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DIRECT OXIDATIVE DEPROTECTION OF TETRAHYDROPYRANYL ETHERS USING HEXAMETHYLENETETRAMINE-BROMINE SUPPORTED ONTO SILICA GEL UNDER MICROWAVE IRRADIATION IN SOLVENTLESS SYSTEM

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DIRECT OXIDATIVE DEPROTECTION OF TETRAHYDROPYRANYL ETHERS USING HEXAMETHYLENETETRAMINE-BROMINE SUPPORTED ONTO SILICA GEL UNDER MICROWAVE IRRADIATION IN SOLVENTLESS SYSTEM

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Primary and secondary tetrahydropyranyl ethers (THP ethers) are converted to their corresponding carbonyl compounds efficiently using hexamethylene-tetramine-bromine supported onto silica gel under microwave irradiation in solvent-free conditions.

Keywords: Carbonyl compounds; microwave irradiation; oxidation; solvent-free conditions; THP ethers

The use of one-pot reactions offers a great success in organic synthesis today. The combination of the one-pot strategy with the use of eco-friendly solid-acid catalysts is now the best tool for the synthesis of specific target compounds with minimum production of pollutants as well as reduction of the cost.¹

Direct oxidation of tetrahydropyranyl (THP) ethers to the corresponding carbonyl compounds has found considerable attention during recent years.²

Hexamethylenetetramine-bromine is an inexpensive reagent that has been used for oxidation of alcohols,³ and the cleavage of oximes⁴ and semicarbazones.⁵

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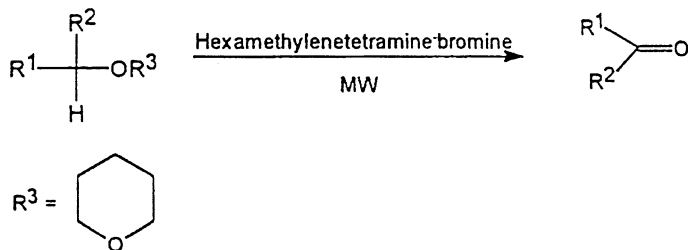
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Microwave irradiation in organic synthesis is a useful technique nowadays.⁶ Dry media using microwave heating have attracted much attention.⁷

Oxidation reactions are less considered under microwave irradiation due to unsafe and uncontrollable experimental conditions.⁸ Impregnation of reagents on solid supports have circumvented this problem and provides an attractive alternative in organic synthesis in view of selectivity and ease of manipulation.⁹

We have recently reported the oxidation of alcohols^{3b} and deoxygenation⁴ and desemicarbozation⁵ using hexamethylenetetramine-bromine under microwave irradiation in solvent-free conditions. In continuation of manipulation of the above supported reagent and in connection with our investigations on organic reactions in solventless system under microwave irradiation,⁹ herein we report our results for the mild, facile, fast, and high-yielding reaction of the direct oxidative deprotection of THP ethers using hexamethylenetetramine-bromine supported onto silica gel under microwave irradiation in solventless system.

The reaction is conducted by mixing hexamethylenetetramine-bromine with silica gel, and adding the neat THP ethers and grinding them thoroughly to make an intimate mixture. By placing the mixture in a microwave oven the reactions are completed in a couple of seconds. In a typical procedure THP ethers of benzyl alcohol were mixed with 2 equivalent of hexamethylenetetramine-bromine supported onto silica gel. The mixture was placed in a microwave oven, the progress of the reaction was monitored by TLC (thin layer chromatography) (using petroleum ether: ethyl acetate 8:2 as eluent). The reaction was completed in 2 min with an 83% yield. To establish the generality of the method, various THP ethers were converted to their carbonyl compounds (Table I). No over-oxidation to carboxylic acid was observed.



In conclusion, we have developed a solid-state method for facile, mild, and rapid one-pot oxidative deprotection of THP ethers

TABLE I Direct Oxidative Deprotection of THP Ethers Using Hexamethylenetetramine-Bromine Under Microwave Irradiation in Solventless System

Entry	Substrate	Time (s)	Product	Yield (%)
1	PhCH ₂ OTHP	120	PhCHO	83
2	CH ₃ (CH ₂) ₂ CH ₂ OTHP	110	CH ₃ (CH ₂) ₂ CHO	75
3	CH ₃ (CH ₂) ₆ CH ₂ OTHP	110	CH ₃ (CH ₂) ₆ CHO	73
4	C ₆ H ₁₃ CH ₂ OTHP	120	C ₆ H ₁₃ CHO	82
5	<i>c</i> -C ₆ H ₁₁ OTHP	120	Cyclohexanone	85
6	(-)-Menthol-THP	90	Menthone	72
7	Cholestroil-THP	90	Cholostenone	65

using hexamethylenetetramine-bromine supported onto silica gel. The reagent is prepared by adding bromine to a chloroform solution of commercially available amine.^{3b} This homogenous nonhygroscopic solid is very stable at room temperature and is not affected by ordinary exposure to light, air, or water, and has no offensive odour of bromine or amine.

EXPERIMENTAL

All compounds are known and were identified with authentic samples. Yields refer to isolated products. Hexamethylenetetramine-bromine was prepared by the reported procedure.^{3b} THP ethers were prepared by the described method.¹⁰

Typical Procedure

Hexamethylenetetramine-bromine (2 mmol) was mixed thoroughly with an equivalent weight of silica gel (mesh 60) in a beaker using a spatula. To this mixture neat benzyl THP ether (1 mmol) was added and mixed to make an intimate mixture. The beaker was placed in a household microwave oven and irradiated for 2 min. The progress of reaction was monitored by TLC using petroleum ether: ethyl acetate 8:2 as eluent. Upon completion of the reaction, CH₂Cl₂ (5 ml) was added. The mixture was filtered and the filtrate was evaporated to afford the benzaldehyde, yield 83%. Caution: although we did not encounter any accident, the use of a microwave oven in an efficient hood is highly recommended.

REFERENCES

- [1] F. Tietze and U. Beifuss, *Angew. Chem. Int. Ed. Engl.*, **32**, 131 (1993).
- [2] a) M. M. Heravi, D. Ajami, and M. Ghassemzadeh, *Synthesis*, **3**, 393 (1999) and references cited therein; b) M. M. Heravi, M. Tajbakhsh, and M. Ghassemzadeh, *Z. Naturforsch.*, **54b**, 393 (1999) and references cited therein.
- [3] I. Yavari and A. Shaabani, *J. Chem. Res.*, 274 (1994); b) M. M. Heravi, D. Ajami, and M. A. Nooshabadi, *Iran. J. Chem. Eng.*, **18**, 88 (1999).
- [4] Y. Sh. Beheshtiha, M. M. Heravi, N. Sarmad, and R. Hekmat-Shoar, *J. Chem. Res.*, 76 (2001).
- [5] M. A. Nooshabadi, K. Aghapoor, M. Tajbakhsh, and M. M. Heravi, *J. Sci., I. R. Iran*, **12**, 1 (2001).
- [6] S. Caddick, *Tetrahedron*, **38**, 10403 (1995).
- [7] J. P. Barnier, A. Loupy, P. Pigeon, M. Ramdani, and P. Jacquault, *J. Chem. Soc. Perkin Trans.*, **1**, 393 (1993).
- [8] A. T. Tsuji and T. Mandai, *Synthesis*, **1** (1999) and references cited therein.
- [9] a) M. M. Heravi, D. Ajami, M. M. Mojtahedi, and M. Ghassemzadeh, *Tetrahedron Lett.*, **40**, 561 (1999); b) M. M. Heravi, D. Ajami, K. Aghapoor, and M. Ghassemzadeh, *Chem. Commun.*, 833 (1999).
- [10] G. J. Neville, *Org. Chem.*, **25**, 1063 (1960).