Ferric chloride induced catalytic cleavage of oximes and hydrazones under solvent-free conditions

D Subhas Bose,* A Venkat Narsaiah & P Ravinder Goud
Organic Chemistry Division III, Indian Institute of Chemical Technology, Hyderabad 500 007, India
Fax: +91-40-7173387, E-mail: dsb@iict.ap.nic.in
Received 8 May 2000; accepted (revised) 9 February 2001

In an solvent-free system, oximes and hydrazones are rapidly transformed into parent carbonyl compounds using ferric chloride adsorbed on silica gel under microwave irradiation in excellent yields.

Regeneration of carbonyl compounds from oximes and hydrazones is a very important transformation in synthetic organic chemistry because of their extensive application in the protection1 and purification of carbonyl compounds2 but also served as intermediates for many reactions such as the preparation of nitriles3 or amides via Beckmann rearrangement.4 As a result, several methods are available based on hydrolytic,5 reductive6 and oxidative7 reactions for the regeneration of carbonyl compounds from such as nitrogen derivatives. Many of these procedures suffer from one or the other drawbacks: toxicity of the reagents, expensive transition metals, long reaction time and difficulties in isolation of products. These limitations prompted us to investigate further new methodology for the deprotection of oximes and hydrazones using ferric chloride adsorbed on silica gel by this procedure to provide the corresponding carbonyl compounds in high yields.

Several examples illustrating this method are summarized in Table I. It is noteworthy that, unlike other oxidative hydrolytic methods, the major drawback of overoxidation of the ensuing aldehydes, is not observed under the reaction conditions. Interestingly, the α,β-unsaturated oxime underwent deoximation very efficiently without effecting the C=C bond and the reaction is essentially chemoselective. Even the sterically hindered camphor oxime has been successfully converted to camphor in good yield.

In summary, we have shown that this FeCl₃ adsorbed on Silica Gel promoted procedure provides an efficient methodology for the rapid cleavage of oximes and hydrazones and demonstrates a useful protocol for the attainment of carbonyl compounds. The other notable advantages offered by this procedure are the reduced reaction times, high yields and mild nature of ferric (III) chloride.

Oximes and hydrazones were prepared by known literature procedures. All resulting carbonyl compounds

---

Note

![Scheme 1](image)

**Scheme I**

Among various mineral supports examined, such as alumina, clay, silica etc., silica was found to give best results. The optimum ratio of the substrate to the reagent for deoximation is found to be 1:0.4 (mole/mole). The reaction remains incomplete if lower amounts of the reagent is used. The role of ferric chloride was confirmed by conducting a blank experiment, where the formation of carbonyl compound was not observed. Ferric chloride is an inexpensive and powerful oxidant used for the transformation of a wide range of functional groups. The use of recyclable silica gel support and the general applicability of this reaction to a variety of oximes and hydrazones under solvent-free conditions are other salient feature of this protocol.

---

1ICT Communication No. 4512
are known compounds; they are identified by comparison of their physical data, IR, and NMR spectra with those of authentic samples.

Ferric chloride adsorbed on silica gel was prepared as described previously.¹

### Table I — FeCl₃-SiO₂ catalyzed cleavage of oximes and hydrazones under solvent free conditions

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Time (min)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH=N-OH</td>
<td>CHO</td>
<td>0.5</td>
<td>93</td>
</tr>
<tr>
<td>2</td>
<td>CH=N-OH</td>
<td>CH=N-OH</td>
<td>0.5</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>CH=N-OH</td>
<td>CH=N-OH</td>
<td>1.0</td>
<td>85</td>
</tr>
<tr>
<td>4</td>
<td>CH=N-OH</td>
<td>CH=N-OH</td>
<td>1.2</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>CH=N-OH</td>
<td>CH=N-OH</td>
<td>1.5</td>
<td>86</td>
</tr>
<tr>
<td>6</td>
<td>CH=N-NMe₂</td>
<td>CH=N-NMe₂</td>
<td>0.6</td>
<td>89</td>
</tr>
<tr>
<td>7</td>
<td>CH=N-NMe₂</td>
<td>CH=N-NMe₂</td>
<td>1.4</td>
<td>84</td>
</tr>
<tr>
<td>8</td>
<td>CH=N-NMe₂</td>
<td>CH=N-NMe₂</td>
<td>1.5</td>
<td>90</td>
</tr>
<tr>
<td>9</td>
<td>CH=N-NHTs</td>
<td>CH=N-NHTs</td>
<td>1.8</td>
<td>92</td>
</tr>
<tr>
<td>10</td>
<td>H₂C₅N₂N₂H₃</td>
<td>H₂C₅N₂N₂H₃</td>
<td>2.2</td>
<td>82</td>
</tr>
<tr>
<td>11</td>
<td>CH=N-HPh</td>
<td>CH=N-HPh</td>
<td>1.5</td>
<td>87</td>
</tr>
<tr>
<td>12</td>
<td>CH=N-HPh</td>
<td>CH=N-HPh</td>
<td>2.5</td>
<td>91</td>
</tr>
</tbody>
</table>

¹Yields refer to isolated pure products.

Re regeneration of carbonyl compounds from oximes and hydrazones: General Procedure: A mixture of neat oxime/hydrazone (5.0 mmole) and ferric chloride supported silica gel reagent (0.6 g) was dissolved in a minimum amount of dichloromethane. After evaporation of the solvent, the dry powder was mixed thoroughly on a vortex mixer in an Erlenmeyer flask and placed in an alumina bath inside a commercial microwave oven (operating at 2450 MHz frequency) and irradiated for a period of 30 s intervals (total period of 0.5-2.5 min). After completion of the reaction (monitored by TLC) the reaction mixture was allowed to reach room temperature, treated with water and extracted with dichloromethane (4 × 5 mL). Removal of solvent and the residue on purificiation by column chromatography on silica gel gave the corresponding carbonyl compounds in 82-93% yield (Table I) and there was no evidence for the formation of any side products. It may be noted that in case of aldehydes, the crude product is filtered through a small bed of neutral alumina with dichloromethane. Moreover, most of the substrates/products decomposition occurs after a prolonged irradiation times.

### References
   (c) Bose D S & Venkat Narasiah A, Synth Commun, 30, 2000, 1153.