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Sulfinic esters: Novel and versatile sulfenylating agents for biologically important thioethers synthesis

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ABSTRACT

Thioethers are one of the most important family of organosulfur compounds that have shown lots of applications in pharmaceuticals, agrochemicals, polymeric materials and organic dyes. Interestingly, over 30 FDA-approved drugs contain at least one thioether motif in their structures and are used to treat a wide range of diseases, from depression to rheumatoid arthritis to acute coronary syndrome. Therefore, looking for novel, efficient, and straightforward methodologies for their synthesis from low cost, readily available, and non-toxic starting materials is very important in organic chemistry. In this context, the reactions between various electrophiles and sulfenylating agents has recently attracted more and more attention as a general and straightforward route for their synthesis. However, most of the existing sulfenylating agents had some disadvantages, such as a foul smell, high cost and being unstable to air and moisture. Recently, sulfinic esters have emerged as odor-less, easily accessible, stable and easy to handle sulfenylating agents and successfully applied in the synthesis of various aliphatic and aromatic thioethers, mainly through the site-selective functionalization of C–H bonds. The purpose of this review is to provide an overview of the available literature on the synthesis of thioethers using sulfinic esters as sulfenylating agents, with special emphasis on the mechanistic features of the reactions. Literature has been surveyed from 2016 to the end of 2022.

1. Introduction

Organosulfur compounds, molecules contain one or more sulfur-carbon bonds, are a special class of organic compounds that widely present in natural environment [1], living organisms, functional materials, pharmaceuticals [2], and agrochemicals [3]. Thioethers are one of the most important classes of organosulfur therapeutic agents which found in more than 30 FDA-approved drugs and use for the treatment/management of various types of diseases such as bacterial infections, gastroesophageal reflux, rheumatoid arthritis, depression, inflammatory, and Parkinson's disease (Scheme 1a) [4]. In addition, this family of organosulfur compounds are acquiring more importance in plant protection field in recent years because of their broad spectrum of agricultural activities, such as antifungal, antibacterial, insecticidal, acaricidal, nematocidal, antiviral, herbicidal, and plant growth-regulating activity (Scheme 1b) [5]. Furthermore, they are valuable precursors for other useful organosulfur compounds such as sulfoxides and sulfones. In light of the above-mentioned chemistry, numerous synthetic methods have been developed to access thioethers [6],

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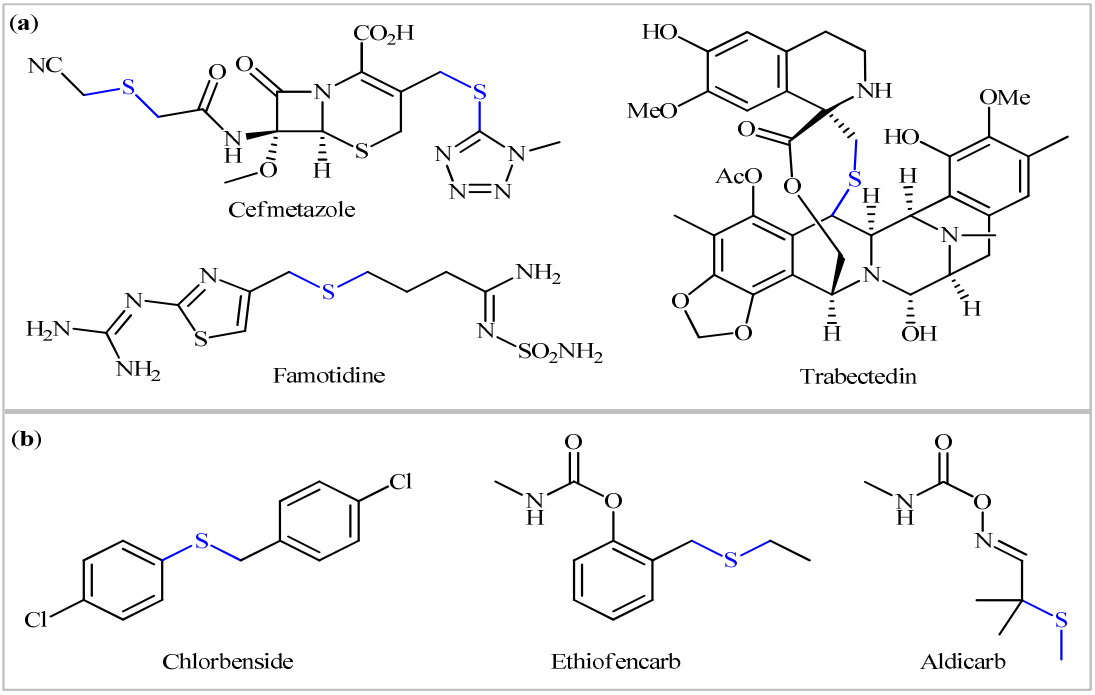
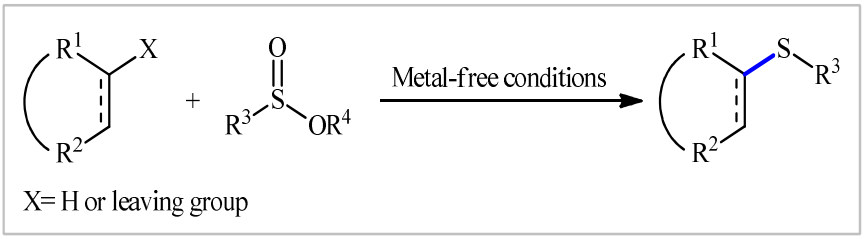


Scheme 1. Selected examples of (a) drug molecules that contain a thioether moiety; (b) thioether-containing pesticides.

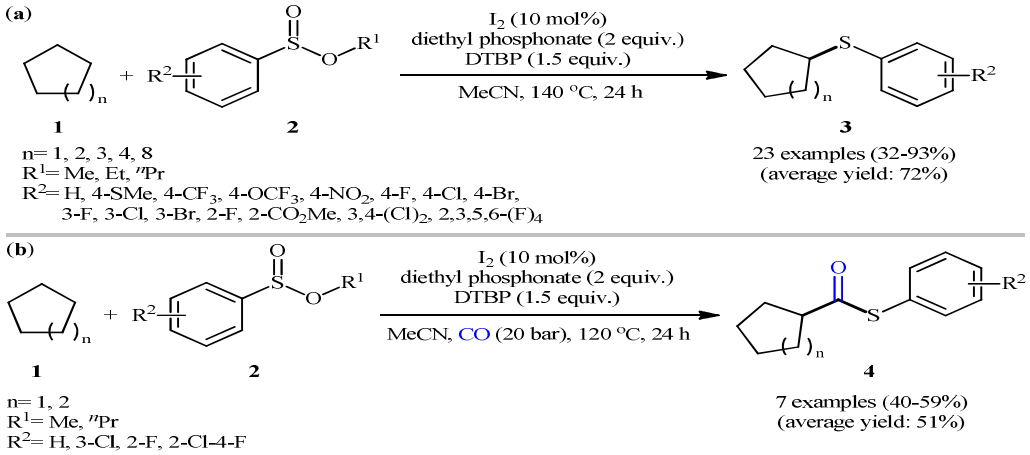
Traditional approaches are based on the condensation of activated organic halides with alkali-metal thiolates that are prepared from thiols in the presence of strong bases [7]. However, the synthetic scope of this classical strategy is limited by its long reaction time, high reaction temperature, and low yield [8]. To overpass these drawbacks, a series of sulfenylation reactions between various types of electrophiles with sulfenylating agents such as sulfenyl halides [9], *N*-hydroxy sulfonamides [10], sulfonyl chlorides [11], *N*-thioimides [12], thiols [13], and disulfides [14] has been developed. Nevertheless, these reactions have some well-known disadvantages [15]: First, some of the sulfenylating agents are unstable to air and moisture, are difficult to be prepared, expensive, or possess unpleasant smelling. This is particularly problematic for largescale synthesis. In addition, many of these reactions involve the use of expensive and/or toxic metal catalysts. Furthermore, some of these reactions suffer from a narrow substrate scope, or yield byproducts unfriendly to the environment. Therefore, the search for alternative sulfenylating agents which address the above-mentioned drawbacks is of great importance. In this context, sulfinic esters have recently emerged as eco-friendly, easily accessible, stable, and odorless sulfenylating agents for the sulfenylation of various aliphatic and aromatic electrophiles under metal-free conditions (Scheme 2). To the best of our knowledge, a comprehensive review has not appeared on this rapidly growing research arena in the literature till date and seems timely to summarize the developments and advances on this field. In connection with previous works on the synthesis of organosulfur compounds [16] and modern organic synthesis [17], herein, we will outline the recent trends in the preparation of thioethers using sulfinic esters as sulfenylating agents.



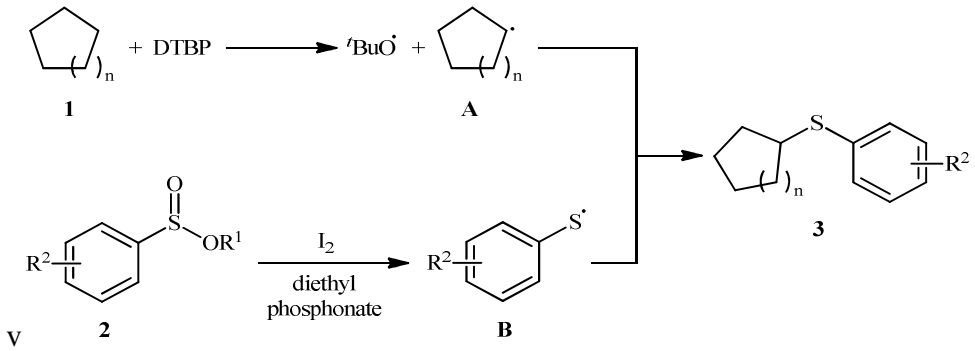
Scheme 2. Sulfinic esters as sulfenylating agents.

2. Sulfenylation of alkanes

Sulfenylation of alkanes using sulfinic esters as sulfenylating agents has been rarely explored. In fact, only one report of such a reaction was published in the literature till date. In this study, Wu and co-workers investigated the possibility of direct conversion of unactivated alkanes to the corresponding thioethers using arylsulfinic esters as sulfenylating agents in a cross-coupling transformation [18]. By employing cyclohexane and methyl benzenesulfinate as the model substrates, the reaction variables were attentively screened. The results demonstrated that the merge of 10 mol% of molecular iodine (I_2) with 2.0 equiv. of diethyl phosphonate and 1.5 equiv. of di-*tert*-butyl peroxide (DTBP) was the most appropriate catalytic system for this transformation. Under the optimized conditions, a panel of 23 alkyl aryl thioethers **3** were obtained in moderate to excellent yields by reaction of various cycloalkanes **1** with alkyl arylsulfinates **2** under an inert atmosphere at 140 °C (Scheme 3a). The results proved that the ring size of cycloalkanes and the electronic effects of the substituents in the phenyl ring periphery of arylsulfinates had no significant impact on the outcome of the reaction. However, nitro substituted substrates did not work well in the reaction and cyclic ethers (1,4-dioxane, THF) and cyclic amines (piperidine, 1-methylpiperidine, pyrrolidine) failed to form any desired products. Unfortunately, the applicability of liner alkanes was not investigated in this synthetic strategy. Interestingly, when the reaction was performed under carbon monoxide (CO) atmosphere, related thioesters **4** were successfully produced without changing the reaction variables (Scheme 3b). According to the author's proposed mechanism (Scheme 4), presumably, the reaction for the formation of thioethers **3** started with the generation of the *t*-butoxy radical ($^tBuO^{\cdot}$) by thermal homolytic cleavage of peroxide (DTBP), which reacts with cycloalkane **1** to provide radical **A**. Simultaneously, alkyl arylsulfinate **2** is reduced by I_2 and diethyl phosphonate to provide the aryl thiol radical **B**. Finally, these two radical species directly coupled to deliver the target thioethers **3**.



Scheme 3. (a) Synthesis of thioethers **3** through sulfenylation of cycloalkanes **1** with alkyl arylsulfinates **2**; (b) carbonylative sulfenylation of cycloalkanes **1** with alkyl arylsulfinates **2** under CO atmosphere.

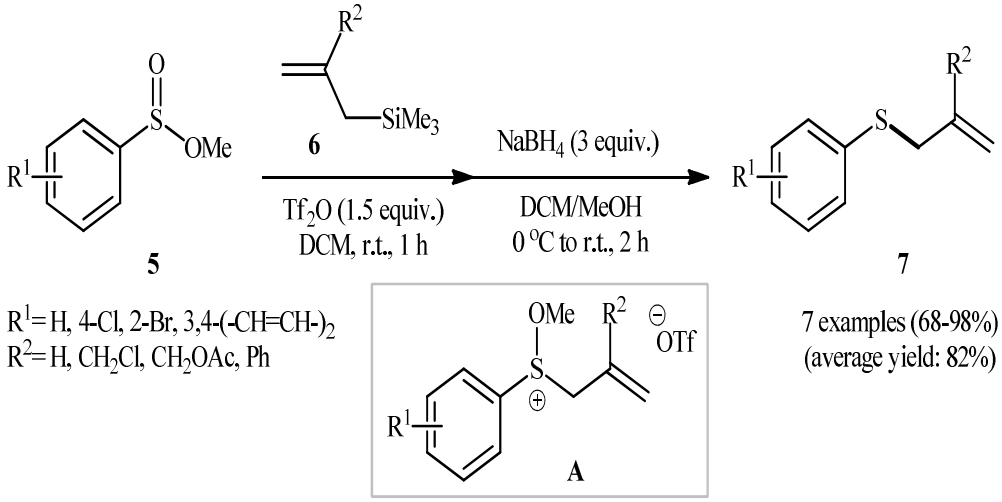


Scheme 4. Proposed reaction mechanism for the formation of thioethers **3**.

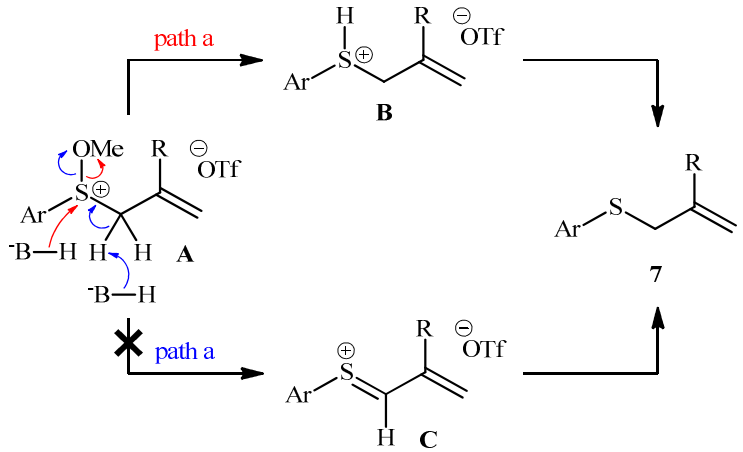
3. Sulfenylation of alkenes

After their seminal work on the preparation of allyl sulfoxides by *S*-allylation of sulfinate esters [19], Yoshida's group demonstrated an interesting one-pot two step synthesis of allyl sulfides from the respective allylsilanes and sulfinate esters through *S*-allylation of sulfinate esters to allyl sulfonium salt followed by reduction with sodium borohydride ($NaBH_4$) [20]. In this investigation, a number of allyl sulfides **7** were obtained in good to almost quantitative yields by reaction of various methyl arylsulfinates **5** with allyltrimethylsilanes **6** in DCM through the action of trifluoromethanesulfonic anhydride (Tf_2O) and subsequent reduction in the binary solvent DCM/MeOH (Scheme 5).

A series of synthetically useful functional groups such as –OAc, –Cl, and –Br were perfectly tolerated by this transformation, thus promising further manipulation of the final products. It should be mentioned that other common reductant such as $NaBH_3CN$, $LiBH_4$, $LiAlH_4$, and $^{i}Bu_2AlH$ were also found to reduce sulfonium salts, albeit with reduced efficiencies. However, Et_3SiH and 1,4-cyclohexadiene were ineffective reductants for this conversion. Based on a series of mechanistic studies conducted (deuteration experiment using $NaBD_4$, ^1H NMR analysis, theoretical calculation), the authors proposed that this reaction proceeds through the intramolecular substitution reaction of the sulfonium sulfur with hydride ion and subsequent deprotonation (Scheme 6, path a). On the other hand, the mechanism shown as path b in Scheme 6 is excludable, since the deprotonation was not observed in the deuteration experiment. To the best of our knowledge, this is the first and only reported example of the sulfenylation of alkenes employing sulfinic esters as sulfenylating agents.



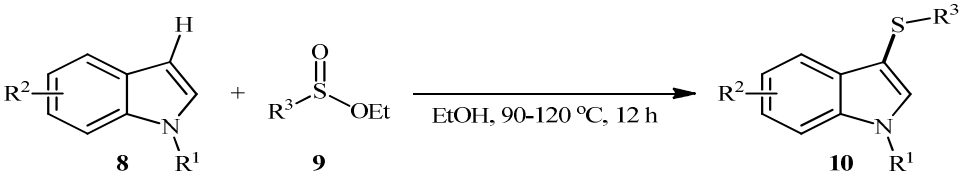
Scheme 5. Yoshida's synthesis of allyl sulfides **7**.



Scheme 6. The plausible mechanistic pathway for the formation of allyl sulfides **7**.

4. Sulfenylation of arenes

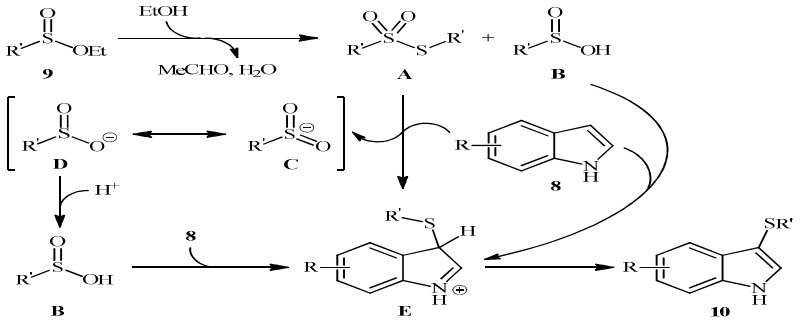
Although, sulfinic esters have been in use as sulfinylating electrophiles in Friedel-Crafts reactions since the early 2010's [21-23], their applicability as sulfenylation agents in such reactions have been explored for first time in 2018 by Zhou, Yang and co-workers [24], who reported highly selective C3-sulfenylation of indoles 8 with ethyl sulfinates 9 to synthesize C3-sulfenylated indole derivatives 10 in modest to high yields, ranging from 38% to 88%, under catalyst-free conditions and without consuming any ligand or additive (Scheme 7). Interestingly, when the C3 position was blocked by substituents, the sulfenylation took place selectively at the C2 of the indole ring. The results demonstrated that the presence of different substituting patterns various positions over the indole ring (C2, C4, C5, C6, C7) did not have strong impact on the reaction outcome. More importantly, both (hetero)aryl- and alkyl-sulfinates were well tolerated in this reaction. The methodology was also compatible with either N-protected or NH-free indoles. However, when Boc- or Bz-protected indoles were used as substrates, the corresponding deprotected (NH-free) indole thioethers were obtained as the sole products. Notably, the reaction can be enlarged to gram scale with negligible decrease in yield. Based on several control experiments, a possible mechanism was suggested by the authors for this regioselective sulfenylation reaction depicted in Scheme 8, the reaction might start with the reduction of sulfinic esters 9 by ethanol to form sulfonothioate A and sulfinic acid B intermediates, which after electrophilic reaction with indole 8 deliver intermediate C and intermediate E. Subsequently, anion D, resonance of intermediate C can react with hydrogen ions to give sulfinic acid C, which also can react with indole 8 to afford intermediate E. Finally, intermediate E converts to the target thioether 10 *via* a deprotonation process.



R^1= H, Me, Bn
R^2= H, 2-Me, 2-Ph, 4-Me, 5-Me, 5-OMe, 5-NO_2, 5-CN, 5-Cl, 5-Br, 6-CO_2Et, 6-F, 6-Cl, 7-Me
R^3= ^{c}Pr, Ph, 4-Me-C_6H_4, 4-^{t}Bu-C_6H_4, 4-OMe-C_6H_4, 4-F-C_6H_4, 4-Cl-C_6H_4, 4-I-C_6H_4, 3-Br-C_6H_4, 3-CF_3-C_6H_4, 2,4,6-$(Me)_3$-C_6H_2, 1-naphthyl, 2-naphthyl, 2-thienyl

29 examples (38-88%)
(average yield: 66%)

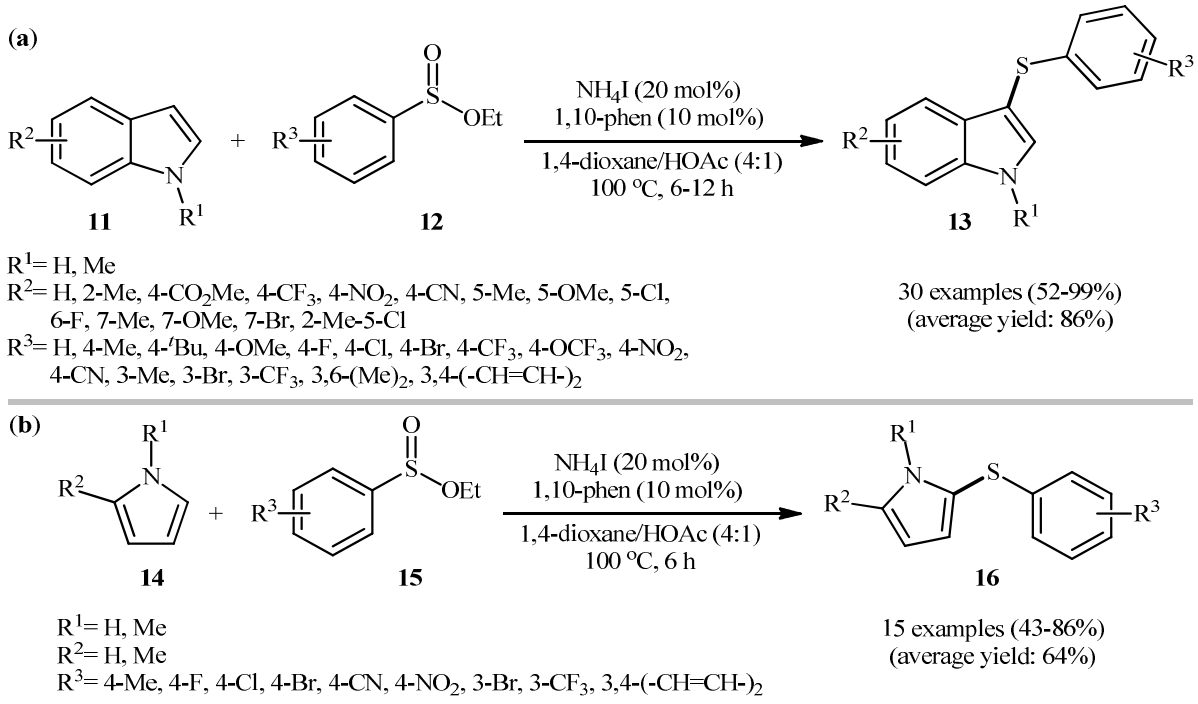
Scheme 7. C3-selective sulfenylation of indoles **8** with ethyl sulfinates **9** under catalyst-free conditions.



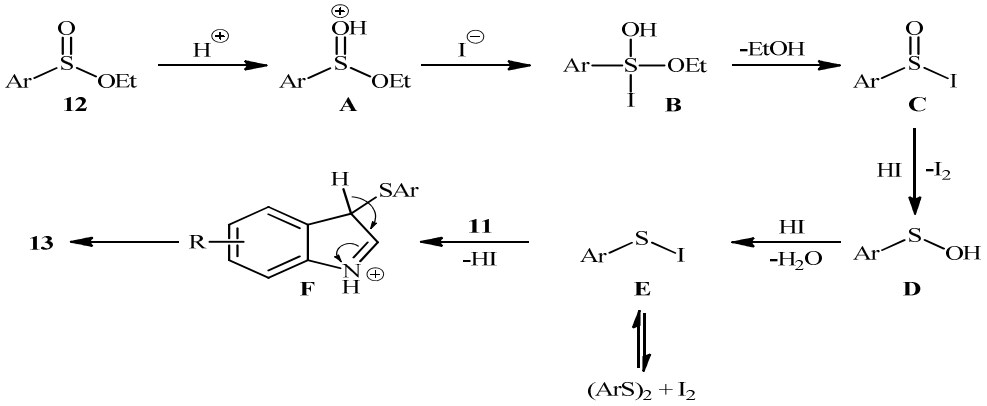
Scheme 8. Mechanistic explanation of the formation of indole thioethers **10**.

Carrying on from this work, Liu-Zhang *et al.* disclosed that the merge of NH_4I and 1,10-phenanthroline (1,10-phen) could be applied as a highly effective catalytic system for the sulfenylation of indoles with sulfinates [25]. KI was also found to promote this C-S coupling reaction, albeit in lower yields. When the reaction was performed in the absence of iodine source, no product was obtained. The results also revealed that the efficiency of this sulfenylation reaction was dramatically dependent on the solvent. Among the various common solvents like toluene, 1,4-dioxane, DMF, DMSO, DCE, EtOH; 1,4-dioxane

proved to be the most efficient for this transformation. Replacing 1,4-dioxane with polar aprotic solvents like DMF or DMSO led to no product at all. Under optimized conditions, various NH-free and N-methyl indoles 11 underwent C3-selective sulfenylation with diverse range of ethyl arylsulfinates 12 to give the corresponding sulfenylated indoles 13 in moderate to almost quantitative yields within 6 h (Scheme 9a). Interestingly, the reaction was equally efficient for both electron-rich and electron-poor arylsulfinates. One 1*H*-pyrrolo[2,3-*b*]pyridine was also tested and gave product in good yield but at higher reaction temperature (120 ^{o}C). Similarly, pyrroles 14 was also found to be suitable substrates for this sulfenylation reaction and selectively gave C2-sulfenylated products 15 in moderate to high yields (Scheme 9b). It should be mentioned that Zhou-Yang's methodology (catalyst-free, EtOH, 90 ^{o}C) was not compatible with pyrrole substrates. In Scheme 10 the authors proposed mechanistic pathway of this C-S bond forming reaction is provided. The reaction initiates with the generation of cationic intermediate A through the protonation of ethyl arylsulfinate 12 under acidic conditions. Subsequently, addition of iodine anion to this intermediate A forms intermediate B, which after losing an ethanol gives arylsulfinic iodide C. Next, reduction of this intermediate C with hydroiodic acid (HI) yields the intermediates D and E. Finally, the electrophilic substitution reaction of indole 11 with intermediate D affords the observed indole thioether 13 through the intermediate F.



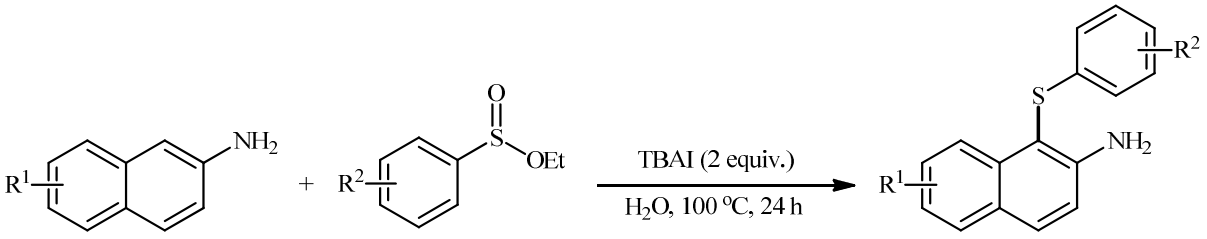
Scheme 9. (a) NH_4I-catalyzed sulfenylation of indoles **1** with ethyl arylsulfinates **2**; (b) regioselective sulfenylation of pyrroles **1** with ethyl arylsulfinates **2** catalyzed by NH_4I/1,10-phen.



Scheme 10. Proposed mechanistic pathway for the reaction in Scheme 9a.

Another example of the direct sulfenylation of aromatic C-H bonds with sulfinic esters was reported by Liu-Gu *et al* in 2020 [26]. In the presence of 2.0 equiv. of

TBAI (*tetra-n*-butylammonium iodide), naphthalen-2-amines **17** reacted with various ethyl arylsulfinates **18** to form the 1-(arylthio)naphthalen-2-amines **19** in good to excellent yields (Scheme 11). Functionalization of thioethers with divers range of important groups such as OMe, CF_3, OCF_3, NO_2, F, Cl, and Br has been successfully achieved by this synthetic strategy that may provide a complementary platform for further modifications of the products to create more complex molecules. Beside good yields and high substrate scope, scalability as well as performing the reaction in water, the most environmentally benign solvent, can be considered as the advantages of this methodology. Noteworthy, apart from naphthalen-2-amines, several other electron-rich arenes (e.g., anilines, indoles, pyrroles, pyrazoles) are compatible with this scenario. However, neither aliphatic- nor heteroaromatic-sulfinates were examined in this procedure. After a series of mechanistic investigations, it was suggested that this reaction most likely proceeds *via* a pathway depicted in Scheme 8.



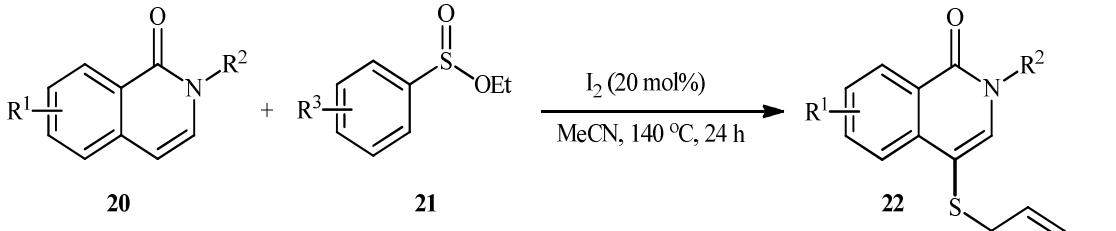
17 **18** **19**

R^1= H, 6-Br
R^2= H, 4-Me, 4-^{t}Bu, 4-OMe, 4-F, 4-Cl, 4-Br, 4-NO_2, 4-CF_3, 4-OCF_3, 3-Me, 3-Br, 3-CF_3, 2,5-$(Me)_2$, 3,4-(-CH=CH-)$_2$

16 examples (68-94%)
(average yield: 84%)

Scheme 11. TBAI-mediated sulfenylation of naphthalen-2-amines **17** with ethyl arylsulfinates **18** in water.

Drawing inspiration from these works, Yang and Tang along with their co-workers developed an efficient regioselective sulfenylation of isoquinolin-1(2*H*)-ones 20 at the C4-position with ethyl arylsulfinates 21 using molecular iodine as an inexpensive catalyst [27]. The reactions proceeded in MeCN at 140 °C, giving fair to quantitative yields of the desired 4-(arylthio)-isoquinolin-1(2*H*)-ones 22 within 24 h (Scheme 12). Concerning the substrate scope, the reaction is very dependent on the electronic-factors of both partners. Generally, compounds bearing strongly electron-withdrawing substituents (e.g., CN, NO_2) afforded less satisfactory results or even no desired product at all. In the proposed mechanism, the authors suggested that this transformation proceeds *via* formation of complex A through the activation of ethyl sulfinate 21 with iodine, which undergoes free radical polymerization to give dimer intermediate B. Subsequently, reductive elimination of this intermediate generates disulfide C by releasing acetaldehyde and hydrogen peroxide. Next, the intermediate C splits into the active iodide species D in the presence of I_2, which then converts into intermediate E through regioselective electrophilic attack by isoquinolin-1(2*H*)-one 20. Finally, elimination of HI from the intermediate E leads to the desired product 22 (Scheme 13).

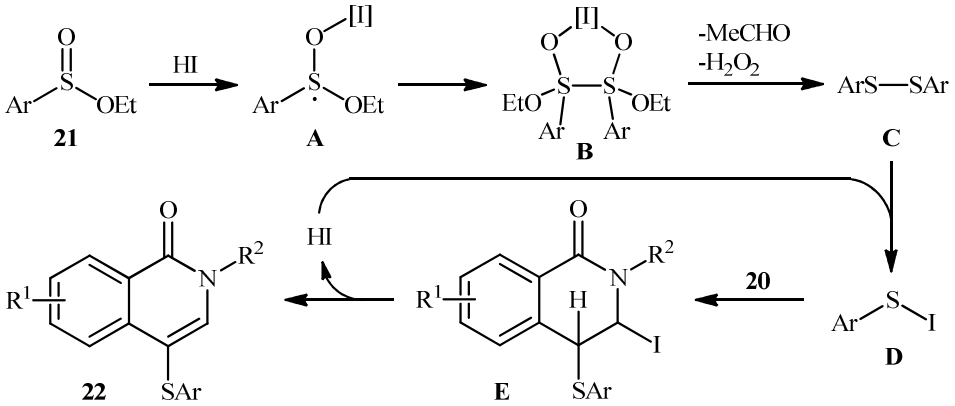


20 **21** **22**

R^1= H, Me, Et, Bn, allyl
R^2= H, 5-NO_2, 6-Me, 6-OMe, 6-Cl, 6-Br
R^3= 4-Me, 4-^{t}Bu, 4-OMe, 4-F, 4-Cl, 4-Br, 4-I, 4-CF_3, 4-CN, 3-Me, 3-Cl, 2-Me, 2-Cl, 2,3-(-CH=CH-)$_2$

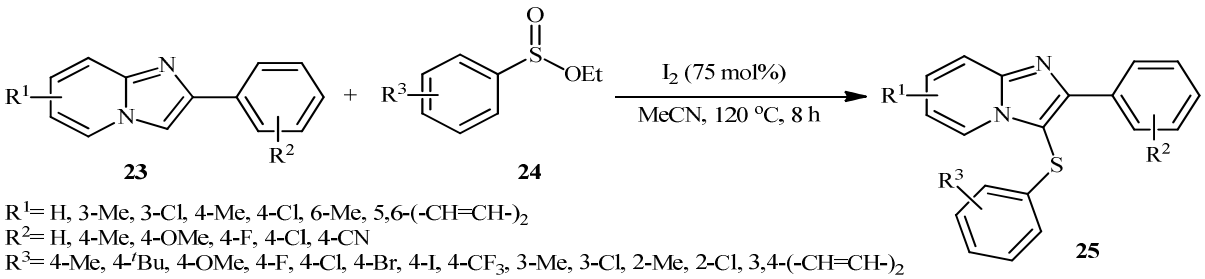
22 examples (17-99%)
(average yield: 70%)

Scheme 12. I_2-catalyzed regioselective sulfenylation of isoquinolin-1(2*H*)-ones **20** with ethyl arylsulfinates **21**.



Scheme 13. Proposed mechanism for the formation of C4-sulfenylated isoquinolin-1(2*H*)-ones **22**.

Recently, the same research team extended the substrate scope of this methodology of direct C-H sulfenylation to imidazo[1,2-*a*]pyridines [28]. Thus, by using 75 mol% of I_2 as a mediator in MeCN, the coupling of various 2-aryl imidazo[1,2-*a*]pyridine derivatives **23** with ethyl arylsulfinates **24** selectively afforded the corresponding 3-(arylthio)-2-arylimidazo[1,2–*a*]pyridines **25** in moderate to high yields (Scheme 14). The results indicated that the electronic character of the substituents in imidazo[1,2-*a*]pyridines as well as ethyl arylsulfinates had negligible effect on the facility of the reaction. Generally, both electron-donating and electron-withdrawing groups were well tolerated. Noteworthy, the *ortho*-substituted arylsulfinates afforded better yields compared to those with a similar substituent in the *meta*- or *para*-position, suggesting the reaction is not affected by steric hindrance. The proposed mechanism for this transformation is analogous to the one depicted for isoquinolin-1(2*H*)-ones.



Scheme 14. Iodine-mediated sulfenylation of imidazo[1,2-a]pyridines 23 with ethyl arylsulfinates 24.

5. Conclusion

Over the past few years, the synthesis of thioether derivatives through the sulfenylation of various electrophiles with sulfenylating agents have attracted considerable attention as cleaner and more sustainable synthetic alternative to traditional procedures which are based on the condensation of activated organic halides with alkali-metal thiolates. However, most of the existing sulfenylating agents are unstable to air and moisture, are difficult to be prepared, expensive, or possess unpleasant smelling. Therefore, there is still further need for developing alternative and/or complementary sulfenylation agents that overpass the current drawbacks.

Along this line, sulfinic esters have recently gained a lot of attention in the light of their easy availability, high stability as well as their non-toxic, odor-less, and non-volatile nature. As illustrated, these compounds have been successfully utilized as effective sulfenylating agents for the synthesis of various aryl-aryl, aryl-alkyl, and alkyl-alkyl thioethers. Interestingly, all reactions covered in this review were performed under metal-free conditions and most of them could be easily scaled up to the gram-scales. These results

clearly show the potential application of this page of thioether synthesis in industry. However, the scope of these emerging of sulfenylation methods is limited, and more efforts are still needed to study its scope and limitations.

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