Manganese (III)-Bis(salicylaldehyde)-4-Methyl-1,2-Phenylenediimine (Mn-BSMP) as an Inexpensive N_2O_2 Type Schiff Base Catalyst for Oxidative Decarboxylation of Carboxylic Acids with (n-Bu_4NIO_4) in the Presence of Imidazol

Karimipour, Gholamreza*[+]**; Montazerozohori, Morteza: Haghighat Naeini, Nasrin**
Department of Chemistry, Faculty of Sciences, Yasouj University,
P.O. box 75918-74831Yasouj, I.R. IRAN

ABSTRACT: *In this study, bis(salicylaldehyde)-4-methyl-1,2-phenylenediimine (BSMP) as a Schiff base ligand of N_2O_2-type and its Mn and Fe complex as M-BSMP catalyst were synthesized and characterized by UV-Vis, IR spectroscopy and elemental analysis. The efficiency of Fe- and Mn-BSMP catalysts was evaluated in the oxidative decarboxylation of arylacetic acids with tetra-butylammonium periodate (n-Bu_4NIO_4) in the presence of imidazol with the mole ratios of M-BSMP: imdazole: n-Bu_4NIO_4: carboxylic acid of 1:2:5:5, respectively in CH_2Cl_2. Using Mn-BSMP instead of Fe-BSMP makes the decarboxylation improved, leading 60-95% of corresponding carbonyl compounds as the sole products.*

KEY WORDS: *Schiff base, Tetrabuthylammonium periodate, Arylacetic acid, Decarboxylation.*

INTRODUCTION

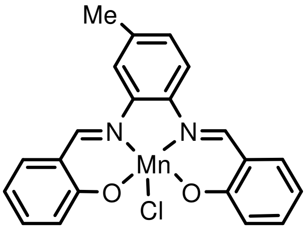
In the last two decades there has been an increasing interest in developing new catalytic processes for oxidation based on the transition metal Schiff base complexes. The synthesis and application of these complexes have been highly considered in inorganic, organic and biological fields [1], because their structures are similar to that of porphyrin and phthalocyanine rings [2]. Moreover, they are good at loading oxygen, resisting bacteria and mimicking enzymes [3]. Catalysts of this kind were easily prepared by condensation of aldehydes and amines, and the produced ligands were metalated by transition metal salts without any complication in its preparation [4]. So, as a continuation of our studies on the oxidative decarboxylation of carboxylic acids by Mn(TPP)X/PhI$(OAc)_2$ [5], Mn(TPP)CN/n-Bu_4NIO_4 [6] and Fe(III)-Schiff base/n-Bu_4NIO_4 [7], we now present M(III)-BSMP (M = Mn and Fe)(Fig.1) as catalyst for the decarboxylation of aryl acetic acids by n-Bu_4NIO_4 as a single oxygen donor in ambient temperature.

---

* *To whom correspondence should be addressed.*

[+] *E-mail: ghkar@mail.yu.ac.ir*

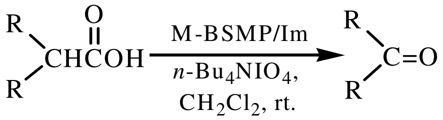
1021-9986/11/4/13 6/\$/2.60



M-BSMP; M= Mn(III), Fe(III)

The synthesis of inexpensive BSMP Schiff base ligand and its complex with Mn (III) and Fe (III), as well as their similarity to the metalloporphyrin catalysts [8] make it potentially useful for the oxidative decarboxylation. Moreover, its catalytic activity could be tuned by introducing electron withdrawing and releasing substituents and bulky groups in the ligand and by changing the central metal atom.

In this catalytic system, various carboxylic acids were selectively converted into the corresponding carbonyl compounds as the sole product without any over-oxidation of the produced carbonyl compounds (Eq. (1)).



$$\mathrm{R_2CHCOOH} \xrightarrow[n\text{-}\mathrm{Bu_4NIO_4},\ \mathrm{CH_2Cl_2},\ \mathrm{rt.}]{\mathrm{M\text{-}BSMP/Im}} \mathrm{R_2C{=}O} \qquad (1)$$

EXPERIMENTAL SECTION

All chemicals were commercial reagent grade from the Fluka Chemical Company. Four dentate ligand, bis(salicylaldehyde)-4-mthyl-1,2-phenylenediimine was synthesized according to the previous report and identified by spectral and physical characterization [17]. ^1H NMR spectra of products were obtained with a Bruker (500 MHz) spectrometer.

Synthesis of [bis (salicylaldehye) 4-Me–1, 2-Phenylenediimine] Mn(III) or Fe(III) Chloride catalyst (Mn(III)-BSMP or Fe(III)-BSMP)

Ligand, bis(salicylaldehyde)-4-mthyl-1,2-phenylenediimine was synthesized according to the previous report [15] by condensing of 2 mmol (0.122g) of salicylaldehyde and 1mmol of 4-methyl 1,2-phenylenediamine) in ethanolic solution. The catalyst was prepared similar to previously reported method via addition of 20 mL ethanolic solution of $MnCl_2.4H_2O$ (5mmol, 0.98g) or $FeCl_3.6H_2O$ (5mmol, 1.35g) to the synthesized ligand (5 mmol, 1.65g) in 20 mL of ethanol. The reaction mixture was severely stirred for 0.5 h and then treated by air bubbling for 6 hours (for Mn-complex). After completion of the reaction as monitored by TLC, the reaction mixture was concentrated and dark brown precipitate of Mn (III)-BSMP was filtered. Physical, spectral and analytical data of Mn (III)-BSMP and Fe (III)-BSMP are as in below:

Mn (III)-BSMP

IR(KBr, cm^{-1}): 3413(m), 1605(vs, C=N), 1535(vs), 1439(m), 1373(m), 1316(s), 1192(m), 1125(m), 1054(m), 923(m), 821(m), 762(m), 618(m), 559(m), 456(m). UV-Vis(CH_2Cl_2, λ_{max}): 210, 250, 334 and 430 nm. M.P.(°C):322-324 (dec.)

Chemical formula: $C_{27}H_{36}ClMnN_2O_3$, Mn (III)-BSMP. H_2O Molecular weight: 526.96, Analytical data: C, 63.4 (calcd.61.54); H, 6.8 (calcd.6.89); N, 5.4 (calcd.5.32).

Fe (III)-BSMP

IR(KBr, cm^{-1}): 3444(m), 3084, 3057, 2973, 2858, 1608(vs), 1582(s), 1536(vs), 1463(m), 1373(m), 1316(s), 1197(m), 1150(m), 1029(m), 915(w), 821(m), 759(s), 611(m), 553(w), 456(m), 507(m). UV-Vis (CH_2Cl_2, λ_{max}): 222, 298, 376 and 422 nm. M.P.(°C):>300 (dec.).

Chemical formula: $C_{27}H_{36}ClFeN_2O_3$, Fe(III)-BSMP. H_2O Analytical data: C, 62.7(calcd.61.43); H, 6.7 (calcd.6.87); N, 5.2(calcd.5.31).

General procedure for oxidative decarboxylation of arylacetic acids with $(n\text{-}Bu)_4NIO_4$ catalyzed by Mn (III)-BSMP or Fe(III)-BSMP

All of the reactions were carried out at room temperature under air in a 25 mL flask equipped with a magnetic stirrer bar. A solution of n-Bu_4NIO_4 (1 mmol) in CH_2Cl_2 (5 mL) was added to a mixture of arylaceticacid (1 mmol) and Mn(III)-BSMP or Fe(III)-BSMP (20% mol) and imidazole (40% mol) in dichloromethane (10 mL). The progress of reaction was monitored by TLC. After the reaction was completed, the reaction mixture was filtered on silicagel and the product was extracted with CH_2Cl_2 or diethyl ether (2 × 20 mL). The carbonyl derivatives were obtained after evaporation of the solvent. Further purification was followed using a silica gel plate. IR and ^1H NMR spectral data confirmed the identities of the products.

RESULTS AND DISCUSSION

Bis(salicylaldehyde) -4- mthyl-1,2- phenylenediimine (BSMP) was prepared as the starting free ligand by reaction of salicylaldehyde and 4-methyl-1,2-phenylenediamine. This N_2O_2 type Schiff base ligand is capable of forming stable Mn (III) and Fe(III) complex with UV-Visible spectrum containing both intra-ligand (210, 250, 334 nm for Mn(III) and 222, 298, 376 nm for Fe(III)) and d-d or d-π^* transition absorption bands (430 and 422 for Mn(III) and Fe(III) respectively).

In comparing with the free ligand, the IR spectra of the M-complexes display certain changes indicating the type of bonds and their structures. The BSMP Shiff base ligand exhibits a broad band at 3418 cm^{-1}(m) originates from -OH stretching. The absence of this band in the M-BSMP indicates deprotonation of phenolic group and coordination of the oxygen atom to the metal ions. However, a slightly broad band observed in Mn-BSMP and Fe-BSMP at 3413 cm^{-1} and 3444 cm^{-1} seem to originate from the coordination of H_2O to the complex [9]. In the free ligand, a strong band at 1617 cm^{-1} is due to the azomethine group (C=N-) which shifts to 1605 cm^{-1} and 1608 cm^{-1} in the complexes indicating coordination through the azomethine nitrogen [10]. The frequencies in 553, 559 cm^{-1} and 456 cm^{-1} are attributed to υ(M-O) and υ(M-N) respectively [11].

Oxidative decarboxylation

Oxidative decarboxylation reactions are ones in which a carboxylate group is removed, forming carbon dioxide. They often occur in biological systems: pyruvate decarboxylation is an oxidative decarboxylation reaction [12], and there are many other examples in the citric acid cycle [13]. Anti-inflammatory drugs such as indomethacin and ibuprofen are decarboxylated during drug metabolism *in vivo* by cytochrome P-450, and the released CO_2 reduces the pain effects [14].

Although a few studies have been reported on the oxidative decarboxylation of carboxylic acids [15], they suffer from the disadvantages of long reaction times and low selectivities.

In this work, CH_2Cl_2 was selected among different solvents due to the facile solvation of starting materials, oxidant and the catalysts in this solvent. We found that no benzophenone product was obtained when diphenylacetic acid was subjected to decarboxylation by n-Bu_4NIO_4. Addition of Mn-BSMP and imidazole (Im) (as co-catalyst) in the reaction mixture improved the decarboxylation, leading to give 95% of the product at optimum conditions. These results clearly demonstrate that n-Bu_4NIO_4 has no oxidation capability to convert carboxylic acids to carbonyl compounds.

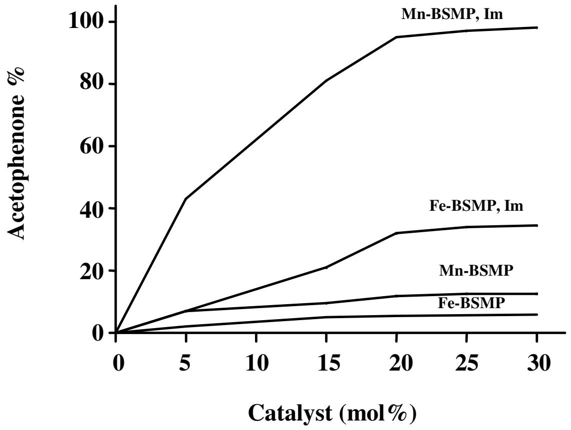
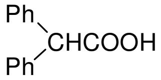
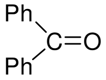
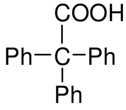
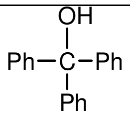
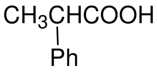
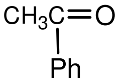
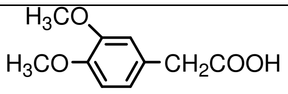
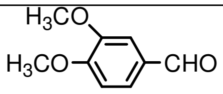
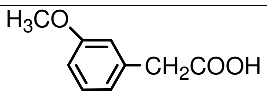
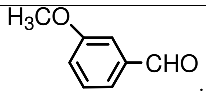
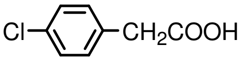
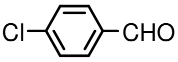
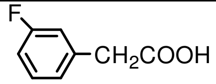
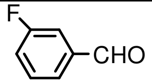
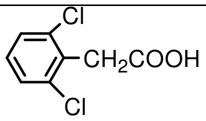
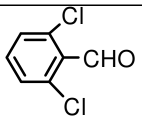
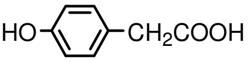
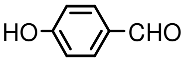
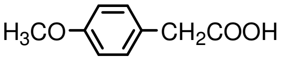
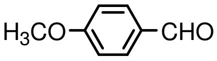
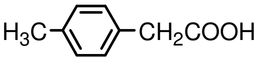
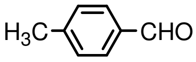
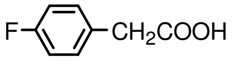
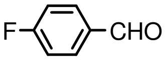


Fig. 1: Oxidative decarboxylation of diphenylacetic acid by Fe- and Mn-BSMP/n-Bu_4NIO_4 catalytic systems in the presence and absence of imidazole (Im).

The efficiency of Fe- and Mn-BSMP catalysts and the exigency of imidazol (Im) as co-catalyst were then tested by changing the concentration of the catalyst in the presence and absence of imidazol ligand. As shown in Fig.1, the yields reach in a maximum value when the mole ratio of Mn-BSMP was 20% mol percent. Further increasing the molar ratio was not effective, so that the benzophenone (%) would not be altered virtually by increasing the molar ratio. Under similar conditions, however, Fe-BSMP was not effective as Mn-BSMP catalyst. The use of Mn-BSMP gave benzophenone in 95%, whereas the product was 32% in the presence of Fe-BSMP (Table. 1). It is notable that the catalytic activity of Fe- and Mn-BSMP catalysts markedly increased in the presence of imidazol ligand, leading to accelerate the oxidation and to increase the yields. For instance, only 12% of benzophenone was obtained by n-Bu_4NIO_4/Mn-BSMP, whereas this reaction affords 95% of benzophenone in the presence of imidazole (Fig. 1). Comparison of the yield by Fe-BSMP in the absence and presence of imidazole give the similar results for the co-catalytic activity of imidazol.

It was reported that nitrogenous ligands such as imidazoles and pyridines improve selectivity, reactivity

Table 1: Oxidative decarboxylation of various carboxylic acids by Fe- and Mn-BSMP/n-Bu_4NIO_4 catalytic system.

Entry	Acid	Product	Mn-BSMP	Fe-BSMP	M.P.(°C) (Lit.)[b]
			P% [a] (Time,min)	P% [a] (Time,min)	
1			95 (50)	32 (140)	48 (47-49)
2	 Ph_3CCOOH	 Ph_3COH	90 (25)	20 (180)	160-162 (160-163)
3	 $CH_3CH(Ph)COOH$	 $CH_3C(Ph){=}O$	95 (70)	20 (180)	18-20 (18)
4			50 (35)	50 (80)	43-44 (43)
5			92 (20)	50 (200)	oil
6			75 (55)	40 (180)	45-47(46)
7			90 (20)	40 (50)	oil
8			80 (20)	20 (180)	68 (67-70)
9			94 (70)	45 (180)	115-118 (116)
10			60 (150)	20 (180)	oil
11			90 (15)	40 (180)	oil
12			80 (120)	20 (180)	oil

a) P% indicate product%, b) Refers to the chemical reagents catalogues of merck, Aldrich and fluka.

and turnover number of metalloporphyrin-mediated reactions, leading to weakening of the M–O bond in the oxidised form of the porphyrin catalysts by donating electron density into the M–O antibonding orbitals, which can account for this improved reactivity observed by Fe- and Mn-BSMP catalysts [16].

In this study, the best results were obtained by Mn-BSMP/n-Bu_4NIO_4 in the presence of imidazol as co-ligand (Fig. 1). However, decarboxylations were also carried out by Fe-BSMP /n-Bu_4NIO_4 catalytic system for confirming the enhanced catalytic activity of Mn-BSMP.

The results are summarized in Table 1. It is notable that the yield and time of reactions are function of the electronic property of the carboxylic acids. Generally, aryl-substituted acetic acids (especially with electron withdrawing groups in their phenyl rings) were more reactive than the less electron rich carboxylic acids and those of containing electron donating groups in their aryl rings. Furthermore, there is no overoxidation of the produced aldehydes was taken place by Mn-BSMP/*n*-Bu_4NIO_4-Im catalytic system (Table 1).

CONCLUSIONS

In summary, we have introduced manganese(III)-bis(salicylaldehyde)-4-mthyl-1,2-phenylenediimine (Mn-BSMP) as an inexpensive N_2O_2 type Schiff base catalyst for oxidative decarboxylation of carboxylic acids in the presence of *n*-Bu_4NIO_4 as a mild and efficient oxidizing agent. Use of Fe-BSMP instead of Mn-BSMP gave lower yield, indicating the inferior catalytic activity of the former. We found that rate and yield for the decarboxylations were significantly affected by the nature of the metal and electronic property of the carboxylic acids and improved by using imidazole as co-catalyst. It is important to note that no overoxidation of the produced aldehydes was achieved under these catalytic conditions.

Aknowledgements

The financial support of this work by Yasouj University Research Councils is acknowledged.

Received : Feb. 8, 2010 ; Accepted : Jan. 24, 2011

REFERENCES

[1] Breslow R., Dong S.D., Biomimetic Reactions Catalyzed by Cyclodextrins and Their Derivatives, *Chem. Rev.* **98**, p.1997 (1998).

[2] (a) Mohajer D., Karimipour G., Bagherzadeh M., Reactivity Studies of Biomimetic Catalytic Epoxidation of Alkenes with Tetrabutylammonium Periodate in the Presence of Various Manganese Porphyrins and Nitrogen Donors: Significant Axial Ligand π-Bonding Effects, *New. J. Chem*., **28,** p. 740 (2004);
(b) Meunier B., Metalloporphyrins as Versatile Catalysts for Oxidation Reactions and Oxidative DNA cleavage, *Chem. Rev*., **92**, p. 1411 (1992);
(c) Kimura T., Kanota N., Matsui K., Tanaka I., Tsuboi T., Takaguchi Y., Yomogita A., Wakahara T., Kuwahara S., Nagatsugi F. Akasaka,T., Preparation and Electrochemical and Optical Properties of Unsymmetrically Substituted Phthalocyanines with One or Two Trithiole Rings and Related Symmetric Derivatives, *Inorg. Chem.*, **47**, p. 3577 (2008).

[3] Doyle M.P., Forbes D.C., Recent Advances in Asymmetric Catalytic Metal Carbene Transformations, *Chem. Rev.,* **98,** p. 911 (1998).

[4] (a) Gomes, M. F. T.; Antunes, O. A. C., Oxidation of α- and β-pinene catalyzed by Mn^{III}(Salen)Cl·H_2O, *Catal. Lett.,* **42**, p. 213 (1996);
(b) Gomes, M. F. T. Antunes, O.A. C., Oxidation of limonene catalyzed by Mn^{III}(Salen)Cl.H_2O, *Catal. Lett.,* **38**, p. 133 (1996.

[5] Karimipour G., Montazerozohoori M, Karami B., Efficient Biomimetic Decarboxylation of Diphenylacetic Acid by [Mn(TPP)X]*n*-Bu_4NIO_4 Catalytic Systems: Effect of Anionic Axial Ligands (X^-), *J. Chem. Res*., **9**, p. 605 (2006).

[6] Karimipour G., Karami B., Montazerozohori M., Zakavi S., Oxidative Decarboxylation of Carboxylic Acids with Tetrabutylammonium Periodate Catalyzed by Manganese (III) *Meso*-Tetraarylporphyrins: Effect of Metals, *Meso*-Substituents, and Anionic Axial Ligands, *Chin. J. Catal*., **28**, p. 940 (2007).

[7] Montazerozohori M., Nasr-esfahani M., Akhlaghi P., Catalytic Oxidative Decarboxylation of Some Benzylcarboxylic Acid Derivative by a New Iron(III) Schiff Base Complex, *Chin. J. Chem*., p. 1007 (2009).

[8] Ortiz de Montellano P.R., Hydrocarbon Hydroxylation by Cytochrome P450 Enzymes, *Chem. Rev.,* **110***,* p. 932 (2010).

[9] Agarwal R.K., Prasad S., Gahlot N., Synthesis Spectral and Thermal Properties of Some Penta-Coordinated Complexes of Oxovanadium(IV) Derived from Thiosemicarbazones of 4-Aminoantipyrine, *Turk. J. Chem*., **28**, p. 691 (2004).

[10] Webster F.X., Silverstein R.M., “Spectrophotometer Identification of Organic Compounds”, 6th ed., John Wiley, New York, **87** (1992).

[11] Nakomoto K., “Infrared and Raman Spectroscopy of Inorganic and Coordination Compounds”, 3rd ed., Wiley Interscience, New York (1978).

[12] Seifert F., Ciszak E., Korotchkina L., Golbik R., Spinka M., Dominiak P., Sidhu S., Brauer J., Patel M.S., Tittmann K., Phosphorylation of Serine 264 Impedes Active Site Accessibility in the E1 Component of the Human Pyruvate Dehydrogenase Multienzyme Complex, *Biochemistry*, **46**, p. 6277 (2007).

[13] Luo W., Yao X., Hong M., Large Structure Rearrangement of Colicin Ia Channel Domain after Membrane Binding from 2D ^{13}C Spin Diffusion NMR, *J. Am. Chem. Soc.*, **127**, p. 6402 (2005).

[14] (a) Komuro M., Nagatsu Y., Higuchi T., Hirobe M., Oxidative Decarboxylation of Carboxylic Acids by Iron Porphyrin - Iodosylbenzene System**,** *Tetrahedron Lett*., **33**, p. 4949 (1992);

(b) Komuro M., Higuchi T., Hirobe M., Application of Chemical Cytochrome P-450 Model Systems to Studies on Drug Metabolism. VIII. Novel Metabolism of Carboxylic Acids via Oxidative Decarboxylation, *Bioorg. Med. Chem*., **3**, p. 55 (1995).

[15] (a) Moghadam M., Tangestaninejad S., Mirkhani V., Mohammadpoor-baltork I., Sirjanian N., Parand P., Moghadam M., Tangestaninejad S., Mirkhani V., Mohammadpoor-Baltork I., Sirjanian N., Parand S., Polystyrene-Bound Mn(T_4PyP): A Highly Efficient and Reusable Catalyst for Biomimetic Oxidative Decarboxylation of Carboxylic Acids with Sodium Periodate , *Bioorg. Med. Chem*., **17**, p. 3394 (2009);

(b) Mirkhani V., Tangestaninejad S., Moghadam M., Moghbel M., Rapid and Efficient Oxidative Decarboxylation o Carboxylic Acid with Sodium Periodate Catalyzedvby Manganese (III) Schiff base Complexes, *Bioorg. Med. Chem*., **12**, p. 903 (2004);

(c) Mirkhani V., Tangestaninejad S., Moghadam M., Karami Z., Efficient Oxidative Decarboxylation of Carboxylic Acids with sodium Periodate Catalysted by Supported Manganese(Ш) Porphyrin, *Bioorg. Med. Chem*. Lett., **13**, p. 3433 (2003);

(d) Bond J.Q., Martin A.D., West R.M., Dumesic J.A., γ-Valerolactone Ring-Opening and Decarboxylation over SiO_2/Al_2O_3 in the Presence of Water, *Langmuir*, **26**, p.16291 (2010).

[16] Ohno T., Suzuki N., Dokoh T., Urano Y., Kikuchi K., Hirobe M., Higuchi T., Nagano T., Remarkable Axial Thiolate Lligand Effect on the Oxidation of Hydrocarbons by Active Intermediate of Iron Porphyrin and Cytochrome P450, *J. Inorg. Biochem.,* **82**, p. 123 and references cited therein (2000).

[17] Archer R.D., Chen H., Synthesis, Characterization, and Luminescence of Europium(III) Schiff Base Complexes, *Inorg. Chem*., **37**, p. 2089 (1998).