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Communication

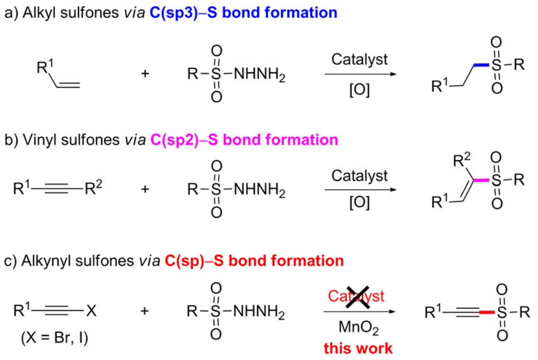
Sulfonylation

MnO$_2$-Promoted Oxidative Radical Sulfonylation of Haloalkynes with Sulfonyl Hydrazides: C(sp)–S Bond Formation towards Alkynyl Sulfones

Pengquan Chen, Chuanle Zhu,* Rui Zhu, Wanqing Wu, and Huanfeng Jiang*[a]

Abstract: A catalyst-free oxidative radical sulfonylation of haloalkynes with sulfonyl hydrazides is reported. It represents an example of C(sp)–S bond formation using sulfonyl hydrazides as sulfonyl radical sources. Various alkynyl sulfones were synthesized in moderate to good yields. Having MnO$_2$ as the oxidant is very critical for this transformation. Remarkably, the self-coupling reaction of haloalkynes through C(sp)–C(sp) bond formation is significantly inhibited under the standard reaction conditions.

Organosulfones are a class of highly valuable compounds and have emerged as privileged building blocks in the area of pharmaceutical and agrochemical chemistry because of their impressive biological activities such as anti-HIV, anticancer, and antibacterial.[1] Owing to their readily removable ability via various desulfonylation methods, they also serve as significant synthetic intermediates in numerous natural-product total syntheses.[2] Therefore, the development of efficient and practical methods for the synthesis of organosulfones has received considerable attention over the past decades.[3] Generally, the generation of a sulfonyl radical and its addition to unsaturated carbon–carbon bonds, such as C–C double bonds and C–C triple bonds, represents one of the most popular and promising methods to construct sulfone derivatives. Among various sulfonyl radical sources such as sulfonyl halides,[4] arylsulfinic acids,[5] arylsulfinic azides,[6] arylsulfinic cyanides,[7] sodium sulfinates[8] and SO$_2$,[9] sulfonyl hydrazides, which are non-corrosive, do not have unpleasant odor, are compatible with water, and provide readily available synthons, have emerged as a friendly and powerful source of sulfonyl radicals under oxidative conditions.[10] Generally, the reactions of these sulfonyl radicals derived from sulfonyl hydrazides with C–C double bonds afforded alkyl sulfone compounds via C(sp^3)–S bond formation (Scheme 1 a),[11] while their reactions with C–C triple bonds delivered the corresponding vinyl sulfone derivatives smoothly through C(sp^2)–S bond formation (Scheme 1 b).[12] Typically, these two types of transformations involved transition metal catalysts, such as Fe and Cu complexes or iodide catalysts, to ensure reactivity and selectivity, and have found broad applications in the field of synthetic and medicinal chemistry. However, the reaction of sulfonyl radicals derived from sulfonyl hydrazides, which provides alkynyl sulfones as products via C(sp)–S bond formation has not been reported yet, despite the fact that alkynyl sulfones are significant motifs in the field of synthetic and medicinal chemistry.[13]



Scheme 1. Oxidative radical sulfonylation of unsaturated bonds with sulfonyl hydrazides.

Owing to the sp hybridization of the C–C triple bonds and the connected halogen atoms, haloalkynes have been served as practical and versatile building blocks and found broad applications in the area of synthetic and material chemistry.[14] As our recent interest for the synthesis of sulfone derivatives,[15] as well as our continuous effort on exploiting the potential reactivities and synthetic applications of haloalkynes,[14] herein, we report a catalyst-free oxidative radical sulfonylation of haloalkynes with sulfonyl hydrazides. To the best of our knowledge, it represents the first example for C(sp)–S bond formation with sulfonyl radicals derived from sulfonyl hydrazides. Using MnO$_2$ as the oxidant is very critical for this transformation, delivering various alkynyl sulfones in moderate to good yields. Additionally, the self-coupling products of haloalkynes through C(sp)–C(sp) bond formation were significantly inhibited.[16]

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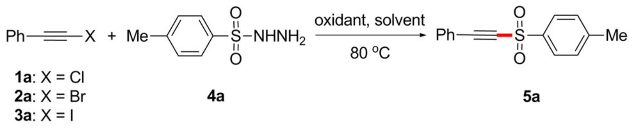
At the outset of our studies, we investigated this catalyst-free oxidative radical sulfonylation of haloalkynes with bromoalkyne **2a** and sulfonyl hydrazide **4a** as the starting materials in DMA (dimethylacetamide) at 90 °C, using TBHP (*tert*-butyl hydroperoxide) as an oxidant, which is known to promote the generation of sulfonyl radicals from sulfonyl hydrazides (Table 1, entry 1).[10] Unfortunately, none of the desired product **5a** was detected by GC-MS or NMR analysis. As expected, no reaction happened in the absence of oxidants (Table 1, entry 2). Next, diverse oxidants such as BQ (benzoquinone), DDQ (2,3-dicyano-5,6-dichlorobenzoquinone), TEMPO (2,2,6,6-tetramethylpiperidine N-oxide), DTBP (di-*tert*-butyl peroxide), I_2, 30% aq. H_2O_2, O_2, $K_2S_2O_4$, and MnO_2 were investigated (Table 1, entries 3–11). To our delight, MnO_2 gave the desired product **5a** in 79% isolated yield. It is worth noting that the organic solvent was also very critical for this C(sp)–S bond formation reaction. The use of other polar solvents such as DMF, DMSO, NMP (*N*-methyl pyrrolidone), MeCN, and THF and nonpolar solvents, such as 1,4-dioxane, DCE (1,2-dichloroethane) or toluene, were ineffective in this reaction, and led to a significantly lower yield of **5a** (Table 1, entries 12–19). By reducing the loading of MnO_2 to 3 equivalents, the yield of **5a** decreased to 63% (Table 1, entry 20). Furthermore, when bromoalkyne **2a** was replaced with chloroalkyne **1a**, no desired product was observed (Table 1, entry 21). Interestingly, the isolated yield of **5a** was further enhanced to 80% with iodoalkyne **3a** as the reactant (Table 1, entry 22).

Table 1. Reaction optimizations.[a]



Entry	Haloalkynes	Oxidants	Solvent	Yield [%][b]
1	**2a**	TBHP	DMA	n.d.
2	**2a**	–	DMA	n.d.
3	**2a**	BQ	DMA	n.d.
4	**2a**	DDQ	DMA	n.d.
5	**2a**	TEMPO	DMA	n.d.
6	**2a**	DTBP	DMA	n.d.
7	**2a**	I_2	DMA	n.d.
8[c]	**2a**	H_2O_2	DMA	n.d.
9	**2a**	O_2	DMA	n.d.
10	**2a**	$K_2S_2O_4$	DMA	8
11	**2a**	MnO_2	DMA	80 (79)
12	**2a**	MnO_2	DMF	39
13	**2a**	MnO_2	DMSO	n.d.
14	**2a**	MnO_2	NMP	n.d.
15	**2a**	MnO_2	MeCN	6
16	**2a**	MnO_2	THF	20
17	**2a**	MnO_2	1,4-dioxane	8
18	**2a**	MnO_2	DCE	n.d.
19	**2a**	MnO_2	toluene	n.d
20[d]	**2a**	MnO_2	DMA	63
21	**1a**	MnO_2	DMA	0
22	**3a**	MnO_2	DMA	82 (80)

[a] A mixture of haloalkyne (0.3 mmol, 1 equiv), **4a** (0.45 mmol, 1.5 equiv), oxidant (4 equiv) and solvent (2 mL) was stirred at 80 °C for 24 h. [b] The yields were determined by GC-MS with dodecane as an internal standard. The numbers in the parentheses show the isolated yield. [c] 33% aq. H_2O_2. [d] MnO_2 (3 equiv). n.d. = not detected.

With the optimized conditions in hand, we next turned our attention to the generality of this catalyst-free oxidative radical sulfonylation of haloalkynes **3** with sulfonyl hydrazides **4** (Scheme 2). First, different haloalkynes **3** were investigated with sulfonyl hydrazide **4a** as the reaction partner. Both electron-donating groups (methyl, propyl, *tert*-butyl and methoxyl) and electron-withdrawing groups (fluoro and chloro) on the phenyl ring of haloalkynes **3** were tolerated under the standard reaction conditions, delivering the corresponding alkynyl sulfones **5a**–**5j** in good yields. 2-Ethynylthiophene-derived haloalkyne was also applicable to this oxidative reaction system and afforded **5k** in 42% yield. Significantly, ethynylcyclopropane-derived haloalkyne was also a good substrate, providing alkynyl sulfone **5l** in 58% yield. Furthermore, the substrate scope was extended to different substituted sulfonyl hydrazides **4** with haloalkyne **3a** as the reaction partner. Gratifyingly, sulfonyl hydrazides with methyl, chloro or bromo groups on the phenyl ring could deliver the corresponding alkynyl sulfones smoothly (**5m**–**5o**).

In 2010, we reported that the self-coupling reaction of iodoalkynes could provide the corresponding diynes in high yields.[16] To cast some light on the mechanism details of this cross-coupling reaction, some control experiments were performed. First, the competition reactions between self-coupling of iodoalkyne **3a** and cross-coupling of iodoalkyne **3a** and sulfonyl hydrazide **4a** were conducted at different reaction temperatures. The reaction temperature could significantly influence the yields of the products (Figure 1). It is worth noting that the yields of self-coupling product **6a** were < 1% in all of these cases, while performing the reaction at 80 °C gave the

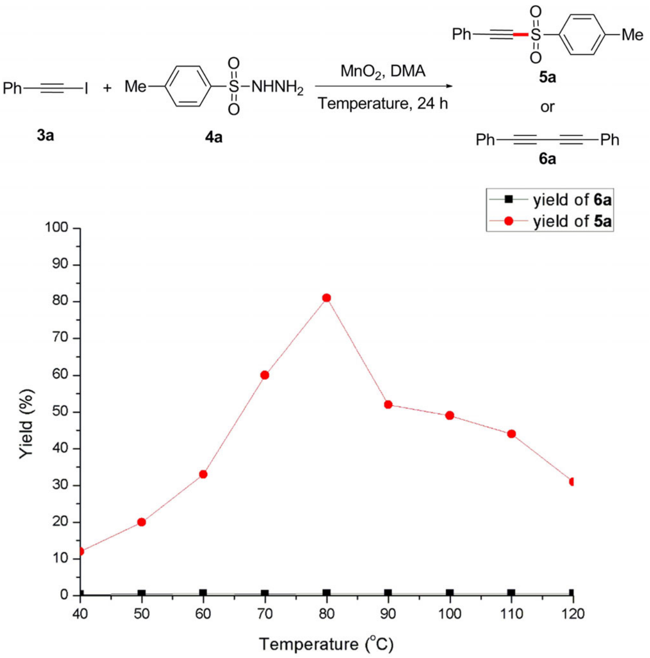
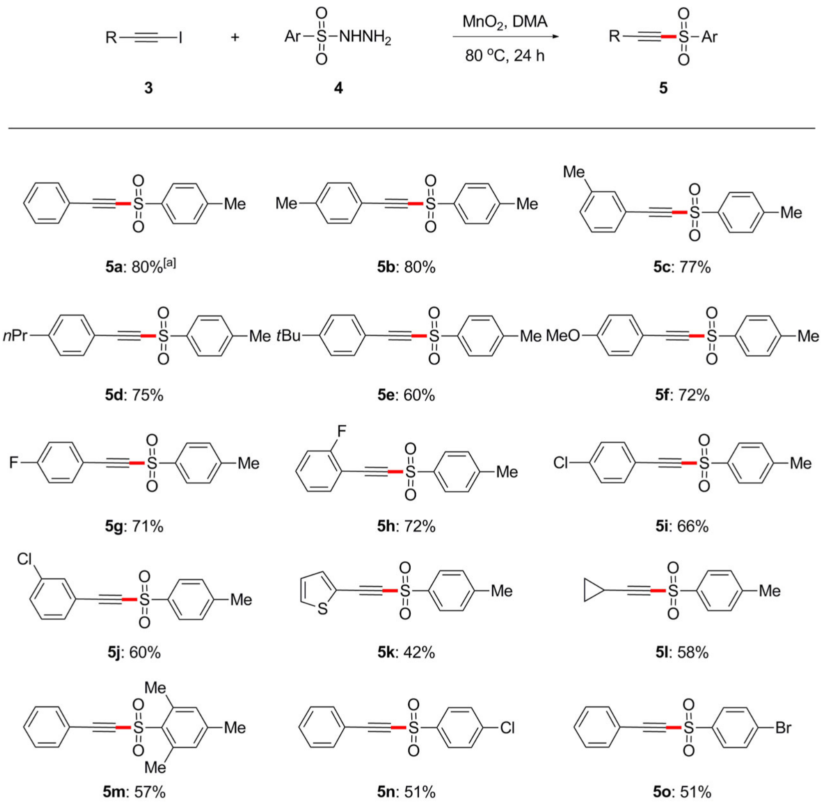
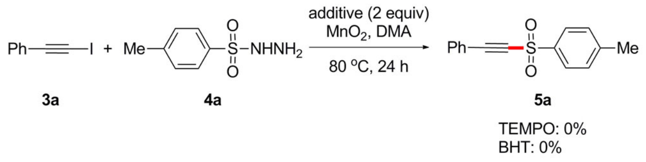


Figure 1. The influence of the reaction temperature.



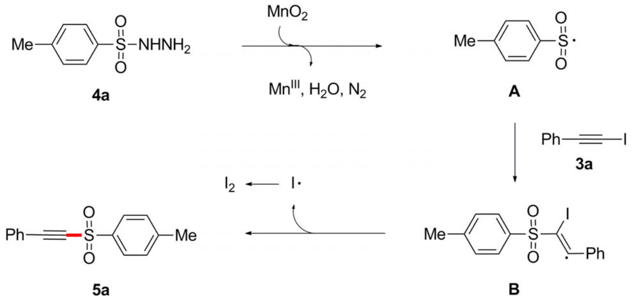
Scheme 2. Substrate scope of haloalkynes and sulfonyl hydrazides. Unless otherwise noted, the reaction conditions were: iodoalkynes **3** (0.3 mmol), sulfonyl hydrazides **4** (1.5 equiv), MnO_2 (4 equiv), and DMA (2 mL) at 80 °C for 24 h. [a] Isolated yield.

cross-coupling product **5a** in 82% GC yield, which indicated that the initial generation of an alkynyl radical was unlikely under our reaction conditions. Furthermore, 2 equivalents of TEMPO or BHT (butylhydroxytoluene) were added to the reaction mixture of iodoalkyne **3a** and sulfonyl hydrazide **4a** under standard reaction conditions, and product **5a** was not observed, further confirming the initial generation of a sulfonyl radical (Scheme 3).



Scheme 3. Control experiments.

On the basis of these experimental results and previous literature,[10,14,16] we tentatively proposed a possible reaction mechanism (Scheme 4). Sulfonyl radical **A** was generated from sulfonyl hydrazide **4a** under oxidative conditions. Subsequent intermolecular addition of the obtained sulfonyl radical **A** to iodoalkyne **3a** gave a vinyl radical intermediate **B**, which further converted to the final alkynyl sulfone product **5a**, releasing an iodo radical. The purple color of the obtained reaction mixture indicated the generation of I_2 under our reaction conditions.



Scheme 4. Proposed mechanism.

In summary, we have reported a catalyst-free oxidative radical sulfonylation reaction of haloalkynes with sulfonyl hydrazides. It represents an example of C(sp)–S bond formation involving sulfonyl hydrazides as the sulfonyl radicals source. Various alkynyl sulfones were synthesized in moderate to good yields. The identification of MnO_2 as the oxidants is very critical for the success of this transformation. Significantly, the self-coupling reaction of haloalkynes through C(sp)–C(sp) bond formation is significantly inhibited under the standard reaction conditions. Efforts are currently underway in our laboratory to investigate the mechanistic details, the synthetic applications of this chemistry, and these results will be reported in due course.

Experimental Section

General Procedure: A 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, iodoalkynes **3** (0.3 mmol), arylsulfonyl hydrazides **4** (0.45 mmol), MnO_2 (1.2 mmol) and DMA (2 mL) was vigorously stirred at 80 °C for 24 h in an oil bath. After the reaction ended, the resulting solution was cooled to room temperature, added EtOAc (30 mL), washed with saturated $Na_2S_2O_3$ aqueous solution (3×10 mL). The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/EtOAc) provided the pure product **5**.

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Keywords: alkynes · C(sp)-S bond formation · organosulfones · radical reactions · sulfonyl hydrazides

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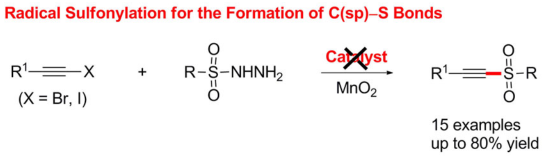

Sulfonylation

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MnO_2-Promoted Oxidative Radical Sulfonylation of Haloalkynes with Sulfonyl Hydrazides: C(sp)–S Bond Formation towards Alkynyl Sulfones

C(sp)—S Bond Formation: A catalyst-free oxidative radical sulfonylation of haloalkynes with sulfonyl hydrazides has been developed. Various alkynyl sulfones were synthesized in moderate to good yields, and MnO_2 was used as the oxidant.