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MICROWAVE-ASSISTED OXIDATION OF ALCOHOLS UNDER SOLVENT-FREE CONDITIONS USING CLAYFEN

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Abstract: Adsorbed on clayfen, alcohols are readily oxidized to carbonyl compounds upon exposure to microwaves under solvent-free conditions. This rapid, selective and environmentally benign method conserves the use of excess solvents and toxic oxidants usually employed. © 1997 Elsevier Science Ltd.

The oxidation of alcohols to carbonyl compounds is an important transformation in organic synthesis and several methods have been explored to accomplish this conversion.[1] In this process, the use of heavy metals and peracids is very common, although selective methods are sought that are not detrimental to the environment.[2,3] In this context, the use of inexpensive supported reagents[4,5] has attracted attention because of the selectivity and the ease of manipulation. Specifically, clay-supported reagents have found widespread acceptance in a variety of heterogeneous reactions.[6,7]

The microwave (MW) enhanced chemical reactions,[8,9] in general and on inorganic solid supports[9-11] in particular, have gained popularity over the usual homogeneous and heterogeneous reactions[6,7] as they can be conducted rapidly and provide pure products in quantitative yields without the use of solvents. Since only the polar reactants adsorbed on the surface of the solid support absorb microwaves, a variety of reagents supported on such surfaces[6,7] can be utilized for the enhancement of organic reactions using an unmodified MW oven.[8] We report here a facile oxidation of alcohols to carbonyl compounds using montmorillonite K10 clay-supported iron(III) nitrate, clayfen,[6,7] under solvent-free conditions in a process that is accelerated by microwave irradiation. The reaction presumably proceeds *via* the intermediacy of nitrosonium ions,[6b] and no formation of carboxylic acids occurs. The experimental procedure involves a simple mixing of neat alcohols with clayfen and irradiating the reaction mixtures in a microwave oven for 15-60 seconds in the absence of any solvent. This extremely rapid, manipulatively simple, inexpensive and selective protocol avoids the use of excess solvents and toxic oxidants. The amount of clayfen used in our reactions is half of that used by earlier workers[7] under heterogeneous conditions that employs large excess of hydrocarbon solvents. Our results are summarized in the **Table**.

The oxidation of benzoin is representative of the general procedure employed. Clayfen (0.125 g) was thoroughly mixed with neat benzoin (0.106 g, 0.5 mmol) in the solid state using a vortex mixer and the material was placed in an alumina bath inside the MW oven[12] and irradiated. Upon completion of the reaction, monitored on TLC (hexane:AcOEt, 10:1, v/v), the product was extracted into methylene chloride. That the effect is not purely *thermal*[12] is supported by the fact that this reaction could be completed in 18 hours in an oil bath at a comparable temperature of 65 °C. The notable exception to these conditions was the case of p-methoxybenzyl alcohol which was completely oxidized to an aldehyde at room temperature. The limitation with aliphatic alcohols, however, still persists and the protocol gives a mixture of compounds.

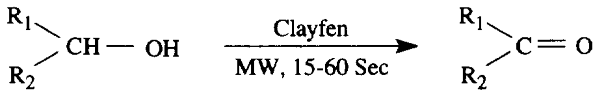

Table. Oxidation of alcohols by clayfen under microwave irradiation

Entry	R_1	R_2	Time (sec)	Yields (%)	I.R. $\nu_{C=O}$ (cm^{-1})
1.	C_6H_5	H	15	92	1705
2.	C_6H_5	CH_2CH_3	30	87	1670
3.	C_6H_5	C_6H_5CO	60	93	1660
4.	p-$CH_3C_6H_4$	H	15	94	1690
5.	p-$CH_3OC_6H_4$	H	–	96	1685
6.	p-$CH_3OC_6H_4$	p-$CH_3OC_6H_4CO$	60	94	1655
7.	Tetrahydrofurfuryl	H	30	90	1730
8.	—$(CH_2)_5$—		30	89	1715

In conclusion, clayfen-mediated solvent-free microwave thermolysis is a convenient, selective and environmentally benign oxidative protocol when compared to the conventional solution phase or heterogeneous reactions.

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