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Strategies for the direct oxidative esterification of thiols with alcohols

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This review paper provides an overview of the main strategies for the oxidative esterification of thiols with alcohols. The review is divided into two major parts according to final products. The first includes the methods for the synthesis of sulfinic esters, while the second contains the procedures for the fabrication of sulfonic ester derivatives.

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1. Introduction

Organosulfur compounds are some of the most versatile building blocks in organic chemistry and occupy a very special place in medicinal, pharmaceutical, and agricultural science.[1,2] In this family of compounds, sulfinic and sulfonic esters are of interest due to their biological and therapeutic activities[3,4] as well as their application as chemical probes in living cell imaging (Scheme 1).[5,6] Furthermore, the title compounds are highly useful synthetic precursors and intermediates in organic synthesis. For example, sulfinic esters were recently applied as efficient sulfenylating agents[7] and sulfonic esters as sulfonylating agents.[8] The classical methods for the synthesize of these classes of organosulfur compounds involve the reaction of sulf(o,i)nyl chlorides,[9,10] sulf(o,i)nic acids,[11,12] or sodium sulfonates[13] with alcohols. However, corrosion, instability, and/or difficult preparability of some of the sulf(i,o)nylating agents limited the utility of these methods.

In the light of the above limitations and due to the versatile synthetic and biological activity of the titled compounds, their synthesis from easily accessible basic starting materials under mild conditions is a field of growing research interest. In this context, recently, the direct oxy-esterification of thiols with alcohols has emerged as an ideal atom- and step-economic strategy for the construction of these compounds which makes the synthetic route more quick and clean than conventional pathways that relay on the use of pre-functionalized starting materials. As a continuation of our previous works on modern synthetic methods in organic chemistry[14] and novel strategies in the preparation of organosulfur compounds,[15] in this review, we will highlight the most important developments on the synthesis of sulfinic and sulfonic esters through the direct oxidative esterification of thiols with alcohols (Fig. 1) with emphasis on the mechanistic features of the reactions, by hoping that it further stimulating research and development of this interesting field. It is noteworthy that, despite wide biological and synthetic importance of sulfenic ester derivative,[16,17] to date no reporting guideline exists for their direct construction from the corresponding thiols and alcohols. Therefore, in this review no comment was made regarding the cross-dehydrogenative coupling between thiols and alcohols.

2. Synthesis of sulfinic esters

In this section we would like to focus on the oxidative esterification of thiols with alcohols into sulfinic esters. To aid the reading, the section is divided into three sub-sections according to catalytic systems. The first includes the electrochemical reactions, the second contains the metal-catalyzed reactions, and the third covers metal-free reactions.

2.1. Electrochemical reactions

Electrochemistry provides some of the greenest, cleanest, and more cost-efficient synthetic strategies, as the use of often hazardous or waste-generating chemical reductants or oxidants can be substituted by electrical power.[18] In this context, electrochemical oxidative cross-coupling reactions have recently attracted tremendous attention as cleaner and more sustainable synthetic alternative to traditional coupling procedures which rely on the use of external oxidants, catalysts or ligands.[19]

The first report on the electrochemical oxidative esterification of thiols with alcohols was published by Nokami and co-workers in 1979,[20] who showed that the treatment of thiophenol **1** with aliphatic alcohols **2** in an undivided cell with platinum electrodes, employing NaOAc as the supporting electrolyte in acetic acid, resulted in the formation of alkyl phenylsulfinates **3** in good to excellent yields (Scheme 2a). The

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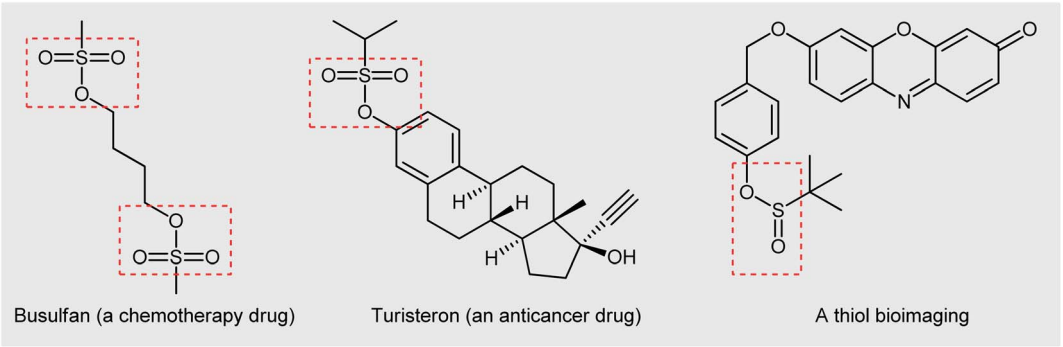

Scheme 1 Selected examples of commercial sulfonic ester drugs and a thiol bioimaging sulfinic ester compound.

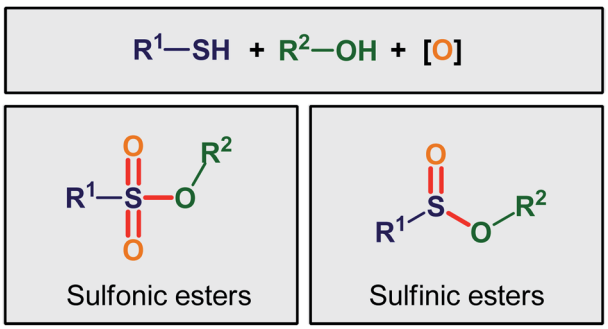

Fig. 1 Direct oxidative esterification of thiols with alcohols.

diphenyldisulfide was also examined under the identical conditions and the desired products were obtained in satisfactory yields. However, the excess use of alcohols would be a significant drawback for this protocol and may limit its range of applications. Moreover, in this preliminary work, only one thiol was employed, without any substrate scope exploration. Four decades later, Gong and Lu along with their co-workers developed a robust electrochemical oxidative cross-coupling between thiophenols **4** and aliphatic alcohols **5** for the synthesis of alkyl benzenesulfinates **6**.[21] In an undivided cell assembled with a graphite rod anode and platinum plate cathode, the best reaction conditions were achieved with tetrabutylammonium tetrafluoroborate ($^{n}Bu_4NBF_4$) as the electrolyte and acetonitrile as the solvent, with a constant current of 12 mA under air atmosphere at room temperature (Scheme 2b). A broad reaction scope was evaluated by testing different groups on the thiophenol ring (*e.g.*, OMe, F, Cl, Br), as well as a variety of aliphatic (primary and secondary) alkyl/benzyl alcohols. Notably, the authors demonstrated the scalability of the reaction since methyl 4-methylbenzenesulfinate could be obtained in 1.62 g scale in excellent yield of 95%. The importance of air atmosphere was evaluated and in the presence of N_2 atmosphere no product was formed. Therefore, they suggested that the source of sulfoxides oxygen comes from air oxygen. The radical trapping experiments with (2,2,6,6-tetramethylpiperidin-1-yl)oxy (TEMPO) confirmed that this reaction most likely proceeds *via* a radical pathway (Scheme 3). Initially, a disulfide intermediate **A** was formed *via* homocoupling of *in situ* generated thiyl radical by the anodic oxidation of starting thiol **4**. In the next step, this intermediate **A** underwent a further single-electron oxidation to form a disulfide radical cation **B**. After that, the newly formed radical **B** was reacted with superoxide radical anion ($O_2^{\bullet-}$), generated from the reduction of O_2 at the cathode, and provided the intermediate **C**. Thereafter, the addition of alcohol **5** to this species **C** gave intermediate **D** which subsequently delivered sulfide anion **E** and intermediate **F**. Finally, reduction of **F** at the cathode gave the desired product **6**.

Shortly afterwards, Ling–Zhong's research group disclosed a similar electrocatalytic oxidative esterification of thiols **7** with alcohols **8** under mild conditions which exhibited considerably better substrate scope when compared to the previous works.[22] The transformation was performed in an undivided cell under a constant current of 6 mA with platinum plates as electrodes employing $^{n}Bu_4NBF_4$ as the electrolyte and DCM as the solvent under an inert atmosphere, which afforded the sulfinic ester products **9** in 58–90% yields. Noteworthy, the constant current affected the reaction dramatically; either increasing or decreasing the constant current led to decreased efficiency. As shown in Scheme 4 this electrochemical reaction is applicable for not only aromatic and heteroaromatic thiols but also aliphatic thiols. However, like previous works, the scope of alcohols was restricted to the use of aliphatic and benzylic alcohols. Based on the experimental results, the authors suggested that alcohols may act not only as reactants but also as oxidants to oxidize the S(II) to S(IV) species. The isotopic labelling experimental using $H_2{}^{18}O$ indicated that oxygen in sulfur could also come from water.

In 2020, Wei and co-workers reported a closely related electrochemical oxidative cross-coupling reaction of thiols **10** with alcohols **11** employing an undivided cell with platinum electrodes and tetrabutylammonium chloride ($^{n}Bu_4NCl$) as the supporting electrolyte.[23] The reaction was conducted in MeCN under ambient conditions and yields of up to 81% were obtained (Scheme 5a). The reaction, however, appears to be limited to aromatic thiols and aliphatic alcohols. The synthetic applicability of the reaction was nicely demonstrated by converting some of the prepared sulfinic esters to thioether, diaryl sulfoxide, trifluoromethyl sulfoxide, and thiosulfonate derivatives. Notably, when the reaction was performed under O_2

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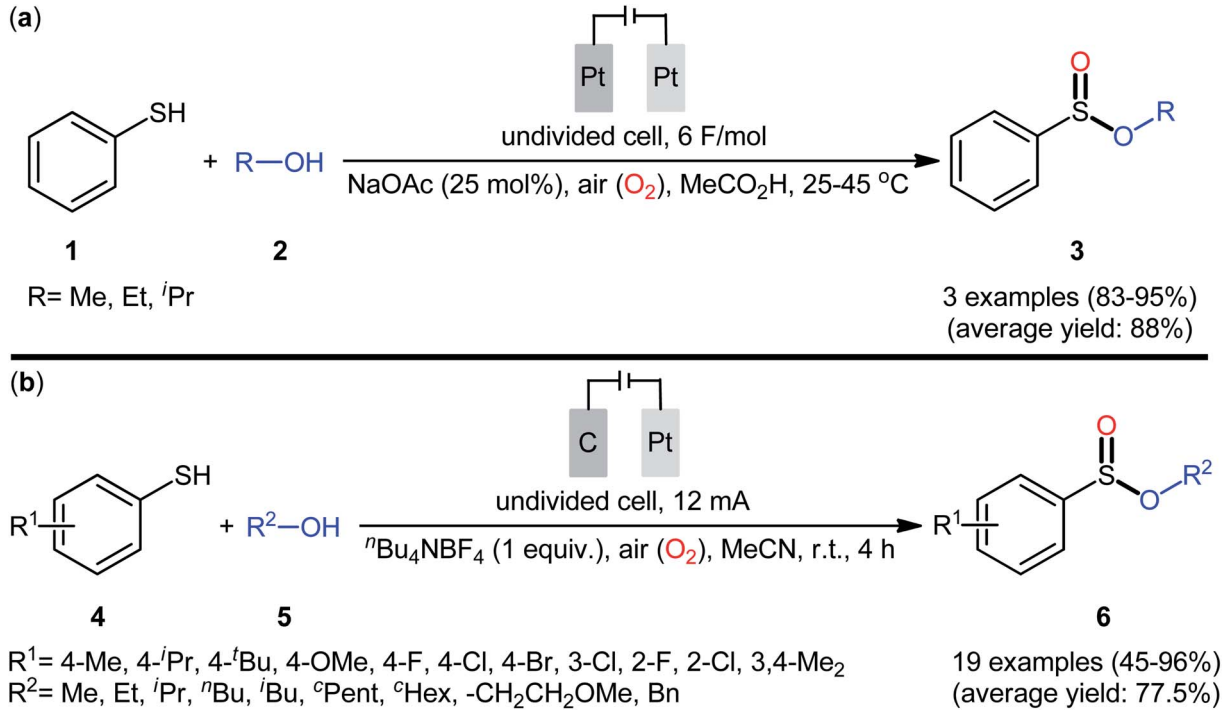
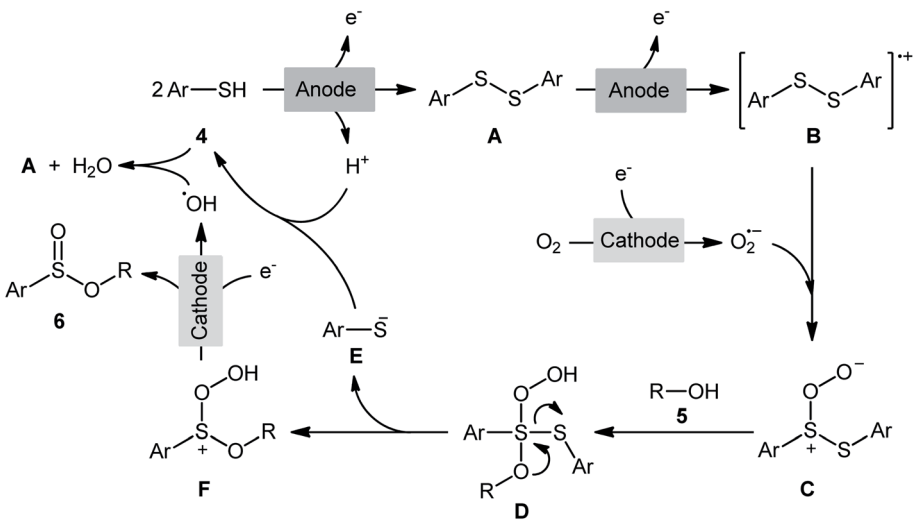


Scheme 2 (a) Electrooxyesterification of thiophenol 1 with aliphatic alcohols 2 to alkyl phenylsulfinates 3; (b) electrochemical synthesis of alkyl benzenesulfinates 6 from thiophenols 4 and alcohols 5.

atmosphere, sulfonates were obtained instead of the desired sulfinates, however, this transformation proceeded more slowly. In the same year, Yang and Wang along with their co-workers demonstrated the similar esterification under electrochemical and catalyst-free conditions.[24] The transformation was carried out in an undivided cell with platinum plate electrodes at room temperature by using $LiClO_4$ as the supporting electrolyte, under 10 mA in MeCN. Under these conditions several thiophenol derivatives **13** carrying various substituents (*e.g.*, OMe, F, Cl, Br) on different positions of phenyl rings were converted to the corresponding alkyl phenylsulfinates **15** in moderate to excellent yields by treatment with aliphatic alcohols **14** (Scheme 5b). However, benzyl thiols were inert under the standard conditions and applicability of aliphatic thiols as starting materials was not investigated in this study. Regarding the reactivity of alcohols, primary alcohols were found to be more reactive than the secondary alternatives. The results also proved that the lengths of carbon chain in alcohols had no impact on the outcome of the reaction. Of note, the authors demonstrated the scalability of the reaction since methyl



Scheme 3 Proposed mechanism for electrosynthesis of sulfinic esters 6.

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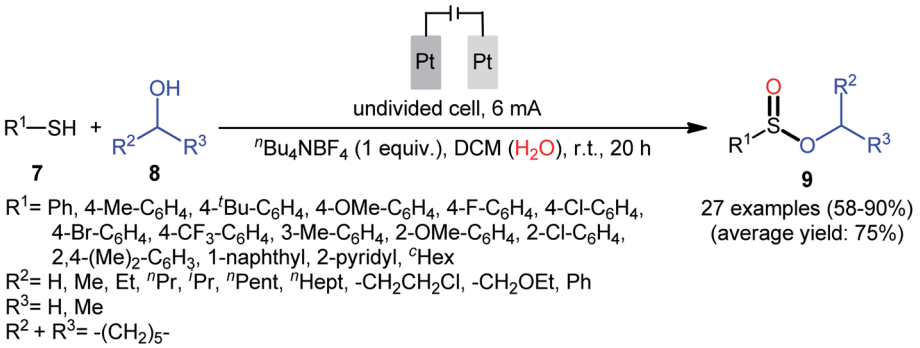
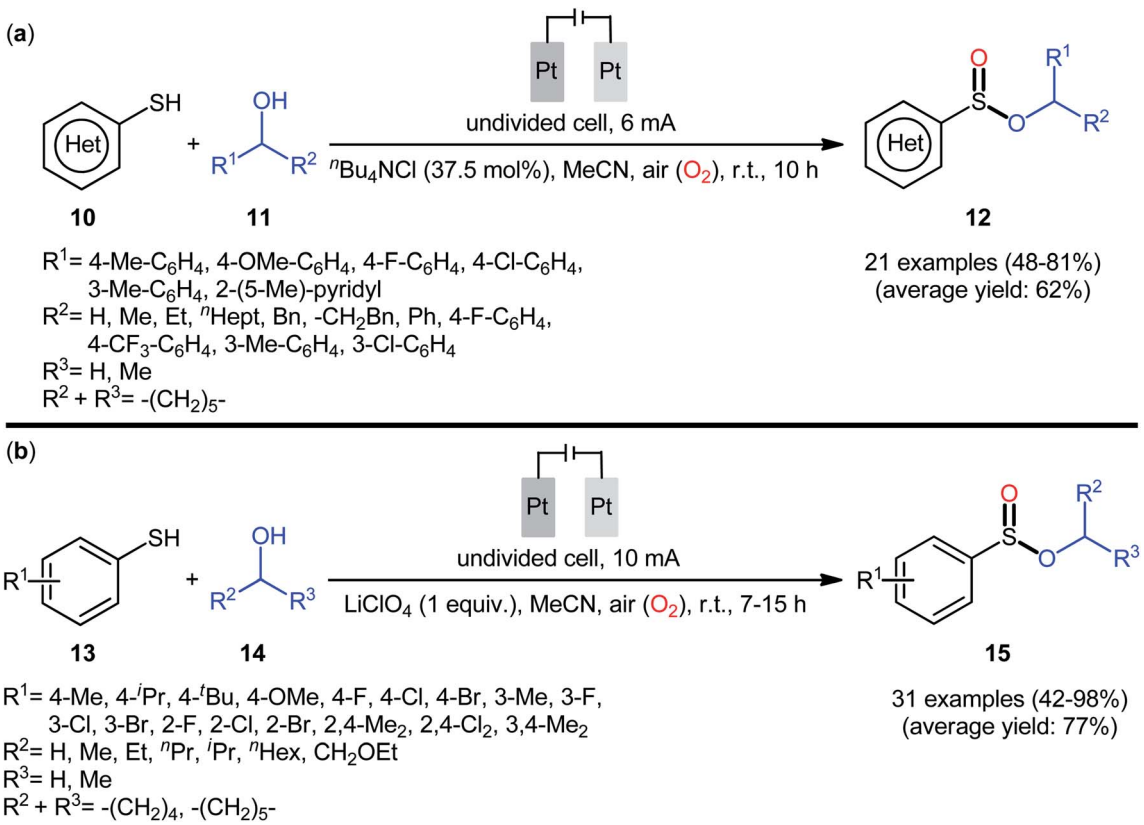


Scheme 4 Ling–Zhong's synthesis of sulfinic esters **9**.

benzenesulfinate could be obtained in 1.43 g scale in high yield of 84%. Based on some control experiments, the O_2 in air proved to be the sole oxygen source.

Concurrently, Kaboudin and co-workers developed an interesting electrochemically enabled nickel-catalyzed methodology for oxidative dehydrogenative coupling between thiols **16** and alcohols **17** under ambient conditions.[25] The efficient combination of $Ni(ClO_4)_2$, 2,2′-bipyridine and $LiClO_4$ with a modified graphite anode and nickel foam cathode in an undivided cell, under constant current of 10 mA, provided the sulfinic esters **18** in modest to high yields, ranging from 35% to 92% (Scheme 6). It is noteworthy that the presence of both catalyst and electricity were crucial for the success of this reaction. No transformation was observed without any of them. Concerning the substrate scope, the protocol limited to the use of only (4-methyl)benzenethiols and simple aliphatic alcohols. Based on a series of control experiments and literature, a plausible mechanism was suggested for the formation of sulfinate esters **18**, as illustrated in Scheme 7. The reaction starts with the formation of a thiyl radical **A** *via* anodic oxidation of the starting thiol **16** and Ni(0) by cathodic reduction of the nickel complex. Next, the interaction of the thiyl radical **A** with Ni(0) in the



Scheme 5 (a) Electrochemical oxidative cross-coupling reaction of thiols **10** with alcohols **11** to sulfinic esters **12**; (b) Yang–Wang's synthesis of sulfinic esters **15**.

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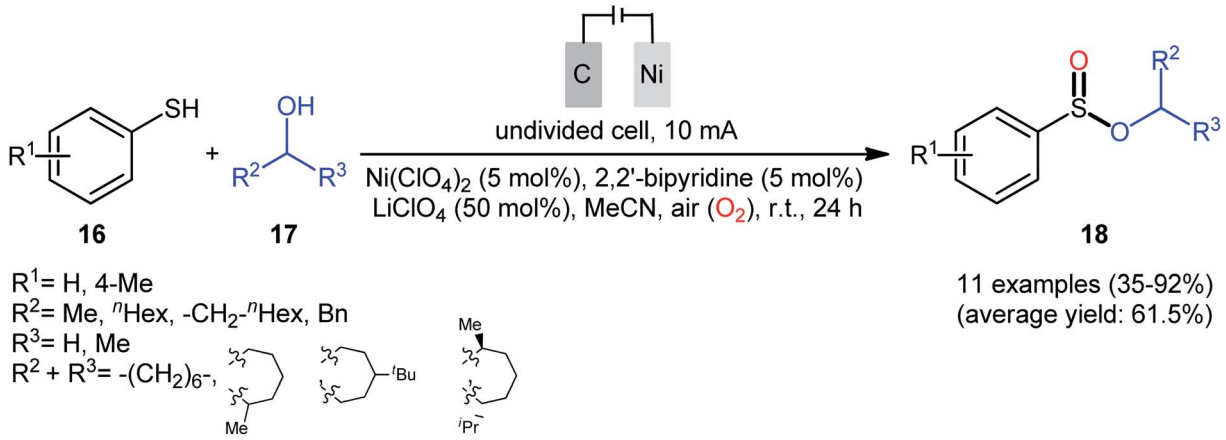


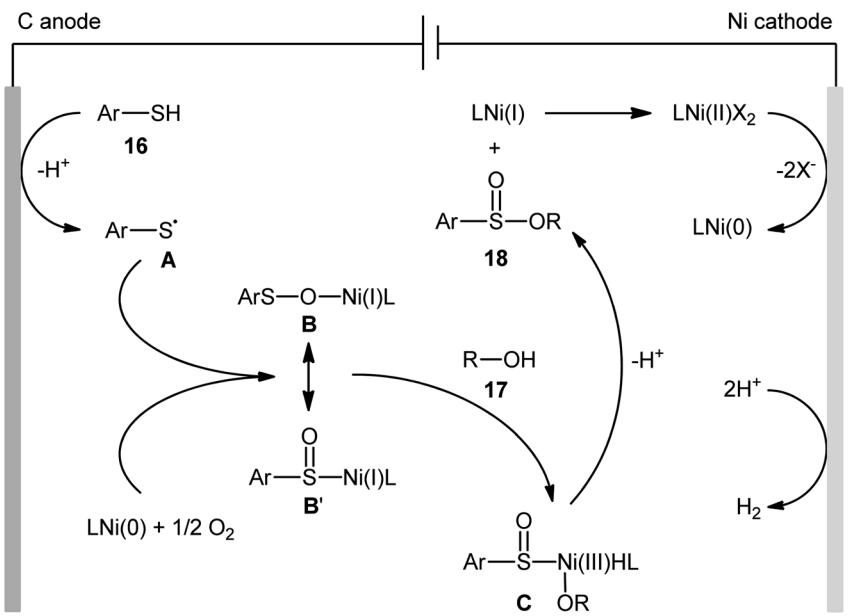
Scheme 6 Electrochemical nickel-catalyzed oxidative cross-coupling between thiols **16** and alcohols **17**.

presence of oxygen gives rise a thiyloxy-Ni(I) complex **B**. Subsequently, the newly formed complex (or its isomer) undergoes an oxidative addition with alcohol **17** to provide a sulfinate-Ni(III) complex **C**. Finally, the reductive elimination of this complex **C** leads to the desired sulfinate ester **18** and regenerates the catalyst.

In the same year, with the aim of designing a metal-free protocol to sulfinic esters through the electrochemical oxidative esterification of thiols and alcohols, Dai and co-workers were able to reveal that a divers set of functionalized sulfinic esters (27 examples) could be prepared in moderate to excellent yields (up to 92%) from the reaction of corresponding (hetero) aromatic thiols with aliphatic alcohols under mild conditions employing an undivided cell with graphite plates as electrodes.[26]

2.2. Metal-catalyzed reactions

Drawing inspiration from the pioneering work by Field and co-workers on $Pb(OAc)_4$-catalyzed one-pot preparation of sulfinic esters from disulfides and alcohols.[27] In 2016, Jang's research group studied the possibility of synthesizing sulfinic esters from the corresponding thiols and alcohols under transition-metal-catalyzed conditions.[28] By considering the coupling of thiophenol with benzyl alcohol as the model reaction, the reaction variables such as catalysts, ligands, additives, and solvents were carefully screened. The results indicated that the merge of 5 mol% of CuI with 10 mol% of triazabicyclodecene (TBD) was the most appropriate catalytic system for this transformation and among the various common solvents (*i.e.*, toluene, dioxane, THF, DMF, DMSO, MeCN); THF was found to be the most suitable solvent. Under optimum conditions, a library of alkyl/benzyl phenylsulfinates **21** were selectively obtained in modest



Scheme 7 Proposed mechanism for reaction in Scheme 6.

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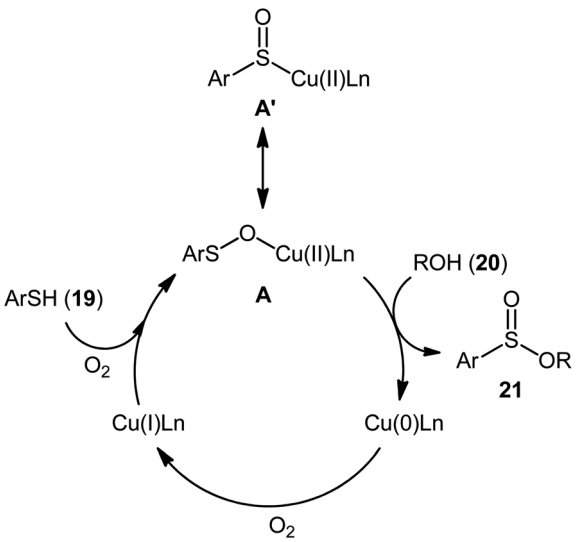
to excellent yields by reaction of various thiophenol derivatives **19** with alkyl/benzyl alcohols **20** under 1 atmosphere of oxygen at 65 °C (Scheme 8). The results indicated that the electron-deficient thiophenols afforded better yields compared to the electron-rich ones and benzylic alcohols gave higher yields than aliphatic alcohols. It should be mentioned that in the case of aliphatic alcohols, the amount of TBD was increased to 1 equivalent. Under the identical conditions, the reactions of aliphatic thiols with benzyl alcohols were also investigated. However, in these cases, benzyl benzoates were obtained instead of the desired sulfinic esters through the oxidation of starting thiols to form the respective thioaldehydes, followed by reaction with benzyl alcohols to afford benzyl benzoates *via* oxidative esterification followed by S–O exchange. Moreover, in this study the authors found some other limitation in their procedure, when they used heteroaromatic thiols (*e.g.*, 2-mercaptobenzimidazole, 2-mercaptopyrimidine, and 4-mercaptopyridine) as substrates. Unfortunately, in all cases no desired product was observed. Based on the experimental results, a plausible mechanism was proposed by the authors for this esterification protocol which involves the following key steps (Scheme 9): (i) oxidation of thiophenol **19** in the presence of the copper catalyst to generate thiyl radical; (ii) formation of thiyloxy-Cu(II) complex **A** (or its isomer) *via* interaction of *in situ* generated thiyl radical with the Cu(I) catalyst; (iii) addition of alcohol **20** to complex **A** (or **A′**) to give the observed product **21** and Cu(0) species; and (iv) oxidation of Cu(0) with O_2 to recover the Cu(I) catalyst and completes the catalytic cycle.

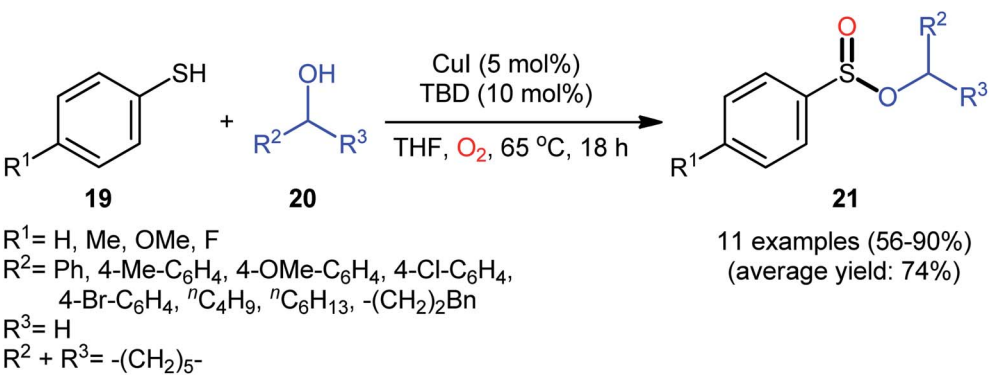
Two years later, Zhang and co-workers introduced ultrafine cobalt nanoparticles supported on N–SiO_2-doped activated carbon (Co/N–SiO_2-AC) as an efficient catalyst for oxidative esterification of thiols with alcohols.[29] Hence, a diverse range of functionalized sulfinic esters **24** were obtained in moderate to excellent yields through the reaction of corresponding thiols **22** with alkyl/benzyl alcohols **23** in the presence of 1.46 mol% Co/N–SiO_2-AC as catalyst and 2 equiv. of K_2CO_3 as a base under O_2 atmosphere at 60–80 °C. As shown in Scheme 10, apart from aromatic and heteroaromatic thiols, aliphatic thiols were also compatible with this scenario. The reaction also showed good tolerance to a number of important functional groups such as the methoxy, amino, fluoro, chloro, bromo, trifluoromethyl, and amid functionalities, and promised its potential applications in the post-functionalization of the end product. It is worthwhile to note that in this methodology alcohols not only were served as substrates but also as solvents. The recycling test established that the catalyst could be recovered and reused for six consecutive reaction runs without loss in catalytic performance. After six recycles, the inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis showed negligible decrease of Co content from 1.08 wt% to 1.05 wt%. The mechanism proposed by the authors to explain the formation of sulfinic esters **24** is depicted in Scheme 11.

2.3. Metal-free reactions

In 1997, Xia and Chen published one of the earliest reports of the metal-free oxidative esterification of thiols with alcohols employing inexpensive phenyliodine(III) bis(trifluoroacetate) (PIFA) as an oxidant under neat conditions.[30] The reactions were carried out under the open air in the absence of any catalyst or ligand, tolerated both aromatic and benzylic thiols **25** and a small library of aliphatic alcohols **26**, and provided the



Scheme 9 Proposed pathway for the formation of sulfinic esters **21**.



Scheme 8 Synthesis of phenylsulfinates **21** *via* Cu-catalyzed oxidative coupling of thiophenols **19** and alcohols **20**.

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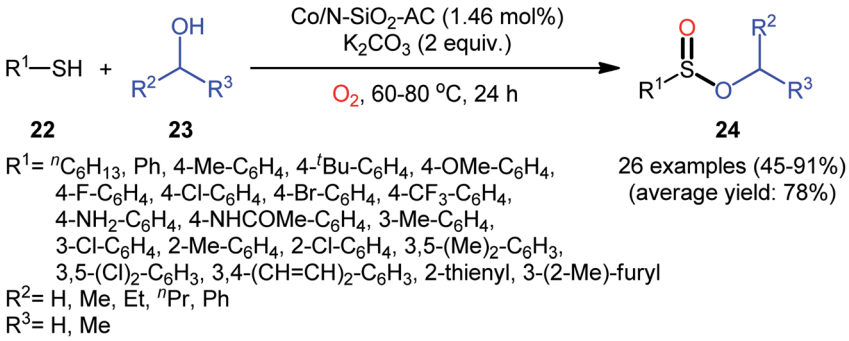
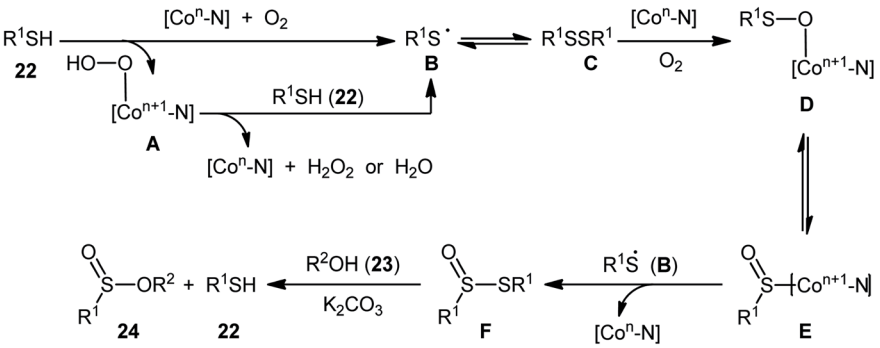


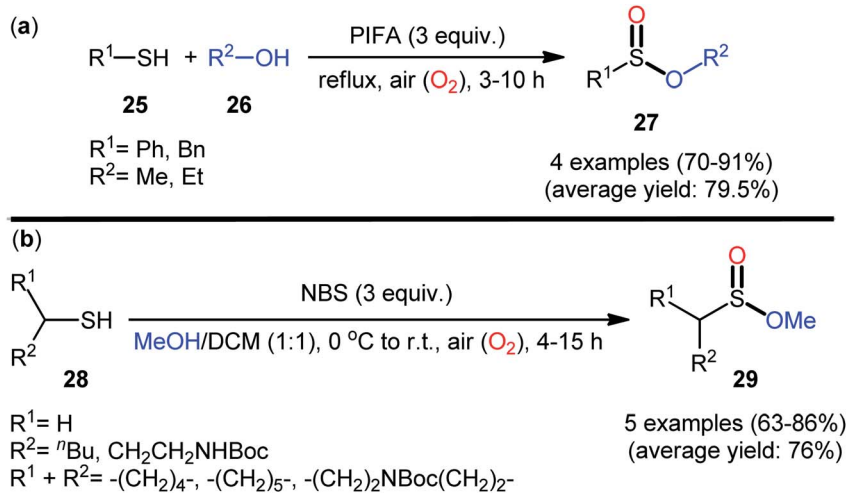
Scheme 10 Cobalt NPs-catalyzed oxidative esterification of thiols **22** with alcohols **23**.

corresponding sulfinic ester products **27** with yield ranging from 70% to 91% yield (Scheme 12a). However, in this seminal work only four examples with limited scope of the substrates were disclosed and no comment was made regarding the mechanism of the transformation. It is worthwhile to note that sulfinic esters can also be achieved in satisfactory yields when disulfides were employed instead of thiol substrates. Twenty-one years later, a similar principle was used by Qin's research team to the synthesis of a series of methyl alkylsulfinates **29** from the respective alkyl thiols **28** using *N*-bromosuccinimide (NBS) as a mediator in the binary solvent MeOH/DCM with ratio 1 : 1 at room temperature (Scheme 12b).[31,32] The prepared sulfinic esters were nicely applied as starting materials to the preparation of primary sulfinamides through reaction with $LiNH_2$ or LHMDS.

In 2018, Zhang and Chen along with their co-workers unfolded the tetra-*n*-butylammonium iodide (TBAI)-mediated oxidative esterification of (hetero)aromatic thiols **30** with *tert*-



Scheme 11 The proposed pathway for Co NPs-catalyzed oxidative cross-coupling of thiols **22** with alcohols **23**.



Scheme 12 (a) Xia's synthesis of sulfinic esters **27**; (b) Qin's synthesis of sulfinic esters **29**.

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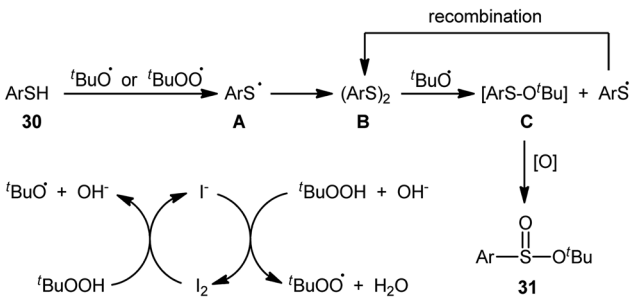
butyl hydroperoxide (TBHP) to synthesize *tert*-butyl (hetero) arylsulfinate derivatives **31** under metal-free condition (Scheme 13).[33] The reaction exhibited broad substrate scope and functional group tolerance, irrespective of whether electron-donating (*e.g.*, Me, Et, ^{i}Pr, ^{t}Bu, OMe and NH_2) or – withdrawing groups (*e.g.*, F, Cl, Br and CF_3) were at different positions of aromatic rings. Moreover, a tolerance for naphthalene-2-thiol (a bicyclic thiol) was also demonstrated. However, aliphatic thiols (*e.g.*, benzylthiol, cyclohexylthiol) were not suitable substrates for this transformation. Unfortunately, the scope and limitation of peroxides were not investigated in this study so that the reaction appears to be limited to only TBHP. It is noteworthy that other iodine sources such as NaI and KI were also effective in this esterification reaction but gave lower yield of products. To gain mechanistic insights, several preliminary experiments were performed and it was confirmed that this reaction most likely proceeds *via* a radical pathway (Scheme 14). Initially, TBHP undergoes decomposition in the presence of iodides to generate *tert*-butoxyl and *tert*-butylperoxy radicals. Next, homolytic bond breakage of thiols **30** under the oxidative conditions leads to thiyl radicals **A**, which after homocoupling affords disulfides **B**. Thereafter, *tert*-butoxyl radical reacts with disulfides **B** to yield *tert*-butoxyl aryl sulfides **C** *via* a radical propagation and regenerate thiyl radicals **A**, which could recombine to disulfides **B**. Finally, the oxidation of the sulfide intermediates **C** delivers the desired (hetero)arylsulfinates **31**.

Concurrently, Srivastava and co-workers disclosed a metal-free, visible-light-induced aerobic oxyesterification of various aliphatic, aromatic and heteroaromatic thiols **32** with alkyl/benzyl alcohols **33** as both substrates and solvents.[34] No additive was used and only 2 mol% of easily available eosin Y organophotoredox catalyst was enough for preparation of a variety of sulfinic esters **34** in 51–95% yields (Scheme 15). The results indicated that aromatic and heteroaromatic thiols were high yielding compared to aliphatic ones and aliphatic alcohols gave higher yields than benzylic ones. Based on some control experiments, the authors suggested a plausible mechanism as shown in Scheme 16. The transformation may start with the formation of excited state of eosin (EY*) *via* the excitation of eosin (EY) under visible light irradiation, which reacts *via* a single electron transfer (SET) process with starting thiol **32** to produce thiyl radical **A**. Subsequently, this highly active radical interactions with superoxide anion radical (generated by one-electron reduction of O_2) to form sulfinyl radical **B**, which after coupling with another molecule of thiyl radical **A** affords sulfinothioate intermediate **C**. Finally, EY – promoted nucleophilic substitution of sulfinothioate **C** by the alcohol **33** affords the expected products **34**.

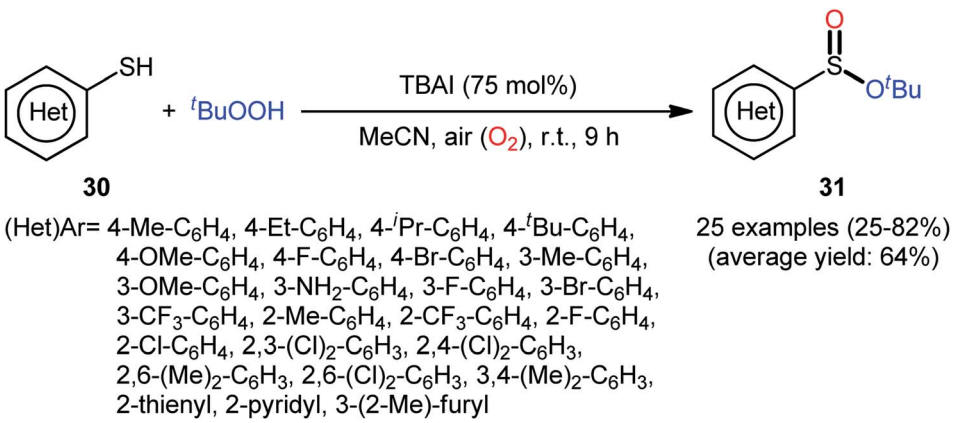
Based on these developments, very recently, Nguyen and co-workers developed a metal-free oxidative esterification reaction of thiols **35** with alcohols **36** using NBS as the mediator and ethyl acetate as the solvent at room temperature (Scheme 17).[35] Although both aromatic and aliphatic thiols were well tolerated under the reaction conditions, the alcohol partners were limited to the use of short-chain alcohols (*i.e.*, MeOH, EtOH, PrOH) as evidenced that butanol totally failed to produce any product under the optimized conditions. Furthermore, under the identical conditions benzyl alcohols were oxidized into benzaldehydes. Note that in some cases performing the process under irradiation of ultrasound slightly improved the efficiency of this reaction in the term of product yields within the shorter times.

3. Synthesis of sulfonic esters

Compared with the relatively well-developed oxy-esterification of thiols with alcohols for the synthesis of sulfinate esters, the direct fabrication of sulfonic esters from those easily available



Scheme 14 The proposed pathway for the formation of (hetero) arylsulfinates **31**.



Scheme 13 TBAI-mediated oxidative esterification of (hetero)aromatic thiols **30** with ^{t}BuOOH developed by Zhang–Chen.

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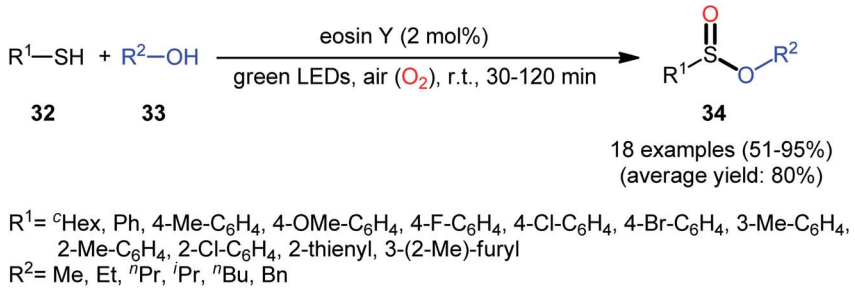
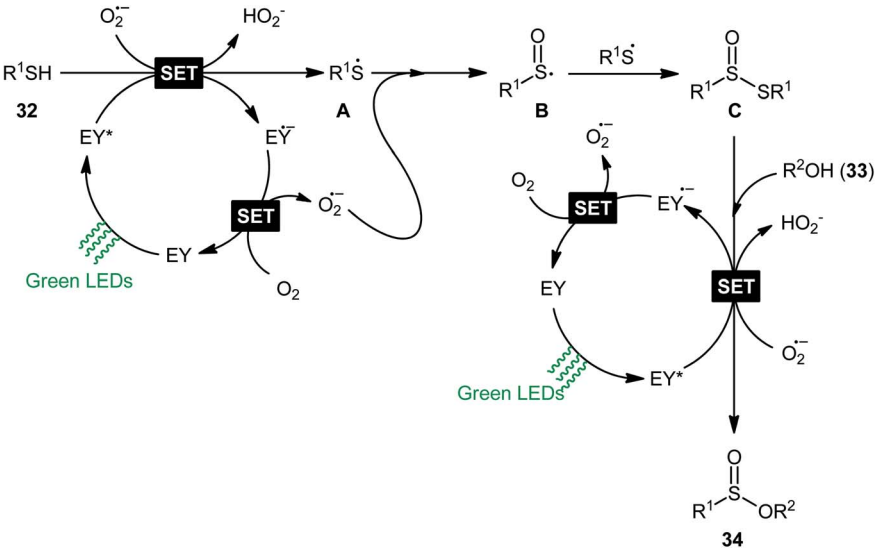


Scheme 15 Visible light-induced aerobic oxyesterification of thiols **32** with alkyl/benzyl alcohols **33**.

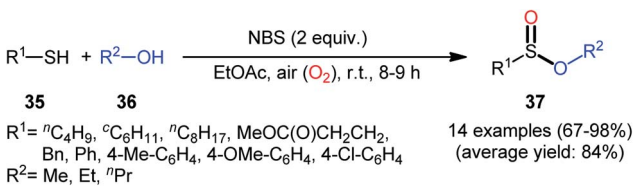


Scheme 16 Mechanistic proposal for the formation of sulfinic esters **34**.

commodity chemicals is still uncommon. In fact, only a handful of reports of such a reaction was published in the literature till date.

One of the earliest reports on this chemistry was published by Bahrami and co-workers in 2012,[36] who described that the treatment of thiols **38** with phenol derivatives **39** in the presence of a combination of Amberlite IRA-400/$POCl_3$/H_2O_2 as the catalytic system resulted in the formation of aryl sulfonic esters **40** in high to almost quantitative yields within 1–20 h (Scheme 18). The reaction is noteworthy in that various aliphatic, benzylic, and aromatic thiols with either electron-donating or electron-withdrawing substituents were well tolerated. Moreover, the procedure allowed to synthesis of disulfonate esters through double dioxy-esterification reaction of corresponding dithiols. Of note, besides alcohols, amines also could be applied as nucleophiles under the identical conditions to form biologically valuable sulfonamide derivatives. Interestingly, a competition experiment using phenol and aniline revealed that phenol reacted preferentially and aniline remained untouched. Similarly, sulfonylation of 4-aminophenol produced the respective sulfonate ester with free NH_2 moiety. Regarding the plausible mechanistic pathway of this transformation, after NMR spectroscopy investigations, it was confirmed that the reaction most likely proceeds *via* a sulfonyl chloride intermediate.

In 2013, Hemmati and co-workers developed a two-step one-pot method for the preparation of sulfonic ester derivatives **43** from the respective thiols **41** and alcohols **42** through oxidative chlorination of thiols to sulfonyl chlorides in the presence of trichloroisocyanuric acid (TCCA), tetrabutylammonium chloride ($^tBu_4NCl$), and water followed by reaction with alcohols under basic conditions (Scheme 19a).[37] Although either aromatic and aliphatic derivatives of both starting materials exhibited good applications under standard conditions and provided the desired products in high to excellent yields, the toxicity of TCCA might limit the application profile of this synthetic strategy. Noteworthy, when disulfides were subjected



Scheme 17 NBS-mediated oxidative esterification of thiols **35** with alcohols **36**.

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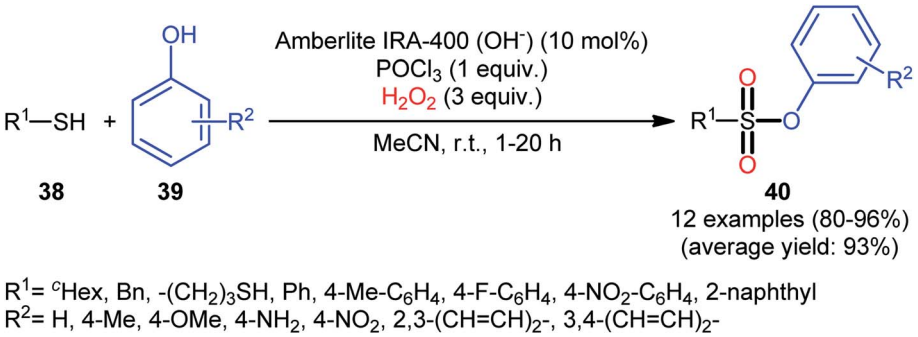
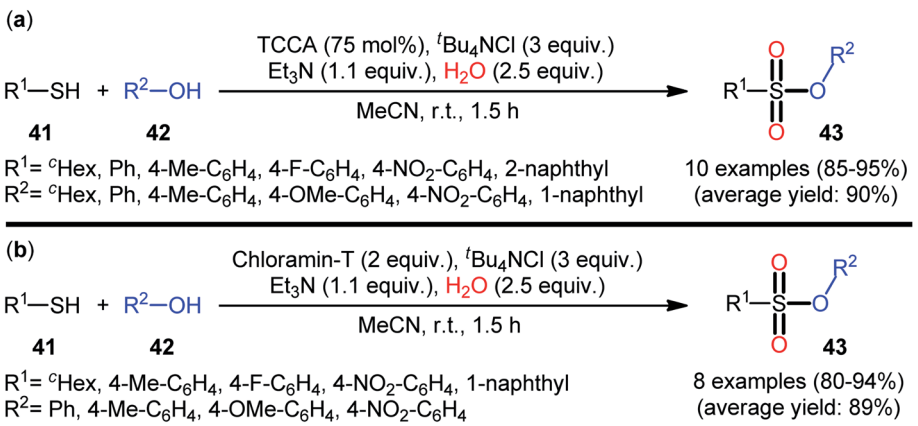


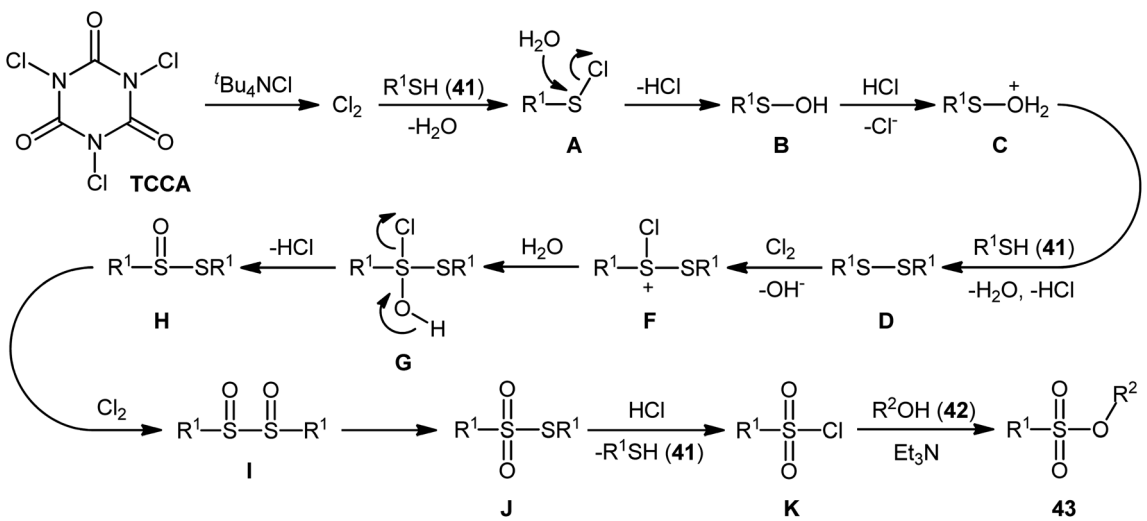
Scheme 18 Amberlite IRA-400/$POCl_3$-mediated oxidative esterification of thiols **38** with phenols **39** in the presence of H_2O_2.



Scheme 19 (a) Hemmati's synthesis of sulfonic esters **43**; (b) Mojtahedi's synthesis of sulfonic esters **43**.

to the reaction in place of thiols, the same set of sulfonic ester products were obtained in close yields. According to the authors proposed mechanism (Scheme 20), the oxygen atom of products originated from water. Another independent one-pot two-step method was published by Veisi and co-workers using Chloramin-T as a chlorinating agent under the same conditions (Scheme 19b).[38] The employed substrates in this work are the same as the ones reported by Hemmati–Mojtahedi group and the product yields are almost similar.

Following these works, Lei and co-workers disclosed an interesting photoinduced oxidative cross-coupling of thiophenols **44** with aliphatic alcohols **45** using 9-mesityl-10-



Scheme 20 The plausible mechanism for the reactions in Scheme 19a.

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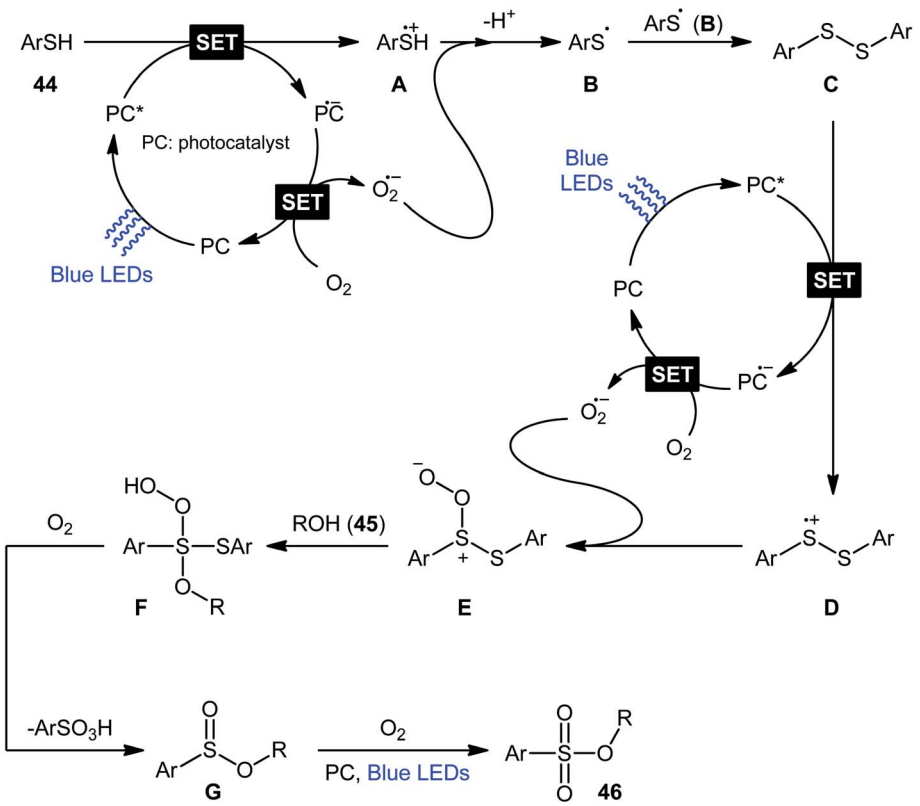
Scheme 21 Photoinduced oxidative cross-coupling between thiophenols **44** and aliphatic alcohols **45**.

methylacridinium ion (Acr^+–Mes) as a photocatalyst under metal-free conditions at room temperature.[39] The reactions proceed under O_2 atmosphere and blue light irradiation providing the alkyl benzenesulfonate compounds **46** in moderate to good yields, ranging from 45% to 70% yield (Scheme 21). Either primary or secondary alcohol substrates were successfully reacted in this system. However, tertiary alcohols failed to produce any product under the conditions employed. Moreover, the scope of thiophenols appears to be restricted to electron-rich ones. To gain mechanistic insights, several preliminary experiments were performed. No products were obtained in the lack of light, photocatalyst, or oxygen. The possibility of a radical pathway was confirmed since the reaction with TEMPO completely prevent the product formation. Furthermore, an isotope labelling experiment with $^{18}O_2$ indicated that the oxygen atoms of S=O bonds originated from the dioxygen. Based on the above results, the authors speculated that the reaction starts with the formation of $Acr^{\bullet}$–$Mes^{\bullet+}$ by intramolecular photoinduced electron transfer from the mesitylene moiety to the singlet excited state of the Acr^+ moiety of the catalyst. Subsequently, the $Mes^{\bullet+}$ moiety oxidizes the thiophenol **44** to form the radical cation **A**, whereas the $Acr^{\bullet}$ moiety reduces O_2 to $O_2^{\bullet-}$. Next, deprotonation of the radical cation **A** provides the corresponding thiyl radical **B**, which undergoes homocoupling to yield a disulfide intermediate **C**. Thereafter, the newly formed intermediate undergoes a further one-electron oxidation to form a disulfide radical cation **D** that, after oxidization affords the thiopersulfinate **E**. Later, nucleophilic attack of the alcohol **45** on the sulfur atom of **E** leads to the intermediate **F**, which then undergoes photooxidative



Scheme 22 Mechanistic proposal for the formation of alkyl benzenesulfonates **46**.

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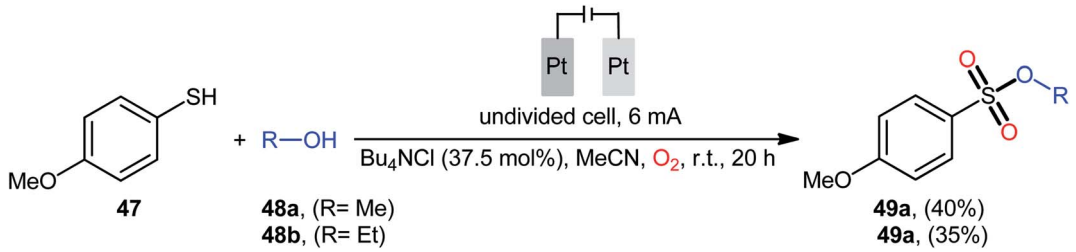

Scheme 23 Electrosynthesis of sulfonic esters **49** from 4-methoxybenzenethiol **47** and aliphatic alcohols **48** under O_2 atmosphere.

fragmentation to yield alkyl benzenesulfinate **G** and benzenesulfonic acid **H**. Finally, further oxidation of benzenesulfinate **G** results in the formation of the expected benzenesulfonate product **46** (Scheme 22).

Recently, in the same paper describing the electrochemical oxidative esterification of thiophenols and alcohols to sulfinic esters employing an undivided cell with platinum electrodes, the group of Xu–Wei reported the successful electrocatalyzed preparation of sulfonic esters **49** through the reaction between 4-methoxybenzenethiol **47** and aliphatic alcohols **48** under O_2 atmosphere (Scheme 23).[23] Although only two low yields examples were disclosed, this paper represents the first example of electrocatalyzed direct dioxy-esterification of thiols. As indicated in previous section, when this reaction was performed in open air the corresponding sulfinic esters were obtained as the sole products. Therefore, of course, O_2 has the key role in the further oxidation of sulfur atom.[40–47]

4. Conclusion

Sulfinic and sulfonic esters, two major kinds of organosulfur compounds containing S=O bonds, have drawn a lot of interest in diverse fields due to their crucial applications in organic synthesis, medicinal chemistry, and cell imaging. Therefore, it is always desirable to develop facile and efficient approaches to the synthesis of these special classes of organosulfur compounds from inexpensive starting materials. As summarized in this review, recently direct oxidative esterification of thiols with alcohols has emerged as an atom-efficient new strategy for the one-pot synthesis of sulfinic and sulfonic esters which beside avoids time and cost consuming prefunctionalization steps merits from low-cost easily accessible starting materials. Nevertheless, despite these advances, there are still many unsolved problems and challenges that need to be addressed. Some of these are listed below: (i) the scope of alcohols was mainly limited to aliphatic and benzylic alcohols. Therefore, of course, further research is needed to development of efficient procedures that are compatible with phenol derivatives; (ii) the synthesis of sulfenic esters *via* cross-dehydrogenative coupling of thiols and alcohols has not been explored thus far. Thus, the development of efficient methods for the direct construction of sulfenic ester derivatives from thiols and alcohols would be highly desirable; and (iii) the number of reported examples on the fabrication of sulfonic esters are narrow and there is an urgent need to study the scope and limitations of this page of sulfonic ester synthesis.

Conflicts of interest

There are no conflicts to declare.

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