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Solid State Oxidative Deprotection of Trimethylsilyl Ethers with Iron (III) Nitrate and Montmorillonite Under Microwave Irradiation

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Abstract: Mixture of iron (III) nitrate and montmorillonite K10 oxidatively deprotect trimethylsilyl ethers to their corresponding carbonyl compounds under microwave irradiation in solventless system, in a short time and good yields.

The protection of certain functional groups, and deprotection of the protected derivatives constitute important processes in synthetic organic chemistry in poly-functional molecules, including the total synthesis of natural products. Thus, large number of protective groups have been developed along with numerous methods for their removals.[1-3] Conversion of hydroxy function to trimethylsilyl ether is one of the most useful and convenient method for protection these groups.[4] Direct oxidation of trimethylsilyl ethers to their corresponding carbonyl compounds has found much attention.[5] Recently, we reported the use of montmorillonite K10 supported bis(trimethylsilyl)chromate for oxidation of alcohols in non-aqueous

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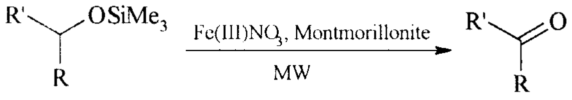
and solvent-free conditions.[6,7] In view of economical, practical, and recent environmental demands,[8] we thought about the significant advantage in using a non-toxic and inexpensive metal salt, such as iron (III) nitrate as oxidizing agent.

The use of clayfen for oxidative dethioacetalization of 1,3-dithialanes and 1,3-dithianes to their corresponding carbonyl compounds under dry condition supported this idea[9]

In continuation of our investigations on new and cleaner chemical processes,[10,11] we report herein the economical, practical, and environmentally acceptable procedure for oxidative deprotection of trimethylsilyl ethers to the corresponding carbonyl compounds (Scheme 1). Thus, upon microwave irradiation of trimethyl-silyl ether (e.g., $C_6H_5CH_2OSiMe_3$) in the presence of montmorillonite K10 and finely grounded $Fe(NO_3)_3$, $9H_2O$, benzaldehyde was produced almost in quantitative yield. The applicability of this method was tested with several aliphatic, and aromatic systems. Interestingly, no overoxidation was observed in the case of primary silyl ethers. Also, bezoin silyl ether, **1b**, was converted to diphenyl α,α-diketone (benzil), **2b**, in 95% yield. The results are summarized in Table 1.



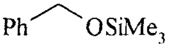
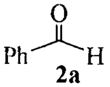
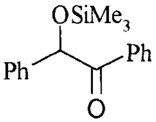
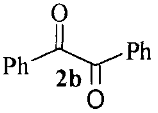
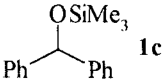
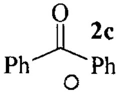
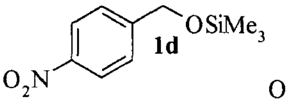
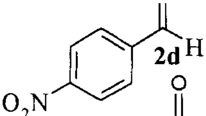
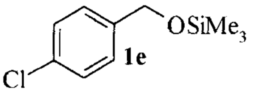
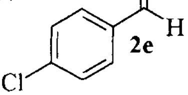
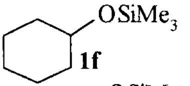
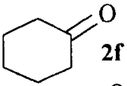
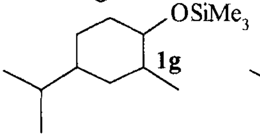
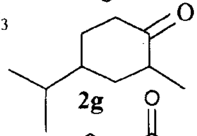
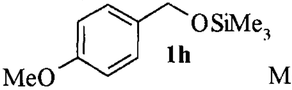
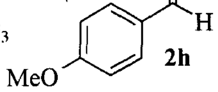
1 (a-h) **2 (a-h)**

Scheme 1

Experimental

Trimethylsilyl ether (1.0 mmol) was added to the mixture of montmorillonite K10 (1.0 g) and finely grounded $Fe(NO_3)_3.9H_2O$, (1.0 mmol, 0.4 g), clayfen,[4] in a 5

Table 1. Oxidative Deprotection of Trimethyl Silyl Ether with Iron (III) Nitrate

Entry	Silyl Ether	Time (sec)	Product	Yield %
1	 1a		 2a	90
2	 1b		 2b	95
3	 1c		 2c	90
4	 1d		 2d	70
5	 1e		 2e	80
6	 1f		 2f	85
7	 1g		 2g	80
8	 1h		 2h	95

mL beaker. The mixture was irradiated in a conventional microwave oven for 10 to 80 sec. at 900 W. The progress of the reaction was monitored by GLC, until the trimethylsilyl ether peak was disappeared. After completion of the reaction, the product was extracted with ether or methylenechloride (2x10 mL),

filtered, and the solvent was evaporated under the reduced pressure to yield the corresponding aldehyde or ketone. All compounds were identified with their NMR and IR spectra. The reaction was also carried out on 10 mmol scale for trimethylsilyl ether 1a. Benzaldehyde was produced with 95% yield after 30 sec.

In conclusion, the present methodology offers an attractive, rapid, efficient, and environmentally benign protocol for direct oxidation of protected alcohols to carbonyl compounds. The notable advantage of this method is the use of iron(III) nitrate instead of pollutant and toxic chromium salt.

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