Letter

# Influence of additional ligands on the two-phase epoxidation with sodium hypochlorite catalyzed by (salen)manganese(III) complexes

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## Abstract

The two-phase epoxidation of olefins with sodium hypochlorite catalyzed by the salen-type Mn(III) complex **1** was examined in the presence of various additional ligands and 4-dodecyloxypyridine 1-oxide (**3**) was found as the most effective one. The system **1–3** was studied by conductometry and UV–Vis spectra. The results support the hypothesis that the disproportionation of the dimeric $\mu$-oxo Mn(IV) complex producing an active oxidant is strongly favoured by the presence of **3**.

*Keywords*: Epoxidation; Hypochlorite; Lipophilic N-oxides; Olefins; Pyridine derivatives; Salen derivatives

## 1. Introduction

The catalyzed epoxidation of olefins has been a subject of intensive studies for the last two decades and sodium hypochlorite activated by metal complexes has been used there as an effective oxygen-donating agent [1]. Foremost, these reactions were promoted by manganese porphyrins [2], however, recently, the salen-type complexes of Mn(III) have become highly valuable catalysts for the regio- and enantioselective epoxidation of conjugated olefins [3–5]. Generally, the efficiency of catalytic system depends on the type of catalyst complex, the structure of olefin being oxidized, the state of equilibrium involving a stoichiometric oxidant, and the presence of additional,

axial ligand, which stabilizes metal–oxo species transferring an oxygen atom to olefin. An important role played by the axial ligand was clearly demonstrated in the porphyrin catalyzed epoxidations [2], but its use with the salen complexes was given only limited consideration. The donor ligands (pyridine, pyridine N-oxide, 4-(imidazol-1-yl)acetophenone) examined by Kochi et al. [3] had little effect on the yields of epoxides. Accordingly, an efficient catalytic system introduced by Jacobsen [4] did not use any additional ligand. However recently, Jacobsen at al. [5] have reported that in some cases the presence of sub-stoichiometric amount of 4-phenylpyridine N-oxide had a beneficial influence on the yield of epoxides. It was also noted that 2-alkylimidazoles were effective as donor ligands in the epoxidation using Mn(III)–salen type catalyst and iodosyl-

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benzene [6], hydrogen peroxide [7] or aerobic conditions [8] applied as terminal oxidants. These reports encouraged us to reveal the results of our studies on the influence of various additional ligands on the two-phase epoxidation with sodium hypochlorite catalyzed by Mn(III)–salen type complex.

## 2. Experimental

The ligand for **1** was prepared in ca 90% yield from di-*tert*-butylsalicylaldehyde and ethylenediamine. Mp. 55°C; $^1$H NMR (CDCl$_3$): 1.28 and 1.43 (ds, 36H, *t*-Bu–), 3.90 (s, 4H, –CH$_2$–), 7.06–7.38 (m, 4H, AB aromatic system), 8.38 (s, 2H, –CH=), 13.1 (br s, 2H, –OH); IR (KBr); 2964, 2872, 1630, 1482, 1476, 1468, 1362, 1272, 1254, 1042, 880. The ligand reacted with Mn(OAc)$_2$·4H$_2$O in abs. ethanol and the product was precipitated by adding solid LiCl. Thus obtained crude product was dissolved in methylene dichloride and recrystallized after addition of hexane. Yield 75%. IR (KBr): 2956, 1612, 1534, 1308, 1252, 1176, 836, 548; UV–Vis (CH$_2$Cl$_2$): 235(34300), 245(37900), 285(18500), 327(15000), 370(6600), 442(4160), 505(1720), 720(210), 820(125); Magnetic prop. (77–298 K): 4.82 $\mu_B$; Anal. Calcd for C$_{32}$H$_{46}$O$_2$N$_2$MnCl: C, 66.14%; H, 7.98%; N, 4.82%; Cl, 6.10%. Found: C, 66.21%; H, 8.02%; N, 4.82%; Cl, 6.10%.



**1**



(R,R)- **2**



**3**
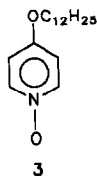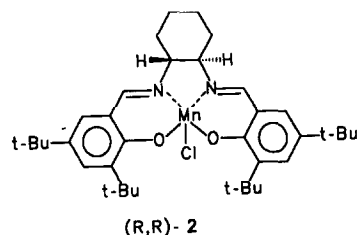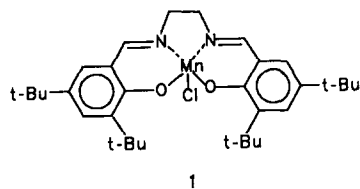
## 3. Results and discussion

The catalytic activity of the complex **1** an achiral analogue of the Jacobsen complex **2**, was examined in the two-phase oxidation of styrene in the absence and presence of various additional ligands and the results obtained are shown in Table 1. Thus, the addition of the proper axial ligand is obviously necessary for the catalytic epoxidation with the system used. Moreover, when 4 mol% of heterocyclic N-ligands (4-*tert*-butylpyridine, 4-dodecyloxypyridine, 1-methylimidazole or 1-decylimidazole) were applied, 80–85% of substrate was recovered and no epoxide was detected. Additionally, there was no essential change in the UV–Vis spectrum of **1** upon the addition of 250 equivalents of 4-dodecyloxypyridine. Nevertheless, when the corresponding N-oxide **3** [9] (250 equiv.) was subsequently added to this solution, the new coordination was clearly seen (Fig. 1). Also, the presence of 4-dodecyloxypyridine has no effect on the spectrum of **1**, when the solution was equilibrated with hypochlorite (see below). All these results demonstrate that **1** used with hypochlorite, unlike the porphyrin analogues [2], shows a strong preference towards the oxygen axial ligands over the nitrogen ones. 4-Dodecyloxypyridine N-oxide (**3**) was particularly effective and a comparison of the structures of the ligands indicates that both the σ-donating power and the lipophilicity contribute to the catalytic activity.

The effect of concentration of **3** on the outcome of the epoxidation under the standard conditions was investigated (Table 2). These results show that the system is effective even in a relatively low

Table 1
Epoxidation of styrene with sodium hypochlorite catalyzed by salen($Mn^{III}$) complex (1 mol%) and additional ligands (4 mol%) [a]

| Entry | Additional ligand | Recovered substrate % | Epoxide % | Carbonyl product % |
|---|---|---|---|---|
| 1 | none | 84 | 8.3 | 3 |
| 2 | pyridine 1-oxide | 82.5 | 9.5 | 4 |
| 3 | 4-ethoxypyridine 1-oxide | 63.5 | 19 | 7 |
| 4 | 4-benzylpyridine 1-oxide | 19 | 45 | 5 |
| 5 | 4-tert-butylpyridine 1-oxide | 2.6 | 85.5 | 6 |
| 6 | 4-phenylpyridine 1-oxide | no | 85.5 | 7 |
| 7 | 4-(1-butylpentyl)pyridine 1-oxide | no | 84 | 8 |
| 8 | 4-dodecyloxypyridine 1-oxide | no | 91 | 6 |

[a] General oxidation procedure: A solution of sodium hypochlorite (commercial bleach, ca 1.8 M NaOCl) was diluted with 0.05 M disodium phosphate to 0.55 M in NaOCl and the pH of the resulting solution was adjusted with 1 M NaOH to 11.3. This cooled solution (5 ml) was added to a solution of salen($Mn^{III}$) complex (1 mol%), additional ligand (4 mol%), tetrabutylammonium chloride (5 mol%) and the corresponding olefin (1 M) in 2 ml of methylene dichloride. The two-phase mixture was stirred magnetically at 0°C for 4 h. The brown organic phase was separated, washed twice with brine (2 ml), and dried over sodium sulfate. This solution was filtered through a short pad of Florisil, washed with methylene dichloride (4 ml). After removal of the solvent, the residue was analyzed by GC/MS and the structure of the product was confirmed by NMR and IR.
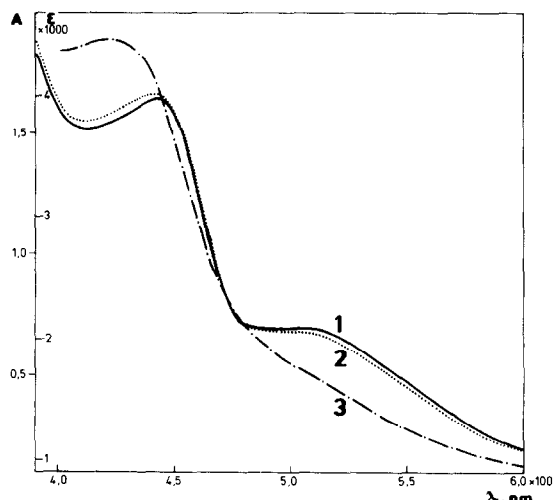


Fig. 1. Absorption spectrum for 1 (0.326 mM) in methylene dichloride (curve 1), in the presence of 4-dodecyloxypyridine (0.0815 M) (curve 2), in the presence of both 4-dodecyloxypyridine (0.0815 M) and 3 (0.0815 M) (curve 3).

3/1 molar ratio and, essentially there is no inhibitory effect up to the 100/1 ratio. On the other hand, amount of the rearranged carbonyl products[1] was substantially reduced when the ratio increased.

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[1] In the oxidation of styrene a mixture of phenylacetaldehyde and acetophenone in ca. 5:1 ratio was found as a by-product (3–9%), (Tables 1, 2 and 3). For α-methylstyrene, a mixture of α-phenylpropionaldehyde and acetophenone (4.5:1) resulted. In all other cases, the corresponding carbonyl by-products were the respective ketones (Table 4).

In order to gain some insight into a role played by the additional ligand, we studied the salen($Mn^{III}$) complex 1–ligand 3 system by conductometry (Table 3) and UV–Vis spectra (Fig. 2 and Fig. 3). Thus, the conductivity of 1 in methylene dichloride was very low, however it increased substantially with the addition of 3. Accordingly, a much less pronounced increase in conductivity was observed when the solution was saturated with water. It seems that both 3 and water replace a chloride ion from the coordination sphere of complex and the cationic manganese species are formed. This process is also reflected in the spectral changes, namely the 442 nm ($\varepsilon$ 4160) band is shifted to the shorter wavelength (Fig. 2). However, an intensity of the d–d band

Table 2
Epoxidation of styrene with sodium hypochlorite catalyzed by salen($Mn^{III}$) complex (1 mol%) and 4-dodecyloxypyridine 1-oxide

| Entry | 4-Dodecyloxypyridine 1-oxide mol% | Recovered substrate % | Epoxide % | Carbonyl product % |
|---|---|---|---|---|
| 1 | 0.00 | 84 | 8.3 | 3 |
| 2 | 0.50 | 30 | 55 | 9 |
| 3 | 1.0 | 12 | 73 | 7 |
| 4 | 4.0 | no | 91 | 6 |
| 5 | 25 | no | 92 | 5 |
| 6 | 100 | 2.4 | 92 | 3 |

Table 3
Conductivity of salen($Mn^{III}$) complex 1 in methylene dichloride [a]

| Entry | Substance added | Conductivity $10^8$ ohm$^{-1}$ cm$^{-1}$ |
|---|---|---|
| 1 | none | 0.189 |
| 2 | $H_2O$ | 2.84 |
| 3 | 3 (4:1) | 19.1 |
| 4 | 3 (25:1) | 99.2 |
| 5 | 3 (100:1) | 277 |
| 6 | NaOCl/$H_2O$ | 13.9 |
| 7 | NaOCl/$H_2O$ and 3 (4:1) | 234 |
| 8 | NaOCl/$H_2O$ and 3 (25:1) | 419 |
| 9 | NaOCl/$H_2O$ and 3 (100:1) | 637 |

[a] Conductance was measured with an RC automatic bridge E-315 (Meratronic, Poland) operating at 1 kHz and using 0.326 mM solution of 1 at 25°C. The readings were corrected for background conductance, e.g. for entry 8: a value of 118.8 $\mu$S was reduced by the conductance measured for a solution of 3 (8.172 mM) in methylene dichloride after it was equilibrated with 0.55 M NaOCl in water, (3.030 $\mu$S).

(ca. 505 nm, $\varepsilon$ 1720) decreased upon gradual addition of 3, may be due to the formation of a six-coordinating complex. The formation of the cationic species is strongly disfavoured by the low polarity of medium (methylene dichloride), and all these effects were observed for relatively high 3/1 ratio. When methylene dichloride saturated with water was used, conductivity for the same 3/1 ratio increased markedly. In addition to the formation of aqua complexes (a hypsochromic shift for the C–T band at 370 nm), we ascribe this rise in conductivity to the increase of medium polarity thus stabilizing ionic species. When 1 in methylene dichloride was equilibrated with an aqueous solution of sodium hypochlorite (0.55 M) at pH 11.3 at 0°C for 5 min both in the presence or absence of 3, substantial spectral changes were observed due to the oxidation of complex and formation of Mn(IV) species [10]. However, these spectral changes were highly dependent on the 3/1 ratio. Thus, in the absence of 3 the complex formed was relatively stable (Fig. 2) and its spectrum reflected the presence of Mn(IV) species only. For the ratio 3/1 equal to 25:1 the oxidized complex was destroyed much faster than in the previous case (Fig. 3). Moreover, spectral data for the later system provided evidence for the presence of Mn(III) species admixed to the

Mn(IV) complexes. The higher concentration of 3 resulted in the faster bleaching of the complexes, so for 3/1 equal to 100:1 this reaction was too fast for detection of the Mn(IV) complexes formed. On the other hand, if the system treated with hypochlorite was, in turn, reduced by the addition of sodium bisulfite, the initial spectrum was reproduced. Thus, tert-butyl-substituted salen-type complex 1 is essentially resistant toward degradation. This conclusion is in agreement with the number of turnovers observed in the catalytic epoxidation. The results support hypothesis [3,5] that when 1 is oxidized with hypochlorite, the dimeric $\mu$-oxo Mn(IV) complexes are mainly formed. These complexes can disproportionate quickly affording equimolar amounts of 1 and the $Mn^V$=O complex, which is actually an active oxidant. Our observations suggest that the state of this equilibrium depends strongly on the presence of an additional axial ligand. Therefore, in the absence of 3 the equilibrium is shifted to the nonionic $\mu$-oxo dimer (as observed from the conductivity, the spectra and the lack of catalysis), while the addition of 3 produces the cationic active oxi-
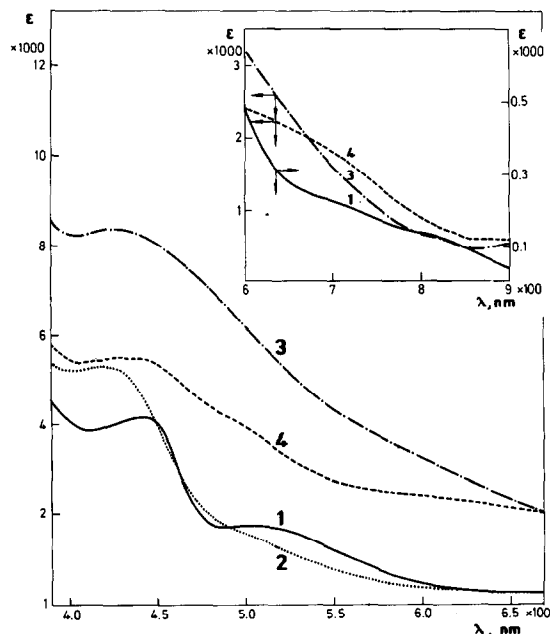


Fig. 2. Absorption spectrum for 1 (0.326 mM) in methylene dichloride (curve 1), in the presence of 3 (0.102 M) (curve 2), saturated with 0.55 M NaOCl in the absence of 3 (curve 3), and saturated with 0.55 M NaOCl in the presence of 3 (1.30 mM) (curve 4).
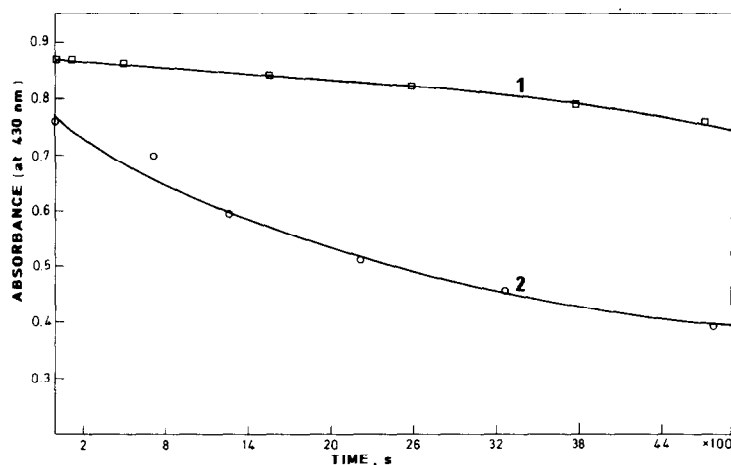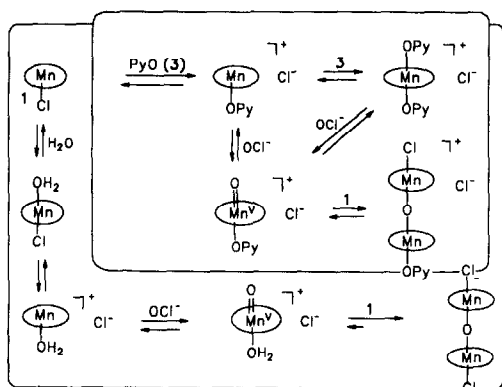
Fig. 3. Time dependence of absorption at 430 nm for **1** (0.326 mM) in methylene dichloride saturated with 0.55 M NaOCl in the absence of **3** (curve 1) and in the presence of **3** (8.16 mM) (curve 2).



Scheme 1.

dant (conductivity, catalysis or without olefin, self-oxidation). Also, the spectrally documented presence of the Mn(III) complexes in the oxidizing mixture confirms the key role played by **3** in the formation of active oxidant. The observed conductivity changes and spectral behavior of the system are in accord with the outcomes of epoxidation so in our opinion rather ionic, than nonionic [5], permanganyl species are responsible for the catalytic process (Scheme 1).

The results reported in Table 4 put some light on the scope and limitations of synthetic utility of the present catalytic system. Thus, electron-rich and sterically demanding olefins were oxidized smoothly to epoxides (entries 4 and 6). Also the exposed nonconjugated double bond was transformed easily into the epoxide function (entry 10). It is noteworthy that in all these cases the

olefins were oxidized completely and the corresponding epoxides were obtained in high yields. The oxidation of cis-stilbene in the presence of additional ligands (4-tert-butyl-, 4-phenyl- or 4-dodecyloxypyridine 1-oxide) led to the values of ratio of cis/trans epoxides in the range of 3.3–2.5, while in the absence of additives this ratio was

Table 4
Epoxides from olefins oxidized with sodium hypochlorite in the catalytic presence of salen(Mn$^{III}$) complex and 4-dodecyloxypyridine 1-oxide [a]

| Entry | Olefin | Recovered substrate % | Epoxide % | Carbonyl product % |
|---|---|---|---|---|
| 1 | styrene | no | 89 | 7 |
| 2 | styrene [b] | no | 94 | 5 |
| 3 | styrene [c] | 62 | 11 | 6 |
| 4 | α-methylstyrene | no | 94 | 6 |
| 5 | indene | no | 84 | 10 |
| 6 | trans-stilbene | no | 94 | 4 |
| 7 | cis-stilbene | no | 80 [d] | 3 |
| 8 | cyclohexene | no | 47 | no, (36) [e] |
| 9 | cyclooctene | no | 41 | 28 |
| 10 | norbornene | no | 95 | 4 |
| 11 | (+)-α-pinene | 60 | 19 | 9 |
| 12 | α-limonene | 73 | 8 | no, (12) [f] |
| 13 | 1-tetradecene | 82 | 8 | 5 |

[a] Reactions were run using 6.5 mol% of the complex (0°C, 6 h).
[b] Reaction carried out in the presence of 1 mol% of the complex.
[c] Reaction carried out in the presence of 0.2 mol% of the complex.
[d] Cis/trans mixture, 57 and 23%, respectively.
[e] The allylic oxidation products were obtained.
[f] p-Cymene was formed.

equal to 1.5. These results additionally support our conclusion concerning N-oxide complexation to the permanganyl species.

Electron-poor and/or sterically hindered olefins were much less susceptible to the reaction. The allylic products formed from cyclohexene as well as the aromatization of $\alpha$-limonene may be caused by the radical-like character of oxidizing species [11]. When the oxidation was carried out using the chiral catalyst **2** (6.5 mol%) and **3** (26 mol%), styrene gave 82% of ( + )-styrene oxide (32% ee) and 4% of aldehyde. In the case of *trans*-stilbene, the corresponding ( − )-epoxide in 89% (16% ee) and ketone (9%) were obtained. Thus, the presence of additional ligand does not improve enantioselectivity. This result is in full agreement with the proposed mode of action for the chiral catalyst and a similar observation has already been published [5].

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