Electrocatalytic Oxidative Transformation of Organic Acids for Carbon–Heteroatom and Sulfur–Heteroatom Bond Formation

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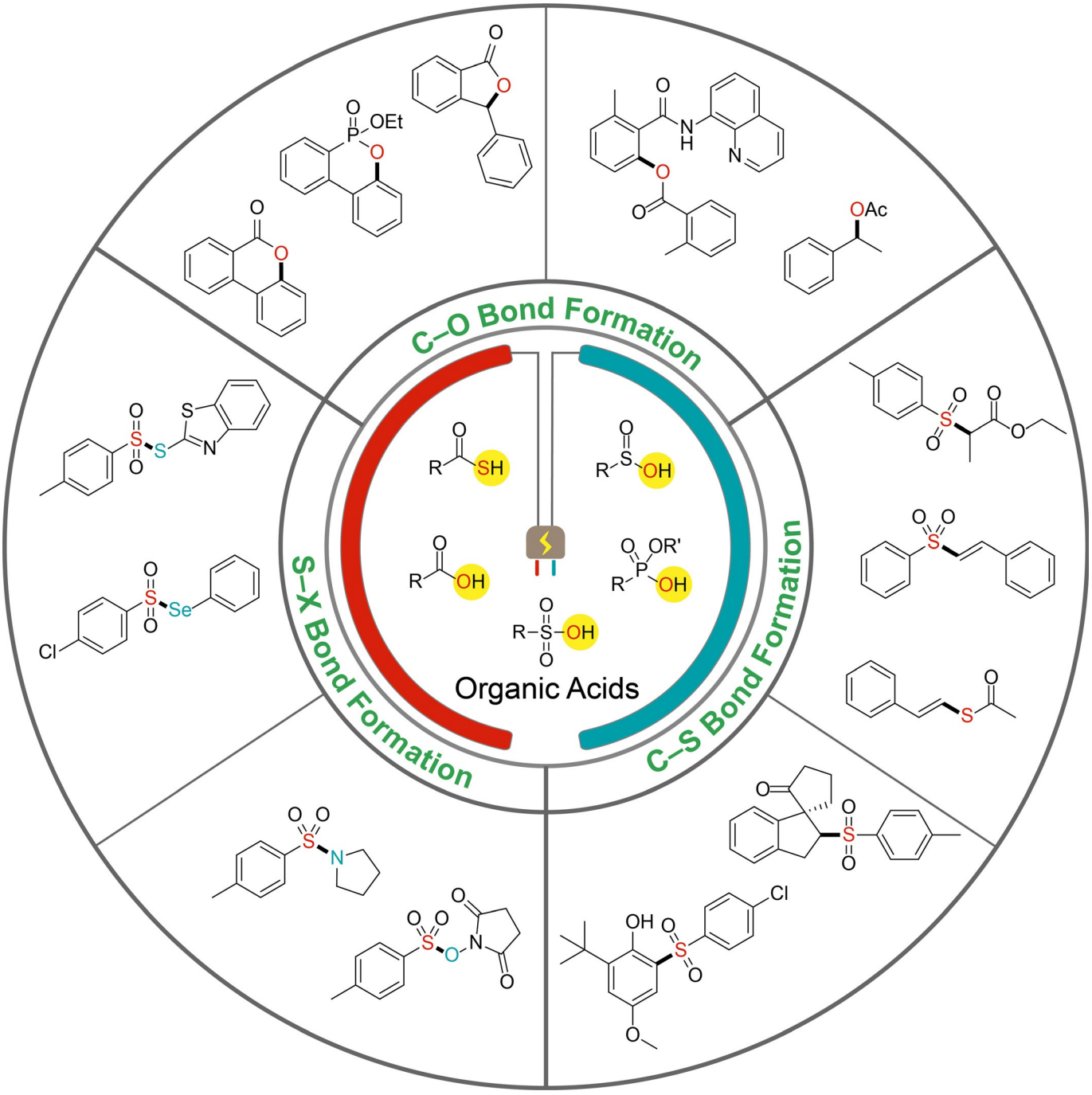

The electrolysis of organic acids has garnered increasing attention in recent years. In addition to the famous electrochemical decarboxylation known as Kolbe electrolysis, a number of other electrochemical processes have been recently established that allow for the construction of carbon–heteroatom and sulfur–heteroatom bonds from organic acids. Herein, recent advances in electrochemical C–X and S–X (X = N, O, S, Se) bond-forming reactions from five classes of organic acids and their conjugate bases, namely, carboxylic, thiocarboxylic, phosphonic, sulfinic, and sulfonic acids, are surveyed.

1. Introduction

Organic electrochemistry represents one of the most powerful and sustainable methods in organic chemistry.[1] Hazardous stoichiometric external oxidants or reductants generally used in conventional organic synthesis can be avoided or used in catalytic amounts through organic electrosynthesis.[2] Among the oxidative coupling reactions, external oxidant-free methods with hydrogen evolution are particularly attractive; these can be realized by employing organic electrochemistry.[3] Additionally, in certain cases, some chemical reagents, such as strong bases or highly active oxidants, can be electrogenerated in situ; these are both environmentally friendly and mechanistically interesting.[4] Recent studies have demonstrated the usefulness of organic electrosynthesis in inert bond functionalization[5] and difunctionalization of alkenes or alkynes.[6]

The electro-decarboxylation of aliphatic carboxylic acids to form dimeric products, known as the Kolbe reaction, has found widespread application in organic electrochemistry.[7] Mechanistically, alkyl radicals are generated and coupled in a classical Kolbe reaction. In recent years, the concept of Kolbe electrolysis has been largely expanded due to the rich chemistry of alkyl radicals.[8] In addition, a number of non-decarboxylative electrochemical transformations of carboxylic acids have also been developed in recent years. Prior to the extrusion of carbon dioxide, the carboxylic acid group can participate in various C–O bond-forming reactions to provide esters and lactones as products. The anodic oxidation of other organic acids, such as sulfinic acids, is very similar to that of carboxylic acids. Sulfinic acids, such as CF_3SO_2Na, were well known to release SO_2 through anodic oxidation. It should be noted that, generally, C–S or S–X, instead of C–O or O–X, bond-forming reactions are observed in the electrolysis of thiocarboxylic acids and sulfinic acids. Herein, recent advances in C–O, C–S, and S–X (X = N, O, S, Se) bond-formation reactions, involving organic acidic functional groups, through electrochemical methods are summarized based on the types of reacting organic acid substrates. The organic acids involved in this review include carboxylic, thiocarboxylic, phosphonic, sulfinic, and sulfonic acids. Representative examples involving C–H functionalization and alkene/alkyne difunctionalization processes are highlighted. Electrochemical reactions involving merely expulsion of CO_2 or SO_2 from respective carboxylic acids or sulfinic acids are out of the scope of this review.

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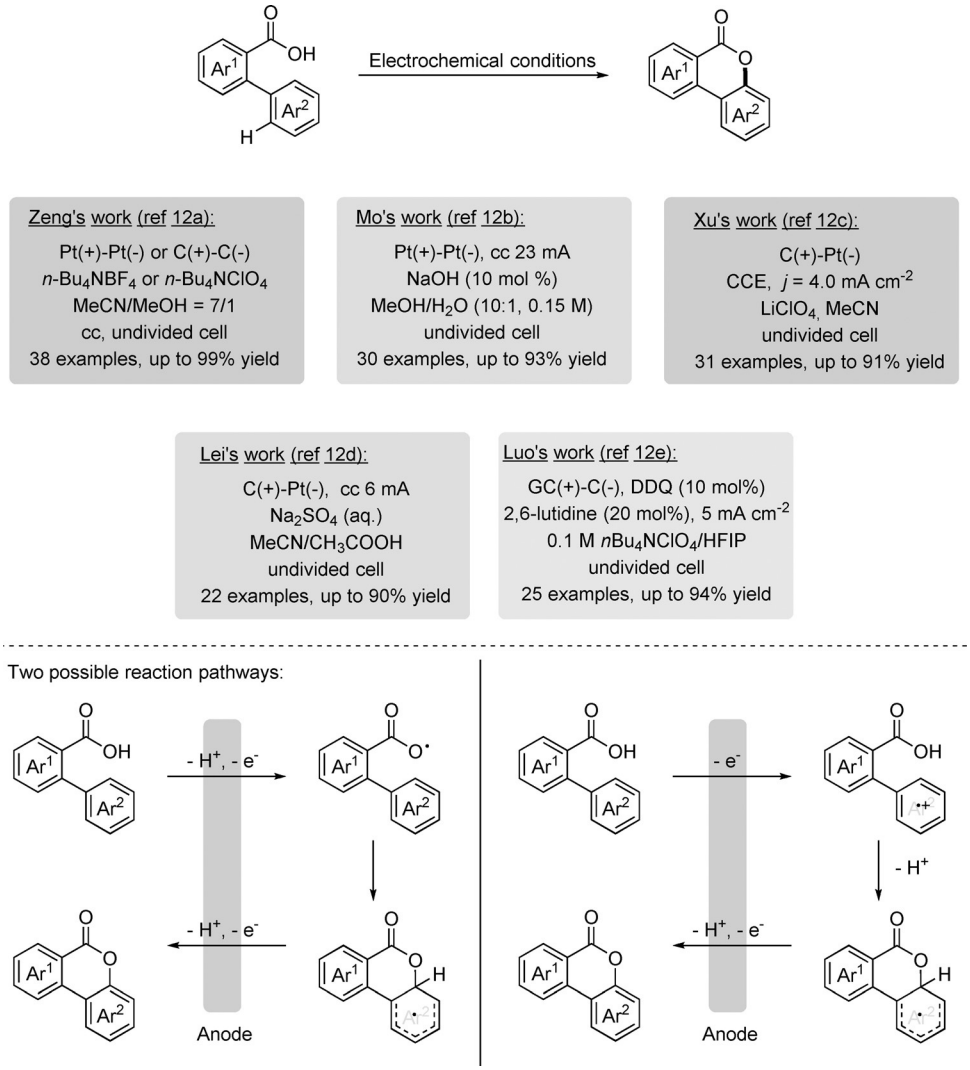
2. Ester C–O Bond Formation through Electrolysis of Carboxylic Acids

2.1. Direct oxidative coupling of carboxylic acids with aryl-C(sp^2)–H bonds

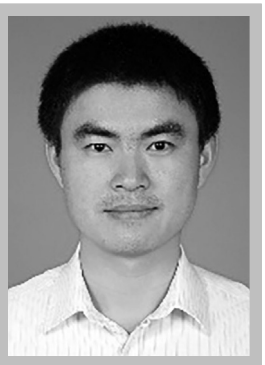
Early studies on this topic, including examples involving transition-metal-catalyzed electrochemical transformations, such as the oxygenation of C–H bonds, have been summarized in other reviews[5a,b,9] and are not included herein. We only focus on recent advances.

The oxidative cyclization of 2-arylbenzonic acid through aryl-C(sp^2)–H bond functionalization is an ideal approach to biaryl lactones.[10] In 2009, anodic acyloxylation based on acid–base reactions between acetic acid or trifluoroacetic acid (TFA) and solid-supported bases was developed.[11] In 2018, several groups independently reported the anodic oxidative cyclization of 2-arylbenzonic acids under transition-metal-free conditions (Scheme 1).[12] Previously, this transformation was achieved by many groups through metal catalysis (Pd, Cu, etc.) in combination with stoichiometric amounts of oxidant. The catalysis system is somewhat complicated and the use of large amounts of oxidant result in safety issues, excessive waste generation, and poor atom economy. In this regard, electrochemistry offers a superior method to that of conventional chemistry.

Constant-current (cc) electrolysis in an undivided cell at room temperature was employed in all of these methods. Zeng et al. reported that the utilization of inexpensive graphite electrodes was quite attractive for large-scale electrosynthesis.[12a] This method was applied to a 40 g scale synthesis. In the report by Mo et al., a catalytic amount of NaOH was used and no further supporting electrolyte was required; this was distinct from that of the other studies.[12b] Lei and co-workers used an aqueous solution of Na_2SO_4 as a cheap and green supporting electrolyte.[12d] Notably, they found that acids, such as



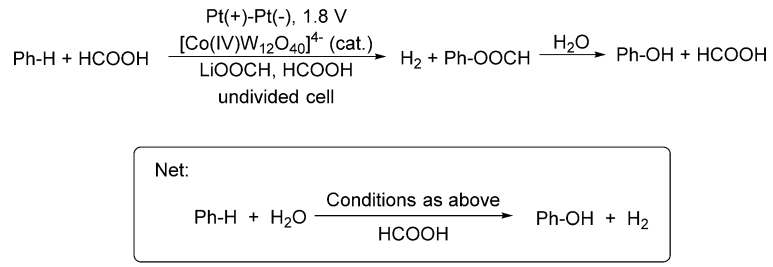
Scheme 1. Oxidative cyclization of 2-arylbenzonic acids. CCE = constant-current electrolysis, HFIP = 1,1,1,3,3,3-hexafluoroisopropanol, cc = constant current, GC = glassy carbon.



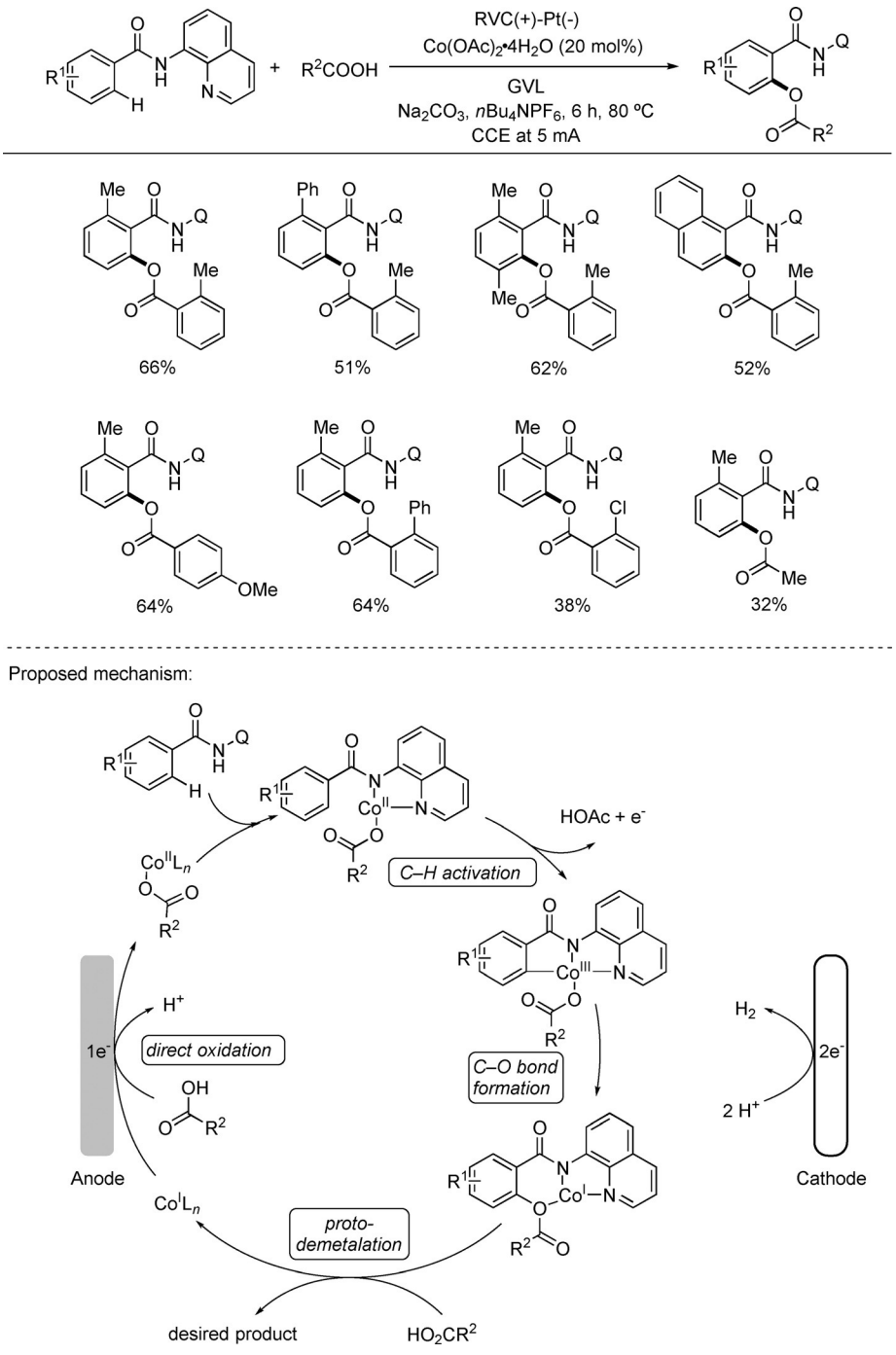
Fanyang Mo obtained his undergraduate and master's degrees in applied chemistry from the Beijing Institute of Technology under the supervision of Professor Zhiming Zhou in 2004 and 2006, respectively. He then moved to Peking University and pursued his Ph.D. studies under the supervision of Professor Jianbo Wang. After receiving his Ph.D. in 2010, he moved to the USA and worked with Professor Qinghai Zhang at The Scripps Research Institute and Professor Guangbin Dong at The University of Texas at Austin from 2010 to 2015. He joined Peking University as Assistant Professor in April 2015. The current research interests of his group include CO_2 utilization in organic synthesis, organic electrochemistry, and the modification of semiconductor oxides for energy and resources utilization.

acetic acid, were beneficial for the reaction. In a study by Xu et al., the electrolysis of 2-phenylbenzonic acid could be conducted on 100 g scale under an air atmosphere.[12c] Luo and co-workers reported the use of a catalytic amount of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and 2,6-lutidine as a redox mediator and base, respectively.[12e] Therefore, indirect electrolysis was used in the method reported by Luo et al., whereas and direct electrolysis was used in the other studies. Notably, the groups of Zeng[12a] and Luo[12e] also reported the electrochemical lactonization of diaryl acrylic acids, which afforded valuable coumarins. As for the reaction mechanism, the most popular proposed mechanism was the generation of carboxylate radicals through anodic oxidation of carboxylate anions, followed by intramolecular radical-trapping cyclization. However, prior anodic oxidation of the aromatic ring containing the reacting C–H bond cannot be ruled out, especially for an electron-rich aromatic ring substituted with a methoxy group, as suggested by Lei and co-workers.[12d]

In 2018, Neumann and co-workers reported an electrocatalytic formylation reaction of benzene and its halogenated de-



Scheme 2. Pathway for the electrochemical hydroxylation of benzene to phenol.



Scheme 3. Cobalt-catalyzed C–H acyloxylation. RVC = reticulated vitreous carbon.

rivatives in the presence of $[Co^{III}W_{12}O_{40}]^{5-}$ as a catalyst and lithium formate as an electrolyte (Scheme 2).[13] The aryl formate products are easily hydrolyzed by water to afford the corresponding phenols and formic acid. Hydrogen was formed at the cathode. Therefore, the sum reaction is an indirect hydroxylation of benzene with water to yield phenol and H_2 as products. It is proposed that the formyloxy radical serves as the reactive species based on an EPR study.

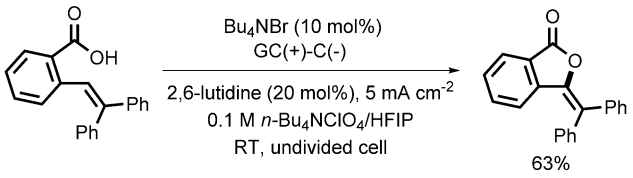
In 2019, Ackermann and co-workers reported the first electrochemical cobalt-catalyzed C(sp^2)–H acyloxylation in biomass-derived γ-valerolactone (GVL) as a renewable solvent (Scheme 3).[14] Electricity serves as a sustainable oxidant with molecular hydrogen as the sole byproduct, in the absence of stoichiometric amounts of metal oxidants. Both aromatic and aliphatic carboxylic acids were amenable substrates. A plausible catalytic cycle was slightly revised from the original paper, according to subsequent related studies.[15] The reaction was initiated by the oxidation of Co^{I} catalyst with carboxylic acid to form carboxylate Co^{II}, followed by coordination with a directing group on the substrate. Further oxidation of Co^{II} to Co^{III} occurs with concomitant activation of the C–H bond. Finally, reductive elimination and proto-demetalation afford the final product and regenerate the Co^{I} catalyst (Scheme 3).

2.2. Direct oxidative coupling of carboxylic acids with vinyl-C(sp^2)–H bonds

In 2018, one example of intramolecular oxidative cyclization of a carboxylic acid with a vinyl-C(sp^2)–H bond was reported by Luo and co-workers (Scheme 4).[12e] Tetrabutylammonium bromide was a better redox mediator than that of DDQ in this case.

2.3. Intramolecular coupling of carboxylic acids with C(sp^2)–X bonds

In 2018, during an investigation into the intramolecular lactonization of 2′-halobiphenyl-2-carboxylic acids, Luo and co-workers found that C–X substitution products were obtained instead of C–H substitution products (Scheme 5).[12e] Halogens, including chloride, bromide, and fluoride, could be viable leaving groups. This type of electrolysis-initiated aromatic radical substitution is relatively rare.



Scheme 4. Oxidative cyclization of a carboxylic acid with a vinyl-C(sp^2)–H bond in the presence of tetrabutylammonium bromide.

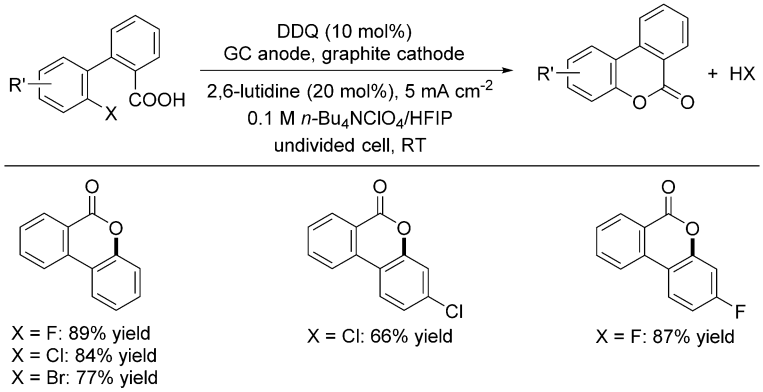
2.4. Electrocatalytic dehydrogenative esterification of carboxylic acids with ketones

In light of the competing decarboxylation of aliphatic acids, it would be significant to construct ester C–O bonds from aliphatic acids to suppress this side reaction. In 2017, Xu and co-workers reported the intra- and intermolecular electrocatalytic dehydrogenative esterification of carboxylic acids with ketones by using an indirect electrolysis strategy (Scheme 6).[16]

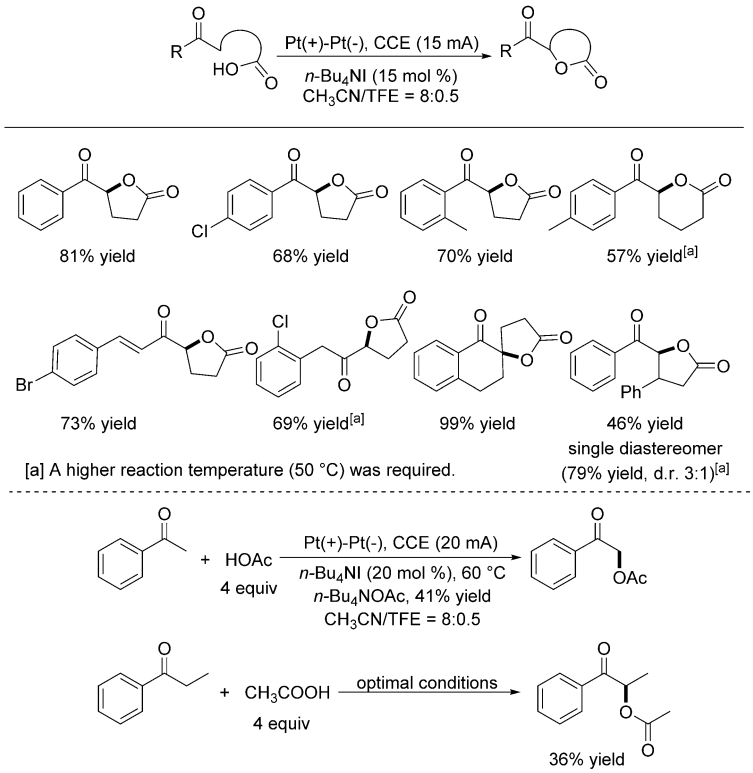
For intermolecular dehydrogenative esterification, both aliphatic and aromatic acids were well tolerated. The mechanism given in Scheme 7 was proposed. Cathodic reduction of the carboxylic acid forms the corresponding carboxylate anion. With nBu_4NI as a mediator, in situ generated I_2 could transform the ketone into α-iodinated ketone. The α-iodinated ketone could also be generated from an acyl hypoiodite intermediate. Final nucleophilic substitution affords the ester product. The utility of this method is illustrated by the synthesis of a natural product, cytosporanone A, on a gram scale.

In 2019, Terent'ev and co-workers reported an electrochemically induced, intermolecular, cross-dehydrogenative C–O coupling of β-diketones and β-ketoesters with carboxylic acids by using KBr as a supporting electrolyte (Scheme 8).[17] They proposed that brominated β-diketones or β-ketoesters served as an important intermediates in this reaction, similar to that reported by Xu et al.[16]

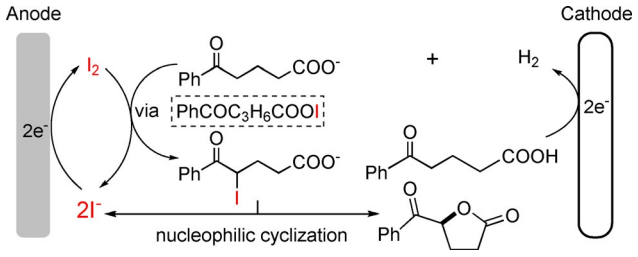
Recently, Wirth and co-workers reported, for the first time, the enantioselective electrochemical lactonization of diketo



Scheme 5. Intramolecular lactonization of 2′-halobiphenyl-2-carboxylic acids.



Scheme 6. Electrocatalytic dehydrogenative esterification of aliphatic carboxylic acids. TFE = 2,2,2-trifluoroethanol.

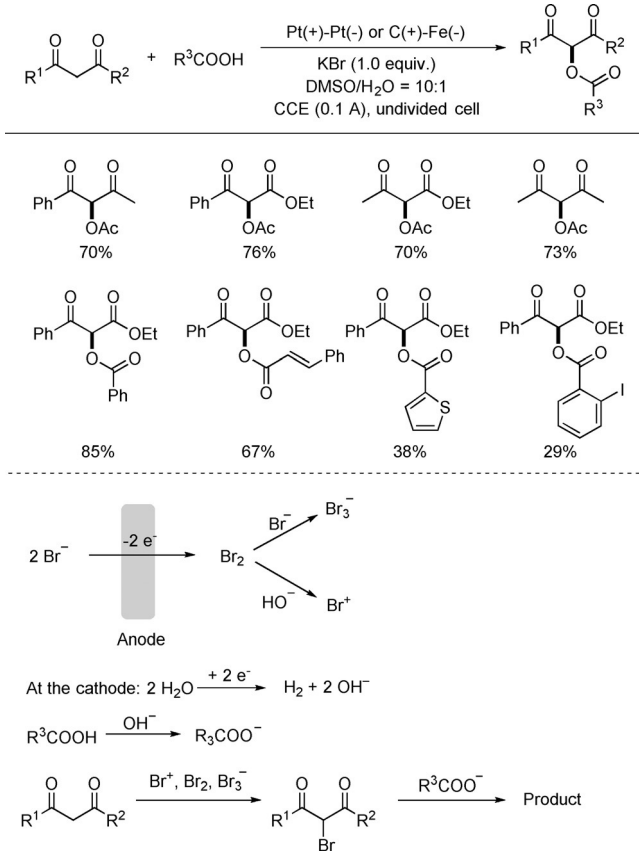


Scheme 7. Proposed mechanism for the electrocatalytic dehydrogenative esterification of aliphatic carboxylic acids.

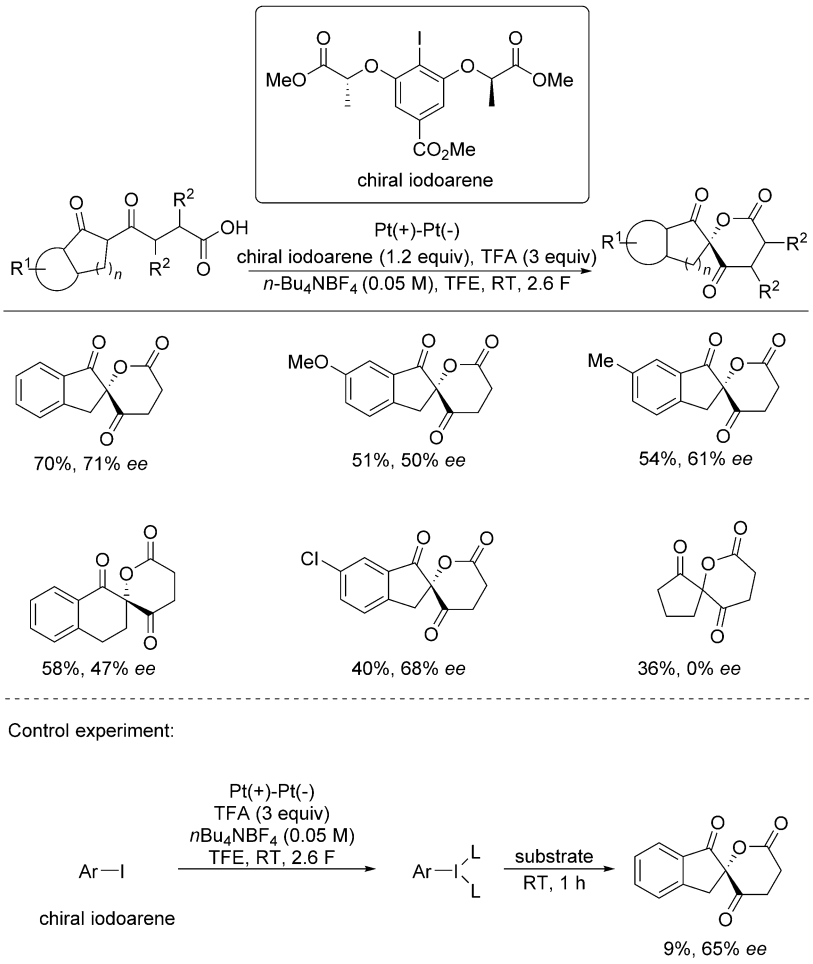
acid derivatives by using chiral iodoarenes as redox mediators (Scheme 9).[18] Cyclic voltammetry (CV) studies show that chiral iodoarene has a lower oxidative potential than that of the substrate; this indicates that hypervalent iodine is first generated in situ in this electrochemical reaction and then works as a homogeneous chiral organocatalyst to catalyze the enantioselective lactonization reaction. Notably, this reaction could also be accomplished by using an electrochemical flow microreactor with a lower supporting electrolyte concentration. In 2019, an efficient cross-coupling reaction of carbon dioxide with amines and aryl ketones was developed to provide a variety of *O*-β-oxoalkyl carbamates in moderate to good yields.[19]

2.5. Esterification of benzylic C(sp^3)–H bonds

In 2018, Zeng and co-workers reported the external oxidant-free electrochemical lactonization of benzylic C(sp^3)–H bonds



Scheme 8. Intermolecular cross-dehydrogenative C–O coupling of β-diketones and β-ketoesters with carboxylic acids.



Scheme 9. Enantioselective electrochemical lactonization of diketo acid derivatives; *ee* = enantiomeric excess.

(Scheme 10).[12a] Lactones with a new quaternary carbon center could be forged in some cases. Notably, an example of the electrochemical lactonization of aliphatic carboxylic acid was given. A plausible mechanism was proposed by the authors. The initial electrogenerated carboxylate radical might trigger a remote 1,5-HAT, resulting in the formation of a stabilized benzylic radical. Final cyclization leads to the product by losing an electron and a proton, possibly via a cation intermediate. It should be mentioned that 2-methylbenzonic acid and 2-ethylbenzonic acid were not suitable for this protocol, which indicated that the stability of the benzylic radical intermediate was very important for this reaction.

In the same year, Muñiz and co-workers also reported an example of the electrochemical lactonization of aliphatic carboxylic acid in higher yield (Scheme 11).[20]

In 2018, Neumann and co-workers reported the acetoxylation of alkylarenes catalyzed by $[Co^{IV}W_{12}O_{40}]^{4-}$ in acetic acid.[13] Dehydrogenation or oxidation of alkylarenes were also observed in these reactions (Scheme 12).

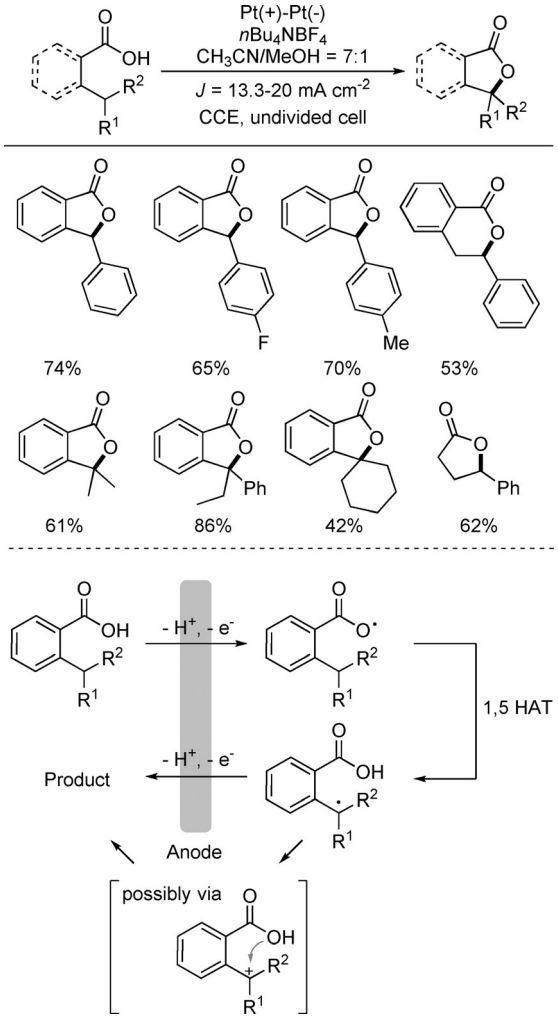
2.6. Esterification of carboxylic acids through difunctionalization of alkenes

2.6.1. Lactone formation through intramolecular trapping of intermediates with carboxylic acids

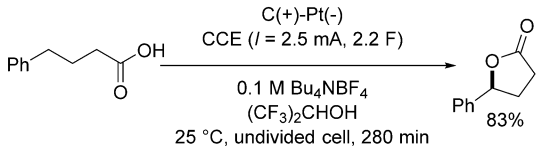
In 2013, Moeller and co-workers reported the anodic coupling of carboxylic acids to electron-rich double bonds (Scheme 13).[21] Although aliphatic carboxylic acids were used as substrates, Kolbe decarboxylation did not appear to be a significant competing pathway. Electron-rich olefins, including ketene dithioacetal, vinyl sulfide, enol ether, and substituted styrene, were all suitable for this reaction. Mechanistically, it is likely that oxidation occurs at the olefin and carboxylate traps the resulting radical cation intermediate. After the second oxidation reaction and nucleophilic attack by methanol or methoxide, the final products are obtained.

Using a similar strategy to that reported by Moeller and co-workers,[21] in 2019, Xu and co-workers reported lactone formation from carboxylic acid containing styrene substrates (Scheme 14).[22] The *endo*-type cyclization in this work deserves attention.

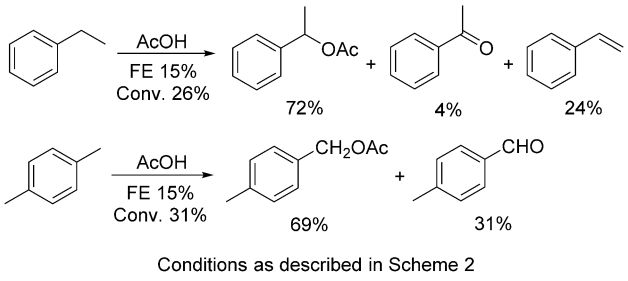
In 2018, Kam and co-workers investigated the effect of *ortho*-substituted side chains bearing nucleophilic groups, such



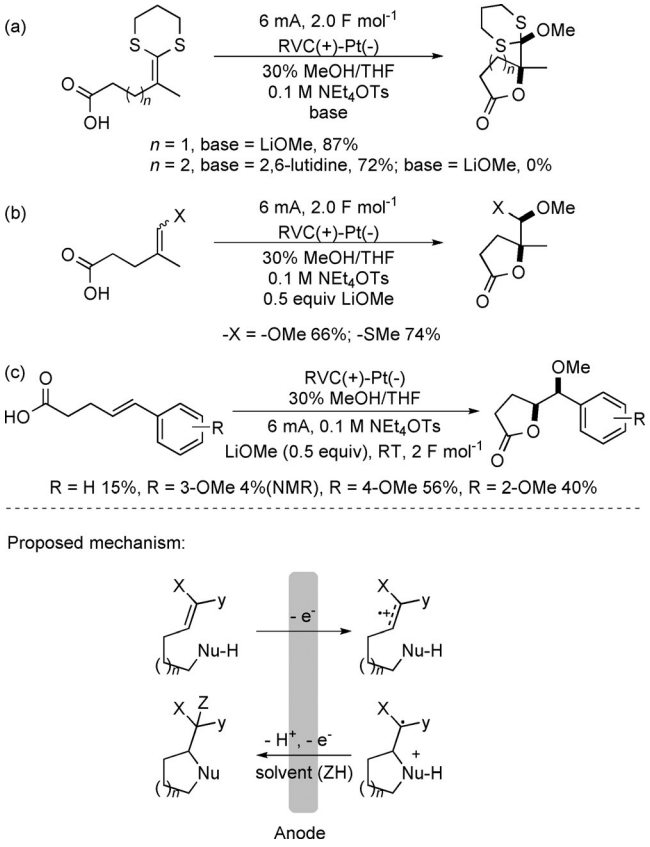
Scheme 10. Electrochemical lactonization of benzylic C(sp^3)–H bonds. 1,5-HAT = 1,5-hydrogen-atom transfer.



Scheme 11. Electrochemical lactonization of aliphatic carboxylic acid.



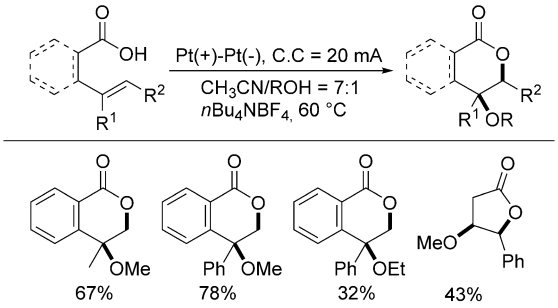
Scheme 12. Electrochemical oxidation of alkylarenes catalyzed by $[Co^{IV}W_{12}O_{40}]^{4-}$ in acetic acid. FE = faradaic efficiency.



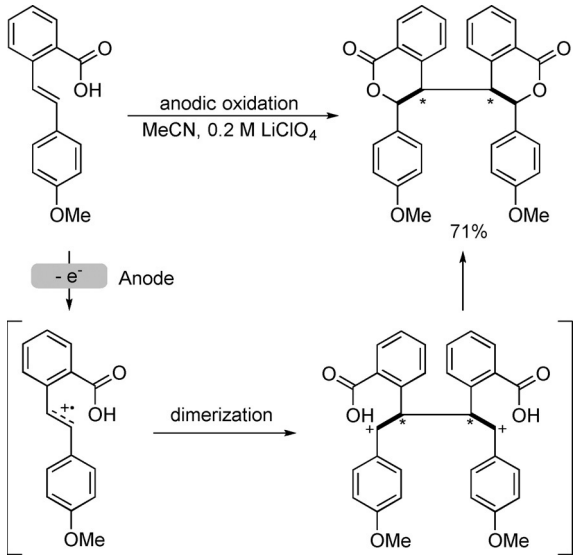
Scheme 13. Coupling of carboxylic acids to electron-rich double bonds. Ts = tosyl.

as CO_2H, on the reactivity of anodically generated 4-methoxy- and 3,4-dimethoxystilbene cation radicals (Scheme 15).[23] With COOH as the ortho substituent, bis-δ-lactones were obtained through a direct intramolecular cation–nucleophile reaction.

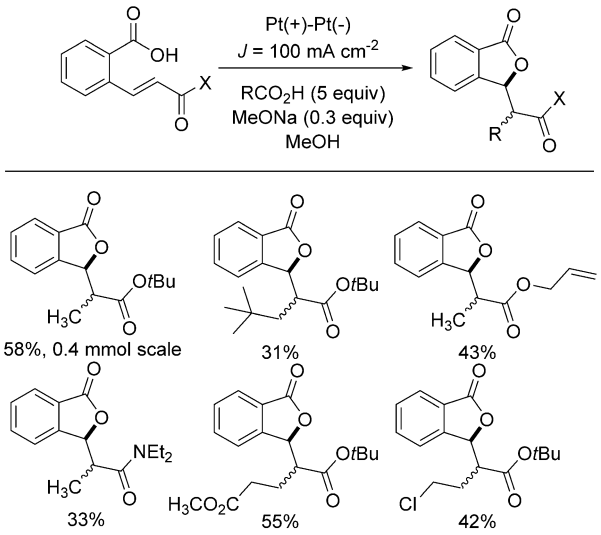
Integration of electrochemical oxidative cyclization and chemical oxidation is an intriguing strategy in the difunctionalization of alkenes. Based on their previous work, in 2013, Yoshida and co-workers reported the integration of electro-oxidative cyclization of alkenes bearing a nucleophilic moiety in the presence of DMSO and chemical oxidation of the resulting alkoxysulfonium ions.[24] The alkoxysulfonium ions can be converted into ketones by treatment with Et_3N through Swern–Moffatt-type oxidation. The reaction is useful for the synthesis



Scheme 14. Electrochemical lactone formation.

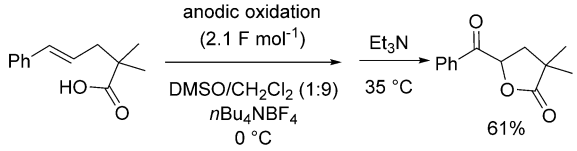


Scheme 15. Reactivity of anodically generated 4-methoxystilbene cation radicals.



Scheme 17. Electrochemical synthesis of phthalides through the anodic activation of aromatic carboxylic acids.

of lactones if the CO_2H group serves as an intramolecular nucleophile (Scheme 16).



Scheme 16. Electro-oxidative cyclization of alkenes.

In 2017, Lam and co-workers reported the electrochemical synthesis of phthalides by using anodically generated aroyloxy radicals in combination with aliphatic carboxylic acid as alkylating agent precursors (Scheme 17).[25] They proposed that aroyloxy and alkyl radicals are key intermediates of this reaction. The electrogenerated alkyl radical from the aliphatic carboxylic acid might oxidize the aromatic carboxylate to form the aroyloxy radical. The possibility of the direct oxidation of the olefin into a radical cation, followed by its capture through nucleophilic attack from the carboxylate, was not favored by a control experiment.

In 2018, Han and co-workers reported the synthesis of thiosubstituted lactones through the electrochemical oxysulfuration of alkenes (Scheme 18).[26] Unsaturated carboxylic acids, including aliphatic and aromatic acids, were all suitable for this reaction. It is likely that the aryl sulfur radical generated from the anodic oxidation of thiophenol triggers the addition reaction. The resulting radical intermediate undergoes further anodic oxidation to afford the carbocation intermediate, which is attacked by the nucleophile to give the final product.

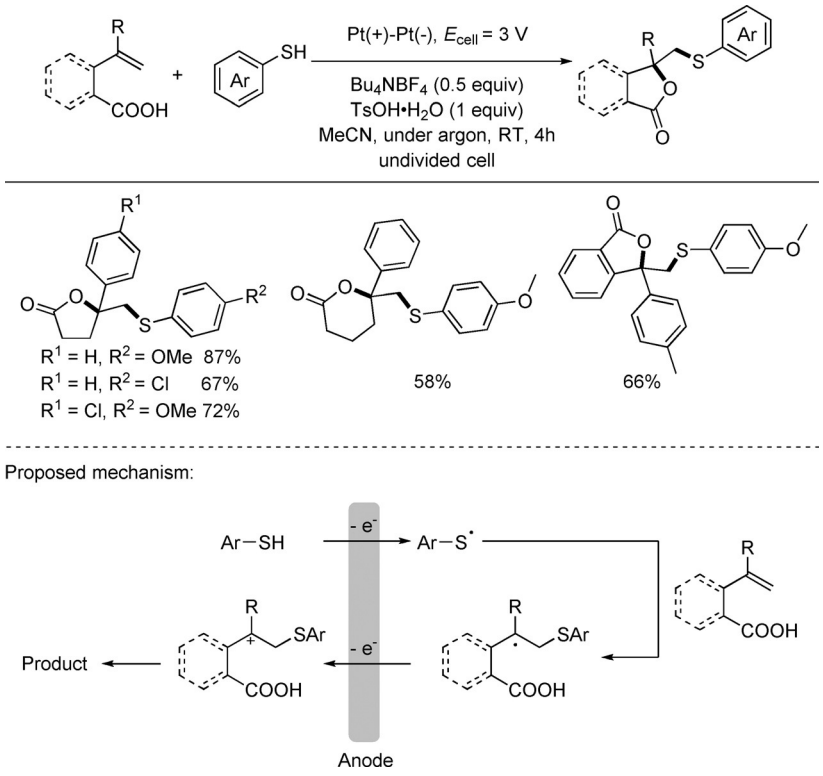
Using a similar strategy, in 2019, Xu and co-workers reported an electrochemical fluoromethylation-triggered lactonization of alkenes under additional supporting electrolyte- and catalyst-free conditions (Scheme 19).[27] With readily prepared CF_2HSO_2Na or CF_3SO_2Na as the fluoromethylating reagents, the desired CF_2H- or CF_3-containing lactones were obtained in an undivided cell under semiaqueous conditions. CV experiments indicated that CF_2HSO_2Na and CF_3SO_2Na were easier to electrochemically oxidize to generate fluoromethyl radicals than that of the alkene moiety. Thus, the R_f radical generated by anodic oxidation of R_fSO_2Na adds to the alkene, followed by further anodic oxidation of the resulting benzylic radical species, to give the benzylic carbocation. Intramolecular trapping by carboxylic acid gives the final product.

2.6.2. Ester formation through intermolecular trapping of intermediates with carboxylic acids

In 2014, Kam and co-workers investigated the electrochemical oxidation of 4,4′-dimethoxystilbene under different conditions.[28] If the reaction was carried out in 25% AcOH/MeCN/0.1 M $LiClO_4$ in the presence of NaOAc (0.25 M), isomeric acetate derivatives were obtained in combined yields of 62% (Scheme 20). The radical cation intermediate was proposed as the key species in this anodic oxidation.

In 2015, DeVos and co-workers reported the divergent paired electrosynthesis of diacid and diol precursors through simultaneous cathodic carboxylation and anodic acetoxylation of conjugated dienes (Scheme 21).[29] As for the acetoxylation reaction, the choice of the TEA salt seemed very important. If an acetate anion was used, no diacetate ester product was observed; if a trifluoroacetate salt was employed, a good yield of diacetoxylated compound product was obtained.

In 2018, Lei and co-workers reported the electrochemical oxidative oxysulfenylation (including acyloxysulfenylation) and aminosulfenylation of alkenes with hydrogen evolution.[30] Neither external chemical oxidants nor metal catalysts were required in these reactions. One example of acyloxysulfenylation



Scheme 18. Synthesis of thio-substituted lactones through electrochemical oxysulfuration of alkenes.

of styrene was reported (Scheme 22). The proposed mechanism was similar with that of Han and co-workers.[26] Notably, the authors pointed out that, although the thiyl radical was the most likely species triggering the reaction, the possibility that the arylbis(arylthio)sulfonium ion served as the key intermediate could not be completely ruled out.

On the basis of this work, Lei and co-workers further developed the electrochemical oxy- and aminotrifluoromethylation of alkenes in the presence of yttrium triflate by using CF_3SO_2Na as a trifluoromethylation reagent.[31] Formic and acetic acid could participate in the electrochemical oxytrifluoromethylation to afford the corresponding CF_3-containing esters (Scheme 23). It is likely that CF_3 radical generated from the oxidation of CF_3SO_2Na at the anode triggers this reaction.

In 2019, the group of Lei reported the electrochemical amino- and oxyselenation of styrenes without any acids or oxidants as additives.[32] Formic, acetic, butyric, benzoic, and cyclopropanecarboxylic acid are all amenable nucleophiles in the oxyselenation of styrene (Scheme 24). Two possible mechanisms involving seleno radical initiated addition or cyclic selenium intermediate were proposed.

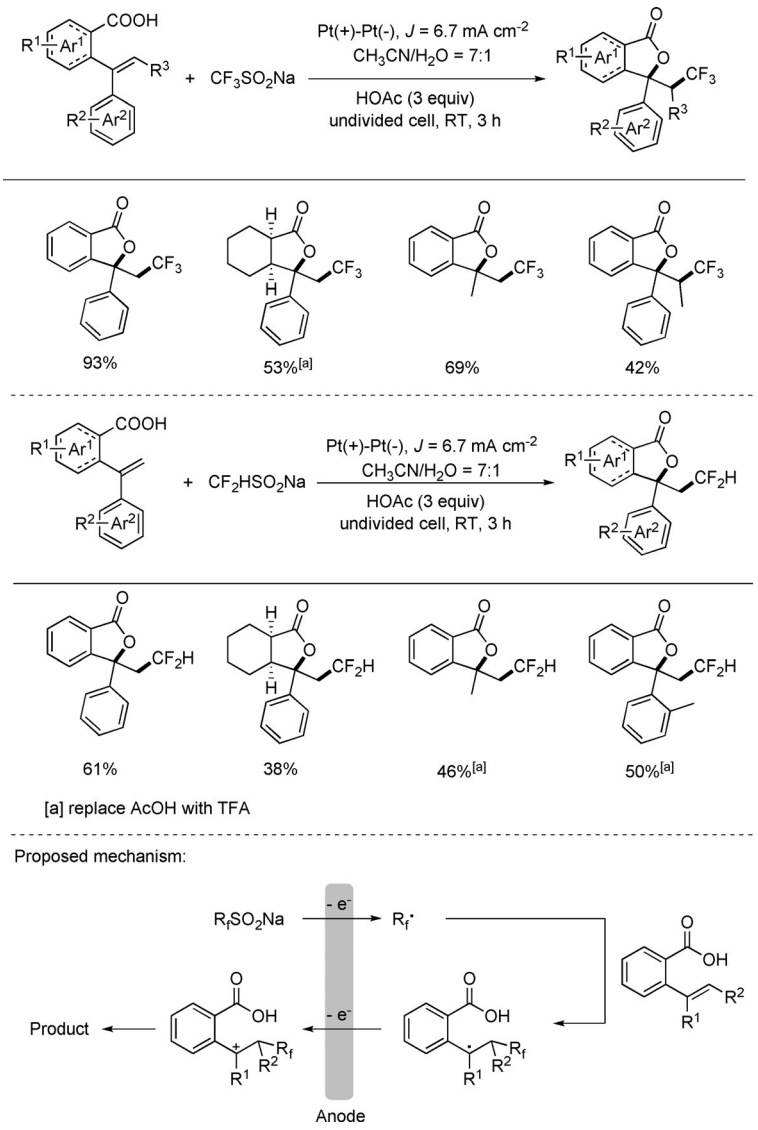
In 2019, Li and co-workers developed an intermolecular 1,2-bromoesterification of alkenes with carboxylic acids and *N*-bromosuccinimide (NBS) under electrochemical oxidative conditions (Scheme 25).[33] They found that TEMPO promoted this reaction significantly. Inorganic bromine sources, such as LiBr, NH_4Br, and KBr, were not suitable for this reaction. A wide range of alkenes, including 1,1- and 1,2-disubstituted ethylene, terminal styrenes, cycloolefins, and aliphatic alkene, were transformed into their corresponding products through C—Br and C—O bond formation. Various carboxylic acids, such as aromatic, cinnamic, aliphatic, and amino acids, were tolerated by the electro-oxidative system. The cyclic bromonium-ion intermediate was proposed as the key species in this transformation.

2.7. Anodic allylic esterification of nonactivated alkenes

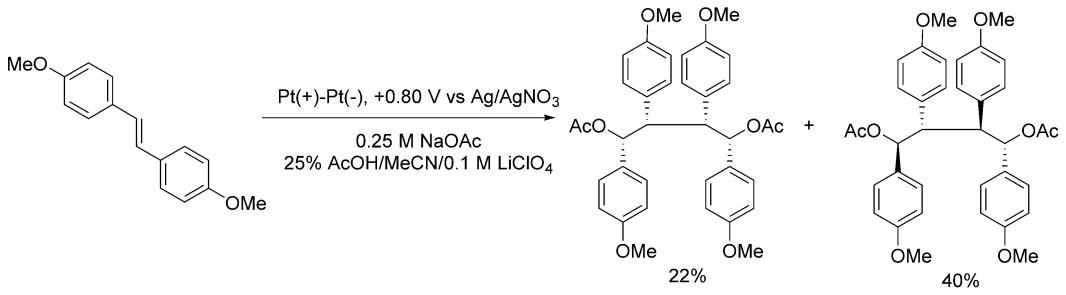
In 2018, Siewert and co-workers reported the anodic allylic esterification and amination of nonactivated alkenes catalyzed by diselenides (Scheme 26).[34] A detailed mechanistic study revealed a plausible mechanism. The selenolactone is proposed as the key intermediate of this reaction. Both intra- and intermolecular anodic allylic esterification were presented in this work. The high regioselectivity of the intermolecular anodic allylic esterification is noteworthy. The required potential to drive the reaction can be adjusted easily, which is an important advantage of this electrochemical reaction compared with conventional methods.

2.8. Electrochemical reactions involving electrogenerated carboxylates

In 2015, Senboku and co-workers reported the electrochemical three-component coupling reaction of benzylic halides, carbon dioxide and DMF by using paired electrolysis (Scheme 27).[35] In this reaction, the carboxylate ion was generated in situ from



Scheme 19. Electrochemical fluoromethylation-triggered lactonization of alkenes.

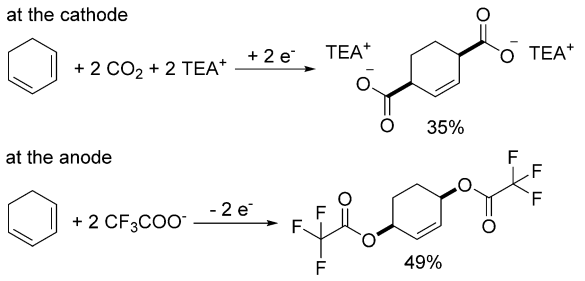


Scheme 20. Electrochemical oxidation of 4,4′-dimethoxystilbene.

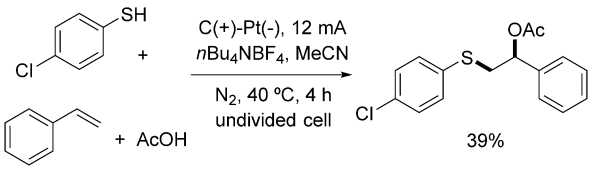
the carboxylation of benzylic halides at the cathode. At the same time, the *N*-acyliminium-ion intermediate was generated through the electrochemical oxidation of DMF at the anode. Coupling of the carboxylate ion with the *N*-acyliminium ion gives the desired coupling product.

3. C–S Bond Formation through Electrolysis of Thiocarboxylic Acids

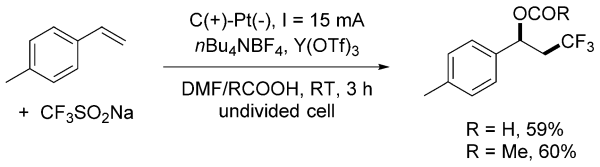
It is well established that the electrolysis of a thiocarboxylic acid can generate the corresponding sulfur-centered radical. In



Scheme 21. Divergent paired electrosynthesis of diacid and diol precursors. TEA = tetraethylammonium.



Scheme 22. Electrochemical oxidative oxysulfenylation of alkenes.



Scheme 23. Electrochemical oxytrifluoromethylation of alkenes.

2017, Wirth and co-workers reported an example of the electrochemical addition of thioacetic acid to phenyl acetylene by using an electrochemical flow reactor without supporting electrolyte (Scheme 28).[36] The thioacetyl radical is stable and adds to phenyl acetylene smoothly to afford thioester. The authors pointed out that it was crucial to use HFIP to stabilize the formed radical. Dimerization of thioacetic acid is observed with other solvents.

In 2016, Zeng and co-workers reported the paired electrosynthesis of 3-amino-2-thiocyanato-α,β-unsaturated carbonyl derivatives from β-dicarbonyl compounds and ammonium carbamodithioate mediated by bromide ions (Scheme 29).[37] In this reaction, bromide is oxidized anodically and the ammonium ion is reduced cathodically. Here, the carbamodithioate anion serves as the thiocyanato group source through the expulsion of H_2S.

4. C–O Bond Formation through Electrolysis of Phosphonic Acids

Compared with the electrolysis of carboxylic acids, the electrolysis of phosphonic acids have received less attention. In 2018, Mo and co-workers reported an anodic oxidation/cyclization of 2-(aryl)arylphosphonic acid monoesters for ethoxy dibenzooxaphosphorine oxide synthesis (Scheme 30).[38] Similar to their previous work on the anodic oxidation/cyclization of 2-arylbenzonic acids, a catalytic amount of NaOH was used in this work. This electrochemical reaction is free from transition metals, external oxidants, and electrolytes. The reaction proceeds at room temperature with hydrogen as the only byproduct. A phosphonic Kolbe oxidation-initiated mechanism was proposed.

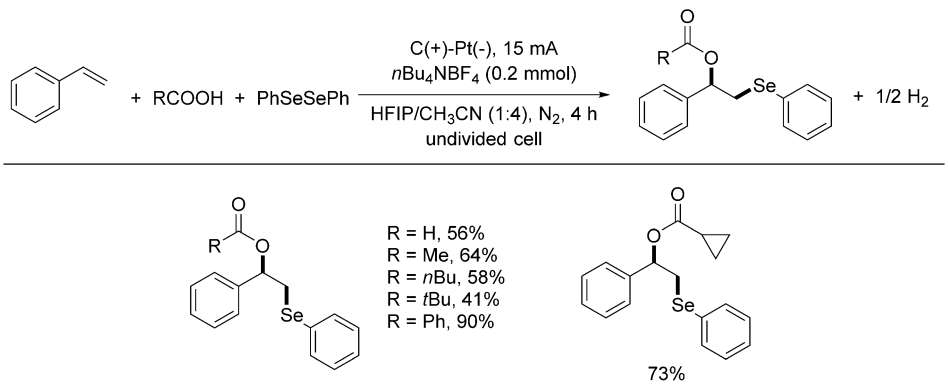
In addition to C–O bond formation through electrocatalytical transformations of carboxylic acids, the electrochemical *N*-acylation of carboxylic acids has also been reported recently.[39]

5. C–S Bond Formation or S–X (X = N, O, S, Se) Bond Formation through Electrolysis of Sulfinic Acids

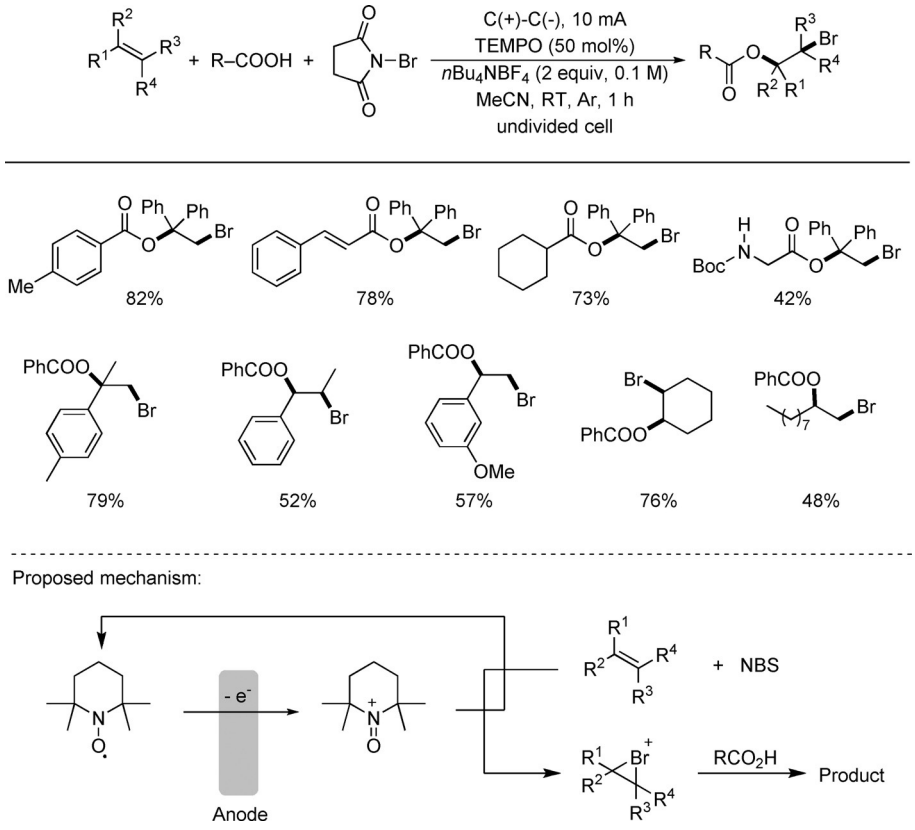
5.1. C–S bond formation through electrolysis of sulfinic acids

5.1.1. Synthesis of vinyl sulfones from sodium sulfinates

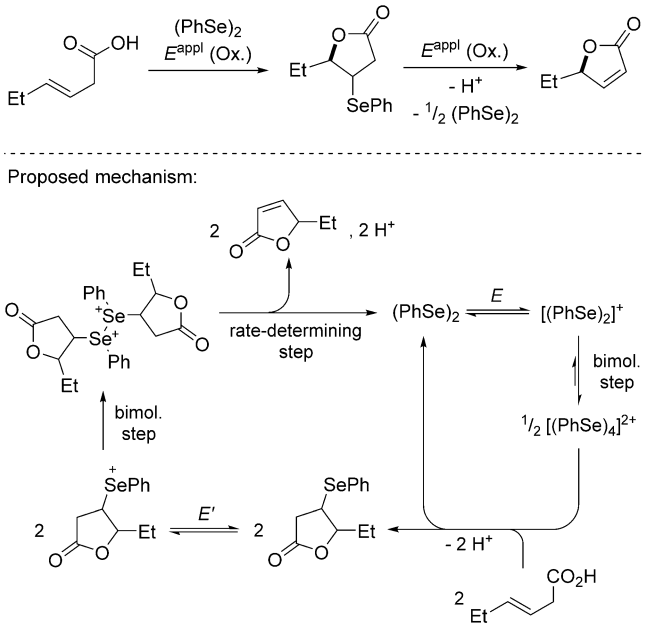
In 2015, Yuan and co-workers reported an electrochemical method for the synthesis of vinyl sulfones from sodium sulfinates and olefins (Scheme 31).[40] With NaI as the supporting



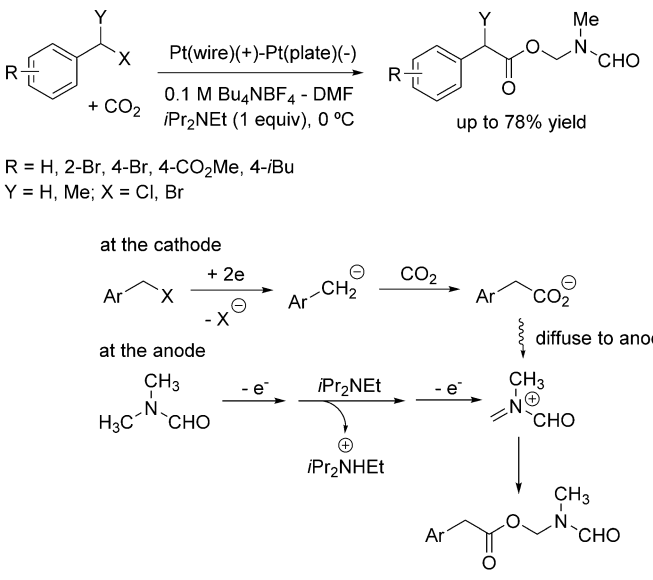
Scheme 24. Electrochemical oxyselenation of styrenes.



Scheme 25. Electro-oxidative 1,2-bromoesterification of alkenes with acids and NBS. TEMPO = (2,2,6,6-tetramethylpiperidin-1-yl)oxyl.

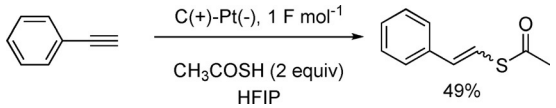


Scheme 26. Anodic allylic esterification and amination of nonactivated alkenes; bimol = bimolecular.

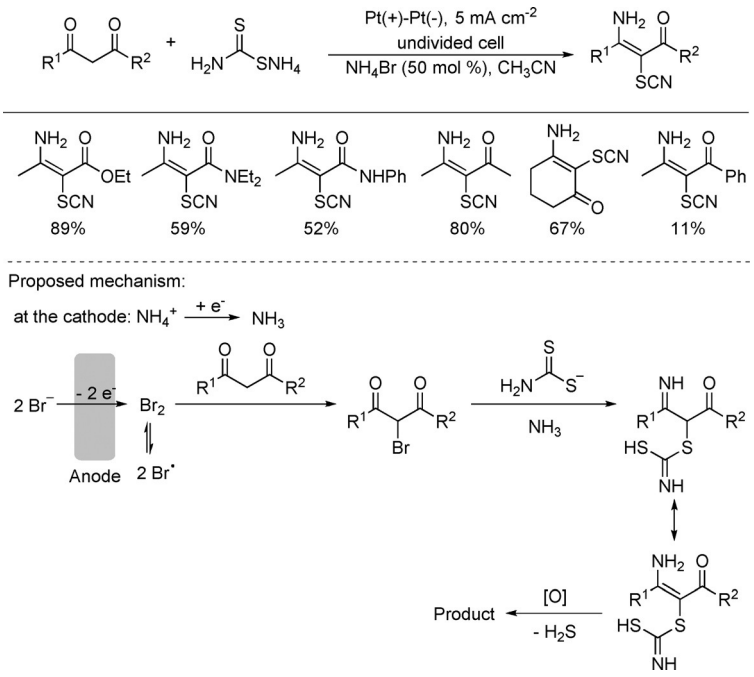


Scheme 27. Electrochemical three-component coupling reaction of benzylic halides, carbon dioxide, and DMF.

electrolyte, the reaction can be performed under transition-metal- and external-oxidant-free conditions. Apart from sodium phenylsulfinates, an aliphatic sodium sulfinate, such as sodium methanesulfinate, is also amenable. In a proposed



Scheme 28. Electrochemical addition of thioacetic acid to phenyl acetylene.



Scheme 29. Electrosynthesis of 3-amino-2-thiocyanato-α,β-unsaturated carbonyl derivatives.

mechanism, in situ electrogenerated I_2 played an important role in this reaction. Additionally, a sulfonyl radical is proposed to be generated from the sulfonyl iodide intermediate. In 2018, in a report on a radical-triggered migration reaction (see Scheme 38, below),[41] Han and co-workers reported an electrochemical synthesis of vinyl sulfone from 1,1-diphenylethylene and *para*-methylbenzenesulfinate without any mediators (Scheme 32).

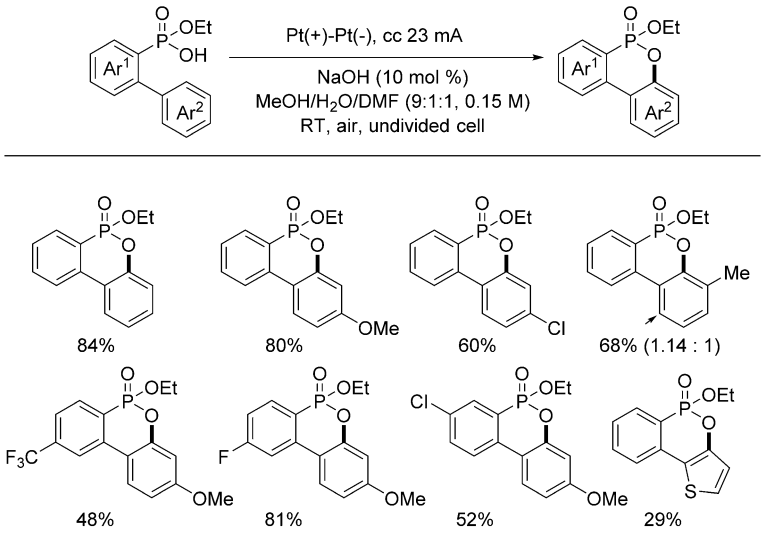
In 2016, Wang and co-workers developed the electrochemical synthesis of (*E*)-vinyl sulfones from cinnamic acids and sodium sulfinates through decarboxylative sulfono functionalization (Scheme 33).[42] Both electronic and steric effects of substituents for cinnamic acids and sodium sulfinates were observed in this reaction. Aliphatic sodium sulfinates (e.g., sodium methanesulfinate and sodium trifluoromethanesulfinate) are not compatible substrates. If styrene was employed as the coupling partner instead of cinnamic acid under the standard conditions of this decarboxylative sulfono functionalization, only a trace amount of vinyl sulfone was obtained. A sulfonyl radical triggered mechanism was proposed.

5.1.2. Synthesis of β-keto sulfones from sulfinates and 1,3-dicarbonyl compounds

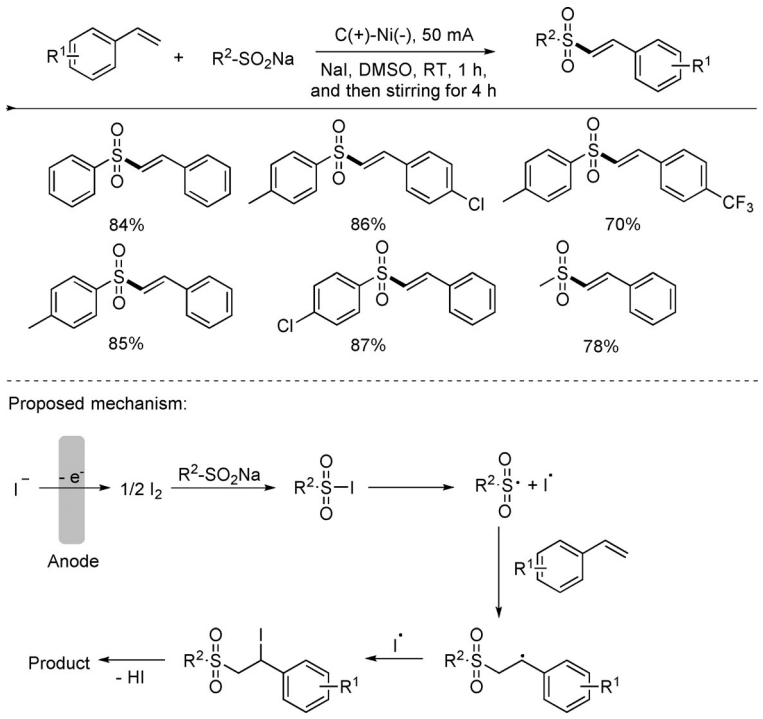
In 2015, Yuan and co-workers reported an efficient electrochemical synthesis of β-ketosulfones from sodium sulfinates and 1,3-dicarbonyl compounds with NH_4I as the supporting electrolyte (Scheme 34).[43] Notably, C–C bond cleavage occurs in this transformation. Iodide salts are necessary for this reaction because no desired product was obtained with NH_4OAc as the supporting electrolyte. The authors proposed that in situ electrogenerated I_2 played an important role and the iodinated 1,3-dicarbonyl compound served as the key intermediate in this reaction.

5.1.3. Difunctionalization of alkenes or alkynes through electrolysis of sulfinic acids

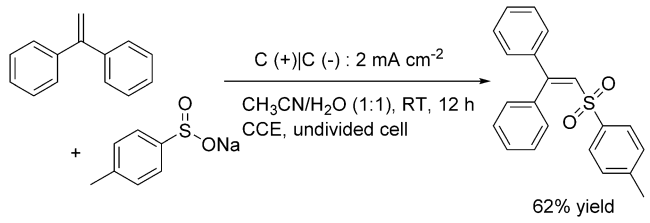
In 2016, Zeng and co-workers developed an efficient electrochemical cyclization method for the synthesis of 3-sulfonyloxindoles through difunctionalization of acrylamide from electrolysis of a mixture of sodium sulfinates and acrylamide under conditions free from transition metals and external chemical oxidants (Scheme 35).[44] A catalytic amount of NH_4Br is employed as a redox catalyst and no supporting electrolyte is re-



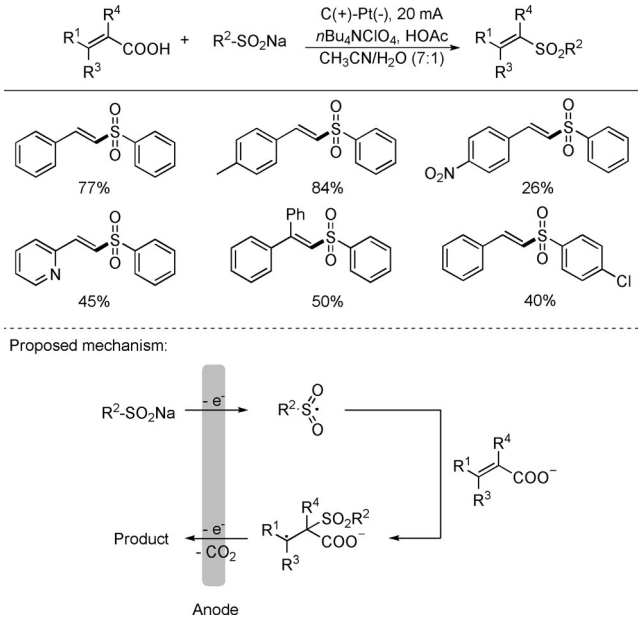
Scheme 30. Anodic oxidation/cyclization of 2-(aryl)arylphosphonic acid monoesters.



Scheme 31. Electrochemical synthesis of vinyl sulfones from sodium sulfinates and olefins.



Scheme 32. Electrochemical synthesis of vinyl sulfone from 1,1-diphenylethylene and *para*-methylbenzenesulfinate.



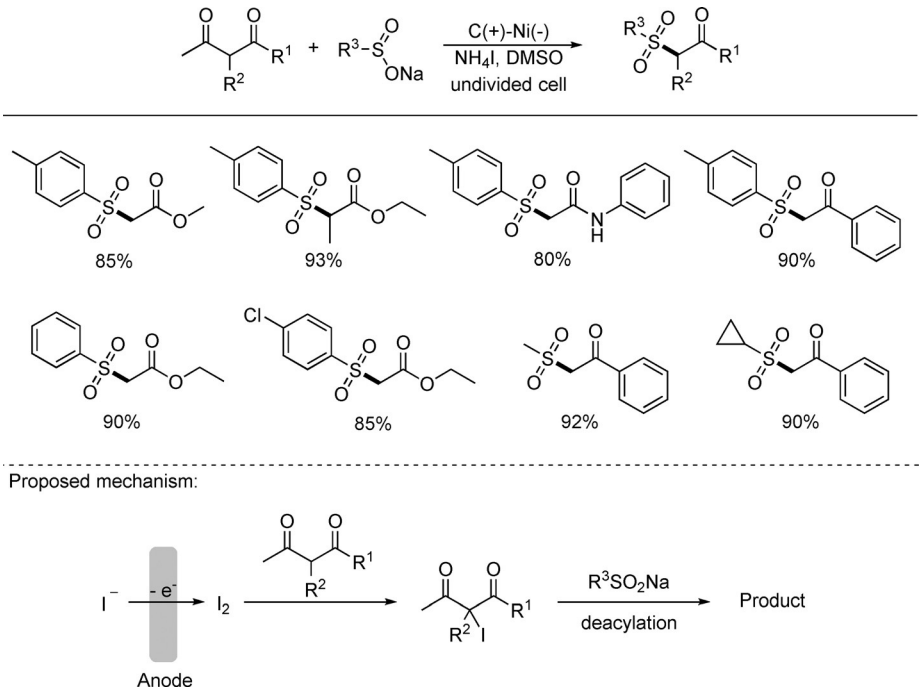
Scheme 33. Electrochemical synthesis of (*E*)-vinyl sulfones from cinnamic acids and sodium sulfinates.

quired. Mechanistically, it is proposed that a sulfonyl radical generated from sulfonyl bromide serves as a key intermediate in this reaction.

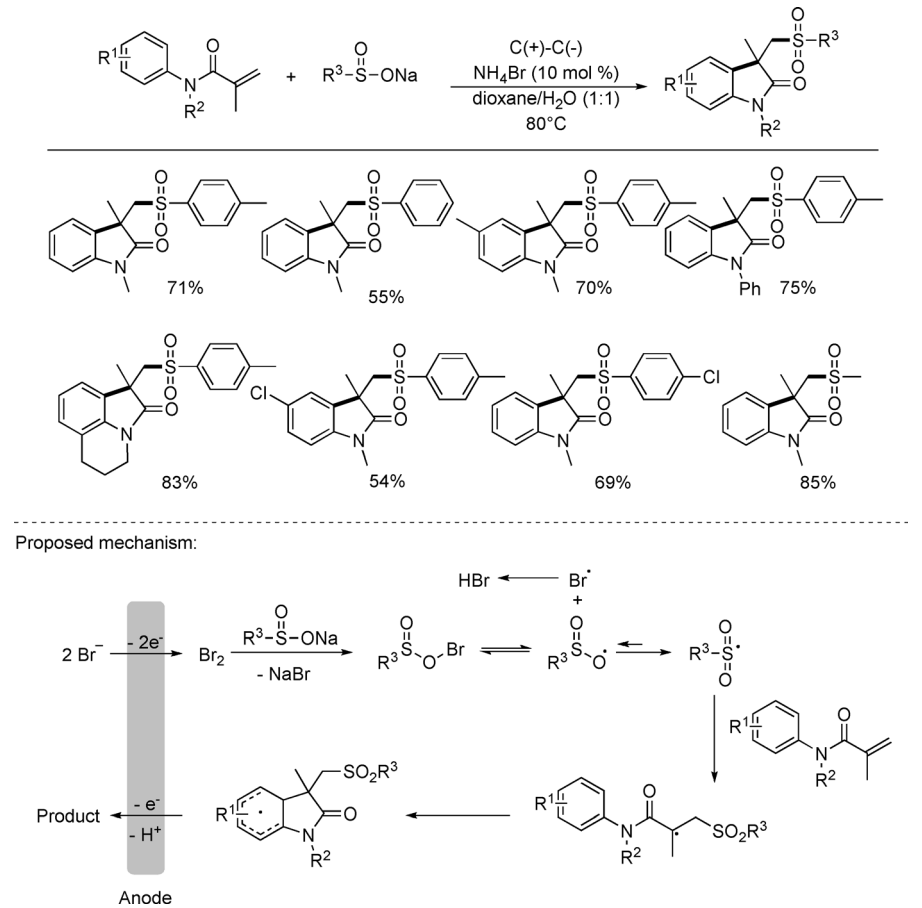
In 2017, Chang and co-workers reported an efficient organic electrosynthesis of tertiary β-hydroxysulfones from functionalized α-methylstyrenes with substituted sodium sulfinates (Scheme 36).[45] With KI as the supporting electrolyte, and a mixture of acetonitrile and water as the solvent, the desired product can be obtained in 85–96% yield under cp electrolysis. The sulfonyl radical generated from sulfonyl iodide added to the double bond of α-methylstyrene to give a benzylic radical, which was followed by loss of one electron to form the stable tertiary carbocation. Upon hydration of the carbocation, the desired product was produced. Notably, the simple styrene is also amenable to this transformation.

In 2019, Li and co-workers reported an electrochemical intermolecular 1,2-aminosulfonylation of alkenes with sulfinates and amines without the need for additive redox catalysts, metal catalysts, and chemical oxidants (Scheme 37).[46] Although arylalkenes were viable substrates in this reaction, aliphatic alkenes had no reactivity. This protocol was applicable to both aryl- and alkylsulfinates. A wide range of primary and secondary amines can undergo the aminosulfonylation reaction. A mechanism involving a sulfonyl radical mechanism was proposed. Amines serve as nucleophiles in this aminosulfonylation reaction.

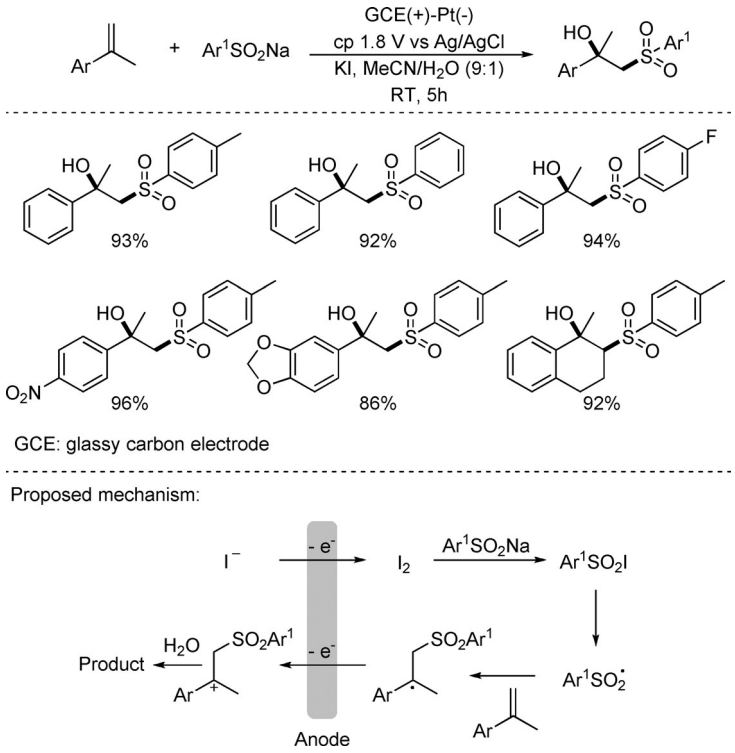
In 2018, Han and co-workers reported an electrochemical 1,2-sulfonylation/alkynylation of alkenes through radical 1,4-al-



Scheme 34. Electrochemical synthesis of β-ketosulfones from sodium sulfinates and 1,3-dicarbonyl compounds.



Scheme 35. Electrochemical cyclization method for the synthesis of 3-sulfonyloxindoles.



Scheme 36. Electrosynthesis of tertiary β-hydroxysulfones; cp = constant potential.

kynyl migration of alkynyl-substituted tertiary alcohols (Scheme 38).[41] Aryl- and alkyl-substituted sodium sulfinates were used as the sulfonyl source in this reaction. Apart from 1,4-alkynyl migration, 1,4-alkenyl migration was also demonstrated. The reaction proceeds smoothly in an undivided cell without the use of any metal catalyst, additive, or external chemical oxidant. This reaction represents the first electrochemical distal radical migration reaction. A possible mechanism was proposed. Anodic oxidation of sodium sulfinate gives the oxygen-centered radical, which resonates to the more stable sulfonyl radical. The sulfonyl radical adds to the terminal position of the alkene to give a radical, followed by 1,4-alkynyl migration.

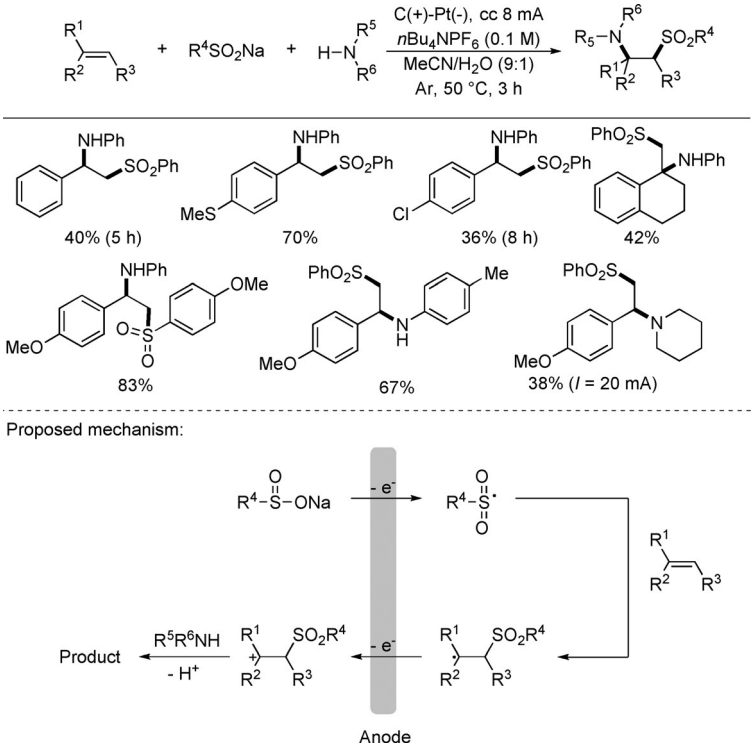
In the same year, Guo and co-workers reported the electrochemical sulfonylation/heteroarylation of alkenes with sulfinic acids through distal heteroaryl *ipso* migration (Scheme 39).[47] Various sulfonated functionalized heteroarenes were prepared in an undivided cell, avoiding the use of any metal catalysts, additives, or external chemical oxidants. A sulfonyl radical initiated mechanism, similar to that reported by Han and co-workers,[41] was proposed.

In 2019, Zhang and co-workers reported the electrochemical sulfonylation/semipinacol rearrangement of allylic alcohols by using sodium arylsulfinates as reagents (Scheme 40).[48] All-carbon quaternary stereocenters were constructed by utilizing this strategy. It is possible that the sulfonyl radical initiates this difunctionalization of alkenes and the radical adduct might be oxidized to carbocation, which subsequently undergoes a cationic 1,2-rearrangement process. Stoichiometric oxidants and transition-metal catalysts were not required in this protocol.

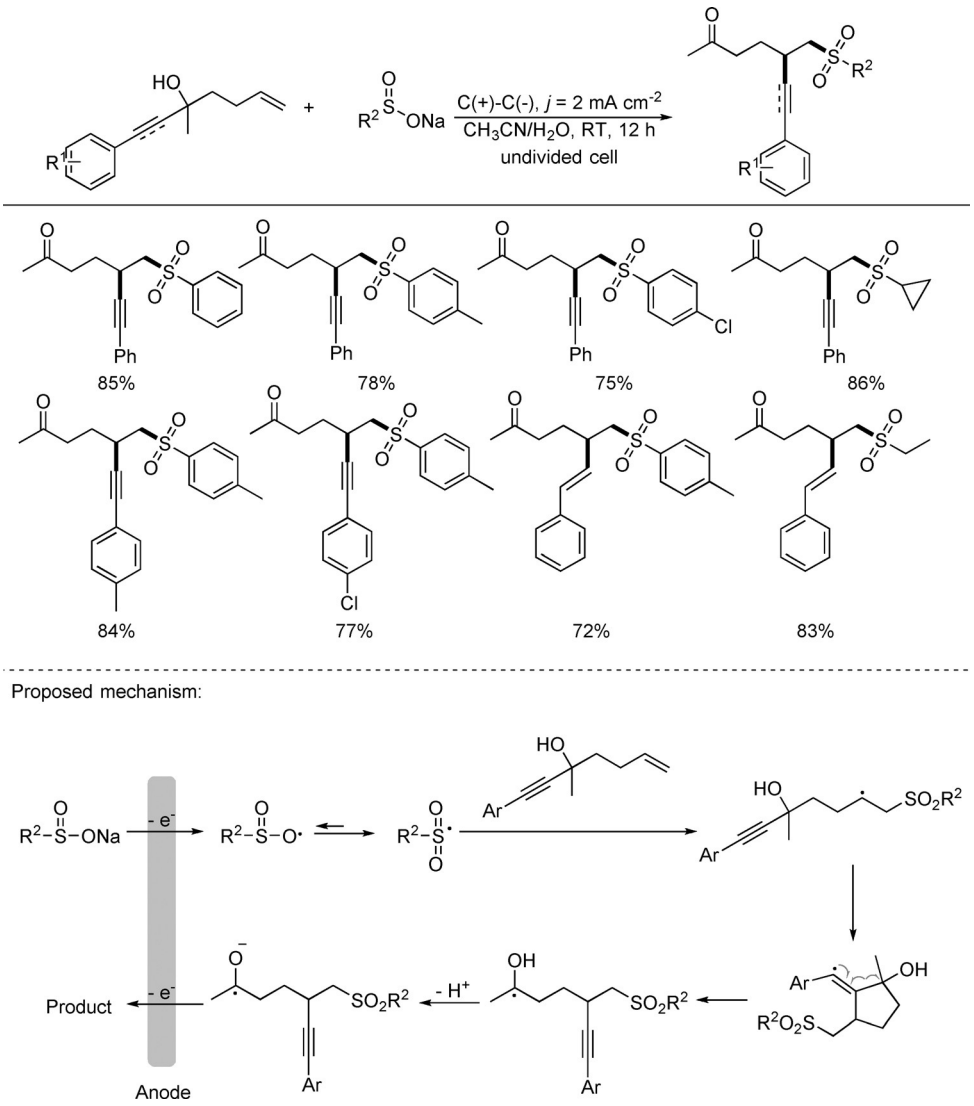
In 2017, Lei and co-workers developed an efficient electrochemical arylsulfonylation reaction of ynones with sulfinic acids under external chemical oxidant free conditions (Scheme 41).[49] A series of sulfonated indenones could be obtained with TBAI as the redox catalyst. A sulfonyl radical initiated tandem reaction mechanism was proposed. Notably, a similar arylsulfonylation product was obtained if the chalcone was used as the substrate to react with benzenesulfinic acid under electro-oxidation conditions.

5.1.4. Arylation of sulfinic acids through electrolysis of sulfinic acids

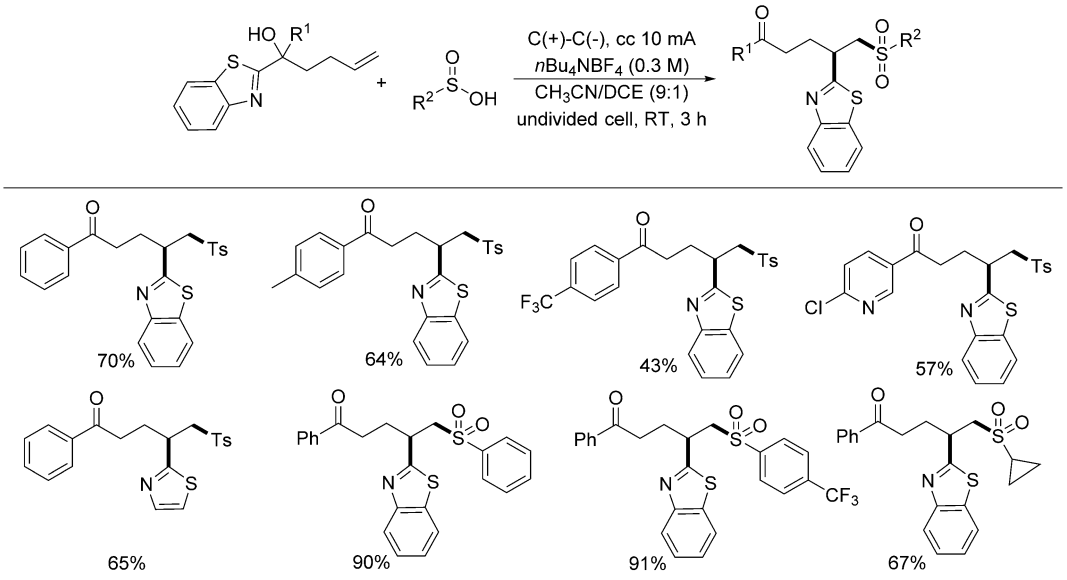
Electrochemical arylation of sulfinic acids is an important method for the synthesis of arylsulfones. Electrogeneration of phenoquinone and its analogues as electrophiles is a popular strategy for the arylation of sulfinic acids.[50] Additionally, in 2017, Yu and co-workers reported the electrochemical α-sulfonylation of 1*H*-indoles with sodium sulfinates by using a catalytic amount of TBAI.[51] Because reviews by the groups of Baran and Waldvogel summarized part of this field,[1a,b] herein we only focus on some representative advances made in recent years and do not reiterate the same content. Notably, for some cases, not only C–S bonds, but also S–N bonds, are constructed in sequential reactions. We discuss these cases in Section 5.3.



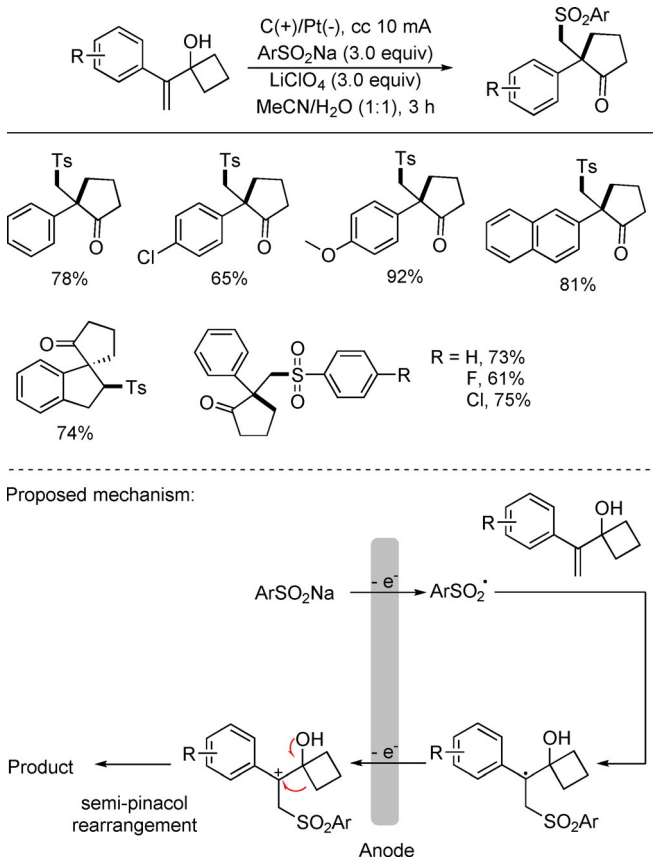
Scheme 37. Electrochemical three-component 1,2-aminosulfonylation of alkenes.



Scheme 38. Electrochemical 1,2-sulfonylation/alkynylation of alkenes through radical 1,4-alkynyl migration.



Scheme 39. Electrochemical sulfonylation/heteroarylation of alkenes with sulfinic acids. DCE = 1,2-dichloroethane.

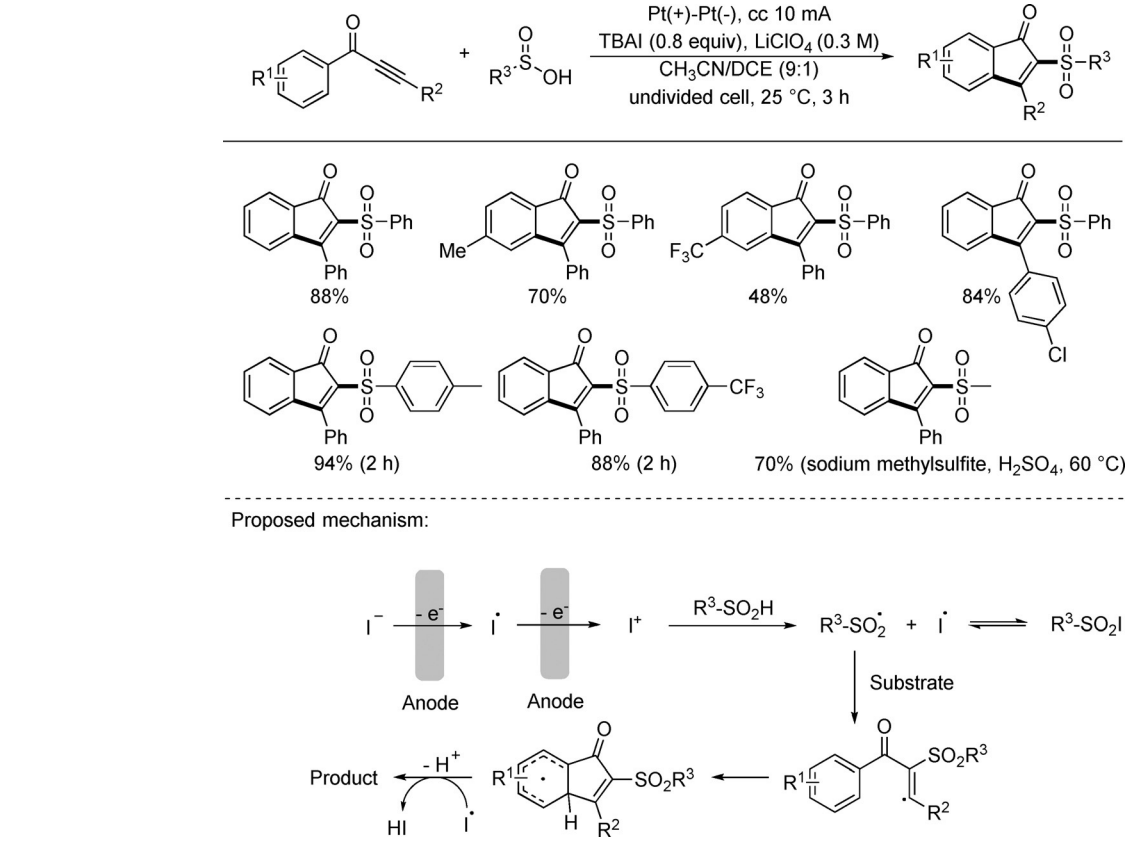


Scheme 40. Electrochemical sulfonylation/semipinacol rearrangement of allylic alcohols.

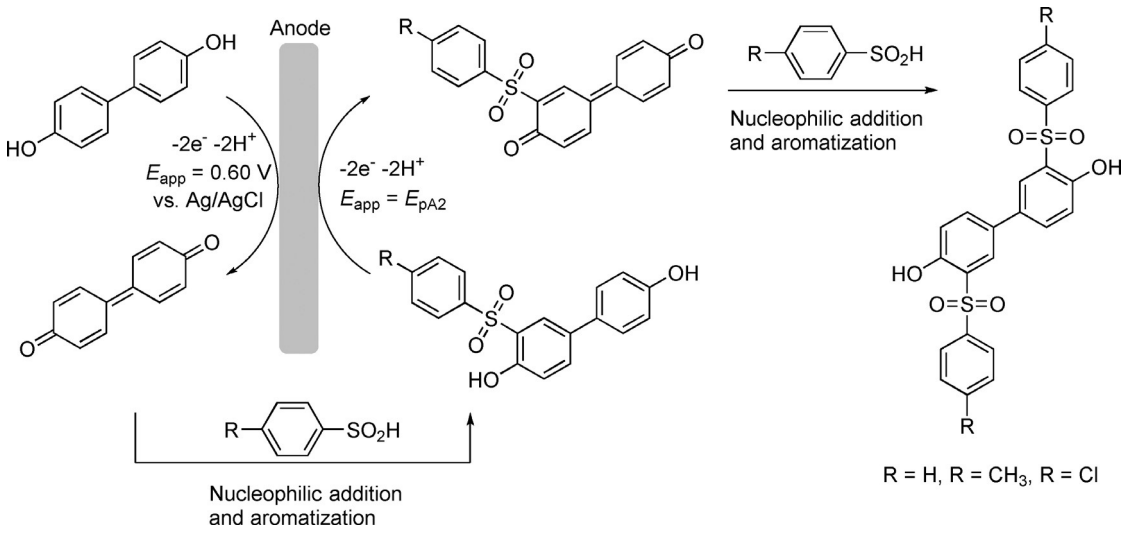
In 2016, Nematollahi and co-workers reported the electrochemical synthesis of arylsulfonyl-4,4′-biphenol and bis-phenylsulfonyl-4,4′-biphenol derivatives through the electrochemical oxidation of 4,4′-biphenol in the presence of arylsulfinic acids as nucleophiles (Scheme 42).[50a] Different products can be obtained, depending on the electrode potential.

In 2017, Momeni and Nematollahi reported the convergent paired electrochemical synthesis of new aminonaphthol derivatives through the oxidation (and reduction) of the acid orange 7 in the presence of arylsulfinic acids as nucleophiles (Scheme 43).[50b] It is proposed that the electrogenerated 1-iminonaphthalen-2(1*H*)-one participates in a Michael addition reaction with arylsulfinic acids to form the 1-amino-3-(phenylsulfonyl)naphthalen-2-ol derivatives.

In 2019, Waldvogel and co-workers developed a novel electrochemical strategy for the synthesis of arylsulfones by direct sulfonylation of phenols with sodium sulfinates (Scheme 44).[52] In this method, the sulfinates are used both as the supporting electrolytes and coupling components. Therefore, additional reagent waste is prevented. HFIP might play a role of stabilizing the radical intermediate. By adding water to the solvent, decomposition of the generated sulfones can be diminished because hydrogen is preferably generated at the cathode. The following mechanism was proposed: Initially, a phenoxyl radical is formed through the electrochemical oxidation of the phenol component. The phenoxyl radical is trapped by nucleophilic attack from the sulfinate anion, which forms a C–S bond. The final product is obtained after a further anodic oxidation



Scheme 41. Electrochemical arylsulfonylation reaction of ynones with sulfinic acids. TBAI = tetrabutylammonium iodide.



Scheme 42. Electrochemical synthesis of arylsulfonyl-4,4′-biphenol and bis-phenylsulfonyl-4,4′-biphenol derivatives.

process. The mechanistic assumption is supported by oxidation potential determinations, which reveal lower oxidation potentials of the phenol components, in comparation with that of the sulfinates.

5.2. S–X (X = N, O, S, Se) bond formation through electrolysis of sulfinic acids

5.2.1. S–N bond formation through electrolysis of sulfinic acids

The electrochemical approach has provided a complementary method to access sulfonamides.[53] In 2016, Zeng and co-workers reported an efficient electrochemical synthesis of sulfonamides via oxidative amination of sodium sulfinates mediated by NH_4I as a redox catalyst (Scheme 45).[54] A wide range of substrates, including aliphatic or aromatic secondary and primary amines, as well as aqueous ammonia, proved to be compatible with this method. External oxidants or corrosive molecular iodine were avoided in this transformation. Later, the groups of Terent'ev[55] and Yuan[56] independently reported similar protocols. Notably, in the report by Yuan and co-workers, with H_2O as the solvent and NaI as the supporting electrolyte, the electrolyte solution could be reused up to 10 times without a clear reduction in yield.

Apart from using halide anions as the redox catalyst, another important strategy in this field is the electrogeneration of nitrogen-centered electrophiles in the presence of sulfinic acids as nucleophiles.[57] We highlight several of the most important advances employing this strategy below.

In 2012, Nematollahi and co-workers reported the electrochemical synthesis of some sulfonamide derivatives through the electro-oxidation of 4-propyl and 4-butyl derivatives of urazole in the presence of arylsulfinic acids as nucleophiles (Scheme 46).[57a] It is proposed that electrogenerated 4-alkyl-4*H*-1,2,4-triazole-3,5-diones are attacked by arylsulfinic acids.

Furthermore, in 2017, Varmaghani and co-workers reported the electrochemical synthesis of two different series of sulfonamides by using 4-(4-nitrophenyl)urazole and arylsulfinic acids as substrates and controlling the potential during electrolysis (Scheme 47).[57b] One series of sulfonamides were obtained through direct electrochemical oxidation of 4-(4-nitrophenyl)-urazole in the presence of arylsulfinic acids and another one were obtained through a paired electrosynthesis. In addition, they also investigated the electrochemical oxidation of 4-cyclohexylurazole in the presence of arylsulfinic acids.

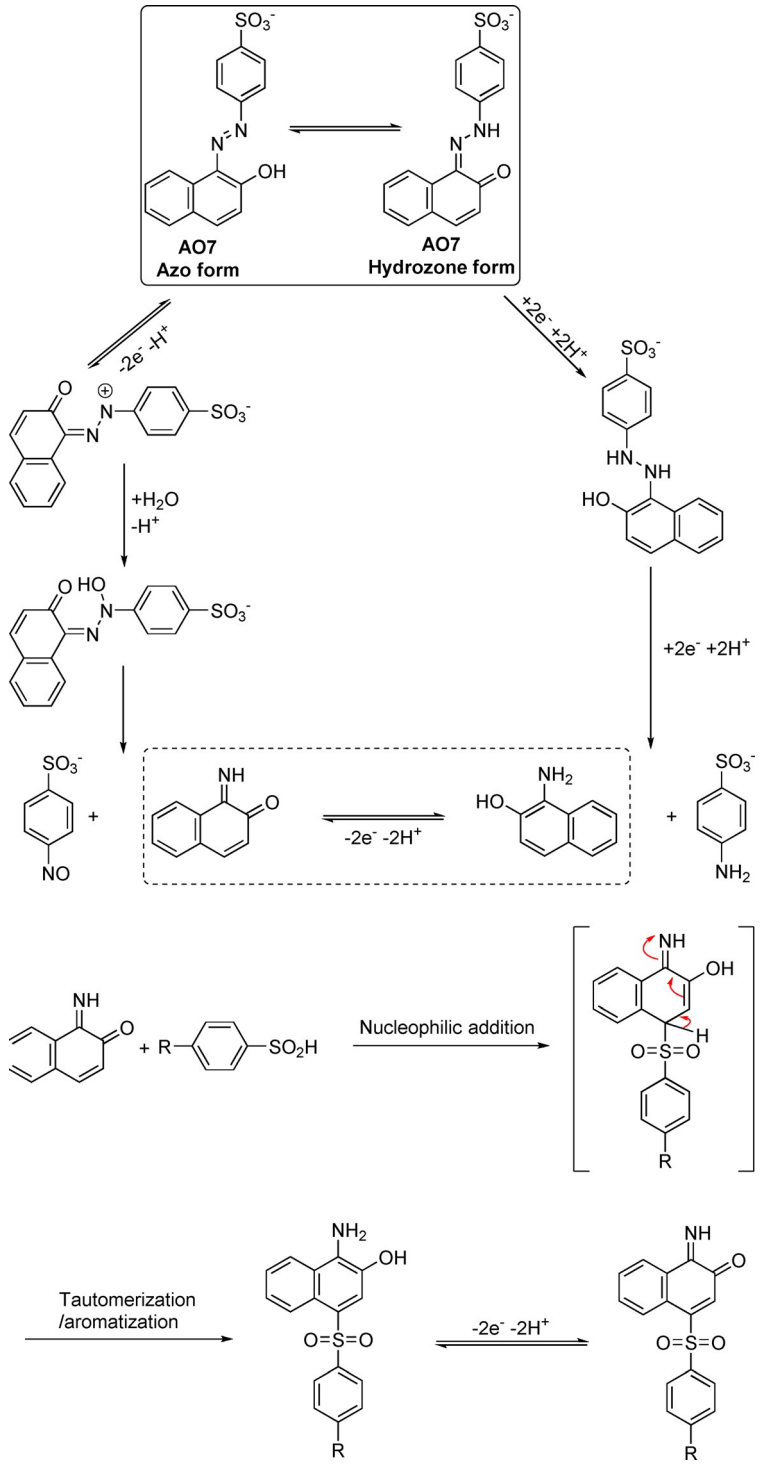
In 2015, Nematollahi and Khazalpour reported the synthesis of disulfonamide derivatives of *N*,*N*-dimethyl-1,4-benzenediamine by electrochemical oxidation of 4-nitroso-*N*,*N*-dimethylaniline (NDA) in the presence of arylsulfinic acids as nucleophiles (Scheme 48).[57c] Interestingly, *N*-arylsulfonyl-3-arylsulfonyl derivatives were obtained by the chemical reaction of NDA with arylsulfinic acids.

In the same year, they also reported the synthesis of *N*-[4-(dimethylamino)phenyl]benzenesulfonamide through the electrochemical reduction of NDA with arylsulfinic acids as nucleophiles (Scheme 49).[57d] This is the first report describing the generation of a Michael acceptor through electrochemical reduction.[57e]

In 2018, Nematollahi and co-workers reported a paired electrochemical method for the synthesis of sulfonamides, diarylsulfones, and bis(arylsulfonyl)aminophenols by using nitrobenzene derivatives and arylsulfinic acids as starting materials (Scheme 50).[57f] For the electrochemical oxidation of nitrobenzene, *p*-nitroaniline, and *p*-nitrophenol in the presence of arylsulfinic acids, the products were sulfonamides, diarylsulfones, and bis(arylsulfonyl)aminophenols, respectively. Therefore, the product selectivity was greatly influenced by the nature of the functional group.

5.2.2. S–O bond formation through electrolysis of sulfinic acids

In 2019, Terent'ev and co-workers reported the electrochemical synthesis of sulfonates from sodium sulfinates and *N*-hydroxysuccinimide (Scheme 51).[58] The yields were lower compared

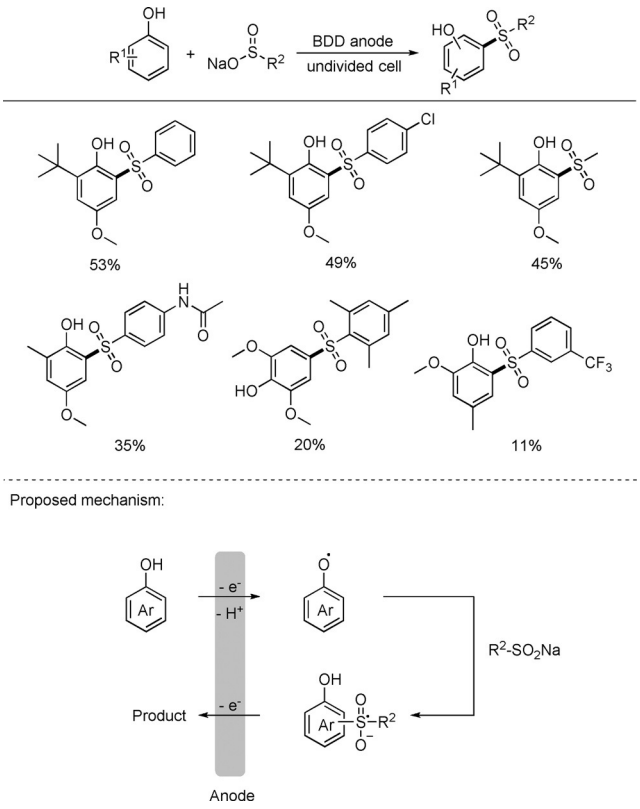


Scheme 43. Electrochemical synthesis of new aminonaphthol derivatives.

with sulfonylhydrazides as the sulfonylation reagent. NH_4Br serves as a supporting electrolyte in this reaction.

5.2.3. S–S/S–Se bond formation through electrolysis of sulfinic acids

In 2019, Sun and co-workers reported the electrochemical oxidative cross-coupling of arylsulfinic acids with thiophenols, providing unsymmetrical thiosulfonates in good to excellent yields (Scheme 52).[59] The reactions of arylsulfinic acids with disulfides or diselenides were also practical under similar conditions to afford thiosulfonates or selenosulfonates. External oxidants or redox catalysts were not required in these reactions.

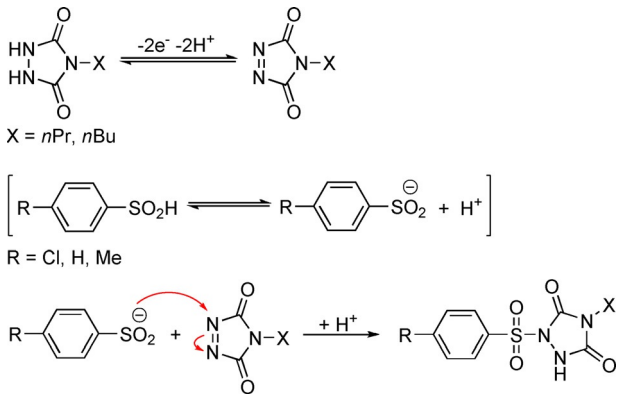


Scheme 44. Electrochemical synthesis of arylsulfones by direct sulfonylation of phenols with sodium sulfinates. BDD = boron-doped diamond.

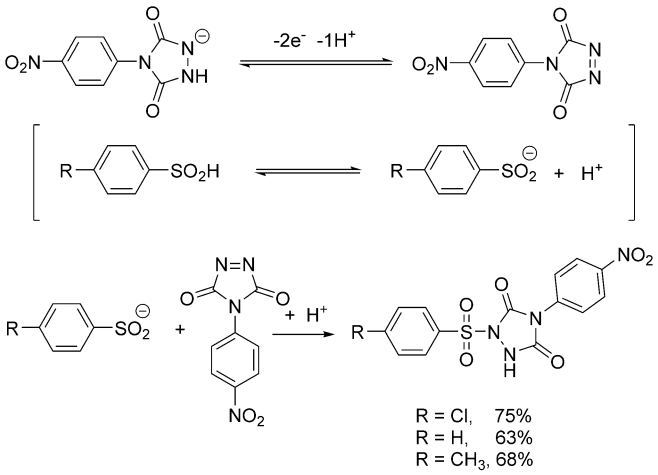
5.3. Sequential C–S and S–N bond formation through electrolysis of sulfinic acids

Electrochemical sequential C–S and S–N bond formation can be realized with the electrogeneration of electrophiles possessing both carbon- and nitrogen-centered electrophilic positions, such as *p*-methylquinoneimine, in the presence of sulfinic acids as nucleophiles.[60]

In 2017, Nematollahi and co-workers reported the synthesis of sulfonyl derivatives of *p*-methylaminophenol through the reaction of electrogenerated *p*-methylquinoneimine with sulfinic acids. Some mono- and bis(or tris)sulfonyl-*p*-(methylamino)-phenol derivatives were obtained by changing the applied potential (Scheme 53).[60a] This method does not deal with organic



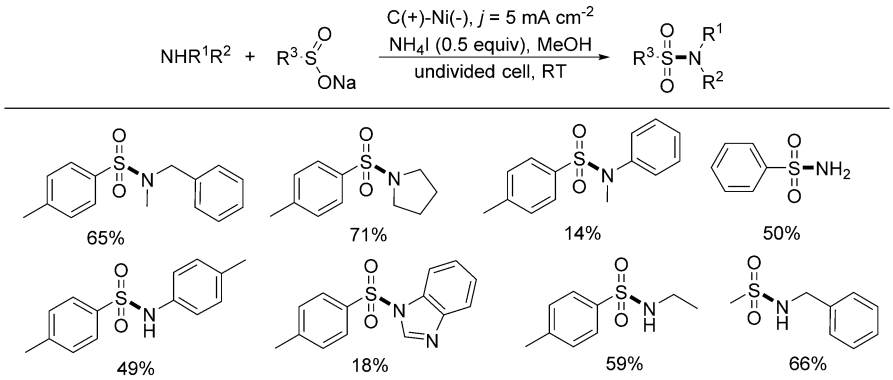
Scheme 46. Electrochemical oxidation of 4-substituted urazoles in the presence of arylsulfinic acids.



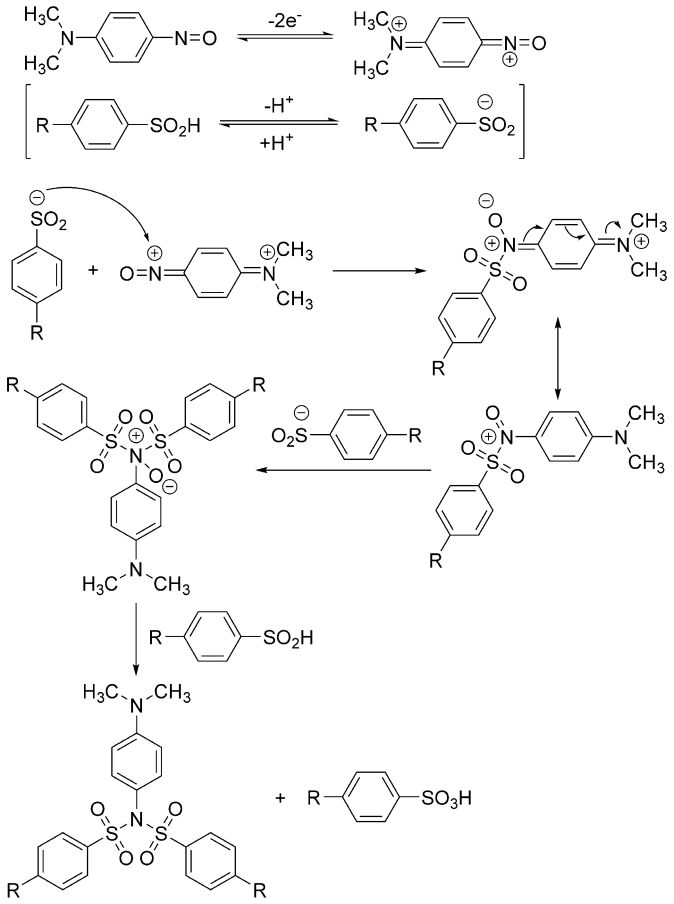
Scheme 47. Electrochemical synthesis of diverse sulfonamide derivatives.

solvents and strong acid/bases. For the synthesis of mono- or bis-sulfonyl-*p*-(methylamino)phenol derivatives, only the C–S bond was formed. For the synthesis of tris-sulfonyl-*p*-(methylamino)phenol derivatives, both C–S and S–N bonds were constructed.

In 2018, Momeni and Nematollahi reported the electrochemical synthesis of new quinonesulfonimide derivatives by the ox-

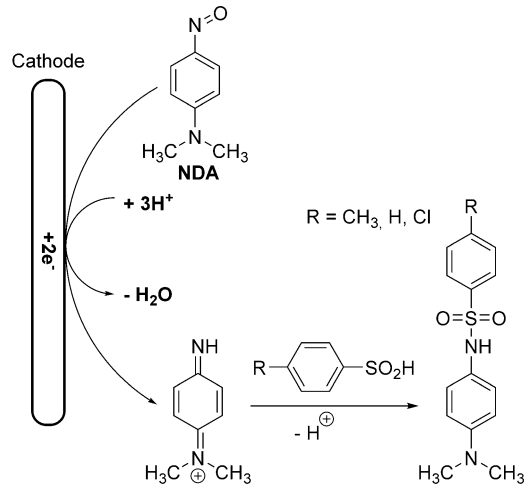


Scheme 45. Electrochemical oxidative amination of sodium sulfinates.

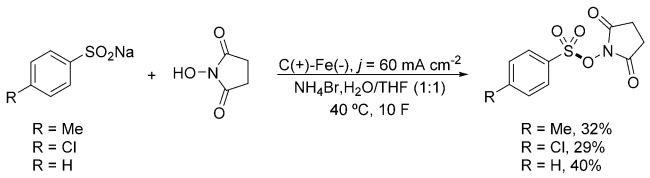


Scheme 48. Electrochemical oxidation of NDA in the presence of arylsulfinic acids.

idation of 4-aminophenyl ether in the presence of arylsulfinic acids under both electrochemical conventional batch and flow cells (Scheme 54).[60b] The lack of use of a supporting electrolyte is an important advantage for an electrochemical flow cell compared with that of a conventional batch cell.

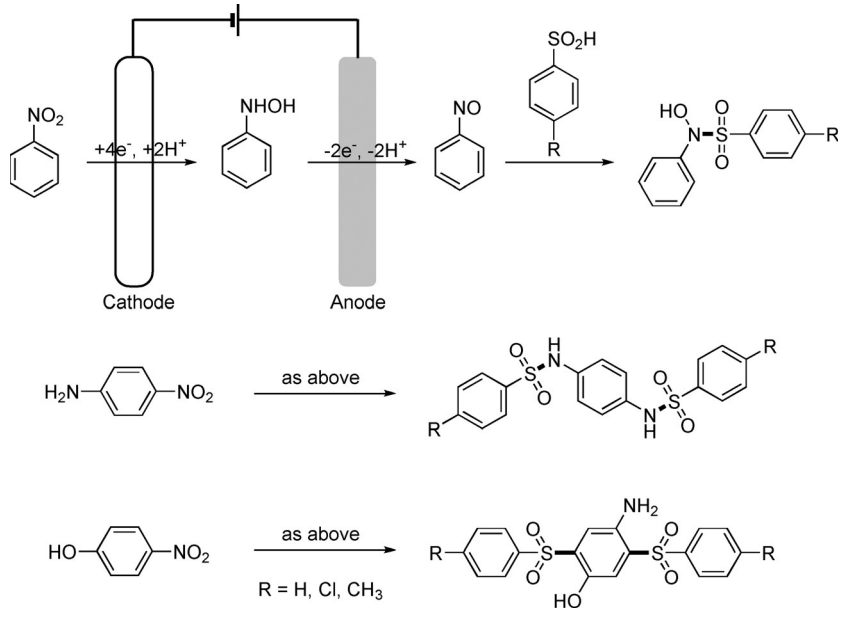


Scheme 49. Electrochemical reduction of NDA with arylsulfinic acids.

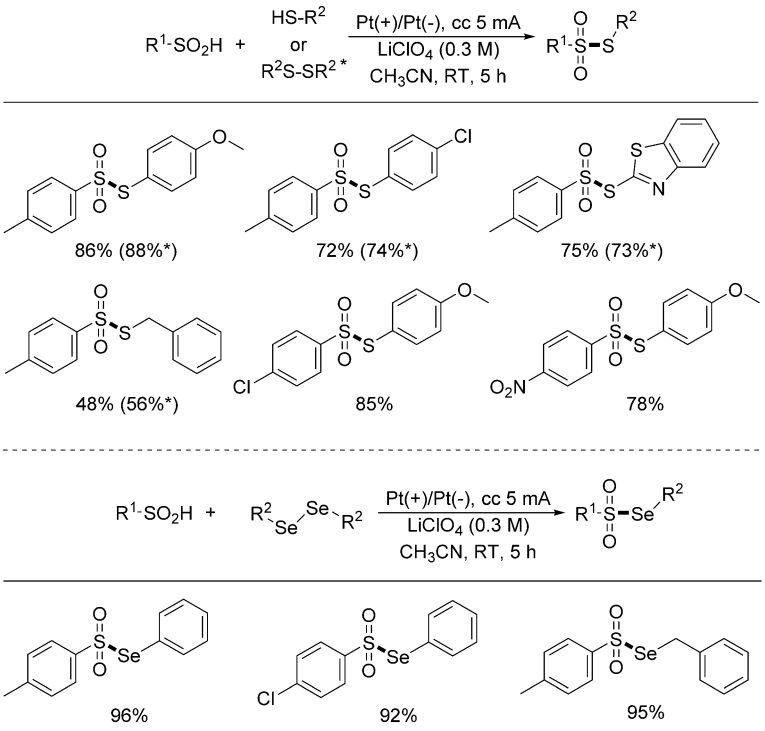


Scheme 51. Electrochemical synthesis of sulfonates from sodium sulfinates and *N*-hydroxysuccinimide.

In 2019, Nematollahi and co-workers reported a tunable paired electrochemical synthesis of benzenesulfonamide derivatives by using reductive-controlled potential electrolysis of dinitrobenzene in the presence of arylsulfinic acids (Scheme 55).[60c] By adjusting the potential, *N*-hydroxy-*N*-(4-ni-



Scheme 50. Electrochemical synthesis of sulfonamides, diarylsulfones, and bis(arylsulfonyl)aminophenols.



Scheme 52. Electrochemical oxidative cross-coupling of arylsulfinic acids with thiophenols.

trophenyl)benzenesulfonamide derivatives and *N*-[4-amino-3-(phenylsulfonyl)phenyl]benzenesulfonamide derivatives could be selectively obtained.

6. C–O Bond Formation through Electrolysis of Sulfonates

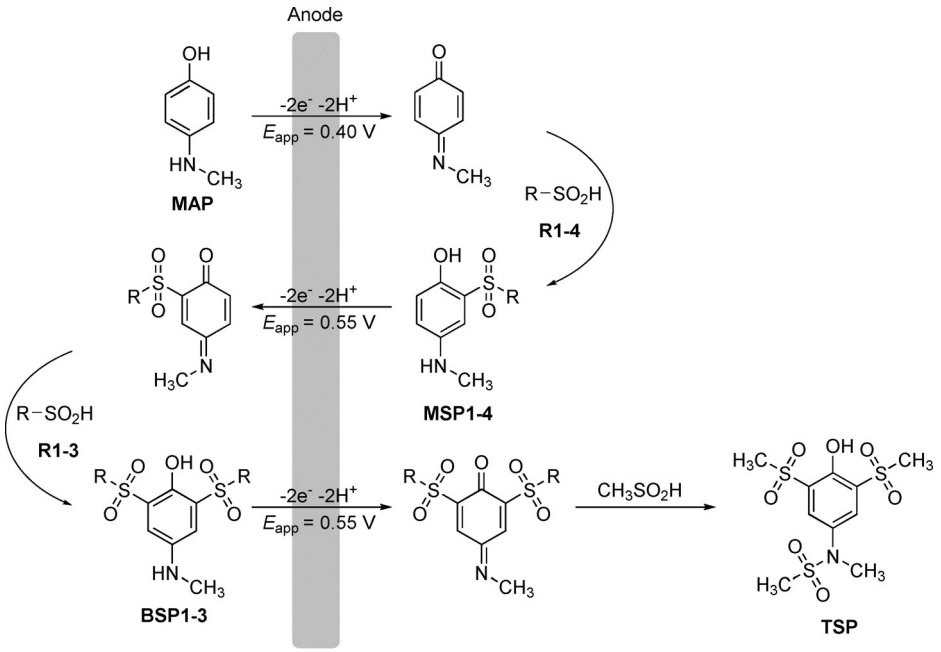
One of the most important applications of electrolysis of sulfonates lies in the electrochemical glycosylation. The use of triflate anions as nucleophiles in the presence of glycosyl cation pools gave α-glycosyl triflates selectively. The triflate group can be displaced by an alcohol to construct a β-selective glycosyl linkage. Because this field has been discussed by other reviews,[1a,61] we do not reiterate it in depth here.

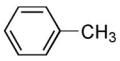
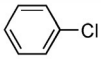
In 2019, Waldvogel and co-workers developed the first electrochemical protocol for the direct synthesis of aryl mesylates by dehydrogenative coupling (Scheme 56).[62] To trap the anodically generated radical cations efficiently, $Bu_4NCH_3SO_3$ in acetonitrile was used as a supporting electrolyte to ensure a sufficient concentration of the methanesulfonate nucleophile. The formation of regioisomeric products was observed in some cases. In the case of biphenyl, the corresponding dimesylated product could be isolated. In addition, anodic formation of aryl benzenesulfonates was also successfully performed.

7. Summary and Outlook

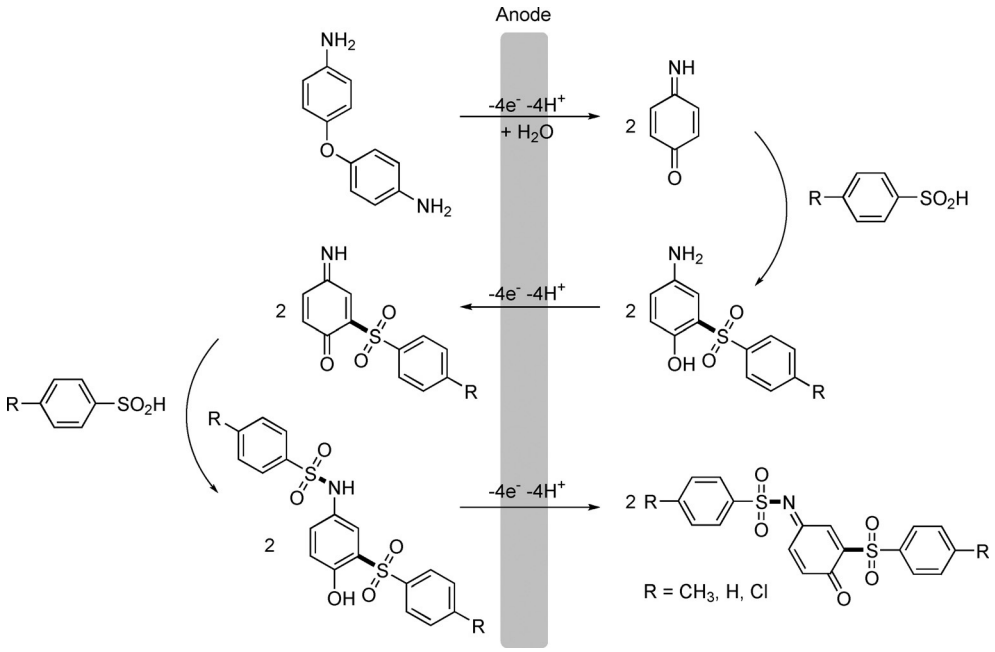
Electrolysis of organic acids has gained increasing attention in recent years and impressive advances have been achieved. Despite the well-known decarboxylation possibility of carboxylates through anodic oxidation, a number of ester-forming reactions involving carboxylic acids have been reported. By employing electricity as the oxidant, many oxidative bond-forming reactions can be performed under conditions free from external chemical oxidants. Furthermore, transition-metal catalysts can also be obviated in many cases. Many challenging transformations, including inert chemical bond functionalization and difunctionalization of alkenes/alkynes, can be realized by using electrochemical methods. As for the design of electrochemical reactions involving transformations of organic acids, it is not limited to anodic oxidation; cathodic reduction and paired electrolysis can also be considered. The most common roles of organic acids in these electrochemical reactions are radical precursors and nucleophiles. Additionally, the scalability of electrosynthesis has been demonstrated in many reactions. Notably, the selectivity of the electrochemical reactions can be finely tuned through several factors, including the electrode potential, which represents a great advantage over other methods. Interestingly, the product selectivity of certain electrochemical reactions can be greatly influenced by the nature of the functional groups and be different from that obtained through conventional chemical reactions.

Several issues remain to be solved in the field of electrochemical functionalization of organic acidic groups. The substrate scope remains limited in some reactions. For some intramolecular reactions, it is challenging to develop the corresponding intermolecular version. There is still much room to develop in the field of inert chemical bond functionalization. For example, electrochemical reactions involving C–C bond cleavage are relatively rare. Furthermore, compared with the difunctionalization of alkenes, the difunctionalization of alkynes has received less attention. Because paired electrolysis can

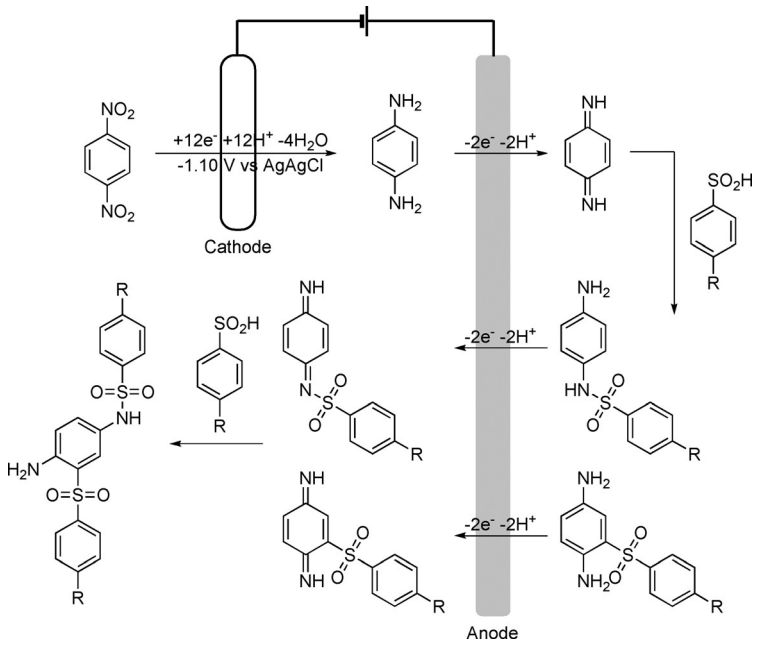


R	Yield [%, isolated product]		
	MSP	BSP	TSP
R1= 	69	77	-
R2= 	65	76	-
R3= 	58	63	-
R4= CH_4	82	-	47

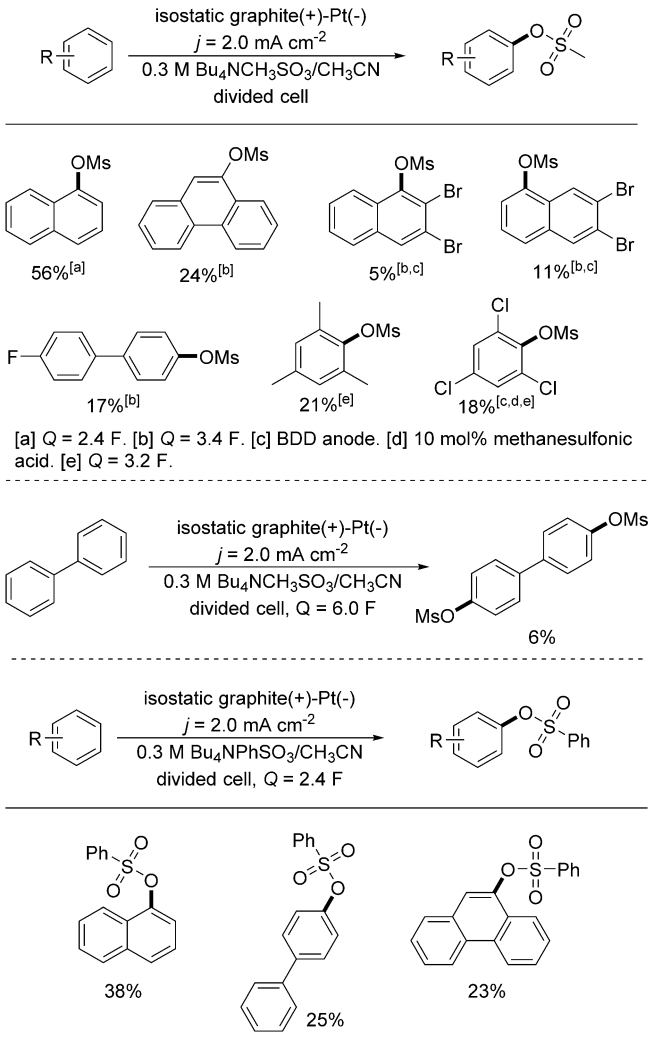
Scheme 53. Synthesis of sulfone derivatives of *p*-methylaminophenol.



Scheme 54. Electrochemical synthesis of quinone sulfonimide derivatives.



Scheme 55. Electrochemical synthesis of benzenesulfonamide derivatives.



Scheme 56. Anodic formation of aryl mesylates through dehydrogenative coupling reactions. Ms = methanesulfonyl.

possess a higher current efficiency than that of single anodic oxidation or cathodic reduction, in theory, it is significant to develop practical paired electrolysis. It is expected that more kinds of mechanistically interesting protocols will be developed. Moreover, more detailed mechanistic studies should be undertaken to help our understanding of these electrochemical reactions. Enantioselective electrochemical transformations remain elusive. For indirect electrolysis, the loading of the redox catalyst is large in some cases. For the reaction solvents, green solvents, such as water, are favored for environmental reasons. Because a supporting electrolyte is required in most electrochemical reactions, it is important to reduce the amount of supporting electrolyte and develop effective recovery methods to save costs. Finally, electrochemical flow reactions deserve more attention due to their unique advantages compared with those of batch reactions.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: electrochemistry · electrosynthesis · organic acids · oxidation · reaction mechanisms

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