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Nano Fe₃O₄/H₂SO₄ as effective catalytic system for deprotection oxime

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ABSTRACT

A simple, rapid, and efficient procedure for the direct conversion of deoxygenation of aldoximes and ketoximes to the corresponding carbonyl compounds with H₂SO₄ in the presence of nano Fe₃O₄. Apparently, nano Fe₃O₄ greatly increases the reaction rate and product yield. The proposed procedure is more advantageous than those described previously due to its clean reaction conditions (without organic solvent), short reaction time and suppression of any side product.

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KEYWORDS

Nano Fe₃O₄;
Oximes;
Carbonyl compounds;
Deprotection.

INTRODUCTION

The field of nanoscience has opened up new areas of interest for the construction of interesting and novel catalytic systems. nanoscale materials make ideal catalytic materials in many ways. Because of two reasons: First, their extremely small size yields a tremendous surface area-to-volume ratio^[1]. Also, when materials are fabricated at the nanoscale, they achieve properties not found within their macroscopic counterparts. Both of these reasons accounts for the versatility and effectiveness of nano-catalysts^[2].

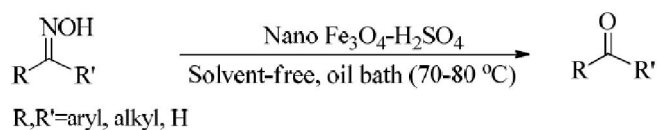
At present, oximes surpass carbonyl compounds and alcohols in both the diversity of reactions and the extent of their application in synthetic chemistry^[3]. They are either colorless liquids, which boil without decomposition, or crystalline solid, and both basic and acidic in character^[4].

Deoxygenation is a method of conversion of oximes

into carbonyl compounds. The deoxygenation reaction is widely used in organic synthesis and analysis, for example, in purification and identification of carbonyl derivatives. deoxygenation in basic media is a less common and less efficient reaction as compared with the acid-catalysed process. However, it is of interest, first of all, as a method for synthesizing carbonyl compounds from oximes that contain groups unstable in the presence of acids^[5].

The important role of oximes as protecting groups has provided motivation to develop deoxygenation agents such as K₃[Fe(CN)₆].3H₂O supported on silica gel^[6], hexachlorodisilane (Si₂Cl₆) in the presence of SiO₂^[7], anhydrous AlCl₃ supported on nano silica^[8], chromic acid supported on aluminum silicate^[9], SCOCC^[10], Amberlyst 15 supported nitrosonium ion^[11], SnCl₂/TiCl₃^[12], Ruthenium Trichloride^[13], MoCl₅ and Zn Powder^[14], KMnO₄/[bmim]Br^[15], silica sulfuric acid/surfactant/paraformaldehyde^[16], montmorillonite-K10 sup-

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Scheme 1

ported CoCl₂^[17], bmimBr-FeCl₃^[18]. However, some of these methods suffer from different disadvantages such as tedious work-up procedure, drastic reaction conditions, long reaction times, undesired chemical yields and use of expensive and toxic reagents. Therefore, a milder, more selective, non-hazardous and inexpensive reagent is still required for such transformation.

In the line of the outlined strategies, herein, we wish to report supported H₂SO₄ on nano Fe₃O₄ as a new promoter system for clean and efficient recovery of carbonyl compounds from oximes at solvent-free conditions in terms of simplicity, mildness and eco-friendly aspects (Scheme 1).

EXPERIMENTAL

General

All solvents and reagents were purchased from commercial sources with the best quality and they were used without further purification. Nano Fe₃O₄ and Oximes are prepared with high purity according to the reported procedures in the literature^[19, 20]. ¹H/¹³C NMR, XRD, SEM and IR spectra were recorded on a 300 MHz Bruker Avance spectrometer in 300.13 and 75.46 MHz, Philips X'pert PW3040/60, Philips XL30 and Thermo Nicolet Nexus 670 FT-IR spectrometer, respectively. Melt-

ing points were determined by Philip-Harris is melting point apparatus and are uncorrected. All products are known and were characterized by their spectral data. All yields refer to isolated pure products. TLC using silica gel 60 GF₂₅₄ aluminum sheet was applied for determination of the purity of substrates and products as well as monitoring the reaction.

A Typical Procedure for Solvent-Free Deoxygenation of benzaldehyde oxime to benzaldehyde Using Nano Fe₃O₄/H₂SO₄ System.

A mixture of nano Fe₃O₄ (2 mmol) and sulfuric acid (H₂SO₄) (0.25 mmol) was ground in a mortar. Benzaldehyde oxime (0.121 g, 1 mmol) was then added to the mortar and grinding of the reaction mixture was continued for 5 min at 60-70°C. TLC monitored the progress of the reaction (eluent; *n*-hexane / EtOAc: 5/3). After completion of the reaction, the mixture was washed with EtOAc (3×5 mL). Evaporation of the solvent affords the pure liquid benzaldehyde in 98% yield (TABLE 2: entry 1).

RESULTS AND DISCUSSION

The effort began with an investigation of nano catalyst deoxygenation of Benzaldehyde oxime to benzaldehyde. The conditions employed and the results of the reactions are presented in TABLE 1.

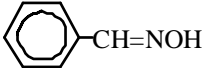
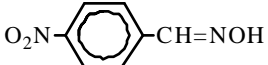
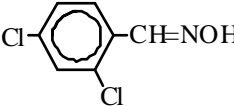
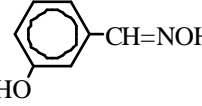
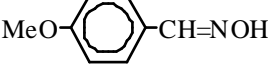
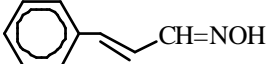
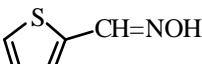
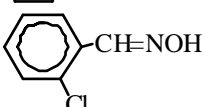
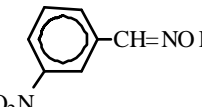
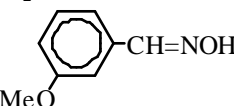
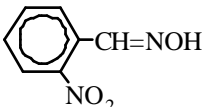
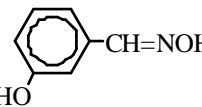
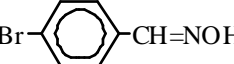
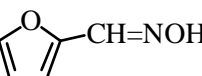
The results show that nano Fe₃O₄/H₂SO₄ system serves as a superior reagent for the deoxygenation of benzaldehyde oxime under solvent free condition (oil bath) (TABLE 1, entry1). It is reported that nano Fe₃O₄ is prone to partial acidic surface. However, the results showed that the acidic conditions gener-

TABLE 1 : Optimization experiments for deoxygenation of aldoxime with nano Fe₃O₄/H₂SO₄.

En	Reaction components	Molar ratio ^a	Condition	Time(min)	Conversion(%)
1	nano Fe ₃ O ₄ /H ₂ SO ₄	2:0.5	Solvent free/oil bath ^b	15	100
2	nano Fe ₃ O ₄ /H ₂ SO ₄	3:0.5	Solvent free/oil bath	15	89
3	nano Fe ₃ O ₄ /H ₂ SO ₄	3:1	Solvent free/oil bath	15	89
4	nano Fe ₃ O ₄ /H ₂ SO ₄	2:0.5	CH ₃ CN/reflux	60	13
5	nano Fe ₃ O ₄ /H ₂ SO ₄	2:0.5	THF/reflux	60	15
6	nano Fe ₃ O ₄ /H ₂ SO ₄	2:0.5	H ₂ O/reflux	60	5
7	nano Fe ₃ O ₄	3	Solvent free/oil bath	30	0
8	H ₂ SO ₄	1	Solvent free/oil bath	30	5
9	Fe ₃ O ₄ /H ₂ SO ₄	3:1	Solvent free/oil bath	45	30

^a All reactions were carried out with the 1mmol of benzaloxime. ^b Temperature of oil bath was 60-70°C.

TABLE 2 : Deoxygenation of aldoximes with nano Fe₃O₄/ H₂SO₄ system^a

En	Substrate	Time (min)	Yield (%) ^b	Mp or bp °C/Torr (lit) ^[21]
1		15	98	178/760 (179/760)
2		25	96	105(104-106)
3		17	98	72(69-73)
4		15	97	103(102-105)
5		15	96	247/760 (247-249/760)
6 ^c		25	89	252/760 (250-252/760)
7		18	92	196/760 (196-198/760)
8		15	98	210/760 (212/760)
9		20	97	59(57-59)
10		20	98	231/760 (231-233/760)
11		22	98	45(43-46)
12		18	97	106(102-105)
13		20	98	59(55-58)
14		25	94	162/760 (162/760)

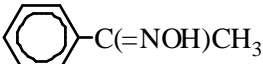
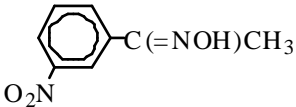
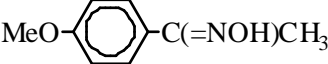
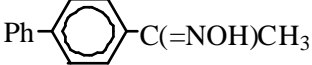
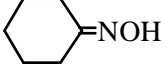
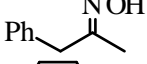
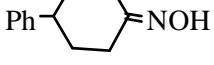
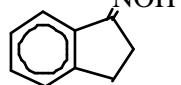
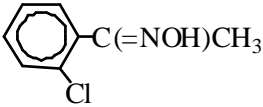
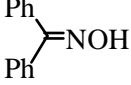
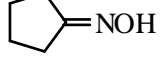
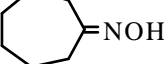
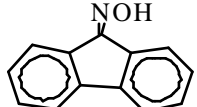
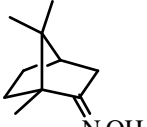
^a All reactions were carried out with the molar ratio of Subs./nano Fe₃O₄/H₂SO₄ (1:2:0.5) under solvent-free conditions. ^b Yields refer to isolated pure products. ^c Completion of the reaction required a molar ratio of Subs./nano Fe₃O₄/H₂SO₄ (1:3:0.5)

ated are not sufficient to promote regeneration of carbonyl compounds from oximes (TABLE 1, entries 3).

H₂SO₄ as an alternative oxidant has achieved increasing attention in the oxidation reaction. Use of sulfuric acid has several advantages. It is a strong oxidizing agent and stable at room temperature^[2].

However, these reagent are performed under excess conditions. Thus, by the combination of nano Fe₃O₄ with H₂SO₄ in a molar ratio of 2.5:0.5, respectively, envisaged that a mixture of nano Fe₃O₄ and H₂SO₄ perfectly and rapidly deoxygenation of aldoximes and ketoximes to corresponding aldehydes and ketones. The studies also showed that using the excess

TABLE 3 : Deoximation of ketoximes with nano Fe₃O₄/H₂SO₄ system^a

En	Substrate	Time (min)	Yield (%) ^b	Mp or bp °C/Torr (lit) ^[21]
1		25	98	200/760 (201-203/760)
2		27	98	80(76-80)
3		35	98	40(36-40)
4		30	98	120(117-123)
5		30	98	154/760 (154-156/760)
6		30	97	215/760 (214-216/760)
7		45	97	80(78-82)
8		40	98	40(38-42)
9		30	98	230/760 (228-229/760)
10		30	98	50(47-50)
11		25	98	130/760(130-131/760)
12		30	98	180/760 (179-181/760)
13		40	96	85(82-85)
14		45	92	176(175-177)

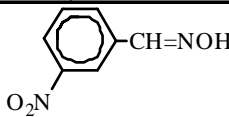
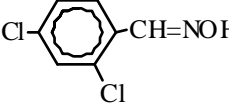
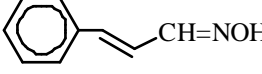
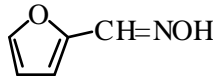
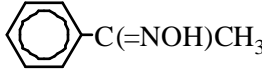
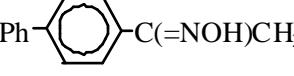
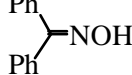
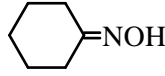
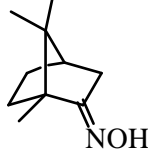
^a All reactions were carried out with the molar ratio of Subs./nano Fe₃O₄/H₂SO₄ (1:2:0.5) under solvent-free conditions. ^b Yields refer to isolated pure products. ^c Completion of the reaction required a molar ratio of Subs./nano Fe₃O₄/H₂SO₄ (1:3:0.5)

amounts of H₂SO₄ did not decrease the reaction time. So, the conditions mentioned in entry 1 were selected as the optimal.

The versatility of this synthetic protocol for deoximation of various aldoximes and ketoximes is shown in TABLES 2 and 3. The results show that all types of aldoximes and ketoximes were deoximated

successfully by nano Fe₃O₄/H₂SO₄ system within 15-45 min to afford the corresponding aldehydes and ketones in excellent yields (97-99%). As it's seen, the α,β -unsaturated oximes underwent deprotection very efficiently without rearrangement of the C=C bond and the reactions are essentially chemoselective (TABLE 2, entry 6), but heterocy-

TABLE 4 : Comparison of deoxygenation of oximes with nano Fe₃O₄/H₂SO₄ system and other reported deoxygenation

En	Substrate	[Time (min)/ Yield (%)]										
		Reference Number	Ref [6]	Ref [7]	Ref [8]	Ref [9]	Ref [10]	Ref [11]	Ref [12]	Ref [14]	Ref [15]	Ref [16]
	Reaction Condition	Ethanol /H ₂ O	H ₂ O	Oil bath	CH ₂ Cl ₂ /reflux	Ethylacetate	dioxane / 70°C	H ₂ O/ THF	CH ₃ CN	solvent free	H ₂ O, u.s.	Oil bath
1		-	240/95	25/92	-	15/89	180/75	-	-	18/95	180/49	20/97
2		-	-	15/93	-	15/83	-	-	-	10/98	-	17/98
3		55/90	-	50/85	360/82	20/81	225/72	-	-	-	-	25/89
4		-	-	40/54	-	-	-	-	-	-	-	25/94
5		75/93	60/95	40/90	180/92	-	60/80	240/96	15/93	52/92	90/93	25/98
6		-	-	110/92	-	-	-	-	-	-	-	30/98
7		105/85	480/99	120/93	120/94	30/90	60/92	-	25/92	55/81	-	30/98
8		-	-	60/92	180/90	10/90	300/70	180/91	15/84	-	90/93	30/98
9		-	-	-	-	-	45/84	-	-	-	-	45/92

clic oximes were not successfully deoxygenated. thiophene oxime for example, produced a moderate yield, further increasing the reaction time and change the molar ratio gave no significant improvement in yields, but rather decomposition occurred (TABLE 2, entry 7,14). As seen, all oximes containing electron releasing or withdrawing groups were deoxygenation easily and efficiently, and so, with the change of the carbon number of the rings (TABLE 3, entry 5, 11, 12), the conversion of oximes to the corresponding carbonyl compounds decreased remarkably.

CONCLUSIONS

As summary, in this paper we have shown the

excellent capability of nano Fe₃O₄/H₂SO₄ system for solvent-free deoxygenation of various oximes to the corresponding carbonyl compounds. these reactions have some other advantages such as low costs, simplicity in process and handling, formation of cleaner products, enhanced selectivity, improved reaction rates and prevent waste solvent generation, hazards, and toxicity make this protocol a useful addition to the present methodologies.

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