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Oxidation of bicyclic arenes with hydrogen peroxide catalysed by Mn(III) porphyrins

Susana L.H. Rebelo [a], Mário M.Q. Simões [a], M. Graça P.M.S. Neves [a], Artur M.S. Silva [a], Pietro Tagliatesta [b], José A.S. Cavaleiro [a,*]

[a] *Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal*
[b] *Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133 Roma, Italy*

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Abstract

Several manganese(III) porphyrin complexes were evaluated as catalysts in the oxidation of indane and tetralin with hydrogen peroxide, in the presence of ammonium acetate as a co-catalyst. Catalysis by Mn(III) *meso*-tetra-2,6-dichlorophenylporphyrins gave rise, in a first stage, to benzylic monooxygenation products (1-alcohols and 1-ketones). However, addition of excess of oxidant gave rise to over-oxidation products and, in certain conditions, hydroxy-keto compounds were selectively obtained. Reactions catalysed by Mn(III) *meso*-tetra-pentafluorophenylporphyrins showed higher capability to generate dehydrogenated products. As a result, 1*H*-indene and naphthalene were formed. To understand the reactions' pathway, the oxidations of 1-indanol, 1-indanone, 2-indanol, 1*H*-indene, 1-tetralol, 1-tetralone, 1,4-dihydroxytetralin and 4-hydroxy-1-tetralone were also considered with manganese (III) *meso*-tetra-2,6-dichlorophenylporphyrin chloride, Mn(TDCPP)Cl, as catalyst.

Keywords: Manganese(III) porphyrin; Oxidation; Hydrogen peroxide; Indane; Tetralin

1. Introduction

The side chain oxidation of alkylaromatics forms the basis of production of various commodity chemicals. Oxidative catalysis has been applied for the activation of this type of compounds in order to obtain more efficient procedures and to replace ecologically dangerous oxidants by more favourable ones [1].

One of the main objectives to carry out the oxidation of indane (**1**) and tetralin (**2**) has been the formation of intermediates for chemical synthesis. Some examples rely on the preparation of chiral benzylic alcohols [2], of 1-tetralone, which is a key intermediate in the commercial production of 1-naphthol [3] and of 2-hydroxy-1-tetralone, used as a building block in the synthesis of aureolic acid antibiotics, exemplified by olivomycin A [4]. More recently, the described anti-parasitic activity of 4-hydroxy-1-tetralone, isolated from a Bolivian plant [5], can extend the application of that type of compounds to other medicinal purposes.

Metalloporphyrins are known to be efficient catalysts for the oxidation of inactivated organic substrates, even at low temperatures [6,7]. When associated with hydrogen peroxide, these systems are still more promising, having in mind the desired cleaner and economical chemistry [8,9].

We have already reported that cheap substrates like terpenes [10,11] and alkylbenzenes [12] can be easily oxidised by using manganese(III) porphyrins as catalysts. This publication now reports the results obtained in the homogeneous oxidation of indane and tetraline with H_2O_2 in the presence of ammonium acetate as co-catalyst. The selected Mn(III) porphyrins for this study are shown in Scheme 1.

* Corresponding author. Tel.: +351 234 370 717; fax: +351 234 370 084.
E-mail address: jcavaleiro@dq.ua.pt (J.A.S. Cavaleiro).

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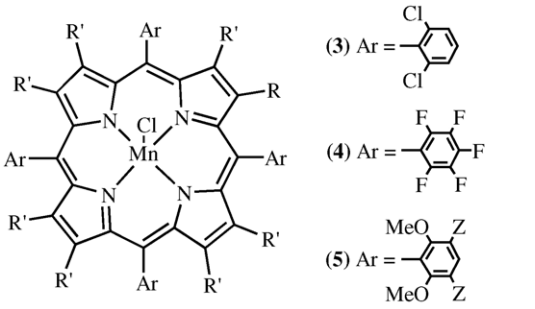


(**3a**)	Mn(TDCPP)Cl	R = R' = H
(**3b**)	Mn(β-NO_2TDCPP)Cl	R = NO_2; R' = H
(**4a**)	Mn(TF_5PP)Cl	R = R' = H
(**4b**)	Mn(β-NO_2TF_5PP)Cl	R = NO_2; R' = H
(**5a**)	Mn(TDMPP)Cl	R = R' = H; Z = H
(**5b**)	Mn(Cl_{16}TDMPP)Cl	R = R' = Cl; Z = Cl

Scheme 1.

2. Results and discussion

2.1. Catalysts synthesis

The free bases of metalloporphyrins **3**–**5** were prepared according to the described procedures [13–15]. Metallation of the free bases leading to the formation of complexes **3**–**5** was performed with $MnCl_2$ according to reported methods [15].

2.2. Oxidation of the substrates

The oxidation reactions were carried out in acetonitrile, at room temperature, with progressive addition of H_2O_2, in the presence of the manganese(III) porphyrin complex and ammonium acetate as co-catalyst. The reactions were followed by GC every 60 min and the addition of H_2O_2 was stopped when the conversion of the substrate remained constant after two successive GC analyses.

2.2.1. Oxidation of indane (*1*)

In the oxidation reactions of indane in the presence of the Mn(III) porphyrins, the conversion of substrate and distribution pattern of the products were found to be dependent on the catalyst structure and on the reaction time (Scheme 2 and Table 1). Different metalloporphyrins led to diverse selectivity for 1-indanol (**1a**) and 1-indanone (**1b**) and, in some cases, interesting selectivity was found for dioxygenation products [1,3-dihydroxyindane (**1c**) and 3-hydroxy-1-indanone (**1d**)] and for products resulting from a dehydrogenation pathway, like 1*H*-indene (**1e**) and 1*H*-indene oxide (**1f**).

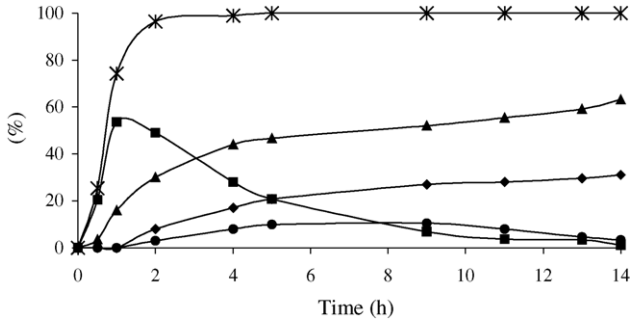


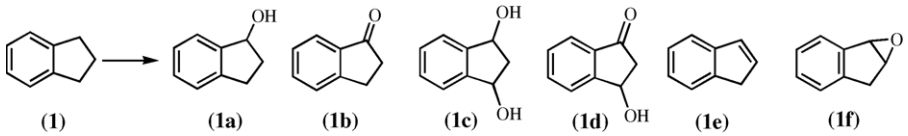
Fig. 1. Conversion and product yield percentages in the course of the oxidation reaction of indane catalysed by metalloporphyrin **3a** [(✳) conversion; (■) **1a**; (▲) **1b**; (●) **1c**; (♦) **1d**]. Reaction conditions: the substrate (0.3 mmol), the catalyst (1 μmol was added to each reaction mixture for three times, at 0, 4 and 8 h) and ammonium acetate (0.2 mmol) were stirred in CH_3CN at r.t. and 0.15 mmol of H_2O_2 (37.5 μl of the diluted solution in use) were added to the reaction mixture every 15 min.

The separation of the indane oxidation products by chromatography afforded pure compounds **1a**, **1b** and **1d**, which were identified by GC–MS and by NMR. Another fraction was obtained and by GC–MS and NMR analysis it was possible to conclude that it was constituted by a diastereoisomeric mixture of *trans*-1,3-dihydroxyindane (**1c**-**1**) and *cis*-1,3-dihydroxyindane (**1c**-**2**) in a ratio of 3:1.

The identity of compound **1e** was confirmed by comparing its mass spectrum with the information available from the GC–MS database and also by GC co-injection of an authentic sample commercially available. Compound **1f** was identified by GC–MS and by comparison with an authentic sample, obtained by oxidation of **1e** with H_2O_2 in the presence of catalyst **3a** and ammonium acetate as the co-catalyst (Table 2, entry 1). This oxidation reaction occurred with full conversion of **1e**, affording **1f** as the only product at a higher substrate:catalyst ratio (600:1) than that used for the oxidation of indane.

The reaction time is an important factor concerning the selectivity for the compounds **1a**–**1d** (Table 1, entries 1 and 2). From Fig. 1 and Table 2, it can be concluded that compounds **1b**–**1d** are formed at the expense of compound **1a**.

In order to understand how the products are formed, the oxidation of potential reaction intermediates was carried out under the conditions used for indane oxidation.



Scheme 2.

Table 1
Indane oxidation with H_2O_2 catalysed by Mn(III) porphyrin complexes **3**–**5**[a]

Entry	Catalyst	*t* (h)	Conversion[b] (%)	Selectivity[b] (%)					
				1a	**1b**	**1c**	**1d**	**1e**	**1f**
1	Mn(TDCPP)Cl (**3a**)	1	74	72	21	0	0	1	6
	Mn(TDCPP)Cl (**3a**)	2	96	48	31	7	8	1	5
	Mn(TDCPP)Cl[c] (**3a**)	6	100	16	52	8	22	0	2
	Mn(TDCPP)Cl[c] (**3a**)	14	100	1	63	3	31	0	1
2	Mn(β-NO_2TDCPP)Cl (**3b**)	1	74	70	17	0	0	10	3
	Mn(β-NO_2TDCPP)Cl (**3b**)	2	95	63	28	0	0	5	4
3	Mn(TF_5PP)Cl (**4a**)	2	55	67	14	0	0	12	7
4	Mn(β-NO_2TF_5PP)Cl (**4b**)	3	41	65	12	0	0	17	6
5	Mn(TDMPP)Cl (**5a**)	2.5	40	58	32	0	0	5	5
6	Mn(Cl_{16}TDMPP)Cl (**5b**)	3.5	56	67	18	0	0	6	8
7	No catalyst	5	0	–	–	–	–	–	–

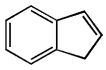
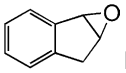
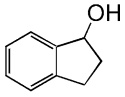
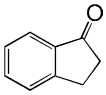
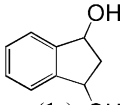
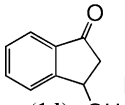
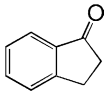
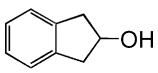
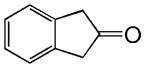
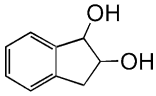
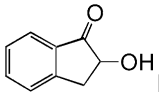
[a] Reaction conditions: the substrate (0.3 mmol), the catalyst (1 μmol) and ammonium acetate (0.2 mmol) were stirred in CH_3CN at r.t. and 0.15 mmol of H_2O_2 (37.5 μl of the diluted solution in use) were added to each reaction mixture every 15 min.
[b] Determined by GC analyses.
[c] Reaction conditions as for Footnote a, but 1 μmol of catalyst was added to the reaction mixture for three times, at 0, 4 and 8 h.

In the oxidation of 1-indanol (**1a**), 1-indanone (**1b**) was the main product, followed by 3-hydroxy-1-indanone (**1d**) and 1,3-dihydroxyindane (**1c**), respectively (Table 2, entry 2). Compound **1e** was not observed and this result allowed us to exclude the possibility of 1*H*-indene to arise from the dehydration of 1-indanol.

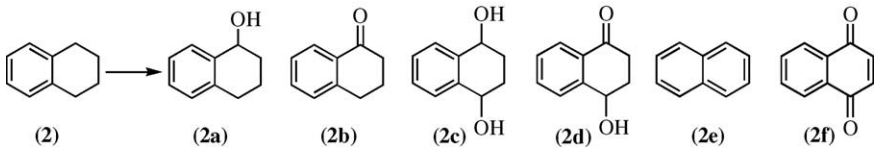
No other products resulting from further oxidation of ketone **1b** have been detected (Table 2, entry 3), suggesting that **1d** was obtained via oxidation of the diol **1c**. Although 2-indanol (**1g**) was never detected during the oxidation reactions of indane, we decided to eliminate the possibility of 1*H*-indene to arise from its dehydration. The oxidation of **1g** (Table 2, entry 4) afforded 2-hydroxy-1-indanone (**1j**) as the major product, followed by 1,2-dihydroxyindane (**1i**) and 2-indanone (**1h**). None of these products were detected during the oxidation of indane. Moreover, we have observed that the oxidation of **1e**, **1a** and **1g**, shown in Table 2, are catalytic processes, since no oxidation products were detected in the absence of the metalloporphyrin.

As far as the efficiency of the catalysts is concerned, we can conclude from Table 1 that catalysts **3** gave rise to almost total conversions after 1–2 h reaction times (entries 1 and 2). With catalyst **3a** significant amounts of 1-indanone (**1b**) and dioxygenated products have been obtained. For longer reac-

Table 2
Results of the oxidation reactions of **1a**, **1b**, **1e** and **1g** with H_2O_2 catalysed by **3a**[a]

Entry	Substrate	[Conversion (%)][b], time	Products [Selectivity (%)][b]			
1	 (**1e**)	[100][c,d], 1 h	 (**1f**) [100]			
2	 (**1a**)	[53][d], 3 h	 (**1b**) [44]	 (**1c**) [25]	 (**1d**) [31]	
3	 (**1b**)	[0], 3 h	No products			
4	 (**1g**)	[22][d], 3 h	 (**1h**) [10]	 (**1i**) [35]	 (**1j**) [49]	

[a] Reaction conditions: the substrate (0.3 mmol), the catalyst (1 μmol) and ammonium acetate (0.2 mmol) were stirred in CH_3CN at r.t. and 0.15 mmol of H_2O_2 (37.5 μl of the diluted solution in use) were added to reaction mixture every 15 min.
[b] Determined by GC analyses.
[c] 0.5 μmol of catalyst were used.
[d] The same reaction was repeated in the absence of the catalyst and no reaction products were observed.



Scheme 3.

tion times, further addition of catalyst **3a** and H_2O_2 resulted in an increase on the yield of **1d** from 8 to 22% (6 h) and 31% (14 h). With porphyrin **3b**, high conversion and high selectivity were achieved for 1-indanol (**1a**) after 2 h of reaction (Table 1, entry 2).

In the presence of catalysts **4** and **5** the indane conversions (40–56%) were lower than those observed with catalysts **3**. The major product was always 1-indanol (**1a**) and no dioxygenated products were obtained. Catalysts **4** were found to be more selective for the dehydrogenated product **1e** and the corresponding oxide **1f**. With porphyrin **4b** (Table 1, entry 4), a 23% selectivity was obtained for **1e** plus **1f**.

2.2.2. Oxidation of tetralin (2)

The oxidation of tetralin with H_2O_2 in the presence of different Mn(III) porphyrin catalysts afforded 1-tetralol (**2a**), 1-tetralone (**2b**), 1,4-dihydroxytetralin (**2c**), 4-hydroxy-1-tetralone (**2d**) and minor amounts of naphthalene (**2e**) and 1,4-naphthoquinone (**2f**) (Scheme 3). The distribution of the obtained products is also dependent on the catalyst and on the total reaction time (Table 3).

Separation of the tetralin oxidation products obtained with catalyst **3a**, by column chromatography, allowed pure compounds **2a**, **2b** and **2d** obtained in separate fractions. These compounds were characterized by MS, ^{1}H and ^{13}C NMR. Further purification of the last fraction collected, containing **2c**, afforded *trans*-1,4-dihydroxytetralin (**2c-1**) and *cis*-1,4-dihydroxytetralin (**2c-2**) in a (1:1) ratio. These two isomers were fully characterized by mass spectrometry and by detailed analysis of the ^{1}H and COSY NMR spectra. Compounds **2e** and **2f** were identified by GC–MS analysis and by GC co-injection of commercially available standards.

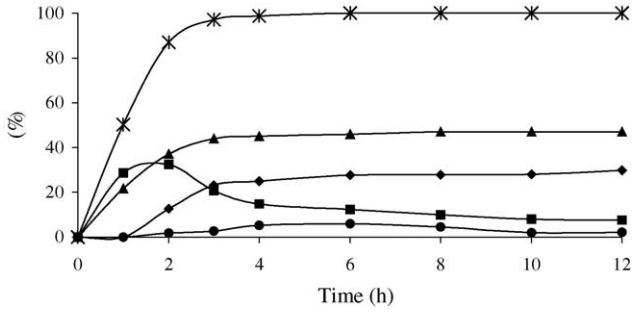


Fig. 2. Conversion and product yield percentages in the course of the oxidation reaction of tetralin catalysed by metalloporphyrin **3a** [(✕) conversion; (■) **2a**; (▲) **2b**; (●) **2c**; (♦) **2d**]. Reaction conditions: the substrate (0.3 mmol), the catalyst (1 μmol was added to each reaction mixture for three times, at 0, 4 and 8 h) and ammonium acetate (0.2 mmol) were stirred in CH_3CN at r.t. and 0.15 mmol of H_2O_2 (37.5 μl of the diluted solution in use) were added to the reaction mixture every 15 min.

The results from Table 3 and the analysis of Fig. 2 suggest that compounds **2b**–**2d** are obtained at the expense of **2a**.

As for indane, we also tried to identify the main reaction pathways for the products formation, by studying the oxidation of **2a**–**2d** in the presence of porphyrin **3a** (Table 4).

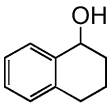
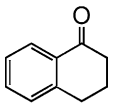
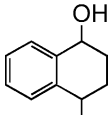
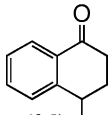
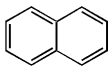
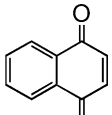
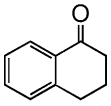
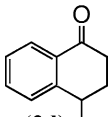
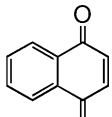
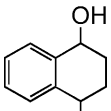
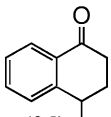
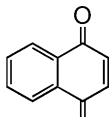
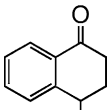
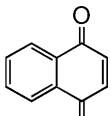
The catalytic oxidation of **2a** occurred with high conversion and afforded **2d** (49%) as the major product, followed by **2b** (26%) and **2c** (13%). Minor quantities of **2e** (4%) and **2f** (5%) were also detected (Table 4, entry 1). These results

Table 3
Tetralin oxidation with H_2O_2 catalysed by Mn(III) porphyrin complexes **3**–**5**[a]

Entry	Catalyst	*t* (h)	Conversion[b] (%)	Selectivity[b] (%)					
				2a	**2b**	**2c**	**2d**	**2e**	**2f**
1	Mn(TDCPP)Cl (**3a**)	2	87	37	43	2	14	0	2
	Mn(TDCPP)Cl (**3a**)	3	97	21	45	3	24	2	4
	Mn(TDCPP)Cl[c] (**3a**)	8	100	11	46	4	28	3	6
	Mn(TDCPP)Cl[c] (**3a**)	12	100	8	47	2	30	4	7
2	Mn(β-NO_2TDCPP)Cl (**3b**)	2	81	56	28	3	8	1	3
	Mn(βNO_2TDCPP)Cl (**3b**)	3.5	96	35	33	7	18	2	3
3	Mn(TF_5PP)Cl (**4a**)	2	76	58	33	0	0	6	2
4	Mn(β-NO_2TF_5PP)Cl (**4b**)	3	39	64	26	0	0	5	3
5	Mn(TDMPP)Cl (**5a**)	4	41	44	55	0	0	0	0
6	Mn(Cl_{16}TDMPP)Cl (**5b**)	3.8	44	77	23	0	0	0	0
7	No catalyst	4.5	0	–	–	–	–	–	–

[a] Reaction conditions: the substrate (0.3 mmol), the catalyst (1 μmol) and ammonium acetate (0.2 mmol) were stirred in CH_3CN at r.t. and 0.15 mmol of H_2O_2 (37.5 μl of the diluted solution in use) were added to each reaction mixture every 15 min.
[b] Determined by GC analyses.
[c] Reaction conditions as for Footnote a, but 1 μmol of catalyst was added to the reaction mixture for three times, at 0, 4 and 8 h.

Table 4
Results of the oxidation reactions of **2a**–**2d** with H_2O_2 catalysed by **3a**[a]

Entry	Substrate	[Conversion (%)][b], time	Products [selectivity (%)][b]				
1	 (**2a**)	[88][c], 6.5 h	 [26] (**2b**)	 [13] (**2c**)	 [49] (**2d**)	 [4] (**2e**)	 [5] (**2f**)
2	 (**2b**)	[8][c], 6 h	 [25] (**2d**)	 [75] (**2f**)			
3	 (**2c**)	[85][c], 4.5 h	 [95] (**2d**)	 [5] (**2f**)			
4	 (**2d**)	[10][c], 11 h	 [85] (**2f**)				

[a] Reaction conditions: the substrate (0.3 mmol), the catalyst (1 μmol) and ammonium acetate (0.2 mmol) were stirred in CH_3CN at r.t. and 0.15 mmol of H_2O_2 (37.5 μl of the diluted solution in use) were added to each reaction mixture every 15 min.
[b] Determined by GC analyses.
[c] The same reaction was repeated in the absence of the catalyst and no products were observed.

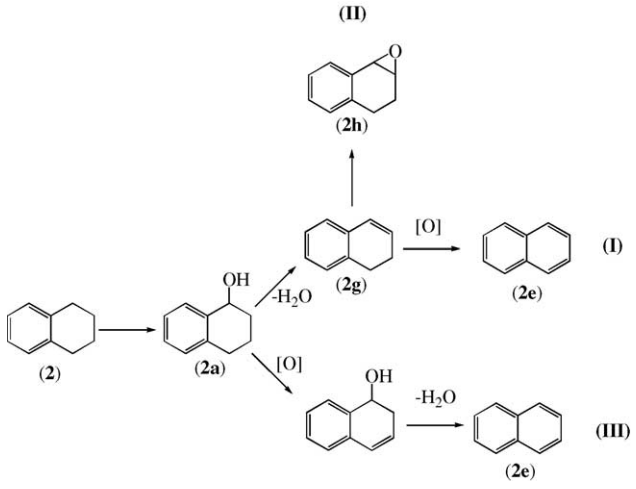
suggest that tetralol is presumably an important primary precursor in the catalytic oxidation of **2**, under such conditions.

The oxidation of 1-tetralone afforded, although in a low conversion (8% after 6 h), the 1,4-naphthoquinone as the major product and the 4-hydroxy-1-tetralone (**2d**) as the minor one (Table 4, entry 2). Compound **2d** was also obtained, but in high yield (95% of selectivity at 85% of conversion of the substrate), from the oxidation of diol **2c** (Table 4, entry 3). These results suggest that the oxidation of that diol is the more facile pathway to **2d**. From Table 4 (entry 4), we can also conclude that further oxidation of **2d** is a difficult process; naphthoquinone was detected but at very low conversion of the substrate and only after 11 h of reaction.

About the formation of naphthalene during the tetralin oxidation reaction, these results (Table 4, entries 1 and 3) suggest that 1-tetralol is a primary precursor of naphthalene, while 1,4-dihydroxytetralin (**2c**) is not. Therefore, the occurrence of naphthalene during the oxidation of 1-tetralol does not result from a double dehydration process, but it arises from alcohol dehydration and dehydrogenation.

In reactions catalysed by $PdCl_2$, the formation of naphthalene from tetralin was justified by an acid catalysed dehydration of 1-tetralol, followed by the catalytic oxidative dehydrogenation of 1,2-dihydronaphthalene [16] (Scheme 4, I). More recently, it was shown that dehydrogenation reactions are also performed in Mn(III) porphyrin oxidative catalysis [12,17]. In some experiments with 1,2-dihydronaphthalene (**2g**) [17], it was observed that the dehydrogenation competes with the epoxidation (Scheme 4, II), affording naphthalene (30%) and 1,2-epoxytetralin (65%), respectively.

However, in our case, the 1,2-dihydronaphthalene (**2g**) or the 1,2-epoxytetralin (**2h**) were never detected during the oxidation of 1-tetralol, even at a trace level. This led us to conclude that the formation of naphthalene from tetralin proceeds through the 1-tetralol intermediate by dehydrogenation of the alcohol as the first process, followed by the dehydration one (Scheme 4, III).



Scheme 4.

In accordance with previous literature data [18,19], naphthoquinone (**2f**) formation can proceed from the oxidation of naphthalene through the formation of 1-naphthol at an intermediate stage. However, recent results from our group [20] showed, under the same conditions used here for the tetraline oxidation, that naphthalene was oxidised to *anti*-1,2:3,4-naphthalene dioxide in 74% yield and only minor quantities of 1,4-naphthoquinone were observed. These results led to the conclusion that the products resulting from the oxidation of naphthalene are not obtained in the oxidation of tetralin. The small amount of 1,4-naphthoquinone observed during tetralin oxidation is probably resulting from the oxidation of compounds **2a**–**2d**.

It was demonstrated that the oxidations of substrates **2a**–**2d** are also catalytic processes, since no oxidation products were detected in the absence of the metalloporphyrin (Table 4).

From Table 3, we can observe that metalloporphyrins **3** are more effective catalysts in the oxidation of tetralin than metalloporphyrins **4** and **5**, since higher conversion rates were obtained. Catalysts **3** were also found to be more selective for the dioxygenated products. Under over-oxidation conditions, by the addition of other amounts of catalyst **3a**, the yield of the ketone **2d** can reach 30%. In the case of the tetralin oxidation, the catalyst **3b** also associates a high percentage of conversion with a good selectivity for the alcohol **2a**, after 2 h of reaction (entry 2).

In the indane and tetralin oxidation studies, the metalloporphyrin stability was determined by the ratio between the intensity of the Soret band at the beginning and after 2 h of reaction. The more resistant metalloporphyrin in the conditions used was always Mn(TDCPP)Cl (42% stability for indane and 28% for tetralin), whereas all the other metalloporphyrins were almost totally degraded (<5% stability).

3. Experimental

3.1. General details

^{1}H and ^{13}C NMR spectra were taken in $CDCl_3$ solutions, using a Bruker Avance 300 at 300.13 and 75.47 MHz, respectively. The chemical shifts are expressed in δ (ppm) values relatively to tetramethylsilane (TMS) as internal reference. Column chromatography was performed on silica gel (Merck silica gel 60, 70–230 mesh). Visible spectra were taken in a UV–vis Uvikom 922, Kontrom Instruments. Mass spectra were obtained using a VG Autospec Q mass spectrometer. GC/MS analyses were performed using a Finnigan Trace GC/MS (Thermo Quest CE instruments) using helium as the carrier gas (35 cm/s). GC-FID analyses were performed using a Varian Star 3400 CX chromatograph and hydrogen as the carrier gas (55 cm/s). In both cases fused silica Supelco capillary columns SPB-5 (30 m × 0.25 mm i.d.; 0.25 μm film thickness) were used. The gas chromatographic conditions were as follows: initial temperature (70 °C) during 1 min; temperature rate (18 °C/min); final temperature (260 °C); injector temperature (260 °C); detector temperature (270 °C). Aliquots were withdrawn from the reaction mixture and injected directly into the injector.

Hydrogen peroxide (30 wt.% solution in water) and acetonitrile were purchased from Riedel de Haën. Indane, tetralin, 1-indanol, 1*H*-indene, 2-indanol, 1-tetralol, naphthalene, 1-tetralone and 1,4-naphthoquinone were purchased from Aldrich. All other chemicals and solvents used herein were obtained from commercial sources and used as received or distilled and dried using standard procedures. Light petroleum was the fraction of bp 40–60 °C.

3.2. General oxidation procedure

In a typical experiment, the substrate (0.3 mmol), the catalyst (1 μmol) and ammonium acetate (0.2 mmol) were dissolved in acetonitrile (2 ml) and stirred at room temperature. Aqueous hydrogen peroxide (30% w/w), diluted in acetonitrile (2:5), was added to the reaction mixture in 37.5 μl aliquots every 15 min. The reaction was followed by GC analysis and was stopped when the product yields remained constant after two successive GC analyses. The reaction mixture was then poured into water and extracted with dichloromethane. The organic phase was dried with anhydrous sodium sulfate and concentrated using the rotary evaporator. The reaction mixtures were separated by silica gel column chromatography. Indane oxidation products were eluted with a (1:1) mixture of dichloromethane:light petroleum, affording **1b** as the first fraction, followed by **1a** and **1d**. Increasing the polarity of the eluent to dichloromethane, **1c** was obtained. For the separation of tetralin oxidation products, solvent mixtures of increasing polarity were used. Compounds **2b**, **2a**, **2d** and **2c** were successively eluted, respectively with dichloromethane:light petroleum (4:1), dichloromethane:light petroleum (9:1), dichloromethane:methanol (24:1) and dichloromethane: methanol (9:1).

3.2.1. 1-Indanol (*1a*)

^{1}H NMR δ: 1.81 (s-broad, 1H, O*H*), 1.89–2.00 (m, 1H, H-2), 2.43–2.54 (m, 1H, H-2), 2.77–2.87 (m, 1H, H-3), 3.01–3.11 (m, 1H, H-3), 5.24 (t, 1H, H-1, J = 6.0 Hz), 7.21–7.26, 7.40–7.43 (2m, 4H, H-4–7). ^{13}C NMR δ: 29.8 (C-3), 35.9 (C-2), 76.4 (C-1), 124.2, 124.9, 126.7, 128.3 (C-4,5,6,7), 143.3 (C-3a), 144.9 (C-7a).

3.2.2. 1-Indanone (*1b*)

^{1}H NMR δ: 2.66–2.70 (m, 2H, H-2), 3.13 (t, 2H, H-3, J = 5.9 Hz), 7.36 (ddd, 1H, H-6, J = 0.6, 7.2 and 7.5 Hz), 7.47 (d, 1H, H-4, J = 7.5 Hz), 7.58 (ddd, 1H, H-5, J = 0.9, 7.2 and 7.5 Hz), 7.75 (d, 1H, H-7, J = 7.5 Hz). ^{13}C NMR δ: 25.7 (C-3), 36.1 (C-2), 123.6 (C-4), 126.6, 127.1 (C-6, C-7), 134.5 (C-5), 136.9 (C-7a), 155.1 (C-3a), 207.1 (C-1).

*3.2.3. trans-1,3-Dihydroxyindane (**1c-1**)*

^{1}H NMR δ: 2.39 (t, 2H, H-2, J = 5.3 Hz), 5.46 (t, 2H, H-1,3, J = 5.3 Hz), 7.36–7.39 (m, 2H, H–Ar), 7.44–7.47 (m, 2H, H–Ar). MS (EI) *m/z* (rel. int., %): 150 ($M^{\bullet+}$, 7), 133 (12), 132 (100), 131 (60), 107 (32), 105 (39), 104 (82), 103 (62), 102 (13), 91 (15), 77 (64).

*3.2.4. cis-1,3-Dihydroxyindane (**1c-2**)*

^{1}H NMR δ: 1.92 (dt, 1H, H-2, J = 4.7 and 13.6 Hz), 2.90 (dt, 1H, H-2, J = 6.4 and 13.6 Hz), 5.10 (dd, 2H, H-1,3, J = 4.8 and 6.4 Hz), 7.36–7.39 (m, 2H, H–Ar), 7.44–7.47 (m, 2H, H–Ar). MS (EI) *m/z* (rel. int., %): 150 ($M^{\bullet+}$, 7), 133 (12), 132 (100), 131 (60), 107 (32), 105 (39), 104 (82), 103 (62), 102 (13), 91 (15), 77 (64).

*3.2.5. 3-Hydroxy-1-indanone (**1d**)*

^{1}H NMR δ: 2,26 (s-broad, 1H, O*H*), 2.64 (dd, 1H, H-2, J = 2.9 and 18.9 Hz), 3.15 (dd, 1H, H-2, J = 6.8 and 18.9 Hz), 5.46 (dd, 1H, H-3, J = 2.9 and 6.8 Hz), 7.48–7.53 (m, 1H, H–Ar), 7.67–7.78 (m, 3H, H–Ar). ^{13}C NMR δ: 47.2 (C-2), 68.6 (C-3), 123.3 (C-4), 125.8 (C-6), 129.6 (C-7), 135.3 (C-5), 136.4 (C-7a), 155.0 (C-3a), 203.1 (C-1). MS (EI) *m/z* (rel. int., %): 148 ($M^{\bullet+}$, 100), 147 (48), 131 (18), 130 (15), 120 (17), 119 (39), 105 (61), 103 (34), 102 (33), 91 (58), 77 (56).

*3.2.6. 1-Tetralol (**2a**)*

^{1}H NMR δ: 1.68 (s-broad, 1H, O*H*), 1.77–1.81 (m, 2H, H-2), 1.89–2.04 (m, 2H, H-3), 2.67–2.88 (m, 2H, H-4), 4.77 (d, 1H, H-1, J = 3.6 Hz), 7.08–7.11 (m, 1H, H–Ar), 7.18–7.21 (m, 2H, H–Ar), 7.41–7.44 (m, 1H, H–Ar).

*3.2.7. 1-Tetralone (**2b**)*

^{1}H NMR δ: 2.11–2.19 (m, 2H, H-2), 2.66 (dt, 2H, H-3, J = 6.1 and 13.1 Hz), 2.98 (t, 2H, H-4, J = 6.1 Hz), 7.26 (d, 1H, H-5, J = 7.5 Hz), 7.31 (t, 1H, H-7, J = 7.5 Hz), 7.48 (ddd, 1H, H-6, J = 1.3, 7.5 and 7.5 Hz), 8.04 (dd, 1H, H-8, J = 1.3 and 7.5 Hz). ^{13}C NMR δ: 23.2 (C-4), 29.6 (C-3), 39.10 (C-2), 126.6 (C-5), 127.1 (C-7), 128.7 (C-8), 132.5 (C-8a), 133.3 (C-6), 144.4 (C-4a), 198.4 (C-1).

*3.2.8. trans-1,4-Dihydroxytetralin (**2c-1**)*

^{1}H NMR δ: 2.02–2.09 (m, 4H, H-2,3), 2.62 (s-broad, 2H, O*H*), 4.76 (s-broad, 2H, H-1,4), 7.32–7.36 (m, 2H, H-5,8), 7.46–7.50 (m, 2H, H-6,7). ^{13}C NMR δ: 28.5 (C-2,3), 68.3 (C-1,4), 128.0 and 128.3 (C-5,6,7,8), 138.9 (C-4a,8a). MS (EI) *m/z* (rel. int., %): 164 ($M^{\bullet+}$, 0.8), 148 (1), 147 (12), 146 (100), 145 (32), 131 (32), 128 (22), 127 (15), 120 (34), 118 (29), 115 (20), 105 (31), 77 (24).

*3.2.9. cis-1,4-Dihydroxytetralin (**2c-2**)*

^{1}H NMR δ: 1.73 (s broad, 2H, O*H*), 1.78–1.88 (m, 2H, H-2,3), 2.29–2.33 (m, 2H, H-2,3), 4.83 (s-broad, 2H, H-1,4), 7.31–7.36 (m, 2H, H–Ar), 7.43–7.50 (m, 2H, H–Ar). ^{13}C NMR δ: 28.3 (C-2,3), 67.9 (C-1,4), 128.3 and 128.4 (C-5,6,7,8), 138.5 (C-4a,8a). MS (EI) *m/z* (rel. int., %): 164 ($M^{\bullet+}$, 0.8), 148 (1), 147 (12), 146 (100), 145 (32), 131 (32), 128 (22), 127 (15), 120 (34), 118 (29), 115 (20), 105 (31), 77 (24).

*3.2.10. 4-Hydroxy-1-tetralone (**2d**)*

^{1}H NMR δ: 2.02 (s-broad, 1H, O*H*), 2.14–2.26 (m, 1H, H-3), 2.38–2.48 (m, 1H, H-3), 2.62 (ddd, 1H, H-2, J = 4.5, 9.6 and 17.3 Hz), 2.96 (ddd, 1H, H-2, J = 4.5, 7.4 and 17.3 Hz), 5.00 (dd, 1H, H-4, J = 2.9 and 4.1 Hz), 7.39–7.48 (m, 1H, H–Ar), 7.58–7.65 (m, 2H, H–Ar), 8.03 (d, 1H, H-8, J = 7.7 Hz). ^{13}C NMR δ: 32.1 (C-3), 35.1 (C-2), 67.9 (C-4), 127.0 and 127.2 (C-7,5), 128.4 (C-8), 131.1 (C-8a), 134.1 (C-6), 145.3 (C-4a), 197.4 (C-1). MS (EI) *m/z* (rel. int., %): 162 ($M^{\bullet+}$, 16), 147 (12), 134 (77), 133 (22), 120 (20), 115 (20), 106 (22), 105 (100), 77 (33), 51 (15).

4. Conclusions

The oxidation of indane, 1*H*-indene, 1-indanol, 1-indanone, 2-indanol, tetralin, 1-tetralol, 1-tetralone, 1,4-dihydroxytetralin and 4-hydroxy-1-tetralone with hydrogen peroxide, in the presence of manganese(III) porphyrins, was studied, under mild conditions, using ammonium acetate as the co-catalyst. The conversion and selectivity of the reactions were found to be strongly dependent on the catalyst structure and on the reaction time. In reactions with catalysts **3**, high substrate conversions were obtained and the formation of dioxygenated products was observed.

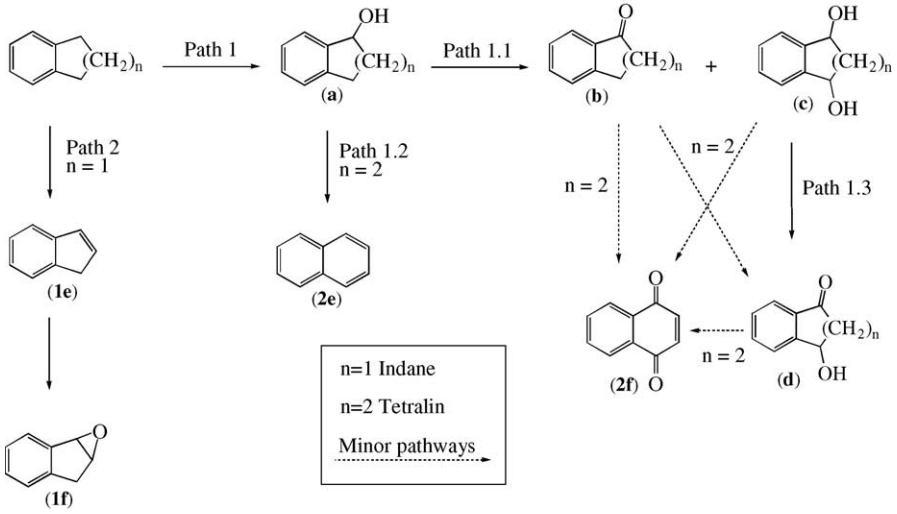
As far as we know, catalytic oxidation of indane and tetralin has been reported to give uncomplete reactions and only monooxygenated products were described [21,22]. However, the biocatalytic oxidation of benzocycloalkanes by enzymes from intact bacterial cultures was reported to produce mono and dioxygenated products, with high stereoselectivity [2,23]. It is an interesting result to obtain a selective multioxygenation of inert substrates in a single step reaction with chemical catalysts.

The described methodology, using porphyrin **3a**, allows the simple and selective preparation of 1-ketones and 4-hydroxyketones which are important compounds from the synthetic and biological points of view. Dioxygenated products were also obtained from the oxidation of 1-indanol and 1-tetralol in the presence of this catalyst. With porphyrin **3b** it was possible to achieve the highest yields for 1-alcohols, also important precursors for chemical synthesis [2].

Compounds resulting from oxidative dehydrogenation were also observed, particularly with the metalloporphyrins of type **4**, affording indene and indene oxide or naphthalene.

All studies performed on the oxidation of several potential reaction intermediates allowed us to establish a general reaction pathway which is shown in Scheme 5.

We have observed that the main pathway consists of successive benzylic oxidations (Scheme 5, path 1). Firstly there is the hydroxylation leading to the 1-alcohol (path 1), and this is then oxidised to the 1-ketone and to the dihydroxy analogues (path 1.1). The dihydroxyderivatives can then be



Scheme 5.

converted into the corresponding hydroxyketones (path 1.3). The ketones (**b)** and the hydroxyketones (**d**) are hardly oxidised under the conditions described.

The formation of the alkene and its further epoxidation have been observed, as minor pathways, mainly with indane (path 2). The production of naphthalene came from 1-tetralol, by the dehydrogenation/dehydration pathway (path 1.2).

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References

[1] R.A. Sheldon, in: B. Meunier (Ed.), Biomimetic Oxidations Catalysed by Transition Metal Complexes, Imperial College Press, London, 2000, p. 613.
[2] N.I. Bowers, D.R. Boyd, N.D. Sharma, P.A. Goodrich, M.R. Groocock, A.J. Blacker, P. Goode, H. Dalton, J. Chem. Soc., Perkin Trans. 1 (1999) 1453.
[3] H.G. Franck, J.W. Stadelhofer, Industrial Aromatic Chemistry, Springer-Verlag, Berlin, Heidelberg, 1988, p. 313.
[4] S. Ramesh, R.W. Franck, J. Chem. Soc., Chem. Commun. (1989) 960.
[5] A. Fournet, A.A. Barrios, V. Munoz, R. Hocquemiller, F. Roblot, A. Cave, Plant. Med. 60 (1994) 8.
[6] B. Meunier, A. Robert, G. Pratviel, J. Bernadou, in: K.M. Kadish, K.M. Smith, R. Guilard (Eds.), The Porphyrin Handbook, vol. 4, Academic Press, New York, 2000, p. 119.
[7] J. McLain, J. Lee, J.T. Groves, in: B. Meunier (Ed.), Biomimetic Oxidations Catalysed by Transition Metal Complexes, Imperial College Press, London, 2000, p. 91.
[8] W.R. Sanderson, Pure Appl. Chem. 72 (2000) 1289.
[9] P. Battioni, J.P. Renaud, J.F. Bartoli, M. Reina-Artiles, M. Fort, D. Mansuy, J. Am. Chem. Soc. 110 (1988) 8462.
[10] R.R.L. Martins, M.G.P.M.S. Neves, A.J.D. Silvestre, A.M.S. Silva, J.A.S. Cavaleiro, J. Mol. Catal. A: Chem. 137 (1999) 41.
[11] R.R.L. Martins, M.G.P.M.S. Neves, A.J.D. Silvestre, M.M.Q. Simões, A.M.S. Silva, A.C. Tomé, J.A.S. Cavaleiro, P. Tagliatesta, C. Crestini, J. Mol. Catal. A: Chem. 172 (2001) 33.
[12] S.L.H. Rebelo, M.M.Q. Simões, M.G.P.M.S. Neves, J.A.S. Cavaleiro, J. Mol. Catal. A: Chem. 201 (2003) 9.
[13] A.M.A.R. Gonsalves, J.M.T.B. Varejão, M.M. Pereira, J. Heterocycl. Chem. 28 (1991) 635.
[14] M. Autret, Z. Ou, A. Antonini, T. Boschi, P. Tagliatesta, K.M. Kadish, J. Chem. Soc., Dalton Trans. (1996) 2793.
[15] J.W. Buchler, in: D. Dolphin (Ed.), The Porphyrins, vol. 1, Academic Press, New York, 1978, p. 398, and references cited therein.
[16] K. Takehira, T. Hayakawa, H. Orita, M. Shimizu, Bull. Korean Chem. Soc. 8 (1987) 254.
[17] V. Maraval, J.-E. Ancel, B. Meunier, J. Catal. 206 (2002) 349.
[18] T. Higuchi, C. Satake, M. Hirobe, J. Am. Chem. Soc. 117 (1995) 8879.
[19] J.F. Bartoli, V.M. Mansuy, K.B. Ozette, M. Palacio, P. Battioni, D. Mansuy, Chem. Commun. (2000) 827.
[20] S.L.H. Rebelo, M.M.Q. Simões, M.G.P.M.S. Neves, A.M.S. Silva, J.A.S. Cavaleiro, Chem. Commun. (2004) 608.
[21] F. Bedioui, J. Devynck, C. Bied-Charreton, J. Mol. Catal. A: Chem. 113 (1996) 3.
[22] D. Mohajer, A. Rezaeifard, Tetrahedron Lett. 43 (2002) 1881.
[23] D.R. Boyd, N.D. Sharma, P.J. Stevenson, J. Chima, D.J. Gray, H. Dalton, Tetrahedron Lett. 32 (1991) 3887.