Microwave-assisted deoximation under solvent-free conditions using Bi(NO$_3$)$_3$·5H$_2$O supported onto montmorillonite K-10

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Oximes are oxidatively deprotected by bismuth nitrate supported onto montmorillonite K-10 to the parent carbonyl compound in high yields upon exposure to microwave irradiation in solventless system.

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The formation of oximes is a common method of isolation, protection and deprotection of carbonyl compounds. This is especially true with the isolation and purification of natural products. Hence after isolation and purification, regeneration of the carbonyl group from its derivative under mild condition is an important process in organic chemistry. There has therefore been considerable interest in the development of mild, fast and environmentally benign methods for this conversion. A number of methods have been documented for the oxidative cleavage of oximes, each has its own merits and drawbacks. Bismuth (III) nitrate-copper (II) acetate has been recently used as an oxidizing agent. Bismuth (III) nitrate supported onto montmorillonite K-10 along with Cu(OAc)$_2$ in a mixture of acetone - water has been reported as a non-toxic and inexpensive reagent for the deprotection of ketoximes. Although this reagent seems to be very promising and attractive, it suffers from the drawback of using organic solvent and long reaction time. For example, in the case of deprotection of benzil oxime it takes 21 hr.

Recently, there has been a growing interest in the application of microwave irradiation in organic synthesis enhancement in solventless system. The concept of utilizing reagents adsorbed on inert inorganic support for the rapid organic reactions under microwave irradiation have been of interest in many laboratories. In this communication, we report that bismuth nitrate supported onto montmorillonite K-10, a relative non-toxic, insensitive to small amounts of water and inexpensive reagent can efficiently and rapidly deprotect oximes under microwave irradiation in solvent free condition (Scheme I).

The reactions were carried out by exposure of well-mixed Bi(NO$_3$)$_3$·5H$_2$O, montmorillonite K-10 and oximes to microwave irradiation in specified time (Table I). The reactions proceeded smoothly providing high yields of carbonyl compounds. It should be mentioned that in the absence of mineral supports, the attempted deprotection under microwave irradiation either failed or resulted to a poor yield with bismuth (III) nitrate even after prolonged reaction periods. In view of the established beneficial effects of the reagent on solid supports, various mineral supports such as silica gel, alumina and with Bi(NO$_3$)$_3$ were examined. We explored that montmorillonite K-10 is the best support for proceeding of the clean and rapid deoximation. It is motivationally to mention, under conventional heating the reactions are sluggish. For example, benzaldehyde oxime was deoximationed partly after 10 hr in the same condition.

An additional benefit of this reaction is the selective deprotection of benzylic aldoximes and ketoximes to the corresponding carbonyl compounds. No overoxidation to carboxylic acid was observed. This method is not successful for the deoximation of aliphatic aldoximes and ketoximes. The reaction did not also work for oxime of thiophen carbaldehyde (Entry 7).

\[
\text{ArNOH} + \text{Bi(NO}_3\text{)}_3\cdot5\text{H}_2\text{O} \xrightarrow{\text{Montmorillonite K-10, MW}} \text{ArO} 
\]

Scheme I
In conclusion, deoximation with Bi(NO$_3$)$_3$.5H$_2$O supported onto montmorillonite K-10 under micro-
wave irradiation in solvent-free conditions is a rapid,
manipulatively simple and selective protocol when
compared with conventional solution phase and
heterogeneous reaction which suffer from the use of
pollutant organic solvent (acetone), Cu(OAc)$_2$, long
reaction time and moderate yields.

**Experimental Section**

A commercial microwave oven (900 W) was used
for irradiation of the reaction mixture. All products
are known compounds and identified by comparison
with authentic samples.

**General procedure for deprotection of oximes**

Montmorillonite K-10 (0.5 g) and bismuth nitrate
pentahydrate (0.2 g, 0.4 mmole) were mixed
thoroughly in a mortar and the oxime (1 mmole) was
added and mixed. The reaction mixture was
transferred to a 25 mL beaker and irradiated in a
conventional microwave oven (900 W) for the
specified time (Table I). The progress of the reaction

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**Table I — Oxidative cleavage of oxime with Bi(NO$_3$)$_3$.5H$_2$O under microwave irradiation**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate$^a$</th>
<th>Carbonyl compound $^b$</th>
<th>Reaction time (sec)</th>
<th>Yield (%)$^c$</th>
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<td></td>
<td></td>
<td>100</td>
<td>63</td>
</tr>
<tr>
<td>2</td>
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<td></td>
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<tr>
<td>7</td>
<td></td>
<td>No reaction</td>
<td>240</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ All substrates were synthesised by known literature procedure.

$^b$ All products were characterized by comparison of their m.p, IR, and $^1$H NMR spectra
with those of authentic sample.

$^c$ Yields refer to isolated products.
was monitored by GLC or TLC (hexane-AcOEt, 8:2). After completion of the reaction, the product was extracted with ether, filtered, and the solvent was evaporated under reduced pressure to yield the corresponding carbonyl compounds.

**Precaution**

Although the reactions were safe in our hands, it is advised to use the microwave oven in an efficient hood.

**Acknowledgement**

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**References**


