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Efficient Oxidative Decarboxylation of Carboxylic Acids with Sodium Periodate Catalyzed by Supported Manganese(III) Porphyrin

Valiollah Mirkhani,^{a,*} Shahram Tangestaninejad,^a Majid Moghadam^b and Zohreh Karimian^a

> ^aDepartment of Chemistry, Isfahan University, Isfahan 81744, Iran ^bDepartment of Chemistry, Yasouj University, Yasouj 75914-353, Iran

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Abstract—Oxidative decarboxylation of carboxylic acids by a supported manganese (III) porphyrin was investigated. In the chemical system using 5,10,15,20-tetrakis(4-aminophenyl)porphyrinatomanganese (III) chloride supported on crosslinked chloromethylated polystyrene, [Mn(H₂NTPP)-CMP], as catalyst, carboxylic acids are converted to the corresponding carbonyl compounds via oxidative decarboxylation with sodium periodate. © 2003 Elsevier Ltd. All rights reserved.

Introduction

Many hydrocarbon oxidation systems mimicking cytochrome P-450 dependent mono-oxygenases using iron and manganese porphyrins as catalysts and various oxygen atom donors such as PhIO, ClO⁻, H₂O₂ or IO₄⁻ have been reported.^{1–5} High yields and rates have been obtained with these biomimetic systems making them useful for complete conversion of various substrates and potentially useful preparative oxidations in organic chemistry. However, difficulty of recovery and instability are two major drawbacks of these expensive catalysts. These limitations have prevented practical application of metalloporphyrin catalysts in synthesis. One way to prepare commercial metalloporphyrin catalysts is to immobilize them onto insoluble supports. Such immobilization can improve the catalyst stability and show other advantages with respect to recovery and reuse.⁶⁻⁹

Recently, we have reported the use of supported manganese (III) porphyrin/periodate systems in epoxidation of alkenes and hydroxylation of alkanes.^{10–15} In our interest in the oxidative decarboxylation of carboxylic acids,^{16,17} in this paper we report the use of [Mn(H₂NTPP)-CMP]/periodate system for oxidative decarboxylation of carboxylic acids in 1:1 CH₃CN/H₂O mixture.

This heterogeneous catalyst exhibits a high activity and stability in the oxidative decarboxylation of carboxylic acids with $NaIO_4$ in the presence of imidazole as axial ligand (Scheme 1).

Results and Discussion

1) Oxidative decarboxylation of carboxylic acids with sodium periodate catalyzed by $[Mn(H_2NTPP)-CMP]$

The ability of this supported manganese(III) porphyrin as catalyst in the oxidative decarboxylation of aryl carboxylic acids initially investigated with 2-phenylbutyric acid in the presence of sodium periodate. Among the 1:1

$$\frac{R}{R'}C-COOH \xrightarrow{[Mn(NH_2TPP)-CMP] / NalO_4}{Imidazole / CH_3CN / H_2O, RT} \xrightarrow{R}{R'}C-OH + \begin{bmatrix} R\\ R'\\ R'' \end{bmatrix} + CO_2$$

in the case of R''=H

Scheme 1.

^{*}Corresponding author. Tel.: +98-9133-108960; fax: +98-7412-223048; e-mail: moghadamm@mail.yu.ac.ir

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mixture of methanol, ethanol, acetone, and acetonitrile with water, the 1:1 acetonitrile/water mixture was chosen as solvent, in which higher carbonyl yield was observed. The effect of different axial ligands upon the oxidation rate decreased in the order:

Table 1. Oxidative decarboxylation of $\alpha\text{-aryl}$ carboxylic acids by $[Mn(H_2NTPP)\text{-}CMP]/NaIO_4$

Run	Substrate	Product	Time(h)	Yield ^a (%)
1	PhCH ₂ COOH	Ketone	3	90
2	Ph CHCOOH Ph	Ketone	3	94
3	Ph CHCOOH H ₃ C	Ketone	3	93
4	Ph CHCOOH H ₅ C ₂	Ketone	3	93
5	Ph CCOOH Ph H OH	Ketone	2	95
6	CI-CH ₂ COOH	Ketone	4	91
7	CI	Ketone	4	90
8	СН ₃ О-СН ₂ СООН	Ketone	2.5	93
9	но-СН2СООН	Ketone	2.5	90
10	COOH	Ketone	5	91
11	СН2СООН	Ketone	6	89
12	СООН	Alcohol	5	83
13	CH ₂ COOH	Ketone	8	77
14	CH ₃ O CH ₃ O CH ₂ COOH CH ₂ COOH	Ketone	8	80
15	$\begin{array}{c} H_3C \\ H_1C \\ H_2C \\ H_3C \\ H \end{array} \xrightarrow{\begin{tabular}{c}} CH_3 \\ H_1C \\ H \\ H_3C \\ H \\ \end{tabular}$	Ketone	6	94

imidazole >4-t-butylpyridine >4-methylpyridine >2methylpyridine > pyridine. Control experiments showed that in the absence of imidazole, this catalytic system is less efficient in the oxidative decarboxylation of carboxylic acids. The optimum conditions used for the oxidation of 2-phenylbutyric acid with this heterogenized system, was catalyst, oxidant, imidazole and substrate in a molar ratio of 0.025: 2: 0.2: 1, respectively.

The results which are summarized in Table 1 show that this catalytic system can be applied to decarboxylation of a wide range of aryl substituted acetic acids in good yields at room temperature. It was found that the principal product was carbonyl derivative (except for 1-Naphthoic acid) and only small amount of the alcohol derivative was obtained. This is due to the oxidation of alcohols to carbonyl compounds by metalloporphyrinoxidant system.¹⁸

Room temperature oxidative decarboxylation of antiinflammatory drugs such as Indomethacin and Ibuprofen (Run 14,15) afforded corresponding carbonyl derivatives as the major products in 80 and 94% yields, respectively. Such oxidative decarboxylation pathway has been also observed during drug metabolism in vivo.^{19,20}

Comparison of this heterogeneous system with previously reported homogeneous systems^{16,17} showed that in this heterogeneous system the yields are higher than that of homogeneous system, whereas the reaction times are longer.

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

Even though the reaction mechanism is interesting, at the present time it is obscure to us, and we have not been able to assign any reasonable mechanism in our studies.

Catalyst reuse and stability

The stability of $[Mn(H_2NTPP)-CMP]$ was studied in repeated oxidative decarboxylation reactions. The oxidation of diphenylacetic acid was chosen as a model substrate for studying of catalyst reuse and stability. The reaction was carried out as described above. At the end of the reaction, the catalyst was removed by filtration and washed with water and acetonitrile and

Table 2. The results of $[Mn(H_2NTPP)-CMP]$ catalyst recovery and the manganese leached in the decarboxylation of diphenylacetic acid with sodium periodate

Run	Conversion (%) ^a	Mn leached (%) ^b	Time (h)
1	94	1	3
2	92	0.7	3
3	90	0.5	3
4	90	0	3

^aGLC yield based on starting diphenylacetic acid.

^bMeasured by atomic absorption spectrometry and based on initial manganese concentration.

^aIsolated yields.

reused. The dried catalyst was consecutively reused four times. After the use of catalyst for four consecutive times, the carbonyl yield was 90%. The amount of leached Mn (1.2%) was determined by atomic absorption spectrometry (Table 2).

Experimental

The porphyrin ligand, 5,10,15,20-tetrakis-(4-aminophenyl) porphyrin, was prepared and metalated according to the literature procedures.^{21,22} Carboxylic acids were obtained from Merck or Fluka and were passed through a column containing active alumina to remove peroxidic impurities.

Preparation of polystyrene-bound manganese (III)5,10,15,20-tetrakis-(4-aminophenyl) porphyrin

A 2.0 g of chloromethylated polystyrene crosslinked with 2% divinylbenzene (Merck) was suspended in 100 mL DMF and 1.67 g (2.48 mmol) manganese (III) 5,10,15,20-tetrakis-(4-aminophenyl)porphyrin and 5 mL triethylamine was added. The mixture was refluxed for 72 h in the dark under N₂ atmosphere while stirring magnetically and then cooled to room temperature. The dark green colored resin was suction filtered, washed thoroughly with DMF, methanol and acetone, respectively, and dried under vacuum at room temperature for 24 h. Elemental analysis (Mn) showed that the supported catalyst contained about 15.4% (w/w) of covalently bound manganese porphyrin.

General procedure for oxidative decarboxylation of α aryl substituted carboxylic acids. A 25 mL flask was charged with carboxylic acid (1 mmole), polystyrenebound manganese porphyrin (150 mg), imidazole (0.2 mmol) and CH₃CN (10 mL). After addition of sodium periodate solution (2 mmole in 10 mL H₂O), the mixture was stirred magnetically at room temperature for 2–8 h. Progress of the reaction was followed by TLC. After the reaction was completed, the polymer beads were filtered off and the filtrates were extracted with CH₂Cl₂ and were purified by silica gel plate or silica gel column (eluent: CCl₄–Et₂O). The identities of products were confirmed by IR and ¹H NMR spectral data.

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