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'Zeofen', a user-friendly oxidizing reagent

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A variety of alcohols are oxidized to the corresponding carbonyl compounds in excellent yields by zeofen under classical heating and microwave irradiation in solventless system.

Oxidation of alcohols to carbonyl compounds is a fundamental transformation in organic synthesis and, because of its significant role, the development of newer methods is attracting much current interest[1–4] in spite of the availability of numerous methods reported in the literature.[5,6] The use of heavy metals and peracids is very common.[7,8] However, a drawback of such oxidants and their use in multistage organic synthesis in spite of their power is their lack of selectivity. For instance, overoxidation of aldehydes to carboxylic acids[9] and degradation of unsaturated substrates are often unavoidable side reactions.[10] In addition to their lack of selectivity, oxidants based on chromium[11] and manganese[12] are corrosive, irritants and toxic.[13]

In view of economic, practical and recent environmental demands,[14] we saw significant advantage in using a non-toxic and inexpensive metal salts such as iron(III) nitrate. Some early success in the use of clayfen for oxidation of alcohols[15] supported this idea.

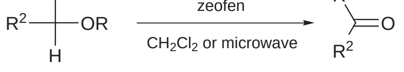
Reagents impregnated on mineral supports have gained popularity in organic synthesis because of their selectivity and ease of manipulation.[16,17] Recently we reported the use of zeolite catalyzed[18] and microwave enhanced chemical reactions[19] on organic solid supports.[20] We report here a facile oxidation of alcohols to carbonyl compounds using zeofen [short for zeolite HZSM-5 supported iron(III) nitrate] in CH_2Cl_2 at room temperature and under microwave irradiation in a solventless system.

To prepare zeofen, $Fe(NO_3)_3.9H_2O$ (0.80 g, 2 mmol) and a weight equivalent of HZSM-5 zeolite[21] were crushed together so as to form an intimate mixture (zeofen). This new reagent can be stored in a dark brown bottle and is stable without suffering from the problem of slow decomposition that clayfen does.[22] In a typical reaction 1–1.2 equiv. of zeofen was added to a stirring solution of an alcohol in dry CH_2Cl_2 at room temperature. After the completion of the reactions (monitored by TLC) the reagent was filtered off and washed with CH_2Cl_2. Evaporation of solvent gave the corresponding carbonyl compounds. It should be pointed out that in the absence of zeolite, the reaction was sluggish and even at reflux temperature a considerable amount of starting material was recovered unchanged. Different types of alcohols were converted to their corresponding carbonyl compounds by this procedure in high yields. The results are presented in Table 1.

Although there has been growing interest in applying microwave dielecteric heating to accelerate organic reactions,[23] oxidation reactions are less often considered as candidates for microwave irradiation due to their unsafe and uncontrollable experimental conditions.[24] It has been shown that polar reactants adsorbed on the surface of solid supports absorb microwaves.[25] In connection with our interest in using microwaves to increase the rates of reactions,[19] we have investigated the above oxidation under microwave irradiation. The oxidation reactions were carried out simply by mixing 1–1.2 equiv. of zeofen with 1 equiv. of an alcohol in a beaker under microwave irradiation (900 W) for 2 min. For example, benzyl alcohol was oxidized to benzaldehyde in almost quantitative yields after 10 s. It is noteworthy to mention that in the absence of zeolite, the reaction was slow and, more seriously, molten ferric nitrate and/or its degradation product(s) adhered to the walls of the reaction vessel, forming an intractable solid mass which made the isolation of carbonyl compounds difficult and led to erratic results. Indeed when iron(III) nitrate was used without zeolite the conversion of benzyl alcohol to benzaldehyde was only 50% under conditions otherwise similar to those described above. Clearly zeolite aided the reproducibility and high activity of iron(III) nitrate. To assess the generality of this oxidation a variety of alcohols were reacted under these conditions, which yielded the corresponding carbonyl compounds in excellent yields. Table 2 summarizes the data for oxidation of alcohols under microwave irradiation in a solventless system.

In conclusion, zeofen can be easily prepared from inexpensive and non-toxic materials and serves as an excellent oxidizing agent for various types of alcohols at room tem-

Table 1 Oxidation of alcohols to carbonyl compounds by zeofen in CH_2Cl_2[a]



	Alcohol	t/min	Product	Yield[b] (%)
1	$PhCH_2OH$	20	PhCHO	99 (90)
2	$4\text{-}MeC_6H_4CH_2OH$	20	$4\text{-}MeC_6H_4CHO$	93 (88)[c]
3	$2\text{-}NO_2\text{-}5\text{-}MeC_6H_3CH_2OH$	20	$2\text{-}NO_2\text{-}5\text{-}MeC_6H_3CHO$	92 (85)[c]
4	(DL)-PhCH(Me)OH	30	PhCO(Me)	89 (80)
5	Ph_2CHOH	40	Ph_2CO	90 (82)
6	$PhCH{=}CHCH_2OH$	40	PhCH=CHCHO	77 (67)
7	$PhCH_2CH(Ph)OH$	40	$PhCH_2COPh$	91 (88)
8	Cyclohexanol	60	cyclohexanone	82 (78)[c]
9	2-Methylcyclohexanol	60	2-methylcyclohexanone	85 (76)[c]
10	(−)-Menthol	60	menthone	85 (78)

[a] Reaction using 1–1.2 equiv. of zeofen in CH_2Cl_2. The physical data of the isolated products are in agreement with those of authentic samples. [b] Yields are based on GLC analysis. Figures in parenthesis are yields of isolated products. [c] Yields based on isolation of the 2,4-DNPH derivative.

Table 2 Oxidation of alcohols using zeofen under microwave irradiation in a solventless system[a]

	Alcohol	t/s	Product	Yield[b] (%)
1	$PhCH_2OH$	10	PhCHO	99 (92)
2	$4\text{-}MeC_6H_4CH_2OH$	20	$4\text{-}MeC_6H_4CHO$	97 (88)[c]
3	$2\text{-}NO_2\text{-}5\text{-}MeC_6H_3CH_2OH$	20	$2\text{-}NO_2\text{-}5\text{-}MeC_6H_3CHO$	95 (82)[c]
4	(DL)-PhCH(Me)OH	30	PhCO(Me)	90 (82)
5	Ph_2CHOH	20	Ph_2CO	92 (80)
6	$PhCH{=}CHCH_2OH$	60	PhCH=CHCHO	81 (87)
7	$PhCH_2CH(Ph)OH$	60	$PhCH_2COPh$	91 (88)
8	Cyclohexanol	120	cyclohexanone	85 (81)[c]
9	2-Methylcyclohexanol	120	2-methylcyclohexanone	84 (78)[c]
10	(−)-Menthol	120	menthone	88 (80)

[a] Reaction using 1–1.2 equiv. of zeofen under microwave irradiation in a solventless system. The physical data of the isolated products were in agreement with those of authentic samples. [b] Yields are based on GLC analysis. Figures in parentheses are yields of isolated products. [c] Yields based on isolation of the 2,4-DNPH derivative.

perature in solvent and under solvent-free conditions using a house-hold microwave oven. Solvent-free microwave irradiation has an advantage over conventional heating, offering a practical and environmentally benign protocol, decreasing reaction time and in some cases giving cleaner reactions and easier work up.

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