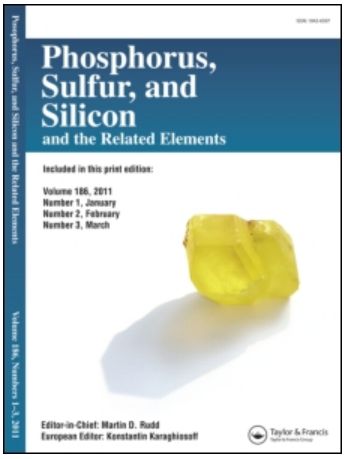

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Microwave-Assisted Eco-Friendly Cleavage of Acetals Using Supported Potassium Ferrate

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MICROWAVE-ASSISTED ECO-FRIENDLY CLEAVAGE OF ACETALS USING SUPPORTED POTASSIUM FERRATE

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An environmentally benign process for the cleavage of acetals under microwave irradiation using clay supported potassium ferrate in dry media is reported.

Keywords: Acetals; carbonyl compounds; eco-friendly condition; microwave irradiation; potassium ferrate

Protection and the subsequent deprotection of a functional group is fundamental and almost inevitable in multistage organic synthesis.[1]

Protection of the carbonyl groups in the form of acetals from nucleophilic attack is usual practice in multistep organic synthesis to exploit its electrophilic properties.[2] Therefore an efficient catalytic cleavage of acetals would be of great importance. Although literature enumerates quite a number of methods of such deprotection,[3] careful scrutiny of the reaction procedure reveals some drawbacks.

The implementation of chemical processes following environmentally benign strategies represents a great challenge in organic synthesis today.[4] The use of environmentally friendly solid acid catalysts[5] especially under microwave irradiation in solvent free conditions is now the best way for the synthesis of specific target compounds with minimum production of pollutants as well as reduction of cost.

The synthesis and ability of potassium ferrate (K_2FeO_4), a high-valent iron salt for oxidizing organic substrates in non-aqueous media

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has been recently studied.[6] Reagents adsorbed on mineral supports have gained popularity in organic synthesis due to their selectivity and ease of manipulation.[7] Montmorillionite clays have been extensively used as efficient support for a variety of organic reactions.[8]

In continuation of our ongoing program to develop the use of surface active catalysts along with the development of eco-friendly synthetic protocols utilizing microwave irradiation in a solventless system,[9] herein we wish to report the use of montmorillionite K-10 supported potassium ferrate as a new catalyst for the cleavage of acetals under microwave irradiation in a solventless system.

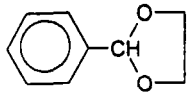
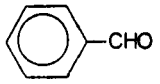
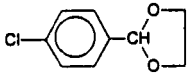
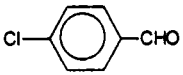
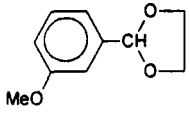
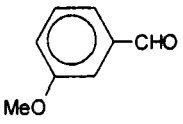
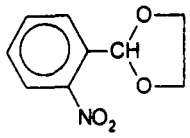
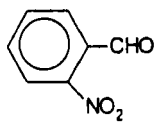
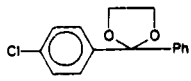
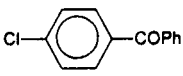
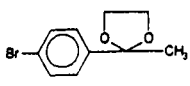
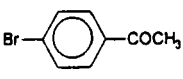
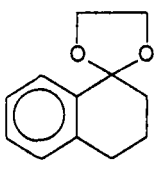
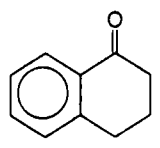
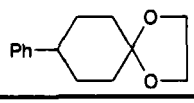
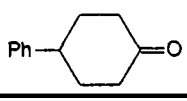
RESULTS AND DISCUSSION

Potassium ferrate (K_2FeO_4), a sixvalent iron compound can be easily prepared by oxidizing ferric nitrate with sodium hypochlorite and the subsequent treatment with potassium hydroxide.[6] This iron compound is a black-purple powder that remains stable in the air for long periods of time provided that moisture is excluded. By contrast with other transition metals, iron is known to be nontoxic.[10] Association of ferric nitrate with montmorillionite[9a] and zeolite[9c] has been reported from our laboratory leading to design of Zeofen as a versatile oxidizing agent.[1]

Among numerous solid supports we found montmorillionite K-10 is a suitable associate for potassium ferrate to perform oxidation.[12] During the course of this study we have observed that the acetals are also susceptible to clay supported potassium ferrate under microwave irradiation in a solventless system. We have found the 1:3, substrate/reagent ratio is suitable for successful cleavage of acetals. It is noteworthy to mention that the reaction remains incomplete when clay is not used with the reagent even for prolonged reaction under microwave irradiation. However the reactions proceed in few minutes when the montmorillionite K-10 is used. Our results are summarized in Table I.

In summary this methodology for the cleavage of acetals has many advantages over the existing methods and will make a useful and important addition to the present procedures. The main advantages of this method are mild reaction conditions, short reaction times, excellent yields and most importantly using relatively harmless iron salt in the absence of hazardous organic solvents.

TABLE I Cleavage of acetals using potassium ferrate supported onto montmorillionite K-10 under microwave irradiation in solventless system

Substrate[a]	Product[b]	Time (min)	Yield[c] (%)
		5	92
		10	90
		8	95
		10	86
		8	92
		5	90
		5	80
		6	85

[a]All substrates were synthesized according to reported procedure.

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

[c]Yields refer to isolated products.

EXPERIMENTAL

All products are known compounds and their physical data were essentially identical with those of authentic samples. Acetals were synthesized according to known procedure. Microwave irradiation was carried out in a National Oven, Model 5250 at 900W.

CLEAVAGE OF ACETALS BY POTASSIUM FERRATE SUPPORTED ONTO MONTMORILLIONITE K-10

General Procedure

In a small beaker an appropriate acetal (2 mmol), potassium ferrate (6 mmol) and montmorillionite K-10 (0.5 g) were intimately mixed. The mixture was placed in a household microwave oven for the indicated time. The progress of the reaction was monitored by TLC, using hexane : ethyl acetate, 8:2. The crude product was suspended in CH_2Cl_2 and filtered. The filtrate was evaporated to dryness under reduced pressure. The crude product was passed through a small column of silica gel, using hexane : ethyl acetate, 8:2 to afford the corresponding carbonyl compound (Table I).

CAUTION

Although this procedure worked safely in our hands, using a microwave oven in an efficient and safe hood is advised.

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