Iron-Catalyzed Sulfenylation of Indoles with Disulfides Promoted by a Catalytic Amount of Iodine

Xiao-Li Fang, Ri-Yuan Tang, Ping Zhong, Jin-Heng Li*

College of Chemistry and Materials Science, Wenzhou University, Wenzhou 325035, P. R. of China
Fax +86/731(8872101; E-mail: jhl@hunn.edu.cn
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Abstract: Selective sulfenylation of indoles with disulfides using iron(III) fluoride combined with iodine has been developed for the synthesis of sulfenylindolines. In the presence of iron(III) fluoride and iodine, a variety of disulfides underwent the reaction with indoles selectively to afford the corresponding sulfenylindolines in good to excellent yields. Moreover, reactions of indoles with 1,2-diphenyldiselenolane were also conducted under the same conditions, which smoothly afforded 3-selenylindolines in good yields.

Key words: iron(III) fluoride, sulfenylation, indoles, disulfides, sulfenylindolines, iodine

Sulfenylindolines are an important class of compounds due to their potential utilization in many major therapeutic areas, such as in the treatment of heart disease, cancer, HIV and obesity. The majority of the methods for the synthesis of sulfenylindolines involve the direct sulfenylation of the indole nucleus with various electrophilic sulfur reagents. The traditional electrophilic sulfur reagents include sulfenyl chlorides, quinone mono-\( O,S \)-acetals and \( N \)-thiophthalimides; however, methods using these sulfur reagents are limited by both the instability, inaccessibility and/or incompatibility of the substrates, and the undesired byproducts.

For example, sulfenyl chlorides, particularly with certain functionalities, are often unstable and difficult to prepare, and the sulfenylation reactions result in an equivalent of thiol byproduct. Similar disadvantages are presented in the use of quinone mono-\( O,S \)-acetals and \( N \)-thiophthalimides. Thus, alternative ways are conducted with the activated disulfides or thiol\( ^{9} \) in situ using a stoichiometric amount of a promoter, such as sodium hydride, \( N \)-chlorosuccinimide, \( N \)-phenyldiindolylmethane bis(trifluoroacetate) or Selectfluor\textsuperscript{10c}. Although these transformations allow for access to sulfenylindolines in moderate to good yields, the high promoter loadings, along with undesired toxic byproducts, hardly make them attractive procedures. The sulfenylation of indoles with disulfides, for instance, usually requires an excess amount of a strong base (often NaH), besides generating an equivalent of undesired thiol byproduct. In view of economy and the environment, the development of transition-metal-catalyzed sulfenylation of indoles may be mandatory. In 1989, an example of alkylthiation of indole with dimethyl disulfide using copper(I) iodide catalyst at 132–160 °C was reported.\textsuperscript{6b} Subsequently, Uemura and co-workers have developed an efficient protocol for the sulfenylation of indoles with thiols in the presence of VO(acac)\(_2\), 2,6-di-tert-butyl-p-cresol, potassium iodide and oxygen, but an excess amount of the thiol is required and undesired disulfide byproducts are formed.\textsuperscript{10d} Very recently, Yadav and co-workers reported an iron(III) chloride catalyzed sulfenylation reaction using indoles and thiols as the reaction partners;\textsuperscript{10c} however, the reaction is limited to aryl thiols and benzyl thiol, which have a foul smell and a pungent flavor. Here, we report a novel and efficient synthesis of sulfenylindolines from the reaction of indoles with disulfides using inexpensive and environmentally benign iron catalysts,\textsuperscript{13} inefficient catalysts in the earlier reports, combined with a catalytic amount of iodine (Scheme 1).

The reaction of 1H-indole (1a) with 1,2-diphenyldisulfane (2a) was investigated to explore the optimal conditions, and the results are summarized in Table 1. Initially, a series of Lewis acids, including \( \text{FeCl}_{3}, \text{Cu(OTf)}_{2} \), \( \text{AuCl}_{3} \) and \( \text{AgOTf} \), were tested (entries 1–4). We found that 35% of the 1H-indole (1a) was consumed with disulfide 2a and iodine in 36 hours to afford the target product 3 in 20% yield (entry 1), and that the other Lewis acids were inferior to iron(III) chloride (entries 2–4); however, no reaction was observed in the absence of a Lewis acid catalyst (entry 5). Accidentally, 1 mol% of iodine was found to enhance the yield of 3 to 75% (87% conversion of 1a, entry 6). Although substrate 1a was converted completely at a loading of 100 mol% of iodine, a mixture of products was observed (entry 7). Among the amounts of iron(III) chloride and the reaction temperatures examined, 20 mol% of iron(III) chloride combined with 80 °C gave the best results (entries 6 and 8–10). Incomplete consumption of 1H-indole (1a) when using iron(III) chloride, even with the aid of iodine, prompted us to evaluate other iron catalysts (entries 11–14). We were delighted to observe that substrate 1a could be converted completely with disulfide 2a, giving product 3 in 90% yield, using iron(III)
fluoride combined with iodine (entry 14); however, sub-
strate 1a could not be converted completely using
Fe(acac)₃, FeBr₃, Fe or 10 mol% of FeF₃ (entries 11–13
and 15). A number of other solvents were also examined
(TTHF, DCE, toluene, DMSO, DMF; entries 16–20), and
they were less effective than acetonitrile. We found that
iron(III) fluoride was less effective in the absence of
iodine (entry 21), while 61% yield of product 3 was isolated
using 1 mol% of iodine alone (entry 22). These results
suggest that PhSI may be generated in situ, improving the
reaction.⁵⁻¹⁰

As shown in Table 2, the scope of both the indole 1 and
disulfide 2 partners for the selenylation reaction was
screened under the standard reaction conditions. Initially,
a variety of disulfides were examined with 1H-indole (1a)
(entries 1–11). The results demonstrated that diaryl disul-
phides 2b–h, bearing either electron-donating or electron-
withdrawing groups, underwent 3-selenylation with 1H-
indole (1a), iron(III) fluoride and iodine smoothly in good
to excellent yields (entries 1–7). It is noteworthy that the
selenylation of substrate 1a with 1,2-di(pyridin-2-yl)disul-
fane (2i) was also successful, in 88% yield (entry 8). To
our delight, the reaction conditions are compatible with
dialkyl disulfides (entries 9–11). 1,2-Dibenzyldisulfane
(2j), for instance, underwent the reaction with 1H-indole
(1a), iron(II) fluoride and iodine smoothly in 93% yield
(entry 9). Then, substituted indoles 1b–h were investigat-
ed (entries 12–23). It was found that several groups, in-
cluding bromo, ethyl and methyl, were tolerated well
under the standard reaction conditions (entries 12–18 and
21–23), but both nitro and ester groups gave unsatisfacto-
ry results (entries 19 and 20). Thus, the bromo-substituted
substrate 1b was treated with disulfides 2a, 2c or 2g to
afford the corresponding products 15–17 in 92%, 90% and
93% yield, respectively (entries 12–14), while methyl 1H-
indole-2-carboxylate (1f) gave the target product 23 in
only 20% yield (entry 20). The reaction of 1-methyl-1H-
indole (1g) with disulfide 2a, iron(III) fluoride and iodine
was also conducted smoothly in 71% yield (entry 21). Fi-
nally, 2-selenylation of the 3-substituted indole 1h was
evaluated under the standard reaction conditions (entries
22 and 23). It was interesting to discover that 3-methyl-
1H-indole (1h) was a suitable substrate to react with 1,2-
diphenylsulfane (2a) and 1,2-di(pyridin-2-yl)disulfane
(2i) in good yields.

3-Selenylation of indoles with 1,2-diphenylsulfane was
also tested under the standard reaction conditions, and the
results are summarized in Scheme 2. In the presence of
iron(III) fluoride and iodine, two indoles 1a and 1b under-
went the 3-selenylation reaction with 1,2-diphenylsulfane
(27) smoothly to afford the corresponding 3-
selenylindoles in good yields.

A working mechanism, as outlined in Scheme 3, was pro-
posed on the basis of reported mechanisms.⁶⁻¹¹ The rea-
tion can take place in the presence of iodine alone (Table
1, entry 22), which suggests an electrophilic addi-
tion process. Initially, the reaction of RSSR (2) with io-

dine (entry 21), while 61% yield of product 3 was isolated
using 1 mol% of iodine alone (entry 22). These results
suggest that PhSI may be generated in situ, improving the
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1, entry 22), which suggests an electrophilic addi-
tion process. Initially, the reaction of RSSR (2) with io-
dine affords RSI (A) in situ (Scheme 3), which is followed by electrophilic addition to yield intermediate B. Deprotonation of intermediate B gives the desired product and HI. HI undergoes reaction with RSSR (2) to give an active RSI (A) and an inactive RSH intermediate. We deduce that FeX₃ plays two roles in the reaction: (1) as a catalyst for the electrophilic addition to give intermediate B, and (2) as a promoter by reacting with HI and RSSR to afford the active RSI species, intermediate C and the stable HX (X = Br, Cl, F). The activity order of FeX₃ (FeF₃ > FeCl₃ > FeBr₃) may be dependent on the Lewis acid

Table 2 Synthesis of Sulfenylindoles by Iron(III) Fluoride/Iodine Catalyzed Sulfenylation of Indoles 1 with Disulfides 2

<table>
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<th>Entry</th>
<th>Indole</th>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>Disulfide</th>
<th>R⁴</th>
<th>Product</th>
<th>Yield (%)</th>
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<td>H</td>
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<td>H</td>
<td>H</td>
<td>2c</td>
<td>4-MeOC₆H₄</td>
<td>5</td>
<td>96</td>
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<td>H</td>
<td>H</td>
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<td>H</td>
<td>H</td>
<td>2e</td>
<td>4-FC₆H₄</td>
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<td>H</td>
<td>H</td>
<td>2f</td>
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<tr>
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<td>H</td>
<td>H</td>
<td>2g</td>
<td>4-O₂NC₆H₄</td>
<td>9</td>
<td>96</td>
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<tr>
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<td>2i</td>
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<td>26</td>
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</table>

a Reaction conditions: 1 (0.4 mmol), 2 (0.2 mmol), FeF₃ (20 mol%) and I₂ (1 mol%) in MeCN (3 mL) at 80 °C for 36 h.
b Isolated yield based on the indole 1.
c >95% of 1e was recovered.
d >65% of 1f was recovered.
properties (FeBr3 > FeCl3 > FeF3). Study of the detailed mechanism is in progress.

In summary, we have developed a novel protocol for the synthesis of sulfenylindoles via iron-catalyzed sulfonylation of indoles with disulfides, with the aid of iodine. In comparison with reported results,6–11 the present iron(III) fluoride/iodine system has the advantages of high efficiency, simple operation, inexpensiveness and regioselectivity for the sulfonylation of indoles. Moreover, using the iron(III) fluoride/iodine system, 3-selenylations of indoles with 1,2-diphenyldiselenane can also be conducted efficiently to afford the corresponding 3-selenylindoles in good yields.

NMR spectroscopy was performed on a Bruker Avance-300 spectrometer operating at 300 MHz (1H NMR) and 75 MHz (13C NMR). TMS was used as internal standard and CDCl3 was used as the solvent. GC-MS analysis was performed on a Shimaatsu TOF IIIQ spectrometer. LC-MS analysis was performed on a Bruker Bio-TOF II spectrometer. Mass spectrometric analysis was performed on a Bruker Bio-TOF II spectrometer. HRMS (ESI): m/z calcd for C14H10FNS [M + Na]+: 266.0410; found: 266.0401; m/z (%) = 243 (100) [M+].

Iron-Catalyzed Sulfonylation of Indoles 1 with Disulfides 2 in the Presence of Iodine; General Procedure

A mixture of an indole 1 (0.4 mmol), a disulfide 2 (0.2 mmol), FeI2 (20 mol%) and I2 (1 mol%) in MeCN (3 mL) was stirred at 80 °C for 36 h until complete consumption of the starting material, as monitored by TLC. After the reaction was finished, the mixture was poured into EtOAc (15 mL) and washed with sat. Na2S2O3 soln (5 × 5 mL). The combined organic layer was dried (anhyd Na2SO4) and concentrated under reduced pressure. The residue was purified by flash column chromatography (hexane–EtOAc) to afford the corresponding 3-selenylindole product.

3-(p-Tolylthio)-1H-indole (4)10h
White solid; mp 133.2–133.1 °C. 
1H NMR (300 MHz, CDCl3): δ = 8.38 (br s, 1 H), 7.59 (d, J = 7.9 Hz, 1 H), 7.44–7.39 (m, 2 H), 7.20–7.17 (m, 3 H), 6.90 (d, J = 7.8 Hz, 1 H), 6.74–6.71 (m, 2 H).
13C NMR (75 MHz, CDCl3): δ = 163.0 (d, J = 247.5 Hz, 1 C), 142.2, 136.5, 131.0, 129.9 (d, J = 8.4 Hz, 1 C), 128.9, 123.3, 121.2 (d, J = 12.2 Hz, 1 C), 119.5, 112.6 (d, J = 23.8 Hz, 1 C), 111.7 (d, J = 13.5 Hz, 1 C), 102.3.
LRMS (EL, 70 eV): m/z (%) = 243 (100) [M+].

3-(4-Acetylphenoxy)phenylthio)-1H-indole (5)10b
Yellow solid; mp 150.1–151.0 °C.
1H NMR (300 MHz, CDCl3): δ = 8.47 (br s, 1 H), 7.48 (d, J = 7.9 Hz, 1 H), 7.43–7.37 (m, 2 H), 7.22–7.10 (m, 4 H), 6.73–6.67 (m, 2 H), 3.74 (s, 3 H).
13C NMR (75 MHz, CDCl3): δ = 150.4, 145.9, 134.5, 130.5, 129.8, 128.7, 125.9, 123.8, 123.5, 112.9, 111.6, 102.8.
LRMS (EL, 70 eV): m/z (%) = 225 (100) [M+].
3-[4-Chloro-2-nitrophenylthio]-1H-indole (10)
Orange solid; mp 154.0–155.3 °C.
1H NMR (300 MHz, CDCl3): δ = 8.74 (br s, 1 H), 8.24 (d, J = 2.3 Hz, 1 H), 7.56–7.45 (m, 3 H), 7.29 (t, J = 8.1 Hz, 1 H), 7.20–7.14 (m, 2 H), 6.87 (d, J = 8.7 Hz, 1 H).
13C NMR (75 MHz, CDCl3): δ = 141.8, 138.9, 133.5, 131.8, 130.3, 129.1, 128.4, 125.5, 123.6, 121.5, 119.2, 112.1, 100.9.
LRMS (EI, 70 eV): m/z (%) = 304 (23) [M+ + 1], 205 (33) [M+ – Br].


5-Bromo-3-[4-nitrophenylthio]-1H-indole (17)
White solid; mp 175.8–178.0 °C.
1H NMR (300 MHz, CDCl3): δ = 8.74 (br s, 1 H), 8.02 (dd, J = 7.0, 1.9 Hz, 2 H), 7.67 (s, 1 H), 7.55 (s, 1 H), 7.39–7.36 (m, 2 H), 7.11 (dd, J = 7.0, 1.9 Hz, 2 H).
13C NMR (75 MHz, CDCl3): δ = 149.2, 145.0, 135.2, 132.4, 130.3, 126.6, 125.1, 124.0, 121.8, 115.0, 113.5, 100.0.
LRMS (EI, 70 eV): m/z (%) = 350 (22) [M+ + 2], 348 (23) [M+], 269 (100) [M+ – Br].

7-Ethyl-3-(phenylthio)-1H-indole (18)10b
Brown oil.
1H NMR (300 MHz, CDCl3): δ = 8.09 (s, 1 H), 7.45–7.41 (m, 1 H), 7.40 (s, 1 H), 7.13–7.03 (m, 7 H), 2.89–2.81 (m, 2 H), 1.36 (t, J = 7.5 Hz, 3 H).
13C NMR (75 MHz, CDCl3): δ = 139.3, 135.4, 130.4, 128.9, 128.7, 127.0, 125.9, 124.8, 121.6, 117.4, 103.1, 22.8, 13.8.
LRMS (EI, 70 eV): m/z (%) = 253 (100) [M]+, 238 (53) [M+ – CH3].

2-Methyl-3-(phenylthio)-1H-indole (19)14
White solid; mp 110.9–111.2 °C (Lit.14 109–110 °C).
1H NMR (300 MHz, CDCl3): δ = 8.07 (s, 1 H), 7.52 (d, J = 7.6 Hz, 1 H), 7.15–7.00 (m, 8 H), 2.42 (s, 3 H).
13C NMR (75 MHz, CDCl3): δ = 141.3, 139.4, 135.5, 130.3, 128.8, 125.6, 124.6, 122.2, 120.7, 119.0, 110.8, 99.2, 12.1.
LRMS (EI, 70 eV): m/z (%) = 239 (100) [M]+.

2-Methyl-3-(p-tolyloxy)-1H-indole (20)14
Brown solid; mp 98.2–100.0 °C.
1H NMR (300 MHz, CDCl3): δ = 8.01 (br s, 1 H), 7.54 (d, J = 8.3 Hz, 1 H), 7.24–7.06 (m, 3 H), 6.95–6.93 (m, 4 H), 2.41 (s, 3 H), 2.21 (s, 3 H).
13C NMR (75 MHz, CDCl3): δ = 141.1, 135.7, 135.5, 134.4, 130.4, 129.6, 125.9, 122.2, 120.7, 119.0, 110.8, 101.2, 20.9, 12.1.
LRMS (EI, 70 eV): m/z (%) = 253 (100) [M]+.

2-Methyl-3-(4-nitrophenylthio)-1H-indole (21)
Pale-yellow solid; mp 144.8–147.2 °C.
1H NMR (300 MHz, CDCl3): δ = 8.48 (s, 1 H), 7.98 (dd, J = 8.2, 2.2 Hz, 2 H), 7.43 (d, J = 7.6 Hz, 1 H), 7.37 (d, J = 7.6 Hz, 1 H), 7.24–7.14 (m, 2 H), 7.08 (dd, J = 8.2, 2.2 Hz, 2 H), 2.50 (s, 3 H).
13C NMR (75 MHz, CDCl3): δ = 149.9, 144.8, 141.7, 135.6, 129.6, 124.9, 123.9, 122.7, 121.1, 118.5, 110.0, 96.9, 12.1.
LRMS (EI, 70 eV): m/z (%) = 284 (100) [M]+, 269 (50) [M+ – CH3].
Methyl 3-(Phenylthio)-1H-indole-2-carboxylate (23)\textsuperscript{4d}

White solid; mp 173.1–174.9 °C.

1H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 8.1\) Hz, 1 H), 2.39 (s, 3 H).

13C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta = 136.3, 133.8, 131.2, 129.9, 128.9, 128.6, 125.6, 122.9, 120.8, 120.3, 131.2, 129.9, 128.9, 128.6, 125.6, 122.9, 120.8, 120.3, 111.3, 98.0.

LRMS (EI, 70 eV): \(m/z\) (%) = 239 (100) [M\textsuperscript{+}].

5-Bromo-3-(phenylseleno)-1H-indole (26)\textsuperscript{15}

Pale-brown solid; mp 153.0–153.8 °C.

1H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta = 8.53\) (br s, 1 H), 8.42 (d, \(J = 4.1\) Hz, 1 H), 7.61 (d, \(J = 7.9\) Hz, 1 H), 7.40–7.35 (m, 2 H), 7.27–7.25 (m, 1 H), 7.18–7.16 (m, 1 H), 7.00 (d, \(J = 5.1\) Hz, 1 H), 6.69 (d, \(J = 8.1\) Hz, 1 H), 2.39 (s, 3 H).

13C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta = 160.6, 149.5, 137.1, 128.4, 123.6, 120.3, 120.1 (2 C), 119.9 (2 C), 119.7, 119.5, 111.0, 9.4.

LRMS (EI, 70 eV): \(m/z\) (%) = 240 (27) [M\textsuperscript{+}], 130 (100).

HRMS (ESI): \(m/z\) calcd for C\textsubscript{14}H\textsubscript{12}N\textsubscript{2}S [M + Na\textsuperscript{+}]: 263.0613; found: 263.0601.

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