SUPPORTING INFORMATION

Iron-catalyzed selective oxidation of sulfides to sulfoxides with polyethylene glycol/O\textsubscript{2} system

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Supporting information

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1. General experimental methods

Caution

Experiments using compressed gases O₂ are potentially hazardous and must only be carried out by using the appropriate equipment and under rigorous safety precautions.

Materials

The sulfides were purchased from Sigma-Aldrich and Aladdin. The various Iron catalysts were purchased from Aladdin with >98% purity (Cu content was determined to be 0.013% w/w by using ICP method). The other organic compounds from Tianjin Guangfu Fine Chemical Research Institute were used without further purification except for the solvents, which were distilled by the known method prior to use.

NMR spectra were recorded on a Bruker 400 or Varian 400 spectrometer in CDCl₃. ¹H and ¹³C NMR chemical shifts (δ) are given in ppm relative to TMS. ¹H and ¹³C positive chemical shifts (δ) in ppm are downfield from tetramethylsilane (CDCl₃: δC = 77.0 ppm; residual CHCl₃ in CDCl₃: δH = 7.26 ppm). GC-MS were recorded on a Thermo Finnigan Polaris Q GC/MS. GC analyses were performed on a Shimadzu GC-2014 equipped with a capillary column (RTX-17, 30 m×0.25 μm) using a flame ionization detector. ICP was measured on a ICP-9000 (N+M) Inductively coupled plasma emission spectrometer. Column chromatography was performed by using silica gel 200-300 mesh with ethyl acetate/petroleum as eluant.

2. Conventional organic solvents and 18-crown-6 used for sulfide oxidation

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Temp (°C)</th>
<th>Conv (%)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sulfoxide</td>
<td>Sulfone</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>CH₂Cl₂</td>
<td>60</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>CH₃CN</td>
<td>80</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>CH₃OH</td>
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<td>0</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>CH₃CH₂OH</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>(CH₃CH₂O)₂</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>1, 4-dioxane</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>CH₃CN/CH₃OH</td>
<td>80</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>CH₃CN/CH₂CH₂OH</td>
<td>80</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

a All the experiments were carried out with 0.5 mmol (62 mg) of thioanisole, PEG-1000 (0.3 mmol, 300 mg.), Fe(acac)₃ (2 mol%, 2.4 mg), O₂ (2 MPa), 6 h. b Determined by GC using area normalization.
Table S2 Oxidation of thioanisole in 18-crown-6\footnote{All the experiments were carried out with 0.5 mmol (62 mg) of thioanisole, 18-crown-6 (300 mg), Fe(acac)$_2$ (2 mol\%, 2.4 mg), O$_2$ (2 MPa), unless otherwise noted. \footnote{Determined by GC using area normalization.} \footnote{without Fe(acac)$_2$.} \footnote{TEMPO (0.05 mmol) was added.}}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temp (°C)</th>
<th>T(h)</th>
<th>Conv (%)\textsuperscript{b}</th>
<th>Yield (%)</th>
<th>Sulfoxide</th>
<th>Sulfone</th>
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<tbody>
<tr>
<td>1\textsuperscript{c}</td>
<td>100</td>
<td>12</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>100</td>
<td>2</td>
<td>96</td>
<td>90</td>
<td>6</td>
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</tr>
<tr>
<td>3\textsuperscript{d}</td>
<td>100</td>
<td>2</td>
<td>&lt;1</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

3. $^1$H NMR and $^{13}$C NMR charts for products

(Methylsulfinyl)benzene  \textsuperscript{2a}

![$^1$H NMR and $^{13}$C NMR charts for products](image-url)
**13C NMR (100.6 MHz, CDCl3)**

\[
\begin{array}{c}
\text{S} \\
\text{O} \\
2a
\end{array}
\]

(Methylsulfonyl)benzene

**1H NMR (400 MHz, CDCl3)**

\[
\begin{array}{c}
\text{O} \\
\text{S}
\end{array}
\]
1-Methyl-4-(methylsulfinyl)benzene  2b
1-Methoxy-4-(methylsulfinyl)benzene 2c

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1-Chloro-4-(methylsulfinyl)benzene  \(2d\)
13C NMR (100.6 MHz, CDCl₃)

4-(Methylsulfinyl)benzonitrile 2e

1H NMR (400 MHz, CDCl₃)
Sulfinyldibenzene 2f

$^{13}$C NMR (100.6 MHz, CDCl₃)

$^1$H NMR (400 MHz, CDCl₃)
$^{13}$C NMR (100.6 MHz, CDCl$_3$)

1-(Propylsulfinyl)propane  \( 2g \)

$^1$H NMR (400 MHz, CDCl$_3$)

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$^{13}$C NMR (100.6 MHz, CDCl$_3$)

Dimethyl sulfoxide 2h

$^1$H NMR (400 MHz, CDCl$_3$)
$^1^3$C NMR (100.6 MHz, CDCl$_3$)