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Synthesis of *ortho*-Phenolic Sulfilimines via an Intermolecular Sulfur Atom Transfer Cascade Reaction

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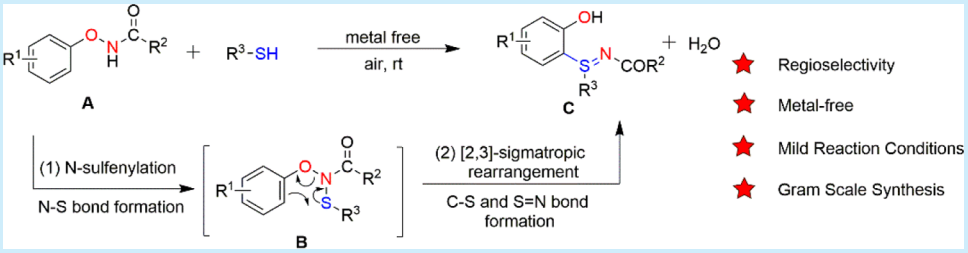


ABSTRACT: To expand the toolbox for the synthesis of *ortho*-phenolic sulfilimines, sigmatropic rearrangements were introduced to the field of sulfilimine chemistry. Herein we report a N−H sulfenylation/[2,3]-sigmatropic rearrangement cascade reaction. This mild reaction enables commercially available thiols to serve as the sulfenylation reagent and generates water as the sole byproduct. Moreover, the reaction has a wide substrate scope and can be conducted on a gram scale with excellent reaction efficiency.

In recent years, there has been increasing interest in developing synthetic methods to prepare sulfilimines (sulfimides),[1] which are valuable building blocks in organic synthesis[2] and serve as functional groups in biologically active agents.[3] Recently, Yoshida reported that sulfilimines can stabilize benzyl cations for the subsequent cross-coupling reaction.[4] Hudson and coworkers identified an interesting biologically relevant role of sulfilimine bonds in collagen IV networks (Figure 1).[5] The potential effect of sulfilimine cross-

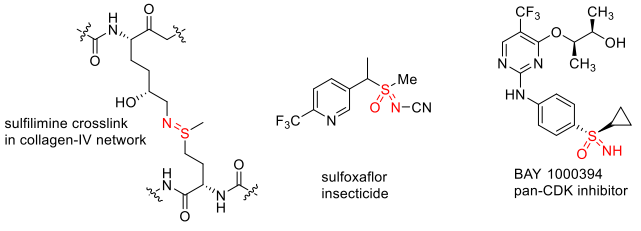
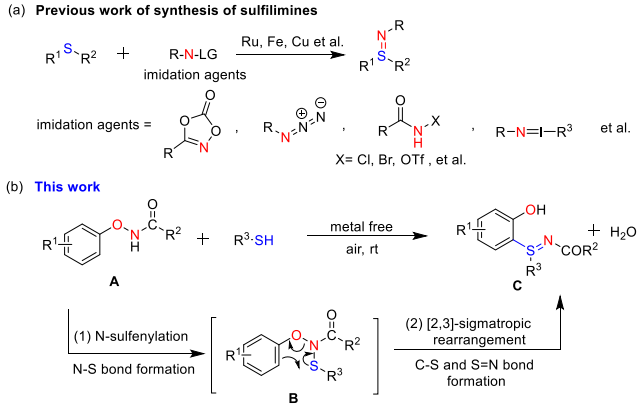


Figure 1. Sulfilimine and sulfoximine derivatives in biologically active agents.

linking in Goodpasture disease has attracted attention in medicine as well.[6] In addition, the sulfoximine group, which could be easily obtained by oxidation of the sulfilimine group, has been considered a widely neglected opportunity in medicinal chemistry (Figure 1).[7] Sulfilimines are typically prepared by the imidation of thioethers (Scheme 1a).[8,9] However, most of these methodologies suffer from the use of hazardous reagents[9c−e,g] and expensive transition-metal catalysts.[9h−k] Therefore, the development of a mild and efficient method for the synthesis of sulfilimines is still highly desirable.

Scheme 1. Strategies for the Formation of Sulfilimine Derivatives



Sigmatropic rearrangements triggered by the cleavage of X−Y (X, Y = C, O, N, S, I) bonds serve as an efficient strategy for synthesizing complex molecules,[10,11] especially those contain-

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ing heteroatoms.[12,13] O−NHAc (oxyacetamide) has been proven to be a multitasking functional group.[14,15] The potential of the O−N bond of oxyacetamide to participate in sigmatropic rearrangements was observed in a few cases,[14c,e,g,15g] and we envision that the strategy can be applied in the synthesis of structurally diverse sulfilimines.

Previously, we developed a biocompatible method for the synthesis of sulfilimines that required prefunctionalized sulfenylation reagents.[14c] From a green and sustainable synthetic standpoint, the use of commercially available thiols as the sulfenylation reagent is more attractive.[16] Herein we report a transition-metal-free regioselective transformation for the construction of *ortho*-phenolic sulfilimines via direct the C−H/S−H cross-coupling of *N*-phenoxyacetamide with thiols (Scheme 1b). This reaction makes full use of the excellent site selectivity, the oxidative O−N bond, and the amination functionality of the oxyacetamide moiety (O−NHAc) at room temperature.

Our initial study began with *N*-phenoxyacetamide **1a** and 4-chlorothiophenol **2a** in the presence of CsOAc in THF at room temperature under air for 16 h. To our delight, we obtained an interesting *ortho*-phenolic sulfilimine product **3aa** in 23% yield (Table 1, entry 1). Next, we screened a series of

Table 1. Optimization of the Reaction Conditions[a]

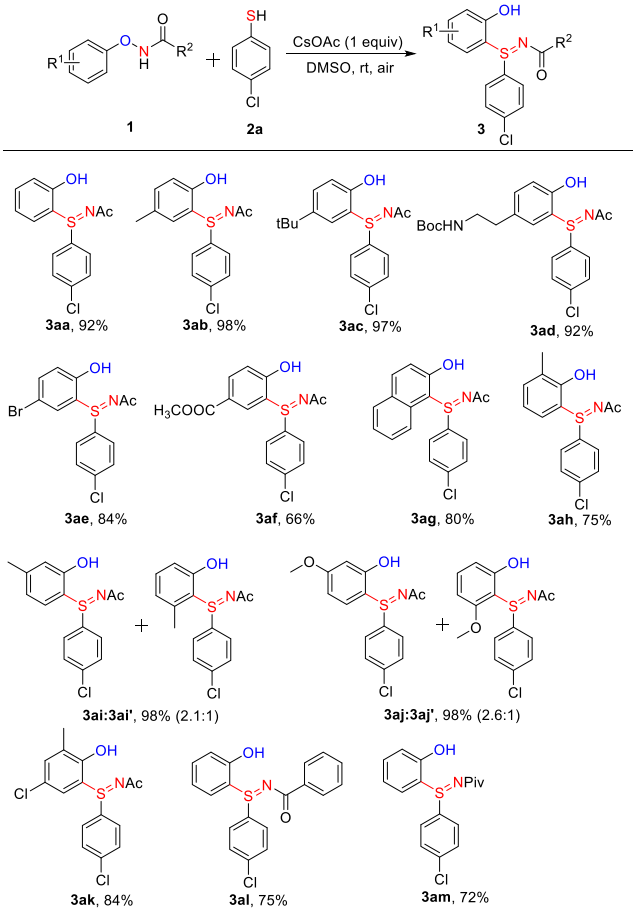
entry	additive	reaction time (h)	solvent	yield (%)
1	CsOAc	16	THF	23
2	PivOH	16	THF	0
3	NaOAc	16	THF	0
4	Et_3N	16	THF	0
5	CsOAc	16	$PhCH_3$	0
6	CsOAc	16	DCE	0
7	CsOAc	16	MeOH	trace
8	CsOAc	16	CH_3CN	51
9	CsOAc	16	DMSO	96
10	CsOAc	16	DMSO	74[b]
11	CsOAc	16	DMSO	96[c]
12	CsOAc	3	DMSO	28
13	CsOAc	6	DMSO	76
14	CsOAc	10	DMSO	95
15	CsOAc	10	DMSO	92[d]
16		10	DMSO	trace
17	CsOAc	10	DMSO	trace[e]

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol) and additive (1 equiv) in solvent (1 mL) at room temperature under air. Yield as determined by ^{1}H NMR spectroscopy using 1,4-dimethoxybenzene as an internal standard. [b]0.5 equiv of CsOAc was used. [c]2.0 equiv of CsOAc was used. [d]Isolated yield. [e]Under N_2.

additives, such as PivOH, NaOAc, and Et_3N, but did not obtain better results (entries 2−4). Surprisingly, solvent has a significant effect on this reaction; whereas DMSO greatly promoted this process, other solvents, such as $PhCH_3$, DCE, and MeOH, were not effective, and all of the starting material *N*-phenoxyacetamide (**1a**) remained. An equivalent amount of CsOAc is sufficient for this transformation when changing the amount of CsOAc. The reaction time screening indicated that 10 h is enough for this transformation. When the cascade reaction was conducted without a base (entry 16) or under a nitrogen atmosphere (entry 17), almost no product **3aa** was obtained, which indicates that the base and O_2 are essential in this transformation.

With the optimum conditions in hand, various aryloxyamide substrates were tested for this cascade reaction (Scheme 2).

Scheme 2. Substrate Scope of Aryloxyamides[a]



[a]Reaction conditions: **1** (0.2 mmol), **2a** (0.4 mmol), and CsOAc (1 equiv) in DMSO (1 mL) at room temperature for 10 h. Yields of isolated products are given.

The electronic effects of the substituents on the aromatic ring were found to significantly affect the reaction. *N*-Phenoxyacetamides with electron-donating groups, such as methyl (**3ab**) and *tert*-butyl (**3ac**), afforded the corresponding products in excellent yields ranging from 92 to 98%, whereas electron-withdrawing groups, such as bromo (**3ae**) and ester (**3af**), gave the products in good yields ranging from 66 to 84%. The naphthyl-substituted substrate not only gave a good yield but also resulted in high regioselectivity, which functionalized only the *ortho*-C−H at the C-1 position (**3ag**). Substituents at the ortho position (**3ah**) gave the corresponding products in lower yield than substituents at the meta (**3ai**, **3ai′**) and para positions (**3ab**). In addition, for meta-substituted substrates with two different ortho sites, two regioisomers (**3ai**/**3ai′**, **3aj**/**3aj′**) with ratios of 2.1:1 and 2.6:1 were obtained, indicating that steric hindrance might play an important role in the reaction. The dual-substituted substrate (**3ak**) was also well tolerated. Notably, when the acetyl group was replaced by benzoyl (**3al**) or the bulkier pivaloyl group (**3am**), the reaction also proceeded smoothly in 75 and 72% yields, respectively.

Subsequently, the scope of thiols in this reaction was explored (Scheme 3). To our delight, a variety of thiols with

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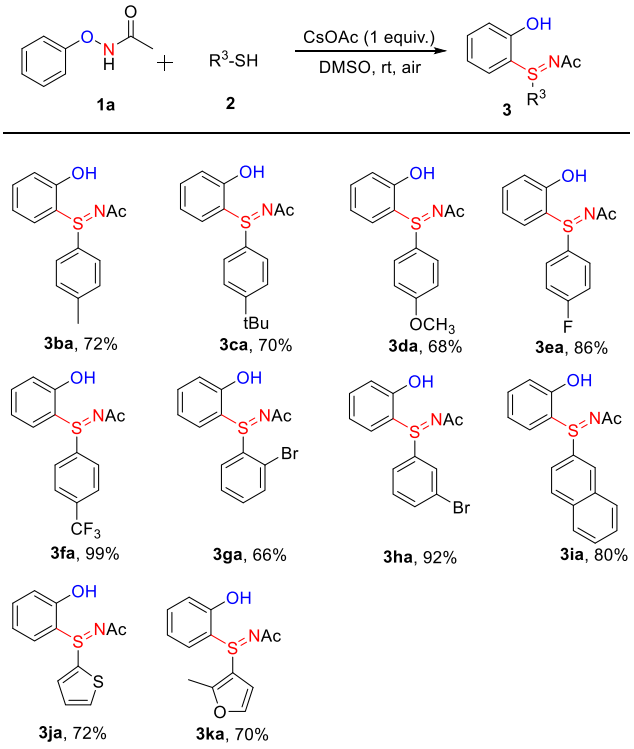
Scheme 3. Substrate Scope of Thiols[a]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), and CsOAc (1 equiv) in DMSO (1 mL) at room temperature for 10 h. Yields of isolated products are given.

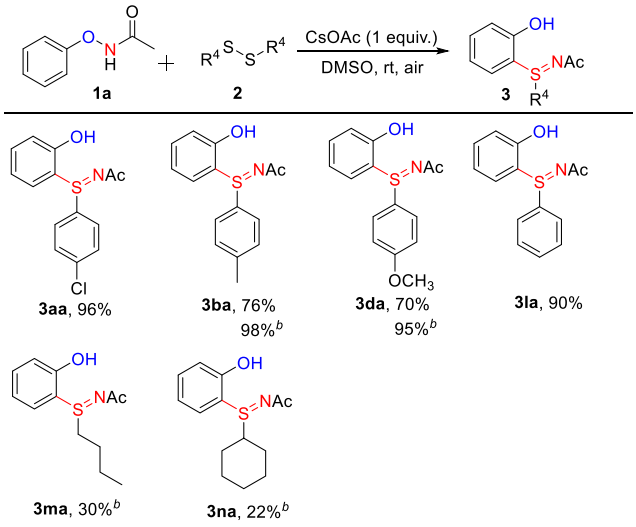
ortho, meta, or para substituents were able to react smoothly with *N*-phenoxyacetamide, affording the desired *ortho*-phenolic sulfilimines in good to excellent yields (**3ba**−**ia**). A reverse electronic effect of the substituents was observed. The electron-deficient thiols gave the desired products in higher yield than the electron-rich thiols. Notably, heteroaryl-bearing thiols (**3ja**, **3ka**) also worked well in the reaction and gave the corresponding products in good yields.

Encouraged by the successful coupling of thiols with *N*-phenoxyacetamide, we then extended this transformation to disulfides (Scheme 4). An electron-deficient diaryl disulfide (**3aa**) gave the desired product in a higher yield than electron-rich diaryl disulfides (**3ba**, **3da**). Notably, the electron-rich diaryl disulfides could be almost fully transformed into the corresponding products when the reaction temperature was 40 °C (**3ba**, **3da**). We were pleased to find that dialkyl disulfides (**3ma**, **3na**) also worked for this reaction, although the yields were very low.

Considering the mild reaction conditions and the high atom economy of this protocol, we performed gram-scale reactions between **1a** and **2a** or **2b**, affording the corresponding products in 90 (**3aa**) and 86% (**3ba**) yields, respectively (Scheme 5). Therefore, this protocol could serve as an efficient and practical method for the synthesis of various *ortho*-phenolic sulfilimines and has the potential to be applied in the green chemical industry.

We conducted detailed control experiments to understand the mechanism of this cascade reaction. When N−H was replaced by N−Me, no product was obtained, which suggested that N−H was essential for this reaction (Scheme 6a). Additionally, 4-chlorothiophenol (**2a**) was completely converted into di(*p*-chlorophenyl) disulfide (**2o**) in the absence of

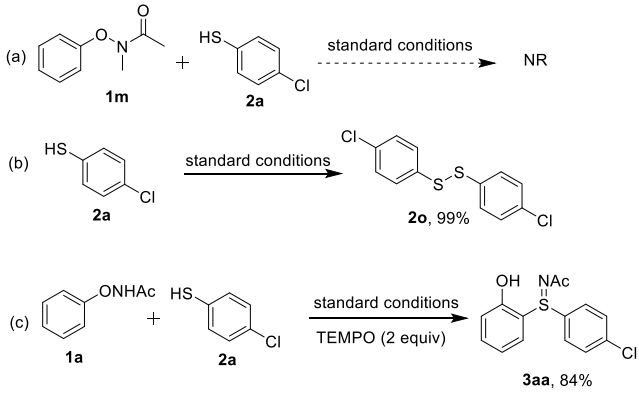
Scheme 4. Substrate Scope of Disulfides[a,b]



[a]Reaction conditions: **1a** (0.2 mmol), **2** (0.3 mmol), and CsOAc (1 equiv) in DMSO (1 mL) at room temperature for 10 h. Yields of isolated products are given. [b]The reaction temperature is 40 °C.

Scheme 5. Gram-Scale Synthesis

Scheme 6. Control Experiments



N-phenoxyacetamide (**1a**) under standard conditions (Scheme 6b). Then, the treatment of di(*p*-chlorophenyl) disulfide (**2o**) with *N*-phenoxyacetamide (**1a**) led to **3aa** in 96% yield, indicating that di(*p*-chlorophenyl) disulfide might be an intermediate in this transformation (Scheme 4). To further explore the mechanism, the reaction of *N*-phenoxyacetamide (**1a**) with 4-chlorothiophenol (**2a**) was examined without CsOAc (Table 1, entry 16) or air (Table 1, entry 17), and the expected product **3aa** was not observed. Moreover, the reaction of *N*-phenoxyacetamide (**1a**) with 4-chlorothiophenol (**2a**) was tested in the presence of TEMPO, and the coupling product **3aa** decreased only slightly to 84%, indicating that a radical process was not involved this reaction system (Scheme 6c).

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On the basis of the aforementioned observations and together with previous reports on sp^2 C−H sulfenylation, a plausible mechanism was proposed and studied by density functional theory (DFT) calculations (Figure 2). Initially, the

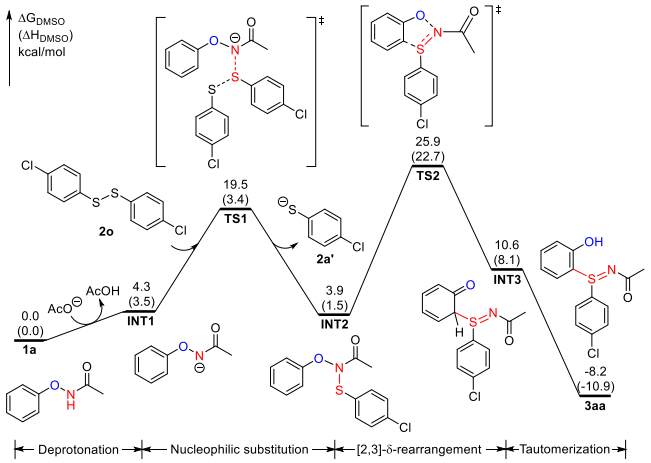

Figure 2. Free-energy profile of the intermolecular sulfur atom transfer cascade reaction. Free energies and enthalpies (in parentheses) are given in kilocalories per mole.

N−H bond of *N*-phenoxyacetamide (**1a**) was deprotonated by AcO^- to form the intermediate **INT1**. Under standard conditions, 4-chlorothiophenol (**2a**) was oxidized to di(*p*-chlorophenyl) disulfide (**2o**). Subsequently, the anionic intermediate **INT1** underwent nucleophilic substitution to di(*p*-chlorophenyl) disulfide (**2o**) via transition state **TS1** with a 15.2 kcal/mol barrier, leading to the formation of a N−S bond (intermediate **INT2**). Next, cleavage of the O−N bond and electrophilic [2,3]-*δ*-rearrangement of intermediate **INT2** proceeded to give intermediate **INT3** with a 22.0 kcal/mol barrier (transition state **TS2**).[14c] Finally, the intermediate **INT3** easily underwent tautomerization to produce **3aa**. The DFT studies indicated that the rate-limiting step of this reaction is the electrophilic [2,3]-*δ*-rearrangement (**TS2**), and the free-energy barrier is 25.9 kcal/mol, which is energetically feasible under standard conditions. The substituent effects of aryloxyamides (Scheme 2) and disulfides (Scheme 4) were also studied by DFT calculations and found to be consistent with the experimental results (Table S1 in the Supporting Information).

In conclusion, we developed a novel strategy for the synthesis of *ortho*-phenolic sulfilimines under mild conditions. The reaction shows excellent chemoselectivity and a broad substrate scope for *N*-aryloxyamides, aryl/heteroaryl thiols, and diaryl/dialkyl disulfides. Moreover, this atom-economical cascade reaction uses commercially available thiols as a sulfur source and generates water as the sole byproduct. Importantly, the reaction can be conducted on a gram scale with excellent reaction efficiency. The further application of the atom transfer cascade in other useful transformations is underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c01032.

Experimental procedures, characterization data, and NMR spectra of all compounds (PDF)

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Author Contributions

⊥F.X., Y.Z., and Y.S. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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