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Active Manganese Dioxide on Silica: Oxidation of Alcohols under Solvent-free Conditions Using Microwaves†

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Abstract: Alcohols are rapidly and selectively oxidized to the corresponding carbonyl compounds by silica supported active manganese dioxide under solvent-free conditions using microwaves.

The oxidation of alcohols to carbonyl compounds is an important transformation in organic synthesis and because of its significant role, the development of newer oxidative protocols[1] continues to receive attention in spite of the availability of several methods to accomplish this objective.[2-5] The use of supported reagents[6] has gained popularity because of the improved selectivity, reactivity and associated ease of manipulation. Since only the polar reactants adsorbed on the surfaces of various mineral supports absorb microwave energy, a variety of reagents supported on such surfaces can be utilized for the enhancement of organic reactions using a simple microwave (MW) oven.[7,8] Microwave-enhanced chemical reactions,[7,8] especially on inorganic solid supports and that are conducted under solventless conditions,[7e-f,8] have attracted attention recently. They offer several advantages over the conventional homogeneous and heterogeneous reactions in view of the rapid reaction rates and higher yields of the ensuing pure products.

Active manganese dioxide[9] is a potentially useful oxidant and has been used for the oxidation of a variety of compounds.[10] We report herein a facile and selective oxidation of alcohols to carbonyl compounds using silica-supported manganese dioxide (MnO_2) under solvent-free conditions in a process that is accelerated by microwave irradiation; the drying of this reagent at elevated temperatures is known to enhance the activity.[10] We examined various mineral supports such as clay, alumina, and silica and found that silica provides the best results in terms of formation of pure products. Also, the yields obtained are comparable to those reported for related reactions.[10] In the absence of support, the isolation of products from the ensuing residues is rendered difficult and the oxidation is also accompanied by the formation of minor contaminants. The reagent, however, does not discriminate between 1° and 2° alcohols as revealed by the oxidation of an equimolar mixture of benzyl alcohol and diphenylmethanol with MnO_2 that is barely enough to oxidize one component. The procedure involves a simple mixing of neat alcohols with silica-supported MnO_2 and irradiating the mixtures in a MW oven for 20-60 sec in the solid state. Our results for this rapid oxidative protocol are summarized in the **Table**.

The oxidation of benzyl alcohol is representative of the general procedure employed. MnO_2 'doped' silica (1.25 g, 5 mmol of MnO_2 on silica gel, Selecto Scientific, 230-400 mesh with large surface area of $600 m^2/g$) is thoroughly mixed with benzyl alcohol (108 mg, 1 mmol) and the material is placed in an alumina bath inside the MW oven and irradiated for 20 seconds. Upon completion of the reaction, monitored on TLC (hexane:AcOEt, 10:1), the product is extracted into methylene chloride, solvent removed and the residue passed through a bed of silica gel (4 cm) to afford exclusively benzaldehyde. The overoxidation to carboxylic acid is not observed. The same reaction could be completed in 2 h at a comparable temperature of 55 °C in an oil bath.

CAUTION: In view of the hazards associated with an active oxidant due caution is recommended for its use at elevated temperatures; the localized temperature may be much higher than the bulk temperature of the bath in the microwave oven and we suggest that the oven be operated at a lower power and for a shorter duration of time.

In conclusion, MnO_2-mediated solvent-free microwave thermolysis is a rapid and selective oxidative protocol for alcohols when compared to the conventional solution phase or heterogeneous reactions.

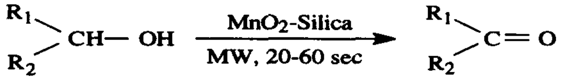

Table. Oxidation of alcohols to carbonyl compounds by MnO_2-silica[a] and using microwaves

Entry	R_1	R_2	Mole Ratio	Time (sec)	Yields (%)
1	C_6H_5	H	1:5	20	88
2	C_6H_5	CH_2CH_3	1:4	60	84
3	C_6H_5	C_6H_5	1:4	45	85
4	C_6H_5	C_6H_5CO	1:5	50	86
5	p-$CH_3C_6H_4$	H	1:4	45	81
6	p-$CH_3OC_6H_4$	H	1:4	30	83
7	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4CO$	1:5	45	85
8	$C_6H_5CH{=}CH$	H	1:4	50	67
9	Hydroquinone		1:4	36	76

[a] 0.348 g of manganese dioxide and 0.652 g of silica were ground in a pestle-mortar to prepare 35% MnO_2-Silica.

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