



Trends in  
**Applied Sciences  
Research**

ISSN 1819-3579



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## Polymer (PVP) Supported Ferric Chloride as a Heterogeneous Catalyst for Selective Deprotection of Aldoximes and Hydrazone

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**Abstract:** Oximes and hydrazones undergo selective deprotection to afford the corresponding carbonyl compounds in excellent yields (85-98%) and short reaction times 1.5-5.0 h using polymer (PVP) supported Ferric chloride as a heterogeneous catalyst.

**Key words:** Aldoximes and hydrazones, polymer (PVP) supported ferric chloride, carbonyl compounds

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### INTRODUCTION

Regeneration of carbonyl compounds from oximes and hydrazones is a very important transformation in synthetic organic chemistry due to their extensive application in the protection (Greene and West, 1991) and the purification of carbonyl compounds (Cheronis and Entrikin, 1963). These carbonyl compounds served as intermediates for many reactions such as the preparation of amides via Beckman rearrangement (Donaruma and Heldt, 1960; Bosch *et al.*, 1995). Oxime synthesis from non-carbonyl compounds (Kabalka *et al.*, 1990a) provides an alternative pathway to aldehydes and ketones. The hydrolytic stability of oximes has inspired the development of several deoximation reagents (Bandgar *et al.*, 1996b) such as trimethylammonium chlorochromate (Bose and Srinivas, 1997c; Rao *et al.*, 1983d) dinitrogen tetraoxide (Shim and Kim, 1987e, pyridinium chlorochromate (PCC) (Maloney *et al.*, 1978f), chromium trioxide-chlorotrimethylsilane (Aizpurua *et al.*, 1985g), clay-supported Ferric nitrate (Laszlo and Polla *et al.*, 1985h), titanium silicate-1 (Joseph *et al.*, 1994i), tertiary butyl hydroperoxide (Barhate *et al.*, 1997j), N-haloamides (Bandgar *et al.*, 1997k) and manganese triacetate (Ayhan *et al.*, 1997l) with certain limitations. Or the regeneration of carbonyl compounds several methods are available based on hydrolytic (Donaldson *et al.*, 1983), reductive (Curran *et al.*, 1984) and oxidative (Bose and Srinivas, 1998a; Bose and Venkat Narsaiah, 1999b, 2000c). Many of these procedures suffer from one or the other drawbacks toxicity of the reagents, expensive transition metals long reaction time and difficulties in isolation of products (Drabowicz, 1980a; Ayhan and Tanyeli, 1997b; Bose and Srinivas, 1998c). These limitations are prompted us to investigate further new methodology for the deprotection of oximes and hydrazones using readily available and safer reagents which lead to high recovery of carbonyl compounds.

### MATERIALS AND METHODS

#### Catalyst Preparation

Cross linked poly (4-vinylpyridine) (1 g) was dissolved in 10 ml of standard solution of 0.1M of FeCl<sub>3</sub> in water. After the solution had been stirred for 30 min at 30°C. The solid PVP-Fe (III) was filtered to obtain. The excessive ferric ions in complex were washed by deionized water. The solid powder was dried under vacuum at 65°C for 24 h. The absorbed amounts are ferric ions in complex were obtained using UV spectrophotometer.

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### General Procedure

A mixture of oxime/ hydrazone (5.0 mmol) and PVP supported ferric chloride (0.6 g) was dissolved in a minimum amount of dichloromethane. The reaction mixture was vigorously stirred at room temperature for specified time (Table 1). The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was allowed to reach room temperature treated with water and extracted with  $\text{CH}_2\text{Cl}_2$  (4×5 mL). The combined organic phase was washed with brine, dried ( $\text{Na}_2\text{SO}_4$ ) and the solvent was removed in *vacuo* to afford the crude product, which was purified by column chromatography on silica gel eluted with ethyl acetate-hexane (1:5).

Table 1: Cleavage of oximes and hydrazones using polymer supported  $\text{FeCl}_3$ .

























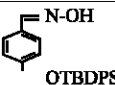

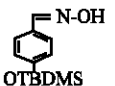

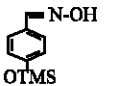

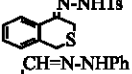



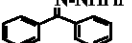

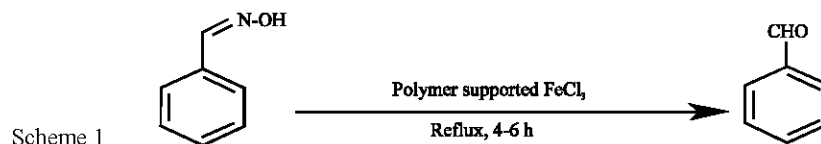
Entry	Aldoximes	Aldehydes	Time (h)	Yield (%)
1			4.0	98
2			4.0	95
3			4.0	90
4			5.0	92
5			4.0	94
6			5.0	92
7			4.5	94
8			4.0	90
9			40	90
10			4.0	89
11			4.0	87
12			4.0	88

Table 1: Continued

13			5.0	90
14			5.0	92
15			5.0	94
16			2.2	85
17			1.5	87
18			2.5	90



## RESULTS AND DISCUSSION

Recently, the use of solid supported reagents (Clark, 1994; Caddick, 1995a; Boruah *et al.*, 1997b; Bose and Jayalakshmi, 1999c; Varma *et al.*, 1997; Bose *et al.*, 1999a; Bose and Raveender Goud, 1999b) has received considerable importance in organic synthesis because of their ease of handling, enhanced reaction rates, greater selectivity, simple workup and recoverability of catalysts. Among the various heterogeneous catalysts, particularly, polymer supported reagents have advantages of low cost, ease of preparation and catalyst recycling. Since the reaction is heterogeneous in nature, the catalyst can conveniently be separated by simple filtration.

Herein we wish to report a facile conversion of oximes and hydrazones to corresponding carbonyl compounds using polymer supported  $\text{FeCl}_3$  as a heterogeneous catalyst (Scheme 1).

$\text{FeCl}_3$  is an inexpensive and powerful oxidant used for the transformation of a wide range of functional groups. A wide range of structurally varied oximes and hydrazones have been subjected to cleavage with  $\text{FeCl}_3$  supported on polymer to provide the corresponding carbonyl compounds it is note worthy that unlike other oxidative hydrolytic methods. The major drawback of over oxidation of ensuing aldehydes is not observed under the reaction conditions. Interestingly the unsaturated oxime under went deoxygenation very efficiently without effecting the  $\text{C} = \text{C}$  bond and the reaction is essentially chemo selective. Oximes and hydrazones were prepared by known literature procedures. All resulting carbonyl compounds are identified by comparisons of their physical data, IR and NMR spectra with those of authentic samples. Polymer supported  $\text{FeCl}_3$  was prepared by using known procedure (Wu *et al.*, 2003). The catalyst was recovered by simple filtration and reused for 3-4 times with consistent activity.

## CONCLUSIONS

In summary, we have shown that the polymer supported  $\text{FeCl}_3$  provides an efficient methodology for the rapid cleavage of oximes and hydrazones to regenerate carbonyl compounds. Present methodology offers very attractive features such as reduced reaction times, higher yields and economic viability of the catalyst and mild nature of  $\text{FeCl}_3$  when compared with conventional methods as well as with other catalysts, which will have wide scope in organic synthesis. The simple procedure combined with ease of recovery and reuses of this catalyst make this method economic, benign and a waste-free chemical process. The operational simplicity of the procedure is also attractive. The catalyst can be prepared easily with readily available inexpensive reagents. To our knowledge, this is first time report of an efficient general method for the rapid cleavage of oximes and hydrazones by using a simple heterogenous catalyst.

All other products were characterised by spectral (NMR and IR) data and by comparison with those of authentic samples and also by the mixed melting points with the authentic samples.

## ACKNOWLEDGMENT

The authors are thankful to K.M.M.S. Prakash, NIH Fellow, School of Medicine, Wayne State University, USA for his valuable discussion.

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