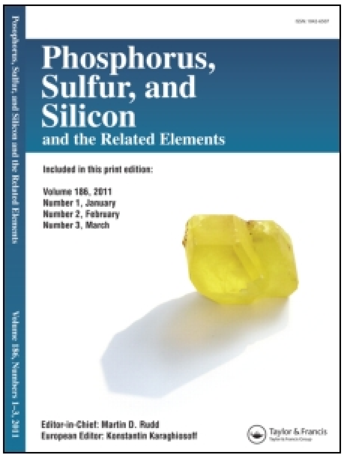

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Solid State Deoximation with Clay Supported Potassium Ferrate Under Microwave Irradiation

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SOLID STATE DEOXIMATION WITH CLAY SUPPORTED POTASSIUM FERRATE UNDER MICROWAVE IRRADIATION

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An environmentally benign process for the regeneration of carbonyl compounds from oximes is described.

Keywords: Clays; deoximation; microwave irradiation; oximes; potassium ferrate

Oximes, which are readily obtained from carbonyl compounds, have significant potential as intermediates in organic synthesis.[1] In the last decade, oximes have attracted much attention by being not only used to purify and isolate carbonyl compounds, but also to protect and activate carbonyl groups.[2] These reaction added attractions after the report of the Barton reaction in which oximes are obtained at non-activated hydrocarbon site.[3] Therefore an efficient catalytic deoximation can be considered as an alternative pathway to aldehydes and ketones.

The literature enumerates many routes for the transformation of oximes to carbonyl compounds,[4] each of which has its own merits and drawbacks. One of the most serious drawbacks of these methods is the use of a chromium reagent. They are inherently toxic[5] and handling of their complexes are potentially dangerous (risk of ignition and explosion).[6] Prompted by stringent environmental protection laws in recent years, there has been increasing emphasis on the design and the use of ecofriendly solid acid-base catalysts that work in the absence of

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organic solvents in a short time to reduce the amount of toxic waste and by-products arising from the chemical processes.[7]

Reagents deposited on mineral supports have been proven to be efficient in solvent-free conditions under microwave irradiation[8] and have attracted much attention because of their enhanced reactivity, selectivity, and ease of manipulation.

In contrast with other transition metals, iron is singled out to be nontoxic.[9] Potassium ferrate (K_2FeO_4), a six-valent iron compound, can be easily prepared by oxidizing ferric nitrate with sodium hypochlorite and subsequent treatment with potassium hydroxide.[10] It is the best known member among the family of iron(VI) derivatives.

We have recently reported potassium ferrate supported onto montmorillonite K-10 as a mild, efficient and inexpensive reagent for oxidative deprotection of trimethylsilyl ethers in non-aqueous conditions.[11] During the course of our investigation in this field[8c-d] and particularly in the exploitation of implementation of organic reactions under microwave irradiation, we wish to extend the utility of supported potassium ferrate in cleavage of oximes under microwave irradiation (Figure 1).

We have studied different substrate/reagent ratios and found that 1:2 is suitable for the successful transformation of oximes to carbonyl compounds. It is also noteworthy to mention that the reactions are incomplete when they are done in the absence of montmorillonite under microwave irradiation even with higher ratios of reagents. In a typical procedure an appropriate oxime (2 mmol) and potassium ferrate (4 mmol) along with an equivalent weight of montmorillonite K-10 were mixed together in an Erlenmeyer flask and irradiated for the indicated time (Table I) to afford the corresponding carbonyl compound. The Table shows some of the aldehydes and ketones regenerated from the corresponding oximes by this method. Even the sterically hindered benzophenone oxime and camphor oxime were converted to their corresponding carbonyl compound.

In summary, the present procedure for the oxidative cleavage of oximes shows significant advantages over the existing method. The main advantage of this method is use of a relatively harmless iron compound in solventless system which brings eco-friendly chemical reaction along with short reaction time, mild condition, easy work up

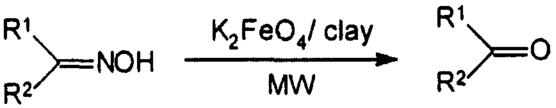
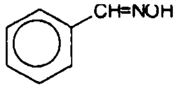
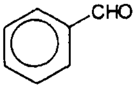
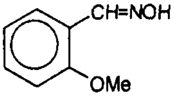
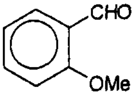
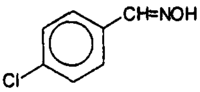
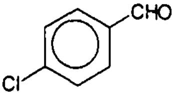
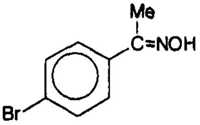
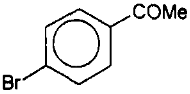
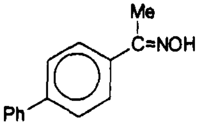
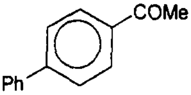
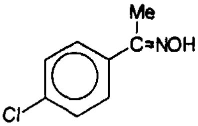
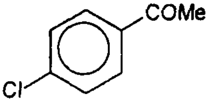
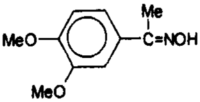
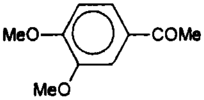
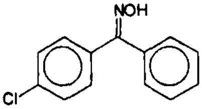
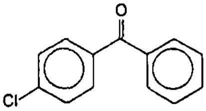
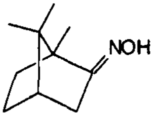
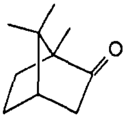


FIGURE 1

TABLE I Substrate and Products from Reactions of Oximes with Potassium Ferrate under Microwave Irradiation in Solventless System

Entry	Substrate[a]	Carbonyl compound[b]	Time (min)	Yield (%)
1			5	95
2			5	88
3			8	82
4			8	90
5			10	92
6			8	91
7			5	85
8			8	82
9			10	81

[a] All substrates were prepared by known literature procedures.

[b] All products were characterized by comparison of their physical and spectroscopic data with authentic samples.

[c] Yields refer to isolated products.

procedure and excellent yields. With these advantages we believe the method can be considered as a useful and important addition to the present methodologies.

EXPERIMENTAL SECTION

Potassium ferrate was prepared according to the reported procedure.[10] KOH, $Fe(NO_3)_3.9H_2O$ and potassium permanganate were analytically pure reagents and purchased from Aldrich, England. All products were known and characterized by comparison of their physical and spectroscopic data with those of authentic samples.

DEOXIMATION OF OXIMES (GENERAL PROCEDURE)

An appropriate oxime (2 mmol) was mixed with potassium ferrate (4 mmol) and equivalent weight of montmorillonite K-10 in a watch glass. The mixture was transferred into a small beaker and placed in a microwave oven for the indicated time. The crude product was extracted with CH_2Cl_2 and filtered. The filtrate was evaporated to dryness. The crude product was passed through a small column of silica gel to afford the corresponding carbonyl compound.

Caution

Although we did not experience any accidents, and the reactions worked safely in our hands, we advise to use the microwave oven in a suitable hood and suggest that the microwave oven be operated in multiples for shorter reaction times (1 min) because of the possible higher localized temperature.

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