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

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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.

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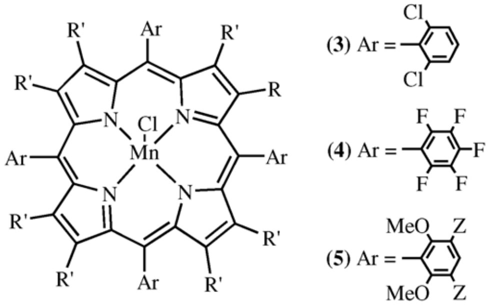


(**3a**)	Mn(TDCPP)Cl	R = R' = H
(**3b**)	Mn(β-NO_2TDCPP)Cl	R = NO_2; R' = H
(**4a**)	Mn(TF_5PP)Cl	R = R' = H
(**4b**)	Mn(β-NO_2TF_5PP)Cl	R = NO_2; R' = H
(**5a**)	Mn(TDMPP)Cl	R = R' = H; Z = H
(**5b**)	Mn(Cl_{16}TDMPP)Cl	R = R' = Cl; Z = Cl

Scheme 1.

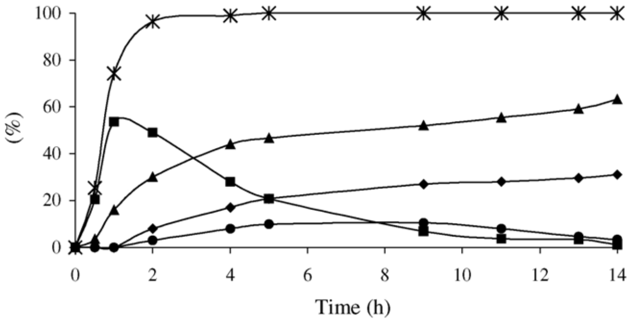


Fig. 1. Conversion and product yield percentages in the course of the oxidation reaction of indane catalysed by metalloporphyrin **3a** [(✱) conversion; (■) **1a**; (▲) **1b**; (●) **1c**; (♦) **1d**]. Reaction conditions: the substrate (0.3 mmol), the catalyst (1 µmol was added to each reaction mixture 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.

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*)

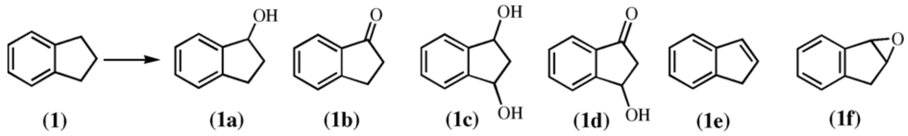
In the oxidation reactions of indane in the presence of the Mn(III) porphyrins, the conversion of substrate and distribution pattern of the products were found to be dependent on the catalyst structure and on the reaction time (Scheme 2 and Table 1). Different metalloporphyrins led to diverse selectivity 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**).

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.