SHORT PAPER

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Regeneration of carbonyl compounds from oximes on clayfen under conventional heating and microwave irradiation[†]

Majid M. Heravi*, Dariush Ajami and Mohammad M. Mojtahedi

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

A new and effecient method for cleavage of oximes has been achieved by a simple reaction of an oxime with clayfen in dichloromethane and under microwave irradiation in solventless system.

In 1985, Laszlo and co-workers reported clayfen as a versatile oxidizing agent.[1] Clayfen is an efficient and selective agent for producing aldehydes and ketones from primary and secondery alcoholes.[2] A large number of imino derivatives such as hydrazones and semicarbazones have been oxidatively cleaved by clayfen.[3] A slight adoptation of this procedure should allow its extension to an other imine family such as oxime.

Oximes are extensively employed for characterization and purification of carbonyl compounds.[4] Their synthesis from non-carbonyl compounds offers an alternative route to aldehydes and ketones.[4b,c,5]

In recent years cleavage of oximes to regenerate the parent carbonyl compounds has received much attention.The hydrolytic stability of oximes has promoted the development of several deoximation reagents such as pyridinium chlorochromate,[6a]pyridinium chloromate–hydrogen peroxide,[6b] triethylammonium chlorochromate,[6c] chromic anhydride–chlorotrimethylsilane,[6d] bismuth trichloride,[6e] wet silica supported sodium periodate,[6f] activated MnO_2,[6g] TBHP,[6h] Des-Martin periodinane[6i] and tetrabutylammonium peroxy disulfate.[6j]

Considering the synthetic utility of clayfen which has become readily accessible in recent years we thought that oximes might undergo Beckmann rearrangment when subjected to this acidic and ionic reagent.[7]

The results of our investigation suggest that alternative modes of cleavage seem to happen which results in the desired oxidative regeneration of the carbonyl compounds. For example, when benzaloxime and 0.66 equivalent of clayfen are refluxed in CH_2Cl_2 for couple of hours, benzaldehyde was obtained in almost quantitative yield. To assess the generality of the method, variety of aldoximes and ketoximes were treated with clayfen in nonaqueous conditions to afford the corresponding aldehydes and ketones in good to high yields (Table1).

Microwave irradiation[8] in organic synthesis is a useful technique.[9] Drying media using microwave heating have attracted much attention.[10] Adsorbed on clayfen, alcohols can be readily oxidized to carbonyl compounds upon exposure to microwave under solvent free conditions.[10] In continuation of our current investigations on organic manipulation, using microwave in solventless system,[11] we now report a solid state oxidative cleavage of oximes using clayfen under microwave irradiation. Clayfen and oximes were mixed together in a beaker. Microwave irradiation of oxime on clayfen under solvent-free conditions provides a fast, efficient and simple method for regeneration of carbonyl compounds. A variety of oximes were oxidatively cleaved by this method (Table 1).

In conclusion clayfen can be used as an excellent deoximation reagent for various type of oximes in refluxing solvent under solvent free conditions using a household microwave oven. Solvent free conditions have the advantage over conventional heating, offering a practical and environmentally benign protocol, that decreases reaction time and in some cases gives cleaner reactions and easier work up. In addition, by development of a continuous microwave reaction for organic synthesis, this work may make industrial applications where the absence of solvent and low cost of the method may lead to environmental and economic advantages.

Caution: Although we did not have any accidents using clayfen, it is advisable to using a hood for reaction. The clayfen shoud be freshly prepared and not stored for long.

Experimental

All products were known compounds and identified by comparison with authentic samples. Yields refer to isolated products.Clayfen was prepared according to referred procedure.[1]

Cleavage of oximes using clayfen under non-aqueous condition: To a stirred solution of oxime (10 mmol) in dicholoromethane (25 mL) freshly prepared clayfen [6g:corresponding to 6.6 mmol of iron (III) nitrate] was added. A slightly exothermic reaction happens immediately. This mixture is refluxed for 3 h until completion of the reaction (monitored by TLC).The reaction mixture was filtered after cooling and the solid residue was washed with CH_2Cl_2 (10 mL). The combined filtrated was evaporated to dryness under reduced pressure. The residue was filterd through a silica gel pad to afford the corresponding carbonyl compound (Table 1).

Cleavage of oxime using clayfen under microwave irradiation: In a small beaker oxime (10 mmol) and freshly prepared clayfen reagent (6.6 mmol of iron(III) nitate) were mixed together to make an intimate mixture. The beaker was placed in a household microwave oven for the specified time. The residue was washed with CH_2Cl_2 (10 mL) and filtered. The filtrate was evaporated to dryness to afford the corresponding carbonyl compound.

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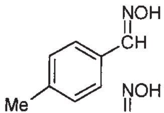
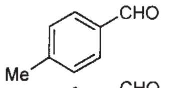
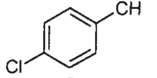
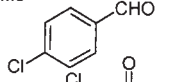
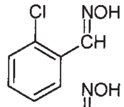
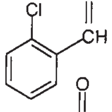
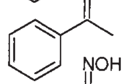
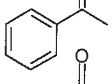
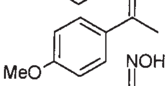
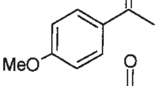
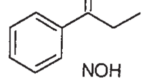
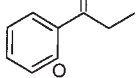
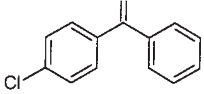
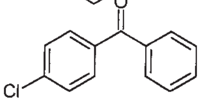
* To receive any correspondence E-mail: mmheravi@azzahra.ac.ir.

[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

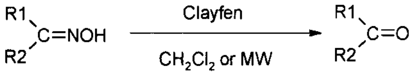
Table 1 Oxidative cleavage of oximes with clayfen under classical heating and microwave irradiation in dry media

Entry	Substrate[a]	Carbonyl compound[b]	In Ch_2Cl_2		Dry media	
			Reaction time (min)	Yield[c] (%)	Reaction time (s)	Yield[c] (%)
1			40	90	60	91
2			40	86	60	90
3			40	85	60	89
4			40	86	60	86
5			40	84	60	86
6			40	83	60	88
7			40	86	60	89

[a]All substrate were synthesised by known literature procedure.

[b]All products were characterized by comparison of their m.p, IR and 1 H MNR spectra with those of authentic sample.

[c]Yields refer to isolated products.



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