

EPOXIDATION OF OLEFINS WITH TETRA *n*-BUTYL-AMMONIUM PERIODATE IN THE PRESENCE OF TETRAKIS (4-SUBSTITUTED PHENYL) PORPHYRINATO-MANGANESE (III) ACETATES AND IMIDAZOLE

Mohajer, Daryoush* and Bagherzadeh, Mojtaba

Department of Chemistry, Shiraz University, Zip code 71454, Shiraz, I. R. Iran

ABSTRACT: *The epoxidation of olefins with tetra n-butylammonium periodate, n-Bu₄NIO₄, is catalyzed by six different tetrakis (4-substituted phenyl) porphyrinatomanganese(III) acetate, Mn(T4-XPP)OAc, complexes in the presence of imidazole as an axial ligand with low to high yields and complete selectivity at room temperature. While the electronic effects of the highly electron-withdrawing NO₂ substituents are clearly reflected in the reduction of epoxidation yields, other substituents, i.e MeO, Me, Cl, and Br, do not significantly modify epoxide yields relative to Mn(TPP)OAc and give very similar results.*

KEY WORDS: *Epoxidation, Tetra n-butylammonium periodate, Manganese porphyrins, Catalyses.*

Cytochrome P-450 dependent monooxygenases catalyze the reductive activation of dioxygen by NADPH and the insertion of one oxygen atom into organic compounds [1]. Metalloporphyrins have been used as epoxidation and hydroxylation catalysts, in an attempt to mimic the behaviour of cytochrome P-450, with some degree of success [2]. These biomimetic oxidation reactions were carried out by various single oxygen donors such as iodosylarenes [3-7], peracids [8-9], alkylhydroperoxides [10-12], hydrogen peroxide [13-15], hypochlorites [16-19], amineoxides [20-21],

periodates [22-25], perchlorate [22], oxaziridines [26] and monopersulfate [27-28].

This article is concerned with the use of various [Mn(T4-XPP)OAc] (X=H, MeO, Me, Cl, Br, NO₂) (Fig. 1) catalysts with tetra n-butylammonium periodate, n-Bu₄NIO₄, as a source of oxygen for epoxidation of olefins in the presence of imidazole in a single phase, CH₂Cl₂, at room temperature.

The oxidation reactions were performed in a 5 mL round bottomed flask equipped with stopper and magnetic stirrer. Solid n-Bu₄NIO₄ (1 mmol) was

* To whom correspondence should be addressed.

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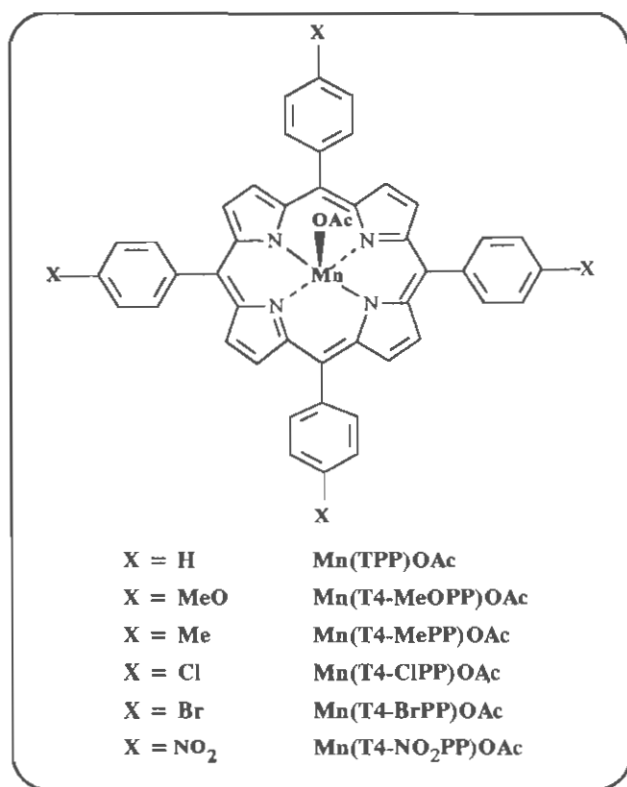


Fig. 1

added to a solution of olefin (0.5 mmol), catalyst (0.006 mmol) and imidazole (0.06 mmol) in methylene chloride (2 mL) under air at room temperature. The solution was stirred vigorously at a constant speed for the required time. Magnetic stirrer was stopped before each aliquot (2 μ L) was withdrawn from the reaction mixture and products were determined by gas liquid chromatography.

In order to find the optimum condition for epoxidation reaction, various molar ratios of Mn-porphyrins, $n\text{-Bu}_4\text{NIO}_4$, imidazole and olefins were examined [33]. The best molar ratio for catalyst : imidazole : olefin : $n\text{-Bu}_4\text{NIO}_4$, was found to be 1 : 10 : 83.3 : 166.6.

The results of epoxidation reaction of some olefins catalyzed by Mn(TPP)OAc are shown in Table 1. No oxidation of the allylic C-H bond leading to alcohols and ketones has been detected. In order to determine the relative reactivities of terminal and internal olefins, we performed epoxidations of oct-1-ene, hep-1-ene, and *cis*-hex-2-ene, as substrates. As the results in Table 1 show in the oxidation of the mono-substi-

tuted terminal olefins and the di-substituted *cis*-hex-2-ene, electronic effect is the dominant factor and the latter shows much greater reactivity. On the other hand, the relative reactivities of cyclohexene and 1-methylcyclohexene with two and three substitutions on double bond, respectively, reflect the importance of steric effects, and the less hindered cyclohexene shows higher reactivity. Furthermore, the greater activity of *cis*-stilbene compared to that of *trans*-stilbene toward oxidation, is another reflection of the importance of steric factors in these reactions. It appears that the rather bulky phenyl groups in the *trans* isomer greatly restricts its approach to the active oxidizing Mn-center.

Table 1 also shows that epoxidation of *trans*-stilbene oxide is a stereospecific process, and only gives the *trans*-stilbene oxide. However, epoxidation of *cis*-stilbene leads to a mixture of *cis*- and *trans*-stilbene oxides, which may imply the occurrence of an olefin derived

Table 1: Epoxidation of various olefins with $n\text{-Bu}_4\text{NIO}_4$ catalyzed by Mn(TPP)OAc / imidazole system in CH_2Cl_2 .^a

Substrate	Conversion % ^b	Epoxide yield % ^b
Cyclooctene	99	99(92) ^c
Cyclohexene	90	90
1-Methylcyclohexene	76	76
Styrene	78	78
α -Methylstyrene	94	94(87) ^c
Norbornene	85	85
(+)-Comphen	40	40
Hep-1-ene	23	23
Oct-1-ene	14	14
<i>cis</i> -Hex-2-ene	77	77
<i>cis</i> -Stilbene	79	64 ^d (15) ^c
<i>trans</i> -Stilbene	23	23 ^e

- a) All reactions were performed at ambient temperature for 5 h, the molar ratios are given in the experimental section.
 b) Conversions and yields are based on the starting olefins.
 c) Isolated yield
 d) *cis*-Stilbene oxide
 e) *trans*-Stilbene oxide

Table 2: Epoxidation of various olefins by $n\text{-Bu}_4\text{NIO}_4$ catalyzed by meso-tetrakis (4-substituted phenyl) porphyrin manganese (III) acetate/imidazole systems^a

Mn(III)(Porph)OAc	Cyclooctene oxide yield %	Cyclohexene oxide yield %	Styrene oxide yield %	α -Methyl styrene oxide yield %	(+)-Comphen oxide yield %	Oct-1-ene oxide yield %
Mn(TPP)OAc	99	75	78	94	40	14
Mn(T4-MePP)OAc	94	67	72	94	31	11
Mn(T4-MeOPP)OAc	93	67	71	97	22	8
Mn(T4-ClPP)OAc	94	71	82	95	36	11
Mn(T4-BrPP)OAc	91	74	83	95	35	9
Mn(T4-NO ₂ PP)OAc	71	37	60	87	25	7

a) All reactions are carried out at room temperature for 5 h. the molar ratio of compounds is given in the text.

Yields are based on the starting olefins.

carbon radical intermediate species [34]. Free rotation around the C-C could lead to the formation of the more stable *trans*-epoxide isomer.

To test the electronic effects of the phenyl groups in oxygenation reactions, six different tetra *para*-substituted tetraphenylporphyrinato manganese (III) acetate and Mn(TPP)OAc complexes, with very similar steric environment at the active metal center, were used as catalysts in epoxidation of olefins by $n\text{-Bu}_4\text{NIO}_4$ in the presence of imidazole. Results of epoxidations are illustrated in Table 2. In general, substitution of the *para*-H of the phenyl groups of the porphyrin ring by electron-releasing methoxy, and methyl groups and by moderate electron-withdrawing chlorine, and bromine groups does not significantly change the epoxidation yields. Whereas the strong electron-withdrawing substituent, nitro group, reduces the activity of the catalyst. As the *para*-phenyl substituents are relatively far from the active metal center, their electronic effects are very weakly reflected in the catalytic processes. However, for nitro groups with very strong σ - and π -acceptor ability and with great influence upon the porphyrin ring, epoxidation is greatly diminished.

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