Synthesis and Remarkable Properties of Iron β-Polynitroporphyrins as Catalysts for Monooxygenation Reactions

J. F. Bartoli, P. Battioni, W. R. De Foor and D. Mansuy

Laboratoire de Chimie et Biochimie Pharmacologiques et Toxicologiques, URA 400, Université René Descartes, 45 rue des Saints-Pères, 75270 Paris Cedex 06, France

Two new porphyrins bearing several electron-withdrawing β-substituents were obtained in one step, in yields of about 50%, by nitration of *meso*-tetra(2,6-dichlorophenyl)porphyrin ($TDCPPH_2$) and *meso*-tetrapentafluorophenylporphyrin ($TFPPH_2$) with HNO_3; the iron(III) complex of β-hexanitro-$TDCPPH_2$ was a remarkable catalyst for the epoxidation of cyclooctene with diluted H_2O_2 (complete conversion and 97% yield in 0.5 h) in the absence of any cocatalyst, and for the hydroxylation of alkanes, *e.g.* heptane, by O_2.

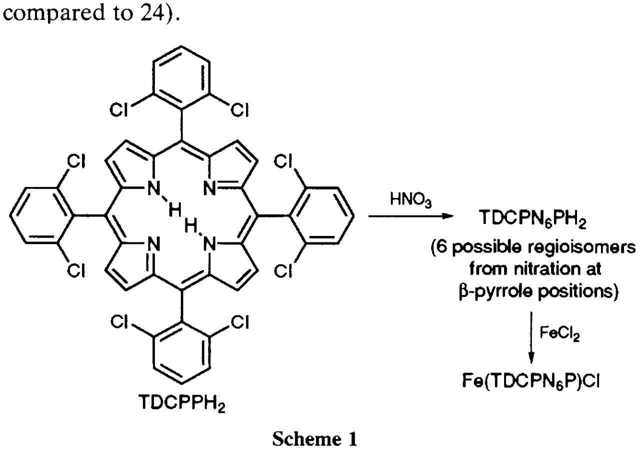
Many systems using iron or manganese *meso*-tetraarylporphyrins as catalysts with various oxygen atom donors have been shown to efficiently mimic cytochrome P450-dependent monooxygenases.[1] Recently, iron *meso*-tetraarylporphyrins bearing 8 halogen substituents on the pyrrole β-positions have been found to be much better catalysts for the hydroxylation of unreactive alkanes with PhIO, peracids or O_2 than the corresponding iron porphyrins without β-halogen substituents.[1g,2,3] In that context, it was tempting to prepare iron *meso*-tetraarylporphyrins bearing strong electron-withdrawing substituents on the β-pyrrole positions and to study their properties as oxidation catalysts. This communication describes an easy access to some new porphyrins bearing 4–6 β-nitro substituents from the reaction of $TDCPPH_2$ and $TFPPH_2$ with HNO_3, and reports preliminary results on the remarkable properties of their iron complexes as oxidation catalysts, one complex being able to catalyse alkene epoxidation by H_2O_2 without the need of cocatalyst. It is noteworthy that a patent recently appeared[4] on the possible preparation of β-polynitroporphyrins upon the direct reaction of NO_2 with metal complexes of $TFPPH_2$, but no description of the products was given.

In a typical experiment, 100 equiv. of red fuming HNO_3 were added dropwise over 8 h to a solution of $TDCPPH_2$[†] (5 mmol dm^{-3}) in pure $CHCl_3$ at room temp. The reaction was followed by visible spectroscopy, as the introduction of nitro groups on β-pyrrole positions was accompanied by a redshift of the Soret peak of the porphyrin. Final Soret peaks at 448 nm (in the case of $TDCPPH_2$) and 430 nm (in the case of $TFPPH_2$) were observed after stirring the reaction mixture for 24–48 h. These peaks remained unchanged on further addition of HNO_3. Such a reaction performed on $TDCPPH_2$ led to a 90:10 mixture of β-hexanitro- and β-pentanitro-$TDCPPH_2$ (from ^1H NMR), with a 70% yield. The main product was purified by column chromatography on silica (CH_2Cl_2–cyclohexane); UV–VIS (451 and 546 nm), ^1H NMR and mass spectra and elemental analysis (C, H, N) were in complete agreement with a β-hexanitro-$TDCPPH_2$ structure. For instance, the mass spectrum (CI, NH_3) showed an isotopic cluster centred at m/z = 1160 for the molecular ion, with an isotopic distribution identical to that calculated for β-hexanitro-$TDCPPH_2$, and an isotopic cluster centred at 1115 for the main fragment ($M - NO_2$). The ^1H NMR spectrum (in $CDCl_3$) showed three sets of signals for the pyrrole, phenyl and NH protons with the expected 2 H : 12 H : 2 H ratio. The chemical shifts (δ 7.75 and 7.65) and shape of the phenyl H signals were very similar to those found for $TDCPPH_2$, indicating that the *meso* phenyl groups remained intact during the reaction. The presence of several signals for the pyrrole H atoms (three singlets at δ 8.88, 8.8 and 8.6) showed that the product was a mixture of regioisomers obtained by the introduction of six β-nitro substituents on the pyrrole rings (six possible regioisomers).

Reaction of $TFPPH_2$[†] with HNO_3 under similar conditions mainly led to a mixture of the regioisomers derived from the introduction of one nitro group on each pyrrole ring (55% yield). The UV-VIS (430, 534, 579, 607 and 665 nm), ^1H NMR [singlets at δ 9.09, 9.02 and 8.99 (4 H) and broad singlet at δ −2.85 (2 H)] and mass [EI, 70ev; m/z = 1154 (M, 2%) and 1109 ($M - NO_2$, 100%)] spectra were in complete agreement with a β-tetranitro-$TFPPH_2$ structure.[‡] All attempts to obtain $TDCPPH_2$ substituted by more than six β-nitro groups or $TFPPH_2$ substituted by more than four β-nitro groups by using more HNO_3, higher temperatures or longer reaction times in reactions between HNO_3 and these porphyrins or their Zn^{II} or Fe^{III} complexes, were unsuccessful.

The iron(III) complex of β-hexanitro-$TDCPPH_2$, $Fe(TDCPN_6P)Cl$ (Scheme 1), proved to be a good catalyst for the hydroxylation of heptane by PhIO. It led to a total hydroxylation yield of 66%, superior to that of Fe(TDCPP)Cl (38%) but less than that observed with $Fe(TDCPCl_8P)Cl$[†] (78%)[8] (Table 1). However, the most spectacular property of $Fe(TDCPN_6)Cl$ was its capacity to catalyse the epoxidation of cyclooctene with diluted H_2O_2 in the absence of any cocatalyst. Addition of 3 equiv. H_2O_2 to cyclooctene in CH_2Cl_2–MeCN led to its almost complete conversion into cyclooctene epoxide in less than 0.5 h at room temp. Under identical conditions, Fe(TDCPP)Cl and Fe(TFPP)Cl gave very low epoxidation yields, and even $Fe(TDCPCl_8P)Cl$ was a poor catalyst for this reaction (20% yield) (Table 1). It is remarkable that $Fe(TDCPN_6P)Cl$ alone gave results similar to those of the best reported metalloporphyrin systems for cyclooctene conversion into its epoxide by H_2O_2, which involve Mn(TDCPP)Cl and a cocatalyst like imidazole.[9] The iron(III) complex of β-tetranitro-$TFPPH_2$, $Fe(TFPN_4P)Cl$, was less efficient than $Fe(TDCPN_6P)Cl$ for this reaction.

$Fe(TDCPN_6P)Cl$ was also a better catalyst than $Fe(TDCPCl_8P)Cl$ for the oxidation of alkanes by O_2 at 90 °C, under moderate O_2 pressure.[§] As shown in Table 1, Fe(TDCPP)Cl was unable to catalyse the oxidation of cyclohexane under these conditions whereas $Fe(TDCPCl_8P)Cl$ led to cyclohexanol and cyclohexanone (177 and 140 turnovers per 2 h), and $Fe(TDCPN_6P)Cl$ was two times more active than $Fe(TDCPCl_8P)Cl$. The superiority of $Fe(TDCPN_6P)Cl$ was more obvious in the case of heptane hydroxylation, as this catalyst was found to be eight times more efficient that $Fe(TDCPCl_8P)Cl$ (187 turnovers per 2 h compared to 24).



Scheme 1

Table 1 Oxidation of hydrocarbons, catalysed by the iron porphyrins Fe(TDCPP)Cl, Fe(TDCPCl$_8$P)Cl and Fe(TDCPN$_6$P)Cl

	Reaction and products/% yield				Reaction and products/turnovers (per 2 h)			
	Heptane + PhIO[a]			Cyclooctene + H_2O_2[c]	Cyclohexane + O_2[d]		Heptane + O_2[d]	
	Heptanols (1-/2-/3-/4-ol ratio)	Heptanones[b]	Total yield	Cyclooctene epoxide	Cyclohexanol	Cyclohexanone	Heptanols (1-/2-/3-/4-ol ratio)	Heptanones
Fe(TDCPP)Cl	26 (0.5:57.5:30:12)	6	38[e]	5	<1	<1	<1	<1
Fe(TDCPCl$_8$P)Cl	68 (1:42:41:16)	5	78[e]	20	177	140	6 (1:39:38:22)	18
Fe(TDCPN$_6$P)Cl	56 (1:49:33:17)	5	66	97	370	270	70 (1:38:38:23)	117

[a] Heptane : PhIO : iron porphyrin = 800 : 20 : 1 in CH_2Cl_2 (catalyst concentration 2 mmol dm^{-3}), 1 h at room temp. Yields were based on the amount of PhIO used (PhIO was totally consumed in each reaction); total yields were calculated assuming that 2 moles of PhIO were necessary for ketone formation. [b] Only the total yield of heptanones was given; the ratio between 2-, 3- and 4-heptanone was equal to that found for the corresponding alcohols. [c] Cyclooctene : H_2O_2 : catalyst = 100 : 300 : 1 in CH_2Cl_2–MeCN (1 : 1) (2 mol dm^{-3} catalyst), 1 h at room temp. H_2O_2 was progressively added (3 additions of molar equivalents relative to cyclohexane); if more H_2O_2 was added, the catalyst began to be destroyed. Yields are based on the initial quantity of cyclooctene. [d] A solution of catalyst (2 mol dm^{-3} in 10 ml benzene and 40 ml alkane) was stirred in an autoclave under 10^6 Pa of O_2 at 90 °C for 2 h. Results are given in mole of products formed per mole of catalyst per 2 h. [e] Results from ref. 8.

The aforementioned results describe an easy one-step access to a new series of porphyrins bearing several electron-withdrawing substituents on the β-pyrrole positions by nitration of the readily accessible TDCPPH$_2$ and TFPPH$_2$ with HNO_3 at room temp. in yields around 50%. By using a large excess of HNO_3, β-hexanitro-TDCPPH$_2$ and β-tetranitro-TFPPH$_2$ are the main products obtained. However, the use of a smaller excess of HNO_3 leads to mixtures of derivatives of TDCPPH$_2$ with four or five β-nitrogroups, and mixtures of TFPPH$_2$ derivatives containing two or three β-nitro groups.

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Footnotes

† TDCPPH$_2$,[5] TFPPH$_2$[6] and TDCPCl$_8$PH$_2$ [tetra-(2,6-dichlorophenyl)-β-octa-chloroporphyrin],[7] and their iron complexes, were prepared as described previously.

‡ This structure was confirmed by the mass spectrum [Cl, NH_3: m/z = 1216 (M − H, 100%)] and elemental analysis (C, H, N) of the Zn^{II} complex of the isolated porphyrin.

§ These conditions were similar to those described by Lyons *et al.*[3] for alkane oxidation by O_2 catalysed with iron polyfluorinated porphyrins. The marked increase in catalytic activity that we observed upon introduction of β-nitro groups on Fe(TDCPP) is in agreement with recent comments on iron polyfluorinated porphyrins.[4]