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Ammonium Chlorochromate Adsorbed on Montmorillonite K-10: Oxidative Deprotection of Tetrahydropyranyl Ethers Using Microwaves in a Solventless System

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Summary. Tetrahydropyranyl ethers were rapidly and selectively oxidized to the corresponding carbonyl compounds by clay supported ammonium chlorochromate under solvent free conditions using microwaves.

Keywords. Ammonium chlorochromate; Montmorillonite; Tetrahydropyranyl ethers; Microwave.

Introduction

Introduction and removal of protective groups constitute important processes in the synthesis of polyfunctional molecules including the total synthesis of natural products [1]. Tetrahydropyranylation of hydroxy groups has been recognized as a useful and representative method for the protection of alcohols and phenols due to the remarkable stability of tetrahydropyranyl (*THP*) ethers under a variety of conditions such as strongly basic media, *Grignard* reagents, and oxidation and reduction by inorganic hydrides [2]. Many catalysts have already been proposed for the tetrahydropyranylation of alcohols and the cleavage of *THP* ethers to their parent alcohols [3]. However, there are only few reports dealing with the direct oxidation of *THP* ethers to the corresponding carbonyl compounds [4]. Montmorillonite K-10 clay has been widely used as a catalyst for a variety of acid catalyzed organic reactions [5] and as a mineral solid support [6].

Recently, there has been a growing interest in employing reagents impregnated on mineral supports using microwaves in dry media [7]. Organic solvents are not only expensive, but often also flammable, toxic, and environmentally hazardous. In addition, solvent free reactions under microwave irradiation are especially appealing as they provide an opportunity to work in open vessels and on a large scale [8].

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Montmorillonite K-10 supported ammonium chlorochromate has been used for the oxidation of alcohols to carbonyl compounds [9]. In continuation of our ongoing efforts to develop environmentally benign solventless methods using solid supports and microwave activation [10], we envisioned the applicability of montmorillonite K-10 supported ammonium chlorochromate for the oxidative deprotection of *THP* ethers under solvent free conditions using microwaves. Herein we report our results.

Results and Discussion

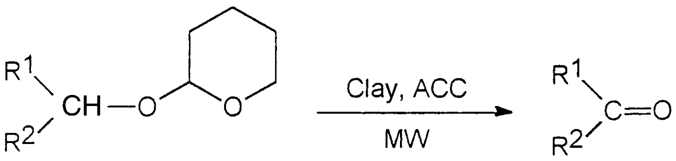
Ammonium chlorochromate adsorbed on montmorillonite K-10 was prepared according to a previously reported procedure [9]. Among the various solid supports examined such as alumina, zeolites, or silica gel, montmorillonite K-10 was found to work best. The reaction was performed by mixing the finely ground supported reagent with neat *THP* ethers. This mixture was irradiated with microwaves to afford the desired compounds in a very fast reaction in excellent yields (Table 1, Scheme 1). It is noteworthy to mention that in the absence of clay the reaction is very sluggish, and considerable amounts of alcohols are recovered unchanged even after extended microwave irradiation. Moreover, in the absence of support the isolation of products from the ensuing residues is difficult.

The oxidative deprotection of benzyltetrahydropyranyl ether is representative of the general procedure employed. Montmorillonite K-10 supported ammonium chlorochromate mixed with benzyltetrahydropyranyl ether was irradiated to afford exclusively benzaldehyde in 94% yield within 20 s. An over-oxidation to the corresponding carboxylic acid was not observed. The same reaction in solution requires heating to 50°C for a period of 1 h.

In conclusion, the present methodology offers an attractive, fast, effecient, and environmentally friendly procedure for the direct oxidative cleavage of *THP* ethers to the corresponding carbonyl compounds.

Table 1. Oxidative deprotection of *THP* ethers with montmorillonite K-10 supported ammonium chlorochromate under microwave irradiation in a solventless system

Substrate	Reaction time / sec	Product	Yield / %
$PhCH_2O$*THP*	20	PhCHO	94
$4\text{-}MeC_6H_4CH_2O$*THP*	20	$4\text{-}MeC_6H_4CHO$	92
$2\text{-}NO_2\text{-}5\text{-}Me\text{-}C_6H_3CH_2O$*THP*	50	$2\text{-}NO_2\text{-}5\text{-}MeC_6H_3CHO$	80
PhCH(Me)O*THP*	50	PhCOMe	88
$PhCH{=}CHCH_2O$*THP*	100	PhCH=CHCHO	78
PhCH(O*THP*)Ph	100	PhCOPh	88
Cyclohexanol-*THP*	120	Cyclohexanone	89
2-Methylcyclohexanol-*THP*	120	2-Methylcyclohexanone	90
Benzoin-*THP*	120	Benzil	88
(−)-Menthol-*THP*	100	(−)-Menthone	85



Scheme 1

Experimental

Ammonium chlorochromate supported on montmorillonite K-10 was prepared by a reported method [9]. Yields refer to isolated products. The obtained compounds were identified by comparison of their physical data with authentic samples. *THP* ethers were prepared according to described procedures [3b].

Oxidative deprotection of tetrahydropyranyl ethers; general procedure

Montmorillonite K-10 supported ammonium chlorochromate was thoroughly mixed with 0.192 g benzyltetrahydropyranyl ether (1 mmol), and the mixture was placed in a beaker inside a microwave oven (900 W) for 20 sec. After completion of the reaction as monitored by TLC (hexane:AcOEt = 8:2) the product was extracted with CH_2Cl_2, the solvent was removed, and the residue was chromatographed over silica gel using hexane:AcOEt (8:2) to afford 94% benzaldehyde.

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