Efficient and Mild Oxidation of Sulfides to Sulfoxides by Iodosobenzene Catalyzed by Cr(salen) Complex

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Abstract: Cr(Salen) I is found to be an efficient catalyst for the oxidation of various sulfides to sulfoxides with iodosobenzene as terminal oxidant. Both aryl and alkyl sulfides are selectively converted into sulfoxides in excellent yields (>90%).

Key words: sulfide, sulfoxide, Cr(salen), oxidation, selectivity

The selective and catalytic oxyfunctionalization is a pivotal reaction in organic synthesis that has received much attention over the years. Transition metal complexes can serve as excellent catalysts for various oxidative processes provided they are equipped with an appropriate organic ligand. A large number of salen type metal complexes were used for numerous organic transformations. The selective oxidation of organic sulfides to sulfoxides without any overoxidation to sulfones is a challenging research in synthetic organic chemistry because of the importance of sulfides as intermediates in biologically active compounds. Oxovanadium(IV), Mn(III), Ti(IV), and some highervalent chromium complexes have been widely used as catalysts for oxidation of sulfides. Oxorhenium(V) dithiolates with tert-butyl hydroperoxide have been reported as an oxidizing agent. The combination of mercury(II) oxide/iode has served as a good oxidizing agent of sulfides. The role of hexafluoropropan-2-ol with H2O2 for sulfoxidation has been reported in the literature. Photochemical oxidation of sulfides has been studied. We have recently reported a mild and efficient oxidation of sulfides with periodic acid catalyzed by FeCl3.

In recent years Cr(salen) complexes and hypervalent iodine atoms have been employed to oxidize various organic substrates. To the best of our knowledge, there is no report on the formation of sulfoxides by using Cr(salen) complexes from a synthetic point of view. In continuation of our interest in the oxidation studies by salen-type metal complexes, we would like to report here an efficient and selective oxidation of sulfides to sulfoxides utilizing 3,5-disubstituted Cr(salen) (1, Figure 1)/PhIO.

Various sulfides were subject to oxidation under the stoichiometric condition given in Table 1. Unsubstituted and substituted thioanisoles (entries 1–4) underwent very smooth oxidation with over 98% yield. The substituents on the phenyl group showed no significant effect on reaction time (entries 2–4). But nitro and cyano substituents show little rate retardation due to their electron withdrawing property (entries 5 and 6). Diphenyl sulfide underwent clean oxidation to the corresponding sulfoxide with longer reaction time due to steric hindrance (entry 7). When compared with PhIO/KBr system, our method requires less reaction time for the oxidation of diphenyl sulfide and gave a better yield. Further, the PhIO/KBr system shows no or very little reaction with the substrates carrying electron-withdrawing substituents at the p-position.

Such rate retardation has already been clearly observed in the oxidation of diphenyl sulfide with longer reaction time giving low yield. The insertion of a methylene group into diphenyl sulfide reduced the steric hindrance as indicated by a little shorter reaction time (entries 8 and 9). Some linear dialkyl sulfides (entries 10–12) underwent smooth oxidation very quickly (20–25 min) with excellent yield. To test the activity of the present catalyst, a model run was carried out with thioanisole without catalyst and was found that no sulfoxidation reaction had taken place within the typical reaction time. The in situ formation of (salen)oxochromium(V) complex is responsible for the sulfoxidation reaction. This hypervalent Cr(V)=O state transfers oxygen to the substrate for the sulfoxidation (Scheme 1).
Table 1  Oxidation of Sulfides into Sulfoxides

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sulfide</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Time</th>
<th>Yield of Sulfoxide (%)&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ph</td>
<td>Me</td>
<td>Me</td>
<td>2 h</td>
<td>99</td>
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<tr>
<td>2</td>
<td>p-MeC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Me</td>
<td>Me</td>
<td>2.5 h</td>
<td>99</td>
</tr>
<tr>
<td>3</td>
<td>p-BrC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Me</td>
<td>Me</td>
<td>2.5 h</td>
<td>99</td>
</tr>
<tr>
<td>4</td>
<td>p-CIC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Me</td>
<td>Me</td>
<td>2.5h</td>
<td>98</td>
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<tr>
<td>5</td>
<td>p-NO&lt;sub&gt;2&lt;/sub&gt;C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Me</td>
<td>Me</td>
<td>4 h</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>p-CNC&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Me</td>
<td>Me</td>
<td>3.5h</td>
<td>91</td>
</tr>
<tr>
<td>7</td>
<td>Ph</td>
<td>Ph</td>
<td>Ph</td>
<td>6 h</td>
<td>94</td>
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<tr>
<td>8</td>
<td>PhCH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Ph</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>3 h</td>
<td>94</td>
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<tr>
<td>9</td>
<td>PhCH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>PhCH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>2.5 h</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Me(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Me(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>20 min</td>
<td>96</td>
<td></td>
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<tr>
<td>11</td>
<td>Me(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>Me(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;</td>
<td>20 min</td>
<td>95</td>
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<tr>
<td>12</td>
<td>Me(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;7&lt;/sub&gt;</td>
<td>Me(CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;7&lt;/sub&gt;</td>
<td>25 min</td>
<td>94</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Reagents and conditions: Cr(salen)(I)/PhIO/Sulfide/CH<sub>2</sub>Cl<sub>2</sub> = 0.1 mmol:1.1 mmol:1 mmol:3 mL.

<sup>b</sup> Isolated yield.

N,N'-Ethylenebis(3,5-di-tert-butylsaliyclideneimino)chromium(III) Chloride (1)

The new catalyst 1 was prepared analogous to the reported<sup>13a</sup> method for the unsubstituted catalyst. To a suspension of bis(3,5-di-tert-butylsalicylidene)ethylenediamine (492 mg, 1 mmol) in THF (25 mL) was added a suspension of anhyd CrCl<sub>3</sub> (246 mg, 1.2 mmol) in THF (20 mL) with vigorous stirring under N<sub>2</sub> at r.t. (ca. 20 °C) for 3 h. Then the dark brown solution was allowed to reflux in the presence of air for 3 h. The residue was suspended in H<sub>2</sub>O (30 mL) and the undissolved brown colored material was collected by filtration and washed with H<sub>2</sub>O (3 × 10 mL). After filtration and concentration of the filtrate with rotary evaporator, a brown material was precipitated on cooling overnight, which was collected and dried under reduced pressure to afford the required complex 1; yield: 90%; mp >300 °C.

IR (KBr): 2923, 1641, 1461, 1170, 836 cm<sup>-1</sup>. Anal. Calcd for C<sub>32</sub>H<sub>46</sub>ClCrN<sub>2</sub>O<sub>2</sub> (578.18): C, 66.49; H, 7.96; N, 4.8. Found: C, 66.29; H, 7.8; N, 5.2.

Oxidation of Sulfides to Sulfoxides with (Salen)Cr(III) (1)/PhIO; General Procedure

Cr(salen) 1 (58 mg, 0.1 mmol) and sulfide (1 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) and the solution was stirred for 5 min. To this solution was added PhIO (242 mg, 1.1 mmol) at once. The reaction was monitored by TLC at regular intervals and continued for reaction time mentioned in Table 1. After removal of the solvent, the residue was purified by silica gel flash chromatography (EtOAc) to afford the sulfoxide. All the sulfoxides thus obtained were identified by comparing NMR data with values reported in the literature<sup>6,14a</sup> and those of the authentic samples<sup>16</sup> (Table 1).

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References


