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Mild and efficient oxidation of alcohols with sodium periodate catalyzed by polystyrene-bound Mn(III)porphyrin

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Abstract—Mild and efficient oxidation of primary and secondary alcohols with sodium periodate catalyzed by Mn(TPyP), [manganese(III)tetra(4-pyridyl)porphyrin], supported on chloromethylated polystyrene, [Mn(TPyP)-CMP], at room temperature were reported. This catalyst can be reused consecutively four times in the oxidation of 4-chlorobenzyl alcohol in 97% yield without significant loss of its activity.

1. Introduction

The development of an efficient model of systems mimicking the activity of cytochrome P-450 has been one of the areas of most intense research activity.[1] Many metalloporphyrin complexes, mainly iron and manganese, proved to be able to catalyze oxidation reactions with single oxygen atom donors such as $PhIO$, ClO^-, H_2O_2 or IO_4^-.[2–7] 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 anchor them onto solid supports. The possibility of recovery and recycling these expensive catalysts has positive effects from the economical and environmental points of view. Further benefit is the ease of product isolation and purification.

Recently, we have reported the use of supported manganese(III)porphyrin/periodate systems in epoxidation of
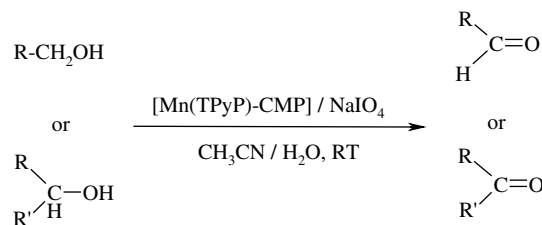
Scheme 1.

alkenes, hydroxylation of alkanes, oxidative decarboxylation of carboxylic acids and oxidation of amines to azo compounds.[8–16] High catalytic activity of Mn(TPyP)-CMP in the alkene epoxidation and alkane hydroxylation[16] prompted us to explore the potential of this catalyst in the oxidation of alcohols with sodium periodate in 1:1 CH_3CN/H_2O mixture at room temperature (Scheme 1).

2. Results and discussion

2.1. Oxidation of alcohols with sodium periodate catalyzed by MnTPyP-CMP

We first investigated the ability of this supported manganese(III)porphyrin as catalyst in the oxidation of 4-chlorobenzyl alcohol in the presence of sodium periodate. Among the 1:1 mixture of methanol, ethanol,

Table 1. Effect of solvent on the oxidation of 4-chlorobenzyl alcohol with Mn(III)porphyrin/NaIO$_4$ system

Entry	Solvent	Time (min)	Yield (%)[a]
1	CH$_3$CN/H$_2$O	45	100
2	CH$_3$COCH$_3$/H$_2$O	45	77
3	CH$_3$OH/H$_2$O	45	21
4	CH$_3$CH$_2$OH/H$_2$O	45	17
5	CHCl$_3$/H$_2$O	45	6
6	CCl$_4$/H$_2$O	45	4

[a] GC yields.

Table 2. The effect of different axial ligands on the oxidation of 4-chlorobenzyl alcohol with Mn(III)porphyrin/NaIO$_4$ system

Entry	Axial base	Time (min)	Yield (%)[a]
1	Imidazole	45	100
2	1-Methylimidazole	45	90
3	4-*t*-Butyl pyridine	45	34
4	Pyridine	45	15
5	No axial base	45	7

[a] GC yields.

acetone and acetonitrile with water (single-phase systems), chloroform and carbontetrachloride (two phase systems with Bu$_4$NBr as phase transfer catalyst), the 1:1 acetonitrile/water mixture was chosen as the solvent in which higher carbonyl yield was observed (Table 1). The manganese porphyrin is not an efficient catalyst

for oxidation of alcohols without adding imidazole as axial ligand because imidazole coordinates to Mn and activates the catalyst. The effect of different axial ligands upon the oxidation rate of 4-chlorobenzyl alcohol was also investigated. The results showed that the imidazole is the best (Table 2). The optimum condition used for the oxidation of 4-chlorobenzyl alcohol with this heterogenized system, was catalyst, oxidant, imidazole and substrate in a molar ratio of 1:100:10:50. During the course of oxidation, the reaction solution remained colorless and there was no evidence for leaching of the catalyst from polymeric support into solution. This fact was also investigated by examining the UV–vis spectrum of the filtered reaction mixture.

This heterogeneous catalyst can be applied to a wide variety of primary and secondary alcohols. As shown in Table 3, benzyl alcohol and substituted benzyl alcohols are converted to their corresponding aldehydes efficiently. In the case of benzyl alcohol, after 45 min, only benzaldehyde was obtained in 90% yield. In longer reaction times (1 h), the obtained products are 63% benzaldehyde and 35% benzoic acid. The results show that the substituents have no significant effect on the oxidation of benzylic alcohols. In the case of linear alcohols such as *n*-octanol, the resulted products are 17% octanal and 51% octanoic acid. A good selectivity observed in the case of cinnamyl alcohol and only alcoholic group is oxidized and no epoxide yield was obtained.

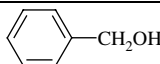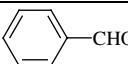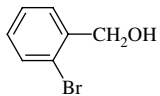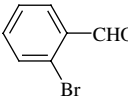**Table 3.** Oxidation of alcohols with NaIO$_4$ catalyzed by MnTPyP-CMP at room temperature
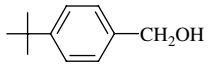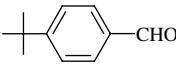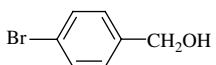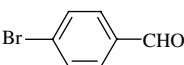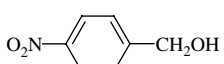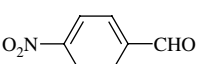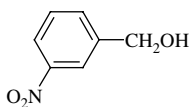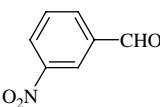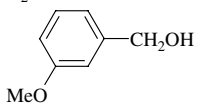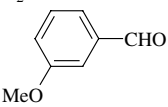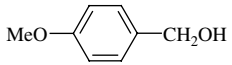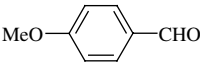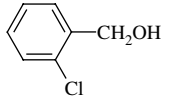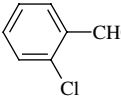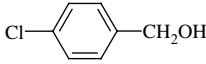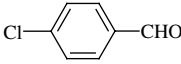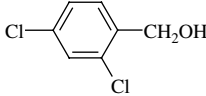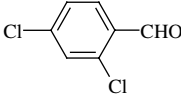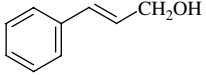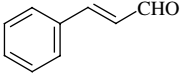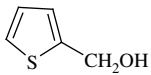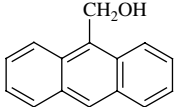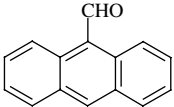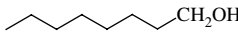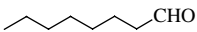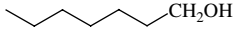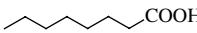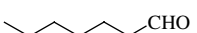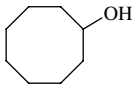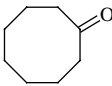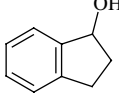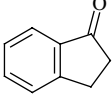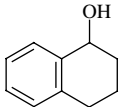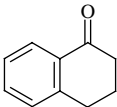
Entry	Alcohol	Product (%)	Yield (%)[a]	Time (min)
1	(phenyl)—CH$_2$OH	(phenyl)—CHO	90	45
2	(2-Br-phenyl)—CH$_2$OH	(2-Br-phenyl)—CHO	100	70
3	(4-*t*-Bu-phenyl)—CH$_2$OH	(4-*t*-Bu-phenyl)—CHO	100	70
4	Br—(phenyl)—CH$_2$OH	Br—(phenyl)—CHO	100	45
5	O$_2$N—(phenyl)—CH$_2$OH	O$_2$N—(phenyl)—CHO	100	45
6	(3-O$_2$N-phenyl)—CH$_2$OH	(3-O$_2$N-phenyl)—CHO	96	60
7	(3-MeO-phenyl)—CH$_2$OH	(3-MeO-phenyl)—CHO	92	60
8	MeO—(phenyl)—CH$_2$OH	MeO—(phenyl)—CHO	100	30
9	(2-Cl-phenyl)—CH$_2$OH	(2-Cl-phenyl)—CHO	94	90

Table 3 (*continued*)

Entry	Alcohol	Product (%)	Yield (%)[a]	Time (min)
10	Cl—C₆H₄—CH₂OH	Cl—C₆H₄—CHO	100	45
11	(2,4-dichlorobenzyl) CH₂OH	(2,4-dichlorobenzyl) CHO	80	90
12	C₆H₅—CH=CH—CH₂OH	C₆H₅—CH=CH—CHO	91	90
13	thiophene-2-CH₂OH	thiophene-2-CHO	75	70
14	anthracene-9-CH₂OH	anthracene-9-CHO	70[b]	60
15	heptyl-CH₂OH	heptyl-CHO	17	150
		heptyl-COOH	51	
16	hexyl-CH₂OH	hexyl-CHO	10	150
		hexyl-COOH	50	
17	cyclohexanol (OH)	cyclohexanone (O)	70	110
18	cycloheptanol (OH)	cycloheptanone (O)	67	120
19	cyclooctanol (OH)	cyclooctanone (O)	68	120
20	1-indanol (OH)	1-indanone (O)	71	120
21	1-tetralol (OH)	1-tetralone (O)	81	90

[a] GLC yield based on starting alcohol.
[b] Isolated yield.

Polystyrene-bound tetra (4-pyridyl)porphyrinato manganese(III) was also used for oxidation of secondary alcohols and their corresponding ketones were obtained in good yields.

2.2. Catalyst reuse and stability

The stability of the supported catalyst was monitored using multiple sequential oxidation of 4-chlorobenzyl alcohol with sodium periodate. For each of the repeated reactions, the catalyst was recovered, washed exhaus- tively with water, methanol, acetonitrile and diethyl ether, respectively, and dried before being used with fresh 4-chlorobenzyl alcohol and sodium periodate. The catalyst was consecutively reused four times without a detectable catalyst leaching or a significant loss of its activity (Table 4).

This polystyrene-bound Mn–porphyrin can be used as a robust, reusable and active heterogeneous catalyst in the oxidation of primary and secondary alcohols with sodium periodate.

Table 4. The results of [Mn(TPyP)-CMP] catalyst recovery and the manganese leached in the oxidation of 4-chlorobenzyl alcohol with sodium periodate

Run	Conversion (%)[a]	Mn leached (%)
1	100	0
2	100	0
3	98	0
4	97	0

[a] GLC yield based on starting alcohol.

Blank experiments in the absence catalyst or in the absence of $NaIO_4$ showed that only negligible amounts of oxidation products were detected.

3. Experimental

All materials were commercial reagent grade. Alcohols were obtained from Merck or Fluka. All of these tetra(4-pyridyl)porphyrin was metalated and supported according to the literature procedure.[16,17]

Reactions were quantified by GLC (Shimadzu 16 A) using a 3 m Silicon DC-200 packed column with a FID detector using decane as internal standard.

3.1. Typical procedure for oxidation of alcohols with $NaIO_4$ catalyzed by MnTPyP-CMP

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 $NaIO_4$ (2 mmol) in H_2O (10 mL) was added to a mixture of alcohol (1 mmol), MnTPyP-CMP (20 μmol) and imidazole (0.2 mmol) in CH_3CN (10 mL). The progress of reaction was monitored by GLC. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and filtered. The resin was thoroughly washed with CH_2Cl_2 and combined washings and filtrates were purified on silica-gel plates or silica-gel column. IR and ^1H NMR spectral data confirmed the identities of the products.

3.2. Catalyst reuse and stability

The stability of MnTPyP-CMP was studied in repeated oxidation reactions. The oxidation of 4-chlorobenzyl alcohol 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 reaction, the catalyst was removed by filtration, washed with water and acetonitrile and reused. After the use of catalyst for four consecutive times, the aldehyde yield was 97%. No manganese was detectable in the filtrates by atomic absorption spectrometry.

4. Conclusions

In this paper we have demonstrated the utility of Mn(TPyP)-CMP catalyst in the oxidation of primary and secondary alcohols to carbonyl compounds with $NaIO_4$. This catalytic system has some advantageous over the previous reported systems[18–21] such as: (i) mild reaction conditions (room temperature); (ii) simple preparation of the catalyst from commercially available materials (porphyrin and polystyrene resin) and it seems binding of porphyrin pyridyl groups to polystyrene resin is a good method to model the microenvironment of active centre of cytochrome P-450; (iii) nontoxicity of the catalyst; (iv) the use of supported metalloporphyrins provides an easy way to recover and recycle the catalyst from the reaction media and (v) the catalytic activity of this catalyst in the oxidation of secondary alcohols has been found to be higher compared with corresponding non-supported manganese(III)porphyrin.[22]

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