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Manganese(III) Porphyrin Catalysts for the Oxidation of Terpene Derivatives: A Comparative Study

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A comparative study involving four manganese(III) porphyrin catalysts combined with two different oxidants (sodium hypochlorite and potassium monopersulfate) has been performed in the epoxidation of three terpene derivatives. The catalytic oxidation of α-pinene produces selectively 100% of the epoxide or 65% of allylic oxidation products, only by modification of the substituents on the *meso*-positions of the metalloporphyrin catalyst. The catalytic oxidation of the 5-vinyl-2-norbornene is regio- and stereoselective, producing only the *exo*-2,3-epoxy-5-vinylnorbornane. With α-terpinene, a conjugated di-olefin, an oxidative dehydrogenation reaction was surprisingly observed, producing *p*-cymene as a major compound.

Key Words: **manganese(III) porphyrins; epoxidation; oxidative dehydrogenation; α-pinene; 5-vinyl-2-norbornene; α-terpinene.**

INTRODUCTION

Porphyrins are macrocyclic molecules consisting on the assembly of four pyrrole rings. The large number of accessible synthetic porphyrin ligands has created a large research field. Metalloporphyrins are widely used in the area of oxidation catalysis (1). The key concept consists of using simple oxidants as single oxygen atom donors to generate high-valent metal–oxo species active in metalloporphyrin-catalyzed oxidations. In 1979, Groves *et al.* published the first article on the use of iodosylbenzene as a simple oxygen atom donor in olefin epoxidation and alkane hydroxylation catalyzed by an iron(III) porphyrin complex (2). Since then, several other oxidants have been used such as sodium hypochlorite (3), potassium monopersulfate (4), hydrogen peroxide (5), and *t*-butylhydroperoxide (6).

The modification of the substituents on the *meso*-positions of the porphyrin macrocycle is known to induce a change in the rate and the selectivity of catalytic oxidations (the *meso*-positions of a porphyrin correspond to the interpyrrolic methyne positions) (1). Thus, we decided to carry out a comparative study in the oxidation of three terpene derivatives involving four different manganese(III) porphyrin complexes (Fig. 1) combined with two oxidants. Oxidation products of terpenes are useful intermediates in fragrance industries.

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EXPERIMENTAL AND METHODS

Methods

The conversions of α-pinene, α-terpinene, and 5-vinyl-2-norbornene and the yields of the differents oxidation products were determined by gas chromatography (GC). GC analyses were performed with an Intersmat IGC 120 FDL instrument equipped with a capillary column Alltech AT-WAX 30 m × 0.25 mm. Peak areas were measured with an integrator Spectra-Physics SP 4290. GC/MS analyses were performed with a HP 6890/MSD 5973 instrument equipped with a capillary column HP-5MS 30 m × 0.25 mm. ^{1}H NMR spectra were recorded on a Bruker AM 250 spectrometer. UV-visible spectra were recorded on a HP 8452A diode array spectrophotometer. Chemicals were purchased from Aldrich and Fluka. Sodium hypochlorite solution was supplied from Prolabo as an aqueous solution containing about 3.5% of active chlorine (0.5 M). Curox ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was a gift from Peroxid-Chemie, Germany.

Synthesis and Characterization of Catalysts

The (*meso*-tetraphenylporphyrinato) chloromanganese(III) Mn(TPP)Cl is commercially available. The *meso*-tetramesitylporphyrin H_2TMP and the *meso*-tetrakis(2,6-dichlorophenyl)porphyrin H_2TDCPP were prepared using a previously described procedure (7). The *meso*-tetrakis (*ortho*-nitrophenyl)porphyrin H_2TNPP was synthesized using the same procedure as for H_2TMP. The crude product was purified by chromatography over a dry column of basic alumina using first dichloromethane as eluent, and then dichloromethane with 0.5% methanol (yield = 3%). ^{1}H NMR ([D_6] DMSO): δ (ppm) −2.70 (s, 2H, NH), 8.28 (m, 8H, Harom), 8.68 (m, 8H, Harom), 8.85 (s, 8H, Hpyr). UV-visible (CH_2Cl_2): λmax (nm) 422. $C_{44}H_{26}N_8O_8$ requires:

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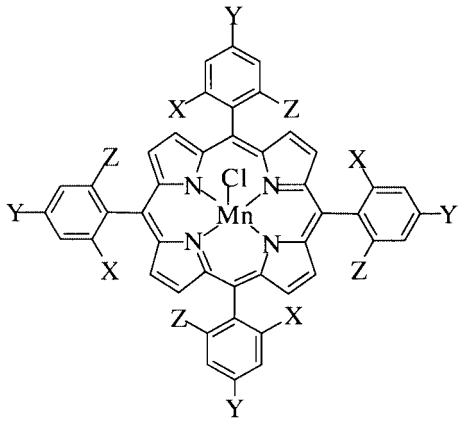


X = Y = Z = CH_3, Mn(TMP)Cl

X = Z = Cl, Y = H, Mn(TDCPP)Cl

X = NO_2, Y = Z = H, Mn(TNPP)Cl

X = Y = Z = H, Mn(TPP)Cl

FIG. 1. Structure of the four Mn(III) porphyrins used as catalysts.

C, 66.50; H, 3.30; N, 14.10. Found : C, 66.12; H, 3.15; N, 14.07.

The chloromanganese(III) porphyrin complexes Mn (TMP)Cl and Mn(TDCPP)Cl were prepared using dimethylformamide as a solvent as described (8, 9). Mn(TNPP)Cl was synthesized using the same procedure and purified by chromatography over a dry column of silica gel. The elution was performed first with a mixture dichloromethane/hexane (90/10, v/v) and then with a mixture of dichloromethane/methanol (98/2, v/v) (yield = 60%). UV-visible (CH_2Cl_2) : λmax (nm) 484. Despite several attempts at purification, inorganic residue remained in the sample. The elemental analyses indicated that the C/H/N ratio was correct, but the loading of inorganic impurities was estimated to be 10–15% based on the comparison of the ε value of the Soret band of this metalloporphyrin with other similar complexes prepared in the group.

General Procedure for Catalytic Oxidation Reactions Using NaOCl as Oxidant

All experiments were carried out at room temperature, under an air atmosphere, in a 50 ml round bottle equipped with a magnetic stirring bar. Either 1.1 or 1.75 mmol of a 0.5 M NaOCl solution was added to a solution of porphyrin complex (5 μmol), benzyldimethyltetradecylammonium chloride (BDTAC) (0.015 mmol), 4-*t*-butylpyridine (0.15 mmol), olefin (1.0 mmol) and an internal standard for gas chromatography in 0.5 ml of dichloromethane. The internal standards used were alkanes or halogenated benzene derivatives (*n*-undecane or chlorobenzene). The reactions were monitored by gas chromatography analyses of aliquots of the organic phase.

General Procedure for Catalytic Oxidation Reactions Using $KHSO_5$ as Oxidant

All experiments were carried out at room temperature, under an air atmosphere, in a 50 ml round bottle equipped with a magnetic stirring bar. Porphyrin complex (5 μmol), BDTAC (0.015 mmol), 4-*t*-butylpyridine (none or 0.15 mmol), olefin (1.0 mmol) and an internal standard for gas chromatography were dissolved in 0.5 ml of dichloromethane. A solution of $KHSO_5$ (1.1 or 1.75 mmol) in 3 ml of a 0.25 M phosphate buffer pH 7 was then added. The reactions were monitored by gas chromatography analyses of aliquots of the organic phase.

RESULTS AND DISCUSSION

1. Catalytic Oxidation of a Cyclic Mono-Olefin, α-Pinene

Oxidation of α-pinene **1** has been studied using various methods and generally gives a mixture of products such as its epoxide **2**, verbenol **3**, verbenone **4** (Fig. 2).

For example, the oxidation of α-pinene with oxygen using a homogeneous cobalt catalyst was described by Lajunen and Koskinen, with a verbenone selectivity of over 70% (10). Mn(III) salen complexes have been used, with iodosylbenzene as oxidant, leading to α-pinene oxide with a 55% selectivity (11). Using methyltrioxorhenium and hydrogen peroxide, Jacobs *et al.* described a 90% selectivity in α-pinene oxide (12). In addition, a number of studies have investigated the oxidation of α-pinene using heterogeneous catalysts such as resins (13), silica–titania co-gels (14), and metallosilicates containing molybdenum (15).

1.1. Sodium hypochlorite as oxidant. The use of Mn-(TPP)OAc as a catalyst for the epoxidation of α-pinene with sodium hypochlorite as oxidant has been described in previous papers (16, 17) leading to α-pinene oxide **2** with 80% yield. The results we obtained for the oxidation of the same substrate with NaOCl in the presence of several manganese(III) porphyrin complexes are summarized in Table 1. The catalytic oxidation reactions were carried out at room temperature using 0.5% molar of Mn(III) catalyst and 1.5% molar of 4-*t*-butylpyridine with respect to α-pinene. The addition of pyridine derivatives acting as axial ligand for the metal core of the porphyrin is known to improve

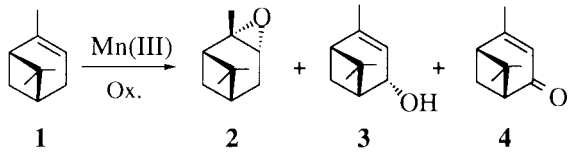


FIG. 2. Catalytic oxidation reaction of α-pinene **1**.

TABLE 1

Catalytic Oxidations of α-Pinene Using NaOCl as Oxidant

Run	Catalyst	Eq. of oxidant vs substrate	Conversion (%)	Yield (%)[a]			T.O.F.[b] (min^{-1})
				2	**3**	**4**	
1	Mn(TMP)Cl	1.75	100	50	36	10	0.8
2	Mn(TDCPP)Cl	1.75	98	67	29	0	1.6
3	Mn(TNPP)Cl	1.75	100	73	0	16	0.5
4	Mn(TPP)Cl	1.75	97	86	3	8	0.5
5	Mn(TNPP)Cl	1.1	100	88	0	12	0.5

[a] Chromatographic yield determined by GC analyses.

[b] T.O.F. = Turn Over Frequency = moles of converted substrate/(moles of catalyst × reaction time per minute).

the rate and the chemo- and stereoselectivity of catalytic reactions (18, 19). An excess of oxidant is generally used, in order to obtain a full conversion of the substrate. The catalytic reactions were performed in a biphasic medium, requiring the use of benzyldimethyltetradecylammonium chloride as phase transfer agent.

First, one should note that the substrate is fully converted in all experiments reported in Table 1 indicating that all the macrocyclic complexes used as catalysts are stable in the reaction medium. The distribution of the oxidation products obtained depends upon the substituents present on the porphyrin ring. The best yield in α-pinene oxide **2** was obtained with the less hindered porphyrin complex, Mn(TPP)Cl (Table 1, run 4). It is worth noting that when the steric hindrance is increased by the substitution of the phenyl rings of the porphyrin (Table 1, runs 1 to 4), the yield of epoxide decreases in favor of the formation of allylic oxidation products **3** and **4**. When bulky substituents are present on the porphyrin ring, as for Mn(TMP)Cl (Table 1, run 1), the approach of the substrate toward the metal–oxo species is tuned by small steric effects between the face of the olefin opposite to the substrate methylene bridge and the mesityl groups of the porphyrin ring leading to an increase of the allylic oxidation compound to the epoxide formation. In association with the steric factor, the electronic properties of the substituents on the phenyl rings of the porphyrin complexes must also be considered. For example, it is interesting to compare runs 2 and 3 of Table 1. The use of Mn(TDCPP)Cl, bearing two bulky chloro substituents that are moderately electron-withdrawing groups, induces the formation of trans-verbenol **3**, but not that of verbenone (Table 1, run 2). In contrast, the use of Mn(TNPP)Cl, bearing only one bulky nitro substituent that is strongly electron-withdrawing, induces the formation of verbenone **4**, but no verbenol is observed (Table 1, run 3). One can suppose that the verbenol formed is immediately reoxidized to produce verbenone quantitatively. A catalytic experiment realized using verbenol as substrate has confirmed this hypothesis, yielding verbenone as the only product.

In run 3, 73% of α-pinene oxide and 16% of verbenone were obtained, with 100% substrate conversion. So, the material balance indicates that 11% of one or several other oxidation products are formed. But these compounds have not been identified by GC analyses and might result from rearrangement of α-pinene oxide. Several articles have reported this weak stability of α-pinene oxide in oxidative conditions leading to rearranged products such as campholenic aldehyde, trans-sobrerol, or trans-carveol for example (20, 21). In order to reduce this phenomenon, a catalytic reaction has been performed with only a slight excess of oxidant (Table 1, run 5). As expected, no over-oxidation of α-pinene oxide was observed and 88% yield of this compound was obtained. It is important to specify that in all these catalytic oxidations of α-pinene, a stereoselective oxidation was observed leading to the formation of α-pinene oxide **2** and verbenol **3**. In all cases, the oxidation occurred on the less sterically hindered side of the olefin, corresponding to an oxygen addition of the high-valent metal–oxo species *anti* to the bridge bearing the two methyl groups (as represented in Fig. 2). In order to complete this comparative study, another oxidant was used with the same Mn(III) catalysts.

1.2. Potassium monopersulfate as oxidant. Potassium monopersulfate is a highly efficient oxygen atom donor. This inorganic peroxide is a stable triple salt $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$ which has a high capacity to generate metal–oxo species when added to metalloporphyrins. Since potassium monopersulfate is water-soluble, the oxidation reactions were performed in a biphasic system, with buffered water/dichloromethane in the presence of benzyldimethyltetradecylammonium chloride as a phase transfer agent. Because a water solution of $KHSO_5$ is very acidic, a solution of this oxidant in a phosphate buffer at pH 7 was used in order to avoid the fast acid-catalyzed opening of the oxirane rings.

When $KHSO_5$ is used in metalloporphyrin-catalyzed oxidations, it is also known that the addition of pyridine derivatives in the reaction mixture increases the rate and modifies the oxidation selectivity (22). Consequently, catalytic oxidation reactions were performed with and without 4-*t*-butylpyridine. In a classical experiment, 0.5% molar of manganese(III) catalyst and 0 or 1.5% molar of 4-*t*-butylpyridine were used with regard to the substrate. The reactions were generally performed with an excess of oxidant and the results are reported in Table 2.

As expected, one can first note that the turn over frequencies (TOF) obtained without addition of 4-*t*-butylpyridine are lower than those observed in its presence in the same experimental conditions (comparison of runs 1 to 4 with runs 6 to 9). The most remarkable increase of the reaction rate has been obtained in the case of Mn(TPP)Cl (Table 2, runs 4 and 9): the catalytic oxidation is almost 20 times faster with 4-*t*-butylpyridine than without. In the runs 1, 4, 7, and 10, the α-pinene conversion was not complete despite the

TABLE 2

Catalytic Oxidations of α-Pinene Using $KHSO_5$ as Oxidant

Run	Catalyst	*t*-Bu-Py	Eq. of oxidant vs substrate	Conversion (%)	Yield (%)[a]			T.O.F.[b] (min^{-1})
					2	**3**	**4**	
1	Mn(TMP)Cl	–	1.75	68	44	3	3	0.4
2	Mn(TDCPP)Cl	–	1.75	100	96	0	0	0.7
3	Mn(TNPP)Cl	–	1.75	100	50	0	9	1.3
4	Mn(TPP)Cl	–	1.75	79	63	3	2	0.7
5	Mn(TNPP)Cl	–	1.1	89	55	5	4	0.7
6	Mn(TMP)Cl	+	1.75	100	34	52	13	2.7
7	Mn(TDCPP)Cl	+	1.75	80	58	21	0	1.1
8	Mn(TNPP)Cl	+	1.75	100	57	2	10	13.3
9	Mn(TPP)Cl	+	1.75	100	100	0	0	13.3
10	Mn(TMP)Cl[c]	+	1.75	68	30	17	5	1.6
11	Mn(TNPP)Cl	+	1.1	92	69	10	12	3.1
12	Mn(TPP)Cl[c]	+	1.75	100	94	2	4	16.7

[a] Chromatographic yield determined by GC analyses.
[b] T.O.F. = Turn Over Frequency = moles of converted substrate/(moles of catalyst × reaction time per minute).
[c] Use of 0.1% molar of catalyst with regard to the substrate instead of 0.5% molar in the others experiments.

use of an excess of oxidant. We decided in these four runs to stop these slow experiments before the full substrate conversion: so these incomplete conversions must not be attributed to a degradation of the catalyst in the reaction medium.

In the experiments realized without 4-*t*-butylpyridine (Table 2, runs 1 to 4), the distribution between the different oxidation products formed cannot be explained as clearly as in the reactions performed with NaOCl considering the steric hindrance and the electronic properties of the porphyrin substituents (Table 1). Products other than α-pinene oxide **2**, trans-verbenol **3**, and verbenone **4** were formed, making these reactions poorly selective, except with Mn(TDCPP)Cl as catalyst (Table 2, run 2) where a 96% yield in α-pinene oxide was obtained with 100% substrate conversion.

In contrast, in the presence of the pyridine derivative, the same steric and electronic effects as those obtained using NaOCl were observed. The selectivity in α-pinene oxide increases when decreasing the steric hindrance on the porphyrin core (Table 2, runs 6 to 9). A 100% yield of **2** was obtained using the less hindered catalyst Mn(TPP)Cl (Table 2, run 9). On the other hand, a 65% yield of allylic oxidation products (**3** and **4**) were observed using the most bulky metalloporphyrin Mn(TMP)Cl (Table 2, run 6). It is interesting to note the large differences observed on selectivity which are due to the only modification of the substituents on the phenyl rings of the macrocyclic ligand using exactly the same experimental conditions, the same oxidant, and the same metal. The experiment performed with Mn(TPP)Cl (Table 2, run 9) is remarkable because its selectivity is totally orientated toward the α-pinene oxide, but also because this reaction is very fast (TOF > 13 min^{-1}). Then, a catalytic reaction was performed with 0.1% molar of Mn(TPP)Cl instead of the 0.5% molar generally used. The turn over frequency obtained in this case was above 16 min^{-1}, but by decreasing the catalyst concentration the reaction selectivity was slightly reduced (Table 2, run 12). Using Mn(TNPP)Cl as catalyst in the presence of 4-*t*-butylpyridine (Table 2, run 8), the TOF value obtained was above 13 min^{-1} but in this case, the epoxide selectivity was very weak. Some unidentified oxidation products coming probably from rearrangement of the α-pinene oxide were formed in 30% yield. By reducing the excess of oxidant used, this phenomenon was eliminated (Table 2, run 11) but then, the reaction became slower.

In the experiments performed with 4-*t*-butylpyridine, GC analyses of the reaction mixtures revealed the presence of a small amount of 4-*t*-butylpyridine-*N*-oxide. However, it has been previously evidenced that the *N*-oxide formed is not a good oxygen atom donor in our experimental conditions (19).

Before ending this study, it is important to specify that the stability of the different oxidation products was checked in the presence of the two oxidants tested: α-pinene oxide **2**, trans-verbenol **3**, and verbenone **4** were all stable. The stability of α-pinene was also examined and weak conversions below 10% were observed after six hours with NaOCl or $KHSO_5$, showing the necessity to use a catalyst in combination with the oxidant to perform the full conversion of the terpene derivatives.

2. *Catalytic Oxidation of a Nonconjugated Di-Olefin, 5-Vinyl-2-Norbornene*

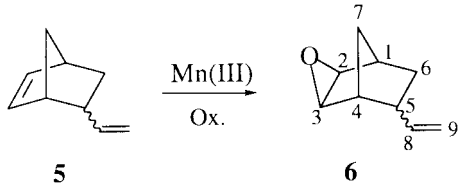
In the second part of this work, we focused our interest in the study of a di-olefin oxidation and our choice has been directed toward the 5-vinylbicyclo[2.2.1]hept-2-ene (5-vinyl-2-norbornene as short name). This compound

is attractive because it possesses two different types of double bonds: one endocyclic and the other being exocyclic and terminal. To our knowledge, there are only a very few examples of catalytic epoxidation systems of 5-vinyl-2-norbornene. Waegell *et al.* reported the use of palladium complexes with molecular oxygen to epoxidize this substrate. They reported a low and slow conversion of 44% of the 5-vinyl-2-norbornene with the epoxidation of the endocyclic double bond in 6 days at 60°C (23, 24). Heteropolyacids such as 12-tungstophosphoric acid or 12-molybdophosphoric acid combined with cetylpyridinium chloride have been reported as catalysts for the epoxidation of 5-vinyl-2-norbornene in the presence of hydrogen peroxide (25). The authors reported a conversion of 90% of the substrate and a 90% selectivity for the intracyclic epoxide.

2.1. Sodium hypochlorite as oxidant. In all experiments realized on 5-vinyl-2-norbornene, only a slight excess of oxidant was used. Our goal was to obtain selectively the epoxidation of the more reactive norbornene intracyclic double bond (Fig. 3).

The experimental conditions used were the same as those for α-pinene oxidation: 0.5% molar of catalyst and 1.5% molar of 4-*t*-butylpyridine with respect to the substrate in a biphasic medium with an ammonium salt as phase transfer agent. The expected oxidation product, 2,3-epoxy-5-vinylbicyclo[2.2.1]heptane **6**, noncommercially available, was synthesized as previously described (26). This epoxidation was realized by using potassium monopersulfate, at 0–5°C with acetone acting both as solvent and reactant. The reaction occurs under nearly neutral conditions to avoid epoxide ring opening. This method leads to a mixture of mono- and diepoxide which can be separated chromatographically. The pure sample of **6** was used as reference in gas chromatography to analyze the catalytic reaction mixtures. The results of our experiments using NaOCl as oxidant are summarized in Table 3.

As expected, the epoxidation reaction occurred regioselectively on the most reactive intracyclic double bond of the norbornene derivative, producing nearly exclusively the compound **6**. The reaction is not only regio- but also stereoselective, giving only the *exo* epoxide. This result can be explained by a combination of steric and electronic effects. It is known that the *exo* face of norbornene is somewhat richer in π electrons than the *endo* face. Since the epoxidation is formally an electrophilic addition, there is a preference for the *exo* face over the *endo* face of the molecule. In addition, the *endo* hydrogen at C_6 and the vinyl substituent at C_5 are viewed as hindering the *endo* approach of the electrophile.



5 **6**

FIG. 3. Catalytic epoxidation of the intracyclic double bond of the 5-vinyl-2-norbornene **5**.

TABLE 3

Catalytic Oxidations of 5-Vinyl-2-Norbornene Using NaOCl as Oxidant

Run	Catalyst	Eq. of oxidant vs substrate	Conversion (%)	Yield of **6** (%)[a]	T.O.F.[b] (min^{-1})
1	Mn(TMP)Cl	1.1	98	98	0.6
2	Mn(TDCPP)Cl	1.1	85	85	0.1
3	Mn(TNPP)Cl	1.1	25	20	0.1
4	Mn(TPP)Cl[c]	1.1	21	21	1.4

[a] Chromatographic yield determined by GC analyses.
[b] T.O.F. = Turn Over Frequency = moles of converted substrate/(moles of catalyst × reaction time per minute).
[c] Rapid degradation of the catalyst.

The two hindered catalysts, Mn(TMP)Cl and Mn(TDCPP)Cl (Table 3, runs 1 and 2), surprisingly gave very good substrate conversions. In addition, the catalytic reactions performed with these two complexes were completely selective and only produced the epoxide **6**. This can be explained by steric considerations: the substrate **5** can only approach the metal center, which is surrounded by bulky substituents, by its less hindered *exo* face, producing then **6** exclusively. Using Mn(TPP)Cl, a rapid bleaching of the organic phase occurred, corresponding to the degradation of the catalyst (Table 3, run 4). In contrast, Mn(TNPP)Cl gave a weak conversion of the substrate but no degradation of the porphyrin catalyst was observed: the reaction was just very slow. For example, using Mn(TNPP)Cl as catalyst, the conversion of the substrate is only 25% in 6.5 h when it is of 98% in 5 h using Mn(TMP)Cl.

2.2. Potassium monopersulfate as oxidant. When using potassium monopersulfate as oxidant, the catalytic reactions were generally faster than with sodium hypochlorite (Table 4).

As observed with NaOCl, Mn(TMP)Cl, and Mn(TDCPP)Cl (Table 4, runs 1 and 2) were the more active and the more selective catalysts and the unique oxidation product observed was the 2,3-epoxy-5-vinylnorbornane **6**. Mn(TNPP)Cl (Table 4, run 3) was less active and less selective, but this complex was stable under the reaction conditions, contrary to Mn(TPP)Cl (Table 4, run 4) which was quickly degraded in the medium.

3. Catalytic Oxidation of a Conjugated Di-Olefin, α-Terpinene

To complete this comparative study, we decided to use a conjugated diene, namely α-terpinene. Using only a slight excess of oxidant, the selective formation of one of the two

TABLE 4

Catalytic Oxidations of 5-Vinyl-2-Norbornene Using $KHSO_5$ as Oxidant

Run	Catalyst	Eq. of oxidant vs substrate	Conversion (%)	Yield of **6** (%)[a]	T.O.F.[b] (min^{-1})
1	Mn(TMP)Cl	1.1	99	99	1.1
2	Mn(TDCPP)Cl	1.1	94	94	1.0
3	Mn(TNPP)Cl	1.1	76	65	0.4
4	Mn(TPP)Cl[c]	1.1	44	43	0.5

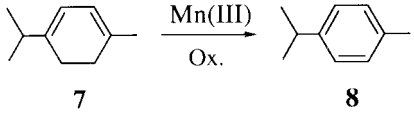
[a] Chromatographic yield determined by GC analyses.
[b] T.O.F. = Turn Over Frequency = moles of converted substrate/(moles of catalyst × reaction time per minute).
[c] Rapid degradation of the catalyst.

possible epoxides was expected. Monoepoxides are the only products observed in the catalytic oxidation of 1,3-cyclohexadiene using the NaOCl/Mn(TPP)OAc system (19).

In the litterature, the catalytic photooxidation of α-terpinene has been described using a TiO_2 suspension in acetonitrile under irradiation (27). In these experimental conditions, a mixture of products is obtained, including ascaridole resulting from the photooxygenation reaction, isoascaridole (bis-epoxide) and *para*-cymene arising from the oxidative dehydrogenation reaction. Using a molybdenum complex, with hydrogen peroxide and sodium hydroxide, Woodward *et al.* described the selective oxidation of α-terpinene in ascaridole (28). The catalytic oxidative dehydrogenation of α-terpinene to *p*-cymene was also described using vanadium and molybdenum mixed heteropolyanions in the presence of oxygen (29) or with *t*-butylhydroperoxide (30).

All the experiments with α-terpinene **7** were realized with 0.5% of catalyst and 1.5% of 4-*t*-butylpyridine with respect to the substrate. The reactions were performed under biphasic conditions using a slight excess of oxidant. In all the catalytic experiments realized, no epoxidation products were observed. The major compound obtained was the *p*-cymene **8**, resulting in an oxidative dehydrogenation of the substrate (Fig. 4).

To our knowledge, only a few examples of oxidative dehydrogenation catalyzed by metalloporphyrins have been previously described. Desaturation of aliphatic hydrocarbons have been reported with cytochrome P450 enzymes as catalysts (31). No example of manganese(III) porphyrin catalyzed oxidative dehydrogenation was found in the litterature.



7 **8**

FIG. 4. Catalytic oxidative dehydrogenation of the α-terpinene **7**.

In GC analyses of the reaction mixtures, the chromatographic yield of **8** is the only one that was determined, the other products being formed in small amounts (see Table 5).

With potassium monopersulfate and sodium hypochlorite, a complete conversion of the substrate was obtained regardless of the metalloporphyrin catalyst used. In the same way as with the two precedently studied substrates, the catalytic reactions were always more rapid with $KHSO_5$ than with NaOCl. Independant catalytic reactions indicated that the yield of **8** ranged from 48 to 72% at full substrate conversion. Nevertheless, GC/MS analyses of the reaction mixtures indicated that no epoxides and no oxygenation products of the substrate at m/z 152 were formed. In contrast, two dehydrogenation compounds at m/z 134 were analyzed by GC/MS. The major product was *p*-cymene and the second one, less abundant, was identified as *p*-mentha-1,3,8-triene **9**. In the case of *p*-cymene, a weight loss of 43 mass units corresponding to an isopropyl fragment was observed on mass spectra, giving a peak at m/z 91. In the case of *p*-mentha-1,3,8-triene, a weight loss of 41 mass units was obtained, corresponding to a methylethenyl fragment, giving a signal at m/z 93.

For the oxidative dehydrogenation catalyzed by Mn(V)=O species, we propose a mechanism similar to that previously described for cytochrome P450 with the initial abstraction of an H-atom on the ring by porphyrin-Mn(V)=O species leading to an intermediate radical (Fig. 5, for the generation of high-valent metal–oxo species in P450 enzymes and related biomimetic models, see Ref. 32). Then, the C-centered radical is oxidized by the Mn(IV)-OH species generated by the H-atom transfer. The loss of a β-proton from the resulting carbocation intermediate generates the new C=C bond.

The yield of **9** was low and estimated to be below 3%. But, if no oxygenation products of the substrate are formed,

TABLE 5

Catalytic Oxidations of α-Terpinene

Run	Catalyst	Oxidant[a]	Conversion (%)	Yield of **8** (%)[b]	T.O.F.[c] (min^{-1})
1	Mn(TMP)Cl	NaOCl	100	54	1.3
2	Mn(TDCPP)Cl	NaOCl	100	54	1.3
3	Mn(TNPP)Cl	NaOCl	100	66	1.3
4	Mn(TPP)Cl	NaOCl	96	72	1.3
5	Mn(TMP)Cl	$KHSO_5$	100	49	2.7
6	Mn(TDCPP)Cl	$KHSO_5$	100	48	4.4
7	Mn(TNPP)Cl	$KHSO_5$	96	57(49)[d]	12.8
8	Mn(TPP)Cl	$KHSO_5$	95	65(47)[d]	12.7

[a] In all the experiments, 1.1 equivalents of oxidant versus the substrate are used.
[b] Chromatographic yields determined by GC analyses.
[c] T.O.F. = Turn Over Frequency = moles of converted substrate/(moles of catalyst × reaction time per minute).
[d] Yields observed 30 minutes after the end of the conversion.

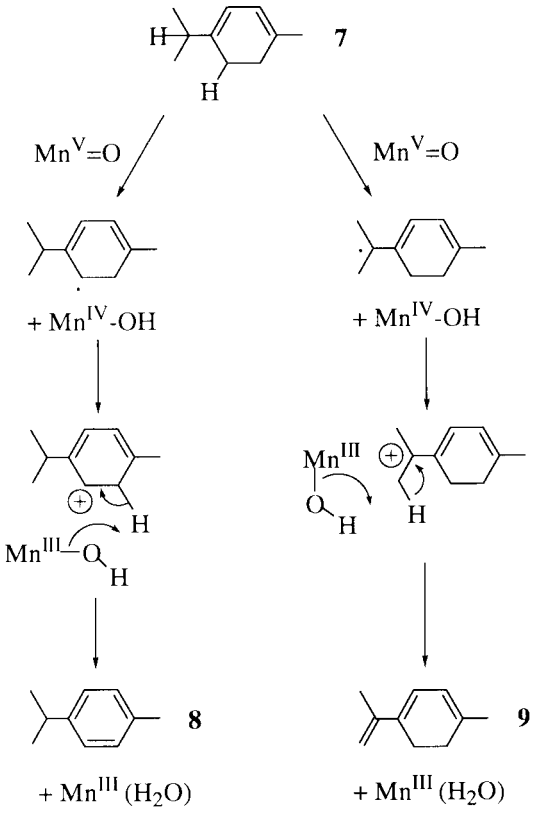


FIG. 5. Proposed mechanism for the oxidative dehydrogenation reaction of the α-terpinene **7**. It should be noted that the abstraction on the other allylic position (on the side of the methyl group) is also possible. Only one route is depicted.

how can we explain that the yield of *p*-cymene is only about 50%? In the runs 7 and 8 of Table 5, the conversion of the substrate was almost complete; so the oxidant has been quasi totally consumed because only a slight excess was used. After a reaction time of 15 minutes, the yield of **8** was 57% using Mn(TNPP)Cl (Table 5, run 7) and 65% using Mn(TPP)Cl (Table 5, run 8). When stirring was maintained, after a period of 30 minutes, we observed that the yield of **8** decreased to 49% for the reaction performed with Mn(TNPP)Cl and to 47% with Mn(TPP)Cl. This phenomenon can not be explained by a catalytic oxidation reaction requiring a stoechiometric amount of sodium monopersulfate since the oxidant excess was too weak (with only 1.1 equivalent of oxidant the substrate was fully converted). Then, we propose that a catalytic amount of Mn(V) = O species in the medium was able to initiate an autocatalytic free radical chain reaction partially consuming the generated *p*-cymene **8**. This free radical chain reaction can lead to several products and its presumed mechanism is depicted in Fig. 6.

In this mechanism, a catalytic amount of Mn(V) = O species initiates the reaction, inducing the abstraction of a hydrogen atom from **8**. The alkyl radical formed can react with oxygen to give the corresponding alkylperoxy radical generating the alkoxy radical **10** after dimerization and Russell fragmentation. The homolytic cleavage of the C–C bond between the ring and the quaternary carbon of **10** (β fragmentation) leads to the formation of acetone and *p*-cresol **11** as previously described in the case of cumene (33). The presence of *p*-cresol was not detected in the GC/MS

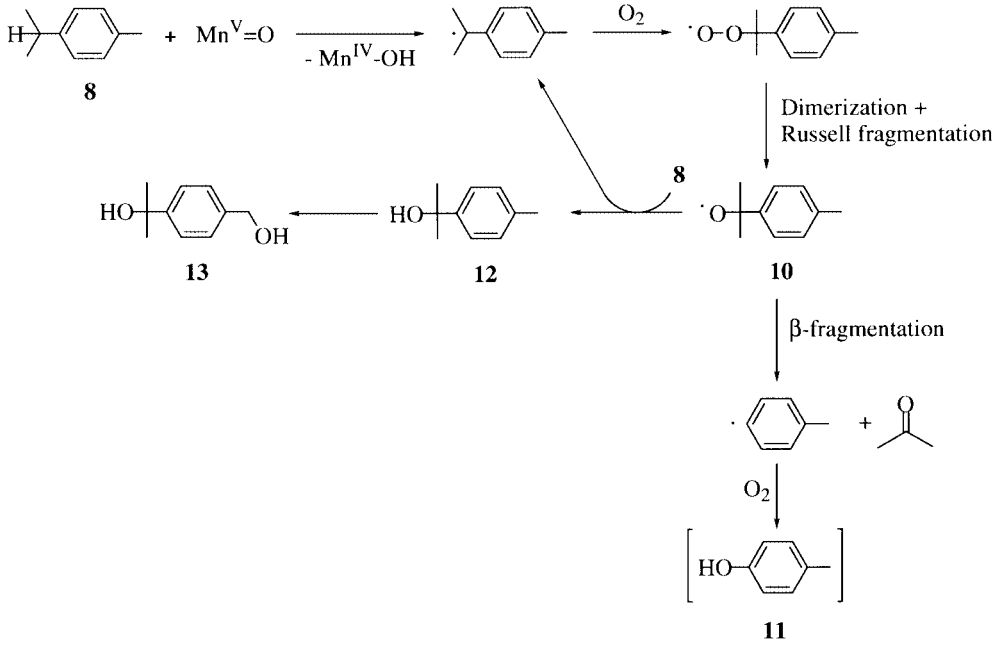


FIG. 6. Proposed mechanism for the autocatalytic free radical chain reaction involving the *p*-cymene **8**.

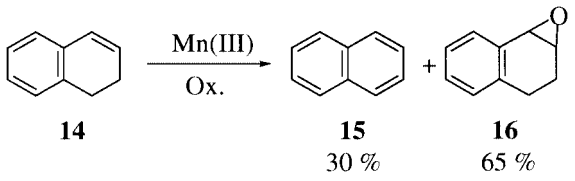


FIG. 7. Catalytic oxidation reaction of the 1,2-dihydronaphthalene **14**.

analyses of the reaction mixtures. In fact, compound **11** is unstable under the oxidative reaction conditions and probably gives the corresponding quinone and polymers. The intermediate alkoxy radical **10** also produced the corresponding alcohol **12** which was observed in GC/MS at m/z 150. The mass spectra of this compound exhibited a fragmentation peak at m/z 91 corresponding to the elimination of the 2-propylalcohol fragment. A further oxidation of this product **12** produced traces of the diol **13** which was observed at m/z 166 in GC/MS.

This free radical chain oxidation explains the limited yield in *p*-cymene observed in these biomimetic reactions and also the formation of the different hydroxylated products arising from its further oxidation. A blank experiment has been performed using *p*-cymene **8** as substrate leading to the formation of the same oxidation products **12** and **13**. In order to complete this study, a catalytic experiment was performed with the 1,2-dihydronaphthalene **14** as substrate (Fig. 7).

In this case, the oxidative dehydrogenation reaction competes with the epoxidation reaction. Substrate **14** reacts in the same way as styrene, which gives the epoxidation product on the vinyl group in high yield (22). In contrast with α-terpinene **7**, substrate **14** already possesses an aromatic ring, thus the epoxidation of the nonaromatic double bond becomes the major reaction (65% of **16**). The naphthalene **15** arising from the dehydrogenation reaction was obtained in 30% yield; **15** was stable in the oxidative conditions, in contrast with *p*-cymene **8**. This difference of stability can be explained by the fact that **15** has no substituents that can undergo hydrogen abstraction in opposition to *p*-cymene which possesses hydrogen atoms in two different allylic positions.

CONCLUSION

Manganese(III) porphyrin complexes are efficient oxidation catalysts for the three studied terpene derivatives. This comparative study allowed us to illustrate the different oxidation products that can be generated using three differently substituted metalloporphyrin catalysts:

- Epoxidation and allylic oxidation reactions were observed with α-pinene (mono-unsaturated substrate). The experiments reported with this terpene derivative allowed us to evidence the strong influence of the metalloporphyrin substituents on the selectivity of the catalytic oxidation reaction (epoxide formation *versus* allylic oxidation).
- Regio- and stereoselective epoxidation is observed in the case of the 5-vinyl-2-norbornene (nonconjugated diene). The intracyclic double bond is the only one to be epoxidized.
- An original oxidative dehydrogenation reaction takes place in the case of the α-terpinene (conjugated diene). Such hydrocarbon desaturation is an unusual oxidation pathway when using metalloporphyrin catalysts.

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