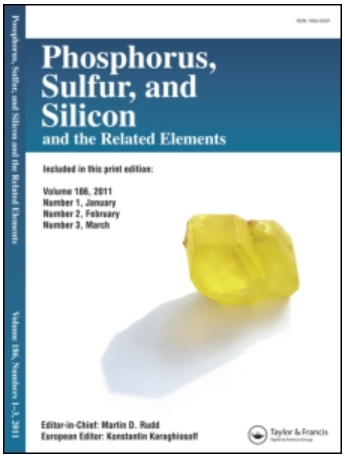

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Microwave Thermolysis: A Rapid and Selective Method for the Cleavage of THP Ethers Using CrO 3 Supported onto Zeolite in Solventless System

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MICROWAVE THERMOLYSIS: A RAPID AND SELECTIVE METHOD FOR THE CLEAVAGE OF THP ETHERS USING CrO_3 SUPPORTED ONTO ZEOLITE IN SOLVENTLESS SYSTEM

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Oxidative deprotection of tetrahydropyranyl ethers (THP ethers) using chromium trioxide supported onto zeolite under microwave irradiation in solvent free condition is described.

Keywords: Chromium trioxide; microwave thermolysis; solventless system; THP ethers; zeolite

An oxidant that is efficient in transferring oxygen, selective in its reactivity, mild toward oxidized product, possesses catalytic activity, and is commercially available would unquestionably be the synthetic chemist's delight. Chromium-based reagents have been extensively used in organic synthesis.[1] The oxidation of primary and secondary alcohols to carbonyl compounds is not frequently accomplished by the use of chromium(VI) reagents in quantities ranging from stoichiometric to a large excess.[2] Since the chromium residues are environmentally hazardous and have the potential danger (ignition or explosion) in term of product isolation and vast disposal,[3] it would be advantageous to develop oxidizing methods using chromium trioxide along with solid supports.

Introduction of reagents on solid supports has opened an attractive avenue in organic synthesis in view of selectivity and associated ease of manipulation.[4] It applied especially to chromium compounds.[5] Microwave heating and its application in organic chemistry for reactions is currently being developed successfully[6] and in recent years there

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has been a tremendous interest in combining this technique with dry conditions[7] where the absence of solvent reduces the risk of hazardous explosion. The protection and selective deprotection of functional groups is of great significance in multistep organic synthesis.[8] The large repertoire of protecting groups available for the hydroxyl functionality[8,9] exemplifies its sensitivity. The protection of hydroxy compounds as THP ethers is common practice in organic synthesis.[10]

Although literature enumerates quite a number of methods for the oxidative deprotection of THP ethers to carbonyl compounds,[11] careful inspection of the reaction procedures reveals some drawbacks. Therefore, introducing a mild, selective, and inexpensive reagent for such functional group transformation still is in much demand.

The oxidation of alcohols to the carbonyl compounds using chromium trioxide supported onto HZSM-5 zeolite has been reported.[12] In this communication, we are pleased to describe our results for the oxidative deprotection of THP ethers by the above reagent in a solventless system under microwave irradiation.

HZSM-5 zeolite was prepared following a previously described procedure.[13] Two equivalents of CrO_3 and a weight equivalent of HZSM-5 zeolite per mmol of benzyl THP ether were mixed throughly and exposed to microwave irradiation for 90 s, which led to the formation of benzaldehyde almost quantitatively. Similar treatment of other THP ethers gave the corresponding carbonyl compounds in a short time in excellent yields. Table I shows some of the aldehydes and ketones, which are oxidatively obtained under microwave irradiation. Overoxidation was not observed with this supported reagent. Cinnamyl THP ether was successfully converted to cinnamylaldehyde in high yield showing that the carbon-carbon double bonds are not prone to cleavage using this method.

TABLE I Oxidative Deprotection of THP Ethers with Chromium Trioxide-HZSM-5 Zeolite Under Microwave Irradiation in Solvent Free Conditions

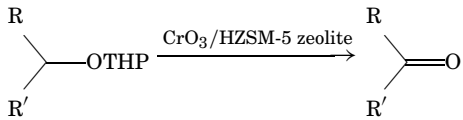
Entry	Substrate	Time (sec)	Molar ratio[a]	Yield (%)
1	$C_6H_5CH_2OTHP$	90	1:2	95
2	2-NO_2-5-Me-$C_6H_3CH_2OTHP$	120	1:2.5	97
3	4-NO_2-$C_6H_4CH_2OTHP$	60	1:2	92
4	2-NO_2-3-Me-$C_6H_3CH_2OTHP$	120	1:2.5	93
5	4-Me-$C_6H_4CH_2OTHP$	120	1:2.5	95
6	$Ph_2CHOTHP$	90	1:2	98
7	*c*-$C_6H_{11}OTHP$	60	1:2	98
8	PhCh=CH–CH_2OTHP	60	1:2	95

[a]Substrate: CrO_3.

It is noteworthy that in the absence of zeolite oxidative deprotection of THP ethers do not occur.

The use of different ratios of substrate/reagent was investigated and it was found that 1:2.5 is suitable for the successful oxidative cleavage. Furthermore, it was noticed that the reactions remain incomplete when they are done in a solvent (CH_2Cl_2), even with a higher ratio of reagent (1:5) and longer reaction time (2 h). However, the reaction proceeds smoothly and efficiently in a very short time under microwave irradiation in solvent free conditions in a few minutes.

In summary oxidative deprotection of THP ethers using CrO_3-HZSM-5 zeolite under microwave irradiation in a solventless system has advantages over previously reported methods and provides a facile, useful, and inexpensive addition to the existing methodologies. The advantages of this procedure are mild reaction condition, excellent yields, short reaction time, a solvent less system, and minimization of side products.



EXPERIMENTAL SECTION

All products are known compounds and are characterized by comparison of their physical and spectroscopic data with those of authentic samples. THP ethers are synthesized via reported procedure.[10a] GC analysis was performed with a Fisson 8000a gas chromatograph with a flame ionization detector using a column 10% carbowax 20M on a chromsorb W/AW, 1.8 M × 6 mm.

Oxidative Deprotection of THP Ethers by Zeolite-HZSM-5-CrO_3

General Procedure

Chromium trioxide (2 mmol) and an indicated equivalent of HZSM-5 zeolite were crushed together in a mortar so as to form an intimate mixture. A neat THP ether (1 mmol) was added to this mixture. The resulting mixture was mixed throughly using a spatula. This mixture was placed in a household microwave oven for an indicated time. The progress of reaction was monitored by TLC using petroleum ether-ethyl acetate. The solvent was evaporated to afford the corresponding carbonyl compound (Table I). (Caution: Although this procedure worked

safely in our hands, it is recommended to use a microwave oven in an efficient and standard hood.)

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