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Clay Supported Cerium(IV) Reagents for Oxidative Deprotection of Tetrahydropyranyl Ethers under Non-Aqueous Conditions

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Summary. Primary and secondary tetrahydropyranyl ethers are efficiently converted to the corresponding carbonyl compounds using clay supported $[Ce(NO_3)_3]_2CrO_4$ and $[Ce(NO_3)_3]_3HIO_6$ in dichloromethane.

Keywords. Oxidative deprotection; Non-aqueous conditions; *BTNCC*; *TTNCPP*.

An Ton adsorbierte Cer(IV)-Reagentien zur oxidativen Entschützung von Tetrahydropyranylethern unter nichtwäßrigen Bedingungen

Zusammenfassung. Primäre und sekundäre Tetrahydropyranylether werden in Dichlormethan durch an Ton adsorbiertes $[Ce(NO_3)_3]_2CrO_4$ oder $[Ce(NO_3)_3]_3HIO_6$ rasch und in guten Ausbeuten zu den entsprechenden Carbonylverbindungen umgesetzt.

Introduction

Tetrahydropyranyl ethers are useful as protecting groups and important building blocks for the synthesis of primary alcohols [1], allylic alcohols [2], and alkyl halides [3]. More recently, the tetrahydropyranylation process (*THP* ether synthesis) has been performed under environmentally friendly conditions with concomitant minimum purification requirement. The methods employed include the use of heterogeneous catalysts such as montmorillonite K-10 [3], sulfonated charcoal [4], H-Y zeolite [5], zinc chloride in alumina [6], envirocat-EPZG [7], natural kaolinite clay [8], and zeolites HSZ [9]. However, the latter has been claimed to effect protection as well as deprotection of hydroxy compounds. We have recently described tetrahydropyranylation of various alcohols using *bis*-trinitratocerium(IV) chromate and *tris*-trinitratocerium(IV) periodate in benzene [10]. Direct oxidation of tetrahydropyranyl ethers to the corresponding carbonyl

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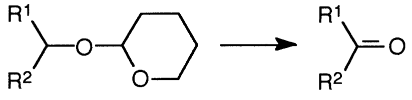

1 **2**

Scheme

compounds is also a useful practical achievement; only few reports on this topic are available [11–13].

Different salts of Ce(IV) are well known as versatile reagents in organic synthesis Ceric ammonium nitrate has been used as an efficient catalyst for protection and deprotection of alcohols with dihydropyran [14]. *Bis*-trinitratocerium(IV) chromate (*BTNCC*) [15] and *tris*-trinitratocerium(IV) paraperiodate (*TTNCPP*) [16] have been prepared as versatile oxidants [15–18]. Although *TTNCPP* has been used for deprotection and direct oxidative deprotection of trimethylsilyl ethers to their corresponding alcohols and carbonyl compounds [18], there is no report on an application of these two catalysts for direct oxidative deprotection of tetrahydropyranyl ethers. In this communication we wish to disclose that montmorillonite K-10 supported *BTNCC* and *TTNCPP* in dichloromethane serve as two mild, efficient, and inexpensive catalysts for direct oxidative deprotection of tetrahydropyranyl ethers to the corresponding carbonyl compounds.

Results and Discussion

A variety of tetrahydropyranyl ethers were treated with catalytic amounts of clay supported *BTNCC* or *TTNCPP*. The corresponding aldehydes or ketones were obtained in high to excellent yields; the results are complied in Table 1. Surprisingly, without montmorillonite K-10 the reaction is very slow, and only negligible amounts of carbonyl compound are obtained. The reaction conditions are particularly mild, and the work-up procedure is exceedingly simple and reduced to a mere filtration.

The possible recycling of the catalysts was investigated in the reaction with **1b**. The catalysts were filtered, washed with dichloromethane, dried, and immediately reused. After allowing the reaction mixture to reflux for 1 h in CH_2Cl_2, **2b** was obtained in 85% with *BTNCC* and 90% with *TTNCPP*. Recycling the catalysts five times afforded **2b** in similar high yield.

In a typical reaction, a mixture of tetrahydropyranyl ether and catalytic amounts of either clay supported *BTNCC* or *TTNCPP* was refluxed in dichloromethane. The progress of the reaction was monitored by GC. After the reaction was complete, the catalyst was filtered off, the solvent was evaporated, and the product was purified by elution with chloroform over a silica gel pad and evaporation of the solvent. A fairly wide range of tetrahydropyranyl ethers were oxidatively deprotected to the corresponding carbonyl compounds in high yields. The reactions proceed reasonably fast, and the conditions are mild enough not to induce isomerizations or oxidations of double bonds.

Table. 1. Oxidative deprotection of tetrahydropyranyl ethers with *BTNCC* or *TTNCPP*

	Substrate	Catalyst	Reaction time (h)	Product	Yield[a] (%)
1a	$C_6H_{11}O$*THP*	*BTNCC*	1	Cyclohexanone	90
1b	$PhCH_2O$*THP*	*BTNCC*	1.5	PhCHO	88
1c	$CH_2{=}CHCH_2O$*THP*	*BTNCC*	1.5	$CH_2{=}CHCHO$	80
1d	$C_7H_{15}CH_2O$*THP*	*BTNCC*	1.5	$C_7H_{15}CHO$	60
1e	$C_3H_7CH_2O$*THP*	*BTNCC*	1	C_3H_7CHO	90
1f	2-Octyltetrahydropyranylether	*BTNCC*	2	2-Octanone	72
1g	(-)-Mentholtetrahydropyranylether	*BTNCC*	2	(-)-Menthone	90
1h	$4\text{-}MeOC_6H_4CH_2O$*THP*	*BTNCC*	1.5	$4\text{-}MeOC_6H_4CHO$	88
1a	$C_6H_{11}O$*THP*	*TTNCPP*	1.2	Cyclohexanone	92
1b	$PhCH_2O$*THP*	*TTNCPP*	1.5	PhCHO	90
1c	$CH_2{=}CHCH_2O$*THP*	*TTNCPP*	1	$CH_2{=}CHCHO$	68
1d	$C_7H_{15}CH_2O$*THP*	*TTNCPP*	1.2	$C_7H_{15}CHO$	85
1e	$C_3H_7CH_2O$*THP*	*TTNCPP*	1.5	C_3H_7CHO	88
1f	2-Octyltetrahydropyranylether	*TTNCPP*	1.2	2-Octanone	75
1g	(-)-Mentholtetrahydropyranylether	*TTNCPP*	1.5	(-)-2-Menthone	90
1h	$4\text{-}MeOC_6H_4CH_2O$*THP*	*TTNCPP*	1	$4\text{-}MeOC_6H_4CHO$	65

[a] Yield based on the isolation of 2,4-dinitrophenylhydrazine derivatives

In conclusion, clay supported *BTNCC* and *TTNCPP* represent two convenient reagents for the one-pot oxidative deprotection of tetrahydropyranyl ethers to the corresponding carbonyl compounds. The notable advantages of this methodology are mild conditions (reflux in CH_2Cl_2), fairly fast reaction times (1–1.5 h), good to high yields, (60%–90%), and reusability of catalysts. We believe that this method could serve as a useful addition to modern synthetic methodologies.

Experimental

Products were characterized by IR and NMR spectroscopy and by direct comparison with authentic samples. *BTNCC* and *TTNCPP* were prepared according to reported procedures [15, 16]. Tetrahydropyranyl ethers were prepared according to Ref. [10].

Oxidative deprotection of tetrahydropyranyl ethers; General procedure

To a solution of tetrahydropyranyl ether **1** (1 mmol) in CH_2Cl_2 (20 ml) in a 50 ml round bottomed flask equipped with a condenser and a magnetic stirrer, a mixture of montmorillonite K-10 (200 mg) and the appropriate catalyst (0.25 mmol) was added. The reaction mixture was refluxed for 1–1.5 h. The progress of the reaction was monitored by GC or TLC (eluent: hexane/EtOAc = 9:1). After completion of the reaction, the catalyst was filtered off and washed with CH_2Cl_2. The filtrate was evaporated, and the resulting crude material was purified on a silica gel plate or a silica gel column with the appropriate eluent. Pure carbonyl compounds **2a–h** were obtained in 60–90% yield (Table 1).

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