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Multicomponent Reactions

Generation of β-Halo Vinylsulfones through a Multicomponent Reaction with Insertion of Sulfur Dioxide

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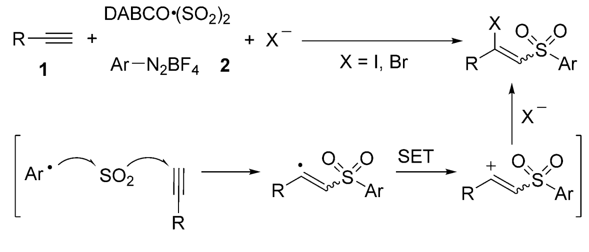
Abstract: A four-component reaction of terminal alkynes, aryldiazonium tetrafluoroborates, sulfur dioxide surrogate of DABCO·$(SO_2)_2$, and potassium halide in the presence of copper(I) chloride (10 mol %) gives rise to β-halo vinylsulfones with good stereoselectivity. The vicinal difunctionalization of alkynes through sulfonylation and halogenation with the insertion of sulfur dioxide works efficiently. A plausible mechanism is proposed, which includes a radical process.

Due to the importance of sulfones in organic synthesis and medicinal chemistry,[1,2] the introduction of a sulfonyl unit into small molecules has attracted much attention. Among the methods for the incorporation of a sulfonyl group, recent efforts have been aimed towards radical reactions from the point of view of reactivity and selectivity. Usually, sulfonyl halides/selenides/azides/cyanides/hydrazides, sulfinates, and sulfinic acids were utilized in the sulfonylative process through reductive or oxidative approaches.[3,4] Recently, using sulfur dioxide as the source for the introduction of the sulfonyl unit into small molecules has been employed as a replacement.[5] For example, compared to the conventional approaches by using sulfonyl compounds for the synthesis of 3-sulfonated coumarins,[6] the strategy through insertion of sulfur dioxide in a radical process for introducing the sulfonyl group was successfully established under more mild condition.[7]

As part of our interests in sulfones, we focused on the exploration of β-halo vinylsulfones due to their versatile reactivity in organic synthesis. It is well known that vinylsulfones have been widely used in organic transformations as well as in pharmaceuticals.[8,9] The elaboration of β-halo vinylsulfones through coupling reactions would provide diverse vinylsulfones. The typical methods for the generation of β-halo vinylsulfones include Knoevenagel-type condensation and Horner–Wadsworth–Emmons reactions.[10] Recent efforts have focused on the sulfonylation of alkynes with sulfonyl compounds or cross-coupling reactions of sulfonyl compounds with alkenes.[11,12] For example, (*Z*)-β-halo vinylsulfones could be obtained through the reaction of alkynes with arylsulfonyl chlorides or arylsulfonohydrazides.[12] As mentioned above, the insertion of sulfur dioxide would be promising and attractive for the incorporation of a sulfonyl group. Therefore, we initiated a program for the generation of β-halo vinylsulfones by using sulfur dioxide as the source.

In the past few years, methods for the synthesis of sulfonyl compounds through the insertion of sulfur dioxide have developed rapidly,[13,14] especially after the sulfur dioxide surrogate of DABCO·$(SO_2)_2$[13a] was used as the source of sulfur dioxide. We have also been involved in this field, with the expectation to provide efficient approaches for the access to sulfonyl-containing pharmaceuticals. Recently, we described an efficient process for the generation of arylsulfonyl radicals using a reaction of aryldiazonium salts with DABCO·$(SO_2)_2$ under mild conditions.[7] During the reaction process, the presence of DABCO was also crucial for the successful transformation. The $DABCO^{+\bullet}$ radical cation generated in situ would act as a carrier for a single electron transfer (SET). Prompted by this result and the importance of β-halo vinylsulfones, we conceived that β-halo vinylsulfones would be formed through a four-component reaction of terminal alkynes, aryldiazonium tetrafluoroborates, sulfur dioxide surrogate of DABCO·$(SO_2)_2$, and metal hailde. The proposed synthetic route is presented in Scheme 1. We envisioned that a radical process would be involved with the insertion of sulfur dioxide. A tandem radical addition of aryl radical to sulfur dioxide and alkyne would provide an alkenyl radical. In the presence of $DABCO^{+\bullet}$ radical cation (generated in situ), an alkenyl cation would be formed, which would be subsequently trapped by halide to produce β-halo vinylsulfones. The stereoselectivity of the final outcome would depend on the steric hindrance during the transformation.



Scheme 1. A proposed synthetic route to β-halo vinylsulfones through a four-component reaction including the insertion of sulfur dioxide.

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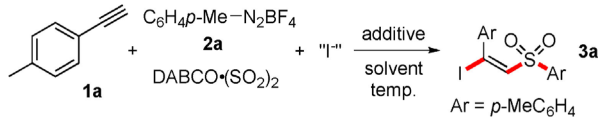
We thus started to explore the practicability of the proposed route in Scheme 1. Initially, a reaction of 1-ethynyl-4-methylbenzene **1 a**, 4-methylphenyldiazonium tetrafluoroborate **2 a**, DABCO·(SO$_2$)$_2$, and sodium iodide in MeCN at room temperature was investigated (Table 1, entry 1). However, we did not observe the formation of the desired product. To our delight, the corresponding product **3 a** was obtained in 17% yield when potassium iodide was used instead of sodium iodide (Table 1, entry 2). We postulated that the presence of a copper salt would facilitate the single electron transfer during the reaction process. Thus, several copper salts were examined as additives. Gratifyingly, the yield was increased to 24% in the presence of copper(I) chloride (10 mol%) (Table 1, entry 4). Further screening of the temperature revealed that the reaction worked efficiently at 80 °C, leading to the desired β-iodo vinylsulfone **3 a** in 62% yield (Table 1, entry 8), whereas compound **3 a** was afforded in 32% yield in the absence of copper(I) chloride (Table 1, entry 10). Reactions in other solvents were explored subsequently (Table 1, entries 11–14). However, the results were inferior. Interestingly, β-iodo vinylsulfone **3 a** was obtained in the (*E*)-configuration exclusively.

Table 1. Initial studies for the reaction of 1-ethynyl-4-methylbenzene **1 a**, 4-methylphenyldiazonium tetrafluoroborate **2 a**, DABCO·(SO$_2$)$_2$, and metal iodide.[a]

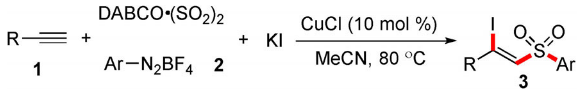


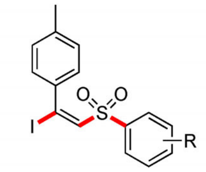
Entry	"I−"	Additive	Solvent	*T* [°C]	Yield [%][b]
1	NaI	–	MeCN	25	0
2	KI	–	MeCN	25	17
3	KI	CuI	MeCN	25	20
4	KI	CuCl	MeCN	25	24
5	KI	CuOAc	MeCN	25	5
6	KI	CuCl	MeCN	45	40
7	KI	CuCl	MeCN	60	47
8	KI	CuCl	MeCN	80	62
9	KI	CuCl	MeCN	90	59
10	KI	–	MeCN	80	32
11	KI	CuCl	DCE	80	trace
12	KI	CuCl	1,4-dioxane	80	trace
13	KI	CuCl	DMSO	80	0
14	KI	CuCl	THF	80	trace

[a] Reaction conditions: 1-ethynyl-4-methylbenzene **1 a** (0.2 mmol), DABCO·(SO$_2$)$_2$ (0.16 mmol, 0.8 equiv), 4-methylphenyldiazonium tetrafluoroborate **2 a** (0.4 mmol, 2.0 equiv), iodide (0.4 mmol, 2.0 equiv), solvent (2.5 mL), under Ar protection. [b] Isolated yield based on 1-ethynyl-4-methylbenzene **1 a**.

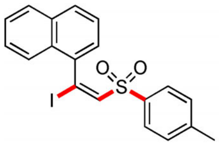
We next explored the scope of this four-component reaction of terminal alkynes, aryldiazonium tetrafluoroborates, DABCO·(SO$_2$)$_2$, and potassium iodide catalyzed by copper(I) chloride under the above optimized conditions (Table 2). From Table 2, it seemed that all reactions worked smoothly to provide the corresponding (*E*)-β-iodo vinylsulfones in moderate to good yields. Various aryldiazonium tetrafluoroborates were good partners in the reaction of 1-ethynyl-4-methylbenzene **1 a**, DABCO·(SO$_2$)$_2$, and potassium iodide. Different functional groups including methyl, methoxy, chloro, bromo, fluoro, and ester were all tolerated under the standard conditions. The structure of product (*E*)-**3 b** was illustrated after X-ray crystallography analysis.[15] Various alkynes were examined subsequently, and the desired products were obtained as expected. It is noteworthy that 2-ethynylthiophene is a good reactant as well, affording the corresponding product **3 k** in 48% yield. However, alkyl-substituted alkynes were not effective during the transformations. This could be rationalized by the lower stability of the alkyl-substituted alkenyl radical intermediate than the corresponding aryl-substituted alkenyl radical.

Table 2. Scope investigation for the reaction of alkynes **1**, aryldiazonium tetrafluoroborates **2**, DABCO·(SO$_2$)$_2$, and potassium iodide.[a]

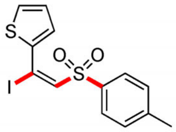




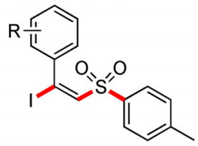
3a: R = 4-Me, 62% yield
3b: R = 4-OMe, 65% yield
3c: R = 4-^{t}Bu, 45% yield
3d: R = H, 55% yield
3e: R = 4-F, 60% yield
3f: R = 4-Cl, 45% yield
3g: R = 4-Br, 55% yield
3h: R = 4-CO$_2$Et, 45% yield
3i: R = 3-Me, 40% yield



3j, 41% yield



3k, 48% yield

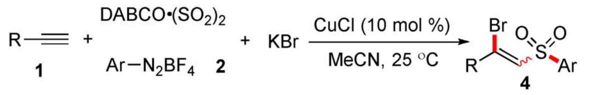


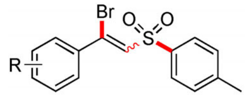
3l: R = 4-OMe, 76% yield
3m: R = 4-Ph, 58% yield
3n: R = H, 60% yield
3o: R = 4-F, 56% yield
3p: R = 4-Cl, 51% yield
3q: R = 4-Br, 58% yield
3r: R = 3-Me, 26% yield
3s: R = 2-Me, 30% yield

[a] Isolated yield based on alkyne **1**.

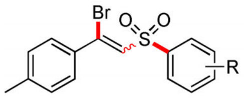
We further evaluated the four-component reaction of terminal alkynes using potassium bromide in an effort to obtain β-bromo vinylsulfones. The results are shown in Table 3. Although the preparation of β-bromo vinylsulfones **4** was accomplished under the copper(I) chloride-catalyzed conditions, a mixture of stereoisomers was provided. As we mentioned above, the stereoselectivity of the final outcome would depend on the steric hindrance during the combination of an alkenyl cation with halide. Thus, it is reasonable that (*E*)-β-iodo vinylsulfones were produced exclusively, whereas β-bromo vinylsulfones were formed as a mixture of stereoisomers. During the transformations, (*E*)-β-bromo vinylsulfones were obtained as the major products. The structure of compound (*E*)-**4 a** was confirmed by X-ray crystallography analysis as well.[15]

Table 3. Scope investigation for the reaction of alkynes **1**, aryldiazonium tetrafluoroborates **2**, DABCO·$(SO_2)_2$, and potassium bromide.[a]





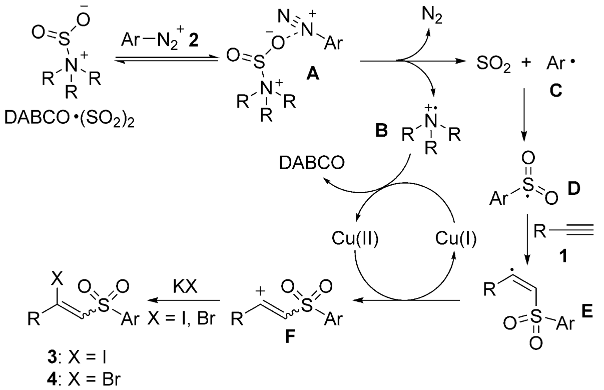
(*E*)-**4a**, R = 4-Me, 41% yield
(*Z*)-**4a**, R = 4-Me, 19% yield
(*E*)-**4b**, R = 3-Me, 27% yield
(*Z*)-**4b**, R = 3-Me, 13% yield
(*E*)-**4c**, R = 2-Me, 40% yield
(*Z*)-**4c**, R = 2-Me, 7% yield
(*E*)-**4d**, R = 4-OMe, 61% yield
(*Z*)-**4d**, R = 4-OMe, 14% yield
(*E*)-**4e**, R = 4-Ph, 40% yield
(*Z*)-**4e**, R = 4-Ph, 8% yield
(*E*)-**4f**, R = H, 35% yield
(*Z*)-**4f**, R = H, 9% yield
(*E*)-**4g**, R = 4-F, 41% yield
(*Z*)-**4g**, R = 4-F, 9% yield
(*E*)-**4h**, R = 4-Br, 32% yield
(*Z*)-**4h**, R = 4-Br, 15% yield



(*E*)-**4i**, R = 4-F, 37% yield
(*Z*)-**4i**, R = 4-F, 22% yield
(*E*)-**4j**, R = 4-Br, 30% yield
(*Z*)-**4j**, R = 4-Br, 6% yield
(*E*)-**4k**, R = 4-CO_2Et, 32% yield
(*Z*)-**4k**, R = 4-CO_2Et, trace

[a] Isolated yield based on alkyne **1**.

Based on our previous report,[7] we envisioned that this four-component reaction might proceed through a radical process. As expected, the model reaction in Table 1 could not take place when 2.0 equiv of 2, 2, 6, 6-tetramethyl-1-piperidinyloxy (TEMPO) was added. Therefore, a plausible mechanism is proposed as shown in Scheme 2. The combination of aryldiazonium cation with DABCO·$(SO_2)_2$ would provide sulfur dioxide, nitrogen, aryl radical, and tertiary amine radical cation **B** through a complex **A**.[7] Then, the addition of aryl radical to sulfur dioxide would occur to produce arylsulfonyl radical **D**, which would attack alkyne **1** leading to the more stable (*Z*)-alkenyl radical **E**.[16] Subsequently, copper (I) chloride would promote the oxidation of alkenyl radical **E** to alkenyl cation **F** by a single electron transfer. Nucleophilic attack of halide to alkenyl cation **F** preferably from the less-hindered side would give rise to the corresponding β-halo vinylsulfone **3** or **4**.



Scheme 2. Investigation of the mechanism.

In summary, an efficient route for the synthesis of β-halo vinylsulfones through a four-component reaction of terminal alkynes, aryldiazonium tetrafluoroborates, sulfur dioxide surrogate of DABCO·$(SO_2)_2$, and potassium halide in the presence of copper(I) chloride (10 mol %) has been developed. The vicinal difunctionalization of alkynes through sulfonylation and halogenation with the insertion of sulfur dioxide works efficiently. The desired β-halo vinylsulfones are generated with good stereoselectivity. (*E*)-β-iodo vinylsulfones are produced exclusively, whereas (*E*)-β-bromo vinylsulfones are obtained as the major products. A plausible mechanism is also proposed, which would undergo a radical process.

Experimental Section

General experimental procedure for the four-component reaction: Potassium halide (iodide or bromide; 2.0 equiv, 66.4 mg), DABCO·$(SO_2)_2$ (0.8 equiv, 38.4 mg) and copper(I) chloride (10 mol %) were mixed with aryldiazonium tetrafluoroborate **2** (2.0 equiv, 0.4 mmol) in a tube and dissolved by MeCN (2.5 mL) under Ar_2 atmosphere (the flask was evacuated and backfilled with Ar_2 three times before MeCN was added). Then alkyne **1** (0.2 mmol) was added to the mixture. The mixture was stirred at 80 °C (potassium iodide) or 25 °C (potassium bromide). After completion of the reaction as indicated by TLC, the mixture was purified directly by flash column chromatography (EtOAc/*n*-hexane, 1:8) to provide the desired product **3** or **4**.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alkyne · aryldiazonium tetrafluoroborate · potassium halide · sulfur dioxide · β-halo vinylsulfone

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[15] CCDC 1534886 [(*E*)-**3b**] and 1540861 [(*E*)-**4a**] contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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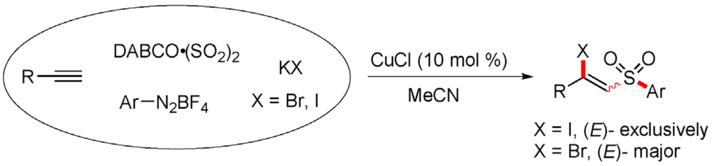

A four-component reaction of terminal alkynes, aryldiazonium tetrafluoroborates, sulfur dioxide surrogate of DABCO·$(SO_2)_2$, and potassium halide in the presence of copper(I) chloride (10 mol%) gives rise to β-halo vinylsulfones with good stereoselectivity. The vicinal difunctionalization of alkynes through sulfonylation and halogenation with the insertion of sulfur dioxide works efficiently.

Multicomponent Reactions

Y. Xiang, Y. Kuang, J. Wu**

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Generation of β-Halo Vinylsulfones through a Multicomponent Reaction with Insertion of Sulfur Dioxide