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AN EFFICIENT CLEAVAGE OF OXIMES INTO CARBONYL COMPOUNDS OVER FERRIC NITRATE - PART 3

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ABSTRACT

A facile and rapid regeneration of carbonyl compounds from oximes occurred over ferric nitrate under irradiation in dry media conditions.

Key words- Carbonyl compounds, Oximes, Ferric nitrate

INTRODUCTION

Oximation of carbonyl compounds is widely used as a protective protocol in synthetic organic chemistry although it is also used for purification as well as characterization of carbonyl compounds. Obviously, deoximation is an important process for the deprotection of carbonyl compounds. Further, since oximes can be synthesized from non-carbonyl compounds as well, (Barton's reaction), therefore, deoximation assumes all the more importance.

Many methods are known for the regeneration of carbonyl compounds from oximes. These include, pyridinium chlorochromate[1], bhromium-trioxdiechlorotrimethyl silane[2], manganese triacetate[3], activated $Mn0_2$[4], dinitrogentetraoxide[5], titanium silicate[6], sodium perborate[7], sodium periodate[8] $SnCI_2$-$Si0_2$[9] etc. Although many of these methods have their own advantages, they suffer from one or the other drawback such as drastic reaction condition, inexpensive reagents, longer reactions times etc. In fact, even if there were not to suffer from any drawback, yet it is always rewarding to explore new methodologies, although the newer methods may turn out to suffer from their own disadvantages.

In earlier communication, we have reported the deoximation over Mont KSF/H_2S0_4 and Mont K10/H_2SO_4 and Ferric nitrate /Ferric chloride. We now report the regeneration of carbonyl compounds from oximes using ferric nitrate alone under microwave irradiation, which to the best of our knowledge has not been reported so far.

To start with, benzaldehyde was found to have been deoximated completely in just 120 seconds of irradiation in an unmodified microwave oven at 240 W. Subsequently, a large variety of oximes of carbonyl compounds were deoximated - 4 hydroxy benaldehyde, 4-chlorobenzaldehyde, 4-methoxy benaldehyde, 2-nitrobenzaldehyde, acetophenone, benzophenone, cyclohexanone, cycloheptanone, α-tetralone (See table). Cinnamaldehyde oxime was chosen as an example of α,β unsaturated oximes. a-tetralone oxime was taken to be a representative example of sterically hindered oxime. All the products are known compounds and were identified on basis of their spectroscopic analyses and by comparison with those of authentic samples prepared by standard routes reported in the literatures. They were further purified by column chromatography. As is evident from the table, the carbonyl compounds were regenerated into more then 90% yield in a few minutes.

Even the a,p unsaturated oxime was transformed efficiently into cinnamadehyde without double bond being attacked. Further more, even the sterically hindered of α -tetralone underwent deoximation in very high yield. To sum up, we have reported a rapid regeneration of carbonyl compounds over ferric nitrate under microwave irradiation. This method should find wide applicability, as the reagent used is a low-cost as well as readily available reagent.

Table-1 : Regneration of Carbonyl compounds from oximes over ferric nitrate [$Fe(N0_3)3;9H_20$] at 240 W

Oximes of	Times(Sec)	Yield(%)
Benzaldehyde	120	95
oc-hydroxy benzaldehyde	125	94
2-hydroxy benzaldehyde	130	93
4-Chloro benzaldehyde	132	93
4-methoxy benzaldehyde	125	92
4-nitro benzaldehyde	135	91
acetophenone	155	92
benzophenone	160	92
cyclopentanone	100	91
cyclohexanone	150	91
cycloheptanone	170	90
a-tetralone	175	90
cinnamaldehyde	150	92

EXPERIMENTAL

Melting points were determined in open capillaries on an electrically heated metal block and are uncorrected. PMR ($CDCl_3$) spectra were recorded on a JEOL FX 90 instrument employing TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer 782 spectrophotometer. The oximes were prepared by standard routes reported in the literature.

In a typical procedure, to benzaldoxime 1 mmol was added 1 mmol ferric nitrate in a 50 ml Erlenmeyer flask. The flask was irradiated at 240 W for 120 second in a unmodified domestic microwave oven, kenstar OM 9925E, 800 W operating at 2450 MHz. Monitoring of the reaction was down by TLC. The flask was taken^out, cooled and 50 ml ether added in it. The mixture'was filtered off the solvent was evaporated to yield the benzaldehyde, which was further purified by column chromatography.

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