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Remarkable Fast Microwave-assisted Zeolite HZSM-5 Catalyzed Oxidation of Alcohols with Chromium Trioxide under Solvent-free Conditions†

Majid M. Heravi,* Dariush Ajami, Kourosh Tabar-Hydar and Mitra Ghassemzadeh

Chemistry and Chemical Engineering Research Center of Iran, P.O. Box 14335-186, Tehran, Iran

A variety of alcohols are oxidized to the corresponding carbonyl compounds in excellent yields by chromium trioxide–HZSM-5 zeolite under microwave irradiation in a solventless system.

Microwave heating and its application in organic chemistry for reactions is currently being developed successfully and in recent years there has been a tremendous interest in this area.[1–4] Remarkable decreases in reaction times and in some cases cleaner reactions and better yields have been reported with microwave irradiation.

Reactions under dry conditions were originally developed in the late 1980s.[5] Synthesis without solvents under microwave irradiation offers several advantages.[6] The absence of solvent reduces the risk of hazardous explosion when the reaction takes place in a closed vessel in an oven. Moreover aprotic dipolar solvents with high boiling points are expensive and are difficult to remove from reaction mixtures. During microwave induction of reactions under dry conditions, the reactants adsorbed on the surface of alumina, silica gel, clay, zeolites or similar material absorb the microwaves whereas the support does not, nor does it restrict their transmission.

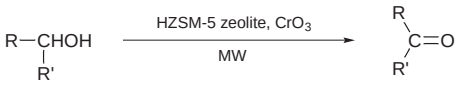
Consequently, such supported reagents efficiently induce reactions under safe and simple conditions with domestic microwave ovens instead of specialized commercial microwave systems that require sealed Teflon bombs.

Zeolites as catalysts have received considerable attention in recent years due to their characteristic properties such as transition state and size selectivity involving level precision, acidity and thermal stability.[6]

The oxidation of alcohols to carbonyl compounds is an important transformation in organic chemistry which is attracting much current interest.[7] Although a large number of reagents are known in the literature for such a transformation there still appears a need either to improve the existing oxidation methods[8] or to introduce newer reagents[9] to permit better selectivity under milder conditions and with easy work up procedures.

The oxidation of alcohols to the corresponding carbonyl compounds using zeolites under non-aqueous conditions has been reported,[10] and we have recently reported on the use of zeolite,[11–14] catalyzed reactions, microwave assisted reactions under solvent free condition[15–17] and chromium based oxidations.[18,19] Armed with these experiences, we now report that HZSM-5 zeolite along with CrO_3 oxidizes various primary and secondary alcohols under microwave irradiation in a solventless system in excellent yields.

HZSM-5 zeolite was prepared following a previously described procedure.[20] The SiO_2/Al_2O_3 ratio (53:1) was determined by X-ray fluorescence prior to the experiments, the zeolite was activated by heating at 400 °C for 8 h. Two equivalents of CrO_3 and a weight equivalent of HZSM-5 zeolite per mol of benzyl alcohol were used and exposed to microwave irradiation for 30 s, which led to the formation of benzaldehyde almost quantitatively. No trace of benzoic acid was observed showing that no over-oxidation occurs. Cinnamyl alcohol was converted to cinnamylaldehyde in 90% yield showing that carbon–carbon double bonds are not prone to cleavage using this method. To establish the generality of the oxidation (Scheme 1) a variety of alcohols were reacted under the conditions specified to yield the corresponding carbonyl compounds in excellent yields over very short times (Table 1). It is noteworthy that in the absence of zeolite the reaction under microwave irradiation is sluggish and considerable amounts of starting materials were recovered unchanged. It is also important to note that at least a weight equivalent of HZSM-5 zeolite is required for satisfactory conversion under microwave irradiation in the solventless system. As far as the relative catalytic ability of different rations of zeolite CrO_3 for various substrates is concerned, the optimized ratio is 1–2 equivalents of HZSM-5 zeolite.



Scheme 1

In conclusion, oxidation with CrO_3–HZSM-5 zeolite under microwave irradiation in solvent-free conditions is a rapid, manipulatively simple, selective and environmentally friendly protocol when compared to the conventional solution phase or heterogeneous condition, and should find utility in contemporary organic synthesis.

Experimental

All oxidation products are known compounds and are identified by comparison of their physical and spectral data. Yields refer to GLC analysis or isolation of their 2,4-dinitrophenylhydrazones. GC analysis

Table 1 Oxidation of alcohols with chromium trioxide–HZSM-5 zeolite under microwave irradiation on solventless system

Entry	Alcohol	*t*/s	Molar ratio[a]	Yield(%)
1	Benzyl alcohol	30	1:1.2	99
2	4-Methylbenzyl alcohol	20	1:1.2	99
3	5-Methyl-2-nitrobenzyl alcohol	80	1:1.2	96
4	Benzhydrol	20	1:1.2	93
5	Benzoin	40	1:1.2	91
6	Cinnamyl alcohol	60	1:1.2	90
7	Menthol	180	1:1.4	89
8	2-Methylcyclohexanol	120	1:1.4	86
9	Cyclohexanol	120	1:1.4	88
10	Octan-1-ol	240	1:1.6	84
11	2-Ethylhexanol	240	1:1.6	78
12	Dodecanol	300	1:1.6	81

[a] Zeolite:CrO_3.

* To receive any correspondence.

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was performed with a Fission 8000a gas chromatograph with a flame ionization detector using a column 10% carbowax 20 M on a chromsorb W/AW, 1.8 MX 6mm.

General Experimental Oxidation Procedure.—Chromium trioxide (2 mmol) and a indicated equivalent of HZSM-5 zeolite were crushed together in a mortar so as to form an intimate mixture. A neat alcohol was added to this intimate mixture. The resulting mixture was mixed thoroughly using a spatula. This mixture was placed on a microwave oven and irradiated (900 W) for an indicated time. The crude product was subjected to column chromatography using hexane–EtOAc (8:2) as eluent affording the corresponding carbonyl compound (Table 1).

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