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Chromium Trioxide on H-Y Zeolite: Rapid Oxidation of Alcohols to Carbonyl Compounds in Solventless System Using Microwaves

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Abstract: In an environmentally benign solventless system, alcohols are rapidly oxidized to carbonyl compounds using HY-zeolite supported chromium trioxide as an oxidant under microwave irradiation.

Chromium based reagents have been extensively used in organic synthesis[1]. The utility of chromium (VI) reagents in the oxidative transformation is compromised due to their inherent toxicity, cumbersome preparation and potential danger (ignition or explosion) in handling of its complexes, difficulties in terms of product isolation and waste disposal.

In recent years the organic reactions on solid supports[2] and those that are assisted by microwaves[3] especially under solvent free condition[4] have attracted attention because of their enhance selectively, milder reaction condition and associated ease of manipulation. However oxidation reactions are less considered under microwave irradiation due to unsafe and

uncontrollable experimental conditions.[4a] Therefore it not surprising that a large number of chromium oxidants impregnated on solid support have been explored.[5]

In continuation of our investigations on organic reactions in solventless system[6-8] and using zeolite as a catalyst,[9-11] we reasoned if HY-zeolite is used in place of H_2SO_4 along with CrO_3 and microwave irradiation in solventless system is chosen instead of classical heating, and if the oxidation occurred it could offer a milder and more environmentally friendly alternative to Jones oxidation. Indeed such a combination when one equiv of CrO_3 and weight equivalent of HY zeolite per mole of neat alcohol was irradiated under microwave irradiation led to formation of the desired carbonyl compounds.

Although the reaction does occur in dichloromethane and chloroform without much difference but in solvent under reflux reactions need at least 1h for completion.

These reactions under microwave irradiation take only 1-10 min to occur. Primary alcohols (allylic and non-allylic as well as benzylic ones did not undergo overoxidation to the carboxylic acid although cinnamyl alcohol gave benzaldehyde (25%) alonge with the desired cinnamyl aldehyde (70%) showing carbon-carbon double bonds are prone to this reagent under mentioned condition.

In summary, HY zeolite supported chromium trioxide under microwave irradiation in solvent-free condition can serve as a very efficient reagent for oxidation of alcohols. The yields are almost quantitative and the reaction conditions are mild and evironmentally benign and isolation of the products are simple and convenient. In addition in view of the current explosive interest in the use of zeolite in various organic transformations the present methodology should find utility in contemporary organic synthesis.

Experimental

All alcohols were available from commercial sources. HY zeolite was prepared from the reaction of commercially available NaY zeolite with NH_4NO_3 and subsequent calcination at 500°C for 12 h. All carbonyl compounds were known and their physical and spectro copic data were compared with those of authentic samples.

Table 1 Oxidation of alcohols with chromium trioxide-HY zeolite under microwave irradiation in solvent-free condition.

Entry	Alcohol	Time (Sec)	Carbonyl Compound	Yield
1	Benzyl alcohol	20	Benzaldehyde	98
2	P-Nitrobenzyl alcohol	600	P-Nitrobenzaldehyde	55
3	o-Hydroxybenzyl alcohhol	180	o-Hydroxybenzaldehyde	95
4	Benzhydrol	600	Benzophenone	95
5	Cinnamyl alcohol	120	Cinnamyl aldehyde	70
6	Cyclohexanol	20	Cyclohexanone	95
7	2-Methylcyclohexanol	20	2-Methylcyclohexanone	90
8	1-Octanol	60	1-Octanal	90
9	2-Ethylhexanol	20	2-Ethylhexanal	88
10	Menthol	240	Menthone	90

Oxidation of Alcohols, General Procedure

Chromium trioxide (1 mmol) and wieght equivalent of HY zeolite were crushed together in a mortar so as to form an intimate mixture. Neat alcohol (1 mmol) was added to this mixture in a beaker and was placed under microwave irradiation for the indicated time (Table 1). The progress of reaction was monitored by TLC. After completion of the reaction, the residue was taken into CH_2Cl_2, filtered, washed with CH_2Cl_2 (5 ml) and the filtrate was evaporated to dryness to give the corresponding carbonyl compounds. Fine purification was achieved by column chromatography using hexane, ethyl-acetate 8:2 as eluent.

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