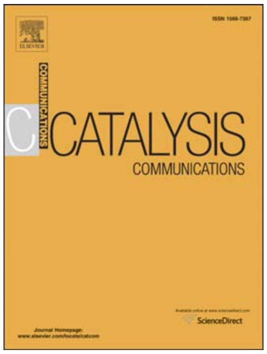

A green and sustainable method for the oxidation of 1,3-dihydrobenzo[*c*]thiophenes to sulfones using metalloporphyrin complexes

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A GREEN AND SUSTAINABLE METHOD FOR THE OXIDATION OF 1,3-DIHYDROBENZO[*C*]THIOPHENES TO SULFONES USING METALLOPORPHYRIN COMPLEXES

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Abstract

Two efficient methods are reported for the oxidation of 1,3-dihydrobenzo[*c*]thiophenes to sulfones in good to high yields using H_2O_2 in the presence of catalytic amounts of porphyrin-based catalysts in ethanol or acetonitrile as solvents at room temperature. The presence of electron-donating or electron-withdrawing groups, in the benzene ring of 1,3-dihydrobenzo[*c*]thiophene, is well tolerated.

Keywords: Thiophenes; Oxidation; Catalysis; Metalloporphyrins; Hydrogen peroxide; Sulfones

1. Introduction

1,3-Dihydrobenzo[*c*]thiophene 2,2-dioxides, also named sulfones, are well-known cyclic diene precursors in Diels-Alder cycloaddition reactions [1,2]. These compounds are stable intermediates for the generation of *ortho*-benzoquinodimethanes (*o*-xylylenes) or benzocyclobutenes, which can be trapped *in situ* by several dienophiles, yielding the corresponding cycloadducts [2]. *Ortho*-benzoquinodimethanes are particularly useful in organic synthesis as transient and highly reactive dienes, generated via chelotropic loss (thermal extrusion) of sulfur dioxide [2]. These compounds have a wide variety of applications, namely in the synthesis of several natural products and heterocyclic compounds [3]. In our group, they have been used in Diels-Alder cycloaddition reactions with several dienophiles such as porphyrin [4,5], fullerene [6], pyrazole [7], chromone [8-10], chalcone [11], and quinolone [12] derivatives. Therefore, the development of new, sustainable methods to perform the oxidation of 1,3-dihydrobenzo[*c*]thiophenes to the corresponding sulfones is of great interest.

Several methods involving different oxidation agents have already been reported to obtain sulfones from the adequate dihydrobenzo[*c*]thiophenes. However, these methods usually require the use of stoichiometric amounts of hazardous oxidants, such as *m*-chloroperbenzoic acid (MCPBA) and solvents (e.g. chloroform, methylene chloride), which generate a large amount of dangerous wastes. The research and application of "Green Chemistry" principles has led to the development of other methods such as the use of hydrogen peroxide (in non-chlorinated solvents), as eco-friendlier alternative oxidation systems, both environmentally and economically desirable [13,14]. Among the catalysts proposed for the oxidation of sulfides, thiophene and benzothiophenes with hydrogen peroxide are those based on water-soluble metallophthalocyanines [15], polyoxometalates [16-18], WOx/ZrO_2 [19,20], titanium-containing molecular sieves [21], vanadium silicates [22],V_2O_5/TiO_2, V_2O_5/Al_2O_3 [23-25], supported $PdCr_2O_3$, MnOx, and Co-Mo/Al_2O_3 [26], and the manganese(IV) complex salt $[L_2Mn_2O_3](PF_6)_2$ (L=1,4,7-trimethyl-1,4,7-triazacyclononane) [27]. Acetic acid [16,17,27], acetonitrile [15,18,19,21,22,25,26], or other polar solvents [19,25] were added to the reaction mixture to enhance the catalytic activity. Oxidation of benzothiophene by hydrogen peroxide in the presence of crown ethers with or without a metal catalyst has been studied as well [28,29]. Recently, we have reported the excellent performance of metalloporphyrins as catalysts in the oxidation of sulfides and recalcitrant benzothiophenes and dibenzothiophenes with hydrogen peroxide [30,31]. Those results and the fact that only a few reports considered the use of iron(III) and manganese(III) porphyrin catalytic systems in the oxidation of organosulfur derivatives [32], prompted us to study for the first time the sulfoxidation of a series of 1,3-dihydrobenzo[*c*]thiophenes with hydrogen peroxide catalysed in the presence of manganese(III) and iron(III) porphyrin complexes, aiming to develop a facile and eco-friendly approach for important diene precursor sulfones.

2. Experimental

2.1. Materials and instrumentation

All solvents and reagents were used as received without further purification. Hydrogen peroxide (30% w/w aqueous solution) and ammonium acetate were purchased from Sigma-Aldrich. The ^{1}H NMR spectra were recorded on a Bruker Avance 300 at 300.13 MHz, using $CDCl_3$ as solvent and TMS as internal reference. The GC-FID analyses were performed on a Varian 3900 chromatograph using helium as the carrier gas (30 cm/s) and a fused silica capillary DB-5 type column (30 m x 0.25 mm i.d., 0.25 μm film thickness). The GC-MS analyses were performed on an Agilent 6890N chromatograph connected to an Agilent 5973 mass quadrupole selective detector operating with an electron impact mode at 70 eV, using helium as the carrier gas (35 cm/s) and a fused silica capillary DB-1 type column (30 m x 0.25 mm i.d., 0.15 μm film thickness).

2.2. Substrate and catalyst synthesis

The selected metalloporphyrin catalysts, chloro[5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinate]manganese(III) and chloro[5,10,15,20-tetrakis(4-dimethylamino-2,3,5,6-tetrafluorophenyl)porphyrinate]iron(III), that will be referred as catalysts (**I**) and (**II**), respectively (Figure 1), were synthesized according to well-established procedures in our laboratory [33,34]. The 1,3-dihydrobenzo[*c*]thiophenes **1-4** (Table 1) were obtained using well established procedures [9,13]. In particular, the experimental procedures for the preparation of thiophenes **2** and **4** as well as the corresponding NMR data are presented in supplementary information (please see ESI).

2.3. Catalytic studies

In the general procedure for the catalytic assays with the substrates **1-4**, the substrate [0.3 mmol for the Substrate/Catalyst (S/C) molar ratio of 300; 0.9 mmol for the S/C molar ratio of 900; 1.8 mmol for the S/C molar ratio of 1800], the internal standard (chlorobenzene, 0.3 mmol) and the catalyst (1.0 x10^{-3} mmol) were dissolved in the appropriate solvent (acetonitrile in the case of manganese catalyst **I** and ethanol for the iron catalyst **II**). Only in the experiments involving the manganese porphyrin a co-catalyst was added to the reaction mixture, namely ammonium acetate (0.12 mmol).

The reaction mixture was kept under magnetic stirring, in the absence of light, and at controlled temperature between 22-25 ºC. Finally, the oxidant [30% (w/w) H_2O_2 aqueous solution diluted 1:10 in the same solvent of the reaction] was progressively added in aliquots corresponding to half of the substrate amount (0.15 mmol each).

3. Results and discussion

The commonly used synthetic procedure to oxidize the 1,3-dihydrobenzo[*c*]thiophenes to the corresponding 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxides or sulfones requires a mixture of oxone and aluminium oxide in refluxing chloroform for 4-6 h which, besides being time consuming, is not an environmentally safe strategy at all. Alternatively, in some cases the oxidation can be performed using *m*-chloroperbenzoic acid (2.2 equiv) in dichloromethane at room temperature, which are both hazardous oxidant and solvent, respectively. Recently, we have demonstrated the success of metalloporphyrin/H_2O_2 catalytic systems in the sulfoxidation of benzo- and dibenzothiophenes [30,31]. Encouraged by our previous results we decided to apply a similar approach to the oxidation of 1,3-dihydrobenzo[*c*]thiophene derivatives **1-4**. Herein we present the results of the catalytic tests with substrates **1-4** using two well-known and very efficient metalloporphyrins: catalysts (**I**) and (**II**) (Scheme 1). The results are summarized in Table 1. Both catalytic systems [catalyst **I**/H_2O_2 and catalyst **II**/H_2O_2] proved to be very efficient, affording excellent conversion values. In fact, for all the substrates, and using a substrate/catalyst (S/C) molar ratio of 300, it was possible to achieve conversions of 99.9 % with both catalysts (**I**) and (**II**). However, the iron complex (**II**) appears to be more efficient as it allows shorter reaction times, under similar reaction conditions.

At the end of the catalysed reactions, all the substrates (**1-4**) are partially or fully converted into the corresponding dioxide products (**5-8**), as represented in Scheme 1. In fact, these results were observed for all the assays performed with catalyst (**I**), for which the GC-MS and ^{1}H NMR analyses of the isolated products confirmed the structure of sulfones **5-8**. In the case of substrate **3**, and for the experiments involving catalyst (**II**), the formation of sulfone **7** was initially detected. However, it was verified that under these conditions the sulfone is not stable, affording several non-identified compounds with lower retention time than the starting thiophene **3**.

In general, when comparing the presently disclosed methodology to obtain 1,3-dihydrobenzo[*c*]thiophene 2,2-dioxides (sulfones) with the already established ones, besides overcoming the principal environmental issues (chlorinated solvents are no longer required, reactions are performed at room temperature and H_2O_2 is used as oxidant) this new methodology is also faster. The procedures followed in the metalloporphyrin catalysed reactions reveal some differences, depending on the metal present in the macrocycle core. These differences are attributed to distinct catalytic species involved for manganese or iron complexes, and are related with the solvent used in the reaction and the presence or the absence of a co-catalyst. For all the assays with catalyst (**I**) an aprotic solvent (acetonitrile) and a co-catalyst (ammonium acetate) are used, while whenever the iron catalyst (**II**) is employed the solvent needs to be protic (ethanol) and the reactions are performed in the absence of a co-catalyst [35].

Considering the above-mentioned differences, in general the use of catalyst (**II**), besides being more efficient, also allows the establishment of a greener procedure. Moreover, in this case, the sulfone easily precipitates in the reaction medium (ethanol), as exemplified in figure 2, thus contributing to a simpler and efficient purification process.

Thinking on the possibility of applying this sustainable procedure to a larger scale conditions, additional scale-up experiments were performed in the presence of the iron catalyst (**II**). Therefore, using substrate **1** as a model reaction, its oxidation was studied using higher quantities of substrate but maintaining the same amount of catalyst (S/C molar ratios of 900 and 1800). Thus, as can be observed in Table 1, the excellent efficiency, namely the selectivity for sulfone **5** (100%) at conversions of 99.9% is maintained for the S/C molar ratio of 900. For the S/C molar ratio of 1800, the results merit also to be highlighted, since with a conversion of 91% the sulfoxide is now the main product (selectivity of 82%). So, depending on the S/C molar ratio, it is possible to favour efficiently the formation of the sulfone or the sulfoxide products.

4. Conclusions

The use of metalloporphyrin catalysts in the sulfoxidation of 1,3-dihydrobenzo[*c*]thiophenes using hydrogen peroxide, as oxidant, proved to be a highly efficient and environmentally friendly approach. For all the substrates tested excellent conversions (99.9%) were observed, generally affording the correspondent dioxide products, which were isolated and characterized.

Despite both catalysts (**I** and **II**) remain highly efficient, in general the iron complex (**II**) proved to be more active in the oxidations and allows also the use of a more sustainable synthetic procedure. The solvent used in the reactions with complex (**II**) is ethanol, no co-catalyst is necessary, and the products precipitate in the reaction medium facilitating its isolation.

Acknowledgments

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A GREEN AND SUSTAINABLE METHOD FOR THE OXIDATION OF 1,3-DIHYDROBENZO[*C*]THIOPHENES USING METALLOPORPHYRIN COMPLEXES

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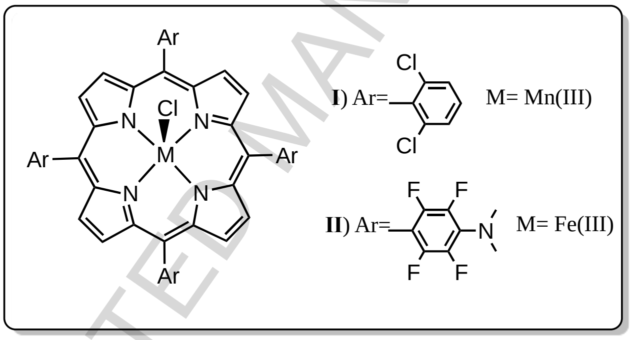


Figure 1- Structure of the catalysts used in the study

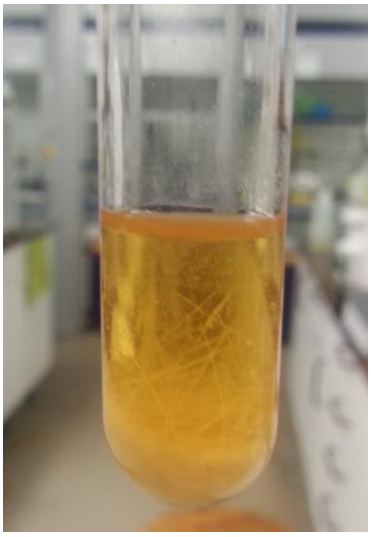
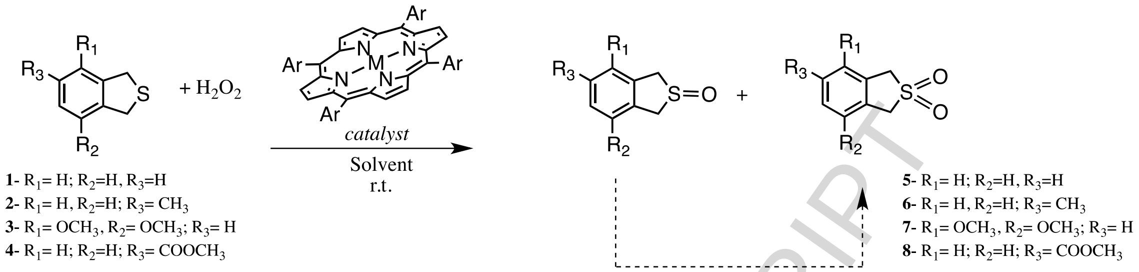


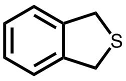
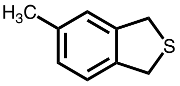
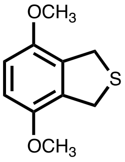
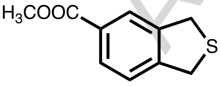
Figure 2- Illustration of the sulfone precipitation at the end of reaction if performed in ethanol



Scheme 1- General sulfoxidation of 1,3-dihydrobenzo[*c*]thiophenes using hydrogen peroxide in the presence of porphyrin catalysts

A GREEN AND SUSTAINABLE METHOD FOR THE OXIDATION OF 1,3-DIHYDROBENZO[*C*]THIOPHENES TO SULFONES USING METALLOPORPHYRIN COMPLEXES

Table 1. Results obtained in the oxidation of substrates (**1-4**) with H_2O_2 catalysed by the metalloporphyrins (**I** and **II**)[a]

Substrates	**Catalyst**	**S/C molar ratio**	**Conversion (%)**	**Product selectivity (%)**		**Time (min)**
				S=O	SO_2	
 **(1)**	**I**	300	99.9	-	100	120
	II	300	99.9	-	100	90
	II	900	99.9	-	100	90
	II	1800	90.9	88	12	90[#]
 **(2)**	**I**	300	99.9	-	100	120
	II	300	99.9	-	100	60
 **(3)**	**I**	300	99.9	18	82	90[§]
	II	300	85.0	*	*	30
 **(4)**	**I**	300	99.9	-	100	120
	II	300	99.9	-	100	90

[a] The substrate (0.3 mmol for the S/C molar ratio of 300; 0.9 mmol for the S/C molar ratio of 900; 1.8 mmol for the S/C molar ratio of 1800) was dissolved in 2.0 mL of the appropriate solvent (CH_3CN for catalyst **I** and ethanol for catalyst **II**) and kept under magnetic stirring at 22-25 ºC in the presence of the catalyst (**I** or **II**, 1.0 x 10^{-3} mmol). The oxidant, diluted 1:10 in the same solvent of the reaction, was progressively added at regular intervals of 15 min in small aliquots, each corresponding to a half-substrate amount. The conversion and selectivity values are the result of at least two essays. [#]Under these conditions the conversion and selectivity values were in the range of ±2.5%. [§]Under these conditions the selectivity values were in the range of ±1%. *The 85% of conversion after 30 min of reaction were determined by GC-MS. Under these conditions, the sulfoxide and the sulfone undergo further oxidation affording several non-identified compounds.

GRAPHICAL ABSTRACT

A GREEN AND SUSTAINABLE METHOD FOR THE OXIDATION OF 1,3-DIHYDROBENZO[*C*]THIOPHENES TO SULFONES USING METALLOPORPHYRIN COMPLEXES

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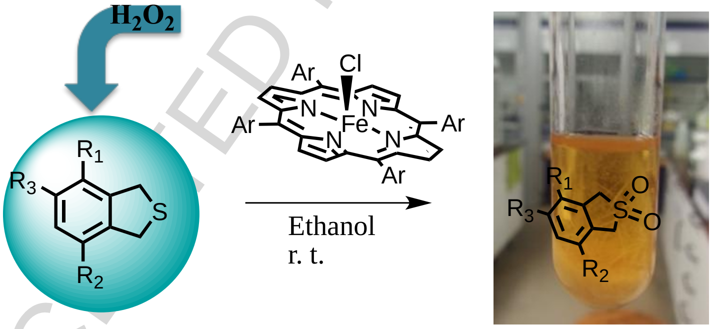

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Highlights

A green and sustainable approach for the oxidation of 1,3-dihydrobenzo[*c*]thiophenes.

Metalloporphyrins and hydrogen peroxide proved to be a highly efficient at r.t..

Excellent conversions (99.9%) were observed, affording the correspondent sulfones.

For the iron(III) porphyrin the products precipitate directly in the reaction medium.

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