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Enantiomeric epoxidation of 4-chlorostyrene with H_2O_2 catalysed by robust chloromanganese(III)-5,10,15,20-tetrakis-[2-chloro-6-(2,3,4,6-tetraacetyl-*O*-β-D-glucosyl)phenyl]porphyrins

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Abstract

Three new chiral manganese(III) porphyrins bearing chloro and glucosyl substituents have been used as catalysts for enantiomeric epoxidation of 4-chlorostyrene in the presence of diluted hydrogen peroxide as oxygen donor. With such complexes enantiomeric excesses (22%) are obtained, in the presence of 4-tert-butylpyridine or 2-methylimidazole with a very low destruction of the catalysts (ca. 5%) after 4 h of epoxidation.

Keywords: Alkenes; Epoxidation; Porphyrins; Asymmetric epoxidation; Chiral induction; Glycosylated porphyrins

1. Introduction

The most attractive aspect of cytochrome P-450 monooxygenases is that they are able to perform chiral recognition and enantioselective oxygenation of alkenes [1]. This can be mimicked using synthetic catalysts. Numerous superstructured metalloporphyrins with a rigid chiral cavity around the metal center are particularly convenient compounds for this purpose [2–4]. The catalytically active species are obtained by reaction of various oxidizing agents with Fe(III) or Mn(III) metalloporphyrins [5].

Attachment of acetylated glucose residues at the *ortho* positions of a substituted *meso*-tetraphenylporphyrin via ether linkages forms chiral binding sites available for the substrate on both faces of the porphyrin ring [6]. Manganese(III) and iron(III) complexes of these porphyrins catalyze the epoxidation of styrene derivatives with enantiomeric excesses from 23 to 33% depending on the atropoisomers when PhIO, $KHSO_5$ or LiOCl are used [7,8].

By contrast, these metalloporphyrins are expected to be insufficiently robust against catalyst destruction when H_2O_2 is used as the source of oxygen at room temperature. Furthermore, H_2O_2 is particularly interesting for two main reasons: (i) water is the side product of H_2O_2 after an oxidation reaction and, (ii) no undesired residues can be formed in bleaching methods, in contrast to processes using a chlorine-containing oxidant such as LiOCl. For these reasons, hydrogen peroxide is regarded as a clean oxidant, suitable for large scale applications, and is a cheap reagent.

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However, the oxygenation catalysts are often bleached by hydrogen peroxide because it is too reactive in transition metal catalyzed oxidations. To overcome this limitation, we have developed new glycosylated compounds whereby electron withdrawing substituents are introduced at each *ortho* aryl position. In fact, introduction of electron-withdrawing substituents on the four *meso* aryl rings (so called second generation catalysts [9–11]) and on the β-pyrrolic positions (third generation catalysts [12–16]) induces a stabilization of metalloporphyrins towards an oxidation degradation during catalysis and also increases the reactivity to the substrate by generating a more electrophilic metal-oxo intermediate.

The main object of the present report is to describe the design and synthesis of new series of tetraphenylporphyrin derivatives bearing acetylated-β-D-glucosyl chiral moieties linked at the *ortho* position and one chlorine atom at the other *ortho'* position of each *meso* phenyl group [17]. In these compounds, regarded as second generation catalysts, the glycosylated residues give a chiral environment of the catalytic site, whereas the presence of chloro atoms reinforces the stability and the reactivity of the catalysts. Oxidative properties towards 4-chlorostyrene were then investigated using H_2O_2 as oxidant and an N-donor molecule as co-catalyst.

2. Materials and methods

2.1. Chemicals

All chemicals used were of reagent grade and were purchased from Aldrich, except for α-1-bromo-2,3,4,6-tetraacetylglucose (Fluka). CH_2Cl_2 was purified by distillation over K_2CO_3 for the free base porphyrin synthesis and over CaH_2 for the oxidation reactions.

Merck silica gel 60 (0.04–0.06 mm) was used for column chromatography. Merck precoated plates (silica gel 60, 2 mm) were used for preparative thin layer chromatography.

4-Chlorostyrene was purified by alumina microcolumn chromatography. The chloro-Mn(III)-5,10,15,20-tetrakis-(2,6-dichlorophenyl)porphyrin [Mn(TDCPP)Cl] derivative was synthesized by a previously described method [18] and was used as reference.

2.2. Instrumentation

Elemental analysis were carried out by the Service Central de Microanalyse du CNRS, Gif-Sur-Yvette, France. ^1H NMR spectra were recorded on a Bruker AM 200 spectrometer and chemical shift values are in ppm relative to TMS.

The enantiomeric excesses (ee's) of the epoxide produced were determined by ^1H NMR using tris-(3-heptafluoropropyl-hydroxymethylene)-*d*-camphorato)europium(III) after isolation of the products.

The column used in GC analysis was a wide bore CP-Sil-5-CB (25 m/0.53 mm) from Chrompack running at 10.8 ml/min of He flow equipped with a flame ionization detector.

Optical spectra in the Soret and visible regions were recorded using a Varian DMS 200 spectrometer.

Cyclic voltammetry studies were carried out with an EGG M 263 potentiostat. All potentials are referred to the saturated calomel electrode. The working electrode was a 3 mm diameter glassy carbon disk. The counter electrode was a platinum wire. The temperature of all experiments was 20°C. The solution were purged with argon and an argon atmosphere was maintained during the experiments.

2.3. Synthesis of 2-chloro-6-hydroxybenzaldehyde 1 [19]

A suspension of 2-chloro-6-fluorobenzaldehyde (10 g, 63 mmol) in NaOH aqueous solution (0.3 M, 700 ml) was magnetically stirred at 75°C for 40 h. The mixture was cooled at room temperature and extracted with ether (2 × 150 ml) to separate the unchanged substrate. The

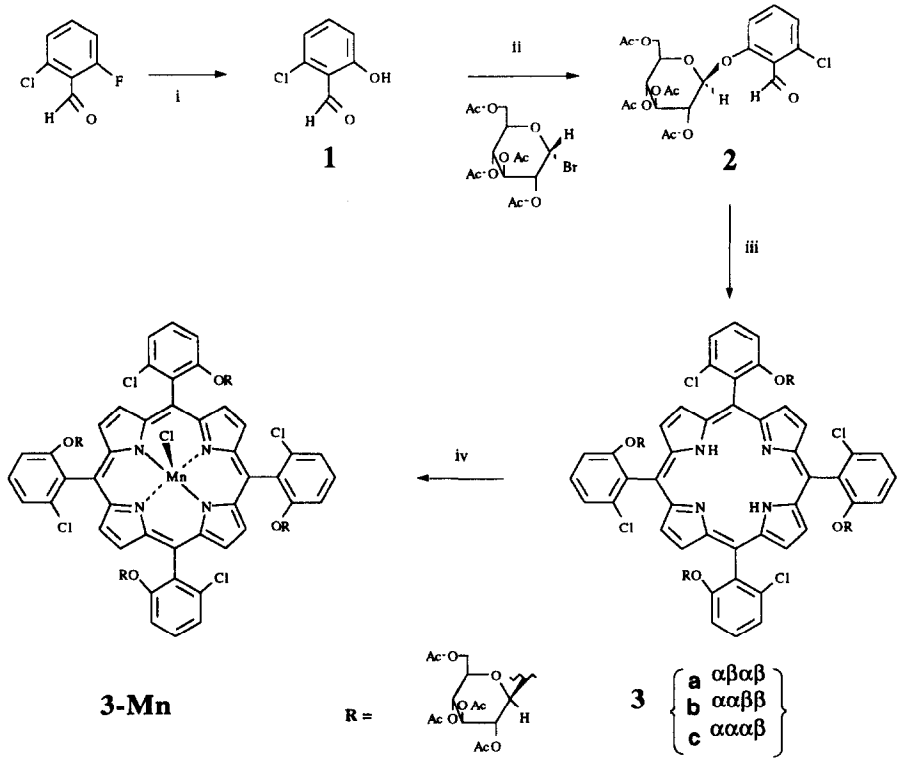
aqueous phase was acidified with concentrated HCl (18 ml) and extracted with ether (3 × 150 ml). The organic phases were dried on Na_2SO_4, filtered and evaporated in vacuum. The solid residue was purified by chromatography on a silica gel column eluted with a mixture of pentane/ether (1/1, v/v) to afford compound **1** as a white solid with 51% yield (5.1 g).

^{1}H NMR ($CDCl_3$) δ ppm 11.9 (1H, s, OH), 10.4 (1H, s, CHO), 7.6–6.7 (3H, m, H phenyl).

2.4. Synthesis of 2-chloro-6-(2,3,4,6-tetraacetyl-β-D-glucosyl)benzaldehyde 2

A solution of compound **1** (6.4 g, 40.9 mmol) in CH_2Cl_2 (45 ml) was vigorously stirred at room temperature with an aqueous solution of NaOH (5%, 63 ml) and tetrabutylammonium bromide (2 g, 5.2 mmol). A CH_2Cl_2 solution (15 ml) of crude compound α-1-bromo-2,3,4,6-tetraacetylglucose (9 g, 22 mmol) was added to the mixture and the resulting solution was stirred for 3 days at room temperature. After separation, the organic layer was washed with aqueous NaOH solution (5%, 2 × 50 ml), water then dried over sodium sulfate. After filtration and evaporation in vacuum the yellow oil was chromatographed on a silica gel column using a mixture of ethyl acetate/hexane (1/1, v/v) to afford compound **2** as a yellow solid after crystallization from ethanol (5.9 g, 55%).

Anal. Calcd for $C_{21}H_{23}O_{11}Cl$: C, 51.81; H, 4.76, Cl, 7.28. Found: C, 51.94; H, 4.77; Cl, 7.36; ^{1}H NMR ($CDCl_3$); δ ppm: 10.35 (s, 1H, CHO), 7.39 (t, 1H, H_4 phenyl), 7.09 (dd, 2H, H_3, H_5 phenyl), 5.31 (m, 2H, $H_{2'}$, $H_{3'}$ 'ose'), 5.16 (m, 2H, $H_{1'}$, $H_{4'}$ 'ose'), 4.21 (m, 2H, $H_{6'}$, $H_{6''}$ 'ose'), 3.85 (m, 1H, $H_{5'}$ 'ose'), 2 (s, 12 H, acetyl)



Scheme 1.

2.5. Synthesis of 5,10,15,20-tetrakis[2-chloro-6-(2,3,4,6-tetraacetyl-O-β-D-glucosyl)phenyl] porphyrins 3

Pyrrole (152 μl, 2.2 mmol) in CH_2Cl_2 (22 ml) and protected β-D-glycosyl benzaldehyde **2** (1.07 g, 2.2 mmol) in the same solvent (22 ml) were added separately to CH_2Cl_2 (240 ml) and purged with argon for 30 min. The mixture was stirred under an argon atmosphere for a further 10 min after which a BF_3–etherate solution (1 ml, 0.5 M) in CH_2Cl_2 was added. The mixture was stirred overnight at room temperature. Chloranil (1 g, 4.06 mmol) was added. After reflux for 4 h, 10 g of silica gel was added to the solution and the solvent was evaporated under vacuum. The absorbed products were placed on the top of a silica gel column and eluted with a mixture of CH_2Cl_2/ether (5/1, v/v) to separate the porphyrins from the reaction mixture. The porphyrin red band was then collected and the atropoisomers were separated by chromatography on a silica gel column using the same eluent. They were purified by thin layer chromatography, eluted once with CH_2Cl_2/ether (5/1, v/v) then twice with toluene/MeCN (3/2, v/v).

The αβαβ, ααββ and αααβ atropoisomers were separately crystallized from CH_2Cl_2/heptane to afford **3a** (1%), **3b** (3%), **3c** (5%) (Scheme 1).

Anal. Calcd for $C_{100}H_{98}N_4O_{40}Cl_4$ (αααβ): C, 56.22; H, 4.63; N, 2.62; Cl, 6.55. Found: C, 57.55; H, 4.77; N, 3.05; Cl, 6.35. ^1H NMR ($CDCl_3$) δ ppm: **3a**: 8.78 (s, 4H, pyr), 8.56 (s, 4H, pyr), 7.73 (m), 7.65 (m), 7.59 (m) (12H, phenyl), 4.76 (t, 4H, $H_{4'}$ 'ose'), 4.66 (d, 4H, $H_{1'}$ 'ose', $J = 8$ Hz), 4.33 (t, 4H, $H_{3'}$ 'ose'), 4.20 (m, 12H, $H_{2'}$, $H_{6'}$, $H_{6''}$ 'ose'), 3.51 (m, 4H, $H_{5'}$ 'ose'), 2.15 (s), 1.85 (s), 1.19 (s), −1.26 (s, 48H, acetyl), −2.74 (s, 2H, NH).

3b: 8.74 (d), 8.66 (d), 8.66 (s), 8.56 (s) (8H, pyr), 7.78 (d), 7.69 (dt), 7.60 (dd), 7.54 (d) (12H, phenyl), 4.92 (d, 2H, $H_{1'}$ 'ose', $J = 8$ Hz), 4.80 (t, 2H, $H_{4'}$ 'ose'), 4.67 (t, 2H, $H_{3'}$), 4.64 (t, 2H, $H_{4'}$ 'ose'), 4.49 (d, 2H, $H_{1'}$ 'ose', $J = 8$ Hz), 4.30 (m, 2H, $H_{3'}$ 'ose'), 4.25 (m, 4H, $H_{6'}$, $H_{6''}$ 'ose'), 4.20 (m, 2H, $H_{2'}$ 'ose'), 4.16 (m, 2H, $H_{2'}$ 'ose'), 4.10 (m, 2H, $H_{6'}$, $H_{6''}$ 'ose'), 3.94 (dd, 2H, $H_{6'}$, $H_{6''}$ 'ose'), 3.75 (m, 2H, $H_{5'}$ 'ose'), 3.43 (m, 2H, $H_{5'}$ 'ose'), 2.17 (s), 2.05 (s), 1.87 (s), 1.78 (s), 1.33 (s), 0.77 (s), −0.10 (s), −1.85 (s) (48H, acetyl), −2.63 (s, 2H, NH).

3c: 8.71 (d), 8.66 (dd), 8.64 (d), 8.60 (d), 8.59 (s), 8.56 (s) (8H, pyr), 7.72 (m), 7.65 (m), 7.52 (m) (12H, phenyl), 5.28 (d), 5.25 (d), 4.97 (d) (3H, $H_{1'}$ 'ose', $J = 8$ Hz), 4.93 (t), 4.89 (t) (2H, $H_{3'}$ 'ose'), 4.86 (m, 2H, $H_{4'}$ 'ose'), 4.65 (t, 1H, $H_{3'}$ 'ose'), 4.50 (d, 1H, $H_{1'}$ 'ose', $J = 8$ Hz), 4.50 (t, 2H, $H_{4'}$ 'ose'), 4.30 (m, 1H, $H_{2'}$ 'ose'), 4.25 (m), 4.23 (m) (5H, $H_{6'}$, $H_{6''}$ 'ose'), 4.19 (t, 1H, $H_{3'}$ 'ose'), 4.12 (m, 1H, $H_{2'}$ 'ose'), 4.10 (m, 2H, $H_{2'}$, $H_{6'}$ or $H_{6''}$ 'ose'), 3.88 (m, 1H, $H_{2'}$ 'ose'), 3.82 (m, 2H, $H_{5'}$ 'ose'), 3.68 (m, 1H, $H_{5'}$ 'ose'), 3.62 (m, 2H, $H_{6'}$, $H_{6''}$ 'ose'), 3.13 (m, 1H, $H_{5'}$ 'ose'), 2.17 (s), 2.15 (s), 2.10 (s), 1.98 (s), 1.90 (s), 1.89 (s), 1.86 (s), 1.74 (s) (24H, acetyl), 1.46 (s, 6H, acetyl), 1.29 (s), 0.86 (s), −0.21 (s), −0.38 (broad), −0.66 (s), −1.46 (broad) (18H, acetyl), −2.61 (s, 2H, NH).

UV–Vis ($CHCl_3$) λ_{max}, nm (ε, 1 $mmol^{-1}$ cm^{-1}): **3a**: 419 (405), 515 (20), 540 (3), 588 (7), 643 (2). at 3b: 419 (384), 514 (21), 537 (3), 589 (7), 644 (1). **3c**: 418 (300), 513 (19), 540 (3), 588 (6), 645 (1).

2.6. Metallation of porphyrins with manganese

The chloromanganese(III) complexes of porphyrins **3a**, **3b** and **3c** were prepared by treatment of the free base ligands (50 mg) with $MnCl_2$ (50 mg) in the presence of 2,6 lutidine (20 μl) in 20 ml of dimethylformamide under argon for 5 h at 140°C [20]. After evaporation of the solvent to dryness, the residue was dissolved in CH_2Cl_2 and washed several times with water and with a saturated NaCl aqueous solution. The organic phase was dried over sodium sulfate, filtered and evaporated. The crude product was chromatographed on silica gel column eluted, first, with a mixture of CH_2Cl_2/acetone (5/1, v/v) to remove unre-

acted ligand and then, with CH_2Cl_2/MeOH (10/1, v/v) to collect the manganese complexes.

After evaporation of solvents, manganese complexes were dissolved in CH_2Cl_2 and washed with a saturated NaCl solution containing few drops of concentrated HCl. The chloromanganese complexes were crystallized from a mixture of CH_2Cl_2/heptane.

UV–Vis ($CHCl_3$) λ_{max}, nm (ε, l $mmol^{-1}$ cm^{-1}): **3a-Mn** (yield, 24%): 376.5 (35), 399.5 (33), 469.5 (60), 566 (8), **3b-Mn** (yield, 40%): 377 (48), 400.5 (44.5), 470.5 (85), 566 (11), **3c-Mn** (yield, 90%): 377 (51), 400 (50), 469 (103), 564.5 (15).

2.7. Experimental conditions for the oxidation reactions

All experiments were carried out at room temperature in a glass vessel equipped with a stirring bar under air atmosphere. Reaction times were measured from the addition of oxidant. At regular intervals, magnetic stirring was stopped, the mixture decanted before withdrawing of an aliquot (10 μl) for GC analyses. At the beginning and at the end of each epoxidation reaction, aliquots (40 μl) were taken to determine by UV–visible spectroscopy the relative amount of manganese complex which had disappeared. The reaction mixtures were analyzed by GC and the epoxidation products were isolated by a silica gel column chromatography under argon with pentane/ether (85/15, v/v) as eluent and enantiomeric excesses were determined in ^1H NMR using a chiral europium(III) salt shift reagent [21].

2.7.1. Standard reaction conditions for epoxidation with H_2O_2

Commercial 30 wt.-% solution of H_2O_2 (200 μmol) were progressively added to 1 ml of CH_2Cl_2 which contains 0.5 μmol of catalyst, 200 μmol of 4-tert-butylpyridine (or 100 μmol of 2-methylimidazole), 10 μmol of benzoic acid and 100 μmol of 4-chlorostyrene.

3. Results and discussion

3.1. Synthesis of new catalyst

The 5,10,15,20-tetrakis[2-chloro-6-(2,3,4,6-tetraacetyl-*O*-β-D-glucosyl)phenyl] porphyrins **3a**, **3b**, **3c** were prepared following the method described by Maillard et al. [6]. This involves, firstly, the preparation of the substituted benzaldehyde **2** bearing the β-D-acetyl glucose as chiral substituent at the *ortho* position and a chlorine atom as electron withdrawing substituent at the *ortho'* position. The condensation of 1-α-bromo-2,3,4,6-tetraacetylglucose with 2-chloro-6-hydroxybenzaldehyde **1**, previously obtained by NaOH hydrolysis from 2-fluoro-6-chlorobenzaldehyde [19], afforded the glycosylated benzaldehyde **2** in 55% yield. This reaction was performed in a heterogeneous phase (mixture of aqueous sodium hydroxide, methylene chloride and nBu_4NBr) by the procedure described by Halazy [22].

The coupling reaction of chloroglucosylated benzaldehyde **2** with pyrrole, by the procedure described by Lindsey [23,24], afforded the corresponding glucosylated porphyrins **3**. This consisted of a high dilution condensation of glucosylated aldehyde **2** and pyrrole in the presence of a Lewis acid catalyst ($BF_3 \cdot Et_2O$) in CH_2Cl_2, in the dark, at room temperature, to give the mixture of porphyrinogens. These compounds were oxidized in situ by treatment of the reaction mixture with tetrachloro-1,4-benzoquinone (*p*-chloranil) to give a mixture of porphyrin atropoisomers in 9% yield.

TLC on silica gel showed that the mixture of compounds **3** contained three chlorotetraglucosylated atropoisomers. They were separated by successive chromatographies on silica gel column and on preparative plates. The three compounds **3a**, **3b** and **3c** were identified by their ^1H NMR spectra as αβαβ, ααββ and αααβ atropoisomers respectively.

The absence of αααα atropoisomer had been observed already when we synthesized the glucosylated porphyrins in which each *meso* phenyl

group was substituted at only one *ortho* position by glycosylated moieties [6]. However thermal atropoisomerization at 80°C of these last compounds in a mixture of toluene/MeCN (10/3, v/v) in the presence of silica gel afforded the αααα isomer [25]. In the case of the new compounds described here, the thermal formation of the αααα atropoisomer was not observed even when each atropoisomer was refluxed in xylene. This absence of αααα atropoisomer was attributed to a very strong steric hindrance introduced both by glucosylated substituents and chlorine atoms.

3.2. Metallation of chloroglucosylated porphyrins by manganese

Since these compounds are insensitive to atropoisomerization, the manganese complexes were prepared at reflux in DMF with $MnCl_2$, under argon according to the Adler method [20]. The metallation yields were low for αβαβ (24%) and ααββ (40%) atropoisomers in which both faces are more sterically hindered than those of the αααβ derivative (90%).

3.3. Asymmetric epoxidation

The epoxidation reactions of 4-chlorostyrene were carried out with the three metalloporphyrins as catalysts using H_2O_2 as oxygen atom donor. Results of the epoxidation reactions are shown in Table 1 which contains also the results obtained with the chloro Mn(III) *meso*-5,10,15,20-tetrakis-(2,6-dichlorophenyl)porphyrin [Mn(TDCPP) Cl] known to have a remarkable stability towards oxidation degradation [10].

Catalytic oxidation of 4-chlorostyrene has been investigated using two methods. The first one, described by Banfi et al. [26], consisted to use 4-tert-butylpyridine as axial ligand and benzoic acid as cocatalyst in the reaction mixture. We have also used 2-methylimidazole as axial ligand in a second method to epoxidize the same substrate. In both cases, the presence of a base such as imidazole or 4-tert-butylpyridine is necessary to observe efficient catalytic reaction. This confirms the key role of the addition of imidazole and pyridine derivatives which considerably enhances the activity of Mn-porphyrins towards hydrocarbons and alkenes oxidation with H_2O_2 as oxidant agent [27]. The main reaction product was 4-chlorostyrene epoxide.

In the presence of 4-tert-butylpyridine, a modest olefin conversion (25–30%) was observed with these glycohalogenated catalysts, weaker that those previously reported for parent complexes bearing only glycosylated residues [8]. The same enantiomeric excesses (22%) were found in both cases. This clearly indicates that the presence of further steric hindrance due to

Table 1
Asymmetric epoxidation of 4-chlorostyrene by Mn(TDCPP)Cl, αβαβ (**3a-Mn**), ααββ (**3b-Mn**), αααβ (**3c-Mn**)

	4-Chlorostyrene/H_2O_2/4-tert-butylpyridine [a]			4-Chlorostyrene H_2O_2/2-methylimidazole [b]		
	Total yield	ee [c]	Turnover number [d]	Total yield	ee [c]	Turnover number [d]
Mn (TDCPP)Cl	66 *	0	132	80	0	160
3a-Mn	24.5	23	64	4	22	8
3b-Mn	31	22	62	5	21	10
3c-Mn	29 **	22	58	5	20	9
Mixture of atropoisomers	23	22	51			

[a] Reaction was performed for 4 h (for *, 2 h 30 min; for **, 5 h 30 min) after addition of H_2O_2 (30% in H_2O, 400 equiv. relative to catalyst) over 15 min at 25°C to a mixture of 100 μmol of 4-chlorostyrene, 200 μmol of 4 tert-butylpyridine, 20 μmol of benzoic acid and 0.38–0.5 μmol of catalyst in 1 ml of CH_2Cl_2. Yields were based on the initial quantity of 4-chlorostyrene.
[b] Reaction was performed for 1 h in the conditions in footnote a, with 100 μmol of 2-methylimidazole which replaces 4-tert-butylpyridine.
[c] Determined in the presence of $Eu(hfc)_3$.
[d] Turnover number = mole of 4-chlorostyrene converted per mole of catalyst.

the chlorine atoms is without influence for the recognition of the substrate.

2-Methylimidazole is a less effective base than 4-tert-butylpyridine as cocatalyst. With this base, the 4-chlorostyrene conversion was very low (4–5%). In fact, this base leads to inactivation of the catalyst because it becomes a competitive substrate for the oxygenation reaction. However, the same ee were observed as in the presence of 4-tert-butylpyridine, suggesting that the ee do not depend on the nature of the added base but on the steric hindrance of the chiral substituents of the *meso* phenyl groups.

Mn(TDCPP)Cl used as reference gave a large yield of epoxide (66%) compared to other metalloporphyrins (Table 1). A low steric hindrance in this latter porphyrin is favorable to high epoxidation of 4-chlorostyrene but any enantioselectivity is obviously lacking. In contrast, the presence of chiral glucosylated substituents and the chlorine atoms around the macrocycle of **3a-Mn**, **3b-Mn** and **3c-Mn**, generate a high steric hindrance which is able to protect the catalyst against oxidative degradation but decrease the catalytic efficiency of these systems.

Moreover, the presence of chlorine atoms as electron-withdrawing substituents on the ligands are expected to render the corresponding metal-oxo active species more electrophilic than the glucosylated metalloporphyrins bearing no chlorine atoms. This effect has been evidenced by cyclic voltammetry. A more positive potential is found by comparing the oxidation process of zinc complexes of chloroglucosylated (E° = 1.40 V) and glucosylated porphyrins (E° = 1.30 V). This difference of 100 mV, in a reversible process, illustrates the electron-withdrawing force of chlorine atoms.

These new chiral catalysts appeared robust and are not degraded when hydrogen peroxide is progressively added to the reaction mixture at room temperature. They were remarkably stable and showed a low degree of destruction (ca. 5%) after 4 h of reaction. Thus a sample of used catalyst could be isolated, purified and committed to another epoxidation to give the same values of ee and yield in the formation of 4-chlorostyrene epoxide. This indicates that the chiral integrity of these catalysts remained intact.

As these new chiral catalysts **3a-Mn**, **3b-Mn** and **3c-Mn** which are difficult to separate by chromatography, induce the same enantioselectivity, a mixture of the three atropoisomers could be used for epoxidation of olefin without modification of ee value. This was confirmed in a separate experiment (Table 1) under the experimental conditions employed with the first method. An enantiomeric excess of 22% was obtained similar to those measured when the three catalysts were separately used.

4. Conclusion

We have reported the preparation of a new chiral porphyrin, bearing both glycosylated residues and chlorine atoms linked at the *ortho* positions of the *meso* phenyl groups. The manganese complexes of the different atropoisomers are able to induce catalytic asymmetric epoxidation of 4-chlorostyrene using H_2O_2 without significant degradation of the catalyst at room temperature within 4 h. This strategy might be extended to the preparation of other porphyrin catalysts in which the presence of electron-withdrawing substituents should induce a remarkable stability under the strong oxidizing conditions used.

Catalytic asymmetric induction is probably the most important aspect of these metalloporphyrin mediated epoxidation. Although the enantiomeric excesses (ee) are rather modest, it has to be noted that the catalysts, which present a high chemical stability, can be reused in several successive catalytic runs.

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