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Rapid and efficient oxidative decarboxylation of carboxylic acids with sodium periodate catalyzed by manganese (III) Schiff base complexes

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Abstract—Rapid and efficient oxidative decarboxylatoin of α-aryl carboxylic acids was observed. In the chemical system containing Mn(III)-salophen complex as catalyst, carboxylic acids are converted efficiently to the corresponding carbonyl derivatives with sodium periodate. The ability of various Schiff base complexes in the oxidative decarboxylation of carboxylic acids was also investigated.

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1. Introduction

Many efficient biomimetic oxidation systems using iron and manganese porphyrins as catalysts, and various single oxygen atom donors such as PhIO, ClO^-, H_2O_2, ROOH or IO_4^- have been reported.[1–10] The high efficiency of some of these systems makes them potentially useful for preparative oxidations in organic synthesis. Recently, mono- and binuclear transition metal complexes derived from ligands other than porphyrins have also been employed as catalysts. The use of metal Schiff base complexes, that is, metal salen and metal salophen to catalyze the oxidation of hydrocarbons by single oxygen atom donors has received much attention. Manganese, chromium, nickel and cobalt Schiff base complexes have been used for these transformations.[11–20]

In continuation of our research on the oxidative decarboxylation of carboxylic acids,[21–23] here we report the rapid and efficient oxidative decarboxylation of α-aryl carboxylic acids mediated by manganese (III) salophen complex.

We have chosen the salophen ligand because it is similar to porphyrin and the electronic and steric nature of the metal complex can be tuned by introducing electron-withdrawing and electron-releasing substituents and bulky groups in the ligand.

This catalytic system exhibits a high activity in the oxidative decarboxylation of α-aryl carboxylic acids with sodium periodate in 1:1 CH_3CN/H_2O mixture in the presence of imidazole as axial ligand (Scheme 1).

The type of metal ion and Schiff base and the nature of reactive intermediate were also investigated.

2. Results and discussion

2.1. Oxidative decarboxylation of carboxylic acids with different metal-Schiff base complexes

In a preliminary approach to the periodate anion activation by metal Schiff base complexes, we decided to investigate the activity of different Schiff base complexes of Fe, Mn, Co and Ni as metal ions. Table 1 summarizes our trials on catalytic oxidative decarboxylation of diphenylaceticacid with $NaIO_4$ in the presence various metal Schiff base complexes (shown in Fig. 1). We found that the nature of the metal ion has an important

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Keywords: Biomimetic oxidation; Schiff base; Oxidative decarboxylation.

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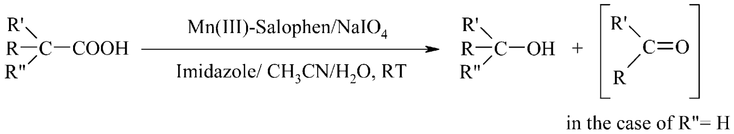


Scheme 1.

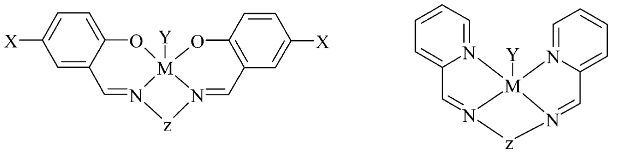
role on the catalytic properties of Schiff base complexes. The use of iron, cobalt and nickel complexes gives small amount of corresponding carbonyl compound in the oxidative decarboxylation of diphenylaceticacid. However, the use of manganese (III) complexes, Mn-BPB [BPB = *N*,*N'*-bis(2-pyridinecarboxamide)-1,2-benzene] and Mn-salophen resulted in a significant amount of diphenylketone after 5 min (31 and 100%).

In comparing the influence of Schiff base ligands on catalytic activity, the hindered Schiff base ligand, salophen, exhibits a significantly greater catalytic power than the unhindered Schiff base ligand, salen. The similar situation have been observed with metalloporphyrin complexes and NaOCl as oxygen donors.[24]

Table 1. Oxidative decarboxylation of diphenylaceticacid by various metal Schiff base complexes with sodium periodate

Schiff base	Yield (%)[a] after 5 min.	Yield (%)[a] after 10 min.	Yield (%)[a] after 30 min.
1	100	100	100
2	36	41	45
3	4	5	6
4	4	4	4
5	4	5	5
6	8	10	11
7	5	8	9
8	31	35	39
9	4	4	4
10	10	11	13
11	5	6	7

[a] GC yields.



	M	z	X	Y
1	Mn	C_6H_4	H	Cl
2	Mn	C_6H_4	NO_2	Cl
3	Fe	C_6H_4	H	Cl
4	Co	C_6H_4	H	-
5	Ni	C_6H_4	H	-
6	Mn	$(CH_2)_2$	H	Cl
7	Fe	$(CH_2)_2$	H	Cl
8	Mn	C_6H_4	H	Cl
9	Fe	C_6H_4	H	Cl
10	Mn	$(CH_2)_2$	H	Cl
11	Fe	$(CH_2)_2$	H	Cl

Figure 1. Transition metal Schiff base complexes used in this study.

2.2. Effect of solvent on the oxidative decarboxylation of diphenylaceticacid

Among the 1:1 mixture of methanol, ethanol, acetone, acetonitrile (single phase systems), chloroform and carbontetrachloride (two phase systems with Bu_4NBr as phase transfer catalyst) with water, the 1:1 acetonitrile/water mixture was chosen as the reaction medium, because metal Schiff base complexes are highly soluble in this solvent and higher ketone yields were observed. The results were shown in Table 2.

2.3. Effect of axial ligand on the oxidative decarboxylation of diphenylaceticacid

One important aspect of this catalytic system is the modification of the decarboxylation rate by addition of small amount of imidazole to the reaction mixture. The formation of diphenylketone in the absence of axial ligand is very slow and the yields are always below 30%, whereas the amount of diphenylketone reaches to 100% in the catalyzed reaction with the imidazole as the axial base.

The effect of different axial ligands upon the oxidation rate decreased in the order: imidazole = 1-methylimidazole > 4-*t*-buthylpyridine > 4-methylpyridine > 2-methylpyridine > pyridine.

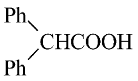
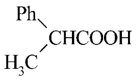
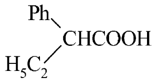
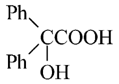
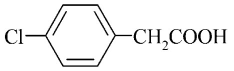
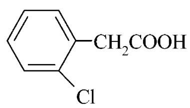
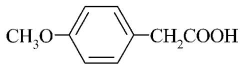
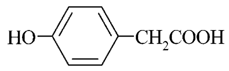
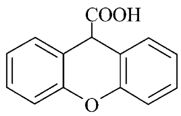
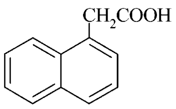
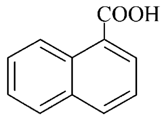
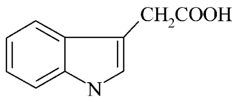
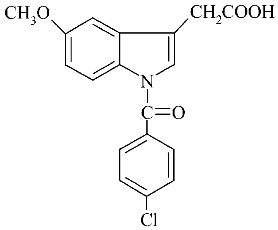
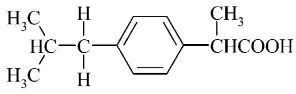
These results may be explained in terms of the greater stability of Mn(salophen)Cl achieved in the presence of imidazole and 1-methyl imidazole. As a result, the main effect of nitrogen donors of the catalytic activity of Mn-catalyst does not seem to be directly related to the basicity of the donors. Behavior of nitrogen donors in catalytic reactions can be explained based on the steric and electronic property of them for ligation to the manganese salophen complexes.

Table 2. Effect of solvent on oxidative decarboxylation of diphenylaceticacid with $NaIO_4$/Mn(salophen) system

Solvent	Yield (%)[a] after 5 min.	Yield (%)[a] after 15 min.
CH_3CN/H_2O	100	100
CH_3COCH_3/H_2O	68	80
CH_3OH/H_2O	45	50
CH_3CH_2OH/H_2O	38	42
$CHCl_3/H_2O$	5	5
CCl_4/H_2O	5	5

[a] GC Yields.

Table 3. Oxidative decarboxylation of α-aryl carboxylic acids by Mn-salophen/ $NaIO_4$

Run	Substrate	Product	Time (min)	Yield[a] (%)
1	$PhCH_2COOH$	Ketone	5	91
2	 $Ph_2CHCOOH$	Ketone	5	94
3	 $Ph(H_3C)CHCOOH$	Ketone	5	93
4	 $Ph(H_5C_2)CHCOOH$	Ketone	5	93
5	 $Ph_2C(OH)COOH$	Ketone	5	91
6		Ketone	5	89
7		Ketone	5	89
8		Ketone	5	90
9		Ketone	5	90
10		Ketone	10	91
11		Ketone	15	90
12		Alcohol	15	84
13		Ketone	30	78
14		Ketone	30	82
15		Ketone	30	92

[a] Isolated yields.

2.4. Oxidative decarboxylation of carboxylic acids with sodium periodate catalyzed by Mn (III)-salophen

The imidazole-modified Mn-salophen/$NaIO_4$ oxidizing system can be applied to decarboxylation of a large number of aryl substituted acetic acids in high yields at short times and room temperatures. All experiments were carried out with 2 equiv of sodium periodate per 1 equiv of carboxylic acid. As shown in Table 3, the yields are between 78–94% and the principal product was carbonyl derivative (except for 1-Naphtoic acid) and only small amount of the alcohol derivatives was obtained.

Oxidative decarboxylation of anti-inflammatory drugs such as Indomethacin and Ibuprophen (Run 14,15) at room temperature afforded corresponding carbonyl derivatives as the major product in 82 and 94% yields, respectively. Such oxidative decarboxylation pathway has been also observed during drug metabolism in vivo.[25,26]

Comparison of this homogeneous oxidizing system with previously reported homogeneous metalloporphyrin systems[21,22] showed that in the Mn-salophen/$NaIO_4$ system the yields are higher than that metalloporphyrin/ $NaIO_4$ systems and the reaction times are shorter, and in the case of heterogeneous metalloporphyrin system[23] the yields are similar whereas the reaction times are shorter.

In the absence of manganese (III)-salophen catalyst, $NaIO_4$ has poor ability to decarboxylate aryl carboxylic acids at room temperature (4–10% yields).

2.5. Oxo manganese (V) species as the reactive intermediate

Although we have assumed the active manganese species to be reactive (salophen)Mn (V) oxo intermediate, [(salophen)$Mn^V = O$], by comparing the present spectral observation with the previous reports,[27] we could not isolate this active species. It is pertinent to point out that to date no (salophen)Mn (V) oxo species have yielded to structural characterization, although Groves et al. and others have characterize oxo manganese (V) porphyrin complexes in recent years.[28]

When a clear brown solution of Mn (III)-salophen in acetonitrile is treated with sodium periodate, it immediately turns dark. The appearance of a new absorption band (with $\lambda_{max} = 520–530$ nm, Fig. 2) is strongly reminiscent of the spectral change obtained during the conversion of the Mn (III)-salophen cation to the corresponding oxomanganese (V) species. Upon standing, the dark brown solution fades to the original light brown within 10 min. When the same experiment is carried out in the presence of diphenylaceticacid, the dark brown solution immediately changed to its original light brown color.

3. Experimental

Schiff base complexes 1–11 (Fig. 1), were prepared as described by Boucher[29] or by the more recently modified methods.[11,30,31] Carboxylic acids were obtained

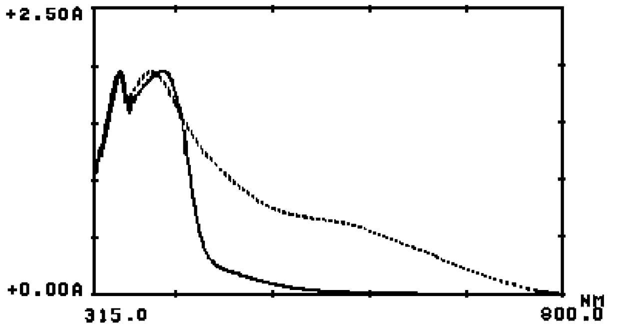


Figure 2. Absorption spectra of [Mn(III)-salophen]Cl in CH_3CN/H_2O. The dashed curve is the same solution immediately after reaction with excess $NaIO_4$.

from Merck or Fluka and were passed through a column containing active alumina to remove peroxidic impurities. The electronic absorption spectra were recorded with a Shimadzu UV-160 spectrophotometer. ^{1}HNMR spectra were obtained with a Brucker AW80 (80 MHz) spectrometer. GLC analyses were performed on a Shimadzu GC-16A instrument using a 2m column packed with silicon DC-200 or Carbowax 20M. IR spectra were recorded on a Shimadzu IR-435 spectrophotometer.

3.1. General procedure for oxidative decarboxylation of α-aryl substituted carboxylic acids

All of the reactions were carried out at room temperature in a 25 mL flask equipped with a magnetic stirring bar. A solution of sodium periodate (2 mmol in 5 mL H_2O) was added to a mixture of carboxylic acid (1 mmol), Mn-salophen (0.067 mmol) and imidazole (0.067 mmol) in CH_3CN (5 mL). Progress of the reaction was monitored by TLC. After the reaction was completed, the reaction products were extracted with CH_2Cl_2 (20 mL) and were purified by silica gel plate or silica gel column (eluent: CCl_4–Et_2O). The identities of products were confirmed by IR and ^{1}H NMR spectral data.

Multi scale oxidative decarboxylation of diphenylaceticacid (5 mmol) was also investigated. The results showed that this compound decarboxylated with sodium periodate in the presence of Mn(salophen)Cl in good yield (92%).

4. Conclusions

Although many oxidation systems that mimic cytochrome P-450 dependent monooxygenase have been reported, Mn(III)salophen/$NaIO_4$ catalytic system have the following advantages: (i) short reaction time (ii) high efficiency for oxidative decarboxylation of carboxylic acids; (iii) ease of preparation of the catalyst.

In comparison with other reported Schiff-base oxidation systems, performance of the novel Mn(III)salophen/$NaIO_4$ system can be described as outstanding. Therefore, in the list of suitable oxidants able to behave like single oxygen donor to Schiff base complex, sodium periodate is among the most efficient.

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