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Electrochemical Sulfonylation/Heteroarylation of Alkenes via Distal Heteroaryl *ipso*-Migration

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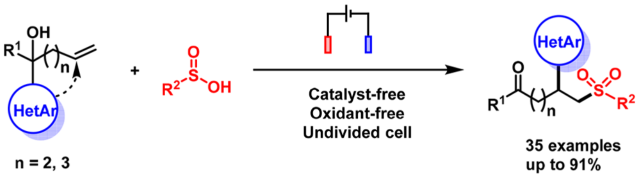
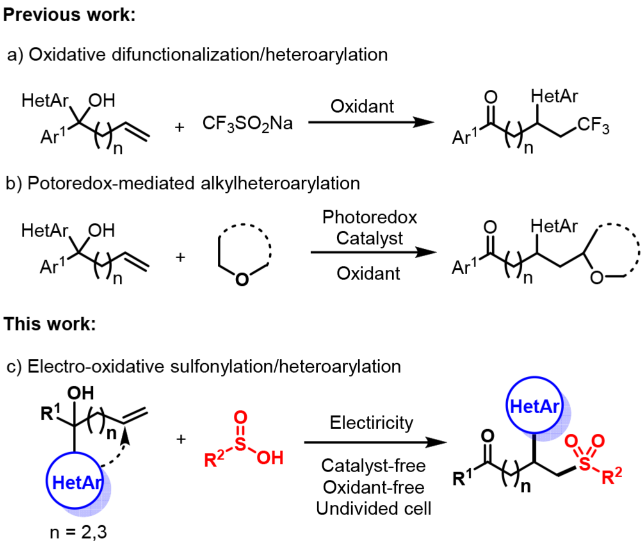
Supporting Information

ABSTRACT: A direct electrooxidative sulfonylation/heteroarylation reaction of alkenes with sulfinic acids, which proceeds through distal heteroaryl *ipso*-migration and C−S and C−C bond formations, is reported. This electro-synthetic method offers an efficient and environmentally friendly entry to prepare various sulfonated functionalized heteroarenes under an undivided cell at room temperature, avoiding the use of any metal catalysts, additives, and oxidants. Preliminary mechanistic studies indicated a radical pathway.



Functionality migration is known as a common workhorse rearrangement transformation in organic chemistry.[1] Not only is it one of the most challenging themes, but it also enables us to reconstruct the molecular frameworks and synthesize invaluable and structurally unique functionalized organic compounds in an efficient way, which are difficult to generate through other methods.[2] Generally, group migration works only at carbon centers adjacent to carbon cations,[3] radicals,[4] or carbenes.[5] For instance, the radical 1,2-arylation migration has been extensively studied.[6] In contrast, long-distance radical aryl migration is currently underdeveloped. In recent years, the remote aryl migration protocol was actively pursued, and a number of elegant cases have been established by Studer,[7a] Liang,[7b] Tchabanenko,[7c] Uneyama,[7d] and others.[7e] Particularly, Zhu[8] and Gu[9] independently reported the intramolecular migration of heteroaryl groups to accomplish the difunctionalization of unactivated olefins (Scheme 1a, b). Despite this progress, these reported methods suffer from the necessity of toxic and stoichiometric radical initiators,[10,11] and oxidants,[12,13] thereby limiting their applicability to a certain extent.[14] Therefore, the development of a practical and green alternative for remote aryl migration is still highly desirable, but is challenging.

Scheme 1. Strategy of Heteroaryl Group Migration



The design and application of efficient and sustainable synthetic strategies toward functional molecules are a hot topic in the organic community. As an ideal alternative to chemical oxidants, electrochemical anodic oxidation represents an environmentally friendly synthetic tool in organic chemistry.[15] Beyond simple replacement of chemical reductants/oxidants, the electrochemical pathway also endows enormous opportunity to realize unprecedented reactivity and selectivity in many C−H functionalization reactions.[16] Recently, significant momentum has been gained by merging electrocatalysis with dehydrogenative coupling for green synthesis, allowing the direct construction of C−N and C−C bonds,[17] and beautiful examples have been independently reported by Lei,[18] Xu[19] and co-workers. In spite of these significant achievements, electrocatalytic C−S bond forming reactions for sulfone synthesis are still rather limited, which requires the selection of suitable sulfonyl sources and the specific design of sulfonyl-radical triggered transformations.[16a,17g] As part of our continuing studies in the synthesis of the sulfone-containing compounds,[20] herein, we report an intermolecular sulfonylation/heteroarylation of the unactivated alkenes through electrochemical oxidation (Scheme 1c). To the best of our knowledge, transition-metal-free and oxidant-free intermolecular sulfonyla-

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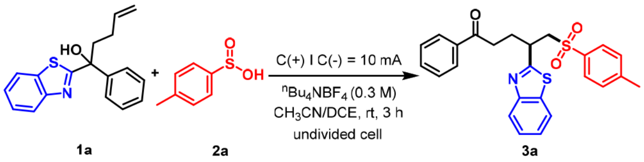
tion/heteroarylation of unactivated alkenes to provide functionalized sulfonated heteroarenes has not been reported to date.

Our study commenced with 1-(benzo[*d*]thiazol-2-yl)-1-phenylpent-4-en-1-ol (**1a**) and 4-methylbenzenesulfinic acid (**2a**) in a 1:3 mol ratio comprised of an undivided cell equipped with a graphite anode and graphite cathode. Initially, the NH_4I (0.8 equiv) was set as the catalyst, $LiClO_4$ as the electrolyte, and CH_3CN/DCE (v/v = 9/1) as cosolvents, which afforded the migration product **3a** only in a trace amount under 10 mA constant current for 3.0 h (Table 1, entry 1). Interestingly, without the addition of NH_4I, the current transformation could proceed smoothly, accessing a 49% yield of the desired product **3a** (entry 2). The following screening of the supporting electrolytes, such as $^nBu_4ClO_4$, $^nBu_4NBF_4$, $^nBu_4PF_6$, Et_4NBF_4, and Et_4NOTs often used in electrocatalysis, were then investigated (entries 3−7), and the results show that $^nBu_4NBF_4$ was proven to be the best one, affording **3a** in 70% yield (entry 4). Next, the effect of solvent was explored, including DCE, CH_3CN, and a cosolvent of CH_3CN/H_2O (v/v = 4/1) (entries 8−10). All these reaction media did not show any improvement in reaction yields compared with the cosolvent CH_3CN/DCE (v/v = 9/1) (entries 8−10 vs entry 4). Further investigation focused on the manipulation of the electrolysis conditions. Either increasing or decreasing the constant current led to the lower conversion (entries 11−12 vs entry 4). Moreover, the effect of the electrode material was probed. It seemed that replacing the graphite anode or graphite cathode with a platinum plate all resulted in lower yields (Table 1, entries 13−15). Finally, the molecular structure of **3a** was identified by single-crystal X-ray diffraction (CCDC 1867118; Figure S2).

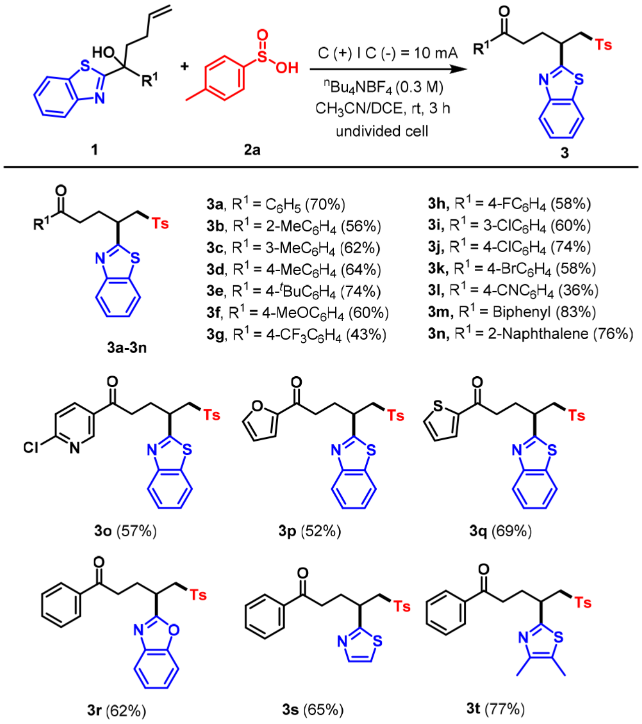
Table 1. Optimization of Reaction Conditions[a]



entry	deviation from standard condition	yield (%)[b]
1	NH_4I as the catalyst, $LiClO_4$ as the electrolyte	trace
2	$LiClO_4$ as the electrolyte	49
3	$^nBu_4ClO_4$ as the electrolyte	48
4	none	70
5	$^nBu_4NPF_6$ as the electrolyte	48
6	Et_4NBF_4 as the electrolyte	30
7	Et_4NOTs as the electrolyte	18
8	DCE instead of CH_3CN/DCE	31
9	CH_3CN instead of CH_3CN/DCE	65
10	CH_3CN/H_2O (v/v = 4/1) instead of CH_3CN/DCE	47
11	5 mA instead of 10 mA, 6 h	63
12	15 mA instead of 10 mA, 2 h	59
13	Pt (+)∣C (−) instead of C (+)∣C (−)	29
14	C (+)∣Pt (−) instead of C (+)∣C (−)	41
15	Pt (+)∣Pt (−) instead of C (+)∣C (−)	26

[a] Standard conditions: graphite SK-50 electrodes, constant current = 10 mA, **1a** (0.25 mmol), **2a** (0.75 mmol), $^nBu_4NBF_4$ (3.0 mmol) in CH_3CN/DCE (10.0 mL, v/v = 9/1) under air at room temperature for 3.0 h. [b] Isolated yield is based on **1a**.

Scheme 2. Scope of Benzothiazole-Substituted Tertiary Bishomoallylic Alcohols[a]

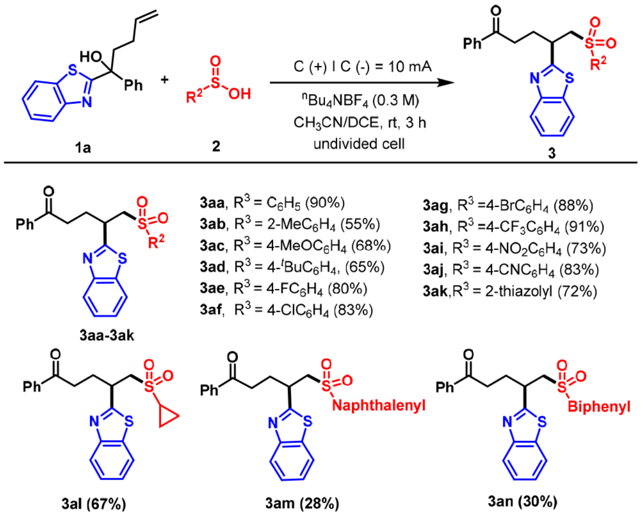


[a] Reaction conditions: graphite SK-50 electrodes, constant current = 10 mA, **1** (0.25 mmol), **2a** (0.75 mmol), $^nBu_4NBF_4$ (3.0 mmol) in CH_3CN/DCE (10.0 mL, v/v = 9/1) under air at room temperature for 3.0 h. Isolated yield is based on **1**.

With the optimized reaction conditions having been identified, we evaluated the scope and limitations of substrates in this electrochemical protocol (Scheme 2). Gratifyingly, electronic characteristics of the aryl group (R^1) have no influence on the migration of the benzothiazolyl group, and a variety of substituents at different positions of the alkynyl (R^1) moiety that are electron-neutral (**3a**−**3e**), -rich (**3f**), and -poor (**3g**−**3l**) efficiently gave the corresponding products **3a**−**3l** with yields ranging from 36% to 74%. To our delight, benzothiazole-substituted tertiary alcohol **1** bearing biphenyl and naphthyl groups led to products **3m** and **3n** in 83% and 72% yields, respectively. Similarly, the reaction exhibited considerable tolerance of a series of heterocyclic functional groups such as pyridyl, furanyl, or thienyl moieties, as the corresponding products **3o**−**3q** were obtained in 52−69% yields. Besides benzothiazole, the other heteroaryl groups such as benzoxazole and thiazoles were then evaluated for this sulfonylation reaction. Delightfully, both of them were suitable for this transformation, giving the migration products **3r**−**3t** with good to excellent yields.

Subsequently, we evaluated whether the reaction could tolerate the modification of the substituents attached to the sulfinic acids **2** (Scheme 3). As anticipated, the reaction of benzothiazole-substituted tertiary alcohol **1a** with a variety of arylsulfinic acids **2** under the standard conditions offered the corresponding sulfonylated products **3aa**−**3aj** in generally good yields. Alternatively, both 2-thienyl and cyclopropyl analogues were proven to be effective, enabling a similar radical-induced migration process to give the corresponding products **3ak** and **3al** in 67% to 72% yields. However, sulfinic acids bearing naphthyl or biphenyl groups seemed reluctant to undergo the current electrocatalytic migration reaction, as the corresponding

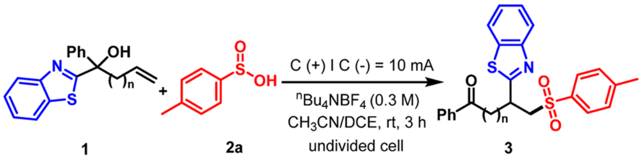
Scheme 3. Scope of Sulfinic Acids[a]



[a]Reaction conditions: graphite SK-50 electrodes, constant current = 10 mA, **1a** (0.25 mmol), **2** (0.75 mmol), $^nBu_4NBF_4$ (3.0 mmol) in CH_3CN/DCE (10.0 mL, v/v = 9/1) under air at room temperature for 3.0 h. Isolated yield is based on **1a**.

products **3am** and **3an** were generated in low yields of 28% and 30%, respectively.

Scheme 4. Transition States of Migration Reaction



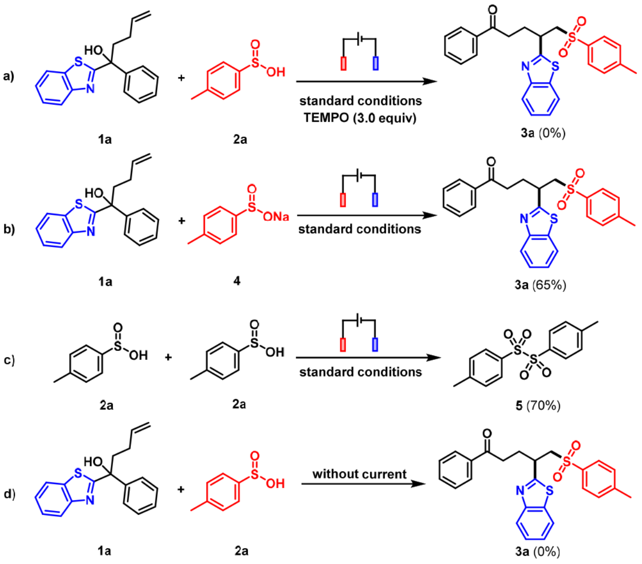
1u, n = 0,	**3u**, yield = (0 %)
1v, n = 1,	**3v**, yield = (0 %)
1a, n = 2,	**3a**, yield = (70%)
1w, n = 3,	**3w**, yield = (54%)
1x, n = 4,	**3x**, yield = (0%)

“3a, yield = (71%)” was revised to “3a, yield = (70%)”

To gain further mechanistic insight into this mechanism, preliminary controlled experiments were conducted. Initially, tertiary alcohols (**1a** and **1u**−**1x**) with different lengths of linear chains were subjected to the reaction of 4-methylbenzenesulfinic acid **2a** under the standard electrocatalytic conditions to understand the migration pathway (Scheme 4). Obviously, the migration of the benzothiazole group could be affected by the chain length of substrate **1**; namely, the corresponding products **3a** and **3w** could be furnished through 1,4- or 1,5-migration (**1a**, *n* = 2; **1w**, *n* = 3) whereas 1,2- and 1,3-migration together with 1,6-migration did not work, and the desired products (**3u**, *n* = 0; **3v**, *n* = 1; **3x**, *n* = 4) could not be obtained. Results from these experiments indicate that the migration favors five- and six-membered cyclic transition states (*n* = 2, 3) while three-, four-, and seven-membered cyclic transition states are disfavored (*n* = 0, 1, 4). These experiment outcomes also support the heteroaryl migration in an intramolecular manner.

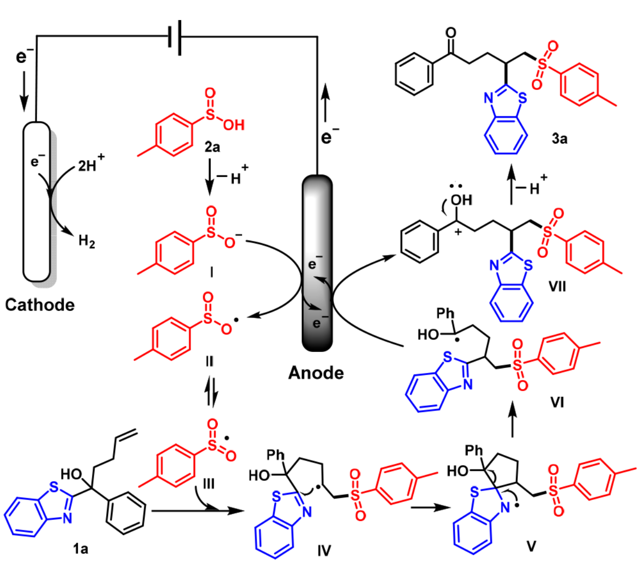
Subsequently, radical trapping experiments were carried out to confirm whether this reaction proceeded through a radical reaction pathway. When 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) as the radical scavenger was subjected to the reaction system under the standard conditions, the reaction was substantially inhibited and the starting material **1a** was almost completely recovered (Scheme 5a). Furthermore, the sodium *p*-tolylsulfinate (**4**) was utilized as the sulfonyl source instead of sulfinic acid **2a** to participate in this reaction under the standard conditions. To our surprise, the sodium *p*-tolylsulfinate showed reactivity similar to that of *p*-toluenesulfinic acid (**2a**), giving the desired product **3a** in 65% yield (Scheme 5b). In addition, without the addition of tertiary alcohol **1**, the coupling product 4,4′-dimethyldiphenyl disulfone (**5**) could be obtained in good yield (70%) (Scheme 5c). Last, the reaction of **1a** with **2a** was conducted under the standard conditions without current, and no desired product could be observed (Scheme 5d). All these results indicate that the sulfinic acid **2a** may undergo a deprotonation process, resulting in sulfonyl radicals.

Scheme 5. Control Experiments



Based on the above results and the literature survey,[21] a reasonable mechanism for electrocatalytic sulfonylation reaction is proposed in Scheme 6. The reaction commences with the deprotonation of sulfinic acid **2a**, giving a sulfonyl ion

Scheme 6. Plausible Mechanism



intermediate **I**. Subsequently, the ion intermediate **I** is oxidized to a new oxygen-centered radical intermediate **II** through a single electron transfer (SET) procedure at the anode. The arylsulfonyl radicals **III** and **II** are resonance structures. The sulfonyl radical **III** undergoes intermolecular radical addition to the benzothiazole-substituted tertiary alcohols to generate intermediate **IV**, which was trapped by the intramolecular heteroaryl group via a five-membered cyclic transition state to generate the spiro *N*-radical **V**. The amino radical triggers the C−C bond cleavage, and the resulting ring opening of the spiro structure generates a ketyl radical **VI**. Single-electron oxidation of **VI** occurs at the anode to the cationic intermediate **VII**. Finally, deprotonation of **VII** afforded the product **3a**.

In summary, we have successfully developed an efficient intermolecular sulfonylation/heteroarylation of alkenes with sulfinic acids via distal heteroaryl *ipso*-migration. This electrochemical protocol avoids the use of the external catalysts and chemical oxidants, resulting in the formation of new C−C/C−S bonds, thereby providing an environmentally friendly way to access a set of sulfonated functionalized heteroarenes. Efforts are underway in our laboratory to extend the application of this method to other migration functionalization reactions.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03191.

> Experimental procedures, More optimization of reaction conditions, Cyclic voltammetry experiment, Faradaic efficiency, X-ray crystallography structure of compound **3a**, Characterization data, Copies of ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra for the products (PDF)

Accession Codes

CCDC 1867118 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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