

Clinoptilolite-Supported Iron(III) Nitrate as a Powerful and Efficient Deoximation Catalyst. Fast Regeneration of Carbonyl Compounds from Oximes*

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Abstract—Clinoptilolite-supported iron(III) nitrate (clinofen) ensures fast and efficient regeneration of carbonyl compounds from the corresponding oximes.

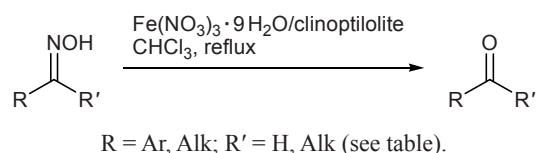
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Oximes are crystalline substances which are widely used for the isolation, purification, and identification of parent carbonyl compounds [1]. Protection of carbonyl functionality via conversion into the corresponding oximes attract considerable attention of organic chemists, taking into account that such derivatives can readily be obtained and are highly stable [2].

Regeneration of carbonyl compounds from their oximes is a quite important problem. In the recent years, numerous reagents have been proposed to effect deoximation (for review, see [3]). Some other reagents, such as thallium(III) nitrate on HZSM-5 zeolite [4], ammonium chlorochromate applied to clay [5], Oxone over wet alumina [6], silica-supported prolinium chlorochromate [7], 2,6-dicarboxypyridinium chlorochromate [8], silica-supported bismuth(III) nitrate in the presence of DABCO [9], etc. [10, 11] were also reported.

Most known methods for the recovery of carbonyl compounds from their oximes have some limitations, including long reaction times, tedious work-up and isolation procedures, and expensive, hazardous, or very toxic reagents. In addition, some procedures require the use of difficultly accessible reagents which must be freshly prepared. Many reagents are not selective for oximes in the presence of unsaturated C=C bonds [12]. In some cases, side overoxidation processes led to reduction of the yield of the target products [13]. Therefore, search for mild, selective, safe, low-expensive, and effective oxidants for the transformation of oximes into the corresponding carbonyl com-

pounds remains an important problem. We recently reported on solvent-free deoximation of oximes using zeofen under microwave irradiation [14]. In the present communication we report on a very convenient and highly effective procedure for oxidative deoximation of ketone and aldehyde oximes to the corresponding carbonyl compounds using clinoptilolite-supported iron(III) nitrate (clinofen) [15] as nontoxic heterogeneous reagent in an organic solvent under moderate conditions (no aqueous media were needed).



As far as we know, this is the first report on the use of clinoptilolite in organic synthesis. Our results (see table) demonstrate such advantages of the proposed procedure as high rate of oxidative deoximation, no formation of overoxidation products, simple experiment, and high yields.

EXPERIMENTAL

All initial oximes were prepared by known methods. The physical and spectral properties of the obtained carbonyl compounds were identical to those reported for authentic samples [16].

Regeneration of carbonyl compounds from the corresponding oximes using clinofen. A mixture of 1 mol of oxime, 1 g of clinoptilolite, and 1 mmol of iron(III) nitrate in 10 ml of chloroform was heated un-

* The text was submitted by the authors in English.

Deoxygenation of aldehyde and ketone oximes using iron(III) nitrate supported onto clinoptilolite (chloroform, reflux)

R	R'	Time, min	Yield, % (GLC data)	mp (bp), °C	
				this work	published data [16]
3-O ₂ NC ₆ H ₄	H	10	99	56	56–59
4-MeC ₆ H ₄	H	2	94	(204)	(204–205)
4-ClC ₆ H ₄	H	12	92	46	47
2-MeOC ₆ H ₄	H	5	96	(238)	(238)
PhCH=CH	H	15	96	(253)	(253)
(CH ₂) ₅		1.5	94	(158)	(156)
4-O ₂ NC ₆ H ₄	Me	15	97	79	80–82
Me(CH ₂) ₈	H	5	95	(209)	(208–209)
Me(CH ₂) ₆	H	2	97	(171)	(171)
2-O ₂ NC ₆ H ₄	H	10	96	44	43.4–44.0

der reflux over a period indicated in table. The mixture was filtered, the filtrate was evaporated, and the residue was recrystallized from appropriate solvent.

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