Regeneration of carbonyl compounds from oximes by chromium trioxide supported onto HZSM-5 zeolite under microwave irradiation in solvent-free conditions

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A new method for the direct conversion of oximes into aldehydes and ketones by treatment with chromium trioxide supported onto HZSM-5 zeolite under microwave irradiation in solventless system is described.

Keywords: oximes, carbonyl compounds, CrO_3, zeolite, microwave irradiation

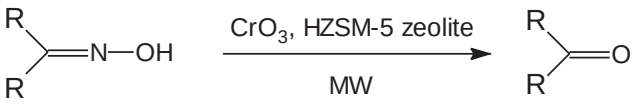
Oxime functionalities are widely used as useful protecting group. They are also extensively used for purification of carbonyl compounds.[1] The oximes also may be used as intermediate for the preparation of amides by the Beckmann rearrangement.[2] The importance of regeneration of carbonyl compounds from oximes assumed added importance after the discovery of the Barton reaction,[3] in which oximes are produced at non-activated hydrocarbon sites. A variety of methods have been developed for the regeneration of carbonyl compounds from oxime,[4] each of them has its merits and drawbacks.

Chromium based reagents have been extensively used in organic synthesis.[5] The utility of chromium(VI) reagents in oxidative transformations is compromised due to their inherent toxicity, cumbersome preparation and potential handling of complexes, difficulties in terms of product isolation and waste disposal. The concept of utilising reagents adsorbed on inert inorganic support to circumvent some of these problems, has been recently employed by several investigators.[6] We have also recently reported the introduction of chromium trioxide on solid support as an attractive alternative for oxidation in view of the selectivity and ease of manipulation.[7]

In continuation of our interest on organic reaction under microwave irradiation under solvent-free conditions,[8] we wish to report a fast, facile and selective regeneration of carbonyl compounds from their oximes. We have recently introduced HZSM-5 zeolite supported chromium trioxide as an efficient reagent for oxidation of alcohols under microwave irradiation in a solventless system.[9]

We now demonstrate that HZSM-5 zeolite supported chromium trioxide can efficiently and rapidly regenerate aldehydes and ketones from their oximes using microwave under solvent-free conditions.

HZSM-5 zeolite was prepared following a previously described procedure.[10] Two equivalents of CrO_3 and a weight equivalent of HZSM-5 zeolite per mole of oxime of acetophenone were exposed to microwave irradiation for 60 s,



Scheme 1

which led to formation of acetophenone almost quantitatively. In the case of the oxime of benzaldehyde no trace of benzoic acid was observed showing that no over-oxidation occurs. To establish the generality of this regeneration of carbonyl compounds from their oximes (Scheme 1) a variety of oximes were reacted in the conditions specified to yield the corresponding carbonyl compounds in excellent yields over very short times (Table 1).

We discovered that in the absence of zeolite the reaction does not proceed even on exposure to microwave irradiation for an extended period of time. The reactions are relatively clean with none of the tar formation typical of some CrO_3 reactions.

In conclusion, the results described in this communication demonstrate the novelty of a zeolite catalyst exercising, unique selectivity, relatively eco-friendly conditions and fast reactions.

Experimental

All compounds were known and are identified by comparison of their physical and spectroscopic data with those of authentic samples. Yields refer to isolated products. Although we did observe any accident, use of microwave oven in an efficient hood is highly recommended.

Oxidative deoximation. General procedure: Chromium trioxide (2 mmol) and an equivalent weight of HZSM-5 zeolite were crushed together in a mortar so as to form an intimate mixture. A neat oxime was added to this mixture. The resulting mixture was placed on a microwave oven and irradiated (900 W) for the indicated time. The crude product was directly subjected to column chromatography using hexane-EtOAc (8:2) as eluent affording the corresponding carbonyl compound (Table 1).

Table 1 Regenration of carbonyl compounds from their oximes using HZSM-5 zeolite supported CrO_3 under microwave irradiation in solventless system

Entry	Substrate	Reaction time/s	Product	Yield/%[a]
1	Benzaldehyde oxime	60	Benzaldehyde	92
2	4-Methylbenzaldehyde oxime	60	4-Methylbenzaldehyde	90
3	4-Chlorobenzaldehyde oxime	60	4-Chlorobenzaldehyde	95
4	Acetophenone oxime	60	Acetophenone	90
5	4-Nitroacetophenone oxime	120	4-Nitroacetophenone	88
6	4-Methoxyacetophenone oxime	60	4-Methoxyacetophenone	92
7	Benzophenone oxime	60	Benzophenone	91
8	Cyclohexanone oxime	120	Cyclohexanone	82
9	Vanillin oxime	120	Vanilline	71

[a]Yields refer to isolated product.

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