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Effect of Bulky Substitution on Catalytic Activity of a Manganese Salen Complex Used in Biomimetic Alkene Epoxidation and Alkane Hydroxylation with Sodium Periodate

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The catalytic activity of Mn(salen)Cl containing *tert*-pentyl groups at the 3,5-positions of the salen ligand in the epoxidation of alkenes and hydroxylation of alkanes was studied at room temperature, using sodium periodate as an oxygen source. The effects of various axial ligands were investigated in the epoxidation of cyclooctene. Imidazole, as a strong π-donor ligand, was the best axial ligand. The effect of different solvents was studied in the epoxidation of cyclooctene in CH_3CN/H_2O solvent mixture. The epoxidation reactions of cyclooctene by different oxygen donors including $NaIO_4$, Bu_4NIO_4, $KHSO_5$, H_2O_2, H_2O_2/urea, NaOCl and *tert*-BuOOH were also studied and $NaIO_4$ was selected as oxygen source. The presence of bulky substituents in the 3,5-positions of the salen ligand was found to increase the catalytic activity of this complex.

Keywords: Manganese salen, Epoxidation, Hydroxylation, Periodate, Bulky substituents.

INTRODUCTION

Transition metal Schiff base complexes have been used to mimic the action of cytochrome P-450 in the oxidation of organic compounds, such as hydrocarbons [1]. P-450 enzymes are known to oxidize a very extensive range of endogenous and exogenous organic compounds, from medium chain alkanes including *n*-heptane and *n*-octane, to steroidal and polyaromatic compounds, as well as very large molecules such as the triterpenes and cyclosporine [2,3]. As key steps in biosynthesis, cellular biochemistry, and metabolism, these reactions are vital in biological systems and are, therefore, very important in the fields of pharmacology and medicine. The Mn(III) salen complexes have attracted much attention in the last few decades because these complexes can catalyze the transfer of oxygen atoms to organic substrates in the presence of different terminal oxidants such as hydrogen peroxide, iodosylbenzene, sodium hypochlorite and *tert*-butylhydroperoxide [4-12]. The nature of the obtained products in these reactions depends on various factors, such as type of axial ligand, counter-ion, substrate, oxidant, solvent and the structure of the salen ligand [13,14].

Selective activation of alkanes, especially under mild reaction conditions, is very difficult due to their chemical inertness. However, the transformation of hydrocarbons using metal-complex catalysts appears to have great potential [15,16]. More specifically, epoxidation of alkenes is one of the most common methods in organic synthesis, since, by highly regio- and stereoselective ring opening reactions, epoxide is readily transformed into a wide array of compounds, and direct oxygen transfer to alkenes is the most widespread means of producing epoxide [17,18].

Chiral Mn(III)-salen complexes are useful catalysts in the asymmetric epoxidation of unfunctionalized alkenes [19,20],

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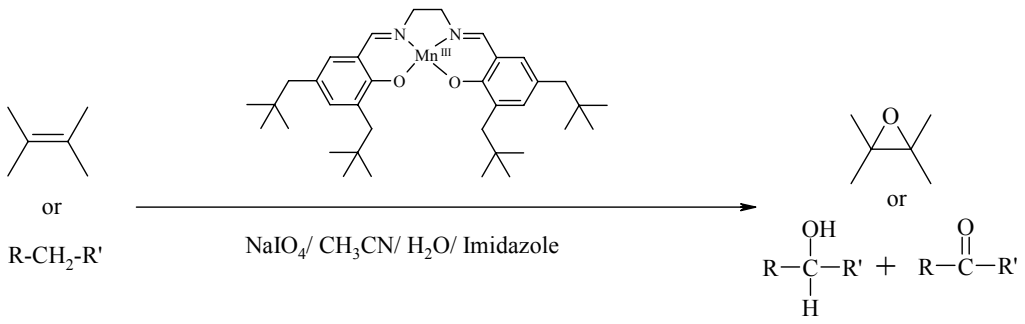


Scheme 1

as demonstrated in the production of biologically and pharmaceutically important compounds such as taxol (taxol side chain) and the calcium channel activator cromakalim [21,22]. Previous reports note that, the substituents on the 3,5-positions of the salen ligand might have direct effects on the electronic properties of manganese(III) salen complexes [23]. There are many reports on the application of catalysts containing the *tert*-butyl group as a unique directing group [24-28]. The *tert*-pentyl group is another simple substituent that is readily obtained from commercially-available inexpensive phenols. A few reports are available on the application of *tert*-pentyl-containing Schiff bases in catalysis [29,30]; however, there is no report on their application in the hydroxylation of alkanes.

In this report, we describe the rapid and efficient epoxidation of alkenes and hydroxylation of alkanes with sodium periodate in the presence of manganese(III) salen catalyst with *tert*-pentyl groups at the 3,5-positions of the salen ligand (Scheme 1).

EXPERIMENTAL

The Schiff base ligands were prepared by refluxing 1:2 molar ratios of the corresponding ethylenediamine and salicylaldehyde derivatives in ethanol as solvent and their purity was checked by ^{1}H NMR and IR spectroscopy [29,31]. The alkenes were purchased from Merck and passed through a column of neutral alumina just prior to use. The electronic absorption spectra were recorded on a Varian Cary NIR. Gas chromotography experiments were carried out with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or carbowax 20 M . FT-IR and ^{1}H NMR spectra were obtained using a Nicolet Impact 400D spectrometer in the range of 400-4000 cm^{-1} and a Bruker AQS 300 MHz, respectively.

Catalysis Experiments

The reactions were carried out at room temperature with constant stirring with a reaction medium composed of 0.5 mmol of alkene or alkane, 0.12 mmol of Mn(III) salen complex as catalyst, 1 mmol sodium periodate in H_2O (2.5 ml) and imidazole (0.14 mmol) in CH_3CN (5 ml).

The progress of the reactions was monitored by GC. At the end of the reaction, the final reaction products were extracted with CH_2Cl_2 and purified on silica gel (plate or column). The identities of the products were confirmed by IR and ^{1}H NMR spectral data. Blank experiments using the same experimental conditions in the absence of either the catalyst or the oxidant were also performed.

RESULTS AND DISCUSSION

Factors Affecting the Catalytic Epoxidation of Cyclooctene with Sodium Periodate

Selecting the oxygen donor, solvent and type of axial ligands in the epoxidation of alkenes catalyzed by these salen complexes is a critical decision.

Effect of terminal oxidant. In this study, we examined the epoxidation of cyclooctene catalyzed by Mn(salen)Cl with *tert*-pentyl groups at the 3,5-positions of the salen ligand by different oxidants including NaOCl, $NaIO_4$, Bu_4NIO_4, H_2O_2, $KHSO_5$, *t*-BuOOH, urea-H_2O_2 (UHP). As shown in Table 1, NaOCl, H_2O_2, *tert*-butylhydroperoxide and urea-H_2O_2 (UHP), in either acetonitrile or dichloromethane, were less efficient

Table 1. Effect of Various Oxidants on the Epoxidation of Cyclooctene Catalyzed by Mn(salen)Cl with *tert*-Pentyl Groups

Oxidant	Solvent	Epoxide yield after 15 min (%)[a]
$NaIO_4$	CH_3CN/H_2O	98
Oxone ($KHSO_5$)	CH_3CN/H_2O	90
H_2O_2	CH_3CN	81
H_2O_2/urea	CH_3CN	34
NaOCl	CH_3CN	79
t-BuOOH	CH_3CN	29
Bu_4NIO_4	CH_3CN	49

[a]GLC yields based on the starting cyclooctene.

Table 2. Effect of Solvent on the $NaIO_4$ Epoxidation of Cyclooctene Catalyzed by Mn(salen)Cl with *tert*-Pentyl Groups

Row	Solvent	Yield after 15 min (%)[a]
1	CH_3CN/H_2O	98
2	CH_3COCH_3/H_2O	73
3	CH_2Cl_2/H_2O	47
4	CH_3OH/H_2O	61
5	CH_3CH_2OH/H_2O	59
6	$CHCl_3/H_2O$	41
7	CCl_4/H_2O	18

[a]GLC yields based on the starting cyclooctene.

oxidizers of cyclooctene. Although $KHSO_5$, a strong, inexpensive and versatile oxidizing agent used in metalloporphyrin-catalyzed oxidations [32], resulted in a good yield in this study, it has some disadvantages. To neutralize its acidity, $KHSO_5$ buffer is needed; however, this can lead to the degradation of the catalyst during the oxidation reactions. In addition, at low pH, the reagent can cause environmental problems. Thus, sodium periodate was selected as the best oxygen source for the following advantages: (i) good oxidation conversion, (ii) inert in the absence of a catalyst and (iii) readily soluble in CH_3CN/H_2O.

Effect of solvent. The epoxidation of cyclooctene was studied in various solvents at room temperature. As is obvious from Table 2, among the binary mixtures of water with methanol, ethanol, acetone and acetonitrile (single phase systems) and with chloroform, dichloromethane and carbon tetrachloride (two phase systems, with Bu_4NBr as a phase transfer catalyst), the 2:1 mixture of acetonitrile/water was chosen as the best reaction medium for its higher epoxidation yield.

Effect of axial ligands. The reactivity of salen catalysts in the epoxidation reactions are not only tuned by substitution of the salen, but also by the addition of donor ligands to the reaction mixture [33,34]. To better understand the role of axial ligands in the activation of the Mn(salen)Cl catalyst, we investigated the effect of different axial ligands upon the

Table 3. The Effect of Different Axial Ligands in the Epoxidation of Cyclooctene by Mn(salen)Cl/$NaIO_4$[a]

Entry	Axial ligand	Epoxide yield after 15 min (%)[b]
1	None	14
2	Triethylamine	31
3	Diethylamine	34
4	Piperidine	49
5	Pyridine	38
6	4-Cyanopyridine	26
7	2-Methylpyridine	44
8	4-Methylpyridine	56
9	4-*tert*-Butylpyridine	81
10	Imidazole	98
11	4(5)-Methylimidazole	91
12	2-Ethylimidazole	82
13	Benzimidazole	96
14	2-Methylimidazole	89
15	Pyrazine	75
16	Quinoline	34
17	Morpholine	41
18	Triphenylphosphineoxide	31
19	DMF	19

[a]Cyclooctene (0.5 mmol), $NaIO_4$ (1 mmol), axial ligand (0.14 mmol) and catalyst (0.12 mmol) in CH_3CN (5 ml)/H_2O (2.5 ml); b) GLC yields based on the starting cyclooctene.

epoxidation of cyclooctene (Table 3).

As seen in Table 3, pure σ-donor amines, with very large pK_b values, are relatively poor co-catalysts in the epoxidation of cyclooctene. Pyridine and methyl-substituted pyridines have weak π-donating abilities and, with pK_b values much smaller than those of σ-donor amines, generally show co-catalytic activities similar to those of amines. The observed order of co-catalytic activities is 4-*tert*-butylpyridine > pyridine >> 4-cyanopyridine, which seems to be directly related to both the σ- and π-donating abilities of these nitrogen donors. Electron-withdrawing substituents, such as CN^-, essentially display no co-catalytic activity. However, substituted pyridines with electron-releasing methyl groups, such as 4-*tert*-butylpyridine, showed 81% conversion in the oxidation of cyclooctene; this is higher than that observed for the unsubstituted pyridine. The addition of Ph_3PO and DMF as donor ligands has no significant effect on the epoxide yield.

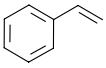
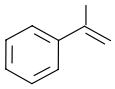
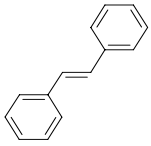
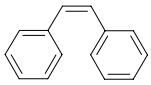
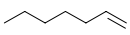
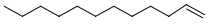
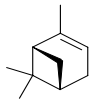
Obviously, among the employed nitrogen bases as axial ligands, imidazoles, which are strong π-donors, display the highest co-catalytic activity in the epoxidation of cyclooctene with sodium periodate. It should be noted that the lower co-catalytic activity of 2-MeImH and 2-EtImH or 4(5)-MeImH are due to the steric properties of the 2-substituent. Bulky and flat BzImH displays co-catalytic activity similar to imidazole.

In fact, the strong coordination of imidazole is expected to increase in the electron density on the central metal and cleave the O-IO_3 bond in $NaIO_4$. However, in the absence of any axial ligand, the amount of cyclooctene oxide was low (14%).

Catalytic Alkene Epoxidation with Sodium Periodate

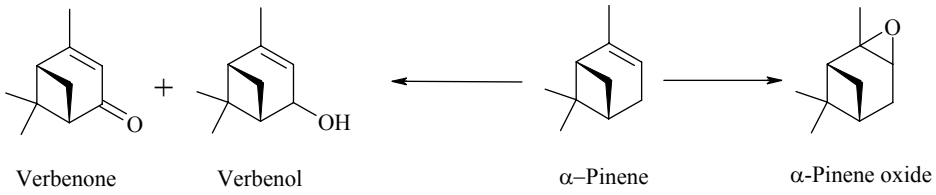
The catalytic alkene epoxidation with sodium periodate in the presence of Mn(salen)Cl with *tert*-pentyl groups at the 3,5-

Table 4. Epoxidation of Alkenes by $NaIO_4$ Catalyzed by Mn(salen)Cl with *tert*-Pentyl Groups *vs*. that by Unsubstituted Mn(salen)Cl in the Presence of Imidazole at Room Temperature

Entry	Alkene	Conversion (%)[a]		Epoxide yield (%)[a]		Time (min)
		Substituted	Unsubstituted	Substituted	Unsubstituted	
1		98	58	98	58	15
2		100	59	91[b]	51[b]	15
3		98	49	93[c]	41[c]	15
4		100	61	95[d]	55[d]	15
5		96	52	96	52	15
6		81	36	81 (*trans*-Epoxide)[e]	36 (*trans*-Epoxide)[e]	15
7		93	46	73 (*cis*-Epoxide)[e] 20 (*trans*-Epoxide)[e]	29 (*cis*-Epoxide)[e] 17 (*trans*-Epoxide)[e]	15
8		89	21	89	21	20
9		56	8	56	8	20
10		98	55	93[f]	49[f]	15

[a]GLC yield based on starting alkene. [b]The by-product is cyclohex-1-one. [c]The by-product is benzaldehyde. [d]The by product is acetophenone. [e]Both ^1H NMR and GLC data approved the reported yields. [f]The by-products are 4% verbenone and 1% verbenol for substituted and 3% verbenone and 3% verbenol for unsubstituted.

positions of the salen ligand was performed at room temperature under air in CH_3CN/H_2O solution. This catalytic system led to the epoxidation of various alkenes in high yields (56-100%), as shown in Table 4. Cyclooctene was oxidized to cyclooctene oxide in 98% yield took 15 min at room temperature. In the oxidation of cyclohexene 91% cyclohexene oxide and 9% cyclohex-1-one were produced. Benzaldehyde and acetophenone were detected as by-products



Scheme 2

in the oxidation of styrene and α-methylstyrene, respectively.

The epoxidation of *trans*-stilbene proceed in a stereospecific manner with complete retention of configuration. In contrast, the epoxidation of *cis*-stilbene is associated with some loss of stereochemistry, affording 73% *cis* and 20% *trans*-stilbene oxides. Evidently, this thermodynamically more stable *trans*-stilbene oxide requires a free rotation about the alkene C-C bond at some intermediate steps, which is more feasible using catalysts with less steric strain [35].

The linear, cyclic and phenyl substituted olefins were used as substrates in this system. As shown in Table 4, electron-rich cyclic olefins are more active than the electron–poor terminal olefins. This reflects the electrophilic nature of oxygen transfer from manganese–oxo intermediate to the olefinic double bond.

In the epoxidation of α-pinene, the major product was α-pinene oxide (93%) and verbenone and verbenol were produced through allylic oxidation as minor products (Scheme 2).

One of the interesting characteristics of salen-based ligands is that, by changing the corresponding diamines and salicylaldehyde ligand precursors, the ligands may be adjusted both sterically and electronically. Recent studies [36,37] have revealed that alterations in the electronic properties of the substituents at the 5,5'-positions of the catalyst can have a significant influence on the oxidation reaction. This can be quantified by evaluating the reduction potentials of metal-salen complexes with electron-donating and electron-withdrawing groups. Only the oxo(salen)chromium(V) ion is stable and can be characterized with certainty, whereas the oxo-metal ions of Mn, Fe and Ru are not. Interestingly, the reduction potentials of metal(III)-salen complexes and oxo(salen)chromium(V) complexes correlate well with the Hammett's σ constants [38]. Thus, we can evaluate the redox potentials by changing the substituent in the salen ligand in order to determine the reactivity of oxo(salen)metal ions. Furthermore, the presence of electron-donating substituents on the catalyst stabilizes the high valent metal-oxo intermediate, attenuating its reactivity to give a relatively milder oxidation.

Oxidation of Alkanes with Sodium Periodate Catalyzed by Mn(salen)Cl with *tert*-Pentyl Groups at the 3,5-Positions of the Salen Ligand

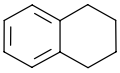
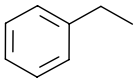
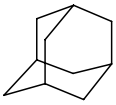
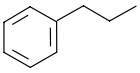
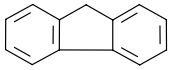
Another reaction of cytochrome P-450 is the direct oxidation of hydrocarbons [2]. High temperatures and pressures are usually necessary for direct functionalization of unactivated C-H bonds in saturated hydrocarbons, therefore, oxidation of alkanes using oxygen sources under mild conditions is a significant achievement. As shown in Table 5, the Mn(salen)Cl/IO_4^- catalytic system effectively catalyzes the biomimetic oxidation of saturated hydrocarbons.

In this catalytic system, cyclooctane, cyclohexane, 1,2,3,4-tetrahydronaphthalene and adamantane were converted to their corresponding alcohols and ketones in high yields. While in the oxidation of ethylbenzene, propylbenzene and fluorene only the corresponding ketones were obtained.

In addition, 1-adamantanol and 2-adamantanone were produced in the oxidation of adamantane [39]. In the oxidation of cyclooctane with molecular oxygen, we found that molecular oxygen is less efficient in the oxidization of cyclooctane (3%). On the other hand, the oxidation of alkanes under argon atmosphere confirmed the obtained data.

This *tert*-pentyl substituted catalyst showed higher activity than the unsubstituted Mn(III)-salen complex in the oxidation of alkenes and alkanes. Under the same reaction conditions, the oxidation of cyclooctene in the presence of unsubstituted Mn(III)-salen gave only 58% cyclooctene oxide. Oxidation of cyclooctane with $NaIO_4$ in the presence of unsubstituted catalyst produced 20% cyclooctanol and 9% cyclooctanone. While

Table 5. Hydroxylation of Alkanes with $NaIO_4$ Catalyzed by Mn(salen)Cl with *tert*-Pentyl Group *vs*. Unsubstituted Mn(salen)Cl in the Presence of Imidazole at Room Temperature

Entry	Alkane	Conversion (%)		Ketone (%)[a]		Alcohol (%)[a]		Time (min)
		Substituted	Unsubstituted	Substituted	Unsubstituted	Substituted	Unsubstituted	
1		67	29	36	20	31	9	40
2		61	18	54	13	7	5	40
3		87[b]	33[b]	87	33	-	-	40
4		43[c]	14[c]	43	14	-	-	40
5		76[d]	28[d]	11	5	65	13	40
6		46[e]	15[e]	46	15	-	-	40
7		67	24	67	24	-	-	40

[a]GLC yield based on the starting alkane. [b]Only α-position was oxidized. [c]The product is acetophenone. [d]The products are 1-adamantanol and 2-adamantanone. [e]The product is ethylphenyl ketone.

this catalytic system is highly active in the epoxidation of linear alkenes such as 1-hexene and 1-dodcene, xidation of these substrates with sodium periodate in the presence the unsubstituted Mn(salen)Cl catalyst led to poorer results (Tables 3 and 4). The higher activity observed with the *tert*-pentyl substituted catalyst is due to the production of more stable oxo-manganese(V) species than the unsubstituted salen complex. It is known that insertion of electron-donating substituents in the 5 position of the aldehyde fragment stabilizes the oxidized species of manganese(III) salen complexes, while introducing of electron-withdrawing groups in the same position destabilizes it. This process is expected to be functioning in the reactive intermediate species, as well [40].

Oxo-Manganese(V) Species as the Reactive Intermediate

Although, we have assumed the active manganese species to be reactive (salen)Mn(V)oxo intermediate, [(salen)Mn^{V}=O], by comparing the present spectral observation with the previous reports [41], we could not isolate this active species. It is pertinent to point out that to date no (salen)Mn(V)oxo species have yielded to structural characterization, although Groves *et al* and others have characterize oxo manganese (V) porphyrin complexes in recent years [42].

When a clear light brown solution of Mn(III)-salen in acetonitrile is treated with sodium periodate, it immediately turns dark. The appearance of a new absorption band (around 500 nm, Fig. 1) strongly resembles the spectral alteration

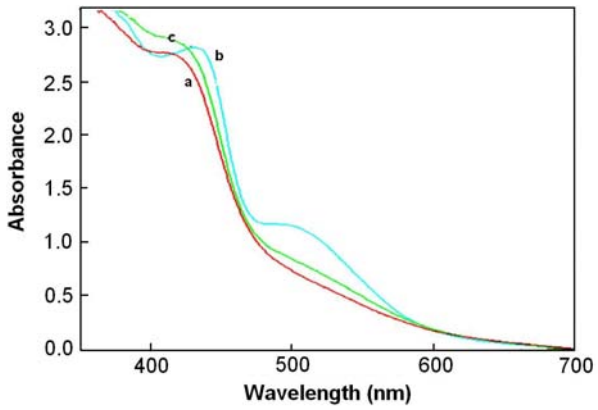


Fig. 1. a) Absorption spectrum of Mn(salen)Cl in CH_3CN (6.0×10^{-3} M) at 25 °C, b) after the addition of excess $NaIO_4$, and c) after the addition of cyclooctene.

obtained when the Mn(III)-salen cation is converted to its corresponding oxo-manganese(V) species. After 15 min, the dark brown solution reverts to the original light brown. However when this reaction occurs in the presence of cyclooctene, the dark brown solution immediately reverts to the original color.

CONCLUSIONS

We have demonstrated the catalytic effectiveness of Mn (III)-salen with *tert*-pentyl groups at the 3,5-positions of the salen ligand in olefin epoxidation and alkane hydroxylation with sodium periodate. Addition of imidazole, as an axial ligand with π-donor capability the highest catalytic activity was obtained. The catalytic activity of substituted Mn(salen) complex was higher than its unsubstituted Mn(III)-salen analogue.

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