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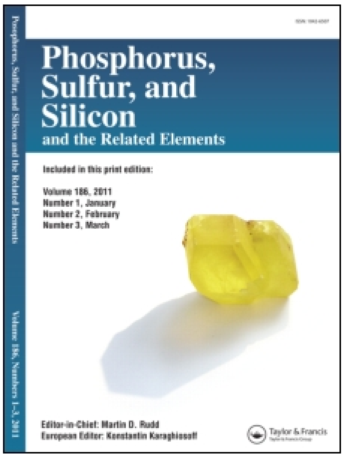

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# Efficient and Selective Oxidative Deprotection of Trimethylsilyl Ethers Using Supported Potassium Ferrate Under Microwave Irradiation

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# EFFICIENT AND SELECTIVE OXIDATIVE DEPROTECTION OF TRIMETHYLSILYL ETHERS USING SUPPORTED POTASSIUM FERRATE UNDER MICROWAVE IRRADIATION

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*Primary and secondary trimethylsilyl ethers are efficiently and rapidly converted to their corresponding carbonyl compounds with supported potassium ferrate under microwave irradiation in solventless system.*

*Keywords:* Deprotection; microwave irradiation; oxidation; potassium ferrate

The trimethylsilyl group is one of the most widely employed protecting groups in multistep organic synthesis and is often used to prepare silyl ethers as volatile derivatives of alcohols and phenols.[1]

Direct oxidation of trimethylsilyl ethers to the corresponding carbonyl compounds has found considerable attention during recent years which exemplifies its significance. Although a large number of reagent are known for such transformation,[2] there still appears a need either to improve the existing oxidative methods or to introduce new reagents to permit better selectivity under milder condition, faster reaction and easier work-up procedure.

Prompted by stringent environment protection laws in recent years, there has been increasing emphases on the use and design of eco-friendly reagents, solid and solvent free reactions.[3]

Application of microwave heating technique is currently under intensive examination.[4] Dry media technique has attracted much attention

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recently since organic solvents are expensive and hazardous, and open vessels can be used.[5]

It has been shown that among transition metals, iron is singled out as nontoxic.[6] Association of ferric salt with zeolite had been pioneered in our laboratory leading to the design of the "zeofen" as a versatile oxidizing reagent.[7] We recently have reported the above reagent for oxidative deprotection of trimethylsilyl ethers.[8] Potassium ferrate ($K_2FeO_4$) is a sixvalent iron compound which can be easily and economically prepared by oxidizing ferric nitrate with sodium hypochlorite and the subsequent treatment with potassium hydroxide.[9] We recently have prepared this reagent by an improved method presented by Laszlo and his coworker,[10] supported onto montmorillonite k-10 and used that for oxidative deprotection of trimethylsilyl ethers.[11] Although this oxidative deprotection proceeds efficiently and smoothly, it suffers from long reaction time (2–11 h). This limitation prompted us to investigate the advantages of microwave irradiation in solvent-free condition. In a typical reaction an intimate mixture of potassium ferrate and benzyltrimethylsilyl ether was irradiated with microwave. Although oxidative deprotection of benzyltrimethylsilyl ethers is observed, considerable amounts of starting material and some bezylalcohol also are present.

More seriously, molten potassium ferrate added to the walls of the vessel making isolation of the products difficult. To circument this problem, potassium ferrate was supported onto montmorillonite k-10. When the supported reagent was mixed with bezyltrimethysilyl ether and the mixture placed in household microwave oven, the reaction was completed in 2 min in 92% yield. The work-up procedure involves addition of $CH_2Cl_2$, mere filtration, evaporation of the solvent, and passing the residue through a small pad of silica gel using suitable solvent. To assess the generality of the method, a variety of trimethylsilyl ethers were treated likewise to afford the corresponding deshielded carbonyl compounds in high to excellent yield (Table I). No overoxidation leading to carboxylic acid was observed. Cinnamyltrimethylsilyl ether was oxidatively deprotected to cinnamaldehyde by this method showing that the carbon-carbon double bond is not prone to cleavage by this method. In summary the present procedure for the cleavage of trimethylsilyl ether has all advantages of using iron salt as eco-friendly and nontoxic material, selectivity, and easy work-up procedure due to impregnation of reagents onto mineral supports as well as very short reaction time without the use of expensive and hazardous organic solvents.

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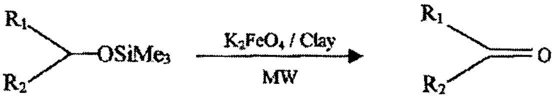
**TABLE I** Oxidative Deprotection of Trimethylsilyl Ethers with $K_2FeO_4$ Supported on Montmorillonite k-10 under Microwave Irradiation in Solvent-Free Conditions



| Substrate | Time (min) | Products | Yield (%)[a] |
|---|---|---|---|
| $PhCH_2OSiMe_3$ | 2 | PhCHO | 95 |
| 4-Me-$C_6H_4CH_2OSiMe_3$ | 2 | 4-Me-$C_6H_4CHO$ | 92 |
| 2-$NO_2$-5-Me$C_6H_3CH_2SiMe_3$ | 4 | 2-$NO_2$-5-Me-$C_6H_3CHO$ | 88 |
| 3-$NO_2$-$C_6H_4CH_2OSiMe_3$ | 5 | 3-$NO_2$-$C_6H_4CHO$ | 82 |
| 3-MeO-$C_6H_4CH_2OSiMe_3$ | 2 | 3-MeO-$C_6H_4CHO$ | 90 |
| 4-Cl-$C_6H_4$-CH ($OSiMe_3$)-$CH_3$ | 4 | 4-Cl$C_6H_4COCH_3$ | 82 |
| c-$C_6H_{11}OSiMe_3$ | 5 | Cyclohexanone | 81 |
| 2-Me-c-$C_6H_{10}OSiMe_3$ | 4 | 2-Methylcylclohexanone | 82 |
| (-)Mentholtrimethylsilyl ether | 5 | (-) Menthone | 85 |

[a] Yields based on isolated product.

(Caution: Although we did not have any problems and the above procedure worked safely in our hands, using a microwave oven in an appropriate hood is recommended).

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## EXPERIMENTAL

Silyl ethers were synthesized from the corresponding hydroxyl compounds according to the literature.[12] All products were known and characterized by comparison of their physical data with those of authentic samples. The reagent was prepared by the impregnation of potassium ferrate on montmorillonite k-10 which was purchased from Aldrich Chemical LTD. Thin layer chromatography was done on precoated silica gel.

### Oxidative Deprotection of Trimethylsilyl Ethers: General Procedure

In a typical procedure, trimethylsilyl ethers (2 mmol) is intimately mixed with potassium ferrate (4 mmol) supported on montmorillonite k-10. The mixture is transferred into a small beaker, and irradiated by microwave (National, 900 w operating at a frequency 2450 MHz) for the indicated time. The progress of reaction was monitored by TLC (pet-ether: ethyl acetate, 80:20). After the completion of reaction the product was extracted with ether and filtered.

Evaporation of solvent gave a crude product which was passed through a short column of silica gel, using pet-ether: ethyl acetate (80:20) as an eluent to afford the corresponding carbonyl compound (Table I).

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