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Oxidative cleavage of alkenes catalyzed by a water/organic soluble manganese porphyrin complex

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Abstract—Tetrakis(4-hydroxyphenyl)porphyrin [TPP–$(OH)_4$] was modified with poly(ethylene glycol) chain as four side arms, such that this compound is soluble in both organic and water solutions. Complexation of this porphyrin with manganese metal ions resulted in the formation of MnCl–TPP–$(PEO_{750})_4$. This complex proved to be an excellent catalyst for the oxidative cleavage of C=C bonds, yielding the corresponding carbonyl compounds with sodium periodate as an oxidant. Mechanistic pathway for this cleavage is discussed.

1. Introduction

Metalloporphyrin species exist ubiquitously in nature and have found a broad spectrum of applications. Amongst, for example, the modeling of cytochrome P-450 for oxygenation of hydrocarbons has received much attention over decades.[1–24] As for the chemical reaction, great efforts have been made to develop new metalloporphyrin-based catalytic systems for the oxidation process, aiming at a higher degree of chemo- and stereoselectivities as well as efficiency under mild conditions.[1–5] In this context, epoxidation and hydroxylation of alkenes catalyzed by metal porphyrin complexes have been a major focus.[6–24]

Recently, porphyrin–Fe and porphyrin–Mn complexes and their corresponding oxo species,[15–17] heterogeneously supported manganese porphyrins[18–20] and poly(ethylene glycol) (PEO) side-chain manganese porphyrins[21] have been widely used as catalysts for either epoxidation or hydroxylation of alkenes under ambient temperatures. However, to our knowledge, there is no precedence concerning the use of manganese porphyrin complexes in the catalytic cleavage of C=C bonds.[22,23] To obtain aldehydes from olefins that are not fully substituted, two common methods are ozonization of olefins followed by a reductive workup and oxidative cleavage with osmium tetraoxide–sodium periodate, both of which, however, required stringent reaction conditions.[22,23] For the safety concern, chemists have been developing alternative methods for the cleavage of C=C, especially on the basis of catalytic approach.[23] Herein we report the preparation of a water/organic soluble metal porphyrin complex MnCl–TPP–$(PEO_{750})_4$, and its high-catalytic activity for the oxidative cleavage of alkenes, resulting in the corresponding carbonyl compounds.

2. Results and discussion

Preparation of MnCl–TPP–$(PEO_{750})_4$ is depicted in Scheme 1. Incorporation of PEO side chain was achieved by direct alkylation of [TPP–$(OH)_4$] with $CH_3(OCH_2CH_2)_{16}OTs$ in 88% yield. ^1H NMR spectra of TPP–$(PEO_{750})_4$ showed characteristic shifts at 8.82 (8H) for the pyrrole methine protons and a singlet at 2.79 ppm for the NH protons in the pyrrole unit. In addition, the integration ratio of ethylene protons for $-OCH_2CH_2-$ versus pyrrole methine protons confirmed the tetraalkylation on the porphyrin moiety. Treatment of TPP–$(PEO_{750})_4$ with $MnCl_2$ under basic conditions afforded the desired complex in 93% yield. Characterization of this complex was performed via UV–vis and elemental analysis. The characteristics UV–vis spectrum of MnCl–TPP–$(PEO_{750})_4$ in CH_2Cl_2 is similar to that of MnCl–TPP, proving the formation of manganese complex.[21,25] This complex is soluble in water as well as in most organic solvents, and its UV–vis spectrum in water is essentially identical to that in dichloromethane.

To examine the catalytic activity, oxidation of alkenes with oxidants over the prepared metal complex was investigated (Table 1). The oxidation reaction of styrene, in the presence of MnCl–TPP–$(PEO_{750})_4$ as the catalyst, was first studied under air or H_2O_2. In this reaction, however, trace of benzaldehyde was obtained as the product even with the addition of imidazole, which acted as an axial ligand for the metal

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Keywords: Oxidative cleavage; Porphyrin; Manganese; Olefin.

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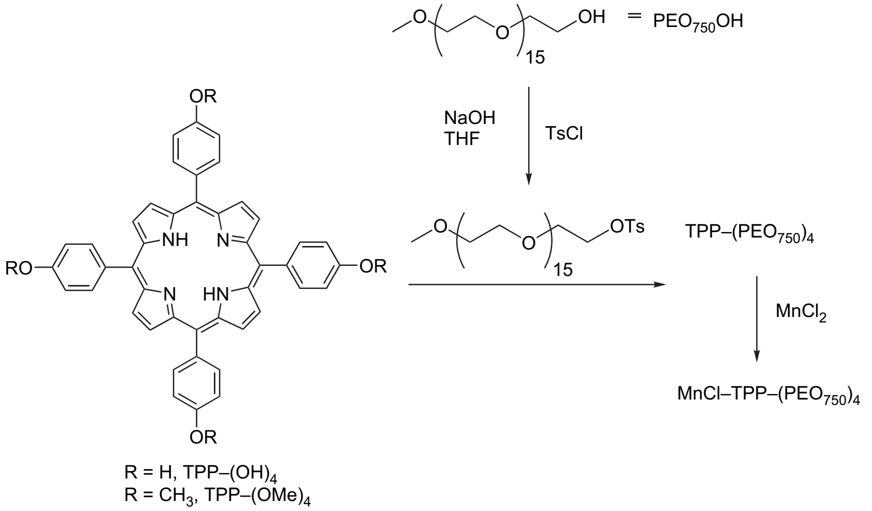

Scheme 1. Preparation of the manganese porphyrin complex.

complex.[26] Alternatively, using sodium periodate as the oxidant in CH_2Cl_2/H_2O (1:1 v/v), a similar catalytic reaction at room temperature revealed better conversion efficiency of turning styrene into a mixture of benzaldehdye and phenylacetaldehyde (see Table 1, entry 1). It is believed that the production of phenylacetaldehyde is mainly via the epoxidation of styrene, followed by the isomerization.[11] Furthermore, as shown in entry 2, the selectivity of the reaction improved significantly by using acetonitrile/water (2:1 v/v) as solvent. For elevating temperatures (see entries 3 and 4), benzaldehyde became the exclusive product under similar conditions.

In view of the above results, the manganese catalytic system with $NaIO_4$ and imidazole in acetonitrile/water rendered the best yield for oxidative cleavage of olefins and was followed in the following studies. Subsequently, various alkenes were tested under this catalytic system and the results are summarized in Table 1. Except for simple 1-alkenes, olefinic substrates underwent the oxidative cleavage to give the corresponding carbonyl compounds in excellent isolated yields. For the phenyl-disubstituted alkene such as 1-diphenylethene, benzophenone (ketones) was observed to be the major product (entry 6). Oxidative cleavage of cycloalkenes proceeded smoothly at room temperature to give the

Table 1. Catalytic oxidation of various alkenes catalyzed by MnCl–TPP–$(PEO_{750})_4$[a]

Entry	Substrate	Cat.[b]	$NaIO_4$[b]	Imidazole[b]	Temp[c]	Product	Yield[d] (%)
1	Styrene (in CH_2Cl_2/water)	0.003	2.5	1.0	rt	PhCHO, $PhCH_2CHO$	44, 30
2	Styrene	0.003	1.5	1.0	rt	PhCHO, styrene oxide	51, 11
3	Styrene	0.003	4.0	1.0	60	PhCHO	66
4	Styrene	0.003	4.0	1.0	80	PhCHO	97
5	m-$ClC_6H_4CH{=}CH_2$	0.003	4.0	1.0	80	m-ClC_6H_4CHO	96
6	1,1-Diphenylethene	0.01	7.0	3.0	80	Benzophenone	99
7	1-Methylstyrene	0.003	4.0	1.0	rt	Acetophenone	99
8	*trans*-Stilbene	0.01	7.0	3.0	80	PhCHO	87
9	2-Vinylpyridine	0.01	7.0	3.0	80	2-Vinylpyridineoxide, 2-Pyridinecarbaldehyde	70, 25
10	Cyclohexene	0.0013	3.0	0.5	rt	1,6-Hexanedial	97
11	Styrene oxide	0.0013	3.0	0.5	rt	PhCHO	99
12	Cyclohexene oxide	0.0013	3.0	0.5	rt	1,6-Hexanedial	96
13	Cyclopentene	0.0013	3.0	0.5	rt	1,5-Pentanedial	99
14	Cyclooctene	0.01	4.0	0.5	rt	1,8-Octanedial	65
15	Benzyl alcohol	0.03	7.0	3.0	80	PhCHO	60
16	Diphenylacetylene	0.01	7.0	3.0	80	—	—
17	1-Phenylcyclohexene	0.01	4.0	0.5	rt	6-Phenyl-6-oxohexanal	77
18	Tartaric acid	0.01	4.0	1.0	rt	—	—
19	Norbornylene	0.01	7.0	1.0	rt	Cyclopentane-1,3-dicarbaldehyde	33
20	(±)-Limonene	0.01	3.0	1.0	rt	(+)-4-Methyl-3-(3-oxobutyl)-4-pentenal	89
21	α-Pinene	0.01	4.0	1.0	rt	(3-Acetyl-2,2-dimethylcyclobutyl)-acetaldehyde	44
22[e]	Styrene	0.003	4.0	1.0	80	PhCHO	97

[a] Reaction conditions: substrate (1 mmol) in CH_3CN (2 ml)/H_2O (1 ml) for 24 h.

[b] In mmol.

[c] Oil bath temperature in °C.

[d] Isolated yield, except entries 1 and 2 by NMR integration.

[e] Under nitrogen atmosphere.