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FULL PAPER

Synthesis of Sulfonated Benzo[*d*][1,3]oxazines by Merging Photoredox Catalysis and Insertion of Sulfur Dioxide

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Abstract. А photocatalytic reaction of N-(2vinylphenyl)amides, DABCO•(SO₂)₂ and arenediazonium tetrafluoroborates for the synthesis of 4-((arylsulfonyl)methyl)-4*H*-benzo[*d*][1,3]oxazines under mild conditions is reported. This synthetic approach is enabled by merging photoredox catalysis and insertion of sulfur dioxide via a radical process. The specific role of photoredox catalysis in this transformation is supported by mechanistic investigations and theoretical calculations.

Keywords: arenediazonium tetrafluoroborate, *N*-(2-vinylphenyl)amide, benzo[*d*][1,3]oxazine, sulfur dioxide, photoredox catalysis

Since the importance of sulfones in agrochemicals, pharmaceuticals, and organic synthesis is established,^[1] the methods for the generation of sulfones are continuously appeared. Typically, the routes to sulfones include oxidation of sulfides and alkylation of sulfinate salts.^[2] However, substrates with sensitive functional groups are usually not tolerated under the oxidative conditions. Additionally, only a few sulfinate salts are commercial available, and they are usually prepared starting from the corresponding sulfonyl chlorides.^[3] In the past decade, using sulfur dioxide as the sulfonyl source has become an efficient and attractive strategy for the synthesis of sulfones.^[4-8] It provides a facile route for the introduction of sulfonyl (-SO₂-) moiety from simple materials. Recently, we are interested in the synthesis of sulfonyl-containing natural product-like compounds starting from sulfur dioxide for further biological evaluations.^[8]

Benzo[*d*][1,3]oxazine is a privileged scaffold, which can be found in many natural products and biologically active molecules.^[9] Due to the importance of sulfonyl compounds in pharmaceuticals,^[1d,e] we conceived that the sulfonated benzo[*d*][1,3]oxazines would be beneficial for our specific biological assays.^[10]





Encouraged by the advances of sulfur dioxide insertion chemistry,^[4-8] we envisioned that sulfur dioxide could be involved in the generation of sulfonated benzo[d][1,3]oxazines. Therefore, we initiated a program for the design and synthesis of sulfonated benzo[d][1,3]oxazines by using sulfur dioxide as the sulfonyl source.

In 2016, our group reported an efficient route for generation of sulfonyl the radicals from arenediazonium tetrafluoroborates and DABCO $(SO_2)_2$ under mild conditions (Scheme 1, eq. a).^[11] It was found that the sulfonyl radicals and tertiary amine (DABCO) radical cation could be produced directly through a single electron transfer (SET) without the addition of any catalysts or additives. The *in-situ* generated arylsulfonyl radicals could be trapped by several partners to provide diverse sulfonyl compounds. Further investigation revealed that the catalyst-free process could not work efficiently for other applications. For example, a fourcomponent reaction of arenediazonium tetrafluoroborates, DABCO•(SO₂)₂, terminal alkynes and potassium halides required the addition of 10

mol % copper(I) chloride as the catalyst (Scheme 1, eq b).^[12] The copper catalyst was supposed to assist the oxidation of the alkenyl radical intermediate to alkenyl cation. Apparently, the introduction of metal catalysis enables broader applications of the developed strategy, combined with the generation of arylsulfonyl radicals. Thus, more valuable functionalized sulfonyl compounds would be obtained through the insertion of sulfur dioxide.

Prompted by the above achievements. we postulated that the oxysulfonylation of alkenes with the *in-situ* generation of arylsulfonyl radicals starting from sulfur dioxide would provide a feasible route to sulfonated benzo[d][1,3]oxazines (Scheme 1, eq c). Initially, a model reaction of N-(2-(prop-1-en-2yl)phenyl)benzamide 1a, benzenediazonium tetrafluoroborate 2a, and DABCO•(SO₂)₂ was carried out in 1,2-dichloroethane (DCE) under catalyst-free conditions (Table 1, entry 1). However, this attempt was unsuccessful. The addition of various copper catalysts under different conditions in this transformation also failed to provide the positive outcome. We suspected that the oxidative ability of the tertiary amine (DABCO) radical cation might be the key issue in the process. Recently, visible-lightinduced reactions under photoredox catalysis have shown power in organic synthesis.^[13] To our surprise, the application of photoredox catalysis with the insertion of sulfur dioxide is still rare.^[14] We noticed that the oxidized forms of the photocatalysts are usually strong oxidants (e.g., $Ru(bpy)_{3^{3+}}$, $E_{1/2}^{III/II}$ = +1.29 V vs SCE, fac-Ir(ppy)₃, $E_{1/2}^{IV/III} = +0.77$ V vs SCE),^[13f] which are stronger than the radical cation DABCO '+ (DABCO, $E_{1/2}^{red} = +0.69$ V vs SCE).^[15] Therefore, we conceived that the merger of photoredox catalysis with the insertion of sulfur dioxide might give a solution for the transformation (Scheme 1, eq c). To our delight, the reaction of N-(2-(prop-1-en-2-yl)phenyl)benzamide 1a. $DABCO (SO_2)_2$ benzenediazonium and tetrafluoroborate 2a in the presence of fac-Ir(ppy)₃(2 mol %) in DCE under the irradiation of visible light provided the desired sulfonated benzo[d][1,3]oxazine **3a** in 18% yield (Table 1, entry 2). This promising result encouraged us for further explorations. After screening other solvents and photocatalysts, it was found that the yield was improved to 55% in the presence of fac-Ir(ppy)₃ in MeCN (Table 1, entries 3Table 1. Initial studies for the reaction of N-(2-(prop-1-en-2-yl)phenyl)benzamide 1a, DABCO•(SO₂)₂ and benzenediazonium tetrafluoroborate 2a^[a]

1a ($ \begin{array}{c} $	F ₄ catalyst solvent hn	O Ph N Ph 3a
Entry	Photocatalyst	Solvent	Yield $(\%)^b$
1	-	DCE	0
2	<i>fac</i> -Ir(ppy) ₃	DCE	18
3	<i>fac</i> -Ir(ppy) ₃	DMF	13
4	fac-Ir(ppy)3	MeCN	55
5	fac-Ir(ppy) ₃	1,4-dioxane	31
6	$Ru(bpy)_3(PF_6)_2$	MeCN	53
7	Eosin Y	MeCN	20
8	Ru(bpy) ₃ Cl ₂	MeCN	51
9 ^c	fac-Ir(ppy) ₃	1,4-dioxane/MeCN	64
$10^{c,d}$	fac-Ir(ppy)3	1,4-dioxane/MeCN	83
$11^{c,e}$	fac-Ir(ppy)3	1,4-dioxane/MeCN	63
$12^{c,f}$	<i>fac</i> -Ir(ppy) ₃	1,4-dioxane/MeCN	nr

Reaction conditions: *N*-(2-(prop-1-en-2yl)phenyl)benzamide **1a** (0.2 mmol), DABCO•(SO₂)₂ (0.2 mmol), benzenediazonium tetrafluoroborate 2a (0.3 mmol), photocatalyst (2 mol %), solvent (2.0 mL), under N₂ atmosphere, room temperature, irradiation with a 35 W compact fluorescent lamp (CFL), 12 h. ^b Isolated yield based on N-(2-(prop-1-en-2-yl)phenyl)benzamide 1a. c1,4dioxane/MeCN (v/v 3 : 1). ^d Benzenediazonium tetrafluoroborate 2a (0.4 mmol). ^e DABCO•(SO₂)₂ (0.16 mmol). ^fThe reaction was carried out in dark.

8). In the meantime, we found that benzenediazoniun. tetrafluoroborate 2a could react with acetonitrile and water, leading to a byproduct of N-phenylacetamide when MeCN was used as the solvent. Thus, we considered to add another solvent into the reaction system, with a hope to hamper the side reaction. To our delight, the yield was enhanced to 83% when 1,4dioxane and MeCN (v/v = 3:1) were used as the cosolvent in the presence of benzenediazonium tetrafluoroborate $\hat{2a}$ (2.0 equivalents) (Table 1, entries 9-11). No desired product was observed when the reaction was carried out in dark (Table 1, entry 12).

Entry	Photocatalyst	Solvent	Yield (
1	-	DCE	0
2	<i>fac</i> -Ir(ppy) ₃	DCE	18
3	<i>fac</i> -Ir(ppy) ₃	DMF	13
4	fac-Ir(ppy)3	MeCN	55
5	fac-Ir(ppy)3	1,4-dioxane	31
6	$Ru(bpy)_3(PF_6)_2$	MeCN	53
7	Eosin Y	MeCN	20
8	Ru(bpy) ₃ Cl ₂	MeCN	51
9 ^c	<i>fac</i> -Ir(ppy) ₃	1,4-dioxane/MeCN	64
$10^{c,d}$	fac-Ir(ppy)3	1,4-dioxane/MeCN	83
$11^{c,e}$	fac-Ir(ppy) ₃	1,4-dioxane/MeCN	63
$12^{c,f}$	<i>fac</i> -Ir(ppy) ₃	1,4-dioxane/MeCN	nr

Table 2. Scope investigation for the reaction of N-(2-vinylphenyl)amides1,DABCO•(SO2)2,andarenediazonium tetrafluoroborates $2^{a,b}$



^{*a*} Reaction conditions: *N*-(2-vinylphenyl)amide **1** (0.2 mmol), DABCO•(SO₂)₂ (0.2 mmol), arenediazonium tetrafluoroborate **2** (0.4 mmol), *fac*-Ir(ppy)₃ (2 mol %) in 1,4-dioxane/MeCN (v/v 3 : 1) (2.0 mL), N₂, rt, irradiation with a 35 W compact fluorescent lamp (CFL), 12 h. ^{*b*} Isolated yield based on *N*-(2-vinylphenyl)amide **1**.

establishing optimized After the reaction conditions, we subsequently explored the reaction scope of this three-component reaction of N-(2-DABCO• $(SO_2)_2$, vinylphenyl)amides 1. and arenediazonium tetrafluoroborates 2 (Table 2). All reactions took place smoothly to afford the sulfonated benzo[d][1,3] oxazines in moderate to good yields. Electronic effects showed minimal influence on the outcome of the transformation. Various functional groups including *tert*-butyl, methoxy, fluoro, bromo, chloro, ester, and even the nitro group^[16] were all compatible under the standard conditions. Furthermore, substrates bearing a hydrogen or phenyl group at the α -position of the styrene reacted with DABCO•(SO₂)₂ and benzenediazonium tetrafluoroborate 2a smoothly, providing the desired products 3t and 3u in 58% and 52% yields, respectively. We further examined the reactions of $DABCO (SO_2)_2$ and benzenediazonium 2a tetrafluoroborate by using N-(2styrylphenyl)benzamide and N-(2-(3-methylbut-2-en-2-yl)phenyl)benzamide as the substrates under the conditions. However, no desired products were obtained and the starting materials were recovered.

To further expand the synthetic potential of this methodology, a reaction of *N*-phenyl-2-(prop-1-en-2-

yl)benzamide **4**, DABCO•(SO₂)₂, and *p*-toluenediazonium tetrafluoroborate **2b** was carried out under the conditions as shown in Table 2 (Scheme 2). As expected, the corresponding *N*-(3-methyl-3-(tosylmethyl)isobenzofuran-1(3*H*)-

ylidene)aniline **5** was produced in 56% yield. Moreover, the (E)-configuration of the product was confirmed by COSY experiment.



(tosylmethyl)isobenzo-furan-1(3*H*)-ylidene)aniline **5**

To obtain more insights of this transformation, the model reaction in Table 1 was performed in presence 2,2,6,6-tetramethyl-1the of piperidinyloxy (TEMPO) under the optimized conditions (Scheme 3, eq a). The standard reaction was hampered, and no desired product of **3a** was detected with the recovery of the starting material **1a**. In order to trap the *in-situ* generated aryl radical and arylsulfonyl radical, 1,1-diphenylethylene was added to the above reaction (Scheme 3, eq b). As a result, ethene-1,1,2-trivltribenzene 6 and (2-(phenylsulfonyl)ethene-1,1-divl)dibenzene 10% were isolated in and 31% vields, respectively, accompanied with the formation of product 3a (33%). These results suggested that the reaction experienced a radical process, and both aryl radical and arylsulfonyl radical were existed in the transformation (Scheme 3).

Based on the above result, a plausible synthetic pathway is proposed in Scheme 4. Arenediazonium tetrafluoroborate would react with DABCO•(SO₂)₂ leading to arylsulfonyl radical **A** and tertiary amine (DABCO) radical cation intermediate **B**.^[11,12] Then arylsulfonyl radical **A** would undergo an addition to the double bond of *N*-(2-vinylphenyl)amide **1** to afford a radical intermediate **C**. We reasoned that radical intermediate **C** would be oxidized by the photocatalyst, producing cation intermediate **D**.



Scheme 3. Mechanistic investigation

Further deprotonation assisted by the released DABCO would promote the intramolecular nucleophilic attack of amide to cation, giving rise to the desired sulfonated benzo[d][1,3]oxazine **3**.



Scheme 4. A plausible mechanism for the synthesis of sulfonated benzo[d][1,3]oxazines

To further illustrate the reaction process, the free-energy changes for the oxidation of radical intermediate C to cation intermediate D by DABCO⁺⁺(path I) or Ir^{IV} (path II) at 298.15 K were calculated through DFT theoretical calculations. From the computational results for the two redox reactions in Table 3, we could conclude that the intermediate C could be oxidized by Ir^{IV} but not by DABCO radical cation B. These two free-energy changes showed that the redox potential of $\mathbf{C} - \mathbf{e} \rightarrow \mathbf{D}$ (E_{OX(D)}) was approximately computed to be 0.75 V, which was between that of DABCO + (DABCO, $E_{1/2}$ red = +0.69 V vs SCE) and Ir^{IV}/Ir^{III} (fac-Ir(ppy)₃, E_{1/2} $^{IV/III}$ = +0.77 V vs SCE). These results gave a strong support to the unique success of photoredox catalysis in this transformation.

Table 3. Free-energy change at 298.15 K for the oxidation of the intermediate C to D by DABCO '+ (path I) or Ir^{IV} (path II).

Reaction	Free Energy Change (eV)
$\mathbf{C} + \mathrm{DABCO}^{++} \leftrightarrow \mathbf{D} + \mathrm{DABCO}$	0.14
$\mathbf{C} + \mathrm{Ir}^{\mathrm{IV}} \leftrightarrow \mathbf{D} + \mathrm{Ir}^{\mathrm{III}}$	-0.11

In summary, we herein report a visible-lightpromoted photoredox approach for the synthesis of sulfonated benzo[d][1,3]oxazines through a threecomponent reaction of N-(2-vinylphenyl)amides, arenediazonium tetrafluoroborates and DABCO•(SO₂)₂ under mild conditions. This transformation takes place smoothly at room temperature under the irradiation of visible light, affording sulfonated benzo[d][1,3]oxazines in good yields. This radical process is efficient, enabled by merging photoredox catalysis and insertion of sulfur dioxide. The photoredox catalysis is found to assist the oxidation of the key radical intermediate, which is supported by density functional theory calculations.

Experimental Section

General experimental procedure for the reaction of *N*-(2-vinylphenyl)amides **1**, DABCO•(SO₂)₂, and arenediazonium tetrafluoroborates **2**: *N*-(2vinylphenyl)amide **1** (0.2 mmol) and arenediazonium tetrafluoroborate **2** (0.4 mmol) were combined with DABCO•(SO₂)₂ (0.2 mmol) and *fac*-Ir(ppy)₃ (2 mol %) in a tube. The tube was evacuated and backfilled with N₂ three times before co-solvent of 1,4-dioxane/MeCN (v/v 3 : 1, 2.0 mL) was added. The mixture was then placed around a visible light bulb (CLF, 25 W) with a distance of 10 centimeters, and was stirred under visible light irradiation for 12 hours at room temperature. After completion of reaction as indicated by TLC, the mixture was purified directly by flash column chromatography (EtOAc/*n*-hexane, I:4) to provide the desired product **3**.

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- [16] CCDC 1527243 contains the supplementary crystallographic data of compound 3i for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif/.

FULL PAPER

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