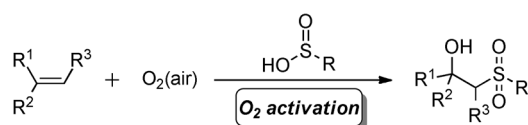


Aerobic Oxysulfonylation of Alkenes Leading to Secondary and Tertiary β -Hydroxysulfones**

Qingquan Lu, Jian Zhang, Fuliang Wei, Yue Qi, Huamin Wang, Zhiliang Liu, and Aiwen Lei*

Dioxygen is not only a green oxidant but also an ideal oxygen source for the functionalization of organic molecules.^[1] Dioxygen activation has been of long-standing interest and has fascinated organic chemists owing to its tremendous potential usage in synthetic chemistry, bioinorganic chemistry, enzymology, and so on.^[1,2] Over the past few decades, significant progress has been achieved. Many transition metals, such as Pd,^[3a,b] Cu,^[3c–i] Ag,^[3j] Mn,^[3k–m] Fe^[3n–j] and others,^[1,4] have been successfully applied to activate dioxygen, whereas organic molecules has been seldom studied in this area (Scheme 1).^[4]



Scheme 1. Dioxygen activation by sulfinic acids for the formation of β -hydroxysulfones.

Seeking dioxygen activation by organic molecules is an extremely attractive and sustainable approach for introducing oxygen functional groups in synthetic chemistry. Moreover, such procedures obviate the need for purification of the products for the residual catalysts and vastly broaden the potential practicality for green synthesis of fine chemicals, especially in the pharmaceutical industry. However, up to now, only a few examples of dioxygen activation by organic molecules have been reported, which mainly focused on the oxidation of simple substrates, such as phenols, organic sulfides, and alkenes.^[5] Great challenges still remain in this

promising field.^[6] In this regard, it is extraordinarily important to find the new reactions to broaden this area. Owing to our continuous interests in dioxygen activation,^[7] we present herein our recent progress in dioxygen activation mediated by sulfinic acids, which illustrates an convenient method towards the synthesis of secondary and tertiary β -hydroxysulfones using simple materials under transition-metal-free conditions.

The chemical structure of β -hydroxysulfone is not only a basic scaffold of numerous pharmaceutically important molecules and synthetically fine chemicals, such as the hugely successful and valuable bicalutamide, Sch42427 and SSY726 etc.^[8] but is also an important precursor in the synthesis of a series of useful biologically active molecules.^[9,10] Generally, β -hydroxysulfones are prepared by the opening of epoxides with sulfinate salts,^[11] the reaction of phenylsulfonylmethyl-metallic reagents with carbonyl compounds,^[12] and chemical or bioreduction of β -ketosulfones.^[13] All of these methods require multistep processes to synthesize starting materials that often produce large amounts of unwanted byproducts, which make them environmentally unfavorable and result in poor functional-group tolerance. As such, tremendous limitations remain in the synthetic scope of β -hydroxysulfone, and efficient approaches towards tertiary β -hydroxysulfone is very rare because of the difficult preparation of starting materials.^[14] Therefore, the development of direct, mild, and environmentally benign processes to access β -hydroxysulfones, and in particular for tertiary β -hydroxysulfones from basic chemical materials, are always highly desirable. To the best of our knowledge, no examples in which β -hydroxysulfones were prepared from direct oxidative difunctionalization of simple alkenes through dioxygen activation by organic molecules have been reported.^[15]

We initially chose α -methylstyrene (**1a**) and benzenesulfinic acid (**2a**) as the substrates to test the reaction (Supporting Information, Table S1). To our delight, **1a** and **2a** reacted smoothly to afford the desirable 2-phenyl-1-(phenylsulfonyl)propan-2-ol (**3aa**) in 46% yield in chloroform under air atmosphere, without any additives. Subsequently, various parameters were screened to optimize the reaction conditions. The experiments showed that bases as an additive seemingly played a key role in promoting the efficiency and pyridine dramatically enhanced the yield to 98%. When other bases, such as DBU, Et₃N, Et₂NH, and LiOH, were applied instead of pyridine, the yield of the desired product more or less decreased. Further screening of the solvents revealed that chloroform was the best solvent for this reaction. It is noteworthy that this reaction could also work well at room temperature, although a longer reaction time was required. Furthermore, when the reaction was carried out under a N₂ atmosphere, only trace amount of desired product was

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[**] This work was supported by the “973” Project from the MOST of China (2012CB725302) and the National Natural Science Foundation of China (21025206, 20832003, and 20972118).

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/ange.201301634>.

formed, which demonstrated the importance of the presence of O₂.

With the optimized conditions in hand, we next explored the scope of the reaction between various sulfinic acids and α -methylstyrene **1a**, and the results are summarized in Table 1. Gratifyingly, a series of aryl sulfinic acids bearing both electron-donating groups (R = OMe, Me) and electron-withdrawing groups (R = F, Cl, Br) furnished to the desired tertiary β -hydroxysulfones in excellent yields (**3ab–3af**). It is noteworthy that Cl and Br substituents on the phenyl ring were well tolerated, which enable a potential application in further functionalization (**3ad–3ae**). Additionally, a more

bulky substrate, 2-naphthylsulfinic acid, also efficiently reacted with **1a** giving the product in 80% yield (**3ag**).

Subsequently, we applied our method to a range of alkenes to prepare an array of tertiary β -hydroxysulfones using *p*-toluenesulfinic acid (**2b**) as the reaction partner. As shown in Table 1, a variety of α -methylstyrene derivatives, including methyl, *tert*-butyl, bromo, and trifluoro groups on the aromatic ring, readily worked well in this reaction (**3bb–3fb**). Notably, a nitro substituent, which is usually unfavorable in reactions with radical participation, was also well tolerated,^[16] affording the corresponding tertiary β -hydroxysulfone **3eb** in 89% yield. The reaction of 2-(prop-1-en-2-yl)naphthalene also proceeded well, giving the desired product in 80% yield (Table 1, **3gb**). Furthermore, this reaction was also applicable to other α -alkylstyrenes, which have steric hindrance at the substituent, as demonstrated by the formation of the desirable products **3hb** and **3ib** in good yields. Encouraged by these promising results, we further applied our developed procedure to synthesize secondary β -hydroxysulfones using styrene and its derivatives as substrates. Pleasingly, *p*-toluenesulfinic acid (**2b**) reacted smoothly with both electron-rich (methyl) and electron-deficient (bromo, chloro, fluoro) group substituted styrenes, and afforded the expected secondary β -hydroxysulfones in excellent yield under slightly modified conditions (**3jb–3ob**). Non-terminal and cyclic styrene derivatives, such as β -methylstyrene and 1,2-dihydronaphthalene, were also effective to give the expected products **3pb** and **3qb** in excellent yield respectively. Delightfully, activated aliphatic alkenes, as a case study of ethyl methacrylate, was also tested, affording the desired product **3rb** in 82% yield. Nevertheless, non-activated aliphatic alkenes such as 1-butene is not amenable to this procedure, which is probably due to the unfavorable factors for the generation of the unstable intermediate.^[14] Furthermore, the identity of product **3fb** was unequivocally established by its X-ray single-crystal structure (see the Supporting Information for details).

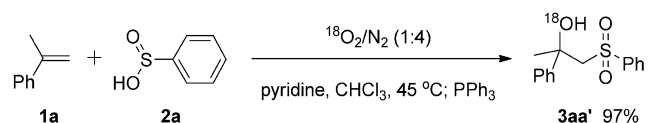
To gain insight into the reaction mechanism, we designed the following experiments. An isotope labeling experiment was first conducted to elucidate the origination of the hydroxy oxygen atom of the β -hydroxysulfones. The reaction of **1a** with **2a** under an ¹⁸O₂/N₂ (1:4) atmosphere under the standard conditions generated the ¹⁸O-labeled product in 97% yield (Scheme 2). This result demonstrated that O₂ took part in this reaction and the oxygen atom in the product came from O₂.

Furthermore, it is well-known that activation of dioxygen mostly proceeded by a radical process.^[3,4] Therefore, when investigating the mechanism of oxidative difunctionalization of alkenes, a radical pathway was also supposed involving in this transformation, and radical trapping experiments supported this assumption. This reaction was extremely inhibited in the presence of 2,2,6,6-tetramethyl-1-piperidinyloxy

Table 1: Substrate scope of the aerobic oxysulfonation of alkenes with various sulfinic acids.^[a]

$\text{R}^1\text{C}=\text{C}(\text{R}^2)\text{R}^3 + \text{HO}-\text{S}(=\text{O})-\text{Ar} + \text{O}_2(\text{air}) \xrightarrow[\text{CHCl}_3, \text{PPh}_3]{\text{pyridine, 45 } ^\circ\text{C}}$		
1	2	3
3aa 98%	3ab 92%	3ac 83% ^[b]
3ad 98% ^[b]	3ae 90% ^[b,c]	3af 98% ^[b]
3ag 80% ^[b]	3bb 91%	3cb 83%
3db 83%	3eb 89%	3fb 60%
3gb 80%	3hb 70% ^[b]	3ib 66% ^[d]
3jb 97% ^[e]	3kb 94% ^[e]	3lb 97% ^[e]
3mb 84% ^[e]	3nb 93% ^[e]	3ob 95% ^[e]
3pb 97% ^[e]	3qb 90% ^[e]	3rb 82% ^[b]
erythro/threo 20:1 trans/cis 35:1		

[a] Unless otherwise specified, all reactions were carried out using **1** (0.20 mmol), **2** (0.40 mmol), and pyridine (0.18 mmol) in CHCl₃ (4.0 mL) at 45 °C for 80 min under 1 atm of air (balloon). Yield of isolated product after PPh₃ workup. [b] *p*-Toluenesulfinic acid (**2b**) (0.80 mmol), pyridine (0.37 mmol), and 4 h were employed. [c] 6 h. [d] **2b** (1.0 mmol) and pyridine (0.9 mmol) were used. [e] **2b** (2.0 mmol) and pyridine (0.92 mmol) were employed at 60 °C.



Scheme 2. ¹⁸O isotope labeling experiment.

(TEMPO) or 2,4-di-*tert*-butyl-4-methylphenol (BHT; see radical trapping experiments in the Supporting Information), which were well-known radical scavengers. These results suggested that the reaction presumably underwent a radical pathway.

To acquire further understanding of the reaction mechanism, we next attempted to use in situ IR to monitor the reaction between **1a** and **2b**. The profiles of relative absorbance (ConcIRT) versus time for individual species is shown in Figure 1. Clearly, when pyridine was added, the absorbance of **2b** immediately decreased sharply, which

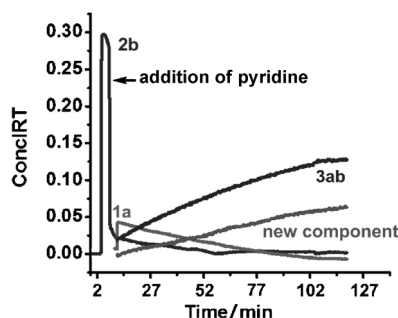


Figure 1. The 2D kinetic profiles of the reaction of **2b** (0.8 mmol), pyridine (0.36 mmol), and **1a** (0.4 mmol) added to CHCl_3 (4.0 mL) at 45°C in succession; the reaction was monitored by in situ IR spectroscopy.

meant that an acid–base neutralizing reaction happened first. When **1a** was added, the signal of **3ab** and a new component increased gradually in intensity with the consumption of **1a**. The IR band of the new component was assigned to pyridinium *p*-toluenesulfonate by comparison with an authentic sample (see the Supporting Information), these results revealed that *p*-toluenesulfonic acid may be also serving as a reductant during the reaction.

The reaction was also monitored by in situ IR spectroscopy in the absence of **1a** (Figure 2). The kinetic profile clearly shows that the signal of **2b** disappeared immediately while pyridine was added. Thereafter, two new bands at 1009 cm^{-1} and 1032 cm^{-1} , which were unambiguously assigned to pyridinium *p*-toluenesulfonate by comparison with an authentic sample, increased proportionally. These results indicated that sulfinic acid was easily oxidized to the corresponding sulfonic acid under the standard reaction conditions and pyridine may also serve as a base to neutralize the sulfonic acid generated in situ.

Based on the aforementioned results and previous reports,^[15,17] a possible reaction pathway is proposed for the formation of β -hydroxysulfones (Scheme 3). First, benzenesulfinic acid reacts with pyridine to release free sulfinyl anion **I**, which could be further oxidized by dioxygen by single electron transfer (SET) to induce the formation of an oxygen-centered radical **II** resonating with sulfonyl radical **III**. Subsequently, the radical addition of **III** to α -methylstyrene (**1a**) affords carbon-centered radical **IV**, which reacts with dioxygen by a redox-transfer process to produce alkylhydroperoxy radical intermediate **V**. And then the generated intermediate **V** affords β -peroxysulfone **VI** by single-electron

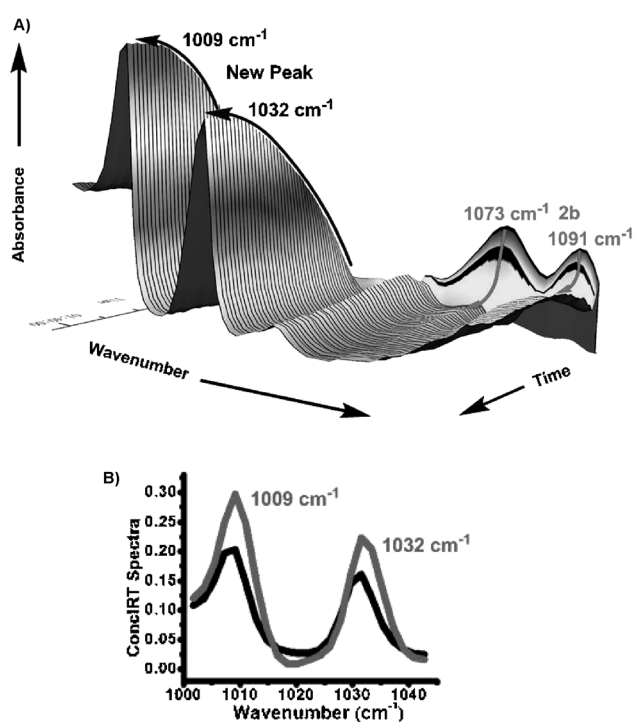
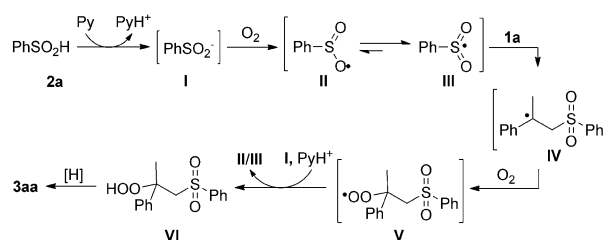


Figure 2. A) The 3D-FTIR profile of the reaction of **2b** (0.4 mmol) and pyridine (0.4 mmol). B) ConcIRT spectra of the new component (black curve) and authentic sample (gray curve).

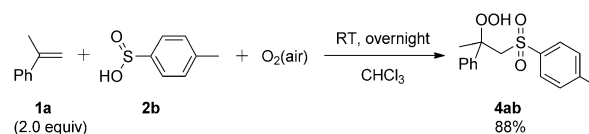


Scheme 3. Proposed mechanism.

transfer (SET) and concomitant proton transfer (PT) from **I** and pyridium benzenesulfonate, furnishes **II/III**. Finally, subsequent reduction by benzenesulfinic acid or workup by PPh_3 , gives the oxysulfonylation product **3aa**.

To probe the feasibility of the pathway and prove the key precursor **VI** is involved in this transformation, we attempt to verify the production of β -peroxysulfone by isolation and characterization. To our delight, β -peroxysulfone **4ab** could be readily isolated in excellent yield by simply changing conditions at room temperature (Scheme 4) and it could be quantitatively transformed to **3ab** after PPh_3 work up.

In conclusion, we have developed a highly attractive and operationally simple intermolecular oxysulfonylation method to construct secondary and tertiary β -hydroxysulfones with



Scheme 4. Isolation of peroxide **4ab**.

readily available reactants, in which β -hydroperoxysulfone was isolated as an important intermediate. The procedure showed a wide range of functional-groups tolerance, and the formation of new C–O and C–S bond in one-pot. The novel method proceeded without any additional initiators and realized dioxygen activation by sulfinic acids, which made this transformation sustainable and environmentally friendly. Radical capture experiments revealed that this reaction might involve a radical process. Ongoing research including further mechanistic details and expanding the substrate scope are currently underway.

Received: February 25, 2013

Revised: April 3, 2013

Published online: May 23, 2013

Keywords: alkenes · dioxygen activation · oxidative difunctionalization · sulfinic acids · β -hydroxysulfones

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