The Application of Sulfonyl Hydrazides in Electrosynthesis: A Review of Recent Studies

Bao-Chen Qian, Chao-Zhe Zhu, and Guang-Bin Shen*

Cite This: ACS Omega 2022, 7, 39531−39561

ABSTRACT: Sulfonyl hydrazides are viewed as alternatives to sulfonic acids and their salts or sulfonyl halides, which are broadly used in organic synthesis or work as active pharmaceutical substances. Generally, sulfonyl hydrazides are considered good building blocks and show powerful value in a diverse range of reactions to construct C−S bonds or C−C bonds, and even C−N bonds as sulfur, carbon, or nitrogen sources, respectively. As a profound synthetic tool, the electrosynthesis method was recently used to achieve efficient and green applications of sulfonyl hydrazides. Interestingly, many unique and novel electrochemical syntheses using sulfonyl hydrazides as radical precursors have been developed, including cascade reactions, functionalization of heterocycles, as well as a continuous flow method combining with electrochemical synthesis since 2017. Accordingly, it is necessary to specifically summarize the recent developments of electrosynthesis with only sulfonyl hydrazides as radical precursors to more deeply understand and better design novel electrochemical synthesis reactions. Herein, electrosynthesis research using sulfonyl hydrazides as radical precursors since 2017 is reviewed in detail based on the chemical structures of products and reaction mechanisms.

1. INTRODUCTION

The application of sulfonyl hydrazides in organic chemistry has witnessed a long history.1 In the Shapiro reaction2−3 and variation of the Wolff−Kishner−Huang Minlon reduction reaction, TsNHNH2 was chosen to reduce the carbonyl group (C=O) to the methylene (CH2) (Scheme 1). In chemical reactions, sulfonyl hydrazides are viewed as alternatives to sulfinic acids4 and their salts5,6 or sulfonyl halides7−11 and are broadly used in organic transformations12,13 or syntheses of active pharmaceutical substances14. Compared with other sulfonic derivatives or sulfonyl halides, sulfonyl hydrazides are easy to handle, stable, moisture-compatible, and noncorrosive. Thus, sulfonyl hydrazides are good building blocks and provide a powerful value in a diverse range of chemical reactions.15 They could work as sulfur sources to introduce various C−S bonds under oxidative conditions16 or take part in cross-coupling reactions to form C−C or C−S bonds,17 and even donate nitrogen atoms serving as nitrogen sources, to form C−N bonds.18,19 In some cases, sulfonyl hydrazides were used as reductants.20

Because of its attractive properties, how to utilize sulfonyl hydrazides has drawn much attention from organic chemists and pharmaceutical scientists. Photoredox catalyzed radical sulfonylation21 and traditional synthetic strategies usually consist of transition-metal catalyzed reactions,22,23 and iodide catalyzed sulfonylation with molecular or ionic iodide16,24,25 are common methods in the application of sulfonyl hydrazides. However, there are many unavoidable problems with these common methods, such as the consumption of stoichiometric amounts of chemical oxidants, the use of metal catalysts sensitive to moisture or oxygen, as well as the output of a substantial number of environmentally hazardous wastes. These unfavorable disadvantages have limited the further applications of these
Therefore, green and practical usage with sulfonyl hydrazides has always been a challenge to be settled. Recently, several reports on the electrochemical application of sulfonyl hydrazides indicated that electrosynthesis could be one of the solutions to this problem. As known to all, the use of external oxidants or reductants could be limited to a certain extent in electrochemical reactions, and there are many advantages for electrosynthesis over traditional methods. 

Therefore, electrosynthesis is green, efficient, and environmental-friendly, and has been widely applied in synthetic methodology development and natural product synthesis.
As a profound synthetic tool, it is indisputable that electrosynthesis has a hopeful future. Due its the important role, there have been several reviews about sulfonyl hydrazides focusing on different aspects. In 2017, Tian et al. reviewed the synthesis of sulfone compounds using sulfonyl hydrazides as sulfonyl sources, and reactions were classified according to the scope of substrates in this review. A recent summary of sulfonyl hydrazides in organic chemistry was prepared by Huang and co-workers in 2020, in which reactions were classified by crucial intermediates. Although electrochemical applications of sulfonyl hydrazides have been mentioned in several reviews, it is still necessary to make a systematic and clear summary of the recent development of electrochemical reactions more effectively. Herein, the electrosynthesis using sulfonyl hydrazides as radical precursors since 2017 is reviewed in detail based on the chemical structures of products and reaction mechanisms.

Sulfonyl hydrazides could be applied in a broad range of fields; we classified these cases into four sections: in section I, sulfonyl hydrazides were used in the syntheses of sulfones, mainly including \( \beta \)-substituted and \( \alpha,\beta \)-unsaturated sulfones through the addition to multibonds; in section II, sulfonyl hydrazides participated in reactions with multifunctional compounds involving radical-triggered cyclization; examples in section III are mainly about the functionalization of heterocyclic compounds with sulfonyl hydrazides, and in the last part, syntheses of sulfonyl derivatives with sulfonyl hydrazides are summarized.

When adopted in electrosynthesis, sulfonyl hydrazides have usually taken part in transformation as radicals, and the generation of sulfonyl radicals was viewed as a key step. To the best of our knowledge, sulfonyl hydrazides could be converted into radicals under electrochemical conditions in two ways, i.e., activated by mediators (path a) or oxidized directly at the anode. Subsequently, sulfonyl radicals were transformed mainly through three routes: they could undergo radical coupling and form products such as sulfonyl derivatives (path I); sometimes they might lose \( \text{SO}_2 \) and form alkyl radicals, and then add to multibonds (path II) to give carbo-radical species, or they can add to multibonds (path III) and produce carbo-radical species (path IV). Carbo-radical species could form products through radical coupling (path IV) or undergo oxidation to form carbo-cation (path V) and afford products via the elimination process or the combination with nucleophiles (path V).

2. SULFONYLATION OF ALKENES AND ALKynes

Sulfones have important applications in organic chemistry or medicinal research, and are involved in a number of reactions and could be used as starting materials to synthesize organic molecules or as medicines directly. When treated with electrochemical methods, sulfonyl hydrazides might be converted into sulfonyl radicals, which could undergo sequential addition to \( \text{C}==\text{C} \) double bonds or \( \text{C}==\text{C} \) triple bonds and generate \( \beta \)-carbon radical species. These radical species could...
be converted into β-functionalized sulfones through various pathways as shown in Scheme 2b. Meanwhile, α, β-unsaturated sulfones which play an important role in organic chemistry also could be obtained via these pathways.

β-Alkoxy sulfones are important intermediates in organic synthesis; in 2018, the Lei group reported a green and efficient synthetic method of the alkoxysulfonylation of alkenes using sulfonyl hydrazides and alcohols by electrochemical anodic oxidation, and this was the first report on such type of reaction (Scheme 3).

In the research, a three-component reaction was carried out in an undivided electrolytic cell charged with a carbon rod anode and a nickel plate cathode with a constant current of 12 mA at room temperature using CH₃CN as solvents and nBu₄NBF₄ (0.1 mmol) as an electrolyte. Under the reaction conditions, sulfonyl hydrazides (10) reacted with alkenes (11) and alcohols (12) to generate β-alkoxy-substituted sulfones (13) with good yields, giving hydrogen and nitrogen gas as the byproducts. Various conditions were attempted when exploring the research, researchers employed a current of different levels, electrode materials, electrolytes, solvents, and amount of methanol; finally, the reported standard conditions were found to be optimal, and nBu₄NBF₄ was found to be the key factor.

Furthermore, the substrates scope and mechanism were also studied. A range of arylsulfonyl hydrazides (10) reacted with alkenes (11) and alcohols (12) to generate β-alkoxyl-substituted sulfones (13) with good yields, giving hydrogen and nitrogen gas as the byproducts. Various conditions were attempted when exploring the research, researchers employed a current of different levels, electrode materials, electrolytes, solvents, and amount of methanol; finally, the reported standard conditions were found to be optimal, and nBu₄NBF₄ was found to be the key factor.

The researchers proposed a mechanism based on cyclic voltammetry (CV) experiments and radical trap experiments, indicating that the sulfonyl hydrazide (10) was first oxidized at the anode, and the N-centered radical (14) was subsequently formed. Then the radical (14) underwent the loss of nitrogen and gave a sulfonyl radical (15), which added to the C=C double bond in the following step and generated the carbocation intermediate (16). The carbocation intermediate (16) combined with an alcohol and lost the proton subsequently. Then the desired product was produced. Meanwhile, reduction of alcohol with the presence of H⁺ occurred at the cathode.

Alkenes bearing a trifluoromethyl group, especially at the α-site, have been widely used in chemical transformation. Due to the strong electron-withdrawing ability of the trifluoromethyl group, application of α-trifluoromethyl alkene in organic synthesis became a challenge, and several electrochemical transformations were introduced recently. In 2021, Yang and co-workers established a protocol for α-trifluoromethyl β-sulfonyl tertiary alcohols, a class of compounds bearing the β-functionalized sulfone moiety and a neighboring −CF3 group (Scheme 4).

To achieve the products, sulfonyl hydrazides (18) were treated with α-trifluoromethyl alkenes (19), and a reaction initiated by iodine radical which was produced in situ at the anode was designed. The reaction was performed in an undivided cell under a constant voltage of 4 V at room temperature, using a C anode and a Pt cathode.
In order to gain a practical method, the researchers studied various factors, showing that when the Pt cathode was replaced with other materials, the yield dropped greatly, indicating that the Pt cathode was crucial to this method. The following investigation of the substrate scope gave a pleasant result showing that sulfonyl hydrazides (18) with either electron-poor or -rich groups on aryl rings worked well under the optimal conditions, while para-substituted hydrazides (20a–20h) worked better than other substrates. When different alkenes were adopted, electron-withdrawing groups (20t–20w) on the phenyl rings showed negative impacts on the yields.

The reaction mechanism was well studied, and various kinds of experiments were conducted. Cyclic voltammetry (CV) experiments on both substrates and KI demonstrated that the oxidation of KI took place first and initiated the transformation. What is more, O\textsuperscript{18} labeling experiments and D\textsubscript{2}O exchange proved that water in the system was not the only source of OH group in the product. Combined with radical trap experiments, a carbon cation species (23) was generated along with molecular N\textsubscript{2}. When styrenes with electron-withdrawing groups (35j–35l) double bonds. By analyzing the reaction conditions and results from substrates screen reactions, it is indicated that the radical (39) produced in the addition step was then oxidized with oxygen to generate \( \beta \)-ketosulfones (41) through a peroxyl radical (40) as the intermediate. Thus, a plausible mechanism was proposed as depicted in Scheme 6.

Among sulfonyl-type compounds, \( \beta \)-keto-sulfones are a class of valuable chemical intermediates.\textsuperscript{60} In 2020, the Xu group reported the oxysulfonylation of alkenes toward \( \beta \)-ketosulfones (35) using sulfonyl hydrazides (33) and styrenes (34) with an electrochemical method (Scheme 6).\textsuperscript{61} To obtain the desired products, an undivided cell equipped with an RVC anode and a Pt cathode was employed. The reaction was conducted in CH\textsubscript{2}CN at room temperature under an air atmosphere, and nBu\textsubscript{4}NBF\textsubscript{4} was used as the electrolyte. The substrates screen showed that the reaction system could work well with a number of styrenes, except those with electron-withdrawing groups (35j–35l). When styrenes with electron-withdrawing groups were charged, an atmosphere of oxygen was necessary instead of air (35j–35l).

The mechanism study showed a similar result with Yang et al.’s research.\textsuperscript{60} The reaction started with the generation of sulfonyl radicals (37), which underwent addition to styrene (38) double bonds. By analyzing the reaction conditions and results from substrates screen reactions, it is indicated that the radical (39) produced in the addition step was then oxidized with oxygen to generate \( \beta \)-keto-sulfones (41) through a peroxyl radical (40) as the intermediate. Thus, a plausible mechanism was proposed as depicted in Scheme 6.

Radicals’ addition to alkynes is an important method to synthesize \( \beta \)-keto sulfones.\textsuperscript{62,63} Compared with traditional...
methods, electrochemical synthesis of $\beta$-keto sulfones might be efficient and green. In 2021, He and co-workers developed an oxysulfonylation of alkynes using sulfonyl hydrazides (42) and alkynes (43) (Scheme 7).
The reaction was carried out in a CH$_3$CN-H$_2$O system in an undivided cell charged with a graphite rod anode and a Pt plate cathode, and nBu$_4$NBF$_4$ was selected as an electrolyte. The conditions were compatible with a broad substrate scope, and $\beta$-keto-sulfones could be produced with acceptable yields when choosing phenylacetylene-type compounds. It could be noted that phenylacetylene with electron-donating groups ($\alpha\beta$-m$\alpha\beta$-$\alpha\beta$s) on the benzene ring gave better results than those with electron-withdrawing groups ($\alpha\beta$-q$\alpha\beta$-$\alpha\beta$s), and aliphatic alkynes ($\alpha\beta$-af, $\alpha\beta$-ag) were not suitable substrates for this reaction. On the other side, the reaction worked well with various kinds of sulfonyl hydrazides, either aryl or alkyl ($\alpha\beta$j) compounds.

The researchers conducted radical trap experiments, isotope labeling experiments, as well as CV experiments, to study the reaction mechanism. In the radical trap experiments, TEMPO, BHT and 1,1-diphenylethylene were used, and both sulfonyl radical and N-centered radical species were detected. Moreover, the isotope labeling experiments with H$_2$O proved the source of the oxygen atom in the product, while the CV experiments explained the reaction procedure. On the basis of the above work, a plausible mechanism was reasonably proposed (Scheme 7).

Similarly, another example of alkoxysulfonylation of alkynes was reported by Zhang and co-workers, using alcohols rather than water (Scheme 8) as a nucleophilic reagent. They performed the reaction in an undivided cell and selected two graphite felt electrodes with a constant current of 5 mA and chose Et$_4$NPF$_6$ in CH$_3$NO$_2$ as the electrolyte system. The reaction system showed a robust application scope with various sulfonyl hydrazides ($\alpha\beta$-a$\alpha\beta$-$\alpha\beta$k), alkynes($\alpha\beta$l$\alpha\beta$-$\alpha\beta$aa), and alcohols ($\alpha\beta$ab$\alpha\beta$-$\alpha\beta$aj). To gain a further understanding of the reaction, control experiments including sulfonyl radicals and vinyl radical intermediates trap experiments, and CV experiments were carried out. Combined with the DFT calculations, a mechanism involving the generation of sulfonyl radical ($\alpha\beta$) and the vinyl radical intermediate ($\alpha\beta$s) was proposed as depicted in Scheme 8.
Meanwhile, an approach to the electrochemical oxidative selenosulfonylation of alkynes was also involved in the same report by Xu et al. (Scheme 9). In this protocol, sulfonyl hydrazides, alkynes, and diphenyl diselenide were treated in an undivided cell charging a graphite anode and a Pt cathode, using nBu$_4$NBF$_4$ as a supporting electrolyte. The reaction had a broad scope of substrates, and most of the selected alkynes and sulfonyl hydrazides with aryl groups.
bearing either electron-donating or electron-withdrawing substituents were tolerated. In addition, aliphatic alkynes (65u, 65v) and sulfonyl hydrazides (65ag) were suitable substrates, although the aliphatic alkynes (65u, 65v) gave the desired products in lower yields. In the proposed mechanism, an alkyn radical (68) was believed to be the key intermediate, which was converted into the product with two possible routes as is shown in Scheme 9, an atom transfer with the diphenyl diselenide (path a) or a radical coupling with the phenyl-selenium radical (70) (path b).

In 2021, Wang reported an electrochemical route to the iodosulfonylation of alkynes via a sulfonyl radicals’ addition to alkynes (Scheme 10). To achieve the target, the reaction was carried out in an undivided cell with two platinum-plate electrodes (10 mm × 10 mm × 0.1 mm) and constant current of 40 mA in a CHCl3-H2O (3:1, v/v) solution. The authors tried a broad scope of substrates, and it was found that reactions with most of the selected alkynes and sulfonyl hydrazides gave the desired products with good yields, except those bearing bulky (75g) or alkyl (75v) groups. With control experiments at hand, a mechanism involving a sulfonyl radical’s addition to a C≡C triple bond was proposed. The mechanism started with the generation of I radical at the anode, and then the sulfonyl hydrazide (73) was activated to generate a sulfonyl radical (78). After the sulfonyl radical’s addition to an alkyn (74), a carbon radical (79) was formed and then gotoxidized at the anode. Lastly, the carbon radical (79) was captured by an iodine radical, and the desired β-iodide sulfone (75) was achieved.

In 2019, Lee reported an electrochemical synthetic protocol for the sulfonylation of tertiary amines toward β-amido-vinyl sulfoines, using sulfonyl hydrazides (81) and tertiary amines (82) as substrates (Scheme 11). To realize the protocol, the substrates were treated in an undivided cell equipped with a graphite anode and a Pt cathode with a constant current of 4 mA (6.2 F mol⁻¹) in DMSO under an acidic condition (acetic acid). nBu4NBF4 (0.1 M) was selected as an electrolyte. In this research, some ary1 hydrazides bearing various substituents including the electron-withdrawing groups (83e–83i) were tested and gave the desired products with good yields. In addition, dealkylation of tertiary amines was a competitive reaction.

A plausible mechanism was proposed with results from CV experiments and control reactions. It was indicated that the key steps in this reaction involved sulfonyl radical’s addition to alkene, which was generated by the electro-oxidation of tertiary amines in situ. At the early stage, sulfonyl hydrazides (81) and tertiary amines (82) were oxidized at the anode and gave sulfonyl radicals (84) and alkenes (87) respectively, and then the addition took place and yielded carbon radical intermediates (88). Then the intermediates (88) underwent with an oxidation and elimination sequence and afforded the target compounds. α-Substituted-vinyl-azides were widely used in organic synthesis and could be converted into various compounds.

In 2020, the Terent’ev group reported the sulfonylation of vinyl azides, converting α-substituted vinyl azides (91) into sulfonyl enamines (92) by reacting with sulfonyl hydrazides (90) under electrochemical conditions (Scheme 12). The reaction was conducted in DMSO/THF (1:1, v/v) under constant current conditions (3.5 F/mol 1, I = 60 mA, j = 20 mA/cm²), and the authors chose NH4I as an electrolyte, a graphite anode, and a stainless steel cathode. To study the substrates scope, they tried different vinyl azides and sulfonyl hydrazides. It was found that vinyl azides with either electron-withdrawing or electron-donating substituents on the aryl rings could afford the desired compounds, and all tried sulfonyl hydrazides also showed good results. However, when substrates with electron-withdrawing groups were chosen, the yields dropped on different levels (92h, 92i, 92s). Moreover, the reaction conditions worked well with the methanesulfonyl hydrazide (92k).

It was quite interesting to learn how the azide group was converted to a sulfonyl radical. The proposed mechanism was illustrated in Scheme 12. In 2019, Lee reported an electrochemical synthetic protocol for the sulfonation of vinyl azides, converting α-substituted vinyl azides (91) into sulfonyl enamines (92) by reacting with sulfonyl hydrazides (90) under electrochemical conditions (Scheme 12). The reaction was conducted in DMSO/THF (1:1, v/v) under constant current conditions (3.5 F/mol 1, I = 60 mA, j = 20 mA/cm²), and the authors chose NH4I as an electrolyte, a graphite anode, and a stainless steel cathode. To study the substrates scope, they tried different vinyl azides and sulfonyl hydrazides. It was found that vinyl azides with either electron-withdrawing or electron-donating substituents on the aryl rings could afford the desired compounds, and all tried sulfonyl hydrazides also showed good results. However, when substrates with electron-withdrawing groups were chosen, the yields dropped on different levels (92h, 92i, 92s). Moreover, the reaction conditions worked well with the methanesulfonyl hydrazide (92k).

It was quite interesting to learn how the azide group was converted to a sulfonyl radical. The proposed mechanism was illustrated in Scheme 12.
the azide group was reduced and an N-centered radical (97) was formed when the sulfonyl radical (96) added to the double bond. At the same time, hydrogen gas was produced at the cathode (Scheme 12).

A similar synthesis of sulfonyl enamines was reported by Chen in 2022 (Scheme 13). This sulfonylation of enamines was conducted under a constant current of 10 mA with LiClO₄ as the electrolyte in a mixed solvent of CH₃CN/H₂O (10:1, v/v), using a carbon anode and a Pt cathode. Substrates with either electron-
donating (102a, 102b, 102c, 102f) or electron-withdrawing groups (102c, 102e–102i, 102n–102s) on the aryl rings all gave corresponding products in medium yields. Meaningfully, products of this reaction were solvent-oriented; when AcOH/H₂O (1:1, v/v) was used instead of CH₃CN/H₂O (10:1, v/v), β-ketosulfones were obtained as products. When conducted in CH₃CN/H₂O (10:1, v/v), aliphatic sulfonyl hydrazides (102u–102y) were also suitable for this protocol.

The reaction was believed to be triggered by the sulfonyl radical (105), and a key intermediate of the carbon radical (107) was generated by the sulfonyl radical’s addition to a C=C double bond. Subsequently, the generated carbon radical (107) was oxidized at the anode, and then a sulfonyl enamine (108) was obtained with loss of H⁺. This proposed mechanism was supported by CV experiments and control reactions.

In 2017, Terent’ev et al. synthesized vinyl sulfones via the sulfonylation of alkenes, choosing alkenes and sulfonyl hydrazides as substrates, in an undivided cell equipped with a graphite anode and an Fe cathode (Scheme 14).⁷⁷ This reaction was conducted under a constant current of 40 mA in an undivided cell in a saturated (NH₄)₂CO₃ solution, using Pt foils (1.0 × 1.5 cm²) as the anode and cathode, and 10 mol % n-Bu₄NI was chosen as the catalyst. By screening a number of substrates, it was found that the reaction was compatible with a broad range of sulfonyl hydrazides (124a–124k) and styrenes (124l–124z) in good E selectivity (E/Z > 99:1). A gram-scale experiment was carried out, and the result showed a potential utility of this reaction.

CV experiments showed that the C=C double bond in the product was formed via an addition–oxidation–elimination procedure. At the beginning, sulfonyl hydrazide (114) was activated at the anode by an iodide cation and yielded a radical species (117) at the anode; in this phase, the sulfonyl iodide (115) was proven to be a key intermediate. The radical (117) also could be gained from the sulfonyl iodide (115) via a sulfonyl anion intermediate (116). Then the radical (117) reacted with an alkene and gave a radical intermediate (119) which was then oxidized and produced a carbon cation species (120). The cation (120) might react with I⁻ to give an iodide compound, which proceeded with the elimination of HI or loss of the H⁺ to produce vinyl sulfones.

Similar to the report of Terent’ev et al., a sulfonylation of alkenes in water was reported by Liao et al. in 2020 (Scheme 15).⁷² This reaction was conducted under a constant current of 40 mA in an undivided cell in a saturated (NH₄)₂CO₃ solution, using Pt foils (1.0 × 1.5 cm²) as the anode and cathode, and 10 mol % n-Bu₄NI was chosen as the catalyst. By screening a number of substrates, it was found that the reaction was compatible with a broad range of sulfonyl hydrazides (124a–124k) and styrenes (124l–124z) in good E selectivity (E/Z > 99:1). A gram-scale experiment was carried out, and the result showed a potential utility of this reaction.

A mechanism was proposed based on the results of control experiments and CV experiments. In control experiments, the authors added radical inhibitors (BHT or TEMPO) to the system or chose presumed intermediates as reactants. Combined with CV experiments, a mechanism consisting of
the generation of radical, C=C bond addition, free radical oxidation, and elimination was proposed. Sulfonyl hydrazides and styrenes were converted into vinyl sulfones via two paths. In the carbon cation path, sulfonyl hydrazides (122) were first activated by the base to give sulfonyl radicals (127), and then the generated sulfonyl radicals (127) added to styrenes; therefore, carbon radical intermediates (128) were yielded. Subsequently, the radical intermediates (128) got oxidized and underwent the loss of H⁺ or HI; in the free radical path, the sulfonyl hydrazides were oxidized by I₂ to give sulfonyl radicals (127); after that, the generated sulfonyl radicals (127) combined with iodide free radicals and yielded species (130), and then the elimination of HI took place, and the target product was afforded.

Decarboxylation of carboxylic acids could be realized by electrochemical methods. Decarboxylative sulfonylation was an efficient strategy for the synthesis of vinyl sulfones when...
charging cinnamic acids as a starting material, and an electrochemical mode of such application was reported by Huang in 2017 (Scheme 16). 74

The reaction was performed with two Pt foil electrodes, nBu_4NBF_4 as the electrolyte in a solvent of DMSO under a constant current of 3 mA. In this reaction, t-BuOLi played an important role in facilitating the oxidation of sulfonyl hydrazides, and this was confirmed by CV experiments. Further studies on the reaction procedure with CV experiments showed that the sulfonyl radical (136) was generated with the aid of a base. It was also noted that the radical (136) added to a double bond at the neighbor position, yielding a carbon radical (138) as the key intermediate. The carbon radical (138) then underwent the oxidation followed by the release of CO_2.

Alkynyl sulfones which showed excellent bioactivity in various fields could be obtained by the sulfonylation of alkynes. 75, 76 In 2019, Tang and co-workers reported a sulfonylation of alkynes using sulfonyl hydrazides (139) and terminal alkynes (140) as substrates (Scheme 17). 77 The substrates reacted in an undivided cell equipped with a RVC anode (100 PPI, 1 cm x 1 cm x 1.2 cm) and a Pt plate cathode (1 cm x 1 cm) with a constant potential of 1.2 V (vs Ag/AgCl) under an O_2 atmosphere, TBAI was selected as an electrolyte, and K_2CO_3 was used as an additive. By investigating various substrates, it was found that the reactions using most of the selected substrates gave desired products with acceptable yields except for alkyl sulfonyl hydrazides (141_k) and alkynes with α-hydrogen atom (141_v).

The authors performed control experiments [CV experiments and electron paramagnetic resonance (EPR) experiments] to study the reaction mechanism. Based on results from these experiments, it was concluded that alkynyl sulfones (141) could be produced through two pathways, and the reaction procedure involved the generation of sulfonyl radicals (146), addition to alkynes and the elimination of iodide. Besides, oxygen did play an important role in this mechanism (path A). Moreover, the authors also evaluated antitumor activity of several compounds (141_f, 141_n, 141_r, 141_t).

3. APPLICATION IN CYCLIZATION REACTIONS

Cyclization involving cascade reactions is widely used in the synthesis of compounds with complicated structures, and it has been used in various reactions. 78, 79 Radical-triggered cascade reactions 80 were common in cascade reactions, and sulfonyl hydrazides have been good sources of free radicals when adopted under electrochemical conditions. In recent years, several annulation reactions using sulfonyl hydrazides and multifunctional arenes were reported.

In 2019, an electrosynthesis involving radical arylsulfonylation/semipinacol rearrangement was reported by Kim and Kim (Scheme 18). In this method, alkenylcyclobutanols (153) and sulfonyl hydrazides (154) were used as substrates, and the reactions were conducted under a constant current of 5 mA with two Pt electrodes in a mixed solvent of THF/H_2O (1:1, v/v), employing NaI as an electrolyte. A substrates screen showed that the reaction conditions were compatible with most of the selected compounds, containing either electron-donating or electron-withdrawing groups.

To gain a further understanding of the ring expansion, CV experiments and controlled reactions were conducted. These experiments showed that sulfonyl hydrazides were activated by I_2, which was produced by anodic oxidation of I^-, and a sulfonyl iodide (156) was formed as the key intermediate. Then a sulfonyl radical (157) was formed via the cleavage of S—I bond.
After that, the sulfonyl radical (157) underwent the addition to a C=C bond, and a carbo-radical (158) was generated. It was presumed that the carbo-radical was oxidated to a carbo-cation (159) followed by a semipinacol rearrangement. Thus, the product was afforded through a ring expansion procedure.

Compounds with indolo-[2,1-a]-isoquinolines structures showed excellent bioactivity and attracted much attention from synthetic chemists. In 2020, Xia and co-workers developed an electrosynthesis route of indole derivatives choosing sulfonyl hydrazides (160) and 2-aryl-N-acryloyl indole derivatives (161) as substrates (Scheme 19). To achieve the goal, the reactions were carried out in an undivided cell charged with a Pt anode and a Pt cathode under a constant current of 10 mA in a mixed solvent of THF/H₂O (3:1, v/v), and KI was used as an electrolyte. The reactions were conducted at room temperature under an air atmosphere. Reactions with compounds (162o−162v) bearing different groups including either electron-donating or electron-withdrawing ones at C-5 of the indole ring all gave desired compounds. In addition, substituents bearing various groups at C-2 of indoles (162w−162ac) could be transformed under the reaction conditions; alkyl sulfonyl hydrazides (162m, 162n) were suitable starting materials, too. Moreover, when KBr was used instead of KI, the corresponding brominated products (162ai−162am) were obtained.

It was predicted that the reaction proceeded with an addition−addition−oxidation−elimination process. To prove that, control experiments and CV experiments were carried out. With those experiments, potential intermediates were determined, and a plausible mechanism was proposed. In this procedure, a sulfonyl radical (164) was first generated at the anode and added to the benzene ring to form a multicyclic structure as a carbo-radical (167) through a 6-endo-trig cyclization. Then the radical intermediate (167) was trans-
formed into a cation species at the anode (168). Lastly, a multicyclic compound was formed with the release of H⁺.

In 2020, an annulation-halosulfonylation of 1,6-enynes toward the synthesis of 1-indanones was reported by Jiang et al. (Scheme 20).²⁶,²⁷ To construct the pentane core, the Jiang group selected 1,6-enynes (170) and sulfonyl hydrazides (171) as substrates. This reaction was carried out in an undivided cell charged with a Pt anode and a Pt cathode under a constant current of 10 mA at room temperature in an air atmosphere, and it was found that a mixed solvent of THF/H₂O was essential.
Both NaI and NaBr were good electrolytes, and iodo- or bromo-groups were introduced, respectively. To study the effect of substituents on the aryl ring or other sites, a variety of compounds were tried under the conditions, and all reactions gave 1-indanone derivatives with acceptable yields and good E/Z selectivity.

The mechanism of this reaction was also investigated. Results of control reactions showed that the sulfonyl radical (174) which triggered the reaction was produced by the oxidation of sulfonyl hydrazides by $I^+$, and the $I^+$ was generated from an $I^−$ by the anodic oxidation. The sulfonyl radical added to the double bond and formed a radical species (177), which underwent addition to the triple bond. Thus, the indanone structure was formed as a vinyl radical (178), and then the radical (178) was oxidized and captured by $I^−$ or reacted with Ts-I to give the product.

Using 1,5-enyne derivatives instead of 1,6-enynes, Jiang’s group developed annihilation-iodosulfonylation of 1,5-enynes toward (E)-spiro-indenes in 2020 (Scheme 21).

Benzoxazines are usually synthesized by transition metal catalysis, Lewis base catalysis, or photoinduced cyclization, and chemists have tried to apply electrochemical methods. In 2020, Huang et al. developed a cascade protocol for the synthesis of benzoxazines (Scheme 22). Sulfonyl hydrazides (192) and acetyl amino-styrenes (193) were chosen to react in an undivided cell equipped with a carbon rod ($\phi = 5$ mm, immersion length: 1.5 cm) anode and a Pt foil ($1 \times 1.5$ cm$^2$) cathode with $j_{\text{anode}} = 0.19$ mA cm$^{-2}$. This reaction was conducted in a CH$_3$CN solution with nBu$_4$NBF$_4$ as an electrolyte at room temperature under N$_2$ atmosphere. Various styrenes and sulfonyl hydrazides were tested, and it was found that sulfonyl hydrazides bearing hydroxy (194l) or amino (194m) groups on the aryl ring were not suitable for this reaction, and other selected compounds, including those bearing either electron-
donating or electron-withdrawing groups on the acyl sites, all afforded the desired product.

This protocol was believed to involve a free radical triggered cascade process, which was confirmed by control reactions including the addition of a radical inhibitor (BHT) to the system. Combined with results from CV experiments, a plausible mechanism involving an addition−oxidation−cyclization−elimination procedure was proposed. The sulfonyl hydrazide (195) was converted into a sulfonyl radical (197) at the anode, and then added to the double bond on the styrene, and a radical intermediate (198) was formed. Next step was the formation of a carbon cation (199) by oxidation of the radical (198) mentioned above at the anode, and the cation (199) then underwent a cyclization and followed by the elimination of H$. Thus, the benzoxazine was constructed in one pot with an efficient and green method.

In some cases, compounds containing the 2-vinylbenzoic acid motif were good building blocks and could be transformed into many meaningful molecules. Recently, in 2022, Chen et al. reported an annulation-sulfonylation of 2-vinylbenzoic acids (202) under electrochemical conditions via a lactonization process (Scheme 23). In contrast to previous reports with sodium sulfonates as the sulfur source, sulfonyl hydrazides were used here. The reaction was performed in an undivided cell with two electrodes with a constant current of 12 mA in a solvent of CH$_3$CN/H$_2$O (10/1, v/v) under an N$_2$ atmosphere, LiClO$_4$ was selected as the electrolyte, and AcOH was chosen as the additive. To investigate the substrates scope, the effects of groups adjacent to the C$\equiv$C double bonds were studied, and aromatic substrates all worked well. However, aliphatic acid derivatives (203aa, 203ab) did not work. Sulfonyl hydrazides were also tested, and it was found that bulky groups (203m, 203n) on the aryl ring might inhibit the reaction.

Control reactions and CV experiments indicated that sulfonyl hydrazide was directly oxidized at the anode and generated a sulfonyl radical (205), and then the radical was added to a double bond and gave a radical species (206). The radical (206) was converted into a cation (207), which was then captured by the −OH group and formed a phthalide with the elimination of H$^+$. The synthesis of heterocycles has always been a popular topic, and it was efficient and applicable to prepare them with cascade reactions. Synthesizing quinolines with electrochemical methods has attracted the attention of chemists. Very recently,
in 2022, Zhang and co-workers reported a synthesis of sulfonylated quinolines under electrochemical conditions with sulfonyl hydrazides through a cascade process (Scheme 24).

The two substrates were treated in an undivided cell equipped with two graphite felt electrodes, Et$_4$NPF$_6$ and nBu$_4$NBF$_4$ as mixed electrolytes under a cell voltage of 3.9 V. The authors chose CoCl$_2$ as an additive and HFIP as a solvent, and this was considered to promote the transformation. The reaction conditions were compatible with a broad range of substrates, and some sensitive groups ($211p$, $211q$) were also tolerated.

A plausible mechanism was proposed based on CV experiments, control reactions, and DFT calculations. The reaction was believed to start with the activation of sulfonyl hydrazides, and then the sulfonyl radical ($214$) was added to the triple bond and gave a vinyl radical ($215$), which was then oxidized and generated a carbocation ($216$). The cation ($217$) was trapped intramolecularly by the nitrogen atom with the loss of H$^+$ and yielded a cyclic intermediate ($218$), which then underwent a ring opening step accompanied by the release of CO$_2$ and gave the desired product ($219$).

Continuous-flow reactions have been applied in synthetic chemistry for a long time, and the nature of electrochemical synthesis makes it suitable to be conducted in a continuous-flow mode and has shown advantages over reactions in batch mode. A continuous electrochemical synthesis of sulfonylated isoquinoline-1,3(2$H$,4$H$)-dione compounds was reported by Guo and co-workers in 2020 (Scheme 25), using a flow electrolytic cell charged with a graphite plate anode and a platinum plate cathode under a constant current of 15 mA. Compared with reactions in batch mode, the flow mode required a lower load of sulfonyl hydrazides and shortened the reaction time with a residence time of 1 min. Interestingly, when conducted in 5 or 10 mmol scale, the flow mode gave the desired product in higher yields (79% vs 52% in 5 mmol scale, 78% vs 44% in 10 mmol scale). The reaction conditions were compatible with most of the common functional groups on the rings of two substrates, e.g., 4-nitrobenzenesulfonyl hydrazide ($222z$). Control reactions indicated that the sulfonyl radical ($224$) was generated at the anode and added to the double bond of the acrylamide ($220$), and a carbon radical
(225) was yielded. The radical (225) center then underwent cyclization with the aryl ring. In the last stage, the desired product was obtained resulting from the loss of electrons and H⁺.

In 2021, an interesting application of sulfonyl hydrazides in the electrochemical synthesis of cinnolines was reported by Guo et al. (Scheme 26). Sulfonyl hydrazides adopted here formed the cinnoline core together with alkynes by the release of SO₂. The protocol consisting of two steps in one pot was carried out in an organocatalytic electrochemical mode, using phenothiazines (231) as a catalyst. In the first step, the sulfonyl hydrazides condensed with the keto group of alkyne derivatives and yielded hydrazone type intermediates, and then the electrochemical conditions (carbon cloth anode, platinum plate cathode, nBu₄NBF₄, 10 mA) were introduced. The authors performed isotope labeling experiments, CV experiments, control reactions, and EPR tests to study the reaction process, especially the electrochemical part. It was proposed that the catalyst was oxidized at the anode first, and then the hydrazone (234) was oxidized by the activated catalyst and yielded an N-centered radical (236), which then added to the triple bond and formed a bicyclic radical (237). The radical (237) then underwent an aryl group migration and got trapped by O₂ after the release of SO₂, and the O₂-trapped species (240) then became an N-centered radical (241) with the loss of O₂. The N-centered radical (241) formed the cinnoline core (242) by an intramolecular annulation and then was transformed into the desired product with the aid of another activated catalyst. The catalyst in this mechanism forms a recycle process between activated and unactivated states at the anode.

4. SULFONYLATION OF HETEROCYCLIC COMPOUNDS

Sulfonylation of heterocyclic compounds is important and common in organic chemistry and is usually achieved by employing sulfinic acids and their derivatives, which usually require transition metals or a large number of oxidants. However, those reagents may lead to environmental problems and can be hazardous to body health. Hence, chemists have been seeking for more effective methods, and there have been several reports on sulfonylation of heterocyclic compounds with electrochemical methods.

In 2018, Lei’s group developed the sulfonylation of arenes/heteroarenes without the application of external oxidants (Scheme 27), and sulfonyl hydrazides (245) and benzofurans (246) were chosen as substrates. These compounds reacted in an undivided cell charged with a graphite rod anode and a nickel plate cathode. This reaction was carried out in a mixed solvent of CH₃CN-H₂O with nBu₄NBF₄ as electrolytes and K₂CO₃ as additives. The subsequent investigation of substrates scope revealed a complex profile of substituent effects, and it was found that groups at the C-3 site were favorable to this reaction. Most of the selected compounds bearing various substituents at the C-3 position afforded desired products. When C-2 substituted compounds were
the conditions, C-3 sulfonylated products (247y) were obtained. The authors also adopted other heterocyclic and aryl compounds, such as electron-rich thiophenes (247ab), pyrroles (247ad), naphthalene (247af), and 1,3,5-trimethoxybenzene (247ag, 247af), and achieved products in acceptable yields. However, indole and its derivatives were not suitable for this reaction.

A plausible mechanism was proposed based on data from radical-trapping experiments and CV analysis. Radical-trapping experiments indicated that a free radical was involved in this reaction. It was concluded that the sulfonyl hydrazide was transformed into a radical species (249) at the anode with the presence of a base, and the radical (249) reacted with an aryl ring to give a radical intermediate (251), and then the radical intermediate (251) was oxidized and a carbon cation was formed. Then the cation underwent the loss of H⁺ and yielded the sulfonylated product.

Heterocyclic N-oxides were widely used in organic reactions, and sulfonyl derivatives sometimes could work as alkylation reagents. In 2019, the Lei group reported an important study on the arylation of quinoline N-oxides at the C-2 site with an electrosynthetic method (Scheme 28).

In contrast with usual electrochemical reactions, the formation of the product involved both anodic oxidation and cathodic reduction in one cell. In this reaction, sulfonyl hydrazides served as aryl free radical precursors and reacted with quinoline N-oxides (254) in an undivided cell under a constant current of 24 mA. The reaction conditions included a graphite anode and a Pt cathode, nBu₄NBF₄ as electrolytes, and a mixed solvent of CH₃CN-HFIP (9:1, v/v). Various sulfonyl...
Hydrazides and quinoline N-oxides were tried, and it was found that aryl sulfonyl hydrazides containing alkyl- (255e, 255f) or halo- (255g−255i) substituents gave desired products in higher yields than other sulfonyl hydrazides. Moreover, sulfonyl hydrazides with 2-thienyl (255b) or 3-pyridyl (255c) groups were compatible with this condition, but the aliphatic compound (255l) did not work. Quinoline N-oxides bearing various groups at different sites all afforded desired compounds with medium yields, however, isoquinoline N-oxide could not give product under the conditions.

Control experiments showed that the oxidation of sulfonyl hydrazides took place at the anode and generated an aryl free radical (257) with the release of N₂ and SO₂, and then the radical (257) added to the quinoline at the C-2 site, and an N-oxide radical (259) was formed. The radical (259) was reduced at the cathode and yielded an N-oxide anion (260), which then captured a proton and underwent the elimination of H₂O.

Functionalization of indazoles could be realized by electrochemical methods. De Sarkar and co-workers developed an electrochemical protocol for the sulfonylation of N₂-aryl 2H-indazoles (263) at the C-3 site in 2020 (Scheme 29).

The protocol was realized by employing an undivided cell, using a graphite anode and a Ni foam cathode with a constant current of 10 mA, and LiClO₄ was chosen as an electrolyte. This reaction was conducted in a mixed solvent of CH₃CN/H₂O (9:1, v/v), and K₂CO₃ was used to provide a basic condition. By adopting various substrates with different substituents, it was found that aryl sulfonyl hydrazides bearing electron-withdrawing or electron-donating groups at the N₂-aryl ring or indazole core all afforded desired products. However, compounds with a nitro group (264h, 264p) on the aryl ring at the N₂-site did not work under such conditions. Meanwhile, reactions with different sulfonyl hydrazides also gave similar results, and methanesulfonyl hydrazide (264e) was suitable for this reaction, too.

Radical trap reactions and CV experiments were also conducted, and a plausible mechanism was proposed. The key step in this reaction was the addition of a sulfonyl radical (267) to an indazole (268) at the C-3 position, and then oxidation of the addition intermediate (269) occurred, followed by the elimination of H⁺. In addition, H₂ was yielded at the cathode as a byproduct.

Compounds with an indole core are always under focus. However, because of the high activity of the indole ring, it was not easy to handle indole derivatives under some conditions. Oxidative coupling is an effective method of indole functionalizations, especially those under electrochemical conditions. In 2019, an electrochemical coupling of indoles (272) and sulfonyl hydrazides (273) was reported by Pan et al. (Scheme 30).

A sulfonyl group was introduced to the C₃ site, and a sulfonyl hydrazide group was introduced to the C₂ site at the same indole ring in one step. To realize this bifunctionalization of the indole ring, the substrates were treated in an undivided cell charged with a Pt anode and a graphite cathode. After testing various materials, NH₄Br was found to be optimal in this reaction, working as an electrolyte. The authors tried various sulfonyl hydrazides and indoles bearing several classical groups, and most of the selected examples showed acceptable results and gave desired compounds with from medium to high yields.

The structure of desired compounds also demonstrated the general mechanism proposed by the authors and other researchers (Scheme 30), especially the process involving the oxidation of sulfonyl hydrazides. Control reactions and CV experiments showed that sulfonyl hydrazide was activated by...
Br\(^*\), which was generated by oxidation of Br\(^-\) at the anode, and then the hydrazide radical (276) reacted with Br\(^*\) twice and gave a sulfonyl radical (279). The indole compound was also oxidized by Br\(^*\), and a 3-indolyl radical (280) was formed. In the last stage, two active species got coupled, and the desired product was obtained. Meanwhile, H\(^+\) was reduced at the cathode.

Due to their unique structure, xanthenes and their derivatives were widely used in chemical research, and recently, they were involved in some C–H activation studies, especially several electrochemical examples, and an electrochemical sulfonylation of xanthenes (284) at the C-9 position using sulfonyl hydrazides as sulfonating reagent was developed by Mo and co-workers in 2022 (Scheme 31).

This oxidative C(sp\(^3\))–H activation was realized by charging a carbon rod anode and a platinum plate cathode under a constant current of 15 mA, using nBu\(_4\)NBF\(_4\) as an electrolyte, as well as a mediator. To handle the acidic proton at C-9, a base was necessary, and MeONa was found to be optimal. Further study showed that the reaction was compatible with a variety of substrates, and aryl sulfonyl hydrazides bearing different substituents all gave the desired products. It should be noted that some experiments (285f–285i) gave better results using Cs\(_2\)CO\(_3\) instead of MeONa. BnSO\(_2\)NHNH\(_2\) and thiophene-2-sulfonyl hydrazide were also tested, but they did not work. When different xanthenes were adopted, most of the selected substrates worked well.

It was believed that the two substrates were coupled in radical form, and two radicals were generated through different pathways. Xanthenes (289) first lost the C-9 proton by reacting with the base, and then the xanthene anions (290) were oxidized and gave radicals (291) by the loss of electrons. The sulfonyl hydrazides were converted into radicals (288) with the aid of iodine radicals, which were formed in situ at the anode. Then the radicals (288 and 291) combined and afforded products. Moreover, the proposed mechanism was demonstrated by control reactions and CV experiments. Some samples made with this method were tested in research on anticancer bioactivity and gave good results.

5. FORMATION OF SULFUR-HETERATOM BONDS

Sulfonic derivatives such as sulfamides, thiosulfonates, and sulfonic esters are a class of common and important compounds in medicinal chemistry, and these compounds are mainly obtained from sulfonic acids or sulfonic chlorides. Besides, sulfonyl hydrazides were also good building blocks in synthesizing sulfonic esters or sulfamides, and electrochemical methods have been applied in preparing these compounds.

In 2016, O. Terent'ev et al. developed an electrochemical approach to the synthesis of sulfamides by the condensation of sulfonyl hydrazides with amines (Scheme 32). This method was realized in an undivided cell equipped with an Fe cathode and a graphite anode in a mode of constant current. To investigate the effect of the electrolyte, a variety of salts were tested, and several of them gave satisfactory results. Among electrolytes (K\(_2\)SO\(_4\), NaI, KI, KBr, NaBr, NH\(_4\)Br, and NH\(_4\)Cl) that worked well, NH\(_4\)Br and NH\(_4\)Cl gave the best results. Moreover, the researchers found that when using primary
Scheme 29. Regioselective Sulfonylation of N2-Aryl 2H-Indazoles

Regioselective Sulfonylation of 2H-Indazoles

Scheme 30. Sulfonylation and Hydrazination of Indoles

Sulfonyl Hydrazides

Scope of R^1 and R^2

Proposed Mechanism

Anode

Cathode

Note: TsHNHH_2 was used in these reactions
amines (295g, 295h), a three-fold excess of amine was crucial to get the desired products. Amino compounds could be prepared from aryl thiols and sulfonyl hydrazides via many ways, and tertiary amines sometimes could be used to introduce amino groups. Application of tertiary amines could promote the tolerance of substrates bearing functional groups sensitive to secondary amines and might avoid some side reactions. In 2017, Sheykhan reported the synthesis of sulfamides, utilizing tertiary amines (297) as sources of amino groups (Scheme 33). The reactions were conducted in an undivided cell charging two graphite electrodes, and Na₂SO₄ was selected as an electrolyte. It was notable that the material of electrodes used here was the same as used in a pencil and was renewable. The synthetic method was compatible with both two substrates bearing common functional groups. Besides, sulfonyl chlorides were also tested and gave the desired products. Mechanism investigation showed that the tertiary amine (299) was oxidized and gave secondary amine (301) via an iminium ion.
intermediate $300$), and the sulfonyl hydrazide was converted into an active species ($302$, $303$) at the anode.

In 2018, Chen and co-workers reported the synthesis of thiosulfonates with an electrochemical method (Scheme 34). The authors used an RVC anode and a Pt cathode in an undivided cell and chose NH$_4$I as the electrolyte, and conducted the reactions in a mode of constant current of 10 mA. With this method, sulfonyl hydrazides ($306$) and aryl thiols ($307$) could be converted into thiosulfonates ($308$), and substrates with various substituents on aryl rings all worked well, giving products in good yields. Furthermore, aliphatic thiols ($308z$, $308aa$) could work well under the conditions, but aliphatic sulfonyl hydrazide ($308n$) did not. Control reactions and CV experiments indicated that mercaptans and sulfonyl hydrazides were...
oxidized at the anode and yielded corresponding radicals (313, 314), and then thiosulfonates were formed by the coupling of two radicals. Another synthesis of thiosulfonates was reported by Terent’ev et al. in 2019 (Scheme 35). 129 Aryl thiols and sulfonyl hydrazides were treated with electrochemical conditions including two Pt electrodes, an NH₄I electrolyte, and a mode of constant current.
Further investigation showed that both aryl and aliphatic thiols (317, 1317m) worked well with the conditions. Moreover, a mechanism study consisting of control reactions and CV experiments demonstrated that this was a radical-involved procedure.

Terent’ev et al. also developed an oxidative coupling method between sulfonyl hydrazides and N-hydroxyimides (327a−327l) or N-hydroxybenzotriazoles (327m−327q) in 2019 (Scheme 36), and the NHPI-type products could be used as good radical precursors and widely applied in organic synthesis.130 The authors chose a graphite anode and an Fe cathode, and selected NH₄Br as an electrolyte. The reaction has a broad scope of substrate and was compatible with most of the selected substrates. It was found sulfonyl hydrazides containing iodide (327h) or a bulky group (327l) gave desired compounds in lower yields due to the decomposition of starting material or steric effects. Further study showed that sodium sulfonates were also suitable for this reaction. The subsequent control reactions and CV experiments revealed that the S−O bond might be formed in two pathways: (i) radical coupling of sulfonyl (329) and N-hydroxy (332) radicals; or (ii) esterification of sulfonyl bromide (328) and N-hydroxy compounds (331), which was indicated by control experiments that the sulfonyl bromide (328) might be a key intermediate.

As efficient substrates in the synthesis of sulfur compounds,131,132 sulfonyl hydrazides were widely used in electrochemical synthesis of sulfonyl halides including sulfonyl fluorides. Recently, in 2022, Lee and Park reported an electrosynthesis of sulfonyl fluorides (335) via the radical pathway under a constant current of 15 mA (Scheme 37).133 The substrates were treated in an undivided cell charged with a graphite anode and a nickel cathode, and nBu₄NI was selected as an electrolyte. To introduce the F atom, Et₃N·3HF was applied here as a fluoride source. By screening a number of sulfonyl hydrazides bearing various substituents, it was found that aryl sulfonyl hydrazides were suitable for this reaction. However, aliphatic compounds (335t−335v) were not compatible with the conditions. Moreover, when sulfonyl hydrazides bearing sensitive groups such as −NO₂ (335l), 8-quinolinyl (335m), and 2-thiophenyl (335r) groups were employed, corresponding products were obtained in good yields under a constant current of 1.0 mA or 10 mA. It was supposed that the product was formed by the combination of a sulfonyl cation (338) and an F⁻ anion. CV experiments and control reactions indicated that the sulfonyl hydrazide was activated by an iodide molecule, which was generated at the anode in situ, and the radical (337) was yielded. Subsequently the radical (337) was oxidized to a sulfonyl cation (338), which was captured by F⁻.

6. CONCLUSION

In conclusion, we have summarized the application of sulfonyl hydrazides in electrochemical synthesis in particular, according to the structure of products and the reaction mechanism. Under electrochemical conditions, sulfonyl hydrazides could take part in various kinds of reactions via free radical mechanisms and could introduce sulfonyl groups, or alkyl groups sometimes. It was found that the application of sulfonyl hydrazides in electrochemical methods was efficient and advantageous over other sulfonyl derivatives. We believe that this review may introduce a clear summary of the electrochemical application of sulfonyl hydrazides to promote wide investigation using sulfonyl hydrazides in the future.

AUTHOR INFORMATION

Corresponding Author
Guang-Bin Shen — School of Medical Engineering, Jining Medical University, Jining, Shandong 272000, P. R. China; orcid.org/0000-0003-0449-7301; Email: gbshen@mail.jnmc.edu.cn

Authors
Bao-Chen Qian — School of Medical Engineering, Jining Medical University, Jining, Shandong 272000, P. R. China
Chao-Zhe Zhu — School of Medical Engineering, Jining Medical University, Jining, Shandong 272000, P. R. China

Complete contact information is available at:
Notes
The authors declare no competing financial interest.

Biographies
Bao-Chen Qian received his Ph.D. degree from University of Chinese Academy of Sciences in 2016, under the supervision of Prof. Chu-Yi Yu. Currently, he is an associate professor at the School of Medical Engineering, Jining Medical University. His research interests include the electrochemical synthesis, synthesis, and bioactivity research of aryl C-glycosides, and DFT computation.

Guang-Bin Shen received his B.S. degree from Ludong University in 2011 and a Ph.D. degree from Nankai University in 2016, under the supervision of Prof. Xiao-Qing Zhu. Currently, he is an associate professor at the School of Medical Engineering, Jining Medical University, Jining, China. Her research interests include dielectric properties of determined diseases in the intersection of medical and engineering fields, and microwave systems, diagnostics, dielectric measurements, and the development of electrochemical sensors.

This study was supported by the doctoral scientific research project of Jining Medical University, Jining Medical University, Jining, China. His research interests include redox mechanisms, electrochemical synthesis, physical organic chemistry, and computational chemistry.

ACKNOWLEDGMENTS
This study was supported by the doctoral scientific research project of Jining Medical University, NSFC cultivation project of Jining Medical University (JYP2019KJ25).

REFERENCES
(1) Hunter, B. A.; Schoene, D. L. Sulfonyl Hydrazide Blowing Agents for Rubber and Plastics. Ind. Eng. Chem. 1952, 44, 119–122.
(2) Adlington, R. M.; Barrett, A. G. M. Recent Applications of the Shapiro Reaction. Acc. Chem. Res. 1983, 16, 55–59.
(3) Shapiro, R. H.; Heath, M. J. Tosylhydrazones. V. Reaction of Tosylhydrazones with Alkylithium Reagents. A New Olefin Synthesis. J. Am. Chem. Soc. 1967, 89, 5734–5735.
(4) Hutchins, R. O.; Milewski, C. A.; Maryanoff, B. E. Selective Desymmetrization of Ketones and Aldehydes Including Hindered Systems with Sodium Cyanoborohydride. J. Am. Chem. Soc. 1973, 95, 3662–3668.
(5) Li, L.-Y.; Leng, B.-R.; Li, J.-Z.; Liu, Q.-Q.; Yu, J.; Wei, P.; Wang, D.-C.; Zhu, Y.-L. Palladium-catalyzed Regioselective Hydro sulfonylation of Allenes with Sulfinic Acids. RSC Adv. 2012, 2, 8443–8448.
(6) Jiang, S.; Zhang, Z.-T.; Young, D. J.; Chai, L.-L.; Wu, Q.; Li, H.-X. Visible-light-Mediated Cross-coupling of Aryl Halides with Sodium Sulfinites via Carboxyl-photoredox/Nickel Dual Catalysis. Org. Chem. Front. 2022, 9, 1437–1444.
(7) Reddy, R. J.; Kumar, A. H. Synthesis and Applications Of Sodium Sulfinites (RSO2Na): a Powerful Building Block for The Synthesis of Organosulfur Compounds. RSC Adv. 2021, 11, 9130–9221.
(8) Liu, W.; Hao, L.; Zhang, J.; Zhu, T. Progress in the Electrochemical Reactions of Sulfonyl Compounds. ChemSusChem 2022, 15, No. e202102557.
(9) Zhao, F.; Tan, Q.; Wang, D.; Deng, G.-J. Metal- and Solvent-free Direct C-H Thiolation of Aromatic Compounds with Sulfonyl Chlorides. Green Chem. 2020, 22, 427–432.
(10) Yang, R.; Yi, D.; Shen, K.; Fu, Q.; Wei, J.; Lu, J.; Yang, L.; Wang, L.; Wei, S.; Zhang, Z. Indole and Pyrrole Derivatives as Prephotocatalysts and Substrates in the Sulfonyl Radical-triggered Relay Cyclization Leading to Sulfonylated Heterocycles. Org. Lett. 2022, 24, 2014–2019.
(11) Joseph, D.; Idris, M. A.; Chen, J.; Lee, S. Recent Advances in the Catalytic Synthesis of Arylsulfonyl Compounds. ACS Catal. 2021, 11, 4169–4204.
(12) Chu, X.-Q.; Ge, D.; Cui, Y.-Y.; Shen, Z.-L.; Li, C.-J. Desulfonylation via Radical Process: Recent Developments in Organic Synthesis. Chem. Rev. 2021, 121, 12548–12680.
(13) Ge, D.; Wang, X.; Chu, X.-Q. SOMOPhilly Alkylation Using Acetylenic Sulfoxones as Functional Reagents. Org. Chem. Front. 2021, 8, 5145–5164.
(14) Lin, S.-Y.; Yeh, T.-K.; Kuo, C.-C.; Song, J.-S.; Cheng, M.-F.; Liao, F.-Y.; Chao, M.-W.; Huang, H.-L.; Chen, Y.-L.; Yang, C.-Y.; Wu, M.-H.; Hsieh, C.-L.; Hsiao, W.; Peng, Y.-H.; Wu, J.-S.; Lin, L.-M.; Sun, M.; Chao, Y.-S.; Shih, C.; Wu, S.-Y.; Pan, S.-L.; Hung, M.-S.; Ueng, S.-H. Phenyl Benzenesulfonylhydrazides Exhibit Selective Indoleamine 2,3-Dioxygenase Inhibition with Potent in Vivo Pharmacodynamic Activity and Antitumor Efficacy. J. Med. Chem. 2016, 59, 419–430.
(15) Yang, F.-L.; Tian, S.-K. Sulfonyl Hydrazides as Sulfonyl Sources in Organic Synthesis. Tetrahedron Lett. 2017, 58, 487–504.
(16) Yang, F.-L.; Tian, S.-K. Iodine-Catalyzed Regioselective Sulfonylation of Indoles with Sulfonyl Hydrazides. Angew. Chem., Int. Ed. 2013, 52, 4929–4932.
(17) Kim, Y.; Song, K. H.; Lee, S. Synthesis of S-aryl Thioureas via Palladium-catalyzed Thiocarbonylation of Aryl Iodides and Aryl Sulfonyl Hydrazides. Org. Chem. Front. 2020, 7, 2938–2943.
(18) Yang, K.; Gao, J.-J.; Luo, S.-H.; Wu, H.-Q.; Pang, C.-M.; Wang, B.-W.; Chen, X.-Y.; Wang, Z.-Y. Quick Construction of a C-N Bond from Arylsulfonyl Hydrazides and Cap^2^-X Compounds Promoted by DMAP at room temperature. RSC Adv. 2019, 9, 19917–19923.
(19) Ruan, H.-L.; Ma, Y.-L.; Man, K.-X.; Zhao, S.-Y. Transition-Metal-Free Radical-Triggered Hydro sulfonylation and Disulfonylation Reaction of Substituted Maleimides with Sulfonyl Hydrazides. J. Org. Chem. 2022, 87, 3762–3769.
(20) Zhao, Z.; Tian, Q.; Chen, Y.; Wu, S.; Zhang, Y.; Cheng, G. Base-Promoted Stereoselective Hydrogenation of Ynamides with Sulfonyl Hydrazide to Give Z-Enamides. J. Org. Chem. 2021, 86, 10407–10413.
(21) Huang, A.-X.; Zhu, H.-L.; Zeng, F.-L.; Chen, X.-L.; Huang, X.-Q.; Qiu, L.-B.; Yu, B. 1-Acryl-2-cyanoindole: A Skeleton for Visible-Light-Induced Cascade Annulation. Org. Lett. 2022, 24, 3014–3018.
(22) Li, M.-M.; Cheng, L.; Xiao, L.-J.; Xie, J.-H.; Zhou, Q.-L. Palladium-Catalyzed Asymmetric Hydro sulfonylation of 1,3-Dienes with Sulfonyl Hydrazides. Angew. Chem., Int. Ed. 2021, 60, 2948–2951.
(23) Yang, Y.; Bao, Y.; Guan, Q.; Sun, Q.; Zha, Z.; Wang, Z. Copper-catalyzed S-methylation of Sulfonyl Hydrazides with TBHP for the Synthesis of Methyl Sulfones in Water. Green Chem. 2017, 19, 112–116.
(24) Xu, Z.-Q.; Wang, W.-B.; Zheng, L.-C.; Li, L.; Duan, L.; Li, Y.-M. Iodine-mediated Aminosulfonylation of Alkenyl Sulfonylamides with Sulfonyl Hydrazides: Synthesis of Sulfonylmethyl Piperidines, Pyrrolidines and Pyrazolines. Org. Biomol. Chem. 2019, 17, 9026–9038.
(25) Wang, F.-X.; Tian, S.-K. Cyclization of N-Arylcarbamates via Radical Arylsulfonylation of Carbon-Carbon Double Bonds with Sulfonyl Hydrazides. J. Org. Chem. 2015, 80, 12697–12703.
(26) Kawamata, Y.; Baran, P. S. Electro synthesis: Sustainability Is Not Enough. Joule 2020, 4, 701–704.
(27) Kingston, C.; Palkowitz, M. D.; Takahira, Y.; Vantourout, J. C.; Peters, B. K.; Kawamata, Y.; Baran, P. S. A Survival Guide for the Electro-curious. Acc. Chem. Res. 2020, 53, 72–83.
(28) Leech, M. C.; Lam, K. Electro synthesis Using Carboxylic Acid Derivatives: New Tricks for Old Reactions. Acc. Chem. Res. 2020, 53, 121–134.
(29) Shi, S.-H.; Liang, Y.; Jiao, N. Electrochemical Oxidation Induced Selective C-C Bond Cleavage. Chem. Rev. 2021, 121, 485–505.
(30) Waldvogel, S. R.; Lips, S.; Selt, M.; Riehl, B.; Kampf, C. J. Electrochemical Arylation Reaction. Chem. Rev. 2018, 118, 6706–6765.
(31) Yan, M.; Kawamata, Y.; Baran, P. S. Synthetic Organic Electrochemical Methods Since 2000: On the Verge of a Renaissance. Chem. Rev. 2017, 117, 13230–13319.
(32) Yuan, Y.; Yang, J.; Lei, A. Recent Advances in Electrochemical Oxidative Cross-coupling with Hydrogen Evolution Involving Radicals. Chem. Soc. Rev. 2021, 50, 10058–10086.

(33) Claraz, A.; Masson, G. Recent Advances in C(sp^3)-C(sp^3) and C(sp^3)-C(sp^2) Bond Formation through Cathodic Reactions: Reductive and Convergent Paired Electrolyses. ACS Organic & Inorganic Au 2022, 2, 126–147.

(34) Munda, M.; Niyogi, S.; Shaw, K.; Kundu, S.; Nandi, R.; Bisai, A. Electrocatalysis as a Key Strategy for the Total Synthesis of Natural Products. Org. Biomol. Chem. 2020, 22, 727–748.

(35) Ritter, S. K. Electrochemistry Gives Chemists More Power. C&EN 2017, 95, 23–25.

(36) Ritter, S. Electrochemistry Got Chemists Charged Up. C&EN 2017, 95, 21.

(37) Zhao, S.; Chen, K.; Zhang, L.; Yang, W.; Huang, D. Sulfonyl Hydrazides in Organic Synthesis: A Review of Recent Studies. Adv. Synth. Catal. 2020, 362, 3516–3541.

(38) Yuan, Y.; Lei, A. Electrochemical Oxidative Cross-Coupling with Hydrogen Evolution Reactions. Acc. Chem. Res. 2019, 52, 3309–3324.

(39) Lanfranco, A.; Moro, R.; Azzi, E.; Deagostino, A.; Renzi, P. Unconventional Approaches for the Introduction of Sulfur-based Functional Groups. Org. Biomol. Chem. 2021, 19, 6926–6957.

(40) Nambo, M.; Maekawa, Y.; Cuddren, C. M. Desulfonylative Transformations of Sulfoxones by Transition-Metal Catalysis, Photocatalysis, and Organocatalysis. ACS Catal. 2022, 12, 3013–3032.

(41) Colomer, I.; Velado, M.; Fernández de la Pradilla, R.; Viso, A. From Allylic Sulfoxides to Allylic Sulfenates: Fifty Years of a Never-Ending [2,3]-Sigmatropic Rearrangement. Chem. Rev. 2017, 117, 14201–14243.

(42) Alba, A.-N. R.; Companyó, X.; Rios, R. Sulfoxones: New Reagents in Organocatalysis. Chem. Soc. Rev. 2019, 48, 2018–2033.

(43) Jilková, A.; Rubešová, P.; Fanfíkl, J.; Fajtová, P.; Rezačová, P.; Brynda, J.; Lepšík, M.; Mertlíková-Kaiserová, H.; Emal, C. D.; Rendsi, A. R.; Roush, W. R.; Horn, M.; Cafrery, C. R.; Mareš, M. Druggable Hot Spots in the Schistosomiasis Cathepsin B1 Target Identified by Functional and Binding Mode Analysis of Potent Vinyle Sulfone Inhibitors. ACS Infect. Dis. 2021, 7, 1077–1088.

(44) Wozel, V. E. G. Innovative Use of Dapsone. Dermatologic Clinics 2010, 28, 599–610.

(45) Munda, M. J.; Ilovaisky, A. I.; Parshin, V. D.; Terent’ev, A. O. Oxidative Sulfonylation of Multiple Carbon-Carbon bonds with Sulfonyl Hydrazides, Sulfonic Acids and their Salts. Adv. Synth. Catal. 2020, 362, 4579–4654.

(46) Jeremias, N.; Mohr, L.-M.; Bach, T. Intermolecular [2 + 2] Photocycloaddition of αβ-Unsaturated Sulfoxones: Catalyst-Free Reaction and Catalytic Variants. Org. Lett. 2021, 23, 5674–5678.

(47) Yue, F.; Dong, J.; Liu, Y.; Wang, Q. Visible-Light-Mediated Alkenylation of Alkylboronic Acids without an External Lewis Base as an Activator. Org. Lett. 2021, 23, 2477–2478.

(48) Yuan, Y.; Cao, Y.; Lin, Y.; Li, Y.; Huang, Z.; Lei, A. Electrochemical Oxidative Alkoxysulfonilation of Alkenes Using Sulfonyl Hydrazines and Alcohols with Hydrogen Evolution. ACS Catal. 2018, 23, 10871–10875.

(49) Yan, G.; Qiu, K.; Guo, M. Recent Advancement in the C-F Bond Functionalization of Trifluoromethyl-containing Compounds. Org. Chem. Front. 2021, 8, 3915–3942.

(50) Zhang, C.; Wang, L.; Shi, H.; Lin, Z.; Wang, C. Iron-Catalyzed Allylic Dehydrogenative Ketone Olefination Coupling. Org. Lett. 2022, 24, 3211–3216.

(51) Luo, C.; Zhou, Y.; Chen, H.; Wang, T.; Zhang, Z.-B.; Han, P.; Jing, L.-H. Photoredox Metal-Free Allylic Dehydrogenative Silylation of α-Trifluoromethylstyrenes with Hydroisoles. Org. Lett. 2022, 24, 4286–4291.

(52) Tian, F.; Yan, G.; Yu, J. Recent Advances in the Synthesis and Applications of α-(trifluoromethyl)styrenes in Organic Synthesis. Chem. Commun. 2019, 55, 13486–13505.

(53) Luo, X.; Wang, S.; Lei, A. Electrochemical-Induced Hydroxysulfonilation of α-CF3 Alkenes to Access Tertiary β-Hydroxysulfones. Adv. Synth. Catal. 2022, 364, 1016–1022.
Benzoxazines. N-allylamides for the Synthesis of CF$_3$-Containing Oxazolines and Disubstituted Alkenes: Asymmetric Synthesis of Selenium-Containing Chiral Lewis Base Catalyzed Enantioselective Selenocyclization of 1,1-para-Quinone Methides (p-QMs) to Access (E)-Spiroindenes.

Y.; Li, Z. Silver or Cerium-promoted Free Radical Cascade Electrochemical Annulation-Iodosulfonylation of 1,5-Enyne-containing Difunctionalization of o-Vinylanilides with Sodium Aryl- or Alkylsulfinate Sources and Electrolytes.]

Transition Metal-Free Synthesis of Sulfonyl- and Bromo-Substituted Indolo[2,1-a]isoquinolines. Syntheses, Steroid Hormone Receptor Binding Alkoxycarbonylation/ Cyclization Reactions.]

Electrochemical Decarboxylative Sulfonylation of Cinnamic Acids with Sodium Sulfinates. J. Org. Chem. 2019, 84, 13465–13472.

Yang, J.; Li, G.; Yu, K.; Xu, B.; Chen, Q. Electrochemical Sulfonylation-Induced Lactonization of Alkenes: Synthesis of Sulfonyl Phthalides. J. Org. Chem. 2022, 87, 1208–1217.

Liao, J.; Yang, X.; Ouyang, L.; Lai, Y.; Huang, J.; Luo, R. Recent Advances in Cascade Radical Cyclization of Radical Acceptors for the Synthesis of Carbo- and Heterocycles. Org. Chem. Front. 2021, 8, 1345–1363.

Zhang, B.; Studer, A. Recent Advances in the Synthesis of Nitrogen Heterocycles via Radical Cascade Reactions Using Isoinitriles as Radical Acceptors. Chem. Soc. Rev. 2015, 44, 3505–3521.

Liu, J.; Wang, M.; Li, L.; Wang, L. Electrooxidative Tandem Cyclization of N-Proargylanilines with Sulfinic Acids for Rapid Access to 3-Arylsulfonylimidoline Derivatives. Green Chem. 2021, 23, 4733–4740.

Ma, Q.; Li, M.; Chen, Z.; Ni, S.-F.; Wright, J. S.; Wen, L.-R.; Zhang, L.-B. An Approach for the Synthesis of 2-Aryl-3-sulfonyl Substituted Quinolines through an Electrochemical Cascade Annulation Pathway. Green Chem. 2022, 24, 4425–4431.

Elsherbini, M.; Wirth, T. Electroorganic Synthesis under Flow Conditions. Acc. Chem. Res. 2019, 52, 3287–3296.

Gütsch, C.; Stenglein, A.; Waldvogel, S. R. Highly Modular Flow Cell for Electrosynthetic Organic Synthesis. Org. Process Res. Dev. 2017, 21, 771–778.

Bajada, M. A.; Sanjós-Orduna, J.; Di Liberto, G.; Tosoni, S.; Pacchioni, G.; Noël, T.; Vile, G. Interfacing Single-atom Catalysis with Continuous-flow Organic Electrolys. Chem. Soc. Rev. 2022, 51, 3898–3925.

Noël, T.; Cao, Y.; Laudadio, G. The Fundamentals Behind the Use of Flow Reactors in Electrochemistry. Acc. Chem. Res. 2019, 52, 2858–2869.

Xu, J.; Yang, Z.; Hua, J.; Lin, Y.; Bian, M.; Li, Y.; Liu, C.; He, W.; Fang, Z.; Guo, K. The Continuous-flow Electrosynthesis of 4-(sulfonylmethyl)isoquinoline-1,3(2H,4H)-diones from N-alkyl-N-methacryloyl Benzamides under Metal-free and Oxidant-free Conditions. Org. Chem. Front. 2020, 7, 3223–3228.

Cai, C.; Lu, Y.; Yuan, C.; Fang, Z.; Yang, X.; Liu, C.; Guo, K. Organocatalytic Electrosynthesis of Cinolones through Cascade Radical Cyclation and Migration. ACS Sustainable Chem. Eng. 2021, 9, 16989–16996.

Karmakar, U.; Samanta, R. Pd(I)-Catalyzed Direct Sulfonylation of Benzylamines Using Sodium Sulfinates. J. Org. Chem. 2019, 84, 2850–2861.

Guo, Y.; Jia, Z.; Tian, L.-L.; Huang, E.-L.; Hua, X.-Q.; Zhu, X.; Shao, T.; Song, M.-P. Iodine-Mediated Difunctionalization of Imidazopyridines with Sodium Sulfinates: Synthesis of Sulfoxides and Sulfoxides. J. Org. Chem. 2018, 83, 338–349.

Jiang, M.; Yuan, Y.; Wang, T.; Xiong, Y.; Li, J.; Guo, H.; Lei, A. Exogenous-oxidant- and Catalyst-free Electrochemical Deoxyxycagenet C2 Sulfonylation of Quinoline N-oxides. Chem. Commun. 2019, 55, 13852–13855.

Zhao, J.; Chen, Z.; He, M.; Wang, D.; Li, L.; Qi, J.; Shi, R.; Lei, A. Metal-free Electrochemical C3-Sulfonylation of Imidazo[1,2-a]-pyridines. Org. Chem. Front. 2021, 8, 3815–3819.

Yin, Z.; Yu, Y.; Mei, H.; Han, J. Electrosynthesis of Functionalized Tetraydrodcarbazoles via Sulfonylation Triggered Cyclization Reaction of Indole Derivatives. Green Chem. 2021, 23, 3256–3260.

Yu, Y.; Fang, Y.; Tang, R.; Xu, D.; Dai, S.; Zhang, W. Electrochemical Oxidative Sulfonylation of N-Arylamides/Amine with Sodium Sulfonates. Asian J. Org. Chem. 2022, 11, No. e202100805.

Yuan, Y.; Yu, Y.; Qiao, J.; Liu, P.; Yu, B.; Zhang, W.; Liu, H.; He, M.; Huang, Z.; Lei, A. Exogenous-oxidant-free Electrochemical
Oxidative C-H Sulfonylation of Arenes/Heteroarenes with Hydrogen Evolution. Chem. Commun. 2018, 54, 11471–11474.

Singh, J.; Patel, R. I.; Sharma, A. Visible Light Mediated C-C Functionalization- and Deoxygenative Strategies in Heterocyclic N-Oxides. Adv. Synth. Catal. 2022, 364, 2289–2306.

Xu, Y.-X.; Liang, Y.-Q.; Cai, Z.-J.; Ji, S.-J. Ruthenium(II)-Catalyzed Chelation-Assisted Desulfitative Arylation of Benzo[h]-quinolines with Arylsulfonyl Chlorides. Org. Lett. 2022, 24, 2601–2606.

Pan, Y.-M. Electrochemically Enabled Chemoselective Sulfonylation, 3699–85

Pan, Y.-M.; Sun, H.-B.; Chen, Z.-F. Electrochemical Sulfonylation of 2H-Indazoles to 3-Sulfonylated 2H-Indazoles. Chem. Commun. 2019, 55, 11091–11094.

Kim, W.; Kim, H. Y.; Oh, K. Electrochemical Radical-Radical Cross-Coupling Approach between Sodium Sulfinites and 2H-Indazoles to 3-Sulfonylated 2H-Indazoles. Org. Lett. 2020, 22, 6319–6323.

Mahanty, K.; Maiti, D.; De Sarkar, S. Regioselective C-H Sulfonylation of 2H-Indazoles by Electrosynthesis. J. Org. Chem. 2020, 85, 3699–3708.

Zhang, Y.-Z.; Mo, Z.-Y.; Wang, H.-S.; Wen, X.-A.; Tang, H.-T.; Pan, Y.-M. Electrochemically Enabled Chemoselective Sulfonylation and Hydrazination of Indoles. Green Chem. 2019, 21, 3807–3811.

Song, Q.; Zhao, H.; Sun, Y.; Jiang, H.; Zhang, M. Direct C(sp3)-H Sulfonylation of Xanthene Derivatives with Sodium Sulfinates by Oxidative Copper Catalysis. Chin. J. Chem. 2022, 40, 371–377.

Das, S.; Roy, S.; Bhowmik, A.; Sarkar, W.; Mondal, I.; Mishra, A.; Saha, S. J.; Karmakar, S.; Deb, I. A radical-radical Cross-coupling Reaction of Xanthene with Sulfonyl Hydrazides: Facile Access to Xanthene-9-sulfone Derivatives. Chem. Commun. 2022, 58, 2902–2905.

Wei, B.; Qin, J.-H.; Yang, Y.-Z.; Xie, Y.-X.; Ouyang, X.-H.; Song, R.-J. Electrochemical Radical C(sp3)-H Arylation of Xanthenes with Electron-rich Arenes. Org. Chem. Front. 2022, 9, 816–821.

Chen, X.; Liu, H.; Gao, H.; Li, P.; Miao, T.; Li, H. Electrochemical Regioselective Cross-Dehydrogenative Coupling of Indoles with Xanthenes. J. Org. Chem. 2022, 87, 1056–1064.

Gao, H.; Chen, X.; Wang, P.-L.; Shi, M.-M.; Shang, L.-L.; Guo, H.-Y.; Li, H.; Li, P. Electrochemical Benzyl C-H Arylation of Xanthenes and Thioxanthenes without a Catalyst and Oxidant. Org. Chem. Front. 2022, 9, 1911–1916.

Wei, W.-J.; Zhong, Y.-J.; Feng, Y.-F.; Gao, L.; Tang, H.-T.; Pan, Y.-M.; Ma, X.-L.; Mo, Z.-Y. Electrochemically Mediated Direct C(sp3)-H Sulfonylation of Xanthene Derivatives. Adv. Synth. Catal. 2022, 364, 726–731.

Terent’ev, A. O.; Mulina, O. M.; Parshin, V. D.; Kokorekin, V. A.; Nikishin, G. I. Electrochemically Induced Oxidative S-O Coupling: Synthesis of Sulfoxones from Sulfonyl Hydrazides and N-Hydroxyimides or N-Hydroxybenzotriazoles. Org. Biomol. Chem. 2019, 17, 3482–3488.

Amri, N.; Wirth, T. Recent Advances in the Electrochemical Synthesis of Organosulfur Compounds. Chem. Rec. 2021, 21, 2526–2537.

Zhang, L.; Cheng, X.; Zhou, Q.-L. Electrochemical Synthesis of Sulfonyl Fluorides with Triethylamine Hydrofluoride. Chin. J. Chem. 2022, 40, 1687–1692.

Park, J. K.; Oh, J.; Lee, S. Electrochemical Synthesis of Sulfonyl Fluorides from Sulfonyl Hydrazides. Org. Chem. Front. 2022, 9, 3407–3413.