized conditions, the TEMPO-adduct **9** was isolated in 21% yield instead of **3a**. The same reaction with BHT, no desired product formation was observed (Scheme 5). These controlled experiments show that, the reaction may proceed through a radical pathway. Further, the complete inhibition of the reaction was observed under argon atmosphere indicates the molecular oxygen is the source for insertion of oxygen in the product **3a**.

Scheme 5. Mechanistic experiments



Based on the above observations and the literature reports[12, 16] a plausible reaction mechanism for dioxygenation of olefin is outlined in Scheme 6. Initially R$_2$NO• radical may be generated from N-hydroxylamine (NHPI, HOBt) under visible light conditions,[16f] which further react with olefin and generate a carbon-centered radical intermediate **A**. The regioselectivity of the reaction solely determines the stability of the benzylic radical generation. In the presence of oxygen, **A** converts to peroxy radical **B**, which may react with N-hydroxylamine to yield the desired product.

Scheme 6. Plausible Mechanism



In conclusion, we have demonstrated dioxygenation of styrenes by employing hydroxylamine promoted by visible light under aerobic conditions at room temperature without metal and additives. The resulted dioxygenated products were further transformed into synthetically useful compounds, such as hydroxy compound and α-oxygenated ketones. Wide range of substrate scope, scalability and high yields are the highlights of present protocol.

Acknowledgments

CSIR-CSMCRI Communication No. 139/2016. S.S, C. R & A. J. are thankful to AcSIR for their Ph.D. enrollment and the “Analytical Discipline and Centralized Instrumental Facilities” for providing instrumentation facilities. S.S and A.J are also thankful to CSIR, New Delhi for their fellowships. We thank DST, Government of India (EMR/2016/000010), and CSIR-CSMCRI (OLP-087) for financial support.

Supplementary Material

Supplementary data (detailed experimental procedure and spectroscopic data) associated with this article can be found, in the online version, at

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Highlights

- Visible-light- induced aerobic dioxygenation of styrenes.
- Synthesis of hydroperoxids and hydroxy compounds
- Metal- and additive-free ambient conditions