

Organic Preparations and Procedures International

The New Journal for Organic Synthesis

ISSN: 0030-4948 (Print) 1945-5453 (Online) Journal homepage: <https://www.tandfonline.com/loi/uopp20>

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To cite this article: Abbas Aminimanesh, Reza Golbedaghi & Leila Hadi (2019): A Selective Method for Catalytic Cleavage of Oximes to Their Carbonyl Compounds Using 10% H₂O₂ and [Mn(L₂₂pyfp)Cl](ClO₄) as a Catalyst, Organic Preparations and Procedures International, DOI: [10.1080/00304948.2018.1549904](https://doi.org/10.1080/00304948.2018.1549904)

To link to this article: <https://doi.org/10.1080/00304948.2018.1549904>



Published online: 13 Feb 2019.



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A Selective Method for Catalytic Cleavage of Oximes to Their Carbonyl Compounds Using 10% H₂O₂ and [Mn(L₂₂pyfp)Cl](ClO₄) as a Catalyst

Abbas Aminimanesh, Reza Golbedaghi, and Leila Hadi

Department of Chemistry, Payame Noor University, P.O. Box 19395-3697, Tehran, Iran

In continuance of our systematic study of oxidation methods^{1–3} we wish to report an easy and selective method for the conversion of aromatic, aliphatic, and cyclic oximes to their corresponding aldehydes and ketones^{4–7} by using the new catalyst {[Mn(L₂₂pyfp)Cl](ClO₄)}⁸ with H₂O₂ as an oxidant (*Scheme 1*).

For this work, the Mn(II) complex was synthesized by the reported procedure⁸ and the structure of the complex is shown in *Figure 1*.

A convenient reaction of an oxime in refluxing CH₃CN with [Mn(L₂₂pyfp)Cl](ClO₄) and H₂O₂ produced the corresponding carbonyl compound in good to excellent yields.

We first checked the catalytic activities of [Mn(L₂₂pyfp)Cl](ClO₄) and hydrogen peroxide toward benzaldehyde oxime in CH₃CN as a test reaction. Benzaldehyde is a suitable target compound, as it is readily over-oxidized to benzoic acid. Thus the formation of benzoic acid is a direct indication of the selectivity of the protocol. Ethanol, methanol, chloroform, acetonitrile and hexane were used as solvents (*Table 1*); our findings suggested that CH₃CN was the best of the solvents examined in terms of time and yields.

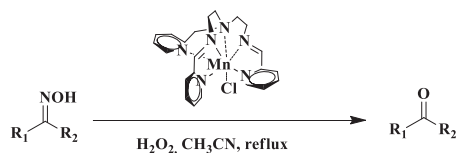
Different molar ratios of the catalyst, benzaldehyde oxime, and H₂O₂ were used (*Table 2*). Stirring of a solution of the catalyst (0.2 mmol), benzaldehyde oxime (1 mmol) and H₂O₂ (7 ml, 10%) in CH₃CN under reflux resulted in the formation of benzaldehyde in quantitative yield within 55 min. Without the Mn-complex catalyst, benzaldehyde was only formed in 20% yield (entry 1) and without H₂O₂ benzaldehyde was not formed at all (entry 2).

The results for deoxygenation of a variety of structures are summarized in *Table 3*.

The results represented in *Table 3* show that the reaction is useful for a variety of aromatic, aliphatic and cyclic oximes. Sterically hindered ketoximes (entries 10, 11, 12) were successfully converted to the corresponding ketones in good yield. Aldoximes are converted to the corresponding aldehydes efficiently (entries 1, 2, 3, 4). Over-oxidation of aldehydes to carboxylic acids and production of the by-products was not observed.

Received January 27, 2018; in final form August 15, 2018.

Address correspondence to Abbas Aminimanesh, Department of Chemistry, Payame Noor University, P.O. Box 19395-3697, Tehran, Iran. E-mail: a_aminima@yahoo.com



Scheme 1. Conversion of oximes to carbonyl compounds by $[\text{Mn}(\text{L}_{22\text{pyfp}})\text{Cl}](\text{ClO}_4)$ and H_2O_2 .

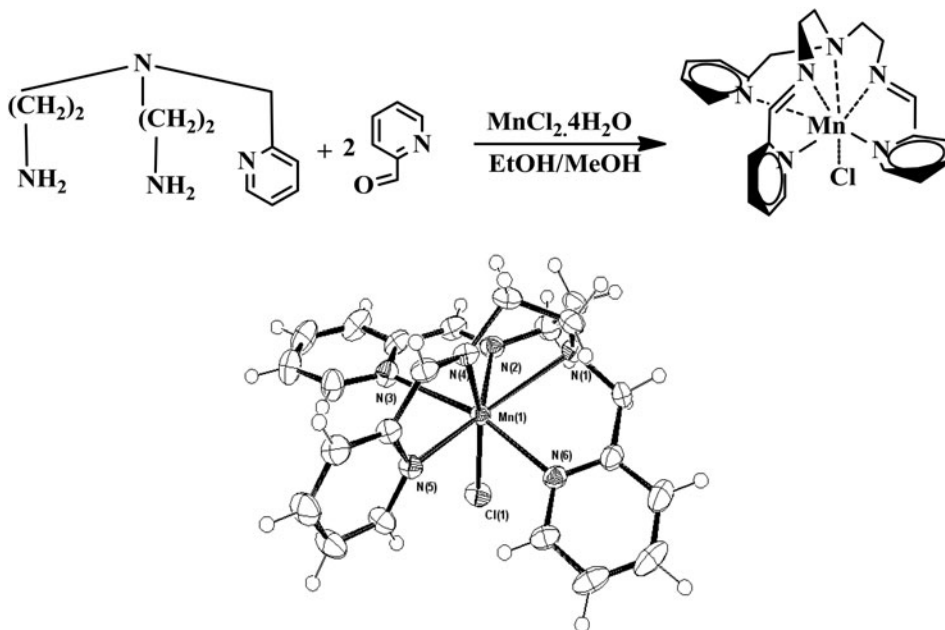


Figure 1. X-ray crystal structure of the $[\text{Mn}(\text{L}_{22\text{pyfp}})\text{Cl}](\text{ClO}_4)$ complex.

Table 1
Optimization of Solvent in Oxidation of Benzaldehyde Oxime to Benzaldehyde

Entry	Solvent	Time (Min)	Yield (%) ^{a,b}
1	C_6H_{12}	90	10
2	CHCl_3	90	20
3	CH_3OH	90	45
4	$\text{C}_2\text{H}_5\text{OH}$	90	50
5	CH_3CN	90	95
6	CH_3CN	55	95
7	Solvent-Free	100	0

^aYields refer to isolated pure products.

^bReaction conditions: oxime (1 mmol), H_2O_2 (10 ml, 10%), $[\text{Mn}(\text{L}_{22\text{pyfp}})\text{Cl}](\text{ClO}_4)$ (0.3 mmol) under reflux conditions.

An important advantage of $[\text{Mn}(\text{L}_{22\text{pyfp}})\text{Cl}](\text{ClO}_4)$ is its simple recovery from the reaction mixture and its reusability. These aspects were tested using acetophenone oxime as a model substrate. The recovery of catalyst was very simple. The carbonyl products are soluble in CHCl_3 or Et_2O , while the catalyst is insoluble. The catalyst was

Table 2
Optimization of Catalyst and Oxidant for Oxidation of Benzaldehyde Oxime to Benzaldehyde

Entry	Amount of $[\text{Mn}(\text{L}_{22\text{pyfp}})\text{Cl}](\text{ClO}_4)$ (mmol)	Amount of H_2O_2 (ml)	Yield (%) ^{a,b}
1	0	10	20
2	0.2	0	–
3	0.05	10	40
4	0.08	10	55
5	0.09	10	62
6	0.1	10	65
7	0.12	10	70
8	0.2	10	95
9	0.3	10	95
10	0.2	7	95

^aYields refer to isolated pure products.

^bReaction conditions: oxime (1 mmol), different amounts of H_2O_2 and catalyst in CH_3CN under reflux for 55 min.

separated by simple filtration from the reaction mixture after each experiment. As shown in *Table 4*, $[\text{Mn}(\text{L}_{22\text{pyfp}})\text{Cl}](\text{ClO}_4)$ is reusable, although by the fourth isolation significant loss of activity was noted.

In conclusion, we have shown a simple and convenient method for the effective conversion of oximes to the corresponding aldehydes or ketones. Formation of by products and over-oxidation of aldehydes to carboxylic acids were not observed. Easy removal of the catalyst $[\text{Mn}(\text{L}_{22\text{pyfp}})\text{Cl}](\text{ClO}_4)$ is another advantage.























Experimental Section

Chemicals were purchased from Merck, Fluka and Aldrich Chemical Companies. All yields refer to the isolated products. All products were known and identified by the comparison of their m.p., b.p., IR and NMR with those reported for the authentic samples.^{9–15} The progress of reaction was monitored by TLC (silica gel as stationary phase and *n*-hexane/acetone 9:1 as solvent). 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.

General Procedure for Deoximation by $[\text{Mn}(\text{L}_{22\text{pyfp}})\text{Cl}](\text{ClO}_4)$

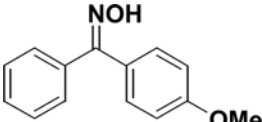
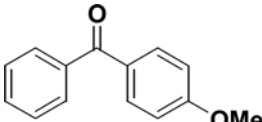
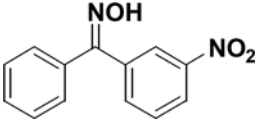
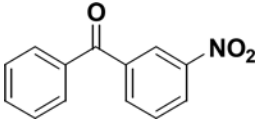
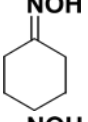
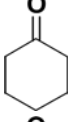
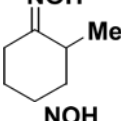
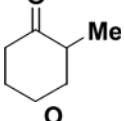
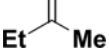
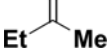
To a solution of oxime (1 mmol) in acetonitrile (10 ml), $[\text{Mn}(\text{L}_{22\text{pyfp}})\text{Cl}](\text{ClO}_4)$ (0.2 mmol, 0.112 g) was added; then hydrogen peroxide (7 ml, 10%) was slowly added. The mixture was then stirred at reflux. The progress of reaction was monitored by TLC (silica gel as stationary phase and *n*-hexane/acetone 9:1 as solvent). After completion of the reaction (*Table 3*), the solvent was removed under reduced pressure and then 10 ml CHCl_3 or THF was added and stirred for 10 min, the mixture was filtered and the solid residue was washed with CHCl_3 or THF (5 ml). Evaporation of the solvent from the residue gave crude products. The pure carbonyl compound was isolated by column

Table 3
Deoxygenation of Oximes by $[\text{Mn}(\text{L}_{22}\text{pyfp})\text{Cl}](\text{ClO}_4)$ and H_2O_2

Entry	Substrate	Product	Time/min	Yield (%) ^{a,b}
1	CH=NOH 	CH=O 	55	95 ⁹
2	CH=NOH 	CH=O 	45	95 ¹⁰
3	CH=NOH 	CH=O 	50	90 ⁹
4	Cl CH=NOH 	Cl CH=O 	85	85 ¹¹
5	NO₂ NOH 	O 	60	90 ⁹
6	NOH 	O 	65	92 ¹⁰
7	NOH 	O 	45	86 ¹²
8	HO NOH 	HO O 	60	85 ⁹
9	Cl NOH 	Cl O 	105	80 ¹⁰
10	O₂N NOH 	O₂N O 	80	70 ⁹
				

(Continued)

Table 3
(Continued).

Entry	Substrate	Product	Time/min	Yield (%) ^{a,b}
11			100	73 ¹³
12			115	60 ¹⁴
13			60	70 ⁹
14			90	60 ¹⁵
15			120	60 ^c

^aOxime (1 mmol), H₂O₂ (7 ml, 10%), [Mn(L₂₂pyfp)Cl](ClO₄) (0.2 mmol), CH₃CN (10 ml) under reflux, 45-120 min.

^bYields refer to the isolated pure products.

^cProduct was separated by distillation under reduced pressure and yield determined as 2,4-dinitrophenyl hydrazone derivative.

Table 4
Reusability of [Mn(L₂₂pyfp)Cl](ClO₄) Catalyst in the Oxidation of Acetophenone Oxime

Run No.	Time (min)	Yield (%) ^{a,b}
1	60	90
2	60	82
3	60	70
4	60	65

^aIsolated yield.

^bOxime (1 mmol), H₂O₂ (7 ml, 10%), [Mn(L₂₂pyfp)Cl](ClO₄) (0.2 mmol), CH₃CN (10 ml) under reflux condition.

chromatography on silica gel (eluent: *n*-hexane/acetone 9:1) in good to excellent yields (Table 3). The yield of butanone product was determined as its 2,4-dinitrophenyl hydrazone derivative. We present analytical data of three selected examples (aromatic aldoxime, aromatic and aliphatic ketoxime, converted in each case to the parent carbonyl compound) from Table 3:

4-Chlorobenzaldehyde. m.p. 44-46 °C, *lit.*⁹ 45-48 °C. IR (KBr): 3421, 3087, 2924, 2857, 2758, 1698, 1574, 1483, 1385, 1207, 815 cm⁻¹. ¹H NMR (90 MHz, CDCl₃) δ (ppm): 7.480-7.716 (dd, 4H), 9.919 (s, 1H).

4'-Hydroxyacetophenone. m.p. 108-110 °C, *lit.*¹² 109-111 °C. IR (KBr): 3243, 3007, 2927, 1674, 1605, 1576, 1511, 1459, 1310, 1250, 1181, 1024, 836 cm⁻¹. ¹H NMR (90 MHz, CDCl₃) δ (ppm): 8.752 (s, 1H), 7.854-6.991 (dd, 4H), 2.578 (s, 3H).

2-Methylcyclohexanone. b.p. 154-157 °C, *lit.*¹⁵ 162-163 °C. IR (KBr): 3402, 2925, 2854, 2359, 1715, 1456, 1375 cm⁻¹. ¹H NMR (90 MHz, CDCl₃) δ (ppm): 2.854-2.515 (m, 4H), 1.979 (m, 3H), 1.602 (m, 2H), 1.108 (s, 3H).

Acknowledgments

We are grateful to the Department of Chemistry of Payame Noor University and Ministry of Science Research and Technology for the financial support.

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