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Electrooxidative Tandem Cyclization of Activated Alkynes with Sulfinic Acids To Access Sulfonated Indenones

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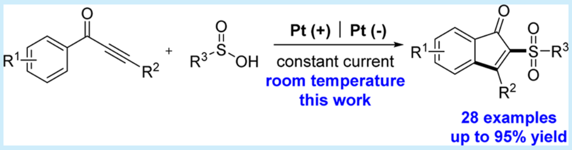
Supporting Information

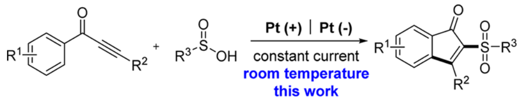
ABSTRACT: An electrooxidative direct arylsulfonlylation of ynones with sulfinic acids via a radical tandem cyclization strategy has been developed for the construction of sulfonated indenones under oxidant-free conditions. This method provides a simple and efficient approach to prepare various sulfonylindenones in good to excellent yields, demonstrating the tremendous prospect of utilizing electrocatalysis in oxidative coupling. Notably, this reaction could be easily scaled up with good efficiency.



During the past decades, oxidative tandem chemistry has ushered in a new epoch in the evolution of chemistry, and it has become one of the most powerful and efficient strategies in organic synthesis.[1] Among the diverse oxidative tandem-mediated synthetic methodologies, strategies utilizing free-radical tandem reactions have proven to be highly valuable for the synthesis of complex carbo- and heteropolycyclic skeletons by avoiding the prefunctionalization process.[2] Despite the promising progress that has been made in recent years, most of the traditional free-radical cascade reactions usually need transition-metal catalysts[3] or stoichiometric oxidants.[4] Therefore, it is still a challenging but attractive task to develop simple, efficient, and oxidant-free reactions to afford a variety of important and structurally diverse compounds.

Indenones, widely existing in many natural products and biologically active compounds, are among the most important classes of carbocycles that have unique biological activity.[5] Functionalized indenones have attracted considerable synthetic interest because of their important applications in asymmetric synthesis, library design, and drug discovery.[6] A variety of synthetic methods have been developed for the construction of these carbocycles.[7] Recently, oxidative radical tandem cyclization of activated alkynes under transition-metal catalysis or metal-free conditions provided a good alternative, and different functional groups such as phosphoryl, cyclohexyl, and thioalcohol groups have been successfully incorporated into the indenone framework. Even so, it is still urgent to develop a transition-metal-free and oxidant-free radical tandem cyclization strategy to construct structurally diverse functional indenones.

Sulfone groups represent one of the most important organic functionalities and are widely found in a number of biologically active compounds, drug molecules, and versatile synthetic intermediates.[7d,8] Therefore, the incorporation of sulfone groups into organic molecules is an important task.[4c,9] Recently, reactions of sulfur-containing substrates with activated alkynes via oxidative radical tandem cyclization have been demonstrated to be efficient methods to synthesize thiolated indenones.[10] However, these reported methods normally suffer from some limitations, such as harsh conditions or the need to use stoichiometric amounts of oxidants to generate sulfonyl radical. As a result, the development of a practical and general protocol to synthesize diverse multisubstituted indenones is still strongly desired.



In this regard, electrocatalysis provides an ideal alternative method.[11] In particular, electrocatalytic oxidative C−H functionalization proved to be an efficient alternative method for classic oxidative coupling methods.[12] However, there is no precedent for the anodic oxidative tandem cyclization of alkynes. As part of our continuing interest in the synthesis of sulfone-containing organic compounds,[13] herein we report a new and efficient oxidant-free direct arylsulfonlylation of ynones with sulfinic acids toward sulfonated indenones in a simple undivided cell under constant current conditions. To the best of our knowledge, this is the first example of constructing sulfonated indenones via electrooxidative tandem cyclization of alkynes.

Initially, 1,3-diphenylprop-2-yn-1-one **1a** and benzenesulfinic acid **2a** were chosen as the model substrates to optimize the reaction conditions (Table S1). By optimizing key reaction parameters, we obtained the best results by performing the reaction under a constant current electrolysis at 10 mA cm^{-2} in an undivided cell using tetrabutylammonium iodide (TBAI) as redox catalyst, $LiClO_4$ as electrolytes, and two platinum plates as

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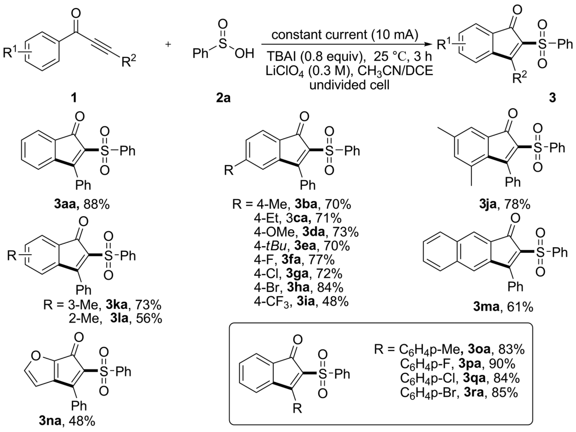
the working electrode and cathode in CH_3CN/DCE at room temperature (Table S1, entry 1). Both increasing and decreasing the constant current would lead to decreased reaction yields (Table S1, entries 2 and 3). Subsequently, replacing TBAI with NH_4I or tetrabutylammonium bromide (TBAB) diminished the reaction yield significantly or suppressed it entirely (Table S1, entries 4 and 5).The variation of the mixed solvent also led to significantly lower yields (Table S1, entries 6 and 7). Additionally, inferior results were observed when the TBAI equivalent was decreased or increased (Table S1, entries 8−10). As for the choice of electrolyte, ammonium salts decreased the reaction efficiency compared with lithium perchlorate (Table S1, entries 11−13). Moreover, the effect of the electrode material was also explored. Lower reaction yields were obtained when the platinum anode or cathode was replaced by carbon (Table S1, entries 14 and 15). Control experiments also showed that no desired product was generated without electricity (Table S1, entry 16).

With the optimized conditions described above, the scope and limitations of the reaction of various ynones with sulfinic acids were investigated, and the results are shown in Scheme 1. First, ynones with different substituents on the 1-positions of the aryl groups were applied as substrates to react with benzenesulfinic acid **2a**. As expected, substrates with electron-donating groups at the para position on the 1-positions of aryl rings were suitable for this protocol, and the corresponding products were obtained in good yields (**3aa−ea**). Halide substituents such as F, Cl, and Br were well tolerated under electrocatalytic conditions, furnishing the sulfonated indenones in high yields (**3fa−ha**). Furthermore, product **3ia** with a strong electron-withdrawing trifluoromethyl group was isolated in 48% yield, which might be due to electronic effects. Subsequently, the substituent group at the meta position of the phenyl ring afforded a single product in moderate yield (**3ja−ka**). *o*-Methyl ynones gave a slightly decreased reaction yield, which might be due to the steric effect of the methyl group (**3la**). Other aromatic ynones were also applied as substrates in this transformation. Both **1m** and **1n** furnished the desired product in good yields (**3ma−na**). Subsequently, the functional group tolerance of the 3-positions of the aryl groups were applied as substrates to react with the benzenesulfinic acid **2a**. An interesting discovery is that electron-donating or electron-withdrawing groups on the 3-positions of aryl rings were suitable for this protocol, and the corresponding products were obtained in moderate to good yields (**3oa−ra**). Unfortunately, lack of access to the desired products may be affected by the conjugation effect when the 3-alkyl-substituted phenylprop-2-yn-1-ones as substrates react with **2a**.

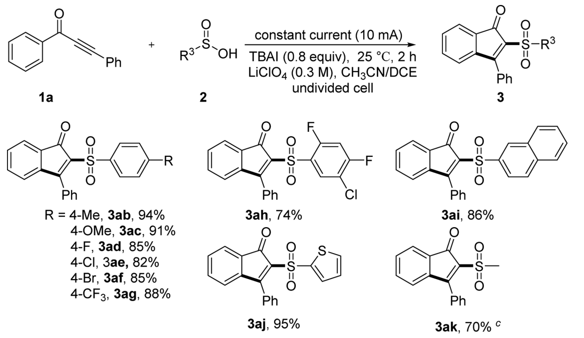
Scheme 1. Results for Electrocatalytic Arylsulfonylation of Ynones with Benzenesulfinic acids 2a[a,b]



[a]Standard conditions: Pt anode, Pt cathode, constant current = 10 mA, **1** (0.25 mmol), **2a** (0.75 mmol), $LiClO_4$ (3 mmol), TBAI (0.8 equiv), MeCN/DCE (10.0 mL, 9/1), 25 °C, 3 h. [b]Isolated yields.

In the next step, the tolerance of the sulfinic acid moiety was also studied (Scheme 2). Both the electron-rich and electron-rich and electron-deficient sulfinic acids were all tolerated in this reaction, thereby facilitating possible further modifications (**3ab−ah**). Moreover, other aromatic sufinic acids such as naphthalene- or thiophene-2-sulfinic acid can also generate the desired products in good yields (**3ai−aj**).

Scheme 2. Results for Electrocatalytic Arylsulfonylation of Ynones with Sulfinic Acids 2[a]

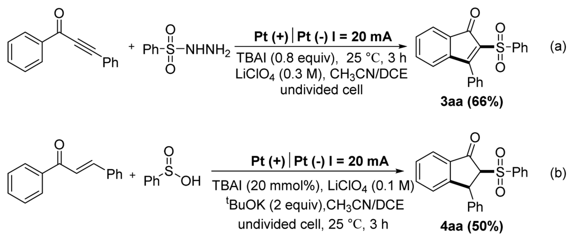


[a]Standard conditions: Pt anode, Pt cathode, constant current = 10 mA, **1a** (0.25 mmol), **2** (0.75 mmol), $LiClO_4$ (3 mmol), TBAI (0.8 equiv), MeCN/DCE (10.0 mL, 9/1), 25 °C, 2 h. [b]Isolated yields. [c]Sodium methylsulfite, H_2SO_4 (0.75 mmol), 60 °C, 3 h.

Notably, a product with relatively high yield was also obtained when the alkanesulfinates, such as sodium methylsulfinates, were used as the substrates (**3ak**). Moreover, the faradaic efficiency is also selectively calculated in 60 ± 5% yield, respectively (Figure S1).

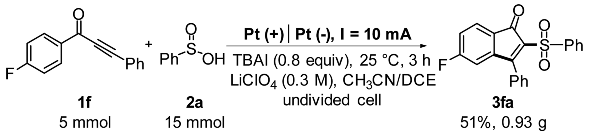
To further show the utility of this strategy, we attempted to apply benzenesulfonyl hydrazide as a coupling partner to react with **1a**. To our delight, the desired product can be obtained in 66% yield when the current is increased to 20 mA (Scheme 3a).

Scheme 3. Substrate Replacement Experiments



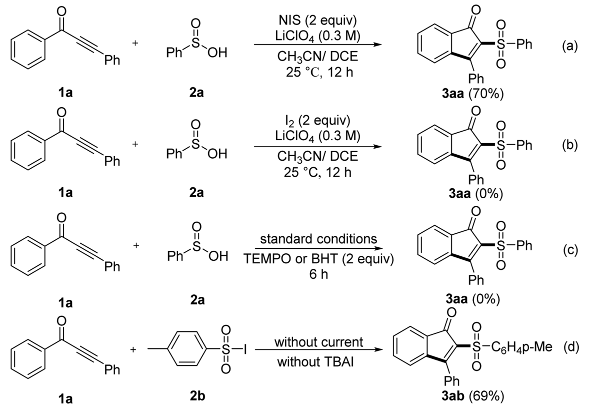
Interestingly, the desired product also could be obtained in 50% yield when the chalcone was used as the substrate to react with benzenesulfinic acid **2a** under the electrooxidation conditions (Scheme 3b). Moreover, the gram-scale reaction between 1-(4-fluorophenyl)-3-phenylprop-2-yn-1-one and benzenesulfinic acid **2a** afforded the desired product in 51% yield (Scheme 4), further highlighting the great potential application of this transformation.

Scheme 4. Gram-Scale Synthesis



To further understand the role of iodine in this oxidative coupling/annulation process, we applied different stoichiometric amounts of iodine sources in the model reaction. To our surprise, an iodine radical source, *N*-iodosuccinimide (NIS), showed reactivity similar to that of TBAI (Scheme 5a,b).

Scheme 5. Control Experiment

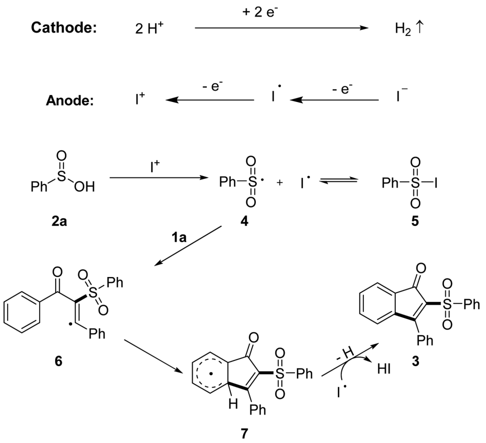


At the same time, no desired product could be obtained by using a stoichiometric amount of I_2 as the oxidant in the absence of current. These results indicated that the I^{+1} species were likely to be involved in the reaction process. Subsequently, radical-trapping experiments were carried out to confirm whether this reaction went through a radical reaction pathway. When a commonly used radical-trapping reagent, TEMPO or BHT, was added into the reaction system, no desired product could be observed even when the reaction time was prolonged to 6 h for the oxidative coupling/annulation of **1a** with **2a** (Scheme 5c). All of the results described above indicate that the reaction probably involves a radical process. At last, the reaction of **1a** with **2b** under the standard conditions without TBAI and current also could give **3ab** in 69% yield (Scheme 5d), which indicates that sulfonyl iodine ought to be the reaction intermediate.

On the basis of the experimental results and previous reports,[14] a plausible reaction pathway is illustrated in Scheme 6. The reaction sequence begins with the anodic oxidation of the iodide ion to form I^{+1} species and its subsequent reaction with sulfinic acid **2a** to afford sulfonyl radical **4** and iodine radical. Subsequently, the addition of sulfonyl radical **4** to 1,3-diphenylprop-2-yn-1-one **1a** generates radical **6**. Intramolecular cyclization of intermediate **6** gives the radical intermediate **7**. Finally, the oxidation of **7** generated the corresponding product **3**.

In conclusion, a convenient and efficient method for the construction of sulfonated indenones via an electrooxidative-mediated arysulfonylation reaction of ynones with sulfinic acids under oxidant-free conditions has been successfully developed. This tandem reaction is constituted by the sequential sulfonylation of alkynes, carbocyclization, dearomatization, and oxidation processes. A series of biologically important sulfone-containing indenones could be conveniently and efficiently obtained in good yields from readily available starting materials with excellent functional group tolerance. Importantly, this reaction can be scaled up in good reaction efficiency, which is beneficial for practical applications.

Scheme 6. Postulated Reaction Pathway



■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.7b01256.

Experimental procedures, optimization of reaction conditions, characterization data, and NMR spectra of the products (PDF)

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Notes

The authors declare no competing financial interest.

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