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Biomimetic Catalytic Decarboxylation of Phenylacetic Acid Derivatives by Manganese(III) Complex

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Bis(2-hydroxyacetophenone)ethylendiimine as a quadridentate Schiff base ligand and its Mn(III) were synthesized and characterized by analytical and spectral data. An efficient homogeneous oxidative decarboxylation of some carboxylic acids was performed by catalytic amount of Mn(III) complex in chloroform, using tetrabutylamonium periodate as oxidant at room temperature.

Key Words: Schiff base, Complex, Catalyst, Decarboxylation, Manganese(III).

INTRODUCTION

Nowadays, Schiff bases as synthetic ligands similar to others such as porphyrin and phthalocyanine, have been used for the synthesis of metal complex catalysts to mimic the reactivity of an expressive number of metalloenzymes[1-9]. The Schiff base metal complexes in combination with various oxygen donors such as sodium periodate, oxone, tetrabutylamonium periodate, H_2O_2, *etc*., have been used for catalytic oxidation of organic compounds such as alkenes, alkanes, alcohols, aldehydes, *etc*. under homogeneous and heterogeneous conditions. Several efficient homogeneous catalytic systems for oxidation of organic substrates based on porphyrinic compounds and manganese or iron Schiff-base complexes as promising catalysts have been reported[1,7-19]. Decarboxylation processes play an important role in different areas of organic synthesis as well as in biochemical reactions. Several reports on this transformation by thermal[20,21], photochemical[22-24] and catalytic methods[25,26] have been reported. Such oxidative decarboxylation pathways have also been observed during drug metabolism *in vivo*[27,28].

In continuation of recently reports on the catalytic oxidation of organic compounds[29-32], herein we report the synthesis of a manganese(III) Schiff base complex with a quadridentate Schiff base ligand and its catalytic activity for the oxidative decarboxylation of a variety of carboxylic acids (**Scheme-I**).

EXPERIMENTAL

Carboxylic acids were obtained from Merck or Fluka and used without further purification. The electronic absorption spectra were recorded with a JASCO UV-570 spectrophotometer. ^{1}H and ^{13}C NMR spectra were obtained with a Brucker 500 MHz spectrometer. IR spectra were recorded on a FT-IR JASCO-680 spectrophotometer. Mass spectra were recorded on Shimadzu 1800. Molar conductivity of complexes was measured by Metrohm 712 model. Elemental analyses (CNHS) of samples were performed using a CHNS-932 elemental analyzer by central instrumental laboratory of Tarbiat Moallem University of Tehran.

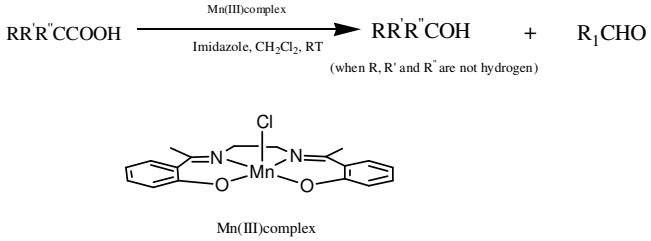
Preparation of the ligand of *bis*(2-hydroxyacetophenone)ethylenediimine: To 5 mmol of 2-hydroxyacetophenoe in 25 mL ethanol, 2.5 mmol of ethylenediamine in 25 mL ethanol was gradually added and the reaction mixture was refluxed. The progress of the reaction was followed by TLC. The reaction mixture was cooled in the refrigerator for 2 h and then the yellow crystals was filtered off and washed with ethanol/water mixture three times to give *bis*(2-hydroxyacetophenone)ethylenediimine in 86 % yield. m.p. (ºC) = 188-190. Characteristic IR (KBr, ν_{max}, cm^{-1}): 3443 (bs, H_2O), 3056 (w, CH-aromatic), 2942 (w, CH-aliphatic), 2884 (w, CH-imine), 1611 (vs, C=N-imine), 1564 (w), 1494 (m), 1435 (m), 1352 (w), 1288 (s), 1235 (s), 1158 (s), 1119 (m), 1058 (m), 1023 (m), 941 (vs), 847 (s), 752 (s), 741 (m), 647 (m). UV (CH_2Cl_2, λ_{max}): 210 (2.7×10^4), 247 (2.7×10^4) and 321 (8.0×10^3) nm. ^{1}H NMR (500 MHz, DMSO-d_6): 15.64 (2H, s), 7.32 (2H, d, J = 7.96 Hz), 7.04 (2H, t, J = 7.85 Hz), 6.63 (2H, d, J = 8.29 Hz) and 6.57 (2H, t, J = 7.85 Hz), 3.76 ppm (s, 4H) and 2.18 (s, 6H) ppm. ^{13}C NMR (500 MHz, DMSO-d_6): 173.01, 163.36, 132.62, 128.51, 119.68, 118.52, 117.59, 50.33 and 15.07 ppm. MS(m/z): 298 (M + 2), 296 (M^+).

Preparation of Mn(III) complex as the catalyst: Manganese complex was obtained by reaction of 5 mmol (1.48 g) of the free ligand and 5 mmol of $MnCl_2 \cdot 4H_2O$ (0.98 g) under air bobbling, based on the literature[7,8,10-12,33,34], under reflux, in ethanol, during 4-6 h. After cooling, the solids were collected by filtration and washed twice with a small portion of ethanol. $[Mn(III)(L)Cl] \cdot H_2O$: IR (KBr, ν_{max}, cm^{-1}): 3413(m, (H_2O)), 3058 (w), 2971 (w), 2882 (w), 1588 (vs, (-C=N)), 1558 (m), 1494 (s), 1435 (m), 1317 (m), 1300 (m), 1235 (s), 1152 (m), 1129 (m), 1082 (m), 941 (w), 870 (s), 823 (w), 752 (s), 67 (m). UV (CH_2Cl_2, λ_{max}): 219 (5.24×10^5), 260 (9.50×10^5), 380 (3.20×10^5) and 540 (8.6×10) nm. Elemental analysis calcd. (%): $C_{18}H_{20}N_2O_3ClMn$: C, 53.68; H, 5.01; N, 6.96; found (%): C, 54.45; H, 5.19; N. 6.59. m.p. (> 300 ºC, dec.). Molar conductivity in methanol is Ω = 20.50 µS/cm.

Typical experimental procedure: To the Mn(III) complex (0.1 mmol, 10 % molar ratio) in chloroform (20 mL), imidazole (0.2 mol, 20 % mmol), 3,4-dimethoxyphenylacetic acid (1 mmol) and then tetrabutylammonium periodate (1 mmol) were added. The reaction mixture was stirred at room temperature until TLC indicated the reaction was completed. The resulting solution was concentrated under reduced pressure to yield a residue, which was passed through a short pad of silica gel using ethyl acetate and hexane (1:2) as eluent to provide analytically pure product in 94 % yield. IR (KBr, ν_{max}, cm^{-1}): 3444 (w), 3184 (w), 3084 (m), 3021 (m), 2975 (w), 2964 (w), 2947 (m), 2892 (m), 2838 (m), 2760 (m), 1680 (vs), 1584 (s), 1509 (s), 1463 (m), 1401 (m), 1348 (m), 1266 (m), 1236 (m), 1151 (m), 1132 (s), 1019 (s), 960 (w), 862 (m), 819 (s), 729 (s), 640 (s). ^{1}H NMR ($CDCl_3$): 9.86 (s, 1H), 7.47 (dd, 1H, *J* = 8.16 and 1.70 Hz), 7.42 (d, 1H, *J* = 1.65 Hz), 6.99 (d, 1H, *J* = 8.17 Hz), 3.99 (s, 3H), 3.96 (s, 3H) ppm. MS (m/z): 166 (M^+), 151, 137, 119, 107, 95, 77, 63, 51.

RESULTS AND DISCUSSION

The ligand was synthesized by condensation of 2-hydroxyacetophenone and ethylenediamine in a 1:2 molar ratio in ethanol under reflux. Elemental analysis, FT- IR and ^{1}H and ^{13}C NMR confirmed the synthesis of ligand. The IR spectral data of the ligand are in accord to its formula structure.



Scheme-I

The broad absorption band centered at around 2500 cm^{-1} is readily ascribed to the O-H stretching. The absorption band at 1611 cm^{-1} due to the asymmetric -C=N vibrational stretching is characteristic frequency of imino-group. The solution NMR data of the ligand is also in good agreement with the structure. The ^{1}H NMR spectrum taken from dimethylsolfoxide-d_6 solution exhibited a singlet at 15.64 ppm for two hydrogens of OH groups of the ligand. The ^{1}H NMR spectrum showed also the expected peaks at 7.32 (d, 2H, *J* = 7.96 Hz), 7.04 (t, 2H, *J* = 7.85 Hz), 6.63 (d, 2H, *J* = 8.29 Hz) and 6.57 (t, 2H, *J* = 7.85 Hz) for benzene ring and 3.76 (s, 4H, $2CH_2$) and 2.18 (s, 6H, $2CH_3$) ppm aliphatic moiety of the ligand. The ^{13}C NMR showed nine signals at 173.01 (C=N), 163.36 (C-OH), 132.62, 128.51, 119.68, 118.52, 117.59, 50.33 and 15.07 ppm in accord with the symmetric structure of the ligand. The electronic spectrum of the ligand showed two bands at 210, 247 and 306 nm that two first bands can be assigned to π-π* of the aromatic ring and the third to imino-group(C=N) bond of the ligand. The synthesis of Mn(III) Schiff base was based on the experimental procedure reported in literature[7,8]. Elemental analysis, IR, UV-visible spectra and conductivity resulted in satisfactory data. The absorption band at 1588 cm^{-1} that can be assigned to the coordinated C=N stretching is characteristic band of the complex. The electronic spectrum of this complex contained three bands at 219, 260(sh), 380 and 540 nm. First three bands were assigned to π-π* of the aromatic rings and imino-groups of the ligand that shifted to lower wavelength with respect to free ligand due to the coordination. The fourth band at 540 nm was assigned to *d-d* electronic transition of the complex. The conductivity measurement in methanol indicates that the Mn(III) complex is neutral (Ω = 20.50 µS/cm)[10-12,33,34]. The NMR of the complexes could not be recorded due to paramagnetic properties of them. After the synthesis and characterization of the Mn(III) complex, its catalytic activity was investigated for the oxidative decarboxylation of a variety of arylacetic acids according to typical procedure, using $(n\text{-}Bu)_4NIO_4$ as oxidant. The reaction mixture was stirred at room temperature until TLC indicated the reaction was complete. For running the reactions, some parameters such as solvent, catalyst, oxidant and auxiliary base amounts must be optimized. As shown in Table-1 various solvents such as dichloromethane, chloroform, acetonitrile, acetone and ethanol were examined for the choice of the suitable solvent. A typical reaction on phenylacetic acid (1 mmol) was performed using the 10 % molar ratio of Mn(III) complex and tetrabutylammonium periodate as oxidant in above solvents. Among the studied solvent, the chloroform was found as the best solvent.

TABLE-1
EFFECT OF SOLVENT ON CATALYTIC OXIDATIVE DECARBOXYLATION OF PHENYLACETIC ACID*

Solvent	Reaction time/(min)	Conversion** (%)
CH_2Cl_2	60	100
$CHCl_3$	45	100
CH_3CN	150	50
CH_3COCH_3	180	56
CH_3CH_2OH	180	44

*Refers to 1mmol phenylacetic acid, 1 mmol $(n\text{-}Bu)_4NIO_4$, 10 and 20 % molar ratios of the catalyst and imidazole. **Based on disappearance and/or recovery of phenylacetic acid.

The effect of catalyst amounts was also demonstrated by performance of a typical oxidative decarboxylation on phenylacetic acid using 0, 5, 6.6, 10, 15 and 20 % molar ratios of Mn(III) complex with respect to substrate in chloroform at room temperature. In the absence of the catalyst, the reaction showed very low progress even after prolonged reaction time. The results showed 10 % molar ratio was as optimum amount

TABLE-2
EFFECT OF CATALYST AMOUNTS OF Mn(III) COMPLEXES IN OXIDATIVE DECARBOXYLATION OF PHENYLACETIC ACID*

Molar ratio of Mn(III) (%) (catalyst to substrate)	Reaction time (min)	Conversion** (%)
0.0	300	<10
5.0	140	55
6.6	105	100
10.0	45	100
15.0	45	100
20.0	40	100

*Refers to 1 mmol phenylacetic acid, 1 mmol $(n\text{-Bu})_4NIO_4$ and 20 % molar ratio of imidazole. **Based on disappearance and/or recovery of phenylacetic acid.

in current conditions. The higher amounts were found not to have a notable effect on reaction time.

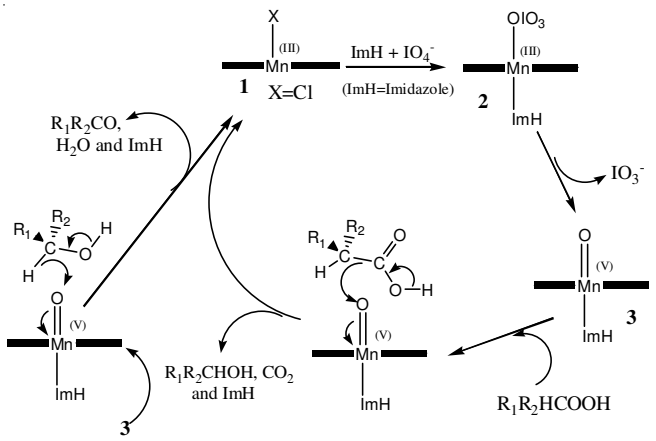
Generally the reaction catalyzed by the Schiff base and porphyrin complexes is improved by the aid of auxiliary bases such as imidazole. Therefore in this work, 0, 10, 20 and 30 % molar ratios (with respect to substrate) of imidazole were examined. The decarboxylation rate of phenylacetic acid in the absence of imidazole is very low (< 30 % conversion) whereas the conversion reaches to 100 % in 45 min by Mn(III) complex and 20 % imidazole as the auxiliary base. Finally among the various ratios of tetrabutylammonium periodate as oxidant to phenylacetic acid as typical substrate including 0.5:1, 1:1 and 2:1 with reaction times of 120 (not completed), 45 and 40 min, respectively, the 1:1 ratio was selected as optimum. After the above investigation, the catalytic oxidative decarboxylation of a variety of carboxylic acids was carried out by the Mn(III)-complex/imidazole/$(n\text{-Bu})_4NIO_4$ system in chloroform that led to good to high yields at relatively short reaction times at room temperature. All experiments were performed with 1 mmol of tetrabutylammonium periodate, 1 mmol of carboxylic acid, 10 % mol ratio of catalyst and 20 % mol ratio of imidazole in chloroform. As shown in Table-3, aldehyde or ketone derivatives were obtained as products with yields between 85-95 % except about the triphenylacetic acid (entry 3) that was converted to triphenylmethanol.

The catalytic mechanism shown in the **Scheme-II** is proposed for the oxidative decarboxylation of carboxylic acids using Mn(III)-complex, **1** as the catalyst. Based on the literature[35,36], we have suggested at first the oxo-compound of [MnV(O)(L)] (**3**) as the direct oxidant in the oxidative decarboxylation is formed by treatment of the tetrabutylammonium periodate with the Mn(III)-complex. The carboxylic acid, $R_1R_2HCCOOH$ approaches *via* its C_1-C_2 to **3** to give the alcohol of R_1R_2HCOH, CO_2 and **1** in the first oxidative step. At the second oxidative step the formed alcohols again is oxidized by the another oxo-compound **3** to produce the aldehyde or ketone as principle product. First step oxidative decarboxylation of triphenylacetic acid (entry 3) lead to a tertiary alcohol (triphenylmethanol) that can not be overoxidized to aldehyde or ketone in our mild conditions. This observation is in agreement with proposed two step mechanism for the oxidative decarboxylation. It seems the mandelic acid (entry 16) with one OH in α-position is directly decarboxylated to benzaldehyde at first step oxidation.

TABLE-3
OXIDATIVE DECARBOXYLATION OF CARBOXYLIC ACIDS USING Mn(III) COMPLEX/IMIDAZOLE/$(n\text{-Bu})_4NIO_4$ CATALYTIC SYSTEM* IN CHLOROFORM AT ROOM TEMPERATURE

Entry	Carboxylic acid	Product**	Time (min)	Yields*** (%)
1	$(Ph)_2CHCOOH$	$(Ph)_2CO$	30	95
2	$PhCH_2COOH$	PhCHO	45	94
3	Ph_3CCOOH	Ph_3COH	20	95
4	$4\text{-}MeC_6H_4CH_2COOH$	$4\text{-}MeC_6H_4CHO$	20	94
5	$4\text{-}MeOC_6H_4CH_2COOH$	$4\text{-}MeOC_6H_4CHO$	45	91
6	$2\text{-}MeOC_6H_4CH_2COOH$	$2\text{-}MeOC_6H_4CHO$	60	89
7	$3,4\text{-}(MeO)_2C_6H_4CH_2COOH$	$3,4\text{-}(MeO)_2C_6H_4CHO$	25	94
8	$3\text{-}ClC_6H_4CH_2COOH$	$3\text{-}ClC_6H_4CHO$	35	92
9	$4\text{-}ClC_6H_4CH_2COOH$	$4\text{-}ClC_6H_4CHO$	35	92
10	$2, 6\text{-}Cl_2C_6H_4CH_2COOH$	$2, 6\text{-}Cl_2C_6H_4CHO$	40	90
11	$3\text{-}FC_6H_4CH_2COOH$	$3\text{-}FC_6H_4CHO$	20	91
12	$2, 6\text{-}F_2C_6H_4CH_2COOH$	$2, 6\text{-}F_2C_6H_4CHO$	20	94
13	$4\text{-}FC_6H_4CH_2COOH$	$4\text{-}FC_6H_4CHO$	25	90
14	$4\text{-}HOC_6H_4CH_2COOH$	$4\text{-}HOC_6H_4CHO$	45	91
15	$PhCH_2CH_2COOH$	$PhCH_2CHO$	25	88
16	PhCH(OH)COOH	PhCHO	40	85
17	EtPhCHCOOH	EtPhCO	40	93

*Refers to 1mmol carboxylic acid, 1 mmol $(n\text{-Bu})_4NIO_4$, 10 and 20 % molar ratios of catalyst and imidazole. **All products are known and their physical and spectral data of them were compared with authentic samples. ***Refers to isolated yields.



Scheme-II

Conclusion

In this paper, the application of new Schiff base complex of Mn(III) as novel homogeneous catalyst in a convenient, efficient and practical method for the effective oxidative decarboxylation of a variety of carboxylic acids is reported. The availability of the reagents, facile synthesis of the complexes, the easy work-up of products and the high yields make this method a useful alternative to literature procedures in this subject.

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