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Clay Supported *Bis*-(trimethylsilyl)-chromate: An Efficient Reagent for Oxidative Deoximation

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Summary. A convenient method for the direct conversion of oximes to carbonyl compounds upon treatment with clay supported *BTSC* under classical heating as well as microwave irradiation in a solvent-free system is described.

Keywords. Oxidative deoximation; Clay supported *BTSC*; Microwave irradiation.

Introduction

Selective protection and deprotection of functional groups is of great importance in synthetic organic chemistry. In the last decade oximes have received much attention, being not only used to purify and isolate carbonyl compounds, but also to protect and activate carbonyl groups [1]. Since oximes can also be prepared from noncarbonyl compounds [2], an efficient method of deoximation can be considered as an alternative pathway to aldehydes and ketones.

The hydrolytic stability of oximes has inspired the development of several reagents, e.g. trimethylammonium chlorochromate [3], dinitrogen tetroxide [4], pyridinium chlorochromate [5], chromium trioxide-chlorotrimethylsilane [6], clay supported ferric nitrate [7], titanium silicate [8], *tert*-butylhydroperoxide [9], N-haloamides [10], manganese triacetate [11], activated MnO_2 [12], sodium periodate-silica [13], bismut trichloride [14] ammonium persulfate-silica gel [15], *Dess-Martin* periodinane [16], and tetrabutylammonium peroxydisulfate [17]. Each of the above reagents has its own merits and drawbacks.

Reagents deposited on mineral supports have gained popularity in organic synthesis due to their selectivity and ease of manipulation [18]. Montmorillonite clays have been extensively used as efficient supports for a variety of organic reagents [18]. Recently we have used supported *bis*-(trimethylsilyl)-chromate (*BTSC*) as an efficient and versatile reagent in organic synthesis [19]. In continuation of our program devoted to the development of surface active catalysts [20] along with environmentally benign synthetic protocols utilizing microwave

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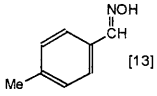
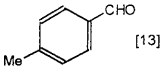
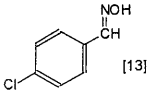
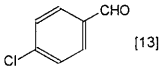
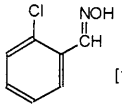
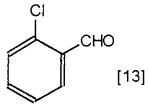
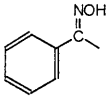
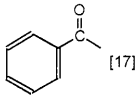
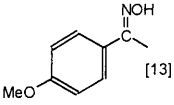
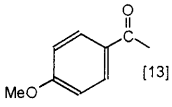
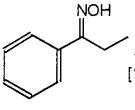
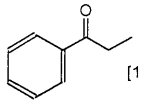
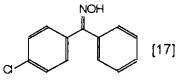
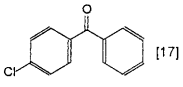
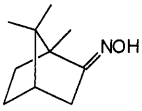
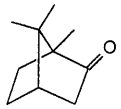
irradiation under solvent-free conditions [21], we report a facile and high-yield deoximation procedure catalyzed by clay supported *bis*-(trimethylsilyl)-chromate at room temperature and under microwave irradiation in a solventless system.

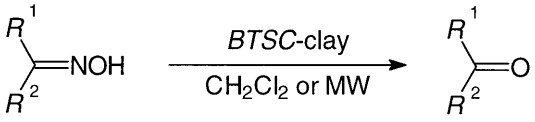
Results and Discussion

In a typical reaction, 1–1.2 equivalents of *BTSC* supported on montmorillonite K10 were added to a stirred solution of oxime in dry CH_2Cl_2 (Scheme 1). The mixture was stirred at room temperature until the reaction was complete; then it was filtered and washed with dichloromethane. Evaporation of the solvent gave the

Table 1. Oxidative cleavage of oximes with clay supported *BTSC* in CH_2Cl_2

Substrate[a]	Carbonyl compound[b]	Reaction time min	Yield[c] %
 [13]	 [13]	40	90
 [13]	 [13]	40	87
 [13]	 [13]	40	88
 [17]	 [17]	40	86
 [13]	 [13]	40	89
 [17]	 [17]	40	87
 [17]	 [17]	40	87
 [9]	 [9]	100	84

[a] All substrates were synthesized by known literature procedures; [b] all products were characterized by comparison of their m.p. as well as their IR and ^{1}H NMR spectra with those of authentic samples; [c] yields refer to isolated products

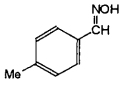
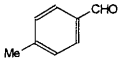
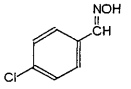
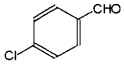
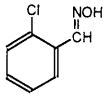
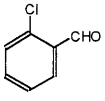
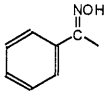
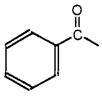
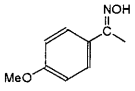
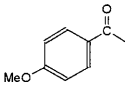
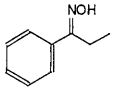
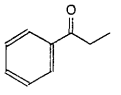
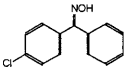
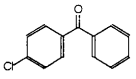
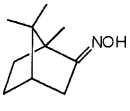
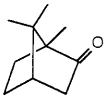


Scheme 1

corresponding carbonyl compounds. Several examples illustrating this method are summarized in Table 1.

In connection with our interest in using microwaves to increase the reaction rates [21], the above deoximation was performed under microwave irradiation in a solventless system by mixing 1–1.2 equivalents of *BTSC*-clay with 1 equivalent of an oxime in a beaker and irradiating for 2 min. It is noteworthy to mention that in the absence of clay in both cases the reactions were seriously sluggish and,

Table 2. Solid state deoximation using *BTSC*-clay under microwave irradiation[a]

Substrate	Carbonyl compound	Reaction time (min)	Yield (%)
		60	93
		60	91
		60	90
		60	89
		60	90
		60	91
		60	92
		240	88

[a] For comments, cf. footnotes to Table 1

moreover, in the latter case molten *BTSC* adhered to the walls of the reaction vessel, forming an intractable solid mass which made the isolation of carbonyl compounds difficult and led to erratic results. To assess the generality of this solid state deoximation, a variety of oximes were reacted under these conditions affording the corresponding carbonyl compounds in high yield and very short reaction times (Table 2).

In conclusion, *BTSC* supported onto montmorillonite K10 is a simple and inexpensive reagent for the oxidative deoximation of oximes at room temperature both in solution and under solvent-free conditions using a household microwave oven. Solvent-free microwave irradiation is advantageous over conventional heating, offering a practical and environmentally benign protocol, decreasing reaction times and, in some cases, giving cleaner reactions and easier work-up.

Experimental

All products are known compounds and identified by comparision with authentic samples. *BTSC* supported on clay was prepared according to the procedure of Ref. [19b].

General procedure for the oxidative cleavage of oximes

To a solution of 10 mmol oxime in 20 cm^3 CH_2Cl_2, 8 g *BTSC* supported on montmorillonite K10 (corresponds to 11 mmol CrO_3) were added. The reaction mixture was stirred at room temperature for 10 min. The progress of the reaction was monitored by TLC (eluent: light petrol ether:ethyl acetate = 8:2). The mixture was filtered, and the solid material was washed with 20 cm^3 CH_2Cl_2. The filtrate was evaporated to dryness, and the crude material was purified on a silica gel pad to afford the corresponding carbonyl compound (Table 1).

Deoximation of oximes with BTSC supported on clay under microwave irradiation in a solventless system

BTSC supported on 1.7 g montmorillonite K10 (corresponding to 2.2 mmol of CrO_3) and 2 mmol oxime were crushed together in a mortar to form an intimate mixture. The mixture was transferred to a beaker and placed under microwave irradiation for the time indicated. The progress of the reaction was monitored by TLC. After completion of the reaction, the residue was taken up with CH_2Cl_2, filtered, washed with 10 cm^3 CH_2Cl_2, and the filtrate was evaporated to dryness. Final purification was achieved by passing the residue through a silica gel pad (Table 2).

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