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Oxygen transfer mechanism in the Mn-salen catalysed epoxidation of olefins

A. Méou, M.-A. Garcia, P. Brun *

Laboratoire de Synthèse Organique Sélective, associé au CNRS, GCOPL, Université de la Méditerranée, Faculté des Sciences de Luminy, 163 Avenue de Luminy, case 901, F-13288, Marseille, Cedex 9, France

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Abstract

The Mn-salen catalysed epoxidation of geraniol and nerol derivatives or similar non-conjugated olefins, with H_2O_2 as oxidant, was studied. Along with the epoxide, rearranged products were isolated and characterised. The formation of these compounds is a strong argument in favour of the formation of an oxametallacycle as an intermediate in these epoxidation reactions. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Epoxidation; Mn-salen complexes; Oxametallacycles

1. Introduction

The Mn-salen catalysed asymmetric epoxidation of olefins, mainly conjugated with an aromatic ring, has been extensively studied since 1990 [1–4]. Most of the published works deal with the influence of the substituents located on the aromatic rings of the ligand and the mechanism of the reaction [5,6].

The epoxidation process can be described by two concerted mechanisms (A and B) and two stepwise ones (C and D) which all involve an oxo-manganese species (Fig. 1) [7]. Similar mechanisms have also been postulated for iron-porphyrin epoxidation of alkenes [8].

We want to report here our results obtained in the epoxidation of trisubstituted, non-conjugated olefins. In these reactions, we have isolated by-products whose structures strongly indicate that, in this case, mechanism A is the most probable.

2. Experimental

2.1. Typical experiment

To a stirred solution of the olefin (1 mmol) and catalyst (0.023 mmol) in CH_3OH or CH_3CN (3 ml) was added dropwise 50% H_2O_2 (0.70 ml) at r.t. The reaction was monitored by TLC. When the consumption of the starting material

* Corresponding author.

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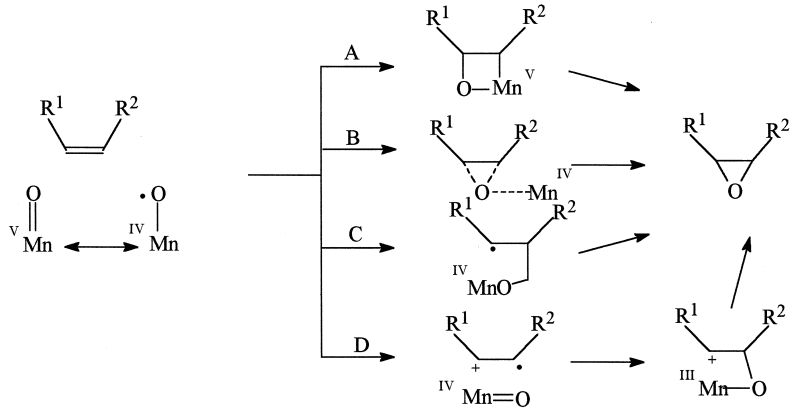


Fig. 1. Mechanistic pathways for the Mn-salen catalysed epoxidation reaction.

did not seem to increase any further (2–3 h), the reaction medium was treated with a 10% aqueous solution of sodium sulfite (5 ml) and extracted with Et_2O (3×5 ml). The organic phase was washed with H_2O (3×3 ml) then dried ($MgSO_4$). The products were isolated and purified by flash chromatography on silica gel (eluent: hexane/Et_2O from 96/4 to 80/20).

All the compounds described in this work have been fully characterised by their spectroscopic data (IR, ^1H and ^{13}C NMR) and by mass spectrometry.

3. Results

During our studies on the epoxidation of geraniol [9] and nerol derivatives catalysed by Mn-salen complexes **1** and **2** (Fig. 2) [6], using H_2O_2 as oxidant, we isolated, along with epoxides, two other products which were identified as a tertiary alcohol and a rearranged aldehyde. With complex **3** [6] no transformation at all was observed. Fig. 3 shows the results for the epoxidation of geraniol derivatives **4a–e**. The same results were obtained with other types of non-conjugated trisubstituted olefins (Figs. 4 and 5). All of the reactions described have been triplicated and the yields (based on starting olefin) of isolated products indicated are averages.

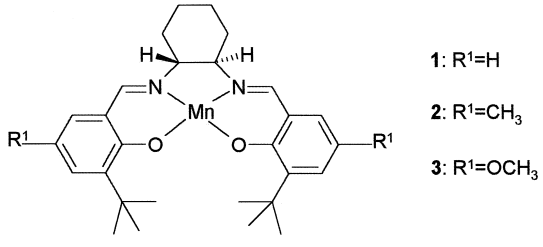
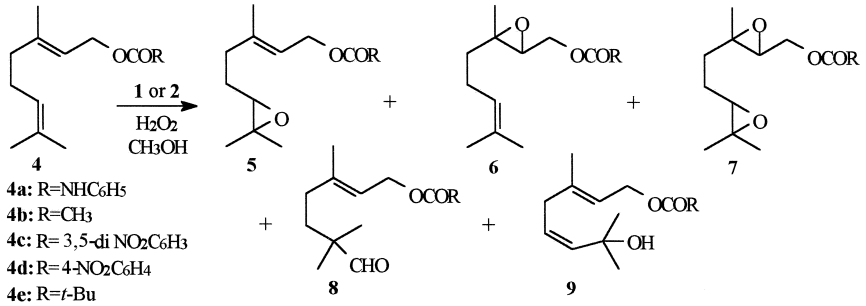


Fig. 2. Structure of the (−)-(1*R*, 2*R*)-Mn-salen complexes used [6].

As can be seen from inspection of Figs. 3–5, the results are almost similar for the different substrates used, except for geraniol acetate **4b** which gives lower yields of epoxide **5b** with the two complexes used. The same types of rearranged aldehyde and alcohol are always formed. It must be noted that the enantiomeric excesses are also similar (50–55%) in all the cases and that the major epoxides **5** and **11** have an (*S*) configuration [9].

4. Discussion

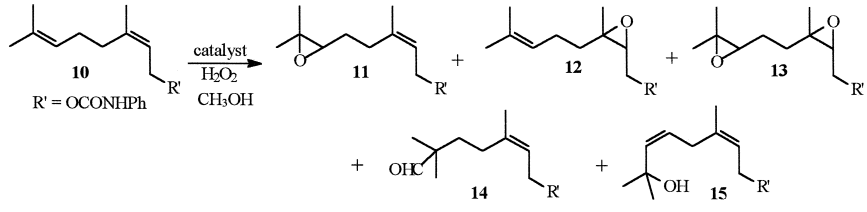
When conjugated olefins are used as substrates in this epoxidation reaction, the most probable mechanism is of the C type, involving the formation of a stabilised radical as an intermediate. This is supported by many results which show that isomerisation and/or typical rearrangements are observed when such radicals are formed [10–13]. With non-conjugated



Substrate	(-)-Mn-salen complex	epoxide **5** (%)	epoxide **6** (%)	diepoxide **7** (%)	aldehyde **8** (%)	alcohol **9** (%)
4a	**1**	55.0	2.5	7.9	3.0	9.0
	1[1]	53.6	3.0	7.9	3.0	9.0
"	**3**	no reaction				
4b	**1**	48.0	2.0	6.0	3.3	10.5
"	**2**	39.0	2.8	4.0	2.0	11.8
4c	**1**	58.0	3.5	9.0	3.5	7.2
4d	**1**	57.0	3.0	7.0	6.0	12.0
4e	**1**	54.6	1.5	2.0	2.0	12.0

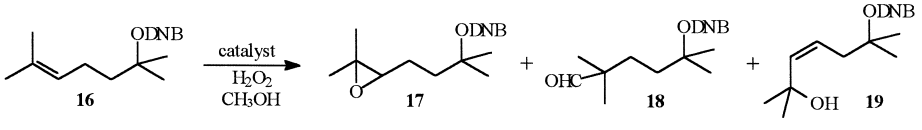
[1] reaction performed in acetonitrile.

Fig. 3. Epoxidation of various geraniol derivatives.



Substrate	(-)-Mn-salen complex	epoxide **11**	epoxide **12**	diepoxide **13**	aldehyde **14**	alcohol **15**
10	**1**	51.0	2.5	8.0	2.6	7.0

Fig. 4. Epoxidation of nerol *N*-phenylcarbamate.



Substrate	(-)-Mn-salen complex	epoxide **17**	aldehyde **18**	alcohol **19**
16	**1**	72.0	5.7	11.0

Fig. 5. Epoxidation of 2,6-dimethyl hept-5-en 2-yl-3,5-dinitrobenzoate.

olefins, the formation of a non-stabilised radical intermediate (path C) or of a radical cation (path D) has been ruled out, essentially by the results observed with vinylcyclopropane [7,14]: indeed this hypersensitive probe does not undergo any rearrangement in the reaction conditions. A radical species is thus not considered anymore as an intermediate in the epoxidation of non-conjugated olefins.

Between the two concerted mechanisms, type B can be excluded. Indeed when the epoxide **5** is reacted with Mn-salen complex **1** or **2** (in the presence of H_2O_2), in the standard reaction conditions, it remains unchanged. In these conditions, an intermediate as the one postulated in mechanism B should be formed: this has been demonstrated and the intermediate characterised in the case of ruthenium–porphyrin complexes [15].

For these Mn^{III}-Salen catalysed epoxidation reactions, a new proposal has been recently presented to explain the mechanism of oxygen transfer from the oxo–manganese complex to the olefin, namely the formation of an oxametallacycle. Such an approach has been proposed and supported on the basis of theoretical calculations [16,17] and experimental results related with the dependence of enantiomeric excess with temperature [18,19]. It is to be noted that such an approach has also been considered since a long time in the case of iron- and manganese-porphyrin catalysed epoxidation reactions [20,21].

Although the existence of these oxametallacycles is still a matter of controversy [22,23], they were postulated as intermediates in many organometallic reactions. For example, this is the case for the dihydroxylation reaction of olefins with $KMnO_4$ [24,25].

In our case, the formation of the tertiary alcohol could be explained by isomerisation of the double bond followed by an allylic oxidation. However such an isomerisation process cannot account for the formation of the rearranged aldehyde. The most reasonable mechanism is thus the type A one, which involves the formation of an oxametallacycle.

When complex **1** or **2** is used, the oxo-manganese bond can approach the *gem*-dimethyl substituted double bond either on its *Si* face (major approach) or on its *Re* face (minor approach). When the *gem*-dimethyl group is on the left side (Fig. 6), clockwise rotation or anti-clockwise rotation leads to two metallacycles with a (*S*) configuration (**A** and **B**) while, when the *gem*-dimethyl group is on the right side, rotations lead to two metallacycles with a (*R*) configuration (**A′** and **B′**) [18].

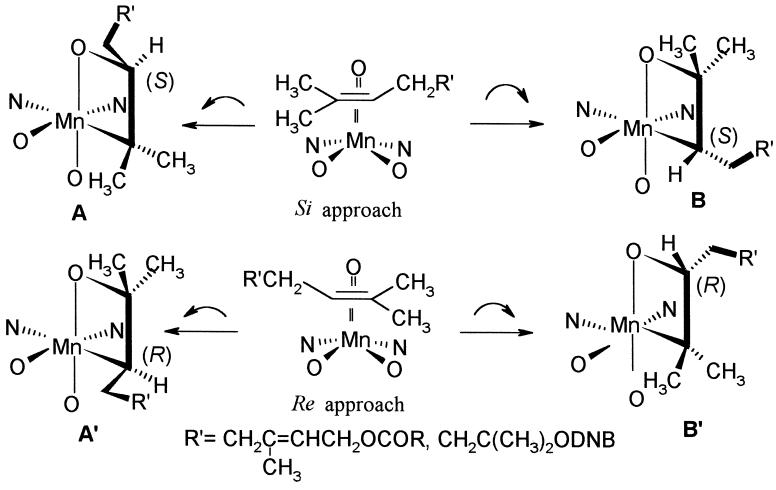


Fig. 6. Formation of the oxametallacycles.

Thus two regioisomeric metallacycles (**A** and **B**) must be considered, in our case, for the formation of epoxides **5**, **11** and **17**. Examination of the models indicates that the favoured approach of the olefin is the one in which the *gem*-dimethyl group is on the left in Fig. 6. Indeed the main interactions developed during the approach of our substrates are those between olefinic substituents and the cyclohexane diamine moiety of the salen complex on one side and the *t*-butyl groups on the other side. This is in agreement with the preferential formation of the (*S*)-epoxide and thus with the geometries of the four-membered rings, as it is known that the reductive elimination, leading to the epoxide, is a process in which configurations are retained. Thus, for the formation of the (*S*)-epoxide, the oxametallacycle intermediate or the oxametallacycle-like transition state must have one and/or the two geometries (**A** and **B**) depicted in Fig. 6.

These structures are in perfect agreement with the last proposal of Katsuki [18]. From these two forms, it is easy to explain the formation of the two isolated by-products (Fig. 7).

If one considers the **A** form, then the formation of the rearranged aldehyde is easy to understand. The assisted cleavage of the O–Mn bond by migration of the suitably positioned side chain gives rise to the aldehyde. In the **B** form, the carbon–carbon bond included in the oxametallacycle is necessarily in a *gauche* orientation with respect to the side chain of the substrate because of the repulsive interactions between that side chain and one phenyl group of the salen ligand. An elimination process involving the hydrogen *anti* to the C–Mn bond leads to the cleavage of that bond and gives rise to the tertiary alcohol with a *cis* double bond. The same pathways can be obviously described, with the same results, starting from the two oxametallacycles **A′** and **B′** involved in the formation of the (*R*)-epoxide. The formation of the proposed metallacycles implies a lateral approach of the olefin toward the oxo-manganese species which is considered to have a pyramidal geometry. After complexation, the system adopts a bipyramidal structure with a phenolic oxygen in an axial position. When complexes **1** and **2** are used, the yield of by-products remains similar. This is in agreement with the fact that the approach of the olefin, and thus the formation of the metallacycle, is not influenced by the presence or the absence of substituents in the 5-position of the salen moiety. When complex **3** (bearing a methoxy group in the 5-position) is used we do not observe any reaction. In this case, steric factors are no more involved and electronic factors should be considered. As proposed before, the reactivity of the oxo–Mn bond vs. the carbon–carbon double bond should be decreased thus explaining the absence of reactivity [26].

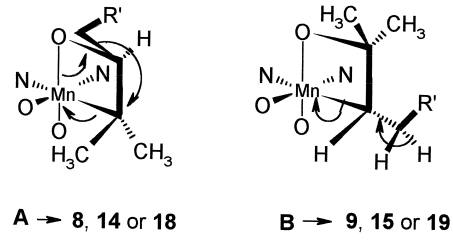


Fig. 7. Pathways leading to the aldehyde and the tertiary alcohol.

5. Conclusion

In this work, we have isolated by-products which are formed during the Mn-salen catalysed epoxidation of various trisubstituted non-conjugated olefins. The formation of these products is closely related with the epoxide formation and thus gives some information on the mechanism of the reaction. Their structure can be readily explained by the intervention of an oxametallacycle, as an intermediate, in the epoxidation process. Such an intermediate had been previously postulated on the basis of indirect evidences. Our results, based on products formation, thus reinforce this hypothesis for the oxygen transfer mechanism in Mn-salen catalysed epoxidation of olefins.

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