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Electrochemical oxidative radical oxysulfuration of styrene derivatives with thiols and nucleophilic oxygen sources

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Oxydifunctionalization of olefins represents a powerful tool and yet a challenging task. Previous methods usually require a stoichiometric amount of a strong oxidant and an expensive transition-metal catalyst. This work describes the first example of the electrochemical oxysulfuration reaction of olefins with thiols and nucleophilic oxygen sources. This electrochemical difunctionalization reaction is conducted under catalyst- and oxidant-free conditions, and shows good substrate generality, affording thio-substituted alcohols, ethers and γ-lactones in good chemical yields and excellent regioselectivities. This work represents a new and green strategy for the difunctionalization of olefins, and also provides a complementary and highly valuable vista for the current methodologies of thio-substituted compounds synthesis.

Electrochemistry has been looked as one of the most direct ways of interacting with molecules, and electrons could interact with nucleus directly at anode and cathode.[1] This specialty of electrochemistry can be regarded as a kind of oxidant or reductant, which means that the organic synthesis could avoid the use of chemical oxidant or reductant in electricity environment. Thus, electrosynthesis has been recognized as a green technology[2] since it does not generate reagent waste.[2a,3] Furthermore, this process can be precisely controlled and conveniently stopped via the variation of voltage. Electrochemistry has been developed for a long history[1,4] and currently is gaining rising attention.[5] The Baran,[6] Waldvogel,[7] Yoshida,[8] Xu,[9] Lei[10] and other groups have independently developed a series of elegant electroorganic dehydrogenation cross-coupling reactions[11] and radical cascade reactions for the C-C,[7,12] C-O,[13] C-N,[6a,8b,10b,14] C-S,[9c,10c,15] N-S,[16] N-N,[6c] and N-P[17] bond formations.

Olefin is a kind of common building block in organic synthesis and fundamental structure unit existing in numerous natural products and pharmaceuticals.[18] The oxidative difunctionalization of the easily available olefins is an attractive method for the construction of the ubiquitous scaffold. Especially the oxydifunctionalization of olefins, such as oxytrifluoromethy-lation,[19] oxyarylation,[20] oxyalkylation[21] and oxysulfuration,[22] have attracted many research interests. Usually, these reported reaction systems need an oxidant and optionally a transition-metal catalyst. The use of large excess of oxidants, expensive and toxic metals or additives usually generates chemical wastes.

Electrochemical difunctionalization of alkenes currently emerged as a new approach for olefin difunctionalization that maximizes substrate generality, avoids using a strong oxidant, and minimizes by-product formation. The pioneering work was reported by the Lin group[23] on the difunctionalization of alkenes in which a single Mn-based electrocatalytic cycle was used to promote the addition to the C-C bond, which provides an environmentally friendly method that converts alkenes to 1,2-diazides, 1,2-dichlorides, and chlorotrifluoromethylated compounds. In the recent years, the S-H activation is also one of the most hot topics in organic chemistry, and a notable development has been made.[10a,24] To the best of our knowledge, the oxysulfuration of alkenes under electrochemical conditions has never been explored. Also, it was found that the use of oxidants in the previous oxysulfuration reactions, thiols/thiophenols can be easily over-oxidized to generate undesirable side products, such as sulfoxides and sulfones.[22a,25] Thus, the use of electrooxidation could provide a solution to the above over-oxidation problem, as the oxidative ability could be conveniently adjusted and by the variation of voltage.[10a] Notably, the Yoshida group developed an addition reaction of diaryl disulfides to carbon–carbon multiple bonds using electrochemistry affording the corresponding diarylthio-substituted compounds in good yields.[26]

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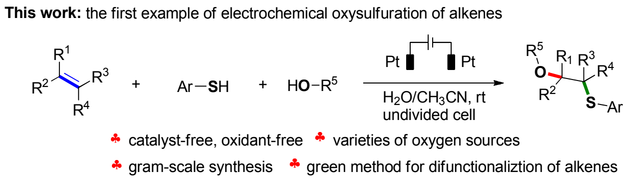
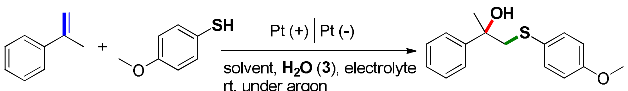
Inspired by recent developments in the area of synthetic electrochemistry[23] and challenged by the problems in the previous systems,[22a,25] we herein reported the first example of electrochemical radical oxysulfuration of olefins with thiols and nucleophilic oxygen sources. This reaction was conducted at room temperature and did not need any oxidative reagent, catalyst or additive. Furthermore, this reaction showed wide substrate scope, broad functional group tolerance, and excellent regioselectivity, which represents a new and green strategy for the difunctionalization of olefins.



Scheme 1 Electrochemical difunctionalization of olefins.

Initially, the electrochemical reaction of prop-1-en-2-ylbenzene **1a** with 4-methoxybenzenethiol **2a** by the use of platinum-plate anode and cathode, and NaCl as an electrolyte, was conducted at 3.0 V cell potential in H_2O/MeCN at room temperature under argon atmosphere for 5 h. The corresponding product 1-((4-methoxyphenyl)thio)-2-phenylpropan-2-ol **4** was obtained in 51% isolated yield (entry 1, Table 1). Then, the voltage for this reaction was screened, and the results in entries 1-3 indicated that 3 v was the best one. Next, it was found that increasing the loading amount of electrolyte NaCl from 0.5 to 1.0 equiv, resulting in a decreased chemical yield (33%, entry 4). To further optimize the reaction conditions, other electrolytes, such as Bu_4NBr and Bu_4NBF_4 were used in the reaction (entries 5-6). Bu_4NBF_4 worked better in this reaction and afforded obviously improved yield (62%, entry 6). When 4 equivalent of thiophenol **2a** was used in the reaction, a further increased yield of product **4** was obtained (76%, entry 7). 80% yield of the product **4** was obtained when the reaction time was prolonged to 8 hours. Finally, when acetonitrile (4 mL) was added as the co-solvent for this reaction, the desired product 4 was obtained in a slightly higher chemical yield (83%, entry 9).

Table 1 Optimization of the reaction conditions.[a]



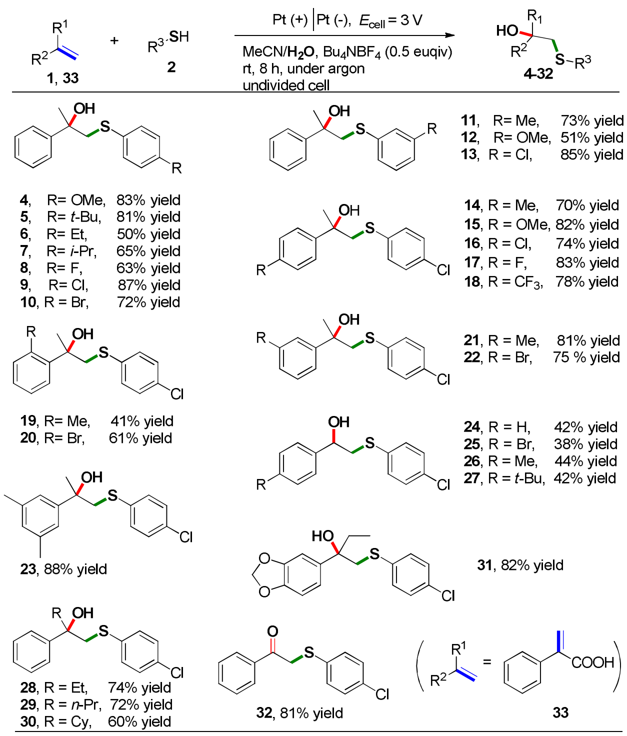
1a **2a** **4**

Entry	Voltage (V)	Electrolyte (equiv)	Time (h)	Yield (%)[b]
1	3.0	NaCl (0.5)	5	51
2	4.0	NaCl (0.5)	5	49
3	5.0	NaCl (0.5)	5	45
4	3.0	NaCl (1.0)	5	33
5	3.0	Bu_4NBr (0.5)	5	56
6	3.0	Bu_4NBF_4 (0.5)	5	62
7[c]	3.0	Bu_4NBF_4 (0.5)	5	76
8	3.0	Bu_4NBF_4 (0.5)	8	80
9[d]	3.0	Bu_4NBF_4 (0.5)	8	83

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.6 mmol), water (2 mL) and MeCN (3 mL) under argon. [b] Isolated yield based on **1a**. [c] 4 equivalent of **2a**. [d] 4 mL of MeCN was added.

With the optimal reaction conditions in hand, we then investigated the substrate scope of this reaction by using various thiophenols, alkenes, and nucleophilic oxygen sources (Table 2).

Table 2 Substrate scope of alkenes and thiols.[a,b]



[a] Reaction conditions: Pt anode, Pt cathode, at 3.0 V cell potential, alkenes (0.2 mmol), thiophenol (0.8 mmol), Bu_4NBF_4 (0.1 mmol), water (2 mL) and MeCN (4 mL) under argon, at room temperature for 8 h. [b] Isolated yields.

Thiophenols **4–10** bearing substituted group, such as methoxyl (**4**), alkyl (**5–7**) and halo (**9–10**) on the *para*-position of the aromatic ring, worked very well in this system resulting in the corresponding product in good yields (50-83%). Reactions of the *meta*-substituted thiophenols also proceeded smoothly to give the desired product with good to excellent yields (51-85%, **11–13**). We then turned our attention to investigate another part of substrate generality by using a

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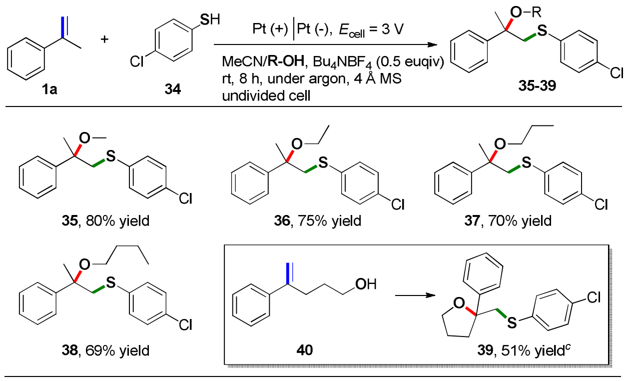
different kind of alkenes in this electrochemical oxidative radical oxysulfuration reaction (**14–32**). It was pleased to find that the *para*-substituted prop-1-en-2-ylbenzenes participated in this reaction very well. Both the electron-donating (**14–15**) and electron-withdrawing groups (**16–18**), even the strong electron-withdrawing group, trifluoromethyl, were well tolerated and afforded the satisfactory results. Next, we investigated the steric hindrance of this reaction by using the *ortho*- and *meta*-substituted prop-1-en-2-ylbenzene as substrates (**19–22**). It was found that there was a strong steric effect in this system, as the obviously decreased yields were obtained for the *ortho*-substituted alkenes (41-61%, **19–20**). Especially, an excellent yield (88%) was obtained when 1,3-dimethyl-5-(prop-1-en-2-yl)benzene was used (**23**). To further extend the alkene scope of the reaction, a series of styrene derivatives were examined in this system. However, obviously lower chemical yields were obtained (38-44%, **24–27**). It is mainly because that this reaction proceeds via a radical process, and the tertiary benzyl radical, generated from sulfur radical addition to styrene, is less stable than quaternary carbon radical. Finally, different terminal olefins were tried in this electrochemical system (**28–32**). Styrenes with different α-substituted alkyl, include ethyl, isopropyl, and cyclohexyl, were all suitable substrates for this reaction, giving the expected product in good yields (**28–30**). Even the reaction of 5-(but-1-en-2-yl)benzo[d][1,3]dioxole also could proceed well to give the corresponding product in a good yield (82%, **31**). In particular, a carbonylation product **32** could be obtained when 2-phenylacrylic acid (**33**) was chosen as the alkene.

As the next objective of our investigation, we sought to demonstrate the generality of our approach that other nucleophilic oxygen sources, such as primary alcohols, could be also applied in this method to construct corresponding ether derivatives (Table 3). To eliminate the impact of water existing in the solvent, 4 Å molecular sieve was added in this reaction. Gratifyingly, a series of primary alcohols reacted very well with alkenes **1a** and thiols **34** to afford the corresponding ethers **35**–**38** in good chemical yields (69-80%). To our delight, when 4-phenylpent-4-en-1-ol (**40**) containing alkenyl and hydroxyl moieties was used as a substrate, a functionalized tetrahydrofuran **39** was obtained in 51% yield.

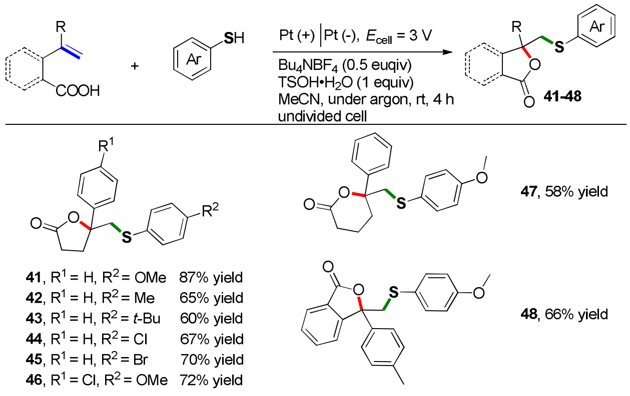
Table 3 Substrate scope of primary alcohols.[a,b]



[a] Reaction conditions: Pt anode, Pt cathode, at 3.0 V cell potential, alkenes (0.2 mmol), thiophenol (0.8 mmol), Bu_4NBF_4 (0.1 mmol), 4 Å molecular sieve (200 mg), alcohol (2 mL) and MeCN (4 mL) under argon at room temperature for 8 h. [b] Isolated yield. [c] 4-phenylpent-4-en-1-ol (**40**) (0.2 mmol), MeCN (6 mL) used.

Thio-substituted γ-lactone is a kind of useful drug molecular framework. It has been proven that there is antiviral activity against poliovirus, RNA virus and herpes simplex virus type 1 (HSV-1).[27] Unsaturated carboxylic acid is a simple, easy to prepare and efficient intermediate to construct these substituted lactone derivatives via cascade thiolation and intramolecular cyclization. Our group developed the first example of thio-substituted γ-lactone synthesis by using unsaturated carboxylic acid in the presence of a chemical oxidant.[28] It gives us the inspiration to demonstrate the application of the current electrochemical oxysulfuration approach in the synthesis of thio-substituted γ-lactones (Table 4). Thus, a series of substituted thiophenols and unsaturated carboxylic acids were tested in this electrochemical system. Generally, both electron-donating group (**41–43**) and electron-withdrawing group (**44–45**) substituted thiophenols were all compatible in this system, and gave the corresponding lactones with good to excellent yields (58-87%). Different kind of unsaturated carboxylic acids, like 5-(4-methoxyphenyl)hex-5-enoic acid and 2-(1-(p-tolyl)vinyl)benzoic acid were also suitable substrates and gave the corresponding lactones with a six-membered ring (**47**) or benzohetercyclic ring (**48**).

Table 4 Application of this method in thio-substituted γ-lactones synthesis.[a,b]



[a] Reaction condition: Pt anode, Pt cathode, at 3.0 V cell potential, unsaturated carboxylic acids (0.2 mmol), thiophenol (0.6 mmol), Bu_4NBF_4 (0.1 mmol), TSOH • H_2O (0.2 mmol) and MeCN (6 mL) under argon at room temperature for 8 h. [b] Isolated yield.

We evaluated the scalability of this electrochemical oxidative radical oxysulfuration of alkenes by performing this reaction on a 5 mmol scale. The reaction of prop-1-en-2-ylbenzene (**1a**), 4-chlorobenzenethiol (**34**) and water proceeded smoothly and the desired hydroxysulfide **9** was obtained in 62% yield (0.86 g, Scheme 2). This result shows the great potential of this electrochemical oxidative radical oxysulfuration of alkenes in practical synthesis.

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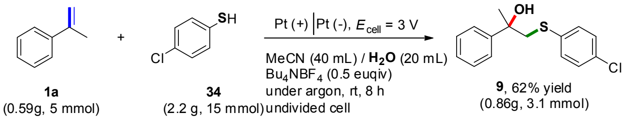
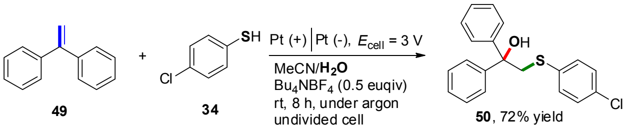


Scheme 2 Gram-scale synthesis.

To get the insight of this electrochemical oxysulfuration reaction, a series of control experiments were conducted (Scheme 3). A radical-trapping experiment has been carried out under standard reaction conditions, with the use of toluylene (**49**) as the radical-trapping reagent (Scheme 3). After the careful isolation of reaction mixture, the trapping product **50** was obtained with 72% yield. Thus, radical intermediates are possibly involved in this electrochemical system. Next, we carried out cyclic voltammetry (CV) experiments to study the redox potential of the substrates (Figure 1). An oxidation peak of **34** in acetonitrile was observed at 1.99 V and reduction peak at -1.33 V. Therefore, between the reaction voltage, the thiophenol may be both involved in oxidation and reduction process in this system.



Scheme 3 Mechanistic studies.

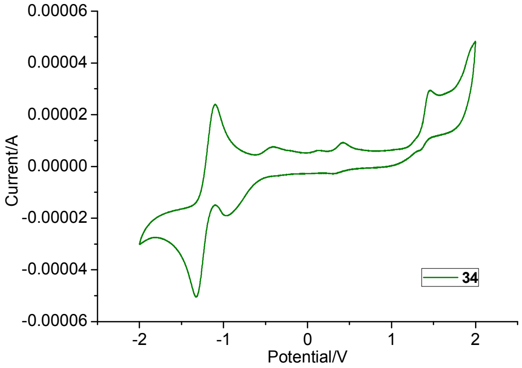
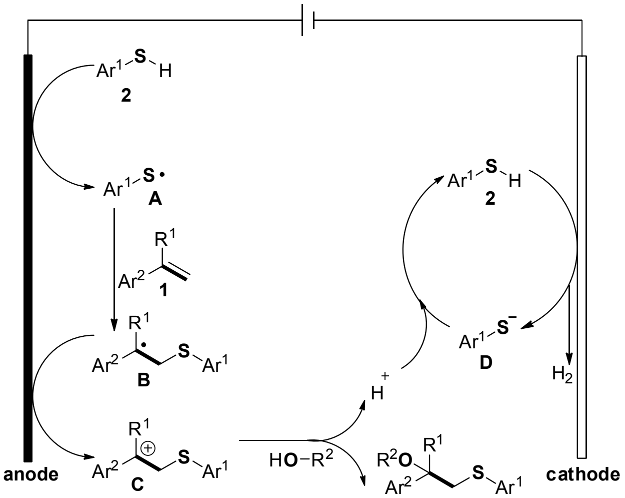


Figure 1. Cyclic voltammetry of **34** (10^{-4} M) in CH_3CN with *n*-Bu_4NPF_6 (0.2 M). Conditions: glassy carbon working electrode, Pt wire counter electrode, SCE reference electrode, scan rate = 0.2 V· s^{-1}.

Based on the previous reports[9,10,22,28] and the above experimental results, a possible electrochemical oxidative radical reaction mechanism is shown in Scheme 4.



Scheme 4 Proposed mechanism.

Initially, the aryl sulfur radical **A** is generated from thiophenol **2** via a SET oxidation at the anode.[10a] Then, this aryl sulfur radical **A** adds to alkene **1** affording the radical intermediate **B**, which is rapidly oxidized to carbocation intermediate **C** at the anode. Then, this carbocation **C** is trapped by the nucleophile to afford the final oxysulfuration product as well as a hydrogen ion. At the same time, thiophenol **2** is reduced to release hydrogen gas and aryl sulfur anion **D** at the cathode, which reacts with hydrogen ion to regenerate thiophenol **2** for the next cycle.

Conclusions

In conclusion, we have developed a mild and electrochemical oxidative reaction for the oxysulfuration of olefins. This method enables the difunctionalization of olefins via cascade two oxidations at anode under catalyst- and oxidant-free conditions. The reaction shows good substrate generality, and several types of nucleophilic oxygen sources are suitable for this transformation. Most importantly, this reaction can be conducted on a gram scale with good reaction efficiency, and such electrochemical system has been successfully applied in the synthesis thio-substituted γ-lactones with high yield. This work represents a new and green strategy for the difunctionalization of olefins, and also provides a complementary and highly valuable vista for the current methodologies of thio-substituted compounds synthesis.

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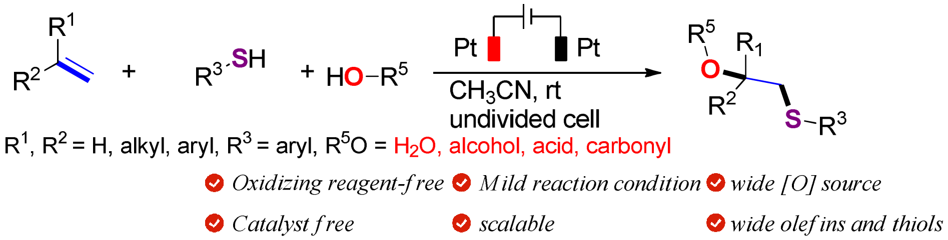

The first example of the electrochemical oxysulfuration reaction of alkenes with thiols and nucleophilic oxygen sources has been reported.