Iodine-Catalyzed Regioselective Sulfenylation of Indoles with Sulfonyl Hydrazides**

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The indole moiety is present in many biologically relevant molecules, and consequently, much attention has been paid to the synthesis of substituted indoles through either construction or modification of indole rings.^[1] The electron-rich nature of indole rings enable them to undergo direct carbonhydrogen bond functionalization with electrophiles to form carbon-carbon and carbon-heteroatom bonds. In this regard, the sulfenylation of indoles has been developed for the synthesis of indole thioethers, some of which serve as potent agents to treat cancer^[2] and allergies,^[3] from sulfenylating agents such as sulfenyl halides,^[4] N-thioimides,^[5] sulfonium salts,^[6] thiols,^[7] disulfides,^[8] quinone mono-O,S-acetals,^[9] and arylsulfonyl chlorides.^[10] Nevertheless, many of these sulfenylating agents are unstable to air and moisture, are expensive, or possess unpleasant odors. Moreover, previously reported sulfenylation reactions of indoles frequently require excess sulfenylating agents, excess additives, or high temperature, suffer from a narrow substrate scope, or yield byproducts unfriendly to the environment. To address such issues, it is highly desirable to explore new sulfenylating agents and reaction conditions for the sulfenylation of indoles.

Sulfonyl hydrazides are readily accessible and exist as stable solids, and they have been widely employed to form hydrazones and heterocycles which have versatile applications.^[11] Moreover, sulfonyl hydrazides can be utilized as reductants^[12] and sulfonyl sources^[13] through the cleavage of their sulfur–nitrogen bonds, and very recently as aryl sources through the cleavage of their carbon–sulfur bonds.^[14] In sharp contrast, little has been published on the cleavage of the sulfur–oxygen bonds of sulfonyl hydrazides for chemical synthesis. In this context, we envisioned that the reductive nature of the NHNH₂ group in the sulfonyl hydrazide might be utilized to remove the two oxygen atoms of the sulfonyl group under certain reaction conditions, and consequently,

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sulforyl hydrazides could serve as effective sulfur electrophiles for the sulfenylation of indoles, wherein water and molecular nitrogen are expected to be generated as environmentally benign by-products [Eq. (1)].

The sulfenylation of indole (1a) with *p*-toluenesulfonyl hydrazide (2a; 1.2 equiv) was selected as the model reaction to test our hypothesis. Initially, the reaction did not occur in ethanol in the presence of 10 mol% iodine and open to air at room temperature. To our delight, heating the mixture at 70 °C led to the formation of 3-(p-tolylthio)-1H-indole (3a) in 86% yield as a single regioisomer. For comparison, the reaction was performed under nitrogen and gave 3a in a slightly lower yield (81%). Reducing the catalyst loading to 5 mol% resulted in a much lower yield (52%). A number of common solvents were examined, but no better yield was obtained.^[15] Moreover, replacing iodine with N-iodosuccinimide (NIS) decreased the yield to 41%,^[16] and even no desired product was obtained when replacing iodine with Nbromosuccinimide (NBS), N-chlorosuccinimide (NCS), or Bu₄NI.

In the presence of 10 mol% iodine, a range of aryl-, heteroaryl-, and alkylsulfonyl hydrazides smoothly underwent sulfenylation with indoles in ethanol to give structurally diverse thioethers in moderate to excellent yields with extremely high regioselectivity (Table 1).^[17] In general, the sulfenylation reaction took place at the C3 position of the indole ring (Table 1, entries 1-25). However, the C2 position of the indole ring was the reaction site of choice when the C3 position was occupied by a substituent (Table 1, entries 26-28). Notably, the reaction tolerated a variety of functional groups such as alkoxy, fluoro, chloro, bromo, iodo, nitro, ester, and nitrile. In a few cases sulfonyl hydrazides decomposed significantly because of slow sulfenylation (see below), and to our delight, acceptable yields were obtained by increasing the amounts of sulfonyl hydrazides from 1.2 to 2 equivalents (Table 1, entries 18, 23, and 28).

While the decomposition of sulfonyl hydrazides proceeded very slowly in ethanol at 70 °C,^[13f] it was dramatically accelerated by iodine. Treatment of **2a** with 10 mol% iodine gave the sulfonothioate **5a** and disulfide **6a** in 44 and 33% yields, respectively (Scheme 1). Moreover, **5a** could be reduced to give **6a** under the same reaction conditions but in only 15% yield, which suggested that there was at least one more intermediate leading to **6a**. To gain more insights, we carried out electron-spray ionization (ESI) mass spectrometric analysis of the iodine-catalyzed reaction mixture of **1a** and

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 $\textit{Table 1:}\ \mathsf{Iodine-catalyzed}\ \mathsf{regioselective}\ \mathsf{sulfenylation}\ \mathsf{of}\ \mathsf{indoles}\ \mathsf{with}\ \mathsf{sulfonyl}\ \mathsf{hydrazides}.^{[a,b]}$

R1	$\frac{1}{\frac{N}{H}} \frac{1}{\frac{l_2(10 \text{ m})}{1}}$		R^2	R ¹		
$R^2SO_2NHNH_2$ 2 EtOH, 70 °C N N R ² 3 H 4 H R ²						
Entry	1 (R ¹)	2 (R ²)	3 or 4	Yield [%] ^[c]		
1	1a (H)	2a (4-MeC ₆ H ₄)	3 a	84		
2	1a (H)	2b (Ph)	3 b	79		
3	1a (H)	2c (4-MeOC ₆ H ₄)	3 c	75		
4	1a (H)	2d (4-FC ₆ H ₄)	3 d	72		
5	1a (H)	2e (4-ClC ₆ H ₄)	3 e	88		
6	1a (H)	2 f (4-BrC ₆ H ₄)	3 f	82		
7	1a (H)	2g (4-IC ₆ H ₄)	3 g	81		
8	1a (H)	2h (4-O ₂ NC ₆ H ₄)	3 h	89		
9	1a (H)	2i (3-O ₂ NC ₆ H ₄)	3 i	90		
10	1a (H)	2j (2,5-Cl ₂ C ₆ H ₃)	3 j	85		
11	1a (H)	2k (2,4,6-Me ₃ C ₆ H ₂)	3 k	63		
12	1a (H)	21 (2-naphthyl)	3	90		
13	1a (H)	2 m (2-thienyl)	3 m	66		
14	1a (H)	2n (Me)	3 n	69		
15	1a (H)	2o [(CH ₂) ₇ Me]	3 o	58		
16	1a (H)	2p (CH ₂ Ph)	3 p	67		
17	1b (1-Me)	2b (Ph)	3 q	88		
18 ^[d]	1c (2-Me)	2b (Ph)	3 r	67		
19	1 d (2-Ph)	2b (Ph)	3 s	87		
20	le (4-Br)	2b (Ph)	3t	82		
21	1 f (5-OMe)	2b (Ph)	3 u	80		
22	1g (5-Br)	2b (Ph)	3 v	89		
23 ^[d]	1h (5-NO ₂)	2b (Ph)	3 w	59		
24	1i (5-CO ₂ Me)	2b (Ph)	3 x	70		
25	1j (6-Cl)	2b (Ph)	3 y	89		
26	1k (3-Me)	2b (Ph)	4 a	91		
27	11 (3-CHPh ₂)	2 b (Ph)	4 b	76		
28 ^[d]	1 m (3-CH ₂ CN)	2b (Ph)	4c	56		

[a] Reaction conditions: indole 1 (0.40 mmol), sulfonyl hydrazide 2 (0.48 mmol), iodine (10 mol%), ethanol (1.0 mL), 70 °C, open to air, 5 h.
[b] No regioisomer was detected by ¹H NMR analysis. [c] Yield of isolated product. [d] 0.80 mmol of sulfonyl hydrazide 2 was used and the reaction was run for 8 h.

Scheme 1. Decomposition of the sulfonyl hydrazide 2a.

2a, and tentatively identified two minor decomposition products of **2a**, 4-MeC₆H₄SO₂H (**7a**), and 4-MeC₆H₄SO₂Et (**8a**), according to the high-resolution mass data.^[15]

Additional experiments were carried out under the developed reaction conditions to determine whether the decomposition products of sulfonyl hydrazides could be transformed into indole thioethers. As demonstrated by the results summarized in Table 2, the four decomposition products of 2a, 5a, 6a, 7a, and 8a, were all transformed into 3a, albeit in much lower yields than that from the reaction of 1a with 2a (Table 1, entry 1). Moreover, some of these reactions gave additional by-products, such as the

Table 2: Reactions of indole (1 a) with the four decomposition products of sulfonyl hydrazide 2a.^[a]



[[]a] Reaction conditions: indole (**1 a**) (0.20 mmol), S source (1 equiv), iodine (10 mol%), ethanol (0.5 mL), 70 °C, open to air, 5 h. [b] Yield of isolated product.

12

14

11

14

trace

28

62

dithioether 9a and sulfone 10a, which were not detected in the corresponding iodine-catalyzed sulfenylation reaction. Thus, it is unlikely for these decomposition products of the sulfonyl hydrazide to serve as major intermediates for the formation of the corresponding indole thioether.

Furthermore, it is unlikely for an indolyl sulfone to serve as an intermediate in the sulfenylation reaction. As shown in Equation (2), our reaction conditions failed to reduce the

$$HN \xrightarrow{O} O \longrightarrow{O} O \to O O$$

sulfone **11a** to give **3a**. This result suggests that the removal of the two oxygen atoms from the sulfonyl group occurs prior to the carbon–sulfur bond formation between the indole and the sulfonyl hydrazide.

The reaction mixture of 1a with 2a became weakly acidic (pH 4-5) as determined by using pH paper. Moreover, the reaction conditions allowed *N*-Boc-*N'*-sulfonylhydrazine (**12a**) to be transformed into 3a in 72% yield by taking advantage of the weak acidity to remove the Boc group [Eq. (3)]. In sharp contrast, no reaction was observed with *N*-

$$Me \xrightarrow{\bigcup_{i=1}^{N} S_{i} - NHNHR} \xrightarrow{indole (1a)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{S} \xrightarrow{Me} (3)$$
12a: R = Boc
13a: R = COPh
$$Me \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)}_{I_2 (10 \text{ mol}\%)} \xrightarrow{I_2 (10 \text{ mol}\%)} \underbrace{I_2 (10 \text{ mol}\%)} \underbrace{I_2$$

benzoyl-N'-sulfonylhydrazine (13a) under the same reaction conditions. These results suggest that the NHNH₂ group is essential for the sulfonyl hydrazide to serve as an effective sulfenylating agent.

On the basis of the above experimental results, we propose the major reaction pathways as depicted in Scheme 2 for the iodine-catalyzed sulfenylation of indoles with sulfonyl hydrazides. Stepwise removal of the hydrogen and oxygen atoms from the SO₂NHNH₂ group in **2** with iodine leads to the formation of the thiodiazonium **17**,^[18]

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8 a

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 $HI + HOI \longrightarrow H_2O + I_2$

Scheme 2. Proposed reaction pathways for the iodine-catalyzed sulfenylation of indoles with sulfonyl hydrazides.

which undergoes a regioselective Friedel–Crafts reaction with 1 to give either the thioether 3 or 4, depending on whether or not a substituent occupies the C3 position of 1. Alternatively, extrusion of molecular nitrogen from 17 gives the sulfenyl iodide 18,^[8b,d] which is attacked by 1 to give either 3 or 4. In these steps, iodine is converted into HI and HOI, the two of which react to give water and regenerate iodine to continue the catalytic cycle.

Possible reaction pathways have also been proposed for the iodine-promoted decomposition of sulfonyl hydrazides (Scheme 3). Oxidation of 2 with iodine and subsequent

$$\begin{array}{c} I & I \\ 0 & (H & H \\ R^{2} \cdot S - N & NH \\ 0 & 2 \\ \end{array} \xrightarrow{} P = 1 \\ 0 & 19 \\ r = 1 \\ r = 1$$

Scheme 3. Proposed reaction pathways for the iodine-promoted decomposition of sulfonyl hydrazides.

extrusion of molecular nitrogen gives 7,^[13f] which undergoes esterification with ethanol (solvent) under acidic conditions to give the sulfinate ester 8. Alternatively, 7 undergoes nucleophilic substitution with 17 (or 18) to give the sulfonothioate 5. Reduction of 17, 18, or 5, by ethanol/iodine gives 6. The generation of HI and 7 as by-products in small amounts by such a reaction pathway accounts for the weak acidity of the reaction mixture.

In summary, we have developed an unprecedented sulfenylation reaction of indoles with sulfonyl hydrazides through the cleavage of sulfur–oxygen and sulfur–nitrogen bonds. In the presence of 10 mol% iodine, a range of aryl-, heteroaryl-, and alkylsulfonyl hydrazides smoothly underwent sulfenylation with indoles to give structurally diverse indole thioethers in moderate to excellent yields with extremely high regioselectivity. The current study paves the way for the use of sulfonyl hydrazides as unique sulfur electrophiles in chemical synthesis.

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- [15] For details, see the Supporting Information.
- [16] The reaction mixture turned purple, and it suggested that iodine was generated from NIS.
- [17] Under the same reaction conditions the reaction with pyrrole and aniline afforded unsatisfactory yields. Moreover, no desired reaction was observed with less reactive aromatic compounds such as furan, phenol, and anisole.
- [18] Since the reaction was not affected by the addition of a stoichiometric amount of 1,1-diphenylethene, a radical intermediate might not be involved in the formation of 17.

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Communications



New S in town: Sulfonyl hydrazides smoothly undergo sulfenylation with indoles in the presence of 10 mol % I_2 to give structurally diverse indole thioethers in moderate to excellent yields with extremely high regioselectivity. This study paves the way for the use of sulfonyl hydrazides as unique sulfur electrophiles in chemical synthesis.

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