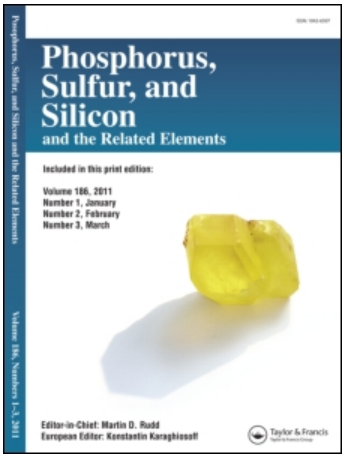

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ZEOLITE-SUPPORTED CHROMIUM(VI) OXIDE: A MILD, EFFICIENT, AND INEXPENSIVE REAGENT FOR OXIDATIVE DEPROTECTION OF TRIMETHYLSILYL ETHERS UNDER MICROWAVE IRRADIATION

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Primary and secondary trimethylsilyl ethers are effeciently converted to the corresponding carbonyl compounds using HZSM-5 zeolite-supported CrO_3 under microwave irradiation in solventless system.

Keywords: Carbonyl compound; microwave irradiation; oxidative deprotection; silyl ethers; solventless system

INTRODUCTION

Trimethylsilyl group is one of the most widely used protection groups in organic synthesis and is often used to prepare silyl ethers as versatile derivatives of alcohols and phenols.[1]

Direct oxidation of trimethylsilyl ethers to the corresponding carbonyl compounds has attracted considerable attention in recent years,[2] but the introduction of new methods, inexpensive reagents, and environmentally friendly conditions for such functional group transformation is still in demand.

Chromium-based reagents have been widely used in organic synthesis.[3] However, due to its inherent toxicity and potential danger in the handling of its complexes, difficulties in terms of product isolation and waste disposal, chemists are reluctant to use it. However, the concept of utilizing a reagent adsorbed on inert inorganic supports has circumvented some of these problems. Therefore, reagents impregnated

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on mineral solid supports have been recently employed by several investigators and laboratories,[4] including our own.[5]

We have recently reported on the fast microwave-assisted zeolite HZSM-5 catalyzed oxidation of alcohols with chromium trioxide under solvent-free conditions.[6] Oxidative deprotection of trimethylsilyl ethers has also been one of the main topics in our laboratory.[2,7] Armed with these experiences, we now report on the use of HZSM-5 zeolite along with chromium trioxide, which oxidatively deprotects trimethylsilyl ethers to afford the corresponding carbonyl compounds.

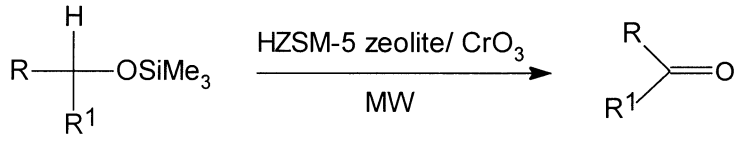
HZSM-5 zeolite was prepared following a previously described procedure.[8] The SiO_2/Al_2O_3 ratio (53:1) was determined by X-ray fluorescence prior to the experiments, and the zeolite was activated by heating at 400°C for 8 h. Two equivalents of CrO_3 and a weight equivalent of HZSM-5 zeolite per mole of benzyltrimethylsilyl ether were used and exposed to microwave irradiation for 2 min, which led to the formation of benzaldehyde almost quantitatively. No trace of benzoic acid was observed, showing that no over-oxidation occurs. To establish the generality of the method, a variety of trimethylsilyl ethers were reacted under the same conditions specified to yield the corresponding carbonyl compounds in excellent yields (Table I).

Among the various supports, such as silica gel, alumina, montmorillonite K-10, HY zeolite, NaY zeolite, and HZSM-5 zeolite, the latter gave the best results regarding yield, reaction time, and selectivity. It is notable that in the absence of solid support the reaction under microwave irradiation is sluggish and a considerable amount of starting material, along with deprotected alcohol and carbonyl compound, even upon extended reaction time, are obtained. It is also noteworthy to mention that at least a weight equivalent of HZSM-5 zeolite is required for satisfactory conversion under microwave irradiation in the solventless system. As far as the reaction catalytic ability of different

TABLE I Oxidative Deprotection of Trimethylsilyl Ethers with HZSM-5 Zeolite

Entry	Substrate	Reaction time min	Product	Yield
1	$PhCH_2OSiMe_3$	1.5	PhCHO	91
2	4-MeO-$C_6H_4OSiMe_3$	1.5	4-MeO-C_6H_4CHO	82
3	2-NO_2-3-OMe-$C_6H_3OSiMe_3$	1.6	2-NO_2-3-OMe-C_6H_3CHO	96
4	2-NO_2-5-OMe-$C_6H_3OSiMe_3$	1.6	2-NO_2-5-OMe-C_6H_3CHO	99
5	4-NO_2-$C_6H_4CH_2OSiMe_3$	2	4-NO_2-C_6H_4CHO	96
6	$Me_3SiOCH_2CH_2CH_2OSiMe_3$	1.5	$OCHCH_2CHO$	99
7	$CH_3(CH_2)_{15}OSiMe_3$	1.8	$CH_3(CH_2)_{14}CHO$	83
8	*c*-$C_6H_{11}OSiMe_3$	2	Cyclohexanone	89
9	$CH_3(CH_2)_6CH_2OSiMe_3$	1.5	$CH_3(CH_2)_6CHO$	93

ratio of zeolite/CrO_3 for various substrates is concerned, the optimized ratio is 1.2 equivalent of HZSM-5 zeolite:



EXPERIMENTAL

Trimethylsilyl ethers were prepared according to a known procedure.[8] All oxidation products were identified by comparison of their physical data with those given in the literature. Yields refer to isolated products. Although we did not observe any accident, use of the microwave oven in an efficient hood is highly recommended.

Oxidative Deprotection of Trimethylsilyl Ether. General Procedure

Chromium trioxide (2 mmol) and 1.5 equivalent of HZSM-5 zeolite were crushed together in a mortar to form an intimate mixture. A neat trimethylsilyl either was added to this mixture. The resulting mixture was mixed thoroughly using a spatula. The mixture was placed in a household microwave oven and irradiated for an indicated time. The crude product was directly subjected to column chromatography using hexane:EtOAc 8:2 as eluent, affording the corresponding carbonyl compound.

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