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Electrochemical Alkynyl/Alkenyl Migration for the Radical Difunctionalization of Alkenes

Yongyuan Gao,[a] Haibo Mei,[a] Jianlin Han,*[a,b] and Yi Pan*[a,b]

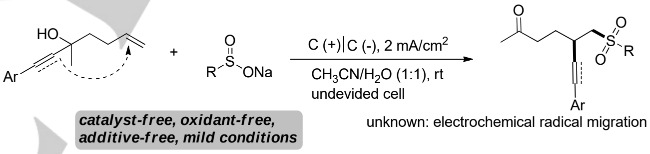
Dedication ((optional))

Abstract: An efficient electrochemical 1,2-sulfonylation/alkynylation of alkenes via radical 1,4-alkynyl migration of alkynyl-substituted tertiary alcohols has been described, which used sodium sulfinates as sulfonyl sources affording the corresponding α-sulfonyl-β-alkynylated products in moderate to excellent yields. This electrochemical reaction proceeded smoothly without the use of any metal-catalyst, additive and oxidant, which represents a new and eco-friendly strategy for the difunctionalization of unactive olefins, and also the first example of the electrochemical distal radical migration reaction.

Distal radical migration strategy represents a particular type of organic transformations in the field of organic synthesis due to its potential application in the construction of complex compounds in an efficient way.[1] Subsequently, the need for advanced approaches and new reagents is at an all-time high. Specifically, the intramolecular radical functional group migration reaction proceeds through the formation of a cyclic intermediate or transition state, which provides an effective strategy for the difunctionalization of C-C double bond in a proper position.[2,3] In the past few years, the elegant works on the vicinal difunctionalization of alkenyl moiety via intramolecular formyl,[4] aryl,[5] cyano,[6] and heteroaryl[7] migration has been developed.[8] Very recently, the Zhu group reported a photoredox-catalyzed radical trifluoromethylative alkynylation of unactivated alkenes via distal alkynyl migration.[9] The Studer group has developed a difunctionalization of alkynyl-substituted tertiary alcohol via 1,4-alkenyl migration.[10] These radical migration reactions mainly focused on the light initiation and metal catalysis, which usually need transition-metal, photocatalyst or additives.

In recent years, electrochemical synthesis has attracted widespread attention in the field of organic synthesis, as electroorganic transformation is considered as one of the green and sustainable synthetic strategies. Electrochemical reaction uses electron as an oxidant, and thus avoids the use of metal-catalysts and a large number of oxidants.[11] In the past years, several types of reactions, such as dehydrogenative cross-coupling,[12] dehydrogenative homo-coupling,[13] electrochemical difunctionalization of alkynes,[14] electrochemical difunctionalization of alkenes,[15] and cascade cyclization reaction[16] have been achieved through electrochemical oxidation. Since electrochemistry represents one of the most intimate ways of interacting with molecules, the development of new electrochemical organic transformations becomes very urgent. Inspired by the above elegant works,[12-16] we envisioned that whether the distal radical migration transformation can be achieved under electrochemical oxidative conditions.

Herein, we provide concrete support for this hypothesis. The first example of the electrochemical radical migration transformation is described (Scheme 1), which proceeds through tandem radical sulfonylation and alkynyl/alkenyl migration. This reaction used sodium benzene sulfinate as the sulfonyl source,[17] and was carried out under mild conditions, without the use of any catalyst or oxidant, to realize α-sulfonyl-β-alkynylation/alkenylation of alkenes. This protocol represents a new example of mild and green radical migration reaction and may provide new opportunities in the fields of electrochemical organic synthesis and alkene difunctionalization.



Scheme 1. Electrochemical radical migration.

Initially, the electrochemical oxidation reaction was carried out with 3-methyl-1-phenylhept-6-en-1-yn-3-ol **1a** and *para*-methylbenzenesulfinate **2a** as model substrates with the use of platinum-plate anode and cathode, and NH_4I as an additive. The reaction can occur at a constant current density of 2 mA/cm^2 in 1,4-dioxane/H_2O (1:1) at room temperature for 12 h, affording the desired product **3a** in 36% yield (entry 1, Table 1). Subsequently, other additives, such as NH_4Br and TBAB, were screened in this electrochemical system, and no obvious improvement on the chemical yield was obtained (entries 2−3). To our surprise, the reaction also proceeded smoothly without the addition of any additives, and the same level of yield was found (46% yield, entry 4). Next, several types of electrodes, including platinum-plate, nickel-plate, iron-plate and graphite plate were investigated for this reaction (entries 5−8). We found that when the graphite electrode was used for both the cathode and the anode, the reaction proceeded very well, and the corresponding product was obtained in 66% yield (entry 8). Then, a series of regular solvents were tested to further improve the reaction efficiency (entries 9−14). We found that the mixture of CH_3CN and H_2O (1:1) was the best choice, and the yield was further increased to 78% (entry 10). In sharp contrast, when CH_3CN was used as the sole solvent, only 12% yield of the corresponding product was obtained (entry 14). Finally, the

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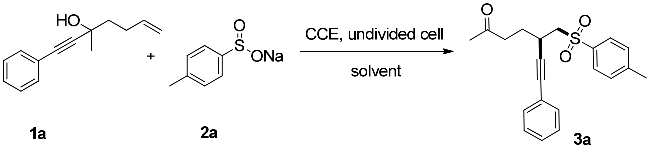
Supporting information for this article is given via a link at the end of the document.((Please delete this text if not appropriate)) variation on the current density and reaction time was not successful, and no improvement on the reaction yield was found.

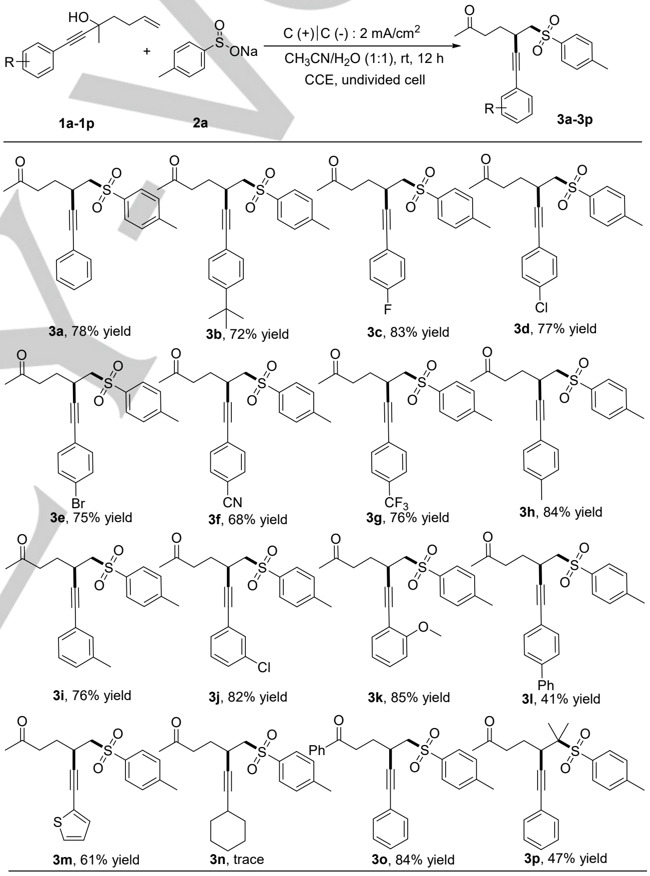
Table 1. Optimization of reaction conditions.[a]



Entry	anode/ cathode	additive (equiv)	electrolyte	Yield (%)[e]
1	Pt/Pt	NH_4I (0.5)	1,4-dioxane/H_2O (1;1)	36
2	Pt/Pt	NH_4Br (0.5)	1,4-dioxane/H_2O (1;1)	41
3	Pt/Pt	TBAB (0.5)	1,4-dioxane/H_2O (1;1)	43
4	Pt/Pt	-	1,4-dioxane/H_2O (1;1)	46
5	C/Pt	-	1,4-dioxane/H_2O (1;1)	48
6	C/Fe	-	1,4-dioxane/H_2O (1;1)	43
7	C/Ni	-	1,4-dioxane/H_2O (1;1)	52
8	C/C	-	1,4-dioxane/H_2O (1;1)	66
9	C/C	-	acetone / H_2O (1:1)	72
10	C/C	-	CH_3CN/ H_2O (1:1)	78
11	C/C	-	THF/ H_2O (1:1)	21
12	C/C	-	CH_3OH/ H_2O (1:1)	62
13	C/C	-	CH_3CN/ H_2O (1:2)	68
14	C/C	-	CH_3CN	12
15[b]	C/C	-	CH_3CN/ H_2O (1:1)	74
16[c]	C/C	-	CH_3CN/ H_2O (1:1)	32
17[d]	C/C	-	CH_3CN/ H_2O (1:1)	75

[a] Reaction conditions: graphite plate anode (1 cm×1 cm×0.3 cm), graphite plate cathode (1 cm×1 cm×0.3 cm), **1a** (0.3 mmol), **2a** (0.9 mmol), additive (0.5 equiv) and solvent (6 mL) were carried out in a undivided cell under an argon atmosphere conducted at a constant current 2 mA/cm^2 for 12 h (3.0 F). [b] 4 mA/cm^2. [c] 1 mA/cm^2. [d] 18 h. [e] Isolated yield.

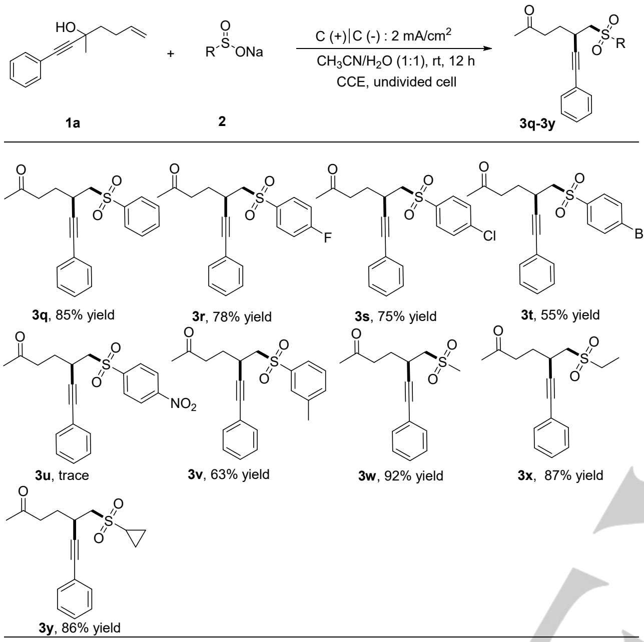
With the optimal conditions in hand, we next examined the substrate scope of various alkynyl-substituted tertiary alcohols by reacting with *para*-methylbenzenesulfinate **2a** (Scheme 2). As presented in Scheme 2, this new electrochemical radical 1,4-alkynyl migration reaction was found to be of a considerable degree of structural generality. Introduction of substituents at the *para*-position of the aromatic ring did not influence the reaction outcome. The substrates bearing the electron-donating groups (*tert*-butyl, methyl, **3b,3h**), and electron-withdrawing groups (fluorine, chlorine, bromine, trifluoromethyl, and cyano, **3c-3g**) worked very well in the reaction, affording the products in good yields (68-84%). In the case of no substituent on the phenyl ring, also good chemical yield was obtained (**3a**, 78%). The position of the substituent on the aromatic ring showed no effect on the reaction efficiency. For example, when the substrates containing *meta*-Me, *meta*-Cl, *ortho*-OMe substituted phenyl ring were used in the reaction, good chemical yields were obtained in 76%, 82%, and 85%, respectively (**3i**, **3j** and **3k**). Moreover, the reaction of a 2-thienyl reactant with *para*-methylbenzenesulfinate **2a** also proceeded smoothly and gave the product in 61% yield (**3m**). It is worth noting the reaction did not proceed when the cyclohexyl alkynyl-substituted tertiary alcohol **1n** was used as the substrate mainly because that the radical adjacent to the aliphatic cyclohexyl group is not stable. Fortunately, 1,6-diphenyl-4-(tosylmethyl)hex-5-yn-1-one was also a suitable substrate and afforded the desired product **3o** in 84% yield. The substrate **1p** bearing substituted C-C double bond was suitable, however only 47% of chemical yield was obtained mainly due to steric hinderance.



Scheme 2. Substrate scope of tertiary alcohols. (Reaction conditions: **1** (0.3 mmol), **2a** (0.9 mmol), CH_3CN/H_2O (6 mL), in an undivided cell under an argon atmosphere at a constant current (2 mA/cm^2) for 12 h (3.0 F). Isolated yields.)

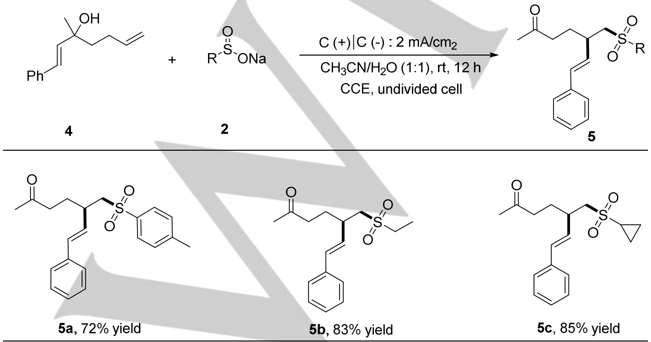
Then, the reaction scope with regard to the sodium sulfinates was explored by reacting with 3-methyl-1-phenylhept-6-en-1-yn-3-ol **1a**. As shown in Scheme 3, most of the examined aryl sulfinates were suitable substrates, affording the desired product in good chemical yields (55-85%). For example, benzenesulfinate and halogenated benzenesulfinates worked very well, and the corresponding products, **3q**, **3r**, **3s,** and **3t** were generated in 85%, 78%, 75% and 55% yields, respectively.

It is worth noting that sodium *para*-nitrophenylsulfinate was not compliant with the reaction, and no desired product **3u** was obtained, which is mainly because that the existence of strong electron-withdrawing group makes the sulfonyl radical unstable. Finally, the alkyl-substituted sodium sulfinates were also found to be suitable substrates for this electrochemical radical reaction, and the excellent yields were obtained (86%-92%, **3w**-**3y**). Especially, in the case of methyl sodium sulfinate, the highest chemical yield was obtained (**3w**, 92 % yield).



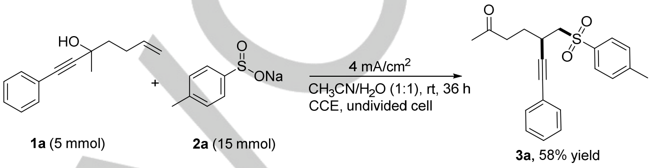
Scheme 3. Substrate scope of sodium sulfinates (Reaction conditions: **1h** (0.3 mmol), **2** (0.9 mmol), CH_3CN/H_2O (6 mL), in an undivided cell under an argon atmosphere at a constant current (2 mA/ cm^2) for 12 h (3.0 F). Isolated yields.)

To further extend the scope of the electrochemical radical migration reaction, we tried to investigate the possibility of the alkenyl migration in this system. To our delight, When (*E*)-3-methyl-1-phenylhepta-1,6-dien-3-ol was used as a substrate to react with sodium sulfinates, the reaction can also proceed smoothly via 1,4-migration, which gave the corresponding products in excellent yields (72-85%, **5a**-**5c**).



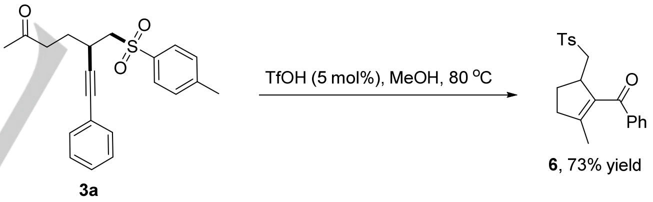
Scheme 4. Reaction of 3-methyl-1-phenylhepta-1,6-dien-3-ol **4** with sulfinates. (Reaction conditions: **4** (0.3 mmol), **2** (0.9 mmol), CH_3CN/H_2O (6 mL), in an undivided cell under an argon atmosphere at a constant current (2 mA/cm^2) for 12 h. Isolated yields.)

The scalability of this electrochemical 1,2-sulfonylation/alkynylation of alkene via radical alkynyl migration was then evaluated by performing 5 mmol scale reaction, which was conducted using inexpensive graphite plate. The reaction can proceed smoothly under a current density of 4 mA/m^2 for 36 hours with a yield of 58% (Scheme 5).



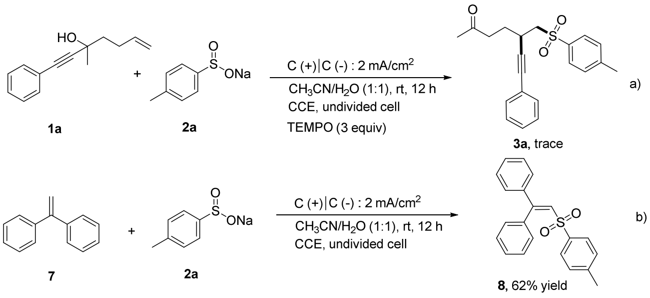
Scheme 5. Large-scale synthesis of reaction conditions: **1a** (5 mmol), **2a** (15 mmol), CH_3CN/H_2O (100 mL), graphite plate anode (5 cm×5 cm×0.5 cm), graphite plate cathode (5 cm×5 cm×0.5 cm), in an undivided cell under an argon atmosphere at a constant current (4 mA/ cm^2) for 36 h (27.0 F). Isolated yields.

We also investigated the follow-up chemistry[18] of this reaction by using **3a** as the starting material (Scheme 6). The cyclization of **3a** in the presence of TfOH afforded the α,β-unsaturated ketone **6** in 73% isolated yield.



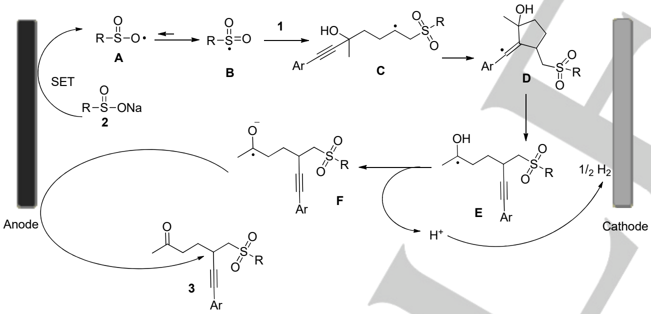
Scheme 6. Follow-up chemistry.

Finally, two control experiments were carried out to get insight into the reaction mechanism. We found that the reaction was totally inhibited when a radical inhibitor TEMPO (3 equiv) was added to the system under standard reaction conditions (Scheme 7a). When 1,1 diphenylethylene was added into the reaction under standard conditions, the adduct of (2-tosylethene-1,1-diyl)dibenzene **8** was isolated in yield 62% (Scheme 7b). These results indicate that the sulfonyl radical is involved in this reaction.



Scheme 7. Control experiments.

Based on the above experimental results and previous reports,[9,10,15] a plausible mechanism for this electrochemical radical migration reaction was proposed in Scheme 8. First sodium sulfinate **2** is oxidized at the anode to give the oxygen-centered radical **A**. The oxygen-centered radical **A** resonates to the more stable sulfonyl radical **B**. Then, the sulfonyl radical **B** adds to the terminal position of the alkene **1** to give the radical **C**. Subsequently, 1,5-radical cyclization of **C** leads to the vinyl radical **D**, which further undergoes the regioselective C–C bond cleavage to generate the radical **E**. Then, dehydrogenation of **E** will produce the ketyl radical intermediate **F**, which is oxidized at anode to afford the final product **3**. It should be mentioned that the catalytic cycle may also proceed via the reduction of intermediate **C** at cathode to form the anion, which then undergoes the Michael addition to alkyne, intramolecular liberation of alkyne, and oxidation to form the final product **3**.



Scheme 8. Proposed mechanism.

In summary, a novel electrochemical radical migration reaction alkynyl-substituted tertiary alcohols has been developed, which proceeded through sulfonylation of alkenes and alkynyl/alkenyl migration. The reaction used sodium sulfinates as sulfonyl sources, without the use of any metal-catalyst, additive, and oxidant, affording the corresponding α-sulfonyl-β-alkynylation product in good yields. The reaction represents a new and green strategy for the difunctionalization of unactive olefins and also the first electrochemical distal radical migration reaction.

Acknowledgements ((optional))

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Keywords: electrochemistry • radical migration • difunctionalization of alkenes • sulfonylation • green method

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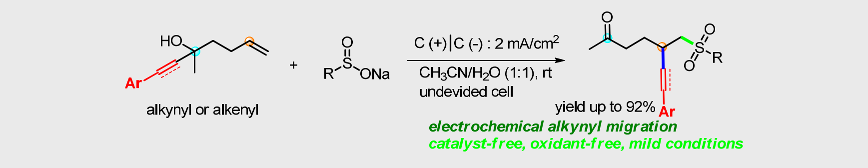

The first example of electrochemical alkynyl migration has been described, which used sodium sulfinates as sulfonyl sources affording the corresponding α-sulfonyl-β-alkynylation product in good yields. The reaction does not need any catalyst, additive, or oxidant, which represents a new and green strategy for the difunctionalization of unactive olefins.

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Electrochemical Alkynyl/Alkenyl Migration for the Radical Difunctionalization of Alkenes