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# Iodophor-catalyzed sulfenylation of indoles with sulfonyl hydrazides for the synthesis of 3-sulfenylindoles†

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An iodophor-catalyzed sulfenylation of indoles using sulfonyl hydrazides as sulfur source to synthesize 3-sulfenylindoles in aqueous phase has been achieved. Notably, iodophor as catalyst and solvent is inexpensive, commercially available and no innocuous to the environment. The method is also easy to operate. Moreover, the synthetic strategy features a wide range of substrates with excellent tolerance to diverse functional groups. A plausible mechanism for the iodophor-mediated 3-sulfenylation of indoles with sulfonyl hydrazides has been proposed. In addition, 3-(phenylthio)-1*H*-indole was obtained on a multi-gram scale.

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## Introduction

3-Sulfenylindoles are widely found in natural products and synthetic pharmaceuticals.<sup>1</sup> In particular, 3-sulfenylindoles attract considerable attention for their medicinal value in the treatment of HIV,<sup>2</sup> cancer,<sup>3</sup> obesity,<sup>4</sup> heart disease<sup>5</sup> and allergies.<sup>6</sup> They are also used as potent inhibitors of tubulin polymerization.<sup>7</sup> In addition, 3-sulfenylindoles are often used as intermediates in organic synthesis.<sup>8</sup> Generally there are two synthetic routes to synthesize 3-sulfenylindoles. One route is the 3-sulfenylation of indole with sulfenylating agents, such as sulfenyl halides,<sup>9</sup> *N*-thioimides,<sup>10</sup> sulfonium salts,<sup>11</sup> thiols,<sup>12</sup> disulfides,<sup>13</sup> or other sources of sulfur.<sup>14,15</sup> However, many of these sulfenylating agents are moisture and air sensitive, highly volatile and have unpleasant odours. In addition, many 3-sulfenylations require harsh reaction conditions, an inert atmosphere, and suffer from low functional group tolerance, or produce by-products that are environmentally unfriendly. Alternatively, 3-sulfenylindoles are synthesized through the annulation/cyclization of 2-(1-alkynyl)-benzenamines with sulfenylating agents such as disulfides and arylsulfonyl chlorides in the presence of transition metal catalysts<sup>16</sup> or a stoichiometric amount of *n*-Bu<sub>4</sub>Ni.<sup>17</sup> However, these strategies are limited to the use of toxic and unstable sulfone halides as reaction partners. To overcome these problems, there is an

urgent need to develop direct 3-sulfenylation of indoles under metal-free and mild conditions using stable and readily available materials.

Sulfonyl hydrazides are stable, commercially available and odourless, and have been extensively used in the synthesis of hydrazones and heterocycles.<sup>18</sup> In addition, by cleaving their sulfur–nitrogen bonds, sulfonyl hydrazides can be used as environmentally friendly sources of sulfur.<sup>19</sup> In 2013, the iodine-catalyzed regioselective sulfenylation of indoles with sulfonyl hydrazides was originally presented by Tian *et al.*<sup>20</sup> The sulfenylation proceeded smoothly in the presence of 10 mol% I<sub>2</sub>, providing a range scope of 3-sulfenylindoles in moderate to excellent yields with extremely high regioselectivity. Subsequently, Wang and co-workers reported the sulfenylation of indoles with sulfonyl hydrazides in water without any catalyst or additive.<sup>21</sup> The method has the low tolerance to steric hindrance of hydrazones and suffers from long time and high temperature. In the same year, Barman *et al.* reported a microwave-assisted synthetic approach for the sulfenylation of indoles with sulfonyl hydrazides, using a DBU-based ionic liquid.<sup>22</sup> Various aryl and alkyl sulfonyl hydrazides smoothly reacted with indoles to afford a series of 3-sulfenylindoles in moderate to excellent yields in only 10 min. Other 3-sulfenylation of indoles with sulfonyl hydrazides has rarely been reported, especially in aqueous phase.

As a common topical disinfectant, iodophor (povidone-iodine in water) is widely used in our daily life. It is inexpensive, commercially available and not harmful to the environment. However, iodophor has rarely been used as a catalyst in organic chemistry. For the sake of environmental benignity and our continuous research interests,<sup>23,24</sup> we present herein the iodophor-catalyzed sulfenylation of indoles with sulfonyl hydrazides for the synthesis of 3-sulfenylindoles in aqueous phase under mild conditions.

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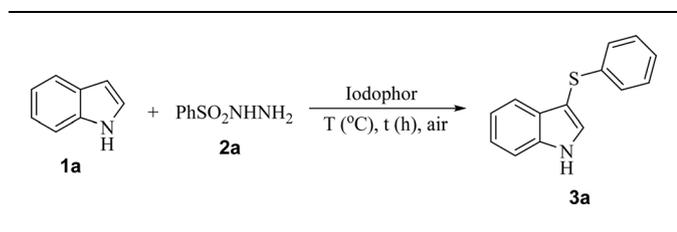


## Results and discussion

The reaction of indole (**1a**) with benzenesulfonyl hydrazide (**2a**) in iodophor and open to air was chosen as a model reaction to screen for the optimal reaction conditions, and the results are summarized in Table 1. Initially, **1a** was treated with **2a** in a 1 : 1 ratio in 2 mL iodophor (0.04 mmol I<sub>2</sub>) at 100 °C for 12 h to give the target product **3a** in 45% yield (Table 1, entry 1). The same reaction in an N<sub>2</sub> atmosphere gave a yield of only 19% (Table 1, entry 2). The result implied that air played an important role in the course of the reaction. Increasing the amount of **2a** improved the yield of product **3a** to varying degrees (Table 1, entries 2–5). The main reason for this is probably that **2a** is less soluble in water. It was found that 1 : 3 was the optimal ratio of **1a** and **2a**, affording product **3a** in 61% yield. Revealing excess sulfonyl hydrazides could increase the yield of 3-sulfonylindoles. The temperature variations suggested that 110 °C was optimal, giving 80% yield of **3a** (Table 1, entries 6–8). Reducing the I<sub>2</sub> loading to 0.02 mmol resulted in a much lower yield (53%) (Table 1, entry 9). Furthermore, the efficiency of the reaction was obviously low with the extension of the reaction time and only 61% yield was obtained (Table 1, entry 10). In comparison, a relatively lower yields were obtained when the reactions of **1a** and **2a** in a ratio of 1 : 2.5 or 1 : 3.5 at 110 °C (Table 1, entries 11 and 12). Finally, the optimized reaction conditions were chosen as follows: indole (**1a**) (1 equiv.) with benzenesulfonyl hydrazide (**2a**) (3 equiv.) and 2 mL iodophor (0.04 mmol I<sub>2</sub>) at 110 °C for 12 h.

The scope of indoles **1** and sulfonyl hydrazides **2** was explored respectively under optimal conditions. First, a series of

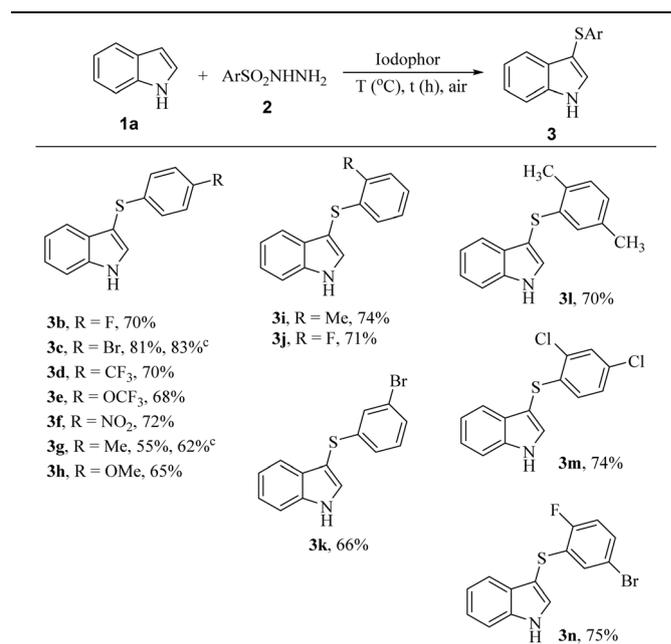
Table 1 Optimization of reaction conditions<sup>a</sup>



Entry	4a : 2a	Iodophor (mL)	T (°C)	t (h)	Yield <sup>b</sup> (%)
1	1 : 1	2 (0.04 mmol I <sub>2</sub> )	100	12	45
2	1 : 1	2 (0.04 mmol I <sub>2</sub> )	100	12	19 <sup>c</sup>
3	1 : 2	2 (0.04 mmol I <sub>2</sub> )	100	12	48
4	1 : 2.5	2 (0.04 mmol I <sub>2</sub> )	100	12	54
5	1 : 3	2 (0.04 mmol I <sub>2</sub> )	100	12	61
6	1 : 3.5	2 (0.04 mmol I <sub>2</sub> )	100	12	58
7	1 : 3	2 (0.04 mmol I <sub>2</sub> )	110	12	80
8	1 : 3	2 (0.04 mmol I <sub>2</sub> )	120	12	60
9	1 : 3	2 (0.04 mmol I <sub>2</sub> )	90	12	55
10	1 : 3	1 (0.02 mmol I <sub>2</sub> )	110	12	53
11	1 : 3	2 (0.04 mmol I <sub>2</sub> )	110	24	61
12	1 : 2.5	2 (0.04 mmol I <sub>2</sub> )	110	12	62
13	1 : 3.5	2 (0.04 mmol I <sub>2</sub> )	110	12	75

<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), **2a** (0.3, 0.6, 0.9 mmol *etc.*), iodophor (2 mL), under air. <sup>b</sup> Isolated yield. <sup>c</sup> Under N<sub>2</sub> atmosphere.

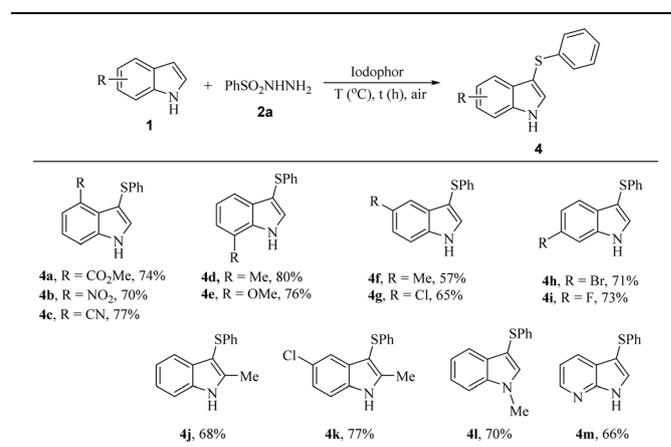
Table 2 Iodophor-catalyzed sulfonylation of indole (**1a**) with aryl sulfonyl hydrazides (**2**)<sup>a,b</sup>



<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), **2** (0.9 mmol), iodophor (2 mL), under air, 110 °C, 12 h. <sup>b</sup> Isolated yield. <sup>c</sup> Reaction time for 18 h.

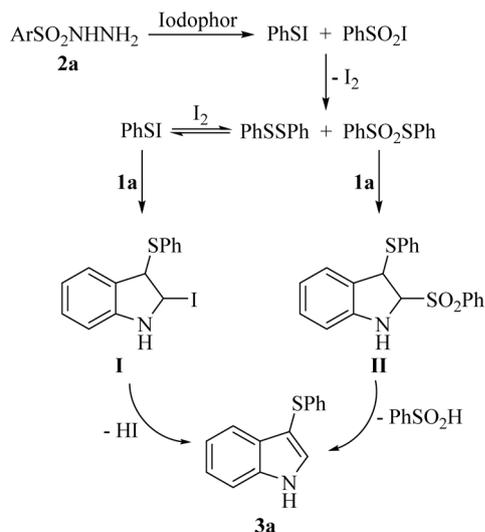
4-substituted aryl sulfonyl hydrazides bearing either electron-deficient groups (F, Br, NO<sub>2</sub>, CF<sub>3</sub> and OCF<sub>3</sub>) or electron-rich groups (Me and OMe) were treated with indole **1a** to afford corresponding 3-phenylthioindoles in good yields (**3b–3h**). In comparison, the substitution effect of electron absorbing groups (**3b–3f**) is slightly better than that of electron-rich groups (**3g** and **3h**). As additional experiments, the sulfonylation for the synthesis of **3c** and **3g** have been investigated for 18 h to give **3c** in 83% yield and **3g** in 62% yield respectively. The yields of **3c** and **3g** have been improved to different degrees, but the

Table 3 Iodophor-catalyzed sulfonylation of indoles (**1**) with benzenesulfonyl hydrazide (**2a**)<sup>a,b</sup>

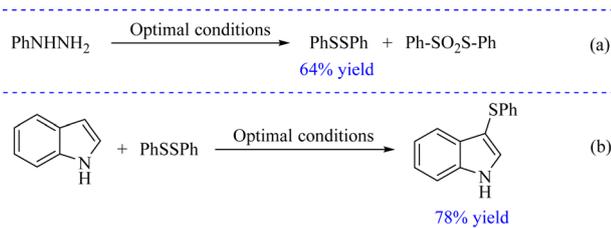


<sup>a</sup> Reaction conditions: **1** (0.3 mmol), **2a** (0.9 mmol), iodophor (2 mL), under air, 110 °C, 12 h. <sup>b</sup> Isolated yield.





Scheme 1 Proposed mechanism for 3-sulfonylation of indoles.

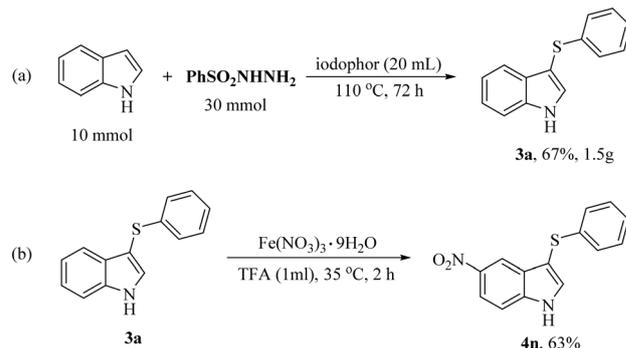


Scheme 2 Control experiments (a) and (b) for proposed mechanism.

electron-withdrawing group still gave a higher yield. A series of 2- or 3-substituted aryl sulfonyl hydrazides **2** were then treated with **1a** to give the desired products **3i–3n** in 66–75% yield. It should be noted that the different positions of the functional groups on the phenyl ring had little influence on the sulfonylation. These results suggest that the synthetic strategy has a high tolerance to different functional groups of aryl sulfonyl hydrazides **2** (Table 2).

Subsequently, the substrate scope of indoles **1** was investigated. Various aryl-substituted indoles were treated with benzenesulfonyl hydrazide (**2a**) under the optimal conditions. Either electron withdrawing groups or electron donating groups on the N-1 (**4l**), C-2 (**4j** and **4k**), C-4 (**4a–4c**), C-5 (**4f** and **4g**), C-6 (**4h** and **4i**) and C-7 (**4d** and **4e**) afforded the desired 3-arythioindoles in moderate to good yields. The results showed that the protocol is highly tolerant to different functional groups of indoles. Among them, electron-rich groups (Me) on the C-5 (**4f**) slightly influenced the reactivity with the lower yield of 57%. In addition, the sulfonylation of biheterocyclic 1*H*-pyrrolo[2,3-*b*]pyridine was investigated to afford the target product **4m** in 66% (Table 3).

Based on our previous work<sup>24</sup> and previous literature,<sup>13,21</sup> a plausible mechanism for the iodophor-mediated 3-sulfonylation of indoles with sulfonyl hydrazides is illustrated in Scheme

Scheme 3 Gram-scale reaction of **3a** and its derivatization.

1. First, benzenesulfonyl hydrazide (**2a**) was initiated by iodophor to afford intermediates PhSSPh (major) and PhSO<sub>2</sub>SPh (minor). On the one hand, PhSI derived from PhSSPh in the presence of I<sub>2</sub> could react with **1a** to give the intermediate **I**. Subsequently **I** rapidly transformed to product **3a** by releasing a molecule of HI. On the other hand, PhSO<sub>2</sub>SPh could react with **1a** without I<sub>2</sub> to give the corresponding product **3a** through intermediate **II**. To further prove the mechanism, the control experiments were carried out. Self-coupling of benzenesulfonylhydrazide occurred under optimal conditions to give the corresponding product PhSSPh in 64% yield (Scheme 2a). PhSSPh was then treated with indole **1a** under optimal conditions to give the desired product **3a** in 78% yield (Scheme 2b). The results of the control experiments supported the proposed mechanism.

The gram-scale reaction was also performed by the reaction of 10 mmol indole (**1a**) with 30 mmol benzenesulfonyl hydrazide (**2a**) in 20 mL iodophor under the optimal reaction conditions. 1.5 g of **3a** was obtained in 67% yield (Scheme 3). Moreover, diverse 3-sulfonylindoles can be obtained by the functionalization of **3a**. For example, **3a** was readily oxidized by Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O to give the corresponding product **4n** in trifluoroacetic acid (TFA). This gram-scale reaction demonstrated the practical applicability of this new protocol for the synthesis of diverse 3-sulfonylindoles.

## Conclusions

In conclusion, we have developed an eco-friendly, mild and effective iodophor-catalyzed sulfonylation of indoles with sulfonyl hydrazides for the synthesis of 3-sulfonylindoles in aqueous phase. Iodophor as catalyst and solvent is inexpensive, commercially available and environment friendly. In addition, this approach has the high tolerance to various functional groups including electron withdrawing groups or electron donating groups. A plausible mechanism for the iodophor-mediated 3-sulfonylation of indoles with sulfonyl hydrazides has been proposed. In addition, the gram-scale sulfonylation of indole with benzenesulfonyl hydrazide offers the possibility for the synthesis of various 3-sulfonylindoles in medicinal chemistry and materials science.



## Experimental section

### General methods

Unless otherwise stated, all reactions were carried out in Schlenk tubes. Melting points were determined using a melting point apparatus and are uncorrected. Chemicals were purchased commercially and were used without further purification. Column chromatography was performed on Qingdao Ocean Chemical silica gel (200–300 mesh).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance III HD 400 MHz spectrometer in  $\text{CDCl}_3$  with tetramethylsilane (TMS) as the internal standard. High resolution mass spectrometry (HRMS) was performed on a Thermo Scientific LTQ Orbitrap XL mass spectrometer, Thermo Fisher Q Exactive.

### General procedure for iodophor-catalyzed sulfenylation of indoles with sulfonyl hydrazides

Indole **1a** (0.3 mmol) and benzenesulfonyl hydrazide **2a** (0.9 mmol) were introduced in a sealed 10 mL reaction tube, and 2 mL iodophor (0.04 mmol  $\text{I}_2$ ) (5% solution of the povidone–iodine in water) was added. The reaction was then continued at 110 °C for 12 h. When the reaction finished, the reaction mixture was cooled to room temperature. Saturated salt solution (10 mL) was then added and extracted with dichloromethane ( $3 \times 10$  mL). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and the organic solvent was evaporated on a rotatory evaporator. The crude was purified by flash chromatography on silica gel (PE/EtOAc) to give the corresponding products **3a**.

### Procedure for the gram-scale reaction of **3a** and its derivatization

Indole **1a** (10 mmol) and benzenesulfonyl hydrazide **2a** (30 mmol) were introduced in a sealed 100 mL round-bottomed flask, and 20 mL iodophor was added. The reaction mixture was then stirred continuously at 110 °C for 72 h. After the reaction finished, the reaction mixture was cooled to room temperature and extracted with dichloromethane ( $5 \times 10$  mL). The combined organic layers were washed with water. The organic phase was then separated and dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered. Subsequently the organic solvent was evaporated on a rotatory evaporator. The crude was purified by flash chromatography on silica gel (PE/EtOAc) to give the corresponding products **3a** in 67% yield (1.5 g).

A mixture of **3a** (3 mmol) and  $\text{Fe}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$  (1.5 mmol) in TFA (1 mL) was stirred for 2 h at 35 °C. After the completion of the reaction, the reaction mixture was neutralized with sodium bicarbonate solution and extracted with ethyl acetate (20 mL). The organic phase was separated and dried over  $\text{Na}_2\text{SO}_4$  and filtered. The filtrate was concentrated and the resulting residue was purified by flash column chromatography on silica gel with PE/EtOAc as eluent to provide the product **4R** in 63% yield.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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