

A RAPID DEOXIMATION OF CARBONYL COMPOUNDS WITH FERRIC CHLORIDE - PART - 4

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ABSTRACT

A rapid regeneration of carbonyl compounds from oximes occurred over ferric chloride under microwave irradiation in dry media conditions.

Key words-

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 deportation of carbonyl compounds. Further, since oxime can be synthesized from non-carbonyl compounds as well, (Braton's reaction), therefore, deoximation assumes all the more importance.

Many methods are known for the regeneration of carbonyl compounds from oximes. These include, pyridinium chlorochromate¹, chromium-trioxidechlorotrimethyl silane², manganese triacetate³, activated MnO₂⁴, dinitrogen tetraoxide⁵ titanium silicate⁶, sodium perborate⁷, sodium periodate⁸, SnCl₂-SiO₂⁹ etc. Although many of these methods have their own advantages, they suffer from one or the other drawback such as drastic reaction conditions, 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 method may turn out to suffer from their own disadvantages.

In a preceding communications, we have reported the deoximation over Mont KSF/H₂SO₄, Mont K10/H₂SO₄, ferric nitrate/ ferric chloride and ferric nitrate. We now report the regeneration of carbonyl compounds from oximes using ferric chloride alone under microwave irradiation, which to the best of our knowledge has not been reported

so far.

In model studies, benzaldehyde was found to have been deoximated completely in just 90 second of irradiation in an unmodified microwave oven at 240 W. Subsequently, a large variety of oximes of carbonyl compounds were deoximated 4 hydroxy benzaldehyde, 4-chlorobenzaldehyde, 4-methoxy benzaldehyde, 2- nitrobenzaldehyde, acetophenone, benzophenone, cyclohexanone, cycloheptanone, α - tetralone (See table) Cinnamaldehyde oxime was chosen as an example of α , β unsaturated oxime. α - tetralone oxime was taken to be a representative example of sterically hindered oxime. All the product 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 than 90% yield in a few minutes.

Even the α , β unsaturated oxime was transformed efficiently into cinnamaldehyde without the double bond being attacked. Further more, even the sterically hindered oxime of α -tetralone underwent deoximation in very high yield.

To sum up, we have reported a rapid regeneration of carbonyl compounds over ferric chloride under microwave irradiation. This method should find wide applicability as the reagent used is a low-cost as well as available reagent. Although similar yields were obtained with ferric nitrate in

Table: Regeneration of Carbonyl compounds from oximes over ferric chloride at 240W.

Oximes of	Times(Sec)	Yield(%)
Benzaldehyde	90	94
cx-hydroxy benzaldehyde	95	93
2-hydroxy benzaldehyde	100	93
4-Chloro benzaldehyde	98	94
4-methoxy benzaldehyde	94	94
4-nitro benzaldehyde	90	90
acetophenone	135	90
benzophenone	155	92
cyclopentanone	140	91
cyclohexanone	135	93
cycloheptanone	140	91
cc-tetralone	142	92
cinnamaldehyde	100	91

our earlier publication, the reaction times are much smaller.

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 chloride in a 50 ml Erlenmeyer flask. The flask was irradiated at 240

W for 90 second in a unmodified domestic microwave oven, kenstar OM 9925E, 80 W operating at 2450 MHz. Monitoring of the reactions was done by TLC. The flask was taken out cooled and 50 ml ether added in it. The mixture was tittered off the solvent was evaporated to yield the benzaldehyde, with was further purified by column chromatography.

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- Maloney J R, Lyle I E, Scavedra J E, Lyle G, *Synthesis*, **212**, (1978)
- Arzupurua J M, Jurirti M, Lecea B, Paloma C, *Tetrahedron*, 2903 (1985) and reference therein.
- Ayha H D, Taneyli E A, *Tetrahedron Lett*, **38**, 7268 (1997) and reference therein.
- Shenada T, Yashihara K, *Tetrahedron Lett*, **36**, 6701 (1995)
- Shim S8, Kim K, Kim Y H, *Tetrahedron Lett*, **28**, 645 (1987)
- Joseph R, Sudalai A, Ravindranathan Y, *Tetrahedron Lett*, **35**, 5493 (1994)
- Bandgar B P, Shaikh S I, Iyer S, *Synthetic Commun*, **26**, 1163 (1996)
- Varma R S, Dahiya R, Saini R K, *Tetrahedron, Tetrahedron Lett*, **38**, 8819 (1997)
- Das N B, Nanda B, Nayak A, *Synth Communication*, **23**, 3647 (2002) and reference therein.