Heterocycles

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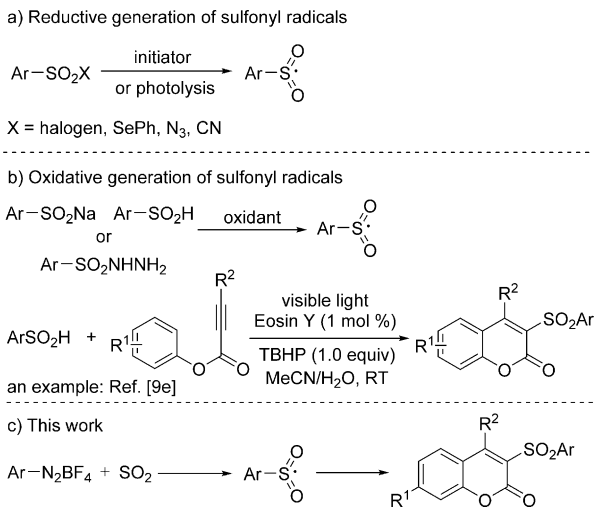
Generation of Sulfonyl Radicals from Aryldiazonium Tetrafluoroborates and Sulfur Dioxide: The Synthesis of 3-Sulfonated Coumarins

*Danqing Zheng, Jiyao Yu, and Jie Wu**

Abstract: *A catalyst-free approach for the generation of sulfonyl radicals from aryldiazonium tetrafluoroborates in the presence of DABCO·$(SO_2)_2$ is realized. The combination of aryldiazonium tetrafluoroborates, DABCO·$(SO_2)_2$, and aryl propiolates affords 3-sulfonated coumarins in good to excellent yields. This tandem reaction process involves radical addition, spirocyclization, and 1,2-migration of esters. Additionally, the in situ diazotization of a number of anilines allows the directional synthesis of desired 3-sulfonated coumarins in a one-pot, two-step process.*

In the past few decades, extensive and continuous effort has been devoted to the syntheses of sulfones because of their diverse range of significant applications in pharmaceuticals, agrochemicals, materials, and imperative synthetic intermediates.[1–4] Notably, the generation of a sulfonyl radical and its addition to unsaturated C–C bonds (such as alkenes and alkynes) contribute much to recent advances in the synthesis of sulfones. Various approaches for the generation of sulfonyl radicals have been extensively developed.[5,6] For instance, sulfonyl radicals can be produced from their corresponding sulfonyl halides, sulfonyl selenides, sulfonyl azides, and sulfonyl cyanides in the presence of radical initiators, light, or catalysts (Scheme 1 a).[6,7] The single-electron oxidation of sulfinates[8] or sulfinic acids[9] and the oxidative cleavage of sulfonyl hydrazides[10] also provide efficient routes for the formation of sulfonyl radicals (Scheme 1 b). The addition of these generated sulfonyl radicals to alkenes or alkynes usually leads to various sulfonated products by different radical trapping processes. For example, sulfinic acids could be used in the reaction of aryl propiolates to provide 3-sulfonated coumarins under visible light.[9e] Meanwhile, the incorporation of sulfur dioxide into small molecules has become an active research field, considering this strategy introduces the sulfonyl moiety from simple sources.[11–13] However, a dearth of methods for the generation of sulfonyl radicals through direct fixation of sulfur dioxide has been revealed.[11b,c] The limited examples focus on the introduction of sulfur dioxide into a Sandmeyer reaction, thus leading to sulfonyl chlorides pioneered by the work of Meerwein et al.[14] This process was largely at the mercy of chosen substrates and highly afflicted by the restricted scope. Moreover, sulfur dioxide was used in the form of toxic gas. In 2014, our group reported a radical process for the formation of N-aminosulfonamides by a metal-free coupling of aryldiazonium salts, the bench-stable sulfur dioxide surrogate DABCO·$(SO_2)_2$ and hydrazines.[13d] The nucleophile was restricted to hydrazines, and we proposed a mechanism that the hydrazine participated in the formation of sulfonyl radicals. Surprisingly, our recent efforts revealed that sulfonyl radicals could be generated under the treatment of aryldiazonium tetrafluoroborates with DABCO·$(SO_2)_2$ in the absence of hydrazines (Scheme 1 c). Herein, we report the formation of sulfonyl radicals from aryldiazonium tetrafluoroborates and DABCO·$(SO_2)_2$, and its application for the synthesis of 3-sulfonated coumarins.



Scheme 1. Methods for the generation of sulfonyl radicals. TBHP = *tert*-butylhydroperoxide.

The coumarin core is recognized as one of the most widely distributed scaffolds in natural products and pharmaceuticals. Its synthesis has attracted a considerable amount of attention.[15] Recently, the generation of coumarin derivatives by the cascade radical addition to aryl propiolates and cyclization has been achieved. Various functional groups such,as trifluoromethyl, difluoromethyl, phosphinoyl, arylsulfonyl, and acyl have been successfully introduced into the 3-position of coumarins.[16] Usually, radical addition and 6-*endo* cycliza-

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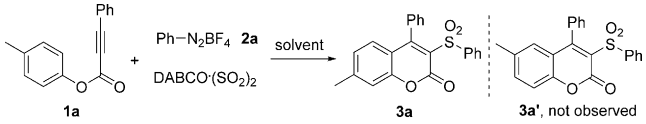
tion were involved to provide the 3-substituted coumarins. More recently, Qiu and co-workers reported a silver-promoted acylation of aryl propiolates with 2-oxoacetic acids for the synthesis of 3-acylcoumarins.[17] Interestingly, they found that the reaction proceeded through radical acylation, 5-*exo* cyclization, and ester migration, which was different from the 6-*endo* cyclization in previous reports. 3-Bromocoumarins and 3-acetonylcoumarins were also successfully obtained in their subsequent work, which was also thought to undergo the 5-*exo* cyclization and ester migration.[18]

Inspired by the copper-catalyzed sulfonyl radical formation developed by Meerwein[14] and our interest in the syntheisis of coumarin derivatives, we began our investigation with the reaction of the phenyl propiolate **1a**, phenyldiazonium tetrafluoroborate (**2a**), and DABCO·$(SO_2)_2$ in the presence of $Cu(OAc)_2$ (10 mol%) in MeCN at 80°C (see Table 1). A product was isolated in 8% yield, and the

Table 1: Initial studies for the reaction of the phenyl propiolate **1a**, DABCO·$(SO_2)_2$, and phenyldiazonium tetrafluoroborate (**2a**).[a]



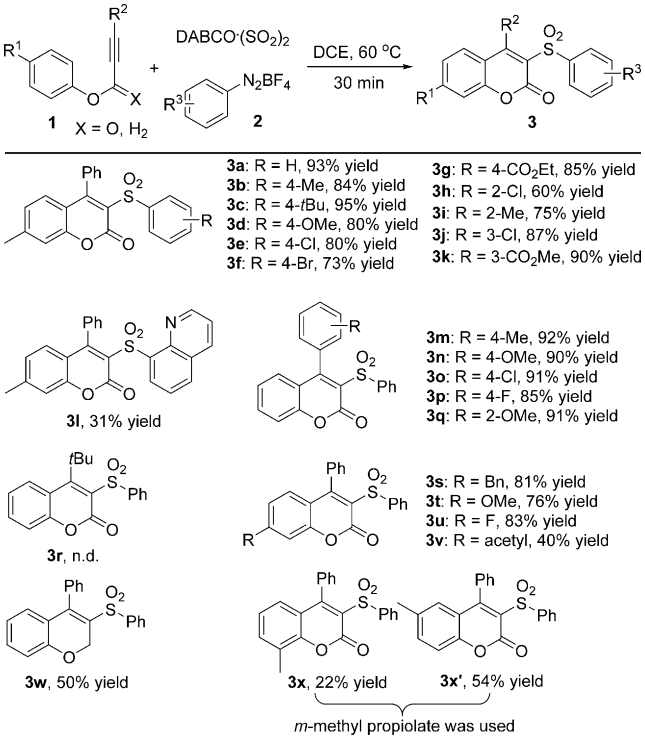
Entry	Solvent	*T* [°C]	DABCO·$(SO_2)_2$	Yield [%][b]
1	MeCN	80	1.2 equiv	10
2	toluene	80	1.2 equiv	61
3	DMF	80	1.2 equiv	42
4	DCE	80	1.2 equiv	80
5	1,4-dioxane	80	1.2 equiv	75
6	DCE	60	1.2 equiv	81
7	DCE	40	1.2 equiv	78
8	DCE	RT	1.2 equiv	50
9	DCE	60	0.8 equiv	59
10	DCE	60	1.6 equiv	85
11	DCE	60	2.0 equiv	93
12	DCE	60	2.5 equiv	92
13[c]	DCE	60	2.0 equiv	50

[a] Reaction conditions: the phenyl propiolate **1a** (0.2 mmol), DABCO·$(SO_2)_2$, phenyldiazonium tetrafluoroborate (**2a**; 0.24 mmol), solvent (1.5 mL), under Ar protection, 30 min. [b] Yield of isolated product based on **1a**. [c] Open to air. DABCO = 1,4-diazabicyclo[2.2.2]octane, DCE = 1,2-dichloroethane, DCM = dichloromethane, DMF = *N*,*N*-dimethylformamide.

a lower yield of 59% (entry 9). Higher yields were obtained as the amount of DABCO·$(SO_2)_2$ was increased, and the employment of 2.0 equivalents of DABCO·$(SO_2)_2$ led to an improved efficiency (entries 10–12). The reaction usually went to completion in 30 minutes. Only 50% yield of **3a** was generated when the reaction took place open to air (entry 13).

With the optimized reaction conditions in hand, the scope of the sulfonated annulation of phenyl propiolates **1** with DABCO·$(SO_2)_2$ and the phenyldiazonium tetrafluoroborates **2** was next investigated. The results are summarized in Table 2. The reaction took place smoothly by using various

Table 2: Investigation of the scope for the reaction of aryl propiolates (**1**), DABCO·$(SO_2)_2$, and aryldiazonium tetrafluoroborates (**2**).[a,b]

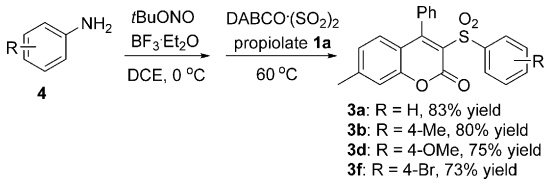


[a] Reaction conditions: aryl propiolate **1** (0.2 mmol), DABCO·$(SO_2)_2$ (0.4 mmol), phenyldiazonium tetrafluoroborate **2** (0.24 mmol), DCE (1.5 mL), under Ar protection, 60°C, 30 min. [b] Yield of isolated product based on **1**.

structural identification suggested that this product was **3a** rather than **3a″**. A control experiment was carried out subsequently, and revealed that the copper catalyst was not necessary for this transformation. A similar yield (10%) was obtained by the treatment of **1a**, **2a**, and DABCO·$(SO_2)_2$ in MeCN at 80°C (entry 1). To our delight, the yield was increased significantly to 61% when toluene was used as solvent (entry 2). Further screening of solvents suggested that DCE was the best fit, increasing the yield of the desired product **3a** to 80% (entry 4). A similar result was obtained when the reaction was performed at 60°C (entry 6). This transformation took place readily at room temperature as well, whereas the yield decreased to 50% (entry 8). Reducing the amount of DABCO·$(SO_2)_2$ to 0.8 equivalents provided aryldiazonium tetrafluoroborates, thus leading to the desired 3-sulfonated coumarins in good yields (**3a–l**). Electronic effects on the aromatic ring of aryldiazonium tetrafluoroborates showed a minimal influence and both electron-withdrawing and electron-donating groups were compatible in this transformation. Moreover, *ortho*-substituted phenyldiazonium tetrafluoroborates were also tolerated, thus generating the desired products **3h** and **3i**, although lower yields were obtained. A heterocyclic aryldiazonium tetrafluoroborate was also employed, thus engendering the sulfonated annulation product **3l** in 31% yield. Reactions of the phenyl propiolates **1** having aryl substituents appended to the triple bond were all efficient, thus leading to the corresponding products **3m–q** in similarly high yields. Surprisingly, alkyl groups such as *tert*-

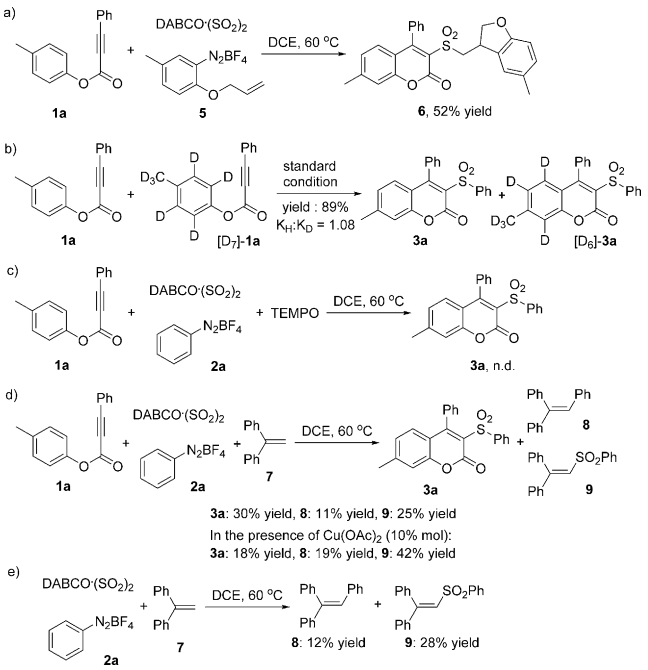
butyl (R^2) led to poor results and no desired product was observed. Reactions of the phenyl propiolates **1** bearing benzyl, methoxyl, and fluoro substituents in the *para*-position of the phenoxy ring with DABCO·$(SO_2)_2$ and **2a** occurred efficiently, thus resulting in the desired products **3s**–**u** in good yields,[19] while a lower yield of 40% was obtained for the substrate with much stronger electron-withdrawing group (acetyl). Pleasingly, the unactivated alkyne (3-phenoxyprop-1-ynyl)benzene **1w** could also be utilized in this transformation, and 45% yield of product **3w** was provided. When *m*-tolyl 3-phenylpropiolate **1x** was employed as the substrate, a mixture of two regioselective products, **3x** and **3x″**, were obtained in 22 and 54% yields, respectively.

Considering the stability problem of aryldiazonium tetrafluoroborates, we next explored the possibility of the utilization of aromatic amines as starting materials by the in situ diazotization process. To our delight, this transformation worked smoothly in a one-pot, two-step format, which afforded the corresponding 3-sulfonated coumarins **3** in good yields. Several anilines (**4**) were applied and the results are presented in Scheme 2.



Scheme 2. Synthesis of 3-sulfonated coumarins by using anilines as the starting materials.

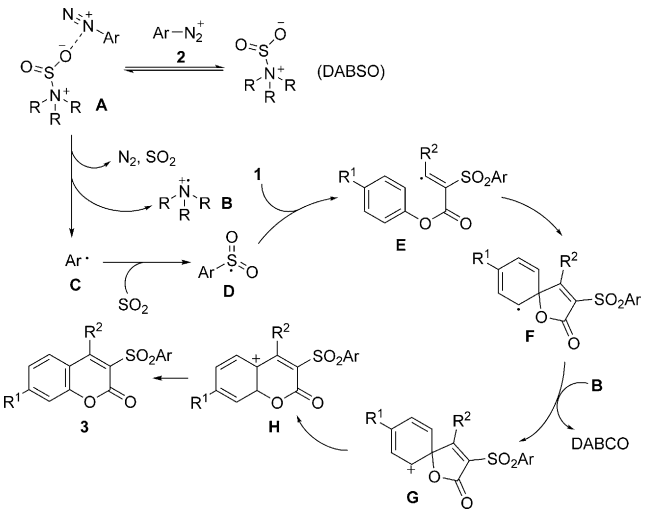
To gain more insight into the mechanism of this annulation, we initially used 2-(allyloxy)-5-methylphenyldiazonium tetrafluoroborate (**5**) in this transformation. Only the cyclized product **6** was produced in 52% yield, whereas the normal product could not be detected (Scheme 3a). This result suggested the involvement of an aryl radical in this process. The kinetic isotope effect was next investigated by a competitive experiment involving equimolar amounts of **1a** and [D_7]-**1a**, and a K_H/K_D of 1.07 was observed [Scheme 3b). This observation indicated that the cleavage of C–H bond on the phenoxy ring was not the rate-determining step. This transformation was terminated when 2.0 equivalents of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) were added to the standard reaction as the additive, thus further proving that the reaction experienced a radical process (Scheme 3c). The yield of **3a** plummeted to 30%, when a milder radical scavenger of 1,1-diphenylethylene (**7**) was added to the reaction system. Ethene-1,1,2-triyltribenzene (**8**) and (2-(phenylsulfonyl)-ethene-1,1-diyl)dibenzene (**9**) were observed in 11 and 25% yields, respectively, thus indicating the existence of both aryl radical and sulfonyl radical in this reaction. To our surprise, the yield of **9** was increased to 42% when this radical trapping experiment was carried out in the presence of 10 mol% of $Cu(OAc)_2$ (Scheme 3d). It seemed that the copper catalyst might benefit from the combination of the sulfonyl radical and **7**. The treatment of DABCO·$(SO_2)_2$, **2a**, and **7** in DCE



Scheme 3. Investigation of the mechanism.

could also lead to the generation of compounds **8** and **9** in 12 and 28% yields, respectively (Scheme 3e). This result proved that the aryl radical and sulfonyl radical could be produced directly from the combination of DABCO·$(SO_2)_2$ and phenyldiazonium tetrafluoroborate.

On the basis of the above experimental observations and previous reports, a plausible mechanism was proposed (Scheme 4). We reasoned that the arydiazonium cation **2** would combine with DABCO·$(SO_2)_2$ to generate the complex **A** through electrostatic interaction.[13d] Then the radical cation intermediate **B**, SO_2, and aryl radical **C** could be produced by the homolytic cleavage of the N–S bond[20] and a single-electron transfer. The combination of **C** and sulfur dioxide would provide the sulfonyl radical **D**, which would



Scheme 4. Proposed mechanism.

attack the triple bond of **1** to afford the intermediate **E**. A subsequent spirocyclization would create the intermediate **F**, which could be oxidized by the radical cation **B** to afford the intermediate **G**.[21] The intermediate **H** was then produced by a 1,2-ester migration and further aromatization would lead to the desired product **3**.

In conclusion, we have demonstrated a catalyst-free approach for the generation of sulfonyl radicals from aryldiazonium tetrafluoroborates in the presence of DABCO·$(SO_2)_2$. The combination of aryldiazonium tetrafluoroborates and DABCO·$(SO_2)_2$ with aryl propiolates affords 3-sulfonated coumarins in good to excellent yields. This three-component tandem reaction process occurs under catalyst-free and additive-free conditions. A plausible mechanism is proposed involving radical addition, spirocyclization and 1,2-migration of esters. Additionally, anilines can be utilized as the replacement of aryldiazonium tetrafluoroborates through an in situ diazotization, thus giving rise to the desired 3-sulfonated coumarins in a one-pot, two-step process. This new discovery will broaden the chemistry of sulfonyl radicals and further applications are anticipated.

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Keywords: diazo compounds · heterocycles · radicals · sulfur · synthetic methods

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