Regeneration of Carbonyl Compounds from Oximes under Microwave Irradiation in Solventless System

Majid M. Heravia, Dariush Ajami, Rahim Hekmatshoar, Yahya Sh. Beheshti, Karim Assadollah, and Mitra Ghassemzadeh

a Department of Chemistry, School of Sciences, Azzaahra University, Vanak, Tehran, Iran
b Chemistry & Chemical Engineering Research Center of Iran, P.O.Box 14335–186, Tehran, Iran

Reprint requests Prof. Dr. M. M. Heravi. E-mail: mmheravi@azzahra.ac.ir
Z. Naturforsch. 55b, 431–433 (2000); received December 20, 1999

Oximes, Deoximation, Carbonyl Compounds

A new, mild, efficient and environmentally benign method for the cleavage of oximes has been achieved by a simple reaction of oximes with wet alumina supported chromium(VI) oxide under microwave irradiations in solvent-free condition.

Introduction

Oximes are one of the most useful employed protecting groups [1] and are extensively used for purification of carbonyl compounds. Their synthesis from non-carbonyl compounds [2] provides an alternative pathway to aldehydes and ketones.

The important role of oximes as protecting group has inspired the development of several deoximation reagents [3] including ammonium persulfate-silica gel [4] supported sodium periodate [5], bismuth trichloride [6], Dess-Martin periodinane [7] and tributylammonium per oxydisulfate [8]. Each of these reagents has its merit and drawbacks. The importance of regeneration of carbonyl compounds from oximes assumed added after the discovery of the Barton reaction [9] in which oximes are produced at non-activated hydrocarbon sites.

In continuation of our investigation on organic manipulations in solventless system [10] we wish to report a solid state deoximation method using wet alumina supported chromium(VI) oxide. Although chromium(VI) oxide has been extensively used for oxidative purposes to the best of our knowledge its use in oxidative deoximation has not been reported.

Results and Discussion

We have recently reported the use of wet alumina supported chromium(VI) oxide as a mild, efficient and inexpensive reagent for oxidative de-protection of trimethylsilyl and tetrahydropyranyl ethers [11]. Armed with these experiences and considering the salient features of solvent free reaction under microwave irradiations [12] we attempted the oxidative deoximation with supported chromium(VI) oxide under these condition.

Among various mineral supports used such as silica, clay, and alumina, alumina was found to give the best results. Surprisingly moistening of the alumina improved the yield drastically. The reaction is conducted by mixing finely ground wet alumina-chromium(VI) oxide with neat oximes. We discovered that in the absence of alumina the reactions do not proceed and in the presence of dry alumina the reactions are sluggish and a considerable amounts of oximes are recovered unchanged at elevated temperature or on exposure to microwave irradiation for an extented period of time. By using wet alumina-chromium(VI) oxide in all cases the reactions are completed by simple mixing and exposure to microwave irradiation. The reactions are relatively clean with no tar formation typical of some CrO3 oxidations.

The irradiation of ketoximes with this reagent afforded carbonyl compounds and did not result in the formation of Beckmann rearranged products [13]. The optimum ratio of the substrate to the reagent for cleavage of oximes was found to be 1:3 (mole/mole). The reactions remained incomplete when lower amounts of oxidant were used. Using conventional heating (oil bath) at 100 °C the reaction can be completed in 24 hours.
Interestingly in these reactions no overoxidation to carboxylic acids was observed. To assess the generality of method several oximes were oxidatively deoximated by this method (Table).

**Experimental**

All compounds employed are known and were identified by comparison of their physical data with those of authentic samples. Yields refer to isolated products.

**Wet Alumina supported chromium(VI) oxide**

Neutral aluminum oxide (10 g, Aldrich, Brockmann I-150 mesh) was shaken with distilled water (2 ml). This mixture (2.4 g) was mixed with CrO$_3$ (0.8 g, 8 mmol) using a pastle and mortar.

**Oxidative deoximation. General procedure**

In a beaker, neat oxime (1 mmol) was mixed thoroughly with the above catalyst (3 mmol) using a spatula. The beaker was placed in a household microwave oven and kept at 900 Watt for the specified time. After the completion of the reaction (confirmed by TLC, hexane:EtOAc 8:2) the product was extracted to CH$_2$Cl$_2$ (2x20 ml) and passed through a small bed of alumina (1 cm) to afford the corresponding carbonyl compound (Table).

**Acknowledgement**

The financial support for this research from the research council of Azzahra University is gratefully acknowledged.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Carbonyl compound</th>
<th>Reaction time (sec.)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Image 1" /></td>
<td>40</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Image 2" /></td>
<td>40</td>
<td>85</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Image 3" /></td>
<td>40</td>
<td>83</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Image 4" /></td>
<td>40</td>
<td>82</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5.png" alt="Image 5" /></td>
<td>40</td>
<td>85</td>
</tr>
<tr>
<td>6</td>
<td><img src="image6.png" alt="Image 6" /></td>
<td>40</td>
<td>84</td>
</tr>
<tr>
<td>7</td>
<td><img src="image7.png" alt="Image 7" /></td>
<td>40</td>
<td>82</td>
</tr>
</tbody>
</table>

Table. Solid state deoximation using wet alumina-CrO$_3$ under microwave irradiation.

a) All substrates were synthesized by known literature procedure.
b) All products were characterized by comparison of their mp., IR and $^1$H NMR spectra with those of an authentic sample.
c) Yields refer to isolated products.
   b) C. G. Rao, A. S. Radhakrishna, B. B. Singh, S. P. Bhalnagar, Synthesis 808 (1983);
   c) S. B. Skim, K. Kim, Y. H. Kim, Tetrahedron Lett. 28, 645 (1987);
   d) J. R. Meloney, R. E. Lyle, J. E. Saavedra, G. G. Lyle, Synthesis 212(1978);
   e) O. A. Olah, O. Liao, C. S. Lee, G. K. Surya Prakash, Synlett 427(1993);
   f) R. Josef, A. Sudalai, T. Ravendranathan, Tetrahedron Lett. 35, 5493(1994);
   g) M. Curini, O. Rosati, E. Pisani, Synlett 333(1996);
   b) M. M. Heravi, D. Ajami, Monatsh. Chem. 130, 709(1999);
   c) M. M. Heravi, D. Ajami, M. M. Mojtabahi, M. Ghassemzadeh, Tetrahedron Lett. 40, 561 (1999);
   d) M. M. Heravi, D. Ajami, M. Ghassemzadeh, Synth. Commun. 29, 1013 (1999);