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Letter

Electrochemically Enabled Sulfonylation of Alkynes with Sodium Sulfinates

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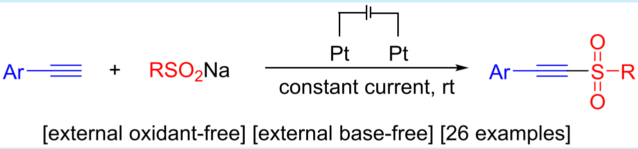
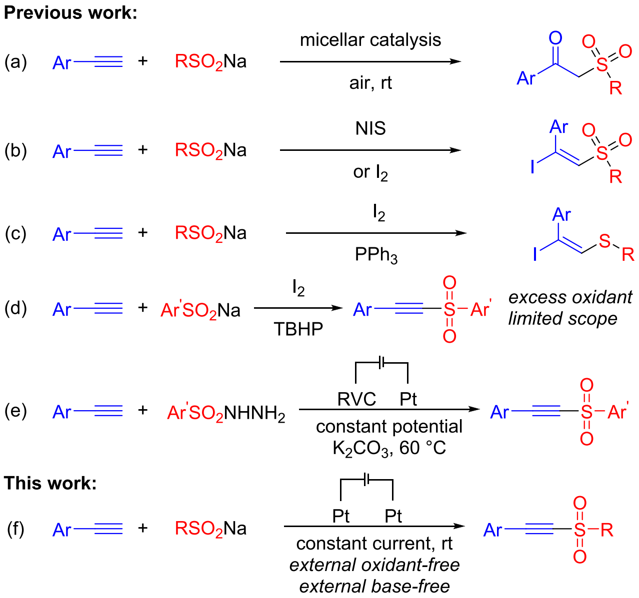
ABSTRACT: An electrochemical sulfonylation of alkynes with sodium sulfinates was achieved for the first time at room temperature. Employing this electrolysis strategy, the reaction occurs efficiently under transition-metal-free, external oxidant-free, and base-free conditions and furnishes diverse alkynyl sulfones in satisfactory yield with broad functional group tolerance.



Sulfones, one of the important organosulfur compounds, are frequently found in natural products,[1] pharmaceuticals,[2] and drug candidates.[3] Among them, alkynyl sulfones are valuable synthetic intermediates in cycloadditions,[4] conjugated additions,[5] cross-coupling reactions,[6] and others;[7] meanwhile, many alkynyl sulfone molecules exhibit remarkable biological activities. Thus several classical synthetic methods, including the oxidation of alkynyl sulfides,[8] oxidation−elimination of selenides,[9] and dehydrohalogenation of vinyl sulfones,[10] have been well established for the preparation of these alkynyl sulfones. However, these protocols generally require predecorated substrates or multiple synthetic steps.

Nowadays, C−S coupling reactions have become a reliable and direct approach to produce alkynyl sulfones. For example, the reactions of alkyl halides or acetylenic acids with sodium sulfinates or sulfonyl hydrazides afforded alkynyl sulfone compounds, which typically use transition-metal catalysts and excess oxidants.[11] In addition, several difunctionalizations of alkynes with sodium sulfonates have been known. In 2014, Lipshutz et al.[12] reported a reaction between arylalkynes and sodium arylsulfinates, providing β-ketosulfones in nanomicelles (Scheme 1a). Jiang[13] and Liu[14] developed a mild iodosulfonylation reaction of alkynes with sodium sulfinates promoted by stoichiometric *N*-iodosuccinimide (NIS) or I_2, respectively (Scheme 1b). In contrast, iodoalkenyl sulfides were isolated from the reaction of alkynes and sodium sulfinates in the presence of excess I_2 and PPh_3, which was discovered by Lu and coworkers (Scheme 1c).[15] In 2016, Kuhakarn and coworkers described an iodine-catalyzed sulfonylation of arylacetylenes with sodium sulfinates using stoichiometric *tert*-butyl hydroperoxide (TBHP) as the oxidant (Scheme 1d).[16] However, electron-deficient arylacetylenes and arylsulfinates were proved to be ineffective substrates. Despite these advances, the development of a direct approach to access alkynyl sulfones from terminal alkynes and sodium sulfinates under mild conditions is still strongly desired. To date, organic electrosynthesis, as an environmentally friendly method, has recently been applied to cross-coupling reactions.[17] Very recently, an elegant electrochemical approach for the sulfonylation of arylalkynes with arylsulfinates was reported by Tang and Huang (Scheme 1e).[18] Whereas this report reflects an external oxidant-free sulfonylation, it requires a reference electrode, an external base, and high reaction temperature. Therefore, we would like to find a very simple electrochemical synthetic protocol to produce alkynyl sulfones

Scheme 1. Coupling Reaction of Alkynes



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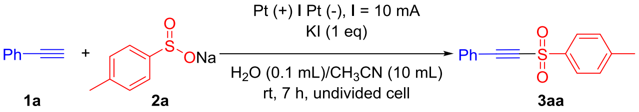
under a design philosophy that is free of metal, external oxidant, and base and has a broad substrate scope.

Herein we report an electrochemically enabled direct sulfonylation of alkynes with sodium sulfinates as the sulfonyl reagent (Scheme 1f). This electrochemical synthesis[19] occurs in an undivided cell under constant current conditions at room temperature. Our method offers efficient access to diverse alkynyl sulfones without any oxidizing reagents, bases, or transition metals. Moreover, sodium sulfinates, which are commercially available, bench-stable, and easily handled, are regarded as a sustainable sulfonyl source for the direct coupling reaction.

Initially, phenylacetylene **1a** and sodium *p*-toluenesulfinate **2a** were chosen as the model substrates to optimize the sulfonylation in an undivided cell, as shown in Table 1.

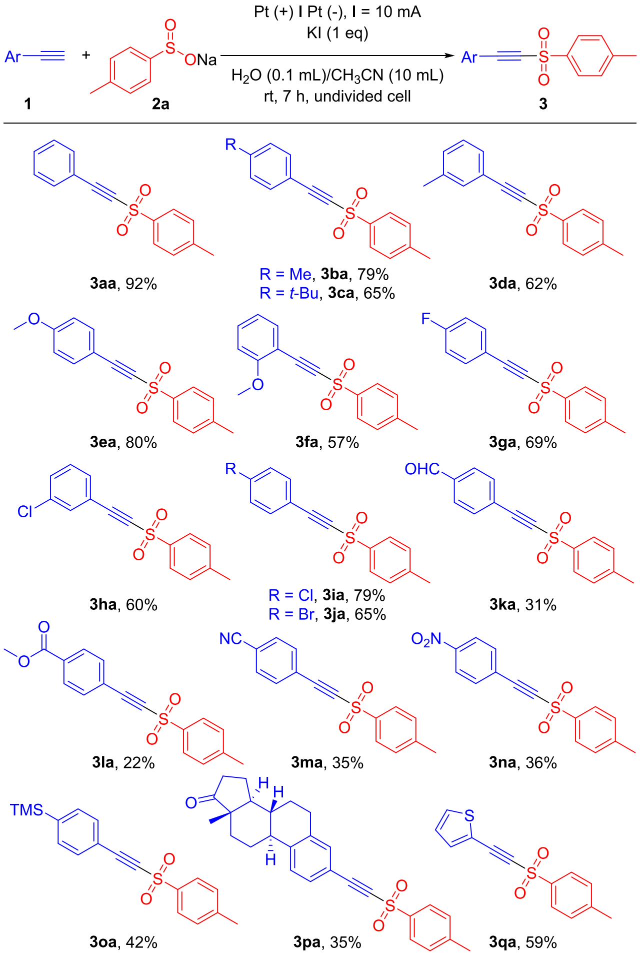
Table 1. Reaction Optimization[a]



entry	variation from standard conditions	yield[b]
1	none	93%
2	graphite as the cathode	22%
3	graphite as the anode	74%
4	C (+) I Ni (−) instead of Pt (+) I Pt (−)	48%
5	TBAI instead of KI	52%
6	NaI instead of TBAI	36%
7	*n*-Bu_4NBF_4 instead of KI	0
8	without H_2O	trace
9	DMSO instead of CH_3CN	0
10	MeOH instead of CH_3CN	0
11	5 mA, 10 h	60%
12	15 mA, 4 h	73%

[a] Standard conditions: **1a** (0.3 mmol), **2a** (3.0 equiv), KI (1 equiv), H_2O (0.1 mL), and MeCN (10.0 mL), undivided cell, 10 mA, rt, 7 h. [b] HPLC yields were determined with naphthalene as the internal standard.

Scheme 2. Scope of Terminal Alkynes[a,b]



[a] Standard conditions: **1** (0.3 mmol), **2a** (3.0 equiv), KI (1 equiv), H_2O (0.1 mL), and MeCN (10.0 mL), 10 mA, rt, 7 h. [b] Isolated yield.

Gratifyingly, the desired acetylenic sulfone **3aa** was indeed isolated in 93% yield with two platinum electrodes under 10 mA current electrolysis at room temperature using KI as the electyrolyte and MeCN/H_2O as the solvent (Table 1, entry 1). A significant decrease in yields was observed when we replaced the platinum electrode with graphite or a nickel electrode (Table 1, entries 2−4). Other iodide salts, such as tetrabutylammonium iodide (TBAI) and NaI, were then examined as the electrolyte. Unfortunately, a lower reaction efficiency was observed (Table 1, entries 5 and 6). No reaction was observed with *n*-Bu_4NBF_4 as the supporting electrolyte (Table 1, entry 7), suggesting that the iodide could also be a redox mediator in this transformation. Only a trace amount of **3aa** could be obtained when the reaction was conducted in anhydrous CH_3CN (Table 1, entry 8), indicating that H_2O was necessary, as it might participate in the reaction process and also increase the solubility of the salts. The sulfonylation did not occur when DMSO or MeOH was used instead of CH_3CN (Table 1, entries 9 and 10). Changing the current was found to reduce the reaction performance (Table 1, entries 11 and 12).

With the optimized electrochemical sulfonylation conditions in hand, we then investigated the scope of terminal alkynes (Scheme 2). When terminal phenylacetylenes **1** was reacted with sodium *p*-toluenesulfinate **2a**, the reaction showed broad compatibility with various substituents on the benzene ring (**3aa**−**oa**). A range of functional groups, including alkyl (**3ba**−**da**), methoxyl (**3ea** and **3fa**), halogen (**3ga**−**ja**), aldehyde (**3ka**), ester (**3la**), nitrile (**3ma**), nitro (**3na**), silane (**3oa**), and ketone (**3pa**), were all left intact under the reaction conditions. In general, terminal phenylacetylenes bearing electron-donating groups were more efficient than those bearing electron-withdrawing groups, and ortho-, meta-, and para-position patterns had little effect on the reaction performance. Notably, natural product estrone could be converted into **3pa** with the developed protocol. Finally, 2-ethynylthiophene **1q** could also be an appropriate candidate, furnishing the corresponding alkynyl sulfone **3qa** in good yield.

Next, we tested a variety of sodium sulfinates under our conditions (Scheme 3). Sodium benzenesulfinate **2b** and sodium *p*-(*tert*-butyl)benzenesulfinate **2c** were found to be effective for the conversion of phenylacetylene **1a** to alkynyl sulfones **3ab** and **3ac**. The reaction of sodium 2,4,6-trimethylbenzenesulfinate **2d** with **1a** afforded the sulfonylation product **3ad** in a lower yield, likely as a result of the increased steric effect. Sodium arenesulfinates bearing halogens (F, Cl, Br), trifluoromethyl (CF_3), and nitrile (CN) were all tolerated in this sulfonylation reaction, affording **3ae**−**ai** in moderate to good yields. Besides arylsulfinates, it was

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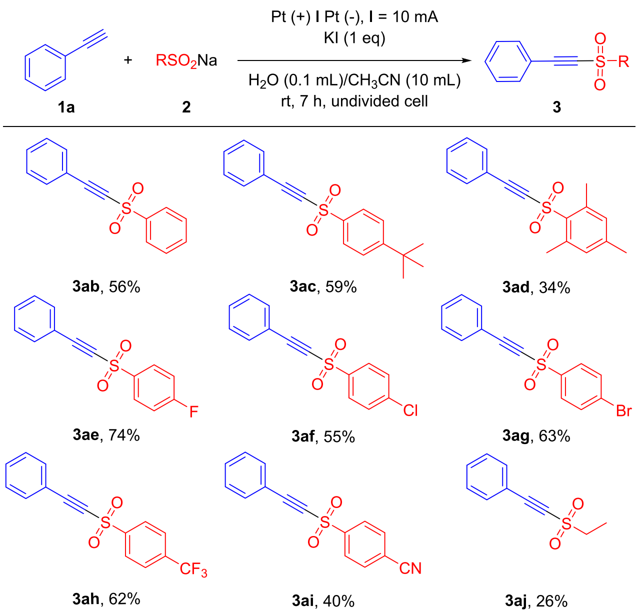
Scheme 3. Scope of Sodium Sulfinates[a,b]

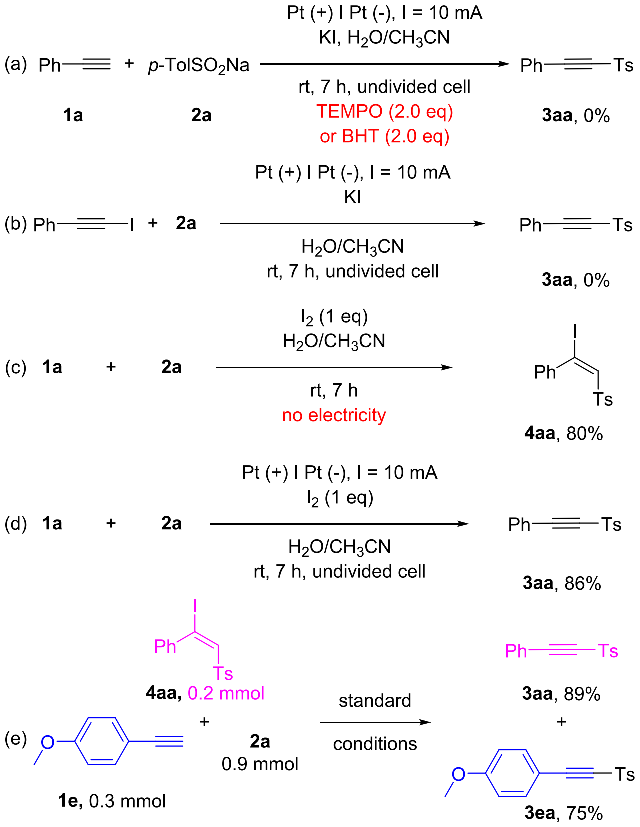


[a]Standard conditions: **1a** (0.3 mmol), **2** (3.0 equiv), KI (1 equiv), H_2O (0.1 mL), and MeCN (10.0 mL), 10 mA, rt, 7 h. [b]Isolated yield.

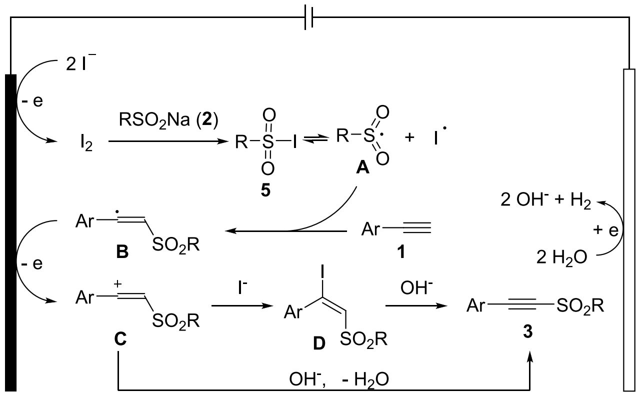
interesting to discover that sodium ethanesulfinate **2j** was also a suitable substrate, leading to acetylenic alkylsulfone **3aj**, which cannot be prepared using a previous electrochemical approach.[18]

To shed light on the reaction mechanism of this electrochemical sulfonylation, several control experiments were carried out (Scheme 4). First, when 2.0 equiv of 2,2,6,6-tetramethyl-1-piperidinoxy (TEMPO) or 2,6-di-*tert*-butyl-*p*-toluenol (BHT) was added to the reaction of **1a** and **2a** under the standard conditions, the desired product **3aa** could not be detected (Scheme 4a), indicating that the sulfonylation might involve a radical pathway. Consequently, phenylethynyl iodide was prepared and subsequently treated with **2a** under the standard conditions, and no reaction was observed (Scheme 4b). This result suggests that phenylethynyl iodide is not involved in this reaction. As expected, only (*E*)-*β*-iodo vinylsulfone **4aa** was isolated from the reaction of **1a** and **2a** in the presence of stoichiometric I_2 without electricity (Scheme 4c), which is consistent with Liu's work[14] (Scheme 1c). In contrast, with electrolysis of the same reaction mixture, acetylenic sulfone **3aa** was furnished in high yield (Scheme 4d). These results indicate that electrolysis is still required after the generation of I_2. Finally, **4aa** was converted to **3aa** in 89% isolated yield under the standard conditions (Scheme 4e), thereby suggesting that it might be an intermediate in this transformation.

Scheme 4. Control Experiments



Scheme 5. Possible Mechanism



On the basis of the previously described experiments and cyclic voltammetric (CV) results (see the Supporting Information), a plausible pathway for this sulfonylation is proposed in Scheme 5. Initially, molecular iodine is formed from the anodic oxidation of iodide anion,[19g] which is confirmed by two oxidation peaks of KI at 1.10 and 1.65 V vs Ag/AgCl (I^- to I_3^- to I_2, red curve, Figure S1). At the same time, sodium sulfinate **2a** does not undergo anodic oxidation (blue curve, Figure S1). Afterward, the *in situ*-generated I_2 reacts with sodium sulfinate **2** to afford sulfonyl iodide **5**, which readily undergoes homolytic cleavage to produce the sulfur-centered sulfonyl radical **A**. The subsequent addition of **A** to alkyne **1** affords vinyl radical **B**, which is then oxidized at the anode, giving vinyl cation **C**.[20] The desired product **3** is finally obtained by a deprotonation of intermediate **C** or **D**. Simultaneously, the cathodic reduction of H_2O produces hydrogen gas and a hydroxide ion.

In conclusion, we have reported an electrochemically direct coupling of terminal alkynes and sodium aryl or alkyl sulfinates at room temperature for the first time. The reaction was performed under mild reaction conditions and does not require any exogenous oxidants, bases, or transition metals. In addition, a range of valuable alkynyl sulfones can be constructed using this eco-friendly protocol, and this protocol tolerated many functional groups.

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■ ASSOCIATED CONTENT

Supporting Information

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Experimental procedures and characterization data (PDF)

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Notes

The authors declare no competing financial interest.

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