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Communication

Visible-light-induced deoxygenative C2-sulfonylation of quinoline N-oxides with sulfinic acids for the synthesis of 2-sulfonylquinoline via radical reactions

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ABSTRACT

A simple and efficient method for the synthesis of 2-sulfonylquinoline from deoxygenative C2-sulfonylation of quinoline N-oxides with sulfinic acid induced by visible light is presented. This protocol shows a broad substrate scope, and desired products with various substituents can be formed in moderate to high yields at room temperature.

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Compared with traditional, heat-promoted organic reactions, visible-light-induced organic reactions are milder, environmentally benign and operationally simpler. Moreover, visible light is a readily available source, so it has promising applications in science and industry [1–5]. In recent years, great progress has been achieved in visible-light-induced reactions. For example, various C–C and C–hetero bond-formation reactions induced by visible light have been successfully achieved [6–21]. Among these, visible-light-induced sulfonylation reactions with sulfinic acids have become a hot topic. In 2015, a visible-light-induced reaction for the synthesis of sulfonated oxindoles [22] and coumarin derivatives [23] using arylsulfinic

acids was developed by Wang's group. Jiang's group [24] developed a visible-light photocatalytic arylsulfonylation and bicyclization reaction of C(sp³)-tethered 1,7-enynes with sulfinic acid which afforded sulfone-containing benzo[a]-fluorene-5-ones in generally good yields [24]. The reaction of terminal alkynes and sulfinic acids mediated by visible light for the synthesis of α -substituted vinyl sulfones with exclusive Markovnikov regioselectivity was reported by Lei and coworkers [25]. Mechanistic investigations showed that radical/radical cross-coupling might be the key step in this transformation. In the absence of additional photocatalyst, three-component reactions of isocyanides, alkynes, and sulfinic

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acids were described by Wang's group [26]. C6-polyfunctionalized phenanthridines with high selectivity were formed. It is interesting that the novel electron donor-acceptor (EDA) complex generated from the reaction of arylsulfonic acid and biaryl isocyanide drives the reaction. Although various sulfonylated compounds have been synthesized via visible-light-induced sulfonylation reactions using sulfonic acids, it is highly desirable to expand the substrate scope of the sulfonylation reaction.

2-Sulfonylquinoline derivatives are important nitrogen-containing heterocyclic compounds in agricultural and pharmaceutical chemistry [27–41]. Therefore, significant efforts have been focused on the development of efficient and economically feasible protocols for their preparation [42–49]. At present, sodium benzenesulfonate [50–53], sulfonyl chlorides [54–56], and sulfonyl hydrazides [57,58], have been shown to be efficient sulfonylation reagents for the preparation of deoxygenative 2-sulfonylquinolines. However, to the best of our knowledge, there is no example of visible-light-induced C2-sulfonylation of quinoline N-oxides with sulfonic acids. Consistent with our interest in green chemistry [59–66], we describe visible-light-induced reactions for the synthesis of 2-sulfonylquinolines using sulfonic acids via a radical mechanism.

Table 1

Optimization of reaction conditions ^a.

Entry	Cat. (2 mol%)	[O] (2 equiv.)	Solvent	Yield (%)
1	Na ₂ .eosinY	TBHP	acetone	83
2	Na ₂ .eosinY	TBHP	DMF	NR
3	Na ₂ .eosinY	TBHP	DMSO	65
4	Na ₂ .eosinY	TBHP	CH ₃ CN	45
5	Na ₂ .eosinY	TBHP	H ₂ O	NR
6	Na ₂ .eosinY	TBHP	DME	NR
7	Na ₂ .eosinY	TBHP	EtOAc	NR
8	Na ₂ .eosinY	TBHP	DCE	88
9	Acid Red 94	TBHP	DCE	27
10	Methylene blue	TBHP	DCE	62
11	Acridine Red	TBHP	DCE	35
12	Eosin Y	TBHP	DCE	24
13	Ru(bpy) ₃ Cl ₂	TBHP	DCE	22
14	Na ₂ .eosinY	TBPB	DCE	27
15	Na ₂ .eosinY	DTBP	DCE	NR
16	Na ₂ .eosinY	K ₂ S ₂ O ₈	DCE	11
17 ^b	Na ₂ .eosinY	TBHP	DCE	52
18 ^c	Na ₂ .eosinY	TBHP	DCE	15
19 ^d	Na ₂ .eosinY	TBHP	DCE	27
20 ^e	Na ₂ .eosinY	TBHP	DCE	NR
21	—	TBHP	DCE	NR
22	Na ₂ .eosinY	—	DCE	NR
23 ^f	Na ₂ .eosinY	TBHP	DCE	89

^a Reaction conditions: quinoline 1-oxide (**1a**) (0.2 mmol), benzenesulfonic acid (**2a**) (0.4 mmol), 8 W blue LED, catalyst (2 mol%), solvent (1 mL), rt, 24 h, isolated yields. ^b 8 W green LED. ^c 8 W UV. ^d 8 W white LED. ^e No light. ^f Catalyst loading 5 mol%.

Initially, to optimize the reaction conditions, the reaction between quinoline 1-oxide and benzenesulfonic acid was examined. As can be seen in Table 1, solvents play an important role in the reaction. The desired product can be obtained with an 83% yield when acetone is used as the solvent (Table 1, entry 1). The use of DMSO and CH₃CN as solvents led to lower yields (Table 1, entries 3 and 4, respectively). To our disappointment, no product was obtained when DMF, H₂O, 1,2-dimethoxyethane (DME), or EtOAc were used as solvents (Table 1, entries 2 and 5–7, respectively). Dichloroethane (DCE) was found to be an excellent solvent for this reaction, providing the highest yield (88%) of the desired products (Table 1, entry 8). Several different catalysts for this reaction were also investigated. Methylene blue was found to be effective in this reaction, yielding moderate product isolation (62%, Table 1, entry 10). Other catalysts, such as Acid Red 94, Acridine Red, Eosin Y, and Ru(bpy)₃Cl₂, were less effective for this reaction (Table 1, entries 9 and 11–13, respectively). An examination of the effects of the oxidant on the reaction was then performed. *tert*-Butyl peroxybenzoate (TBPB), dibutylperoxide (DTBP), and K₂S₂O₈ were less effective than *tert*-butyl hydroperoxide (TBHP) (Table 1, entries 14–16, respectively). Next, different visible-light sources such as green, UV, white, and blue were tested. Blue light showed the best result (Table 1, entries 8 and 17–19, respectively). When the reaction was conducted in the absence of light, catalyst, or oxidant, it was completely inhibited (Table 1, entries 20–22, respectively). Increasing the loading of the catalyst to 5 mol% also did not improve the efficiency of the reaction (Table 1, entry 23).

To survey the versatility of the deoxygenative sulfonylation

Table 2

Reaction scope ^a.

^a Reaction conditions: quinoline 1-oxide (0.2 mmol), sulfonic acid (0.4 mmol), *tert*-butyl hydroperoxide (TBHP, 0.4 mmol), 8 W blue LED, Na₂.eosinY (2 mol%), dichloroethane (DCE, 1 mL), rt, 24 h, isolated yields.

reaction, a variety of quinoline N-oxides and arylsulfonic acids were tested, with the results summarized in Table 2. Quinoline N-oxides with electron-neutral, electron-poor, and electron-rich groups all reacted efficiently with benzenesulfonic acid to generate the corresponding products in moderate to high yields (Table 2, 3a–3h). For substituted sulfonic acids, various groups such as F, Cl, Br, CH₃, and *t*Bu were all suitable for this reaction (Table 2, 3i–3p). Steric hindrance did not have any obvious impact on this reaction, as compounds 3f, 3m, and 3n were obtained in 72%–82% yields. It is interesting to note that naphthalene-2-sulfonic acid also reacted well with quinoline N-oxides, affording the desired products in 77%–80% yields (Table 2, 3q and 3r). Br and CH₃CO are active groups which render the corresponding products ready for further functionalization.

To investigate the mechanism of this transformation, radical-trapping reagents, 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) and 2,6-di-*tert*-butyl-4-methylphenol (BHT), were introduced to the reaction, with no desired product being formed (Scheme 1). This suggests that free-radical intermediates may be involved in the presented transformation. Visible light, photocatalyst, and oxidant also play important roles in the sulfonylation reaction, because the reaction will not proceed if any of these are absent (Table 1, entries 20–22, respectively).

Based on our initial mechanistic studies and previous work [23–25,50–53,59–66], a possible mechanism for visible-light-induced deoxygenative sulfonylation of quinoline N-oxides is diagrammed in Scheme 2. First, excited photocatalyst species Na₂-eosinY* is generated from the irradiation of Na₂-eosinY by visible light. Then, Na₂-eosinY* reacts with TBHP, leading to production of a *tert*-butoxyl radical. Hydrogen can be abstracted by the *tert*-butoxyl radical from sulfonic acid to afford a sulfonyl radical A. Then the sulfonyl radical A reacts with quinoline N-oxide to provide intermediate B. Intermediate B further reacts with the sulfonyl radical to afford intermediate C. Finally, desired product D is obtained from aromatization of C with concomitant release of sulfonic acid. Alternatively, intermediate B could also abstract a hydrogen atom from sulfonic acid. This would produce another equivalent of a sulfonyl radical and lead to the elimination of H₂O from hydrogenated E, affording the desired products. This mechanism may also be possible.

In conclusion, we have described a novel and efficient visible-light-induced reaction for preparation of 2-sulfonylquinoline. Various functional groups were well tolerated in this reaction and the corresponding products were obtained in moderate to high yields. Free-radical intermediates may be involved in the reaction process. Further investigations toward expanding substrate scope and mechanistic study are

Scheme 1. Control experiments.

Scheme 2. Proposed reaction mechanism.

underway in our lab.

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Graphical Abstract

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Visible-light-induced deoxygenative C2-sulfonylation of quinoline N-oxides with sulfinic acids for the synthesis of 2-sulfonylquinoline via radical reactions

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A simple and efficient method for the synthesis of 2-sulfonylquinoline from deoxyquinoline N-oxides with sulfinic acid induced by visible light is presented. This protocol shows a broad substrate scope, and desired products with various substituents can be formed in moderate to high yields at room temperature.

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可见光诱导喹啉-N-氧化物与亚磺酸的脱氧C2-磺酰化通过自由基反应合成2-磺酰喹啉

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摘要: 喹啉类衍生物在有机合成、药物化学以及材料化学等领域一直具有重要作用, 通过喹啉-N-氧化物合成喹啉类衍生物目前已有许多报道, 其中采用金属催化剂实现反应占有很大比例, 但这些方法存在催化剂对空气敏感及环境不友好等问题. 因此, 发展无金属催化反应受到越来越多的重视. 近年来, 光催化反应在有机合成中得到广泛应用. 基于我们在光催化相关反应方面的研究, 本文报道了一种可见光诱导喹啉-N-氧化物与亚磺酸脱氧C2-磺酰化合成2-磺酰喹啉衍生物的合成方法.

我们选用喹啉-N-氧化物与苯亚磺酸为底物进行条件筛选实验, 发现 $\text{Na}_2 \cdot \text{eosinY}$ (2 mol%)为催化剂, 二氯乙烷为溶剂, TBHP (0.4 mmol)为氧化剂, 在蓝光照射下为最优化的实验条件, 目标产物2-磺酰喹啉最高产率为88%. 在该优化反应条件下, 带有供电子或吸电子基团的喹啉-N-氧化物都能与苯亚磺酸反应得到中等至以上产率的目标物, 另外带有不同官能团(F, Cl, Br, CH_3 和 $t\text{-Bu}$ 等)的亚磺酸与喹啉-N-氧化物也都能得到中等以上产率. 当使用苯亚磺酸作为反应底物时也能以较高产率得到相应目标产物. 对照实验显示, 在反应体系中加入自由基捕获剂TEMPO或BHT时反应不能发生, 表明自由基中间体可能参与本反应的转化. 另外在黑暗条件、无氧化剂或者无催化剂下反应也不能发生, 证明这些反应条件是必须的. 基于上述实验结果, 提出了可能的反应机理. 首先光催化剂在可见光照射下形成激发态, 然后与TBHP反应生成叔丁氧基自由基, 再作用于苯亚磺酸使其生成磺酰基并与喹啉氮氧化物反应, 其中通过两步的磺酰基反应, 最后通过芳构化得到目标产物, 光催化剂可以通过TBHP氧化再生完成催化循环.

在此, 我们发展了一种简单高效的合成2-磺酰喹啉衍生物的反应方法, 该方法无需金属催化剂, 可在温和条件下通过可见光诱导实现反应发生.

关键词: 喹啉-N-氧化物; 亚磺酸; 2-磺酰喹啉; 可见光; 自由基反应

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