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N-Methylpiperidinium Chlorochromate Adsorbed on Alumina: A New Deoximation Reagent

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Summary. N-Methylpiperidinium chlorochromate adsorbed on alumina was found to be an efficient and selective reagent for the mild oxidative cleavage of oximes.

Keywords. N-Methylpiperidinium chlorochromate; Deoximation; Supported reagent; Carbonyl compounds.

Introduction

Oximes are easily obtained from carbonyl compounds and have great potential as intermediates in organic synthesis [1]. They are also useful protecting groups in multistep organic syntheses [2] and have found extensive application in the isolation and purification of carbonyl compounds [3]. Their synthesis from non-carbonyl compounds offers an alternative route to aldehydes and ketones [4, 5]. Oximes are hydrolytically stable, and this advantage has inspired the development of several reagents for their oxidative cleavage. In recent years reagents such as trimethylammonium chlorochromate [6], pyridinium chromate-hydrogen peroxide [5], triethylammonium chlorochromate [7], chromic anhydride-chlorotrimethylsilane [8], bismuth trichloride [9], sodium periodate supported on wet silica [10], activated MnO_2 [11], Ti_3HP [12], *Des-Martin* periodinane [13], and tetrabutyl ammonium peroxydisulfate [14] have been reported. Reagents impregnated on mineral solid supports [15, 16] have gained popularity in modern organic synthesis [17]; accordingly, deoximation reactions using solid supports have also been developed [18, 19].

We have recently reported that N-methylpiperidinium chlorochromate adsorbed on alumina is a selective reagent for the oxidation of benzylic alcohols to the corresponding carbonyl compounds [20] as well as that deoximation reactions on solid supports proceed under eco-friendly conditions [21–23]. Armed with these

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experiences, a method for the cleavage of oximes under mild conditions seemed to be at hand.

In this communication we report on N-methylpiperidinium chlorochromate adsorbed on alumina as a new reagent for the cleavage of oximes under non-aqueous conditions.

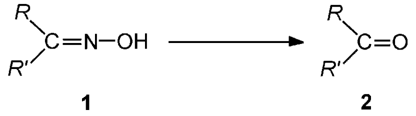
Results and Discussion

In a typical procedure, acetophenone oxime and N-methylpiperidinium chlorochromate supported on alumina were refluxed in dioxane. The progress of the reaction was monitored by TLC using $CHCl_3$:$CCl_4 = 3:1$ as eluent. Filtration, removal of the solvent, and purification of the residue by column chromatography on silica gel afforded acetophenone in almost quantitative yield. Using the reagent without mineral support results in a sluggish reaction, and considerable amounts of starting material are present even after prolonged reaction times. Among various supports (silica gel, montmorillonite K-10, zeolite), alumina was found to give the best results.

To assess the generality of the method, a variety of oximes were treated with this reagent under the same conditions to afford the corresponding carbonyl compound in high to excellent yields (Table 1).

In conclusion, the described procedure has advantages over previously reported methods and provides a facile, useful, and important addition to the existing methodologies. The notable advantages are mild reaction conditions, easy work-up, excellent yields, and minimization of side products.

Table 1. Deoximation with N-methylpiperidinium chlorochromate adsorbed on alumina



Substrate	*R*	*R'*	Product	Reaction time / min	Yield[a] / %
1a	H	Ph	**2a**	30	92
1b	H	4-Cl-Ph	**2b**	60	90
1c	H	2-Cl-Ph	**2c**	40	92
1d	H	4-Me-Ph	**2d**	40	90
1e	Me	Ph	**2e**	60	92
1f	Me	4-OMe-Ph	**2f**	60	90
1g	Ph	Ph	**2g**	80	82
1h	Ph	4-Cl-Ph	**2h**	85	71

[a] Yields refer to isolated and purified products

Experimental

Yields refer to pure isolated products. All compounds are known and were characterized by comparison of their physical and spectroscopic data with those of authentic samples. N-Methylpiperidinium chlorochromate was synthesized according to a reported procedure [20].

Conversion of acetophenone oxime to acetophenone; typical procedure

In a round bottomed flask (50 cm^3) equipped with a condenser and magnetic stirrer, a mixture of 0.315 g acetophenone (1 mmol) in 10 cm^3 dioxane was prepared. N-methylpiperidinium chlorochromate supported on alumina (1 g, prepared by mixing 0.5 g of reagent and 0.5 g of alumina) was added to this solution and refluxed for 60 min. Reaction progress was monitored by TLC (eluent: $CHCl_3$:$CCl_4 = 3:1$). After completion of the reaction the mixture was filtered, and the solid material was washed with 10 cm^3 dioxane. The filtrates were combined and evaporated. The resulting crude material was further purified on a silica gel column with an appropriate eluent to afford the corresponding carbonyl compound (Table 1).

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