SHORT PAPER

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Efficient and practical solvent-free oxidation of alcohols using microwave irradiation†

Mohammad M. Mojtahedi[a], Ali Sharifi[b], Sharif Kaamyabi[b] and Mohammad R. Saidi*[a]

[a]*Department of Chemistry, Sharif University of Technology, PO Box 11365-9516, Teheran, Iran*

[b]*Chemistry and Chemical Engineering Research of Iran, PO Box 14355-186, Teheran, Iran*

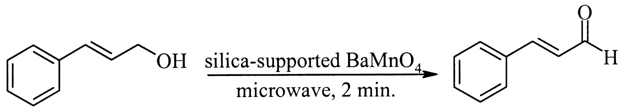
Alcohols are oxidised rapidly to the corresponding carbonyl compounds by montmorillonite KSF or silica supported barium manganate, under solvent-free conditions and microwave irradiation.

Keywords: alcohols, montmorillonite KSF, silica supported barium manganate

The oxidation of alcohols to carbonyl compounds is an important transformation in organic synthesis.[1] Although a large number of reagents are known in the literature for such transformations,[2] the development of newer oxidation methods to permit better selectivity under milder condition and with easy work-up procedure continue to receive great interest.[3]

Since the appearance of the first paper on the application of microwave irradiation in the chemical synthesis,[4] this useful technique has been used for variety of organic reactions and functional group transformation. The initial experiments with microwave techniques were carried out in high dielectric solvents. The focus has now shifted to solvent-free condition in the presence of mineral supports such as montmorillonite or silica, to eliminate or minimise the use of organic solvents.[5-7]

Silica-supported manganese dioxide and montmorillonite K10 clay-supported iron (III) nitrate, clayfen, have been also used for the oxidation of alcohols.[8] In continuation of our investigation on new and cleaner chemical processes,[9] we report here a facile, selective and inexpensive method of oxidation of alcohols to carbonyl compounds using silica- or montmorillonite KSF-supported barium manganate ($BaMnO_4$) under solvent-free conditions in a process which is accelerated by microwave irradiation. Our investigation began with an effort to optimise reaction conditions for the oxidation of alcohol using silica- or montmorillonite KSF-supported $BaMnO_4$ for 1 mmol of substrate. The reaction yield was determined by gas chromatography (GC) analysis using an internal standard. Randomly selected reactions were used to compare the isolated yields to those determined by GC. In each case, the isolated yield was within a few percent of the value determined by GC. The oxidative deprotection of trimethylsilyl ethers **1b** and **1c** to the corresponding carbonyl compounds **2b** and **2c**, are notable reaction under these conditions (Scheme 1).

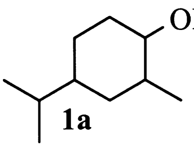
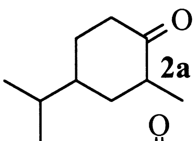
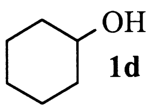
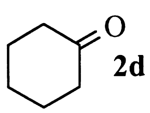
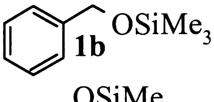
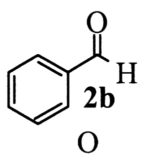
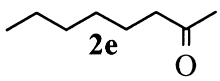
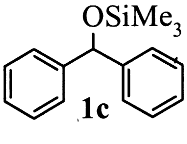
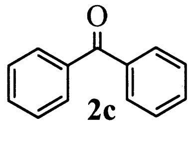
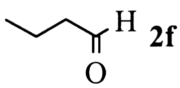
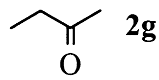


Scheme 1

No over-oxidation had been observed in the case of primary alcohols, and this is the main advantage for using barium manganate. The irradiation time was 2–3 min in all cases. Longer irradiation time may increase the yields in most cases.

When the mixture of benzyl alcohol and cyclohexanol was irradiated over silica-supported barium manganate for 2 min, only benzaldehyde was produced. No cyclohexanone could

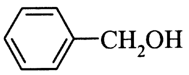
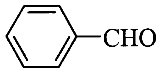
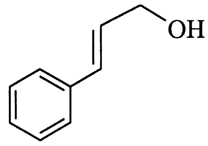
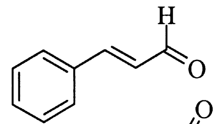
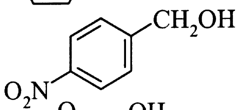
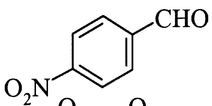
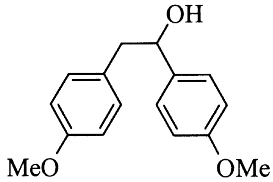
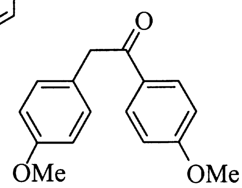
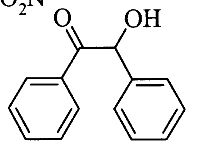
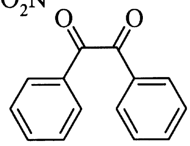
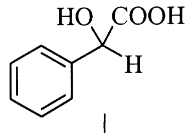
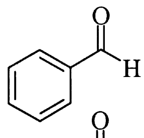
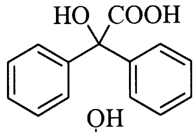
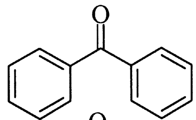
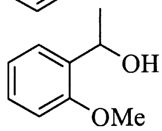
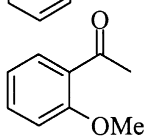
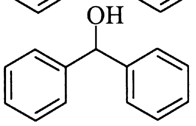
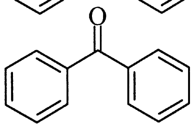
Table 1 Oxidation of alcohols by $BaMnO_4$/KSF under microwave irradiation

Substrate	Product	% Yield	Substrate	Product	% Yield
 **1a**	 **2a**	47	 **1d**	 **2d**	60
 **1b**	 **2b**	70	2-octanol **1e**	 **2e**	40
 **1c**	 **2c**	60	*n*-butanol **1f**	 **2f**	50
			2-butanol **1g**	 **2g**	60

* To receive any correspondence. E-mail: saidi@sharif.edu

† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 2 Oxidation of alcohols by $BaMnO_4$/silica under microwave irradiation

Substrate	Product	% Yield	Substrate	Product	% Yield
		72			61
		53			65
		60			60
		52			55
		56			

be detected in this condition. Also, benzaldehyde was produced when cinnamyl alcohol was irradiated over montmorillonite KSF-supported barium manganate.

Experimental

^1H NMR spectra were recorded in $CDCl_3$ on a Bruker AC 80 spectrometer, using TMS as internal standard. IR spectra were obtained on a Matt Son 1000 Unicam FTIR spectrophotometer.

General procedure for oxidation of alcohol using montmorillonite KSF-supported barium manganate: $BaMnO_4$ (0.75 g), montmorillonite KSF (2.0 g), and an alcohol (1 mmol) was throughly mixed using a vortex mixer. The material was placed in a 50 ml beaker inside a conventional microwave oven and was irradiated for the given time. Upon completion of the reaction, monitored by TLC, the product was extracted into ether, and the solvent was evaporated to afford the carbonyl compound. The results with different alcohols are listed in Table 1.

General procedure for oxidation of alcohol using silica-supported barium manganate: $BaMnO_4$ (0.75 g), silica (2.0 g), and an alcohol (1 mmol) was throughly mixed using a vortex mixer. The material was placed in a 50 ml beaker inside a conventional microwave oven and was irradiated for given time. Upon completion of the reaction, monitored by TLC, the product was extracted into ether, and the solvent was evaporated to afford the carbonyl compound. The results with different alcohols are listed in Table 2.

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