

$K_3[Fe(CN)_6].3H_2O$ supported on silica gel: An efficient and selective reagent for the cleavage of oximes to their corresponding carbonyl compounds in aqueous medium

ABBAS AMINI MANESH* and BEHZAD SHIRMARDI SHAGHASEMI

Department of Chemistry, Payame Noor University, 19395-4697 Tehran, I. R. of IRAN
e-mail: a_aminima@yahoo.com

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Abstract. $K_3[Fe(CN)_6].3H_2O$ supported on silica gel, a new oxidant, for efficient, simple and selective cleavage of ketoximes and aldoximes to their corresponding carbonyl compounds in aqueous medium is described. Further oxidation of aldehydes to carboxylic acid and formation of by-products were not observed. $\alpha - \beta$ unsaturated oxime was deoximated smoothly without oxidation of the double bond.

Keywords. $K_3[Fe(CN)_6].3H_2O$, Silica gel; oxime; aldehyde; ketone.

1. Introduction

Oximes can be prepared from carbonyl and non-carbonyl compounds, and compounds having active methylene groups.^{1,2} These solid compounds are used for isolation, purification and characterization of the parent carbonyl compounds.³ Carbonyl groups can be protected by oximation, and in turn, these oximes can serve as an intermediate for the preparation of nitriles⁴ of amides via the Beckmann rearrangement or to activate the carbonyl group.⁵ Thus, there has been an increasing interest in the development of methods for the conversion of oximes into their corresponding carbonyl compounds and a number of methods and compounds such as 1,3-Dibromo-5,5-dimethylhydantoin,⁶ microwave,⁷ CeO_2-ZrO_2 ,⁸ Potassium bromide and Ammonium heptamolybdate,⁹ Silica Sulfuric acid,¹⁰ $Bi(OTf)_3.4H_2O$,¹¹ Ionic liquid,¹² poly[4-vinyl-*N,N*-dichlorobenzenesulfonamide],¹³ metalloporphyrins,¹⁴ 1,3-Dichloro-5,5-dimethylhydantoin,¹⁵ 2-Nitro-4,5-dichloropyridazin-3(2H)-one,¹⁶ *N*-bromo-*N*-benzoyl-4-toluenesulfonamide,¹⁷ Tetra-*n*-alkylammonium bromates¹⁸ have been explored.

In a nutshell, the regeneration of carbonyl compounds from oximes can be achieved using a variety of methods, including oxidative, reductive, and photochemical techniques.¹⁹ In continuation of our systematic study and research on oxidation methods,^{20–24} we report a new, simple and selective method for the conversion of aliphatic, aromatic and cyclic oximes to their corresponding aldehydes and ketones by

$K_3[Fe(CN)_6].3H_2O$ supported on SiO_2 as a new oxidant (scheme 1).

2. Experimental

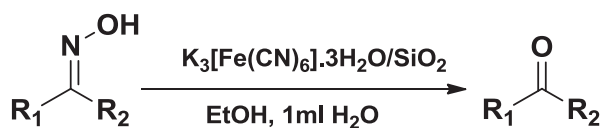
2.1 General methods and materials

In this study, all of the oximes were prepared as reported elsewhere,²⁵ except benzaldehyde oxime, which purchases from Merck (Darmstadt, Germany). IR and ¹H NMR spectra were recorded using a Shimadzu Infrared Spectrophotometer FT-IR Model IR Prestige 21 (KBr pellets) and a 90 MHz Jeol FT-NMR spectrometer, respectively. ¹H NMR chemical shifts were measured relative to TMS. Silica-supported $K_3[Fe(CN)_6].3H_2O$ (oxidant B) was prepared by impregnating 2.0 g of silica with aqueous solutions of $K_3[Fe(CN)_6].3H_2O$ (1 g in 30 mL H_2O). The mixture was stirred overnight at reflux temperature, followed by drying using a rotary evaporator at 110°C which gives yellow powders.

2.2 General Procedure for Deoximation

To a solution of oxime (1 mmol) in ethanol (10 mL), 0.1 g oxidant B (0.393 mmol) was added. Then H_2O (1 mL) was added to the solution. The resulting mixture was stirred at reflux conditions and the progress of the reaction monitored by thin layer chromatography (hexane-acetone, 8:2 v/v). After completion of the reaction, the oxidant was removed by filtration and washed with 2×5 mL ethanol. The solvent was removed from

*For correspondence



R1, R2 = Aromatic, Aliphatic, Cyclic, H

Scheme 1. Cleavage of oximes by $\text{K}_3[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ supported on SiO_2 .

the filtrate and the product was purified by column chromatography.

3. Results and Discussion

In order to optimize the reaction conditions, first of all, 0.2 g oxidant A (0.787 mmol $\text{K}_3[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$) was added to a solution of acetophenone oxime (1 mmol, 0.135 g) in acetonitrile (10 mL). According to the proposed mechanism, H_2O (1 mL) was added to the solution (scheme 2). The resulting mixture was stirred at reflux conditions (the reaction did not proceed after prolonged time at room temperature) and the progress of the reaction was monitored by thin layer chromatography (hexane-acetone, 8:2 v/v). Several trials of oxidant A were tried to find the suitable amount of oxidant for the reaction (table 1).

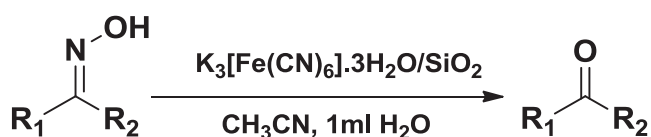
During the optimization of the reaction conditions, we compared the effect of different solvents on the rate and yields of the reactions. Our findings showed that EtOH was generally the best of the solvents tested in terms of yield and time (table 2).

After using oxidant A in EtOH as the suitable solvent, we conducted the reaction for different amounts of oxidant B and oxidant C (table 3). Having analyzed these results, we conclude that the best reaction conditions were achieved when we used 0.1 g of oxidant B in EtOH media in reflux condition. It is noteworthy that, addition of more H_2O to the reaction mixture, does not improve the reaction.

Different conditions for the preparation of oxidant A, B and C are shown in table 3.

3.1 Characterization of the oxidant

The XRD profiles of the samples at 298 K are shown in figure 1. Powder X-ray diffraction (XRD) patterns were



Scheme 2. Optimization of the reaction in acetonitrile.

Table 1. Optimization of Oxidant A.

Entry	Oxidant A (g)	Conditions	Time (h)	Yield (%)
1	0.2	r.t.	5	0
2	0.2	reflux	2.5	73
3	0.1	reflux	3.5	65
4	0.3	reflux	3.45	57
5	0.25	reflux	2.5	85

Table 2. Optimization of solvent.

Entry	Solvent	Time (h)	Yield (%)
1	CH_3CN	2:30	85
2	EtOH	2:15	91
3	CH_2Cl_2	5	0
4	Hexan	5	0
5	MeOH	2:30	86

Table 3. Preparation of oxidant.

Oxidant	SiO_2 (g)	$\text{K}_3[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ (g) ^a
A	2	2
B	2	1
C	2	0.5

^a $\text{K}_3[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ was dissolved in 30 mL of H_2O .

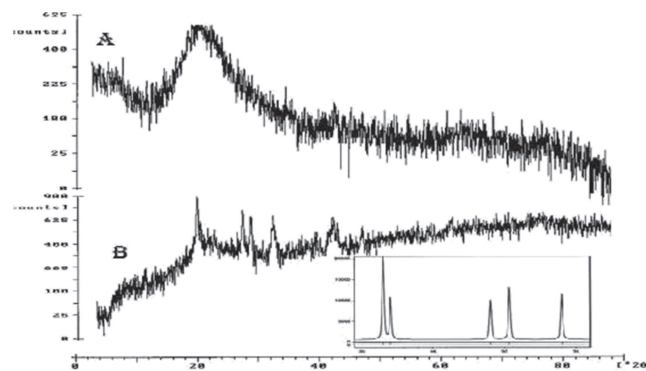


Figure 1. XRD pattern of A: SiO_2 , B: $\text{K}_3[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ supported on silica gel.

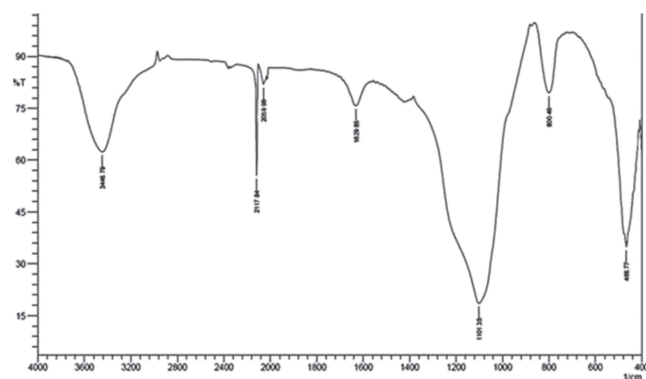












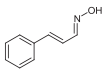
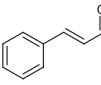




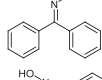
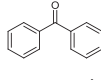
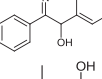
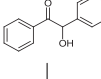


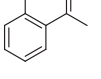
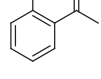


Figure 2. IR (KBr) Spectrum of $\text{K}_3[\text{Fe}(\text{CN})_6]\cdot 3\text{H}_2\text{O}$ supported on silica gel.

Table 4. The results of the conversion of oximes to the carbonyl compounds by oxidant.

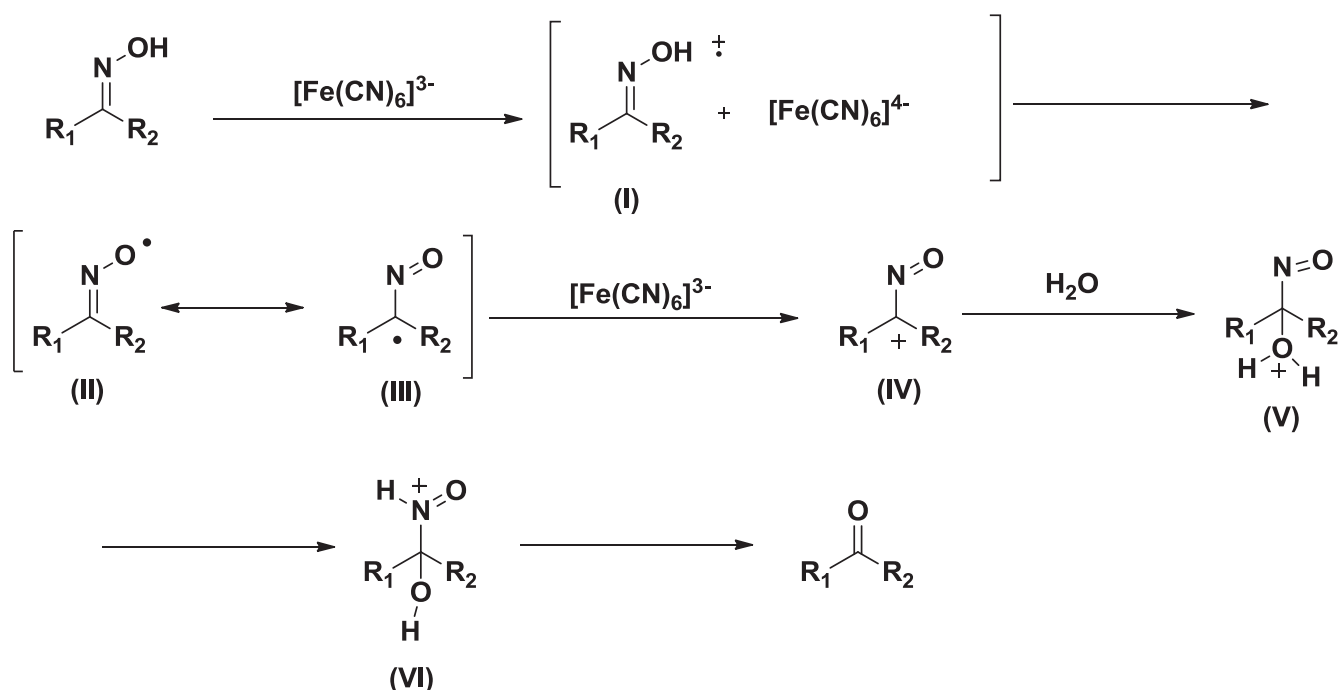
Entry	Oxime	Product	Time (min)	Yield (%) ^{a,b}
1			50	95
2			50	90
3			45	95
4			45	95
5			65	87
6			50	90
7			55	90
8			60	86
9			75	93
10			105	85
11			–	–
12			–	–
13			–	–

^a Products were characterized by their physical constants, comparison with authentic samples and melting points of 2,4-dinitro phenyl hydrazone derivatives and IR and NMR spectra; ^b Isolated yields

recorded on a Philips PW-1840 X-ray diffractometer (XRD) with Cu $K\alpha$ radiation. The intensity data were collected over a 2θ range of $10\text{--}90^\circ$. The XRD results revealed the presence of $K_3[Fe(CN)_6].3H_2O$ over amorphous SiO_2 matrix in the case of $K_3[Fe(CN)_6].3H_2O$ - SiO_2 (see $2\theta = 20 - 40^\circ$), and some overlapped regions.

The particles size of the $K_3[Fe(CN)_6].3H_2O$ on SiO_2 is 82 nm (figure 1). The main features of

$K_3[Fe(CN)_6].3H_2O$ supported on silica gel are connected to the similarity of bands associated with the inorganic backbone including (i) a broad band between 3400 and 3200 cm^{-1} , which is assigned to the O-H stretching mode of silanol groups and also to the remaining adsorbed water, (ii) the intense band related to siloxane stretching of these groups at 1100 cm^{-1} , (iii) a band assigned to Si-O stretching mode of the silanol group at 800 cm^{-1} and (iv) the band around 1650 cm^{-1} ,



Scheme 3. Proposed mechanism of deoxygenation by the oxidant.

assigned to the water bending mode, and (v) an intense band assigned to CN band at 2117 cm^{-1} (figure 2).

3.2 Proposed mechanism

Various methods were adopted for the deoxygenation processes to effectively and suitably obtain the parent or new aldehydes and ketones. Deoxygenation can be achieved using various processes like oxidation, hydrolysis, hydrogenation, etc., using organic and inorganic reagents. Besides, some surface templated processes and photochemical processes were also used to give products in a remarkably effective way.²⁶

Mechanism of deoxygenation by the $\text{K}_3[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ supported on silica gel is similar to other electron transfer type mechanisms that are described elsewhere.²⁷ Proposed mechanism for deoxygenation of variety of oximes to their corresponding aldehydes and ketones (table 4) is shown in scheme 3. The first step is simply the formation of the radical cation (I) of oxime by electron transfer from oxime to the potassium ferricyanide. Alternatively, a sequence can be written involving removal of a proton from (I) followed oxidation of iminoxyl radical (II) or nitroso radical (III) by potassium ferricyanide to give the nitroso carbocation (IV).

Hydration of the carbocation (IV) produces the intermediate (V), and finally decomposition of the (VI) produces carbonyl compounds.

4. Conclusion

It is noteworthy that in this study, over oxidation of aldehydes to carboxylic acid and formation of by-products were not observed. α - β unsaturated oxime (Entry 7) was deoxygenated smoothly without oxidation of the double bond. Furthermore, acid sensitive groups (Entry 4 and 8) remained unaffected during the oxidation reaction. The water insolubility of the reagent and by-products made product recovery easy. Due to sterical hindrance, benzoin oxime (Entry 11), Camphor oxime (Entry 12), and 2-hydroxy acetophenone oxime (Entry 13) could not be converted to their corresponding carbonyl compounds. Also, the reactions did not proceed using $\text{K}_3[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ or SiO_2 alone, even after a prolonged period of time. The striking features of our method are short reaction times, heterogeneous reaction conditions, absence of formation of over oxidation products due to high selectivity and mild nature of oxidant, easy work-up procedure, high yields and preservation of carbon-carbon double bond functional group in the oxime structure.

Supplementary Information

The electronic supporting information can be seen at www.ias.ac.in/chemsci.

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