Microwave assisted deoximation of carbonyl compounds using aqueous hydrochloric acid

Marimuthu Anniyappan, D Muralidharan & Paramasivam T Perumal
Organic Chemistry Division, Central Leather Research Institute, Adyar, Chennai 600 020, India.

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An effective and mild hydrolytic cleavage of oximes to carbonyl compounds is the presence of aqueous hydrochloric acid in acetonitrile under microwave irradiation (MWI) results in good yields.

The protection of carbonyl compounds as oximes is of great interest to organic chemistry as they are readily prepared and highly stable compounds. Oximes are extensively used for purification and characterization of carbonyl compounds. Although quite a good number of methods are available for the conversion of oximes to carbonyl compounds, the discovery of newer, efficient and fast methods is the goal of organic chemists. Some of the methods reported earlier for deoximation of carbonyl compounds consist of oxidative and reductive reactions using various deoximation reagents such as pyridinium chlorochromate, pyridinium chlorochromate-\(\text{H}_2\text{O}\), triethylammonium chlorochromate, Raney Nickel, chromic anhydride chlorortrimethyl silane, dinitrogen tetroxide, Dowex-50, dimethyl dioxirane, \(\text{I}-\text{Bu}\text{t}	ext{yl hydroperoxide}\), ammonium persulphate-silica, Des-Martin periodinane and copper(II)-nitrate-silica.

Some of the reagents suffer from one or the other disadvantages like longer reaction times, difficulties in isolation of products, causing explosion under excessive heating during preparation and lack of ready availability. For example the deoximation of aldoximes using \(\text{NaBiO}_3\)-silica results in a complex mixture of products. A very few methods reported earlier are suitable for this conversion under mild reaction conditions.

Recently, there has been a tremendous interest in the application of microwave irradiation as a source of thermal energy in organic reactions such as Aldol-type condensation, Vilsmeier reaction, Knoevenagel condensation, preparation of aryl vinyl nitriles, rearrangement of aldehydes to nitriles due to the reduction in reaction times, operational simplicity, cleaner reactions, easier work-up and better yields. Herein we report a fast, efficient and simple method for deoximation of different aldoximes and ketoximes with aqueous hydrochloric acid (6N) in acetonitrile under microwave irradiation for 2 minutes to the corresponding carbonyl compounds in excellent yields (Scheme I). There was no evidence for the formation of any side products. The results of cleavage of several oximes by this procedure are summarized in Table I. In conclusion, we have developed a simple and convenient method for the facile hydrolytic cleavage

\[
\begin{align*}
\text{R}^1\text{C}=\text{NOH} & \text{aq. HCl (6N)} \\
& \text{CH}_3\text{CN, MWI, 2 min} \\
& \text{R}^1\text{C}=\text{O}
\end{align*}
\]

Scheme I

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Oximes</th>
<th>Products a</th>
<th>Time (min.)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Acetophenoxime</td>
<td>Acetophenone</td>
<td>2</td>
<td>83</td>
</tr>
<tr>
<td>2.</td>
<td>4-Chloracetophenoxime</td>
<td>4-Chloracetophenone</td>
<td>2</td>
<td>89</td>
</tr>
<tr>
<td>3.</td>
<td>1-Tetraloneoxide</td>
<td>1-Tetralone</td>
<td>2</td>
<td>88</td>
</tr>
<tr>
<td>4.</td>
<td>4-Methylacetophenoxime</td>
<td>4-Methylacetophenone</td>
<td>2</td>
<td>84</td>
</tr>
<tr>
<td>5.</td>
<td>4-Methylbenzaldoxime</td>
<td>4-Methylbenzaldehyde</td>
<td>2</td>
<td>74</td>
</tr>
<tr>
<td>6.</td>
<td>Cyclohexanoxime</td>
<td>Cyclohexanone</td>
<td>2</td>
<td>92</td>
</tr>
<tr>
<td>7.</td>
<td>Cycloheptanoxime</td>
<td>Cycloheptanone</td>
<td>2</td>
<td>85</td>
</tr>
<tr>
<td>8.</td>
<td>3-Nitrobenzaldoxime</td>
<td>3-Nitrobenzaldehyde</td>
<td>2</td>
<td>73</td>
</tr>
<tr>
<td>9.</td>
<td>4-Methoxybenzaldoxime</td>
<td>4-Methoxybenzaldehyde</td>
<td>2</td>
<td>68</td>
</tr>
<tr>
<td>10.</td>
<td>Benzaldoxime</td>
<td>Benzaldehyde</td>
<td>2</td>
<td>72</td>
</tr>
</tbody>
</table>

a All the products were characterized by \(^1\text{H NMR}, ^{13}\text{C NMR, IR, mass spectra and by comparison with authentic samples.}
of a variety of aldoximes and ketoximes using aqueous hydrochloric acid (6N) under microwave irradiation. The main advantages of this method include mild reaction conditions, reduced reaction times, minimisation of side products, cost effectiveness and excellent yields.

Experimental Section

General. A mixture of cyclohexanoneoxime (0.5g, 4.4 mmoles) and 5mL of aqueous hydrochloric acid (6N) in 10mL of acetonitrile taken in a conical flask was placed in a BPL-SANYO domestic microwave oven operating at 80W, with a pulse of 10 sec, each for 2 minutes. After completion of the reaction (monitored by TLC), the product was extracted with dichloromethane (3x10mL), distilled and the crude product passed through a short column of silica gel eluted with 5% ethyl acetate-petroleum ether to get the cyclohexanone in 92% yield.

Acknowledgement

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References