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N-Hydroxy sulfonamides as new sulfenylating agents for the functionalization of aromatic compounds

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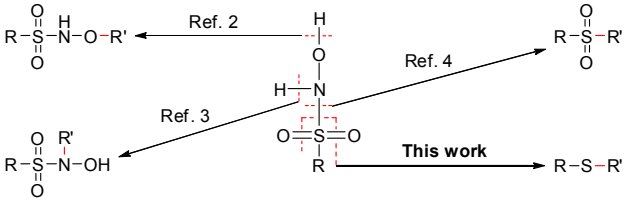
An unprecedented use of *N*-hydroxy sulfonamides as sulfenylating agents has been established. In the presence of catalytic amounts of iodine and *N*-hydroxysuccinimide, *N*-hydroxy sulfonamides participated in sulfenylation with indoles, 7-azaindole, *N*-methyl pyrrole, and 2-naphthol to afford structurally diverse thioethers in moderate to excellent yields with very high regioselectivity.

For a long time much attention has been paid to *N*-hydroxy sulfonamides, particularly Piloty's acid ($PhSO_2NHOH$),[1] owing to their ready accessibility and versatile applications. *N*-Hydroxy sulfonamides have been explored as oxygen nucleophiles,[2] nitrogen nucleophiles,[3] and sulfonyl sources[4] through cleavage of O–H, N–H, and S–N bonds, respectively (Scheme 1). Herein we report a conceptually new synthetic application of *N*-hydroxy sulfonamides to the sulfenylation of aromatic compounds through cleavage of S=O and S–N bonds (Scheme 1). When compared to traditional sulfenylating agents such as thiols, sulfenyl chlorides, and disulfides,[5] *N*-hydroxy sulfonamides are much more amenable to handling because, in general, they are readily accessible solids, free of unpleasant odor, and compatible with moisture.



Scheme 1 Synthetic applications of *N*-hydroxy sulfonamides.

Inspired by our previous discovery on the sulfenylation reactions with sulfonyl hydrazides,[6,7] we envisioned that *N*-hydroxy sulfonamides could serve as alternative sulfenylating agents in a similar manner releasing water and nitric oxide as byproducts via cleavage of S=O and S–N bonds. We selected the sulfenylation of indoles to test our hypothesis since some indole thioethers serve as potent agents to treat cancer[8] and allergy.[9] Other than sulfonyl hydrazides,[6a,7l,m] the sulfenylation of indoles was reported to be realized with sulfenylating agents such as thiols,[10] sulfenyl halides,[11] disulfides,[12] *N*-thioimides,[13] sulfinates,[14] and sulfonyl chlorides.[15] Many of these sulfenylating agents are unstable to air and/or moisture, are expensive, and/or possess unpleasant odors. Moreover, many of these reactions require excess sulfenylating agents and/or additives, suffer from a narrow substrate scope, and/or yield some byproducts unfriendly to environment.

Initially, we employed 10 mol% iodine to catalyze the model reaction of *N*-hydroxy sulfonamide **1a** with indole (**2a**), which occurred in butanol under nitrogen at 120 °C to afford thioether **3a** in 53% yield (Table 1, entry 1). To our surprise, the yield was enhanced dramatically by addition of an *N*-hydroxy imide or an *N*-hydroxy amide (entries 2-5), and particularly, the use of 30 mol% *N*-hydroxysuccinimide (**H1**) gave a 98% yield (entry 2). Replacing iodine with NIS decreased the yield dramatically and even no desired product was isolated when using either TBAI or HI as the catalyst (entries 6-8). A number of organic solvents were examined but no better yield was achieved (entries 9-14). Finally, a control experiment was carried out under oxygen, and the desired product was observed in only a trace amount despite that fact that most of the *N*-hydroxy sulfonamide was consumed through oxidation by the end of the reaction (entry 15).

In the presence of 10 mol% iodine and 30 mol% *N*-hydroxy imide **H1**, a range of *N*-hydroxy arylsulfonamides smoothly participated in sulfenylation with indoles to afford structurally diverse aryl indolyl thioethers in moderate to excellent yields with very high regioselectivity (Scheme 2, **3a-y**). In general, the sulfenylation reaction occurred at C-3 of the indole ring (**3a-o** and **3r-y**). When C-3 was occupied by a substituent, C-2 of theindole ring was the reaction site of choice (**3p** and **3q**). It is noteworthy that the reaction tolerated a variety of functional groups such as an alkoxy group, fluoro, chloro, bromo, iodo, a

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† Electronic Supplementary Information (ESI) available: General information, experimental procedures, characterization data, and copies of ^1H NMR and ^{13}C NMR spectra and a HPLC trace. See DOI: 10.1039/x0xx00000x

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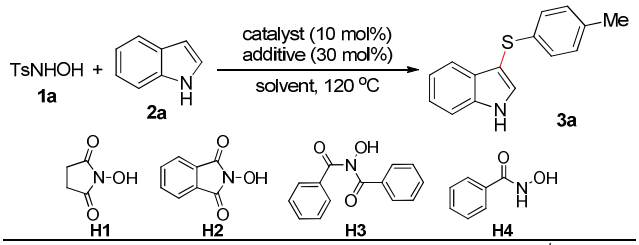
Table 1 Optimization of the reaction conditions[a]

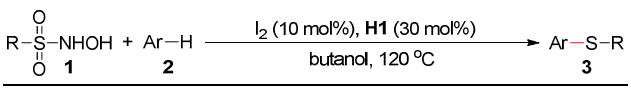


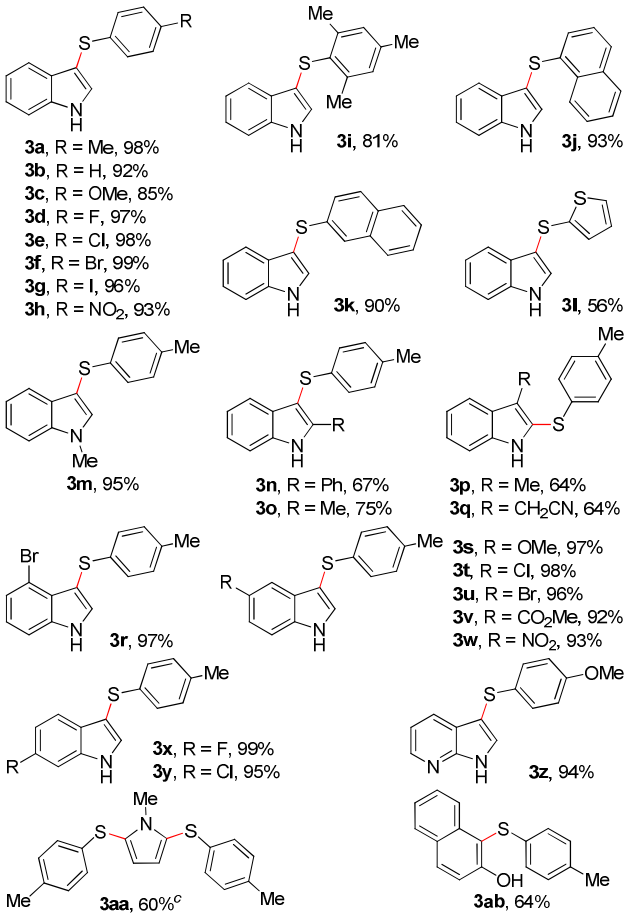
Entry	Catalyst	Additive	Solvent	Yield[b] (%)
1	I_2	none	Butanol	53
2	I_2	**H1**	Butanol	98
3	I_2	**H2**	Butanol	86
4	I_2	**H3**	Butanol	90
5	I_2	**H4**	Butanol	91
6	NIS	**H1**	Butanol	79
7	TBAI	**H1**	Butanol	0
8	HI	**H1**	Butanol	0
9	I_2	**H1**	Cyclohexanol	trace
10	I_2	**H1**	Glycol	trace
11	I_2	**H1**	Glycerol	trace
12	I_2	**H1**	DMF	44
13	I_2	**H1**	DMSO	0
14	I_2	**H1**	Toluene	80
15[c]	I_2	**H1**	Butanol	trace

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), catalyst (10 mol%), additive (30 mol%), solvent (2.0 mL), 120 °C (oil bath), under nitrogen, 15 h. [b] Isolated yield. [c] The reaction was run under oxygen.

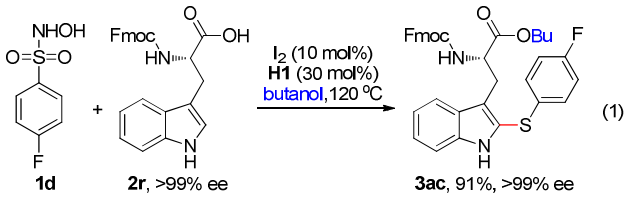
nitro group, a nitrile group, and an ester group. This regioselective sulfenylation reaction was successfully extended to some other electron-rich aromatic compounds such as 7-azaindole (**3z**), *N*-methyl pyrrole (**3aa**), and 2-naphthol (**3ab**). Notably, *N*-methyl pyrrole was very reactive and participated in oversulfenylation to afford bisthioether **3aa** in a good yield with very high regioselectivity.[16] Nevertheless, the sulfenylation reaction was not applicable to less reactive aromatic compounds such as furan, thiophene, *N*,*N*-dimethylaniline, phenol, anisole, and 2-methoxynaphthalene. On the other hand, we failed to observe the sulfenylation reaction with *N*-hydroxy alkylsulfonamides such as *N*-hydroxyhexadecane-1-sulfonamide.

The above conditions were further applied to the sulfenylation of Fmoc-protected *L*-tryptophan **2r** (Fmoc = fluorenylmethyloxycarbonyl). To our delight, a three-component reaction of *N*-hydroxy sulfonamide **1d**, protected *L*-tryptophan **2r**, and butanol (solvent) proceeded via sulfenylation and esterification to afford functionalized α-amino ester **3ac** in 91% yield (eqn (1)). Importantly, no racemization was detected in this case.





Scheme 2 Sulfenylation of aromatic compounds with *N*-hydroxy sulfonamides. [a] Reaction conditions: **1** (0.20 mmol), **2** (0.30 mmol), I_2 (10 mol%), **H1** (30 mol%), butanol (2.0 mL), 120 °C (oil bath), under nitrogen, 15 h. [b] Isolated yields were given. [c] **1a** (2 equiv) was used.



To gain insights into the reaction mechanism, we carried out ^{1}H NMR spectroscopic analysis of the reaction mixture of *N*-hydroxy sulfonamide **1a** with indole (**2a**) in ethanol and found that the *N*-hydroxy sulfonamide decomposed to sulfinic acid **4a**, sulfinate ester **5a**, and thiosulfonate **6a** (Table 2),[17] whose structures were further confirmed by high resolution mass spectrometric analysis.[18] While sulfinic acid **4a** and thiosulfonate **6a** existed in very small amounts throughout the process, sulfinate ester **5a** was generated in a relatively big amount but disappeared by the end of the reaction. In addition, a little more than half of *N*-hydroxy imide **H1** underwent iodine-catalyzed alcoholysis with ethanol to afford diester **7a**,[19] which suggests that hydroxylamine was generated during the reaction.

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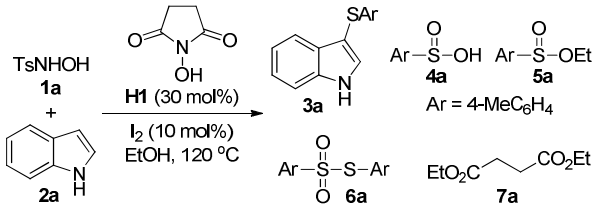
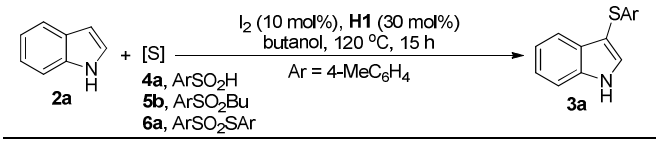
Table 2 ^{1}H NMR spectroscopic analysis of the reaction mixture



Entry	Time (h)	**1a** : **3a** : **4a** : **5a** : **6a**	**H1** : **7a**
1	1	80.8 : 10.9 : 0.7 : 6.8 : 0.8	65.3 : 34.7
2	5	14.9 : 70.7 : 2.8 : 8.5 : 3.1	49.0 : 51.0
3	15	0 : 93.6 : 3.5 : 0 : 2.9	47.1 : 52.9

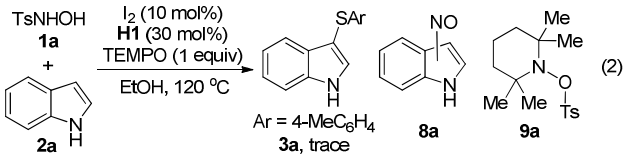
Under the standard conditions, sulfinic acid **4a**, sulfinate ester **5b**, and thiosulfonate **6a** each participated in sulfenylation with indole (**2a**) to afford thioether **3a** (Table 3). It is noteworthy that trace amounts of sulfinic acid **4a** and thiosulfonate **6a** were generated during the reaction of sulfinate ester **5b** according to thin-layer chromatography (TLC) analysis. Moreover, a series of control experiments revealed that iodine rather than *N*-hydroxy imide **H1** was crucial for the sulfenylation of indole (**2a**) with these intermediates.

Table 3 Transformations of intermediates

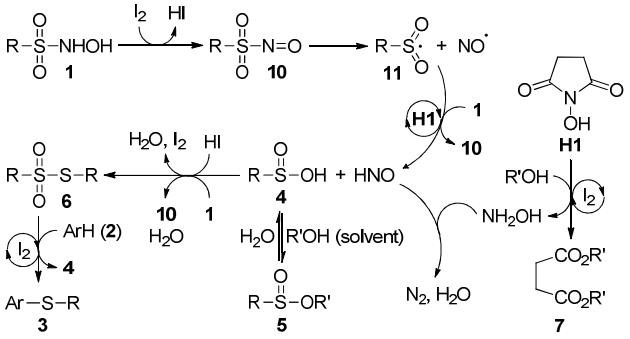


Entry	[S]	Isolated yield (%)		
		Standard	Without I_2	Without **H1**
1	**4a**	57	12	63
2	**5b**	85	0	73
3	**6a**	88	47	88

Addition of one equivalent of 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO), a radical scavenger, to the reaction mixture of *N*-hydroxy sulfonamide **1a** and indole (**2a**) almost inhibited the formation of thioether **3a** (eqn (2)). We further carried out electron-spray ionization (ESI) mass spectrometric analysis of this reaction mixture and tentatively identified nitroso-substituted indole **8a** and TEMPO-Ts (**9a**) according to the high resolution mass data.[18] These results suggest that both nitric oxide radical (NO$^{\cdot}$) and sulfonyl radical Ts$^{\cdot}$ were generated through decomposition of *N*-hydroxy sulfonamide **1a** during the sulfenylation reaction.



On the basis of our experimental results and previous relevant studies, we propose the following reaction pathways for the sulfenylation of aromatic compounds with *N*-hydroxy sulfonamides (Scheme 3). Initially, oxidation of *N*-hydroxy sulfonamide **1** with iodine affords HI and sulfonyl nitroso compound **10**,[4b] homolytic cleavage of which generates sulfonyl radical **11** and nitric oxide radical.[4b] Both radicals undergo *N*-hydroxy imide **H1**-catalyzed hydrogen abstraction from *N*-hydroxy sulfonamide **1** to afford sulfinic acid **4** and HNO.[20] Part of HNO is converted to molecular nitrogen and water through reduction with hydroxylamine,[21] which is generated by iodine-catalyzed alcoholysis of *N*-hydroxy imide **H1** with the alcohol solvent. While sulfinic acid **4** can be converted to sulfinate ester **5** under acidic conditions,[22] the reverse hydrolysis reaction occurs readily as the following reaction progresses.[23] Sulfinic acid **4** is reduced by HI and/or *N*-hydroxy sulfonamide **1** to afford thiosulfonate **6**,[6e] which participates in iodine-catalyzed sulfenylation with aromatic compound **2** to afford thioether **3**.[6e]



Scheme 3 Proposed reaction pathways.

In summary, we have established a conceptually new synthetic application of *N*-hydroxy sulfonamides to the sulfenylation of aromatic compounds through cleavage of S=O and S–N bonds. In the presence of 10 mol% iodine and 30 mol% *N*-hydroxysuccinimide, a range of *N*-hydroxy sulfonamides smoothly participated in sulfenylation with indoles, 7-azaindole, *N*-methyl pyrrole, and 2-naphthol to afford structurally diverse thioethers in moderate to excellent yields with very high regioselectivity. Preliminary mechanistic studies show that *N*-hydroxy sulfonamides first decompose to sulfinic acids and then participate in sulfenylation with aromatic compounds. This study paves the way for the use of *N*-hydroxy sulfonamides as sulfenylating agents in chemical synthesis.

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