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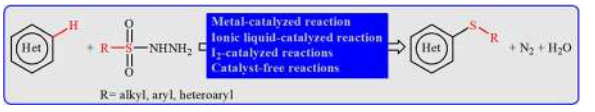
Direct C–H bond sulfenylation of (Het)arenes using sulfonyl hydrazides as thiol surrogate: a review

Akram Hosseinian[a], Sattar Arshadi[b], Shahriar Sarhandi[b], Aazam Monfared[b] and Esmail Vessally[b]

[a]School of Engineering Science, College of Engineering, University of Tehran, Tehran, Iran; [b]Department of Chemistry, Payame Noor University, Tehran, Iran

ABSTRACT

Sulfonyl hydrazides are easily accessible, non-toxic, stable and extremely valuable compounds in organic synthesis that are extensively utilized as sulfonylating and arylating agents (through the cleavage of their sulfur–nitrogen and carbon–sulfur bonds, respectively) for the synthesis of diverse range of biologically active molecules such as biaryls, sulfones, and sulfonamides. These compounds have also been broadly used as environmentally friendly, stable, and odorless sulfenylation agents (through the cleavage of their sulfur–nitrogen and sulfur–oxygen bonds) in the synthesis of synthetically and biologically important thioether derivatives. In this review, we will highlight the most important advances and explorations in the direct C–H bond sulfenylation of (het)aromatic compounds with these compounds during the period 2013 to October 2018. Particular emphasis is placed on the mechanistic aspects of the reactions.



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Sulfonyl hydrazides; thioethers; C–H bond functionalization; sulfenylation agents; molecular iodine

1. Introduction

Sulfur-containing compounds are a special class of organic compounds, which are prevalent in diverse biologically active natural products [1–3], pharmaceuticals [4,5] and agrochemicals [6]. Among the various organosulfur compounds, thioether derivatives (R-S-R') are one of the most important motifs in medicinal chemistry that display a variety of biological and pharmacological activities against cancers, allergies, arrhythmias, inflammations, bacteria, microbes, and viral infections [7]. There are more than thirty thioether-containing medications on the market today [4] and a number of potential drug candidates possessing this unique structural motif are currently undergoing clinical trials.

CONTACT Aazam Monfared dmonfared@gmail.com Department of Chemistry, Payame Noor University, P. O. Box 19395-1697, Tehran, Iran

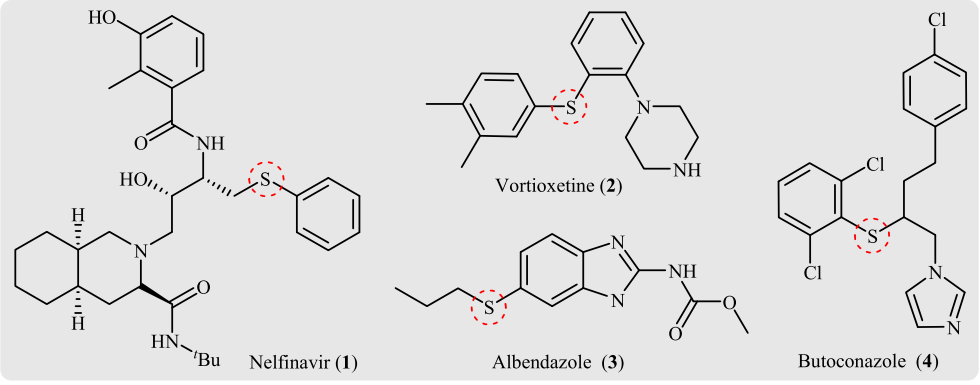


Figure 1. Some biologically active thioethers.

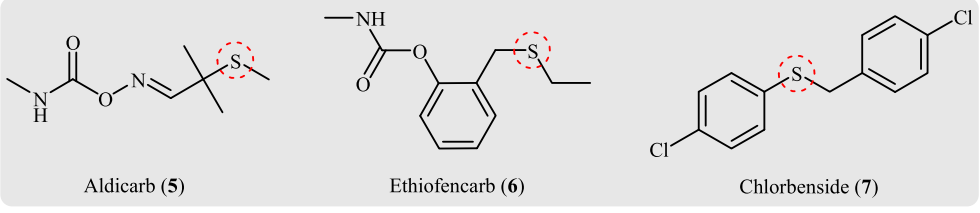


Figure 2. Pesticides containing a thioether group.

A few selected examples of commercial drugs containing this privileged moiety are represented in Figure 1. Those are nelfinavir **1**, (as an ant-HIV agent) [8], vortioxetine **2** (used in the treatment of depression) [9], albendazole **3** (the treatment of parasitic worm infestations) [10], and butoconazole **4** (antifungal agent) [11]. Furthermore, titled compounds have also many applications as pesticides in agriculture. For example (Figure 2), Aldicarb **5** with brand name of Temik is a commercially available pesticide used to control a variety of insects [12]. Ethiofencarb **6** is a thioether insecticide available in a number of countries worldwide which is useful in controlling aphids on fruits and vegetables [13]. Chlorbenside **7** is a synthetic pesticide that commonly used as an acaricide [14].

In addition to the above benefits, thioether derivatives are versatile intermediates in organic synthesis. These compounds were successfully transformed into sulfoxides [15,16], sulfones [17], sulfonium salts [18], benzothiazoles [19], thiophenes [20,21], internal alkynes [22], biaryls [23], and diaryl amines [24].

In light of the widespread synthetic applications and biological activities of thioether derivatives, the development of efficient and practical approaches for the synthesis of these compounds, from inexpensive, simple, and readily available starting materials is highly desirable. Traditionally, these compounds were formed by the condensation of activated organic halides with alkali–metal thiolates [25,26]. Later, sulfenylation reactions between various electrophiles (*e.g.* organic halides, boronic acids, and carboxylic acids) with sulfenylating agents such as thiols, disulfides, sulfenyl halides, *N*-thioimides, and sulfinate salts have been developed [27–30]. However, high cost, toxicity, volatility, and instability of many of these sulfenylating agents limit their applications. To overpass these

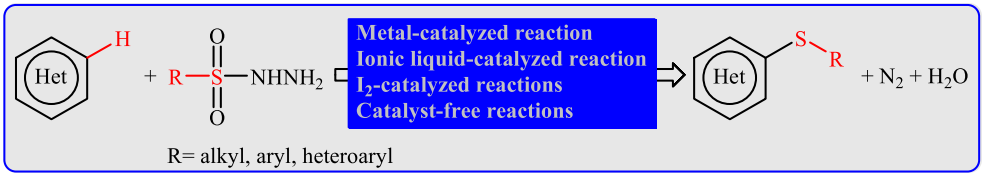


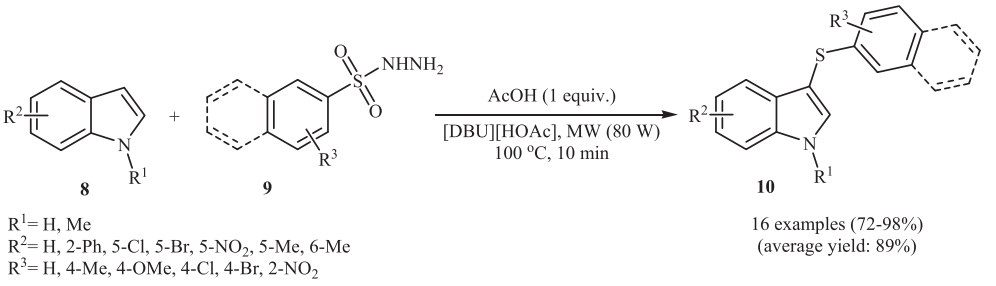
Figure 3. Synthesis of thioethers through direct C-H bond sulfenylation of heteroarenes with sulfonyl hydrazides.

limitations, recently, sulfonyl hydrazides (RSO_2NHNH_2) as readily accessible, high stable, non-toxic, odorless, and structurally diverse sulfenylating agents have been developed for the construction of C–S bonds *via* the cleavage of their S–N and S = O bonds [31–35].

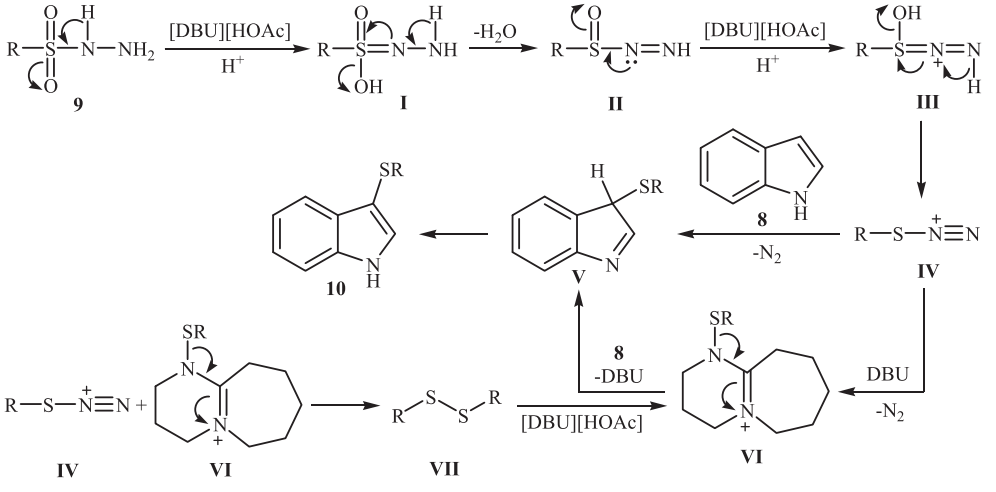
Recently, the direct and selective functionalization of (hetero)arenes through carbon–hydrogen bond activation has become an efficient and attractive method to access substituted (hetero)aromatic compounds [36,37,38,39]. Indeed, in these green and atom-economic reactions the inactive C–H bonds can be treated as a functional group, similar to the traditionally used C-(pseudo)halide bonds and thus reduce the number of synthetic steps, because they avoid the use of prefunctionalized starting materials [38,39]. Since a number of developments in direct C–H bond sulfenylation of heterorenes with sulfonyl hydrazides have occurred from 2013 to present, a comprehensive review on this explosively growing field seems to be timely. In connection with our recent reviews on the carbon–sulfur bond formation reactions [38,40–42] and new methodologies in organic synthesis [43–52], herein, we will highlight the most important advances and explorations on the synthesis of thioethers through the reaction of corresponding (hetero)aromatic compounds with sulfonyl hydrazides *via* C–H bond activation (Figure 3). The review has been classified based on the based on the type of catalysts (*i.e.* ionic liquid catalysts, metal catalysts, iodine-based catalysts). It should be noted that particular emphasis is placed on the mechanistic aspects of the reactions.

2. Ionic liquid promoted reactions

In 2016, Barman and his team reported the first example of ionic liquid-promoted sulfenylation of aromatic C–H bonds with sulfonyl hydrazides [53]. They showed that functionalized indoles **8** underwent very fast sulfenylation with various aryl sulfonyl hydrazides **9** in the presence of 1 equiv. of acetic acid as an additive in non-nucleophilic ionic liquid [DBU][HOAc]. The reactions were carried out under microwave irradiation (80 W) at 100°C, tolerated a range of functional groups (*e.g.* Cl, Br, NO_2, OMe) and generally provided the corresponding 3-sulfenylindoles **10** in high to excellent yields (Scheme 1). Interestingly, alkyl sulfonyl hydrazides were also well tolerated in the transformation. In addition, a gram-scale reaction was also successfully performed. It is noted that ionic liquid pyridine playing a dual role in this sulfenylation; the solvent and the promotor. The authors proposed mechanism for this reaction is depicted in Scheme 2. First, a thiodiazonium intermediate **IV** was formed *via* the reduction of starting sulfonyl hydrazide **9** in the presence of [DBU][HOAc] and AcOH through intermediates **I**-**III**. Subsequently, the electrophilic reaction of this intermediate with indole **8** yields intermediate **V**. In another possibility, nucleophilic addition of DBU to intermediate **IV** can happen to give the



Scheme 1. Barman's synthesis of 3-sulfenylindoles **10**.



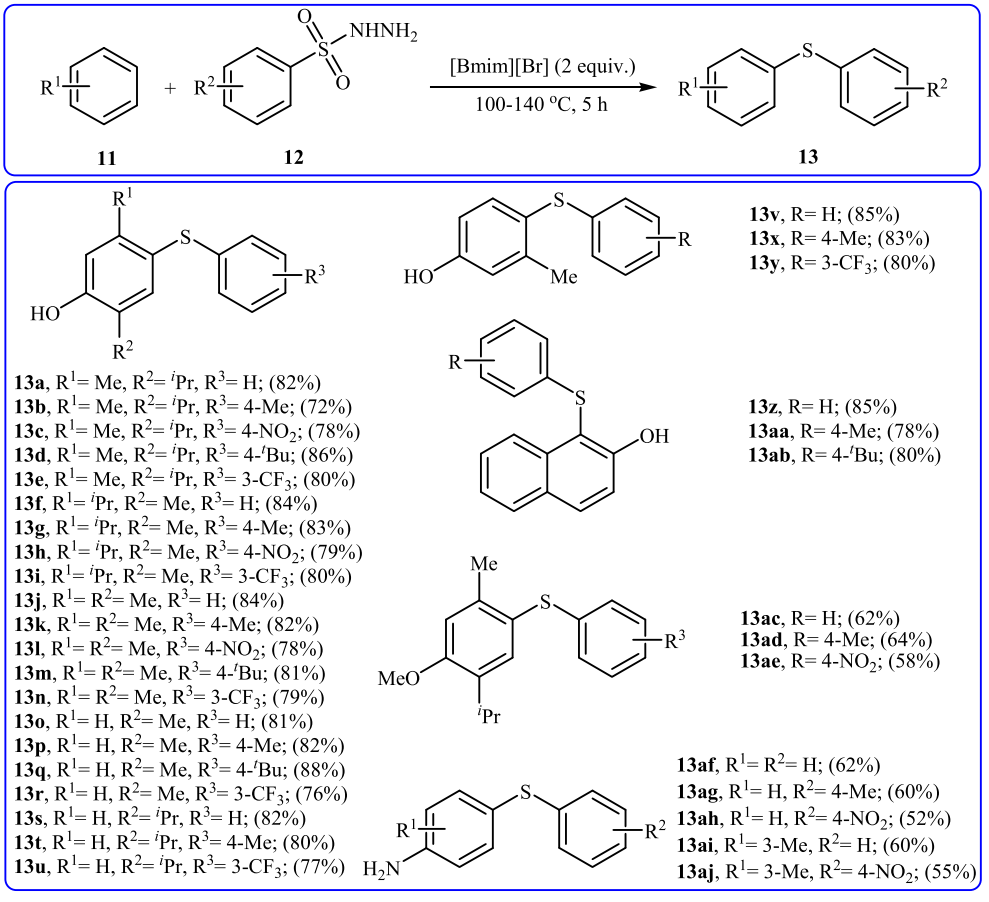
Scheme 2. Mechanism that accounts for the formation of **10**.

sulfonamide intermediate **VI** (this intermediate could also be formed through the reaction of *in situ* generated disulfide **VII** with DBU), which after reaction with indole **8** generates intermediate **V**. Finally, this intermediate **V** release an H^+ ion and affords the expected thioether **10**.

Very recently, Raghuvanshi and Verma extended the substrate scope of this chemistry to simple arenes and obtained a variety of unsymmetrical diaryl sulfides **13** in moderate to high yields *via* the treatment of electron-rich arenes **11** with arylsulfonyl hydrazides **12** in [Bmim][Br] ionic liquid at 100–140°C (Scheme 3) [54]. However, arenes possessing an electron-withdrawing group failed to participate in this reaction. It is noted that this C–S coupling reaction is almost equally efficient for both the electron-rich and electron-poor arylsulfonyl hydrazides. Noteworthy, the ionic liquid was reusable and preserved its activity after recycling for five runs of reaction.

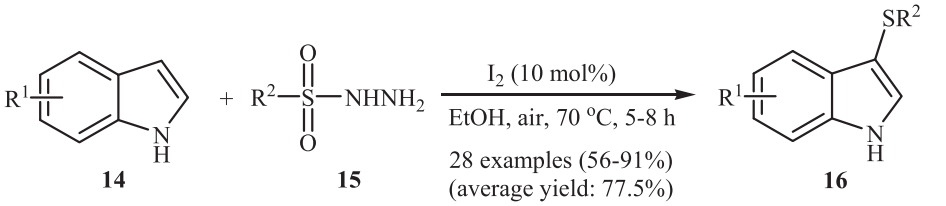
3. Iodine catalyzed reactions

The molecular iodine catalyzed direct C–H bond sulfenylation of (hetro)arenes with sulfonyl hydrazide derivatives is probably the area that has experienced the most growth



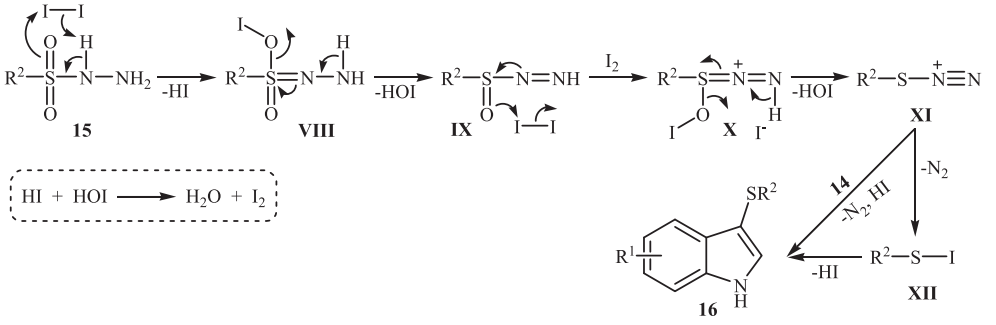
Scheme 3. [Bmim][Br]-promoted sulfenylation of electron-rich arenes **11** with arylsulfonyl hydrazides **12**.

in this field in the last years. In 2013 the first I_2-catalyzed sulfenylation reaction of aromatic compounds with titled sulfenylation reagents was published by Yang and Tian, who showed that the reaction of substituted indoles **14** with various aryl-, heteroaryl- and alkylsulfonyl hydrazides **15** in the presence of 10 mol% of I_2 in EtOH afforded structurally diverse 3-sulfenylindoles **16** in moderate to excellent yields (Scheme 4) [55]. Sensitive and active moieties such as chloro, bromo, methoxy, nitro, cyano and ester functionalities were tolerated well in this system, which provided the opportunity to further functionalize the products using other convenient reactions. A plausible mechanism to explain this transformation is shown in Scheme 5. Initially, stepwise removal of the hydrogen and oxygen atoms from the sulfonyl hydrazides **15** with the help of iodine generates the thiodiazonium intermediate **XI**. Subsequently, regioselective Friedel–Crafts coupling between this intermediate **XI** and indole **14** affords the corresponding thioether **16**. Alternatively, the extrusion of molecular nitrogen from **XI** generates the sulfenyl iodide **XII**, which is attacked by indole **14** to give desired sulfenylated product **16**. In the catalytic process, iodine is converted into HI and HOI, which would react to give water and to regenerate the iodine catalyst.



R^1= H, 1-Me, 2-Me, 2-Ph, 4-Br, 3-Me, 3-$CHPh_2$, 3-CH_2CN, 5-OMe, 5-Br, 5-NO_2, 5-CO_2Me, 6-Cl,
R^2= Me, -$(CH_2)_7Me$, CH_2Ph, Ph, 4-Me-C_6H_4, 4-OMe-C_6H_4, 4-F-C_6H_4, 4-Br-C_6H_4, 4-I-C_6H_4,
4-NO_2-C_6H_4, 3-NO_2-C_6H_4, 2,5-Cl_2-C_6H_3, 2,4,6-Me_3-C_6H_2, 2-naphthyl, 2-thienyl

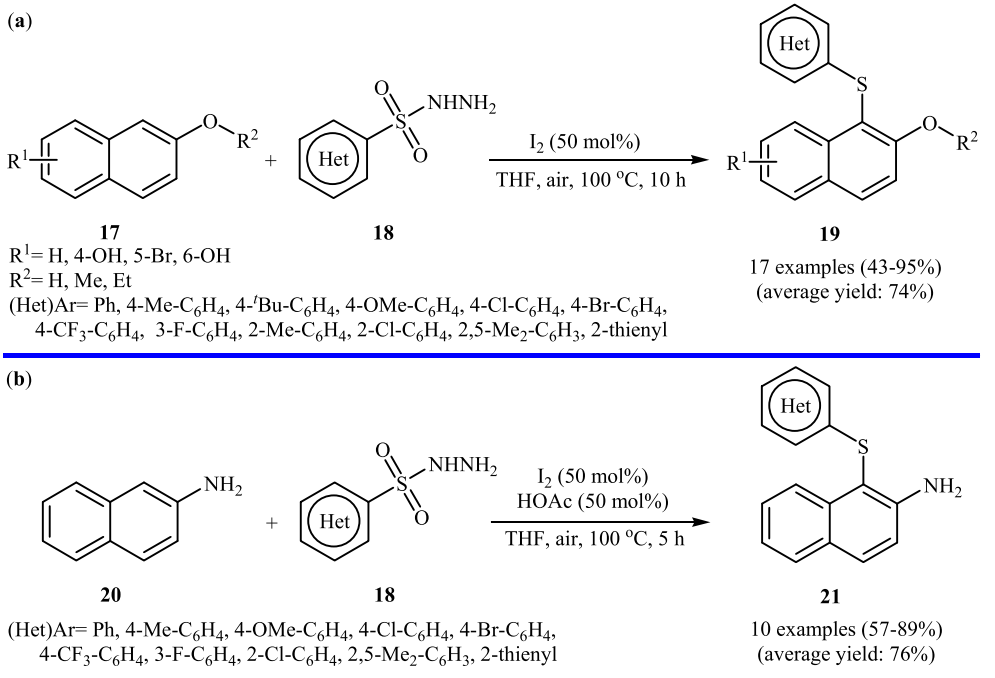
Scheme 4. I2-catalyzed C3-sulfenylation of indoles **14** with sulfonyl hydrazides **15** developed by Tian.



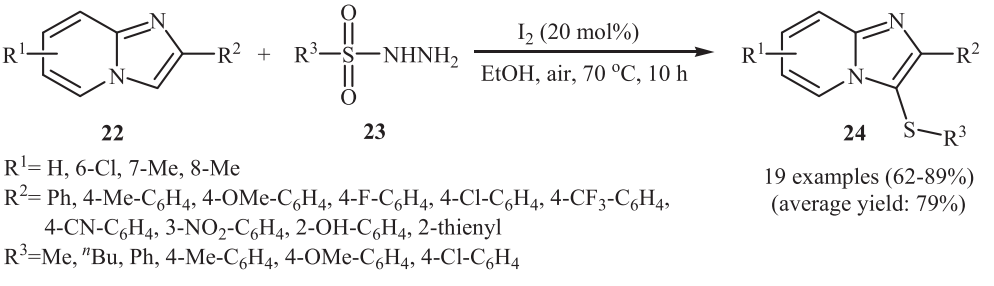
Scheme 5. Suggested mechanism for the formation of 3-sulfenylindoles **16**.

Subsequently, Yan and Huang along with their co-workers described an efficient C–H bond sulfenylation of naphthols **17** with arylsulfonyl hydrazides **18** employing molecular iodine as catalyst and air as oxidant [56]. This sulfenylation reaction afforded the optimum yield in THF at 100°C. Various substituted naphthols and aryl/heteroaryl sulfonyl hydrazides were used to establish the general applicability of the method (Scheme 6(a)). It is noteworthy that sulfenylation of unsubstituted naphthylamine **20** with the same set of sulfonyl hydrazides **18** was also examined using this catalytic system. In this case, the addition of 50 mol% of HOAc as an additive was found to be necessary for the efficiency of the reaction (Scheme 6(b)). In this investigation, the authors reported some limitations in their protocol when they attempted to react arylsulfonyl hydrazides having a strongly electron-withdrawing group (*e.g.* NO_2) and nitrogen-substituted naphthylamine derivatives. In these cases, no formation of target thioethers was observed.

Shortly afterwards, molecular iodine was reported to be an active catalyst for regioselective sulfenylation of imidazo[1,2-*a*]pyridines **22** with various aromatic and aliphatic sulfonyl hydrazides **23** giving the desired 3-sulfanylimidazopyridines **24** in 62–89% yields (Scheme 7) [57]. TBAI and NIS were not effective as the catalysts for this transformation. The best solvent for this system was found to be EtOH. Beside high yields, broad substrate scope, and scale-up ability were the advantages, mentioned for this oxidant- and additive-free synthetic approach. Imidazo[2,1-*b*]thiazoles were also tested in this reaction giving the desired thioethers in high yields.

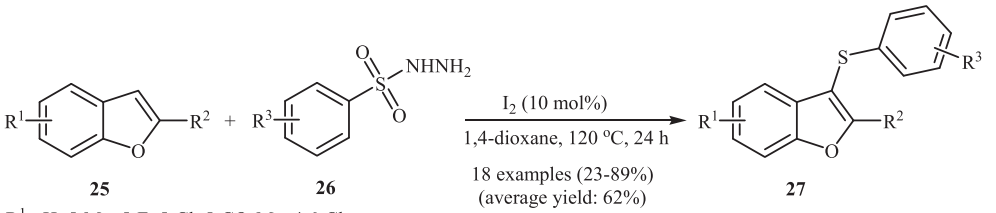


Scheme 6. I_2-catalyzed sulfenylation of substituted (a) naphthols **17**; (b) Naphthylamines **20** with sulfonyl hydrazides **18**.



Scheme 7. Regioselective sulfenylation of imidazo[1,2-*a*]pyridines **22** with sulfonyl hydrazides **23** catalyzed by molecular iodine.

In a related investigation, Zhao-Lu research team found that treatment of 2-substituted benzo[*b*]furans **25** with arylsulfonyl hydrazides **26** in the presence of 10 mol% of I_2 in 1,4-dioxane at 120°C, afforded corresponding 3-sulfanylbenzofurans **27** with yield range from 23% to 89%. (Scheme 8) [58]. Some important information about this reaction is given below: (i) the reaction did not work with aliphatic sulfonyl hydrazides; (ii) depending on the electronic effects of substituents on the benzo[*b*]furans, substrates with electron-donating groups gave higher yields as compared to that with substrates containing electron-withdrawing groups; and (iii) arylsulfonyl hydrazides, bearing both



R^1= H, 5-Me, 5-F, 5-Cl, 5-CO_2Me, 4,6-Cl_2
R^2= ^{n}Bu, Ph, 4-OMe-C_6H_4, 3-CN-C_6H_4
R^3= 4-Me-C_6H_4, 4-OMe-C_6H_4, 4-CF_3-C_6H_4, 4-Cl-C_6H_4, 4-Br-C_6H_4, 3-OMe-C_6H_4, 3-Cl-C_6H_4, 2-Me-C_6H_4

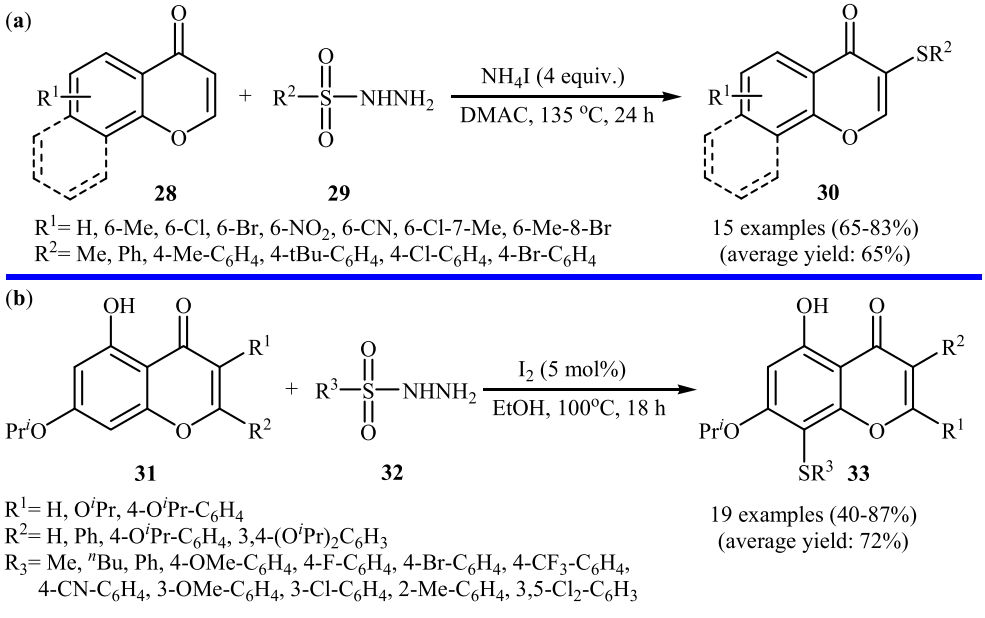
Scheme 8. I_2-catalyzed reaction of benzo[*b*]furans **25** with arylsulfonyl hydrazides **26**.

electron-withdrawing and electron-donating groups, as well as *meta*-, *ortho*-, and *para*-substitutions were well tolerated under the optimized conditions. Interestingly, when 3-substituted benzo[*b*]furans were utilized as substrates, the 2-sulfanylbenzofuran products were obtained in moderate to high yields. It is noteworthy that the 3-sulfanylbenzofuran products could also be obtained through the electrophilic cyclization of 2-alkynylphenol derivatives with arylsulfonyl hydrazidesin the presence of I_2/PTSA (*p*-toluenesulfonic acid) combination as a catalytic system in 1,4-dioxane.

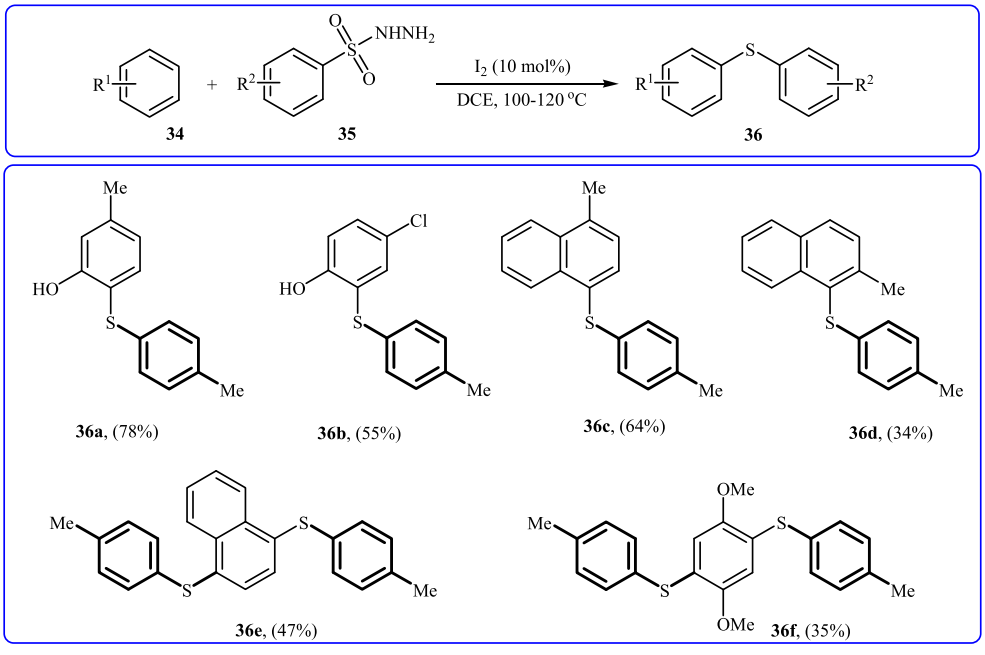
In 2015, an interesting and efficient synthetic methodology for the regioselective C3-sulfenylation of flavones **28** with alkyl/arylsulfonyl hydrazides **29** has been developed by Zhao and co-workers using NH_4I as a mediator in DMAC at 135°C [59]. The respective thioethers **30** were obtained in good to high yields (Scheme 9(a)). For a comparative study, the authors tested this reaction (for the sulfenylation of unsubstituted flavone with benzenesulfonyl hydrazine as a model reaction) using a series of common organic solvents such as MeCN, THF, toluene, DCE, and DMF. However, the yield of the product in these solvents was very low compared to DMAC. When 2,2,6,6-tetramethylpiperidinoxyl (TEMPO) and butylated hydroxytoluene (BHT) were used as radical scavengers in the aforementioned model reaction, high yields were obtained (82% and 81%, respectively), thus indicating that radical intermediates were not involved in these reactions. Based on the control experimental, electrophilic thiodiazonium iodide (RSN≡NI) was proposed as the main intermediate in the catalytic cycle. Later, the group of Zhao-Lu reported that highly substituted flavones **31** could also be sulfenylated by sulfonyl hydrazides **32** in the presence of I_2 as a catalyst in moderate to high yields (Scheme 9(b)) [60]. They found that the reaction is also compatible with dihydroflavone, flavonol, isoflavone, and aurone derivatives.

In 2016, the same research team extended the substrate scope of this chemistry to a variety of simple arenes and obtained a range of diaryl sulfides **36** in modestly to high yields *via* the treatment of electron-rich aromatic compounds **34** (anisoles, phenols, toluenes, and naphthalenes) with arylsulfonyl hydrazides **35** in the presence of catalytic amounts of I_2 in DCE at 120°C [61]. The major drawback reported for this system is the undesired di-sulfenylation reactions of symmetrical arenes with two molecules of sulfonyl hydrazides. Under the standard conditions, the desired thioethers were obtained along with di-thioether side-products. Some reported examples are shown in Scheme 10.

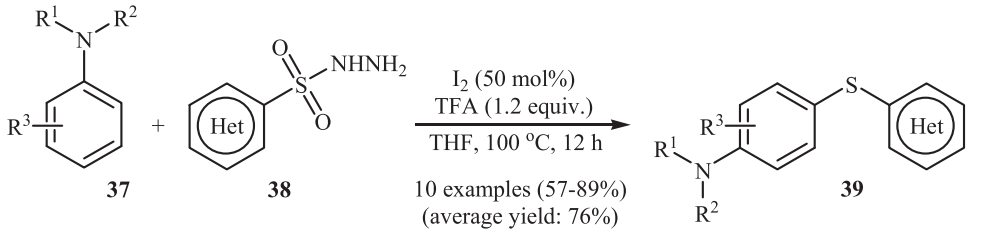
Inspired by these works, Yan and co-workers presented an elegant I_2-catalyzed regioselective *para*-sp^2 C–H sulfenylation of aromatic amines **37** with aryl sulfonyl hydrazides



Scheme 9. (a) NH_4I-catalyzed regioselective C3-sulfenylation of flavones **28** with sulfonyl hydrazides **29**; (b) Zhao's synthesis of sulfenylated-flavones **33**.

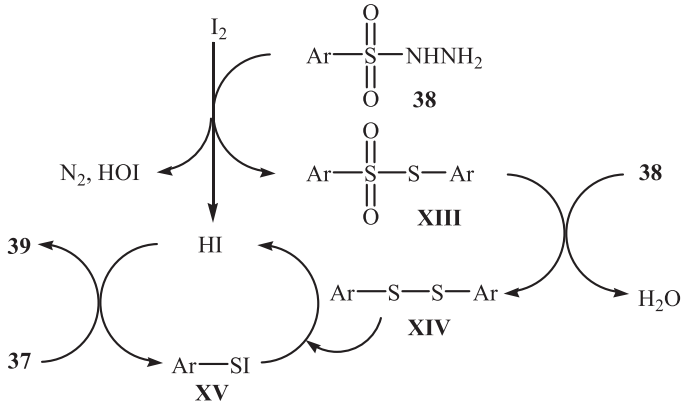


Scheme 10. I_2-catalyzed direct C-H bond sulfenylation of electron-rich aromatic compounds **34** with sulfonyl hydrazides **35**.



NR^1R^2= NMe_2, NEt_2, NEtBn, pyrrole, pyrrolidine, morpholine, piperazine
R^3= H, 2-Me
(Het)Ar= Ph, 4-Me-C_6H_4, 4-^{t}Bu-C_6H_4, 4-OMe-C_6H_4, 4-Cl-C_6H_4, 4-Br-C_6H_4, 4-CF_3-C_6H_4, 3-Me-C_6H_4, 3-F-C_6H_4, 3-Br-C_6H_4, 2-Me-C_6H_4, 2-Cl-C_6H_4, 2-naphthyl, 2-thienyl

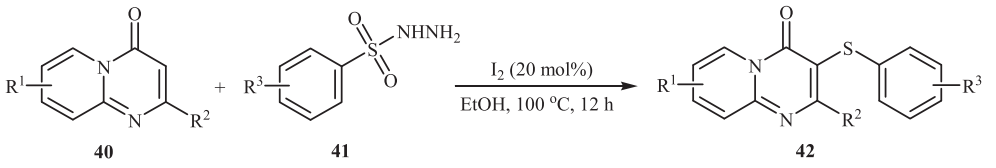
Scheme 11. Iodine-mediated synthesis of thioethers **39** with aromatic amines **37** and sulfonyl hydrazides **38**.



Scheme 12. Mechanistic explanation of the synthesis of aromatic thioethers **39**.

38 using 1.2 equiv. of commercially available TFA as an additive [62]. The reactions were carried out in THF at 100°C, tolerated a series of sensitive functional groups, including fluoro, chloro, bromo, and methoxy functionalities, and afforded the expected thioethers **39** in moderate to excellent yields (Scheme 11). The generality of the process was established by employing various *N*,*N*-disubstituted aromatic amines and (hetero)aryl sulfonyl hydrazides. However, aniline, *N*-methylaniline, 1-phenyl-1*H*-pyrrole, and 4-nitrobenzenesulfonohydrazide failed to enter into the coupling under the optimal reaction conditions. The mechanism proposed to explain this reaction starts with the generation of thiosulfonate intermediate **XIII** *via* decomposition of starting sulfonyl hydrazide **38**, which then undergoes reduction to form the disulfide intermediate **XIV**. Subsequently, reaction of this intermediate with HI gives the sulfenyl iodide intermediate **XV**. Finally, electrophilic substitution between intermediate **XV** and amine **37** affords the observed thioether **39** (Scheme 12).

Very recently, Wang and co-workers reported an analogous methodology for the direct C3-selective C–H sulfenylation of 4*H*-pyrido[1,2-*a*]pyrimidin-4-ones **40** with arylsulfonyl hydrazides **41** (Scheme 13) [63]. In their optimization study, they found that the use of 20 mol% of I_2 as the catalyst in EtOH gave the best results. Examination of the scope of

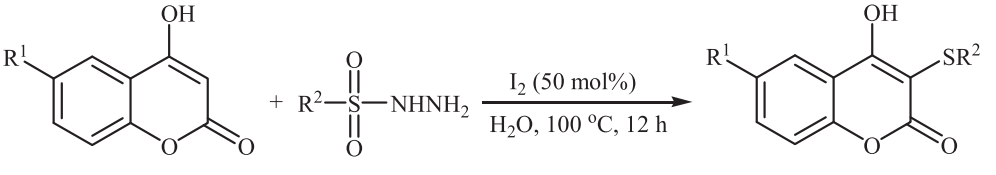


40 41 42

R^1= H, 7-Me, 7-F, 7-Cl, 7-Br, 8-Me, 8-Cl, 9-Me
R^2= H, Me
R^3= H, 4-Me, 4-F, 4-Cl, 4-Br, 3,5-Me_2

25 examples (70-84%)
(average yield: 77%)

Scheme 13. Synthesis of sulfenylated 4*H*-pyrido[1,2-*a*]pyrimidin-4-one derivatives **42** reported by Wang.



43 44 45

17 examples (62-93%)
(average yield: 80%)

R^1= H, Me, F, Cl, Br
R^2= Et, Ph, 4-Me-C_6H_4, 4-OMe-C_6H_4, 4-F-C_6H_4, 4-Cl-C_6H_4, 4-Br-C_6H_4, 4-CF_3-C_6H_4, 3-Cl-C_6H_4, 2-Cl-C_6H_4, 1-naphthyl, 2-naphthyl, 2-thienyl

Scheme 14. Regioselective C3-sulfenylation of 4-hydroxycoumarins **43** with sulfonyl hydrazides **44** in water.

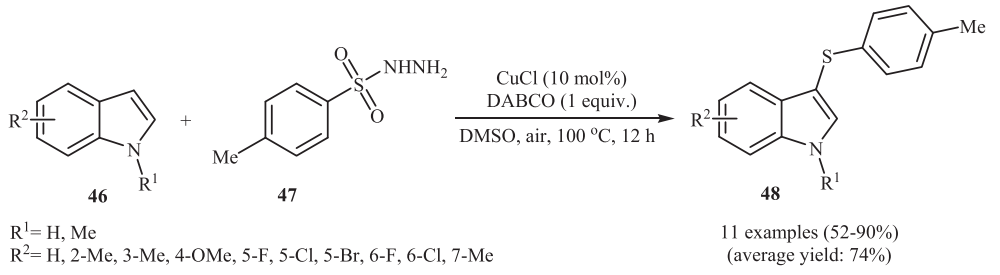
the reaction revealed that a variety of 4*H*-pyrido[1,2-*a*]pyrimidin-4-ones bearing both electron-donating and -withdrawing groups and a range of aromatic sulfonyl hydrazides afforded the sulfenylated 4*H*-pyrido[1,2-*a*]pyrimidin-4-one derivatives **42** in good to high yields. However, 4*H*-pyrido[1,2-a]pyrimidin-4-ones possessing a strong electron-withdrawing -NO_2 group at the C7 position failed to participate in this sulfenylation process.

With the objective of designing an efficient and green procedure to sulfenylated coumarin derivatives through sulfenylation of corresponding coumarins with sulfonyl hydrazides, Yang and Zhou along with their co-workers were able to demonstrate that a number of C3-sulfenylated coumarins **45** could be obtained from the reaction of 4-hydroxycoumarins **43** with sulfonyl hydrazides **44** in the most significant green solvent, water, employing molecular iodine as the catalyst (Scheme 14) [64]. The I_2-catalyzed reaction tolerated both aromatic and aliphatic sulfonyl hydrazides and gave the final products in good to excellent yields. Other catalysts like NH_4I, KI, NIS, KIO_3 and CuI are not effective to afford the thioethers by this reaction. It is noteworthy that 4-nitrobenzenesulfonohydrazide, unsubstituted coumarin and 4-phenyl-coumarin were incompatible in this reaction.

4. Metal-catalyzed reactions

4.1. Copper

In 2014, the group of Jiang reported that copper salts could act as efficient catalysts for sulfenylation reactions of (het)aromatic compounds in which sulfonyl hydrazides were

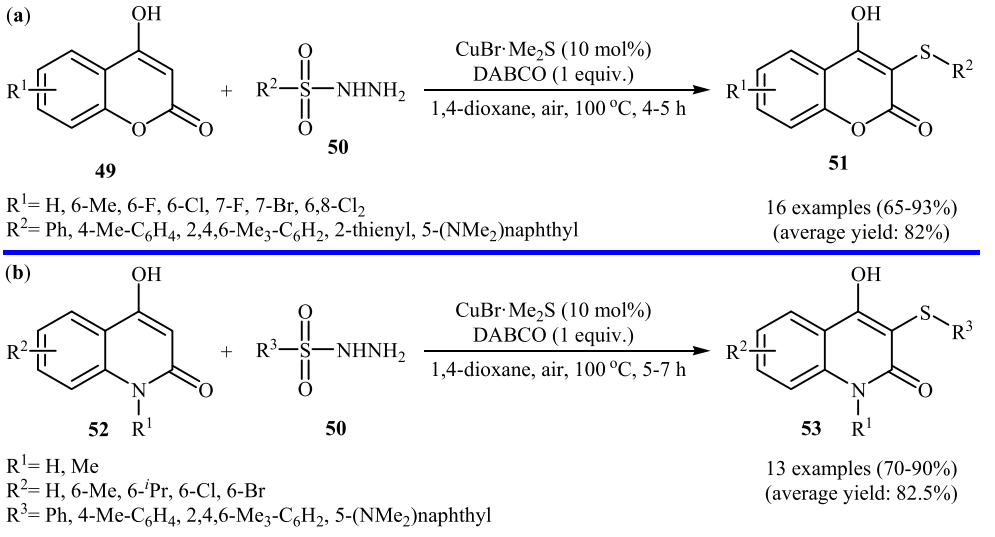


Scheme 15. Cu(I)-catalyzed regioselective C3-sulfenylation of indoles **46** with p-toluene sulfonohydrazide **47**.

used as sulfenylation reagents [65]. Among the various copper catalysts like $CuCl_2$, CuCl, $Cu(OAc)_2$, $Cu(OTf)_2$; inexpensive CuCl was the most efficient for the transformation. In the presence of 10 mol% of CuCl and 1.0 equiv. of DABCO (1,4-diazabicyclo[2.2.2]octane) in DMSO under air, a range of indoles **46** smoothly underwent sulfenylation with *p*-toluene sulfonohydrazide **47** to give structurally diverse 3-(*p*-tolylthio)indoles **48** in fair to excellent yields (Scheme 15). It is worthwhile to note that sulfenylation of electron-rich (hetero)aromatics including substituted anisole, toluene, naphthalenol, pyrimidine, imidazo[1,2-*a*]pyridine derivatives was also achieved with the use of similar reaction conditions.

Shortly afterwards, Lee's research team published an efficient methodology for the preparation of a library of 3-sulfanylcoumarins **51** through Cu-catalyzed sulfenylation of corresponding 4-hydroxycoumarins **49** with arylsulfonyl hydrazides **50** [66]. Considering the catalyst, additive, and solvent, the optimized conditions of this sulfenylation reaction involved using $CuBr{\cdot}Me_2S$ as a catalyst, DABCO as an additive, and 1,4-dioxane as the solvent at 100°C under air for 4–5 h. The optimized protocol tolerated a range of functionalized 4-hydroxycoumarins and both aromatic and heteroaromatic sulfonyl hydrazides and provided the expected products in high to excellent yields (Scheme 16(a)). However, vinyl sulfonyl hydrazides failed to participate in this reaction. The results showed that under this reaction conditions the reaction of 4-hydroxyquinolinones **52** with arylsulfonyl hydrazides **50** afforded the corresponding quinolinone thioethers **53** in high yields (Scheme 16(b)). According to the authors proposed mechanism (Scheme 17), a possible process for the formation of compounds **51** and **53** should involve the formation of thiosulfonate **XVII** and disulfide **XIX** intermediates *via* Cu(I)-catalyzed aerobic oxidation of arylsulfonyl hydrazides **50** through intermediates **XVI** and **XVII**, followed by reaction of the copper catalyst with **XVIII** or **XIX** to give the copper(III) complex **XX**, which after DABCO-mediated transmetallation at the 3-position of 4-hydroxycoumarins or 4-hydroxyquinolinones **49** or **52** to form another intermediate copper(III) complex **XXI**. Next, the reductive elimination of this complex affords **3'** or **5'** and copper (I) complex **XXII**. Then, exchange of copper(I) complex **XXII** with HBr produces sulfinic acid **XXIII** or thiol **XXIV** and generates the copper (I) catalyst. Finally, Keto–enol tautomerzation of intermediate **51'** or **53'** affords the desired product **51** or **53**.

Shortly afterwards, Liu and co-workers found that sulfenylation of electron-rich arenes **54** with arylsulfonyl hydrazides **55** in the presence of catalytic amounts of $Cu(OTf)_2$ in binary solvent HOAc/DCE with ratio 1:2 was possible [67]. Various unsymmetrical diaryl

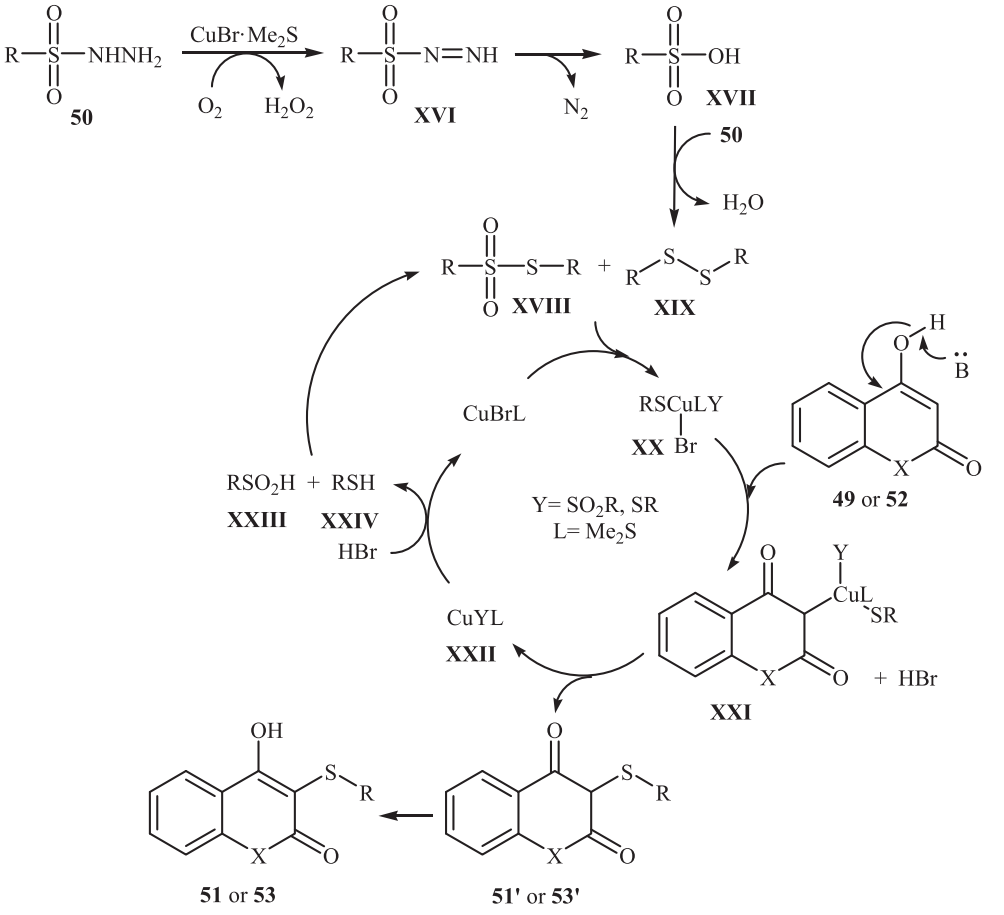


Scheme 16. Lee's synthesis of (a) 3-sulfanylcoumarins **51**; (b) 3-sulfanylquinolinones **53**.

sulfides **56** were obtained in modestly to high yields by this method. However, because of the poor regioselectivity of the reaction, in some cases a mixture of mono- and bis-thioether products were formed. Some reported examples are shown in Scheme 18.

Very recently, Yu and co-workers showed that C5-sulfenylated 8-aminoquinolines **59** could be synthesized from the reaction between unprotected 8-aminoquinolines **57** and arylsulfonyl hydrazides **58** in the presence of 15 mol% of CuI as the catalyst, 3.0 equiv. of Na_2CO_3 as the base in *p*-xylene at 120°C [68]. Generally, the expected products were obtained in moderate to good yields (Scheme 19). However, this protocol for S-arylation of *N*-substituted 8-aminoquinolines was considerably less efficient. The authors have also checked the reaction of unsubstituted 8-aminoquinoline with methyl sulfonyl hydrazide, in place of arylsulfonyl hydrazides under the conditions; however, no reaction was observed. The proposed mechanism for this transformation starts with the generation of the benzenesulfonothioate intermediate **XXV** through a featured reductive coupling of arylsulfonyl hydrazides **58**. Then further reduction of intermediate **XXV** in the presence of **58** furnishes disulfide intermediate **XXVI** which undergoes a homocleavage to give the arylthio free radical **XXVII**. Meanwhile, oxidation of Cu(I) by air oxygen affords Cu(II), which, in the presence of base, coordinates to the 8-aminoquinoline **57** to provide the Cu(II) complex **XXVIII**. Subsequently, the transfer of a single-electron from Cu(II) species to **XXVIII** yields free radical intermediate **XXIX**. Next, the reaction of this intermediate with **XXVII** gives another Cu(II) complex **XXX**, which after intramolecular proton transfer yields the intermediate **XXXI**. Finally, **XXXI** transforms to the final product **59** with regeneration of the Cu(II) (Scheme 20).

In 2018, an elegant and efficient synthetic protocol was reported by Tian and co-workers for the oxidative sulfenylation of various substituted indoles **60** with trifluoromethanesulfonyl hydrazide **61** to afford a diverse range of 3-indolyl trifluoromethyl thioethers **62** using CuCl as a catalyst and DMSO as an oxidant in MeCN (Scheme 21) [69]. The reactions were performed under nitrogen atmosphere, tolerated a variety of sensitive functional groups

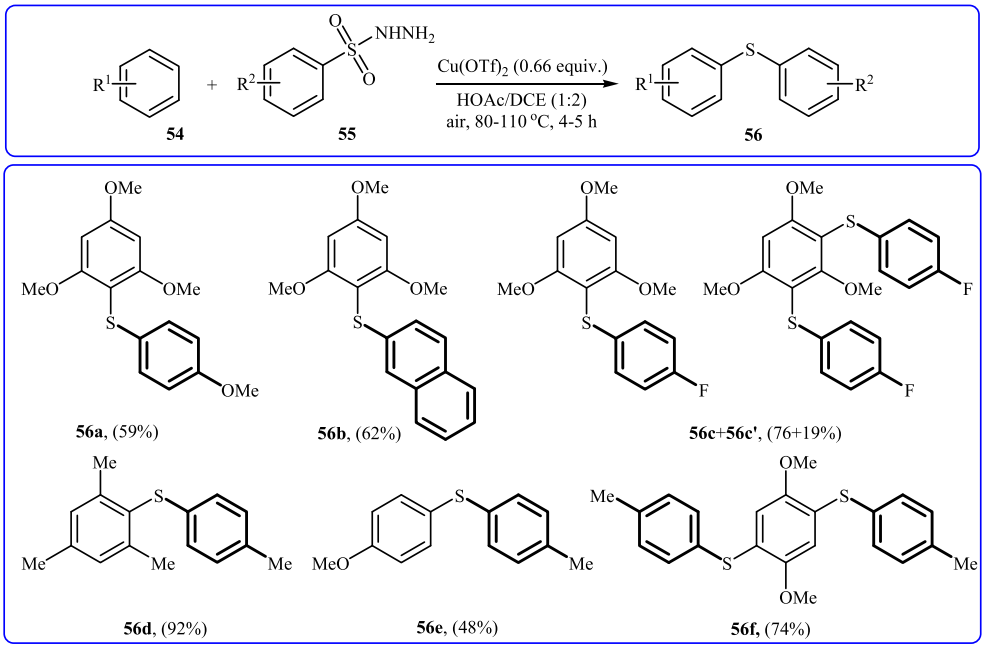


Scheme 17. Proposed mechanism for the Cu(I)-catalyzed sulfenylation of 4-hydroxycoumarins **49** and 4-hydroxyquinolinones **52**.

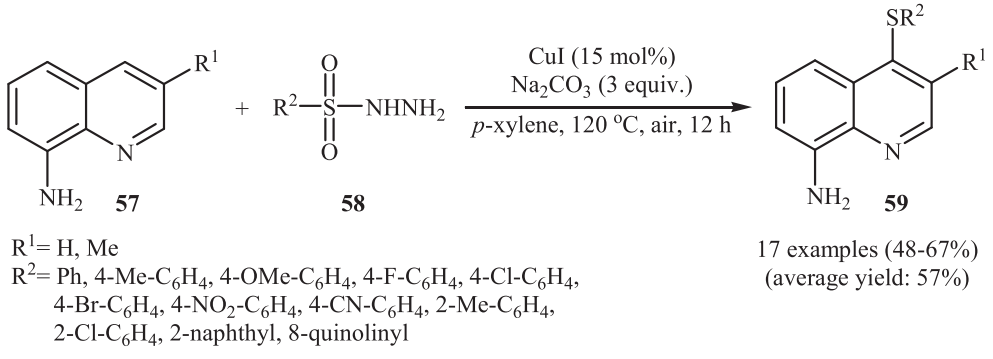
such as F, Cl, Br, OH, OMe, OBn and CO_2Me and provided the target sulfides in moderate to high yields. It should be mentioned that the yield of the reaction is strongly dependent on the oxidant employed. Replacing DMSO with some other oxidants (*e.g.* H_2O_2, TBHP, $K_2S_2O_8$, air, O_2) led to much lower yields or even no desired product at all. The mechanism of this sulfenylation reaction is believed to involve: (i) redox decomposition of the sulfonyl hydrazide **61** to generate disulfide intermediate **XXXII**; (ii) oxidative addition of intermediate **XXXII** to CuCl to produce copper(III) species **XXXIII**; (iii) nucleophilic attack of indole **60** to **XXXIII** to give copper(III) species **XXXIV**; and (iv) reductive elimination of intermediate **XXXIV** to form the thioether product **62** (Scheme 22).

4.2. Cerium

In 2016, Begari and Kumar along with their co-workers disclosed that the $CeCl_3·7H_2O$-NaI system could effectively catalyze sulfenylation of indoles **63** with aryl sulfonyl hydrazides **64** in ethanol at 100°C under air (Scheme 23) [70]. Generally, arylsulfonyl hydrazides

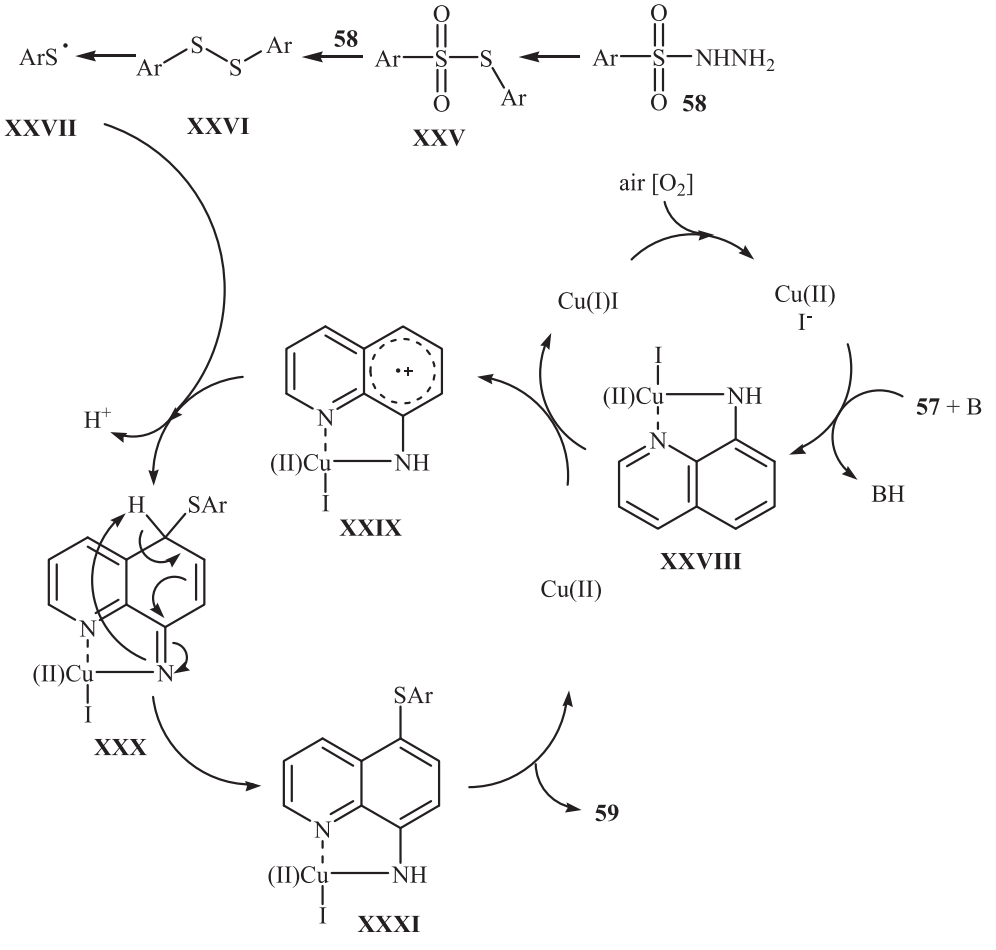


Scheme 18. Cu(II)-catalyzed sulfenylation of electron-rich arenes **54** with arylsulfonyl hydrazides **55**.

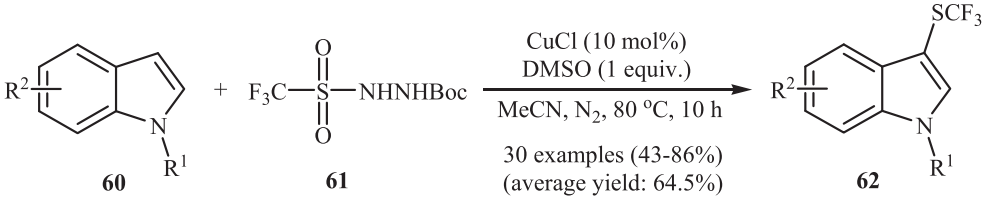


Scheme 19. Synthesis of C5-sulfenylated 8-aminoquinolines **59** *via* the Cu(I)-catalyzed reaction of 8-aminoquinolines **57** with sulfonyl hydrazides **58**.

containing electron-withdrawing as well as electron-donating group were well tolerated under these reaction conditions. Even an alkyl sulfonyl hydrazides reacted well. The results proved that the indoles with electron-donating substituents gave considerably higher yields compared to the electron-withdrawing group containing indoles. It should be mentioned that the reaction regioselectively afforded C3-sulfenylated indoles **65** as sole products, however when C3-position of indole is blocked by a substituent the reaction site will be the C2 position. Interestingly, using $CeCl_3 \cdot 7H_2O$ and NaI individually, the expected products were obtained in very poor yields. Therefore, these reagents have a synergistic effect on the reduction of the sulfonyl hydrazide to the corresponding thiodiazonium. According to



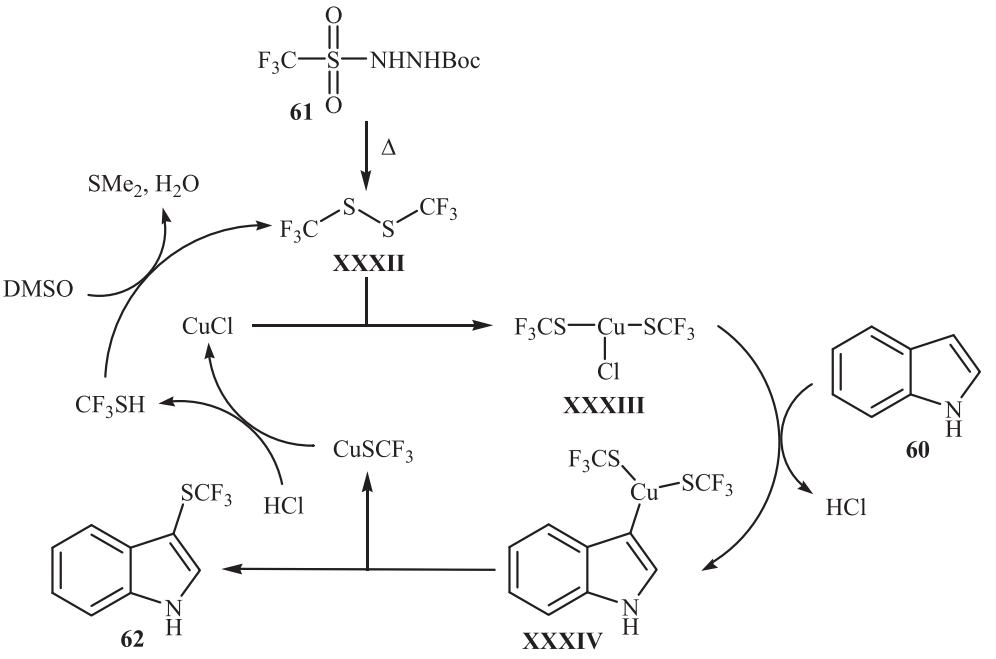
Scheme 20. Mechanistic proposal for the formation of **59**.



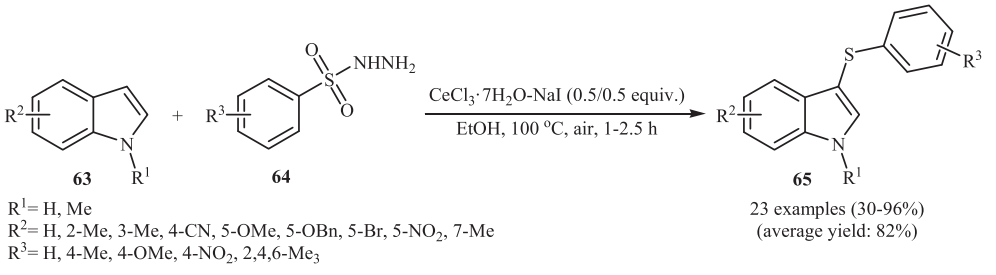
R^1= H, Me, Bn
R^2= H, Me, Ph, 4-Me, 4-OMe, 4-OH, 4-Cl, 4-Br, 4-CO_2Me, 5-Me, 5-OMe, 5-OBn, 5-F, 5-Cl, 5-Br, 5-CO_2Me, 6-Me, 6-OMe, 6-F, 6-Cl, 6-Br, 7-Me, 7-OMe, 5,6-F_2

Scheme 21. Tian's synthesis of 3-indolyl trifluoromethyl thioethers **62**.

the authors proposed mechanism (Scheme 24), this reaction proceeds through the formation of intermediate **XXXV** *via* the coordination of $CeCl_3 \cdot 7H_2O$–NaI system with oxygen atom of sulfonyl hydrazide **64**, following a proton transfer from nitrogen to oxygen to give

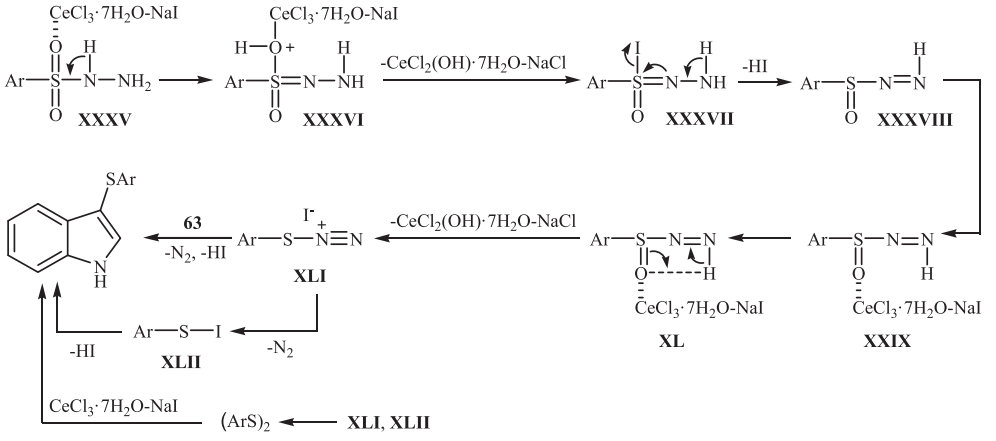


Scheme 22. Mechanistic explanation of the synthesis of thioethers **62**.



Scheme 23. $CeCl_3 \cdot 7H_2O$-NaI-catalyzed direct C-H bond sulfenylation of indoles **63** with sulfonyl hydrazides **64**.

the intermediate **XXXVI**, which then undergoes a nucleophilic attack by iodide to produce intermediate **XXXVII**. Subsequently, the liberation of HI from **XXXVII** gives sulfinyl diazene **XXXVIII** which again coordinates with $CeCl_3 \cdot 7H_2O$–NaI system to afford the intermediate **XXIX**. Then, a proton transfer from nitrogen to oxygen gives intermediate **XL**, which after the release of the $CeCl_2(OH) \cdot 7H_2O$–NaI system affords the thiodiazonium intermediate **XLI**. Finally, a regioselective Friedel Craft's reaction with indole **63** takes place to give the expected product **65**. On the other hand displacement of molecular nitrogen from **XLI** gives the sulfenyl iodide **XLII**, which is attacked by indole **63** to give the C3-sulfenylated indole **65**.

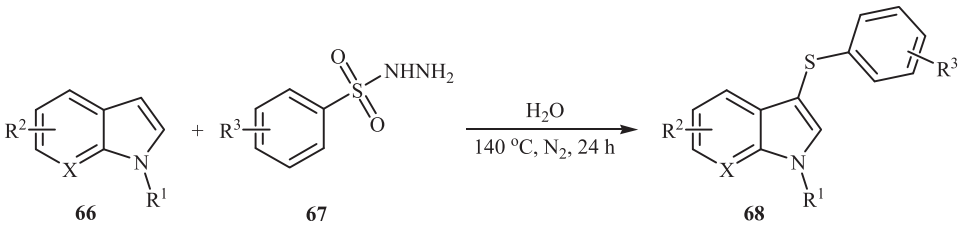


Scheme 24. Proposed mechanism for the reaction in Scheme 23.

5. Catalyst-free reactions

The first report on the catalyst-free C–H bond sulfenylation of heteroarenes with sulfonyl hydrazides was published in 2016, by Yang *et al.* [71]. They showed that simple heating (140°C) of indole derivatives **66** with arylsulfonyl hydrazides **67** in neat water under an inert atmosphere gave the corresponding 3-sulfenylindoles **68** in fair to quantitative yields (Scheme 25). However, heteroaryl- and sterically hindered *ortho*-substituted aryl-sulfonyl hydrazides failed to participate in this reaction. The results demonstrated that the electronic character of the substituents on both the substrates had a relatively little impact on the rate of the reaction. Generally, both electron-rich and electron-poor indoles and arylsulfonyl hydrazides were well tolerated. Moreover, a gram-scale reaction was also successfully performed. In Scheme 26, a reasonable mechanistic pathway for this catalyst-free sulfenylation reaction is suggested by the authors. It consists of the following key steps: (i) transformation of sulfonyl hydrazides **67** into the corresponding disulfide **XLII** and sulfonothioate **XLIII** intermediates under the reaction condition; (ii) dissociation of intermediate **XLIII** into ionic intermediate **XLIV** in the presence of water; (iii) Friedel–Crafts reaction of intermediate **XLIV** with indole **66** and formation of intermediates **XLV** and **XLIV**; and (iv) transformation of intermediate **XLV** into expected product **68** with the release of hydrogen ion.

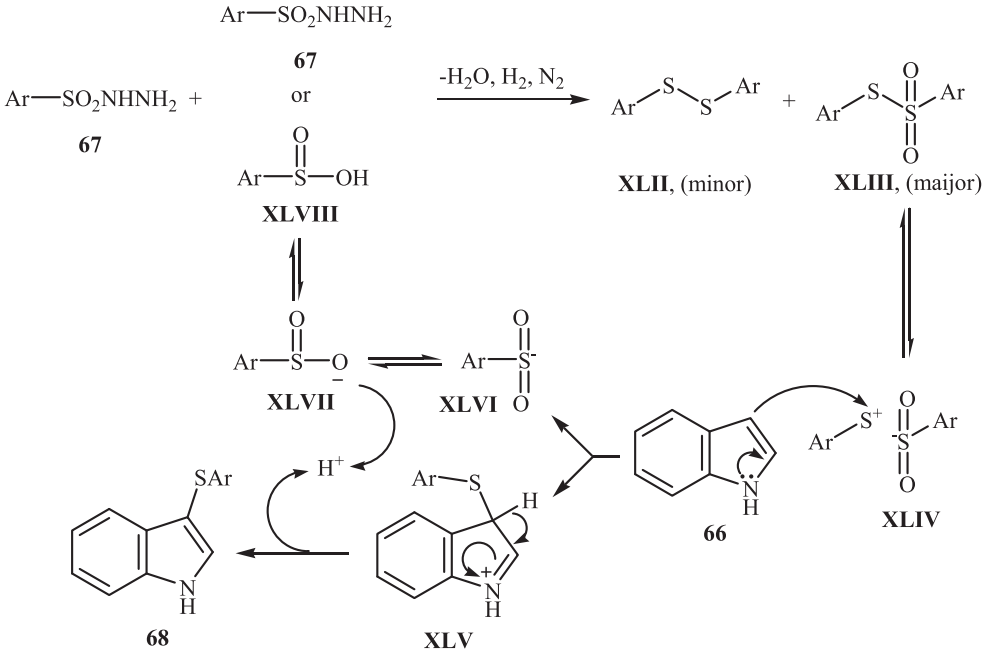
Very recently, the group of Maity reported an analogous methodology for the direct C3-selective C–H sulfenylation of imidazo[1,2-*a*]pyridines **69** with arylsulfonyl hydrazides **70** [72]. In their optimization study, they found that the use of water as solvent under catalyst and additive free condition gave the best results. Examination of the substrates scope revealed that a variety of imidazo[1,2-*a*]pyridines bearing both electron-donating and -withdrawing functional groups and a range of functionalized arylsulfonyl hydrazides afforded the expected 3-(arylthio)-imidazo[1,2-*a*]pyridines **71** in moderate to high yields (Scheme 27). Furthermore, the substrate scope was successfully extended to use imidazo[2,1-b]thiazole derivatives. Interestingly, aliphatic sulfonyl hydrazides were also well tolerated in this transformation. According to the author proposed mechanism, this



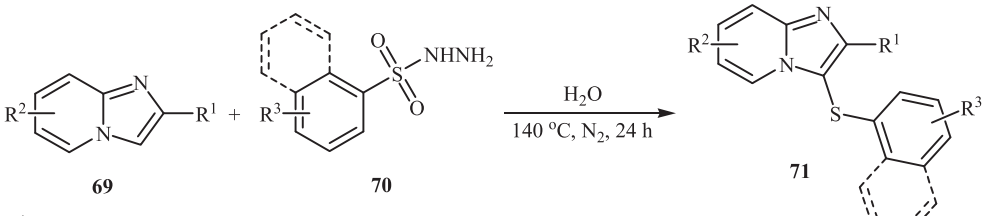
X= CH, N
R^1= H, Me
R^2= H, 2-Me, 4-Me, 5-OMe, 5-Br, 5-CN, 5-NO_2, 6-F
R^3= H, 4-Me, 4-^{n}Pr, 4-^{t}Bu, 4-CF_3, 4-OMe, 4-OCF_3, 4-F, 4-Cl, 4-Br, 4-CN, 4-NO_2, 3-NO_2, 3-F-4-Me, 3-NO_2-4-Cl

27 examples (35-99%)
(average yield: 74.5%)

Scheme 25. Catalyst-free sulfenylation of indoles **66** with sulfonyl hydrazides **67** in water.



Scheme 26. Mechanism that accounts for the formation of 3-sulfenylindoles **68**.



R^1= Me, Ph, 4-Me-C_6H_4, 4-OMe-C_6H_4, 4-tBu-C_6H_4, 4-F-C_6H_4, 4-Br-C_6H_4, 4-CN-C_6H_4, 2-E-C_6H_4, 2-naphthyl, 2-thienyl
R^2= H, 6-Cl, 6-Br, 7-Me, 8-Me, 6,8-Br_2, 6-Br-7-Me
R^3= H, 4-Me, 4-OMe, 4-NO_2

23 examples (36-86%)
(average yield: 70%)

Scheme 27. Catalyst-free synthesis of 3-(arylthio)-imidazo[1,2-*a*]pyridines **71** developed by Maity.

sulfenylation reaction proceeds along the similar mechanistic pathway, which is described in Scheme 26.

6. Conclusion

The direct formation of carbon–sulfur bonds represents a key step in the synthesis of many organosulfur compounds which are prevalent in natural products, pharmaceuticals, agrochemicals and organic materials. Over the past decades, various sulfenylating agents such as thiols, disulfides, sulfenyl halides, N-thioimides, and sulfinate salts have been developed in this chemistry; however, high cost, toxicity, volatility, and instability of many of these sulfenylating agents limit their practical applications. Thus, the development of new sulfenylating agents for these reactions is highly desirable. Sulfonyl hydrazides as inexpensive, readily accessible, high stable, odorless, non-toxic, and environmentally friendly thiolating agents have drawn considerable attention in recent years. As illustrated, these compounds have been successfully utilized in the synthesis of various synthetically and biologically important (hetero)aryl thioethers through direct and selective C–H bond sulfenylation of corresponding (hetero)aromatic compounds wherein H_2O and N_2 are the environmentally benign by-products of this transformation. Interestingly, most of the reactions covered in this review could be scaled up to provide multigram quantities of desired products. However, in some cases, the reactions were limited to the use of aromatic sulfonyl hydrazides since low yields were obtained with aliphatic and sulfonyl hydrazides. We conclude this review by hoping that it will stimulate researchers and serve as inspiration in their future work.

Disclosure statement

No potential conflict of interest was reported by the authors.

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