Microwave-Assisted Oxidation of Alcohols Using Wet Alumina Supported Ammonium Chlorochromate in Solventless System

Majid M. Heravi* and Maryam M. Aghayan

Chemistry and Chemical Engineering Research Center of Iran. P.O. Box 14335-186, Tehran, Iran. Fax: 0098(21) 8037185, E-mail: CCERCI@neda.net.ir

Z. Naturforsch. 54b, 815–817 (1999); received December 2, 1998

Oxidation. Alcohols, Carbonyl Compounds, Wet Alumina, Solventless System, Ammonium Chlorochromate

A simple and selective method for the oxidation of alcohols to carbonyl compounds is described that occurs on wet alumina supported ammonium chlorochromate under microwave irradiation in solventless system.

The oxidation of alcohols to carbonyl compounds is an important transformation in organic synthesis and several methods have been explored to accomplish this conversion [1]. Chromium based reagents have been extensively used in organic synthesis [2]. The utility of chromium (VI) reagents in the oxidative transformation is compromised to their inherent toxicity, cumbersome preparation and potential danger (ignition or explosion) in handling of its complexes difficulties in terms of product isolation and waste disposal. Introduction of reagents [3] on solid supports has circumvented some of these problems and provided an attractive alternative in organic synthesis in view of selectivity and associated ease of manipulation. Therefore it is not surprising that a large number of chromium (VI) based oxidants impregnated on solid support have been explored [4a–i]. Ammonium chlorochromate adsorbed on silica gel in an aprotic solvent oxidizes primary and secondary alcohols [5]. However these reactions under inert atmosphere require 2–4 h for completion [5].

The microwave (MW) enhanced chemical reaction [6, 7] in general and on organic solid supports [8, 9] in particular have gained popularity over the usual homogenous and heterogeneous reactions and they can be conducted rapidly and provide pure products in quantitative yields without use of solvent. Since only the polar reactants adsorbed on the surface of the solid supports absorb microwaves a variety of reagents supported on such surfaces [10, 11] can be utilized for the enhancement of organic reactions using an unmodified household MW oven [6] or continuous microwave reactor for large scale reactions [12].

In continuation of our investigations on organic reactions in solventless system [13–15], we now report a facile and selective oxidation of alcohols to carbonyl compounds using ammonium chlorochromate-wet alumina under solvent free conditions which is accelerated by exposure to microwaves.

The reagent is easily prepared by addition of a weighted aluminium oxide to a solution of ammonium chlorochromate in water and rotary evaporating to dryness. The adsorbed reagent is remarkably effective in oxidizing alcohols to corresponding carbonyl compounds. Interestingly we discovered that in the absence of wet alumina the reactions are slow and considerable amounts of alcohols recovered unchanged.

In few cases the reactions are completed upon simple mixing at ambient temperature and gentle warming but in most cases exposure to microwave irradiation accelerates the reaction (Table).

The reactions are relatively clean with no tar formation typical of many CrO₃ oxidation. No overoxidation to carboxylic acid was observed in the case of primary alcohols. Cinamyl alcohol was converted to cinammaldehyde almost quantitatively showing carbon-carbon double bonds are not prone to cleavage with this reagent.

In conclusion, wet alumina supported ammonium chlorochromate solvent free microwave thermolysis is a convenient, selective and environmentally benign oxidative protocol when com-
Table. Oxidation of alcohols by wet alumina supported ACC under microwave irradiation.

<table>
<thead>
<tr>
<th>Entry</th>
<th>R&lt;sup&gt;1&lt;/sup&gt;</th>
<th>R&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Mole ratio Alcohol/Reagent</th>
<th>Time min</th>
<th>Yield %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>H</td>
<td>1/2</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>4-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>H</td>
<td>1/2</td>
<td>80</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1/2</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1/2</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;CH=CH-</td>
<td>H</td>
<td>1/3</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>C&lt;sub&gt;7&lt;/sub&gt;H&lt;sub&gt;15&lt;/sub&gt;</td>
<td>H</td>
<td>1/1.3</td>
<td>95</td>
<td></td>
</tr>
</tbody>
</table>

Prepared to the conventional solution phase or heterogeneous reactions.

**Experimental**

All products are known compounds and their physical data were essentially identical with those of authentic samples. Yields are based on GLC analysis using a Fisson 8000 a gas chromatograph with a flame ionization detector (with a column 10% carbowax 20 N on chromsorb W/A, 1.8 M×6 mm). Microwave irradiation were carried out in a National oven Model 6755 at 900 W.

**Preparation of alumina supported ammonium chlorochromate**

Neutral aluminium oxide (5 g; Aldrich Brockmann, 150 mesh) was added to the mixture of CrO<sub>3</sub> (1 g; 0.01 mole) and NH<sub>4</sub>Cl (0.53 g; 0.01 mol) in water (2.5 ml) was added at 40 °C. The orange solid was precipitated after 15 min which were filtered off and dried at 70 °C.

**Oxidation of alcohols to carbonyl compounds using wet alumina supported ACC**

In a watch glass, neat alcohol (1 mmol) was mixed with the above catalyst (2 mmol) using a spatula. This reaction mixture was placed in microwave oven and irradiated. An exothermic reaction ensues with darkening of the orange color of the reagent. The completion of the reaction is confirmed by TLC or GC. The product is extracted into hexane (2×10 ml) and is passed through a small bed of silica gel to afford the corresponding carbonyl compounds (Table).


   b) A. McKillop, D. W. Young, Synthesis 1979, 401 and 481;

   b) J. M. Lalancette, G. Rollin, P. Dumas, J. Can Chem. 50, 3058 (1972);
   c) G. Cainelli, G. Cardillo, M. Orena, S. Sandri, J. Am. Chem. Soc. 98, 6737 (1976);
   d) S. Filippo, C. I. Chern, J. Org. Chem. 42, 2182 (1977);
   e) E. Satiniello, F. Ponti, A. Manzocchi, Synthesis 1978, 534;
   f) J. D. Lou, Y. Y. Wu, Chem. Ind. 1987, 531;
   g) Y. S. Cheng, W. L. Liu, S. H. Chen, Synthesis 1980, 223;
   i) T. Brunelet, C. Jouitteau, G. Gellbard, J. Org. Chem. 51, 4016 (1986);


[6] For recent reviews on microwave-assisted chemical reactions, see a) R. A. Abramovich, Org. Prep. Proced. Int. 23, 683 (1991);
   c) G. Majetich, R. Hicks, J. Microwave Power Electromagn. Energy 30, 27 (1995);
   d) S. Caddick, Tetrahedron 51, 10403 (1995);

   b) R. S. Varma, A. K. Chatterjee, M. Varma, Tetrahedron Lett. 34, 4603 (1993);


   b) R. S. Varma, J. Org. Chem. 61, 6360 (1996);
   c) A. Cornélie, P. Laszlo, Synthesis 1985, 909;

    b) A. Cornélie, P. Laszlo, Synthesis 1985, 909;


