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Wet Alumina Supported Chromium(VI) Oxide: A Mild, Efficient, and Inexpensive Reagent for Oxidative Deprotection of Trimethylsilyl and Tetrahydropyranyl Ethers

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Summary. Primary and secondary trimethylsilyl and tetrahydropyranyl ethers are efficiently converted to the corresponding carbonyl compounds using wet alumina supported chromium(VI) oxide.

Keywords. Silyl ethers; Tetrahydropyranyl ethers; Deprotection; Oxidation; Carbonyl compounds.

Chrom(VI)oxid auf feuchtem Aluminiumoxid: Ein mildes, effizientes und billiges Reagens zur oxidativen Entschützung von Trimethylsilyl- und Tetrahydropyranylethern

Zusammenfassung. Primäre und sekundäre Trimethylsilyl- und Tetrahydropyranylether werden durch die Einwirkung von an feuchtem Aluminiumoxid adsorbiertem Chrom(VI)oxid in guten Ausbeuten in die entsprechenden Carbonylverbindungen übergeführt.

Introduction

The trimethylsilyl group is one of the most widely employed protecting groups in organic synthesis and is often used to prepare silyl ethers as volatile derivatives of alcohols and phenols [1]. The protection of hydroxy groups with 3,4-dihydro-2*H*-pyran (*DHP*) also is a method which has found a broad field of application in organic synthesis [1b, 1c, 2].

Direct oxidation of trimethylsilyl ethers and tetrahydropyranyl ethers to the corresponding carbonyl compounds has found considerable attention during recent years [3a–g]. Although a large number of reagents are known for such transformations [3a–g], there still appears a need either to improve the existing oxidation methods or to introduce new reagents to permit better selectivity under milder conditions and with easy work-up procedures. Wet alumina supported chromium(VI) oxide efficiently fulfills these requirements.

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Results and Discussion

In continuation of our investigations on organic reactions utilizing reagents adsorbed on inorganic supporting materials [4–8], we mixed chromium(VI) oxide with alumina and reacted this chromium supported reagent in CH_2Cl_2 with trimethylsilyl and tetrahydropyranyl ethers. In the absence of wet alumina, the reactions are slow, and considerable amounts of starting material and alcohols were recovered unchanged in reactions at room temperature or even under reflux for an extended period of time. As an example, the reaction of trimethylsilyl benzyl ether with dry alumina CrO_3 resulted in the formation of 30% benzylalcohol and 25% benzaldehyde.

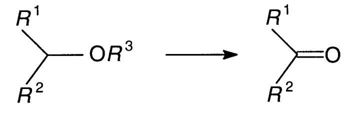
However, when alumina was premoistened and then mixed with chromium oxide, trimethylsilyl benzyl ether was converted to benzaldehyde almost quantitatively in CH_2Cl_2 at room temperature.

To assess the generality of this oxidative deprotection method, a variety of trimethylsilyl and tetrahydropyranyl ethers were reacted under these conditions, yielding the corresponding carbonyl compounds in good to excellent yields (Table 1). Primary trimethyl silyl and tetrahydropyranyl ethers (allylic and non-

Table 1. Oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers with wet alumina supported chromium(VI) oxide

	Substrate	Reaction time (min)	Product	Yield (%)
1a	$C_6H_5CH_2OSiMe_3$	10	C_6H_5CHO	93[b]
1b	4-Me-$C_6H_4CH_2OSiMe_3$	10	4-MeC_6H_4-CHO	91[b]
1c	2-NO_2-5-Me-$C_6H_3CH_2OSiMe_3$	10	2-NO_2-5-Me-C_6H_3CHO	90[b]
1d	*R*,*S*-$C_6H_5CH(Me)OSiMe_3$	15	C_6H_5COMe	89[a]
1e	$(C_6H_5)_2CHOSiMe_3$	10	$(C_6H_5)_2CO$	92[a]
1f	*c*-$C_6H_{11}OSiMe_3$	20	Cyclohexanone	85[b]
1g	2-Me-*c*-$C_6H_{10}OSiMe_3$	20	2-Methylcyclohexanone	83[b]
1h	(−)-Mentholtrimethylsilyl ether	25	(−)-Menthone	83[a]
2a	$C_6H_5CH_2O$*THP*	10	C_6H_5CHO	92[b]
2b	4-Me-$C_6H_4CH_2O$*THP*	10	4-Me-C_6H_4CHO	90[b]
2c	2-NO_2-5-Me-$C_6H_3CH_2O$*THP*	15	2-NO_2-5-Me-C_6H_3CHO	91[b]
2d	*R*,*S*-$C_6H_5CH(Me)O$*THP*	15	C_6H_5COMe	84[a]
2e	$(C_6H_5)_2CHO$*THP*	15	$(C_6H_5)_2CO$	88[a]
2f	*c*-$C_6H_{11}O$*THP*	25	Cyclohexanone	83[b]
2g	2-Me-*c*-$C_6H_{10}O$*THP*	25	2-Methylcyclohexanone	84[b]
2h	(−)-Menthol-*THP*	25	(−)-Menthone	83[a]

[a] Yields based on GLC analysis; [b] yields based on the isolation of the corresponding 2,4-dinitrophenylhydrazine derivative



1a-h: R^3 = $SiMe_3$; **2a-h**: R^3 = *THP* allylic as well as benzylic) did not undergo overoxidation to the corresponding carboxylic acids.

In conclusion, wet alumina supported chromium(VI) oxide represents a convenient reagent for the one-pot oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers to their corresponding carbonyl compounds.

Experimental

Trimethylsilyl and tetrahydropyranyl ethers were prepared according to known procedures [9, 2a]. All oxidation products were identified by comparison of their physical data with those given in the literature. Yields refer either to GC analysis or to isolation of the 2,4-dinitrophenylhydrazine derivative. GC analysis was performed with a fission 8000 gas chromatograph with FID using a 10% carbowax 20 M on chromsorb W/A W column (1.8 m×6 mm). Wet alumina was prepared by shaking neutral alumina oxide (10 g, Aldrich-Brockmann, 150 mesh) with distilled water (2 ml). The reagent was prepared by mixing CrO_3 (0.8 g, 8 mmol) with wet alumina (2.4 g) using pistle and mortar.

Oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers; general procedure

In a flask (50 ml), a solution of 1 mmol of ether in 20 ml CH_2Cl_2 was prepared. Wet alumina supported chromium(VI) oxide (0.06 g) was added, and the mixture was stirred magnetically for 10–25 min. The progress of reaction was monitored by GC or TLC (eluent: hexane/EtOAc, 8:2). The mixture was filtered, and the solid material was washed with CH_2Cl_2. The filtrate was evaporated on a rotary evaporator, and the resulting crude material was purified on a silica gel pad with the appropriate eluent. Pure carbonyl compounds were obtained in yields of 83–93% (Table 1).

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