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Synthesis of Chiral "Twin Coronet" Porphyrins and Catalytic and Asymmetric Epoxidation of Olefins

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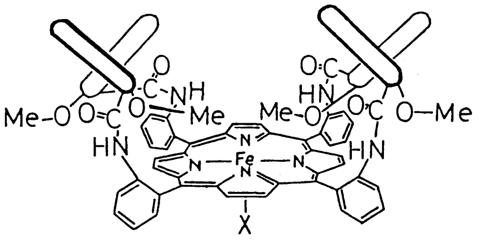
Novel iron porphyrins, "twin coronet" porphyrins, which have chiral hydrophobic cavities consisting of binaphthalenes on their both faces are synthesized, and found to catalyze asymmetric epoxidation of olefins with high enantioselectivity.

A number of synthetic metalloporphyrins have been employed to catalyze oxidation of hydrocarbons with a view to mimic the behavior of cytochrome P-450.(1,2) From X-ray analysis of cytochrome P-450_{CAM},(3) the active reaction center has two different sites, i.e. a substrate/oxygen binding and a thiolate ligand coordinating one. In order to construct a model system which closely mimics the natural ones, five-coordinate iron porphyrin must have ligation sites of both a substrate and an axial ligand.

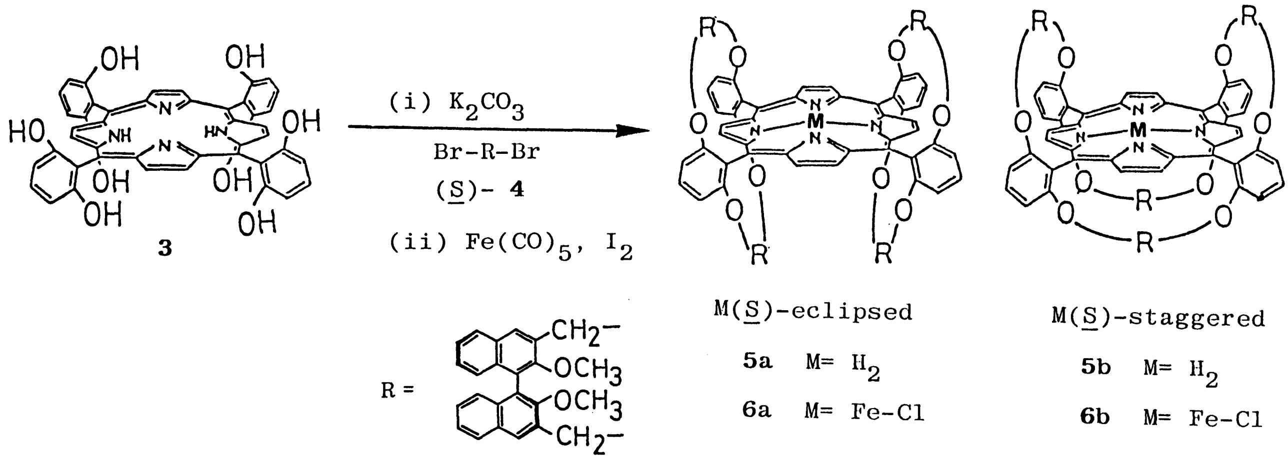
We recently synthesized Iron "BINAP-porphyrin" (**1**), which is modified by binaphthyl groups on one side,(4) and is found to catalyze the shape-(4) and enantioselective epoxidation(5) of various olefins. The catalytic oxidation with **1** is proposed to occur within the chiral hydrophobic pocket. The two binaphthyl groups over the macrocycle can selectively recognize substrates and can block formation of unreactive μ-oxo dimer. Several porphyrins bearing chiral auxiliaries(6) have been synthesized and some of their iron derivatives showed catalytic activity toward chiral epoxidation in low to moderate optical yields.



(**1**) Fe[(S)-Binap$(OMe)_2]_2$TPPX

We report herein synthesis and the spectral features of novel "twin coronet" porphyrins, **5a** and **5b**, which have binaphthalene-pockets similar to that of **1** on their both faces, together with asymmetric epoxidation of prochiral olefins by the corresponding iron complex catalyst **6a**.

meso-Tetrakis(2,6-dimethoxyphenyl)porphyrin (**2**) was prepared from 2,6-dimethoxybenzaldehyde and pyrrole according to Adler's method in 7.1% yield. Cleavage of ethereal linkage was performed with dry pyridinium hydrochloride under refluxed conditions to give the corresponding octahydroxyporphyrin (**3**) in 91% yield. This porphyrin (**3**) is highly symmetrical, and does not have atropisomerism, which is observed in meso-tetrakis(2-hydroxyphenyl)porphyrin.(7)



3

M(S)-eclipsed

5a M= H_2

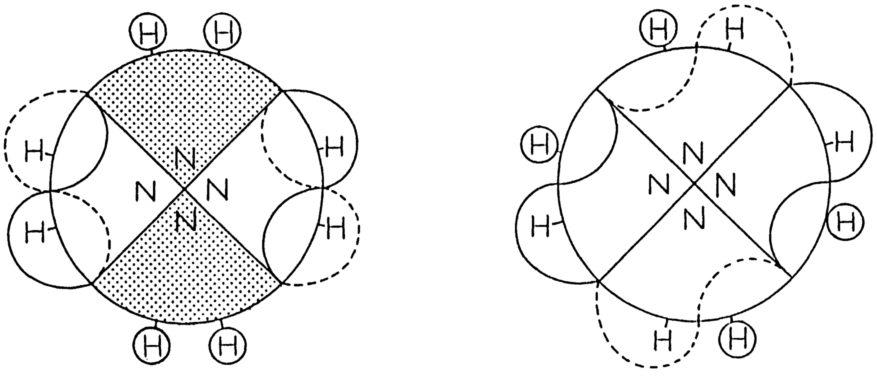
6a M= Fe-Cl

M(S)-staggered

5b M= H_2

6b M= Fe-Cl

To avoid formation of many stereoisomers, an optically active 2,2'-dimethoxy-1,1'-binaphthyl derivative was used as a chiral auxiliary. A THF-acetone solution (6:11 v/v, 425 ml) of meso-tetrakis(2,6-dihydroxyphenyl)porphyrin (**3**) (360 mg, 0.49 mmol) and (S)-3,3'-bis(bromomethyl)-2,2'-dimethoxy-1,1'-binaphthyl (**4**) (1.20 g, 2.40 mmol)[8] was refluxed with excess amount of K_2CO_3 (5.4 g, 0.039 mol) under high-purity Ar atmosphere (O_2< 0.2 ppm), to give two isomeric porphyrins, (**5a**) (4.3%) and (**5b**) (5.3%), which can be separated by silica-gel column chromatography (benzene-CH_2Cl_2). From their ^1H NMR spectra,[9] the less polar isomer and the more polar one were assigned to be H_2(S)-eclipsed (**5a**) and H_2(S)-staggered (**5b**), respectively. Major difference between the two isomers in their ^1H NMR spectra is the signals of the pyrrole β-protons. In H_2(S)-eclipsed (**5a**), two β-protons on one pyrrole ring are equivalent, and there are two sets of equivalent pyrrole rings (Fig. 1). Thus, ^1H NMR signals of their β-protons must be a couple of singlets. On the other hand, four pyrrole rings of H_2(S)-staggered (**5b**) are all equivalent, but each two β-protons on one pyrrole ring are different (Fig. 1). Hence, two doublet peaks of pyrrole β-protons should be observed in H_2(S)-staggered. Based on these spectroscopic features, the structures of the obtained isomers were determined.[9]



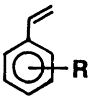
(5a) H_2(S)-eclipsed (5b) H_2(S)-staggered

Fig. 1. Schematic representation (top view) of the structures of 5a and 5b. The sigmoidal curves represent the binaphthyl groups above (——) and below (- - - -) the porphyrin ring.

The iron complexes, Fe-Cl(S)-eclipsed (**6a**) and Fe-Cl(S)-staggered (**6b**), were prepared by treatment of **5a** and **5b** respectively, with Fe(CO)$_5$ and I$_2$ in a dry toluene solution, followed by treatment with a dilute HCl solution.[10]

Epoxidation of olefins by the catalyst (**6a**) and iodosobenzene were performed according to the following procedure; to a CH_2Cl_2 solution (1 ml) of the catalyst (0.001 mmol), an olefin (0.5 mmol), and a GLC internal standard under an Ar atmosphere at 0°C, was added PhIO (0.1 mmol) at once. The corresponding epoxides and aryl acetaldehydes were produced in 26-72% yield based on the initial amount of the oxidant, as shown in Table 1. In every case, the corresponding (R)-epoxide was formed in preference. Especially, good optical yields were obtained in the oxidation of electron-deficient olefins and the excellent ee (80%) was recorded in the case of 2-nitrostyrene. This is the highest value reported so far in the oxidation with related chiral porphyrin catalysts.[6]

Table 1. Asymmetric epoxidation of olefins catalyzed by 6a[a)]

Olefins	Turnover numbers[b)] Epoxide	Aldehyde	Reaction time/h	Epoxide ee/%[c)]	Config.[d)]
 R = H	66	6	1.5	14	R
2-NO$_2$	26	trace	3	80	(R)
F$_5$	36	trace	2	74	R
4-Br	31	5	2	28	(R)
2-OMe	32	16	2.5	0	-
1-vinylnaphthalene	36	trace	1.5	46	(R)

a) All reactions were performed under the reaction conditions described in the text.

b) Turnover numbers, (product mol)/(catalyst mol), were determined by GLC.

c) Optical yields were determined by (i) HPLC equipped with a column packed with a chiral stationary phase, or (ii) ^{1}H NMR measured in the presence of a chiral shift reagent, tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato] europium(III).

d) Absolute configurations were determined by comparison with authentic samples. The configurations in parentheses were estimated from analogy with the chromatographic and/or spectroscopic behavior of (R)-styrene oxide.

Further experiments on asymmetric oxidation with new iron porphyrin systems exhibiting high turnover numbers and high optical yields are now under progress. This work was supported by a Grant-in-Aid for Scientific Reseach, Ministry of Education, Science and Cultures of Japan to Y. N. We would like to thank Dr. Masanori Kawamura, Ono Pharmaceutical Co., for gift of optically active binaphthol.

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8) (S)-Binaphthyl dibromide (**4**) was prepared in 71% yield from PBr$_3$ and (S)-3,3'-bis(hydroxymethyl)-2,2'-dimethoxy-1,1'-binaphthyl, which was synthesized quantitatively by reduction of (S)-(-)-2,2'-dimethoxy-1,1'-binaphthalene-3,3'-dicarboxylic acid dimethyl ester (97% e.e.).

9) **5a:** UV-Vis (CH$_2$Cl$_2$) 329, 420, 513, 540, 587, and 641 nm; ^{1}H NMR (CDCl$_3$) δ= -3.20 (2 H, br s, NH), -1.62 (12 H, s, OCH$_3$), 2.90 (12 H, s, OCH$_3$), 4.38 (4 H, d, J=11 Hz), 4.85 (4 H, d, J=11 Hz), 4.96 (4 H, d, J=9 Hz), 5.30 (4 H, d, J=9 Hz), 6.13 (4 H, d, J=8 Hz), 6.23 (4 H, t, J=7 Hz), 6.64 (4 H, t, J=7 Hz), 6.84 (4 H, d, J=9 Hz), 7.02 (4 H, t, J=7 Hz), 7.18-7.24 (12 H, m), 7.32 (4 H, d, J=8 Hz), 7.45 (4 H, s), 7.73-7.78 (8 H, m), 7.84 (4 H, s), 8.38 (4 H, s, pyrrole β-H), 8.68 (4 H, s, pyrrole β-H); FAB MS m/z 2095 (M$^+$+1).

5b: UV-Vis (CH$_2$Cl$_2$) 329, 420, 513, 540, 587, and 643 nm; ^{1}H NMR (CDCl$_3$) δ= -3.23 (2 H, br s, NH), -1.75 (12 H, s, OCH$_3$), 2.78 (12 H, s, OCH$_3$), 4.63 (4 H, d, J=11 Hz), 4.71 (4 H, d, J=10 Hz), 4.88 (4 H, d, J=11 Hz), 5.28 (4 H, d, J=10 Hz), 5.91 (4 H, t, J=8 Hz), 6.13 (4 H, d, J=8 Hz), 6.54 (4 H, t, J=7 Hz), 6.82 (4 H, d, J=8 Hz), 7.03 (4 H, t, J=7 Hz), 7.12 (8 H, d, J=8 Hz), 7.22 (4 H, s), 7.25 (4 H, t, J=7 Hz), 7.40 (4 H, d, J=9 Hz), 7.73-7.81 (12 H, m), 7.84 (4 H, s), 8.38 (4 H, d, J=4 Hz, pyrrole β-H), 8.52 (4 H, d, J=4 Hz, pyrrole β-H); FAB MS m/z 2095 (M$^+$+1).

10) **6a:** yield 75%; UV-Vis (CH$_2$Cl$_2$) 419, 508, 580, and 648 nm; FAB MS 2150 (M$^+$-Cl+1). **6b:** yield 19%; UV-Vis (CH$_2$Cl$_2$) 422, 508, 577, and 650 nm; FAB MS 2150 (M$^+$-Cl+1).

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