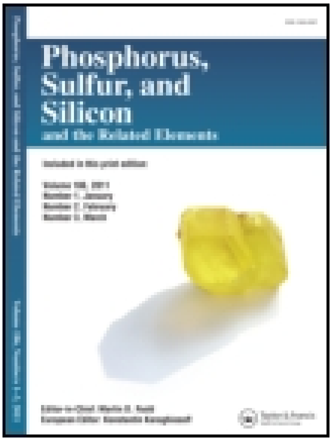

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OXIDATIVE DEPROTECTION OF TRIMETHYLSILYL ETHERS WITH HEXAMETHYLENETETRAMINEBROMI SUPPORTED ONTO SILICA GEL UNDER MICROWAVE IRRADIATION IN SOLVENTLESS SYSTEM

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OXIDATIVE DEPROTECTION OF TRIMETHYLSILYL ETHERS WITH HEXAMETHYLENETETRAMINE-BROMINE SUPPORTED ONTO SILICA GEL UNDER MICROWAVE IRRADIATION IN SOLVENTLESS SYSTEM

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Hexamethylenetetramine-bromine supported onto silica gel rapidly converts trimethylsilyl ethers to their corresponding carbonyl compounds under microwave irradiation in solventless system.

Keywords: Deprotection; hexamethylenetetramine-bromine; microwave irradiation; oxidation

INTRODUCTION

The protection of certain functional groups and the deprotection of the protected derivatives constitute important processes in the multistage synthetic chemistry of polyfunctional molecules, including the total synthesis of natural products.[1] One of the most useful and convenient methods for protection of hydroxy groups is their transformation to trialkylsilyl ethers. Direct oxidation of trimethylsilyl ethers to the corresponding aldehydes and ketones is of great relevance to organic synthesis.

Although various methods have been reported for such a transformation,[2] some of them show limitations such as the requirement

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of aqueous reaction conditions, use of expensive reagents, long reaction times, tedious workup, and low yield of products. Therefore, presentation of new methods and inexpensive and environmentally friendly reagents for such functional group transformation is still in much demand. Hexamethylenetetramine-bromine is an inexpensive reagent, which has been reported as an oxidizing agent.[3] We have recently successfully used this oxidant in deoximation and desemicarbonization reactions.[4]

In recent years, the organic reactions that are assisted by microwave,[5] especially under solventless systems,[6] have attracted attention because of their enhanced selectivity, mild reaction conditions, and associated ease of manipulation.

In continuation of our ongoing efforts in microwave-assisted reactions,[7] herein we wish to report a simple oxidative deprotection of trimethylsilyl ethers with hexamethylenetetramine-bromine supported onto silica gel in solventless system, which is accelerated by microwave irradiations.

In the absence of solid support, the attempted oxidative deprotection of silyl ethers failed with hexamethylenetetramine-bromine under thermal as well as microwave irradiation even after prolonged reaction periods. In view of established beneficial effects of the reagents on minerals,[8] we used silica gel as a support for hexamethylenetetramine-bromine. Hexamethylenetetramine-bromine was mixed intimately with an equivalent weight of silica gel. When this supported reagent was mixed thoroughly with benzylsilyl ether using a spatula in a beaker and placed in microwave oven the reaction was completed in 2 min as confirmed by thin layer chromatography (TLC; hexane:ethyl acetate, 8:2: see Table I Entry 2).

To establish generality of the method, trimethylsilyl ethers of various alcohols were used under the above condition.

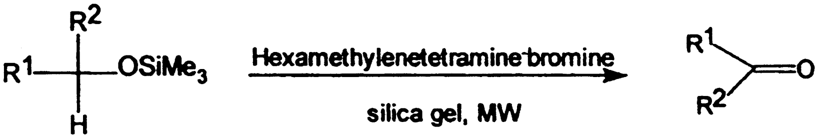
TABLE I Oxidative Deprotection of Trimethylsilyl Ethers with Hexamethylene-tetramine-bromine Supported onto Silica Gel under Microwave Irradiation

Entry	Substrate	Time (s)	Product	Yield[a] (%)
1	$PhCH_2OSiMe_3$	120	PhCHO	93
2	Cyclohexyltrimethylsilyl ether	120	Cyclohexanone	88
3	*n*-$CH_3(CH_2)_6CH_2OSiMe_3$	120	$CH_3(CH_2)_6CHO$	89
4	$CH_3(CH_2)_5CH_2OSiMe_3$	150	$CH_3(CH_2)_5CHO$	72
5	(−)-Menthylsilyl ether	180	Menthone	71
6	Cholestryltrimethylsilyl ether	150	Cholostenone	67

[a] Yields refer to isolated product.

In conclusion, we have developed a solid-state method for facile direct oxidative deprotection of trimethylsilyl ethers using hexamethylenetetramine-bromine supported onto silica gel under microwave irradiation in solventless system.

The reagent could be readily prepared by adding bromine to a chloroform solution of commercially available amine. This homogenous nonhygroscopic solid is very stable at room temperature and is not affected by ordinary exposure to light, air, or water, and it has no offensive odor of bromine or amine (Scheme 1).



SCHEME 1

EXPERIMENTAL

All compounds are known and characterized with their physical data by comparison with those of authentic samples. In view of the hazard associated with an oxidant and evolution of gases during the reaction, caution is recommended for its use at elevated temperature. We suggest that the microwave oven be operated carefully and for a shorter time due to possibility of a high localized temperature.

Oxidative Deprotection of Trimethylsilyl Ethers: General Procedure

Hexamethylenetetramine-bromide supported on silica gel (60 mesh, 2 mmol) was mixed thoroughly with the appropriate trimethylsilyl ether (1 mmol) in a beaker. The beaker was placed in a microwave oven and irradiated for specific time (Table I). The progress of reaction was monitored by TLC. The crude CH_2Cl_2 (5 ml) was added and filtered off. The filtrate was evaporated to dryness to afford the corresponding carbonyl compound (Table I).

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