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Clay Supported *Bis*(trimethylsilyl)chromate: Oxidative Deprotection of Tetrahydropyranyl Ethers under Solvent-Free Conditions using Microwaves

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Summary. Tetrahydropyranyl ethers are rapidly and selectively oxidized to the corresponding carbonyl compounds by montmorillonite K-10 supported *bis*(trimethylsilyl)chromate under solvent-free conditions using microwaves.

Keywords. Clay supported reagent; Oxidation; Deprotection; Dehydropyranylation.

An Ton adsorbiertes *Bis*(trimethylsilyl)chromat: Oxidative Entschützung von Tetrahydropyranylethern unter lösungsmittelfreien Bedingungen und Bestrahlung mit Mikrowellen

Zusammenfassung. Tetrahydropyranylether werden rasch und selektiv durch an Montmorillonit K-10 adsorbiertes *Bis*(trimethylsilyl)chromat unter lösungsmittelfreien Bedingungen und Einwirkung von Mikrowellen oxidativ zu den entsprechenden Oxoverbindungen gespalten.

Introduction

The protection of certain functional groups and the deprotection of the protected derivatives constitute important processes in the synthetic chemistry of polyfunctional molecules including the total synthesis of natural products. The tetrahydropyranyl group is one of the most useful protective groups for alcohols in multi-step organic synthesis [1], and considerable efforts have been made for the development of new methods for their introduction and removal [2–17]. However, there are only few reports dealing with the direct oxidation of tetrahydropyranyl ethers to the corresponding carbonyl compounds [18, 19]. Consequently, there is a need to develop and introduce new methods and reagents for this transformation.

The use of supported reagents [20] has attracted interest because of improved selectivity, reactivity, and associated ease of manipulation. Since polar reactants adsorbed on the surfaces of various mineral carriers absorb microwave energy, a variety of reagents supported on such surfaces can be utilized for the enhancement

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of organic reactions using a simple microwave (MW) oven [21, 22]. Microwave enhanced chemical reactions, especially on inorganic solid supports and under solvent-free conditions [20e, 21] have attracted attention recently. They offer several advantages over conventional homogeneous and heterogeneous reactions with respect to high reaction rates and yields.

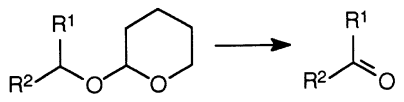
Results and Discussion

Montmorillonite K-10 supported *bis*(trimethylsilyl)chromate has been used for the oxidation of a variety of compounds [23, 24]. We report herein a direct oxidative deprotection of tetrahydropyranyl ethers to carbonyl compounds using montmorillonite K-10 supported *bis*(trimethylsilyl)chromate under solvent free conditions and accelerated by microwave irradiation. We examined various mineral supports such as clays, silica gel, or alumina and found that montmorillonite K-10 provides the best results in terms of formation of pure products. The yields are much higher than those reported for related reactions [18, 19]. In the absence of support, the reaction is very slow, the yield is low, and the isolation of products from the ensuing residues is difficult. The procedure involves simple mixing of neat tetrahydropyranyl ethers with montmorillonite K-10 supported *bis*(trimethylsilyl)-chromate and irradiating the mixture in a MW oven for 20–120 sec in the solid state. The results of this rapid direct oxidative deprotection protocol are summarized in Table 1.

The oxidative deprotection of benzyltetrahydropyranyl ether is representative of the general procedure employed. Montmorillonite K-10 supported *bis*(trimethylsilyl)chromate mixed with benzyltetrahydropyranyl ether was irradiated to afford exclusively benzaldehyde. An overoxidation to carboxylic acid was not observed. The same reaction could be completed in 1 h at a comparable temperature of 55°C in an oil bath.

Table 1. Oxidative deprotection of *THP* ethers with montmorillonite K-10 supported *BTSC*

Substrate	Time (s)	Product	Yield (%)
PhCH$_2$O*THP*	20	PhCHO	92
4-MeC$_6$H$_4$CH$_2$O*THP*	20	4-MeC$_6$H$_4$CHO	90
2-NO$_2$, 5-Me-C$_6$H$_3$CH$_2$O*THP*	40	2-NO$_2$, 5-MeC$_6$H$_3$CHO	85
PhCH(Me)O*THP*	60	PhCOMe	90
PhCH=CHCH$_2$O*THP*	100	PhCH=CHCHO	75
PhCH(O*THP*)Ph	120	PhCOPh	85
Cyclohexanol-*THP*	100	Cyclohexanone	88
2-Methylcyclohexanol-*THP*	120	2-Methycychohexanone	85
Benzoin-*THP*	120	Benzil	80
(–)-Menthol-*THP*	100	(–) Menthone	88



In summary, the presented methodology offers an attractive, rapid, and efficient method for the direct oxidative cleavage of tetrahydropyranyl ethers to the corresponding carbonyl compounds.

Experimental

All compounds used are known; their physical data were compared with those of authentic samples and found to be identical.

Preparation of bis(trimethylsilyl)chromate supported on montmorillonite K-10

To a solution of 6.4 ml (0.03 mol) hexamethyldisiloxane in 20 ml of dry CH_2Cl_2, 3 g (0.03 mol) CrO_3 were added. The reaction mixture was stirred in a 50°C bath for 5 h. Solid CrO_3 dissolved, and the dark red mixture became homogeneous. Montmorillonite K-10 (13 g) pre-dried at 120°C overnight and activated in the microwave oven for 3 min was added to the warm reaction mixture, and the resulting mixture was stirred for further 5 h. The solvent and other volatile components were removed under reduced pressure to afford 19 g of the supported chromium oxidant.

Oxidative deprotection of tetrahydropyranyl ethers; typical procedure

Montmorillonite K-10 supported *bis*(trimethylsilyl)chromate (0.93 g, equivalent to 1.5 mmol) was thoroughly mixed with 0.192 g benzyltetrahydropranyl ether (1 mmol), and the material was placed in a beaker inside the microwave oven (900 W) for 20 s. After completion of the reaction as monitored by TLC (hexane:AcOEt = 8:2) the product was extracted into CH_2Cl_2, the solvent was removed, and the residue was chromatographed on a silica gel column using hexane:AcOEt = 8:2 to afford 92% benzaldehyde.

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