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Solid State Deoximation with Clay Supported Ammonium Chlorochromate: Regeneration of Carbonyl Compounds Using Microwaves in a Solventless System

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Summary. Ammonium chlorochromate adsorbed on montmorillonite K-10 rapidly regenerates carbonyl compounds from their corresponding oximes under microwave irradiation and solvent-free conditions.

Keywords. Deoximation; Ammonium chlorochromate; Montmorillonite; Carbonyl compounds.

Introduction

Oximes which are easily obtained from carbonyl compounds have significant potential as intermediates in organic synthesis [1]. They are also useful protecting groups [2] and extensively used for purification of carbonyl compounds. Since oximes can also be prepared from non-carbonyl compounds [3], their efficient deoximation can be considered as an alternative pathway to aldehydes and ketones. The important role of oximes as protective groups owing to their hydrolytic stability has provided motivation for the search of new deoximation reagents. However, only a limited number of methods is available for the regeneration of aldehydes and ketones from the corresponding oximes under mild reaction conditions [4].

The hydrolytic stability of oximes has inspired the investigation of several deoximation reagents, *e.g.* trimethylammonium chlorochromate [5], dinitrogen tetroxid [6], pyridinium chlorochromate [7], chromium trioxide-chlorotrimethylsilane [8], clay-supported ferric nitrate [9], titanium silicate [10], *tert*-butylhydroperoxide [11], N-haloamides [12], manganese triacetate [13], activated MnO_2 [14], sodium periodate-silica [15], bismuth trichloride [16], ammonium persulfate-silicagel [17], *Dess-Martin* resiodinane [18], and tetrabutylammonium peroxydisulfate [19]. Each of the above reagents has its own merits and some drawbacks.

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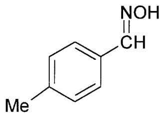
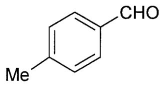
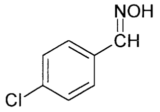
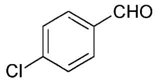
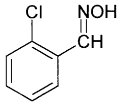
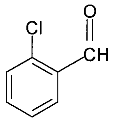
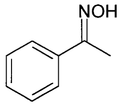
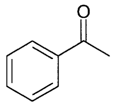
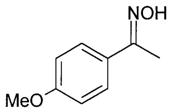
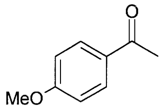
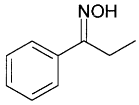
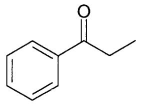
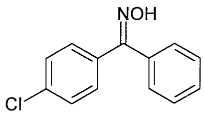
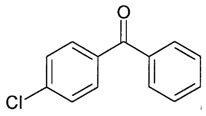
Reagents adsorbed on mineral supports have gained popularity in organic synthesis due to their selectivity and ease of manipulation [20]. Montmorillonite clays have been extensively used as efficient support for a variety of organic reactions [21].

Recently we have used clay supported ammonium chlorochromate as an efficient reagent for the oxidation of alcohols to the corresponding carbonyl compounds [22]. In continuation of our ongoing program to develop the use of surface active catalysts along with the development of environmentally benign synthetic protocols utilizing microwave irradiation under solvent free conditions [23], we here report the use of clay supported ammonium chlorochromate as a new catalyst for the cleavage of oximes under microwave irradiation in the solid state.

Table 1. Substrates and products from reactions with *AAC* supported on montmorillonite K-10 under microwave irradiation

Entry	Substrate[a]	Carbonyl compound[b]	Reaction time (s)	Yield[c] (%)
1			60	90
2			120	88
3			360	90
4			120	94
5			120	90
6			360	80
7			360	80

[a] All substrates were synthesized according to known literature procedures; [b]All products were characterized by comparision of their melting points, IR, and ^{1}H NMR spectra with those of authentic samples; [c]Yields refer to isolated products

Results and Discussion

Heating chromium trioxide and ammonium chloride in water at 40°C results in a nearly homogeneous soloution [24]. Ammonium chlorochromate (*ACC*) supported on montmokrillonite K-10 was conveniently prepared by simply adding montmorillonite K-10 to such a solution [22].

The deoximation reactions were carried out by mixing 2 equivalents of *ACC* supported on montmorillonite K-10 with a neat oxime in a beaker under microwave irradiation for 2 min. For example, benzaldoxime (Table 1, entry 1) was oxidatively deoximated to benzaldehyde in almost quantitative yield. The reaction remained incomplete when lower amounts of the supported oxidant were used or in the absence of montmorillonite K-10, even after prolonged exposure to microwaves (10 min). Moreover, in the absence of support molten ammonium chlorochromate adhered to the walls of reaction vessel, forming an intractable solid mass which made the isolation of carbonyl compounds difficult and led to erratic results. Among various mineral supports examined such as alumina, silica gel, clays, *etc*., montmorillonite K-10 was found to give the best results. To assess the generality of this solid state deoximation, a variety of oximes (Table 1) were reacted yielding the corresponding carbonyl compounds in high yields at very short reaction times. Using an alternate heating mode (oil bath, 100°C) the reaction needed 24 h for completion. Another attractive feature of this method is the recyclability of montmorillonite K-10. After washing off the support, the clay can be recycled for further use.

In conclusion, the present procedure for the deoximation and regeneration of carbonyl compounds has advantages over previously reported methods and provides a facile, useful, and important addition to the existing methodologies. The advantages of this procedure are mild reaction conditions, excellent yields, minimization of side products, and short reaction times.

Experimental

Yields refer to pure products, characterized by their known spectroscopic data. Montmorillonite K-10 was dried and simultaneously activated in a microwave oven for 5 min at 900 W prior to use. *ACC*/montmorillonite K-10 was prepared according to a reported procedure [22].

Deoximation of oximes (general procedure)

Ammonium chlorochromate supported on montmorillonite K-10 (2.6 mmol) was mixed with the neat oxime (1.6 mmol) in a small beaker. The beaker was placed inside a microwave oven operating at full power (900 W) for the indicated time (Table 1). After completion of the reaction (monitored by TLC), the product was extracted with CH_2Cl_2. The filtrate was evaporated to dryness, and the residue was passed through a small bed of silica gel to afford the corresponding carbonyl compounds after removal of the solvent.

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