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An efficient protocol for deprotection of oximes to carbonyl compounds catalyzed by anhydrous AlCl₃ supported on nano silica

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ABSTRACT

Recovery of aldehydes and ketones from oximes is one of the most important reactions in organic synthesis, because oximes are served as an efficient protective group for carbonyl compounds. We report here an efficient and rapid deoximation method using nano SiO₂- AlCl₃ system, for conversion of various oximes to the corresponding carbonyls under solvent-free conditions. © 2013 Trade Science Inc. - INDIA

KEYWORDS

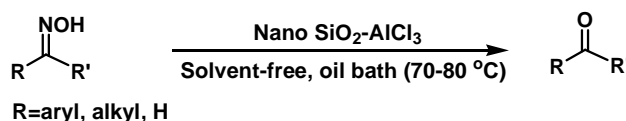
Anhydrous AlCl₃;
Carbonyl compounds;
Deprotection;
Oxime;
Nano SiO₂.

INTRODUCTION

Oximes are extensively used for purification and characterization of carbonyl compound^[1] as well as preparation of amides via the Beckmann rearrangement^[2]. The important role of oximes as protecting groups^[3] has provided motivation to develop deoximation agents such as silica gel confined functional ionic liquids^[4], alumina supported N-methyl piperidinium chlorochromate^[5], ZrCl₄ on wet SiO₂ supported ammonium dichromate^[6], and supported quinolinium flourochromate^[7], alumina supported potassium permanganate^[8], wet SiO₂ supported Mg (HSO₄)₂^[9], N,N-dibromo-N,N-1,2-ethanediybis (p-toluene sulphonamide)^[10], polymer supported peroxotungstate complex^[11], poly (4-vinyl-N,N-dichloro benzene sulfonamide)^[12], cetyltrimethyl ammonium cerium citrate^[13], triscetylpyridinium tetra kis (oxodiperoxotungsto) phosphate^[14]. 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.

On the other hand, one of the most stimulating features of nanotechnology is its potential use in almost any field. The discovery of nanoparticles with varied size, shape, and composition has stretched the limits of technology in ways that scientists would never have dreamt of a century ago^[15]. So, in the line of the outlined strategies, herein, we wish to report supported AlCl₃ anhydrous on nano SiO₂ 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).



Scheme 1

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EXPERIMENTAL

General

All solvents and reagents were purchased from commercial sources with the best quality and they were used without further purification. Nano SiO₂ are prepared in high purity according to the reported procedures in literature^[16]. ¹H, ¹³C NMR and IR spectra were recorded on 300 MHz Bruker Avance and Thermo Nicolet Nexus 670 FT-IR spectrometer, respectively. All products are known and were characterized by their spectral data. Yields refer to isolated pure products. TLC was applied for monitoring of the reactions over silica gel 60 F₂₅₄ aluminum sheet.

A typical procedure for solvent-free deoxygenation of acetophenone oxime to acetophenone using nano SiO₂/AlCl₃ system

A mixture of nano SiO₂ (0.240 g, 4 mmol) and anhydrous AlCl₃ (0.266 g, 2 mmol) was ground in a mortar. Acetophenone oxime (0.135 g, 1 mmol) was then added to the mortar and grinding of the reaction mix-

ture was continued for a moment. The mixture was stirred magnetically in oil bath (70-80 °C) at solvent-free conditions for 40 min. 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 acetophenone in 90% yield (0.116 g, TABLE 3: entry 1).

RESULTS AND DISCUSSION

The literature review shows that the sol-gel process is widely used to produce pure silica particles due to its ability to control the particle size, size distribution and morphology through systematic monitoring of the reaction parameters^[17]. so we prepared nano silica with this method (diagram 1).

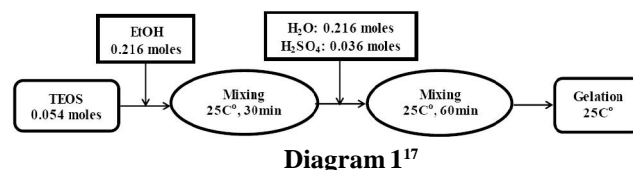


TABLE 1 : Optimization experiments for deoxygenation of benzaldoxime with nano SiO₂/AlCl₃ under different conditions

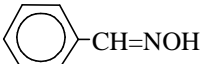
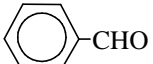
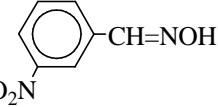
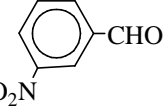
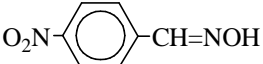

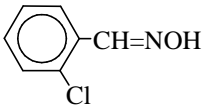
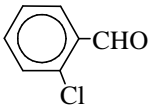
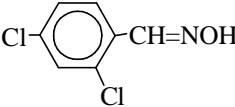
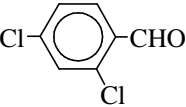
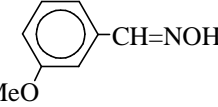
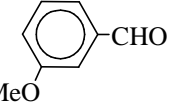
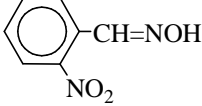
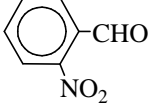
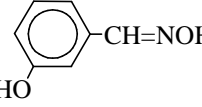
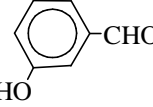
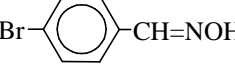
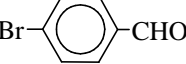
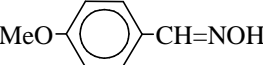

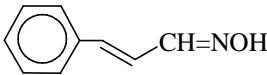
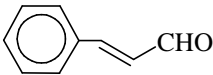
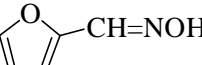
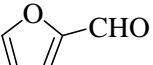
Entry	Reaction components	Molar ratio	Condition	Time(min)	Conversion(%)
1	oxime/AlCl ₃	1:2	Solvent free/oil bath ^a	50	80
2	oxime/SiO ₂ /AlCl ₃	1:4:1.5	Solvent free/oil bath ^a	20	100
3	oxime/SiO ₂ /AlCl ₃	1:4:1	Solvent free/oil bath ^a	25	80
4	oxime/SiO ₂ /AlCl ₃	1:4:2	Solvent free/oil bath ^a	20	100
5	oxime/SiO ₂ /AlCl ₃	1:3:1.5	Solvent free/oil bath ^a	30	50
6	oxime/SiO ₂ /AlCl ₃	1:1:1.5	CH ₃ CN/reflux	60	30
7	oxime/SiO ₂ /AlCl	1:1:1.5	EtOH/reflux	60	30
8	oxime/SiO ₂ /AlCl ₃	1:1:1.5	H ₂ O/reflux	60	60
9	oxime/SiO ₂ /AlCl ₃	1:1:1.5	THF/reflux	60	10

^aTemperature of oil bath was 70-80°C

Continuation of our research program directed to the oximes reactions under mild and green reaction conditions^[18] we found that AlCl₃ anhydrous in the presence of nano SiO₂ dramatically performs deoxygenation of various aldoximes and ketoximes to the corresponding carbonyl compounds at solvent-free conditions. In order to obtain the optimum reaction conditions and showing the influence of the reaction components, we performed deoxygenation of benzaldehyde oxime as a model compound with nano SiO₂- AlCl₃ system under different reaction conditions (TABLE 1). As it's seen,

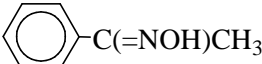
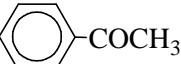
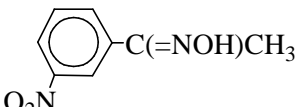
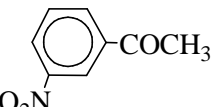
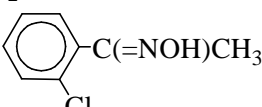
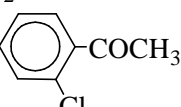
the solely AlCl₃ did not show completed even at the prolonged reaction time (entries 1). However, by the combination of nano SiO₂ with AlCl₃ in a molar ratio of 4:1.5, respectively, deoxygenation of 1 mmol benzaldehyde oxime was carried out perfectly in oil bath (70-80 °C) within 20 min at solvent-free conditions (entry 2). Versatility of this synthetic protocol for deoxygenation of various aldoximes and ketoximes is shown in TABLES 2 and 3. The results show that all types of aldoximes and ketoximes were deoxygenated successfully by nano SiO₂/AlCl₃ system within 15-150 min to afford the cor-

TABLE 2 : Deoximation of aldoximes with Nano SiO₂/AlCl₃ system^a

Entry	Substrate	Product	Time (min)	Yield (%) ^b
1			20	93
2			25	92
3			30	92
4			25	94
5			15	93
6			30	90
7			25	91
8			30	93
9			30	90
10			35	90
11 ^c			50	85
12			40	54

^a All reactions were carried out with the molar ratio of Subs./nano SiO₂/AlCl₃ (1:4:1.5) in oil bath (70 - 80 °C) under solvent-free conditions. ^b Yields refer to isolated pure products. ^c Completion of the reaction required a molar ratio of Subs./nano SiO₂/AlCl₃ (1:6:2)

TABLE 3 : Deoximation of ketoximes with Nano SiO₂/AlCl₃ system^a

Entry	Substrate	Product	Time (min)	Yield (%) ^b
1			40	90
2			50	92
3			60	93

Full Paper

Entry	Substrate	Product	Time (min)	Yield (%) ^b
4			70	94
5			110	92
6			120	92
7			110	93
8			60	92
9			150	92
10			120	93
11			50	95
12			110	93
13			120	90

^a All reactions were carried out under oil bath (70 – 80°C) conditions. ^b All reactions were carried out with the molar ratio of Subs./Nano SiO₂/AlCl₃ (1:4:2)

TABLE 4 : Comparison of deoxygenation of oximes with nano SiO₂/AlCl₃ system and other reported deoxygenation systems

Entry	Deoxygenation systems	Condition	Time(min)/Yield(%)				
			Benzaldehyde-Oxime	4-Nitrobenzaldehyde Oxime	Acetophenone Oxime	Cyclohexanone Oxime	Cinnamaldehyde Oxime
1	Nano SiO ₂ /AlCl ₃	solvent-free	20/94	30/92	40/90	60/94	50/92
2	FeCl ₃ /CH ₃ CN ²⁹	Ultrasound	10/90	10/75	30/93	15/92	-
3	MoCl ₅ /Zn ³⁰	CH ₃ CN	15/91	-	40/93	20/75	-
4	SiO ₂ -OSO ₃ H/Paraformaldehyde ³¹	H ₂ O	-	180/79	90/93	90/93	-
5	SiO ₂ /CrO ₃ ³²	M.W	-	2/57	1/95	1/87	2/91
6	Al(NO ₃) ₃ /NaBr ³³	CH ₂ Cl ₂	-	-	110/98	45/89	-

responding aldehydes and ketones in high to excellent yields (85-95%). In addition, due to the inherent less reactivity of ketoximes versus aldoximes, higher quantities of AlCl₃ (2 mmol) were used in the reactions. In-

terestingly, the α,β -unsaturated oximes underwent deprotection very efficiently without rearrangement of the C=C bond and the reactions are essentially chemoselective (TABLE 1, entry 11), but heterocyclic

oximes were not successfully deoximated. Furfural oxime for example, produced a moderate yields, further increasing the reaction time and change molar ratio gave no significant improvement in yields but rather decomposition occurred (TABLE 2, entry 12). In order to show the efficiency of this deoximation system, we compared our results with those of reported in the literature for $\text{FeCl}_3/\text{CH}_3\text{CN}$ ^[19], MoCl_5/Zn ^[20], $\text{SiO}_2\text{-OSO}_3\text{H/Paraformaldehyde}$ ^[21], $\text{SiO}_2/\text{CrO}_3$ ^[22], $\text{Al}(\text{NO}_3)_3/\text{NaBr}$ ^[23] as shown in TABLE 4.

CONCLUSIONS

In this paper, we have shown the combination system of nano SiO_2 and AlCl_3 anhydrous efficiently performed deoximation of various oximes to the corresponding carbonyl compounds in high yields at solvent-free conditions. Simplicity, excellent yields, mildness and eco-friendly aspects of this synthetic protocol are the advantages which make nano $\text{SiO}_2/\text{AlCl}_3$ system a new addition to the present methodologies in this area.

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