Catalysis Communications 56 (2014) 68–71

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

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

Gustavo da Silva [a,1], Sónia M.G. Pires [a,1], Vera L.M. Silva [a,*], Mário M.Q. Simões [a,**], M. Graça P.M.S. Neves [a,***], Susana L.H. Rebelo [b], Artur M.S. Silva [a], José A.S. Cavaleiro [a]

[a] *QOPNA, Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal*
[b] *REQUIMTE, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre, 4169-007 Porto, Portugal*

ARTICLE INFO

Article history:
Received 14 June 2014
Received in revised form 25 June 2014
Accepted 26 June 2014
Available online 12 July 2014

Keywords:
Thiophenes
Oxidation
Catalysis
Metalloporphyrins
Hydrogen peroxide
Sulfones

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.

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 have 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

---

* Corresponding author. Tel.: +351 234 370 200; fax: +351 234 370 084.
** Corresponding author. Tel.: +351 234 370 713; fax: +351 234 370 084.
*** Corresponding author. Tel.: +351 234 370 710; fax: +351 234 370 084.
E-mail addresses: verasilva@ua.pt (V.L.M. Silva), msimoes@ua.pt (M.M.Q. Simões), gneves@ua.pt (M.G.P.M.S. Neves).

[1] These two authors contributed equally to this work.

http://dx.doi.org/10.1016/j.catcom.2014.06.032

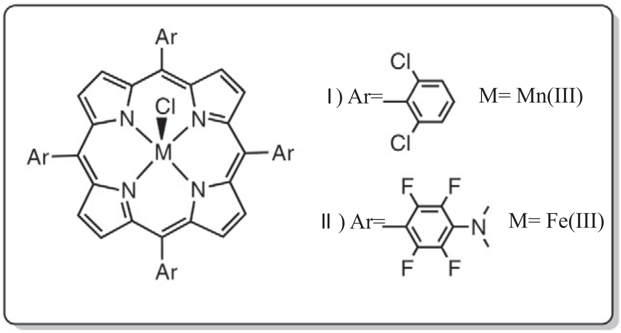


Fig. 1. Structure of the catalysts used in the study.

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 × 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 × 0.25 mm i.d., 0.15 μm film thickness).

2.2. Substrate and catalyst synthesis

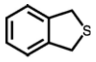
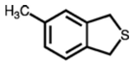
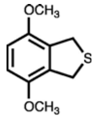
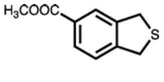
The selected metalloporphyrin catalysts, chloro[5,10,15,20-tetrakis(2,6-dichlorophenyl)porphyrinate]manganese(III) and chloro [5,10,15,20-tetrakis(4-dimethylamino-2,3,5,6-tetrafluorophenyl) porphyrinate]iron(III), that will be referred as catalysts (**I**) and (**II**), respectively (Fig. 1), were synthesized 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 (1.0×10^{-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 and 25 °C. 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.

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[b]
 **(2)**	**I**	300	99.9	–	100	120
	II	300	99.9	–	100	60
 **(3)**	**I**	300	99.9	18	82	90[c]
	II	300	85.0	[d]	[d]	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 °C in the presence of the catalyst (**I** or **II**, 1.0×10^{-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.

[b] Under these conditions the conversion and selectivity values were in the range of ±2.5%.

[c] Under these conditions the selectivity values were in the range of ±1%.

[d] The 85% of conversion after 30 min of reaction was determined by GC-MS. Under these conditions, the sulfoxide and the sulfone undergo further oxidation affording several non-identified compounds.