May, 1987] Bull. Chem. Soc. Jpn., 60, 1649—1659 (1987) 1649

Synthesis and Properties of 5,10,15,20-Tetrakis(3,5-di-*t*-butyl-2-nitrophenyl)porphyrin: Conformational Stabilities of the Respective Atropisomers and Oxygenation Capabilities of the Iron(III) and Manganese(III) Complexes

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(Received July 11, 1986)

The synthesis and properties of new, bulky atropisomeric porphyrins are described. Four atropisomers of 5,10,15,20-tetrakis(3,5-di-*t*-butyl-2-nitrophenyl)porphyrins has been easily separated and purified by column chromatography. The isomers all have different thermal stabilities toward atropisomerization. Below 60 °C, however, they have rather high conformational stabilities, and an iron(III) or manganese(III) ion has been incorporated into each isomer, with a retention of the ligand conformation. By the use of these metal complexes, the catalytic oxygenation reactions, i.e., the epoxidation of olefins (styrene, α-methylstyrene, cyclohexene, and cyclooctene) and the hydroxylation of alkanes (cyclohexane and heptane), have been done in the presence of hypochlorite or iodosylbenzene as an oxidant. Products analyses by GLC show that these new complexes effectively catalyze the oxygenations in higher yields or in more selective ways, than the corresponding TPP complexes.

The cytochrome P-450 family of monooxygenase enzymes have increasingly attracted the attention of chemists because of the versatility of its catalyses, i.e., aliphatic hydroxylation, alkene epoxidation, and heteroatom dealkylation.1) Most of all, an inestimable blessing to inorganic chemists is the fact that iron(II—IV) porphyrin IX serves as an active center throughout enzymatic reactions.2)

So far many efforts have been made to exploit P-450 models which include the metalloporphyrin-iodosylbenzene,3–6) the metalloporphyrin-hypochlorite,7–9) or the metalloporphyrin–O_2-reducing reagent system.10,11) In these model systems, a variety of protected porphyrins have been used as catalysts. As far as atropisomeric porphyrins are concerned, however, limited numbers of the isomers have been employed, and they are not in extensive use at present.12) This is surprising in view of the possible unsymmetrical steric protection afforded on both faces of the porphyrin plane by the use of atropisomerism. One factor in explaining this insufficient use is the lack of easily prepared atropisomeric porphyrin that either have a high conformational stability to heating or show no serious deterioration during catalysis. Two types of new atropisomers, i.e., 5,10,15,20-tetrakis(2-methoxy-1-naphthyl)porphyrin (**2**)13) and 5,10,15,20-tetrakis(2-cyanophenyl)porphyrin (**3**),14) have been reported. Although the four possible isomers of **2** were cleanly isolated, the instabilities of the 2-methoxy-1-naphthyl groups toward such oxidants as iodosylbenzene or hypochlorite hamper the practical use of their metal complexes as catalysts. Inversely, metal complexes of **3** may not be decomposed by the oxidant, but the separation conditions to the respective atropisomers are very severe. Thus, it is of great interest to develop new synthetic entries into atropisomeric porphyrin chemistry that either have new types of polar bulky groups around the porphyrin plane or lead to recoverable, reusable catalysts for P-450 models.

Recently, we described the synthesis of 5,10,15,20-tetrakis(3,5-di-*t*-butyl-2-nitrophenyl)porphyrin (**1**) and the separation of the four possible isomers (Fig. 2).15) Each isomer has a relatively high conformational stability to prolonged heating, and the conversion into the iron complex (**1**–FeX) was done with a retention of the ligand conformation. The thermally stable *hydroxy iron(III) complexes* (**1**–FeOH) were also isolated by the treatment of the corresponding halo iron(III) species (**1**–FeBr or **1**–FeCl) with aqueous sodium hydroxide or with basic alumina. The stability of these complexes was explained as a steric

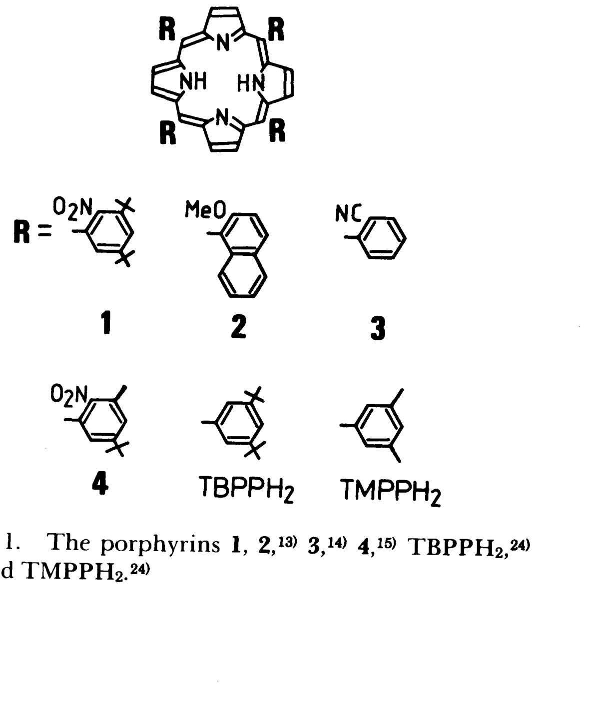


Fig. 1. The porphyrins **1**, **2**,13) **3**,14) **4**,15) $TBPPH_2$,24) and $TMPPH_2$.24)

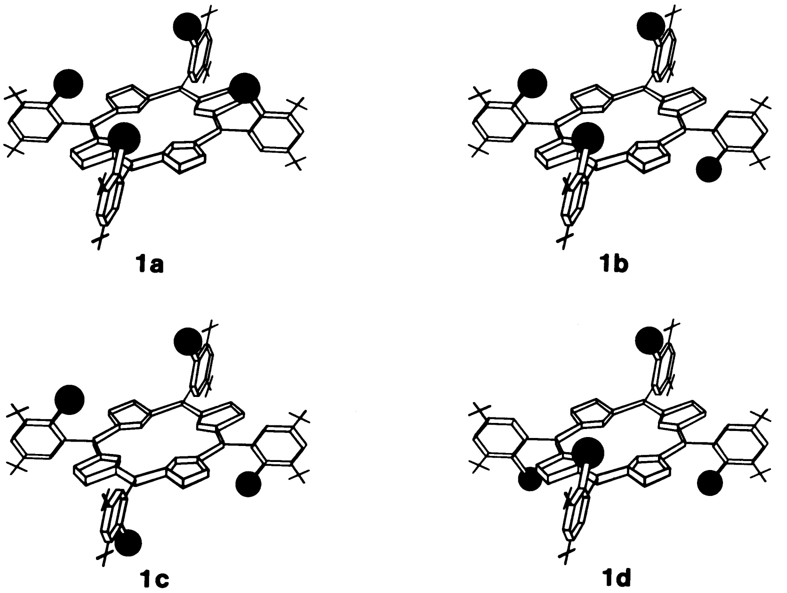


Fig. 2. The four atropisomers of porphyrin **1**: **1a**($\alpha\alpha\alpha\alpha$); **1b**($\alpha\alpha\alpha\beta$); **1c**($\alpha\alpha\beta\beta$); **1d**($\alpha\beta\alpha\beta$).[15]

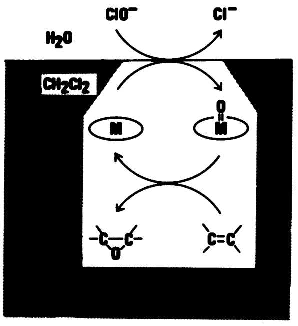


Fig. 3. Olefin epoxidation reaction using hypochlorite.

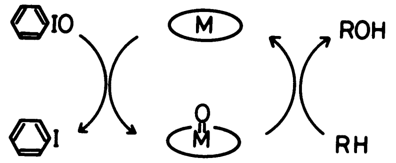


Fig. 4. Alkane hydroxylation reaction using iodosylbenzene.

effect attributable due to *t*-butyl and/or nitro groups.

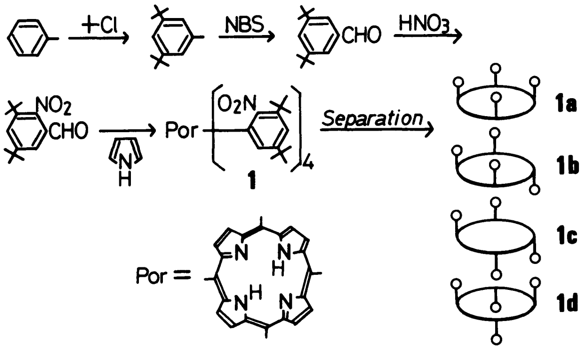
Herein we wish to report details of the syntheses of **1** and their manganese(III) and iron(III) complexes (**1**-MnX or **1**-FeX) and of GLC analyses of the oxygenation products of the styrene, α-methylstyrene, cyclohexene, cyclooctene, cyclohexane, or heptane catalyzed by these complexes in the presence of hypochlorite or iodosylbenzene (Fig. 3 or 4). A preliminary account of the synthetic and spectral work has appeared.[15–17]

Experimental

The synthetic procedure to **1** is shown in Scheme 1.[15]

3,5-Di-*t*-butyl-2-nitrobenzaldehyde. In a 2 dm³, three-necked, round-bottomed flask, powder of 3,5-di-*t*-butylbenzaldehyde (214 g, 0.98 mol) was dissolved, with mechanical stirring, in 0.9 dm³ of sulfuric acid. After the mixture had then cooled to 5 °C, 88 cm³ of nitric acid (Sp. Gr. about 1.38) was added, drop by drop, at such a rate that the temperature did not rise above 10 °C. After the addition was complete, the mixture was stirred for a further 30 minutes and then poured into 6 dm³ of water containing chipped ice. The solid product was separated by filtration with a G3 sintered glass filter and washed with three 1-dm³ portions of water. The solid thus obtained was dissolved in the minimum ammount of the 1:9 chloroform–hexane (about 600 cm³). The solution was then submitted to 3.5×40 cm of 70—230 mesh Merck alumina 90, and the product was eluted from the column with 1:9 chloroform–hexane. The solution was evaporated to dryness, and the residue was purified by vacuum distillation (bp 150—155 °C/1.3 Pa) to give 214 g (83% based on 3,5-di-*t*-butylbenzaldehyde; mp 90—91 °C) as yellow crystals. Found: C, 68.54; H, 8.07; N, 5.37. Calcd for $C_{15}H_{21}NO_3$: C, 68.41; H, 8.04; N, 5.32. ¹H NMR ($CDCl_3$) δ=1.3 (9H, s, 3-*t*-butyl H), 1.4 (9H, s, 5-*t*-butyl H), 7.7 (2H, m, phenyl H), 9.7 (1H, s, CHO). Mass spectrum, *m/z* 263.3.

5,10,15,20-Tetrakis(3,5-di-*t*-butyl-2-nitrophenyl)porphyrin (1). The porphyrin was prepared by a modification of the method of Sorrell's.[18] Two hundred and eighty grams of 3,5-di-*t*-butyl-2-nitrobenzaldehyde were dissolved in 1.3 dm³ of glacial acetic acid in a 3-dm³, three-necked, round-bottomed flask fitted with Allihn condensers and a dropping funnel. The solution was heated and stirred with a magnetic bar. To the boiling solution, 74.5 g of pyrrole (1.1 mol) was added, drop by drop. The resulting black mixture was allowed to reflux for 60 min and then left to stand over-night. The purple brown crystals thus precipitated were filtered by suction and washed with



Scheme 1. The synthetic procedure to porphyrin **1**.

methyl alcohol (ca. 500 cm^3). Yield: 36.0 g (11%). **1** is very easily soluble in chloroform; very soluble in benzene or toluene; soluble in hexane, dioxane, *N,N*-dimethylformamide, or carbon tetrachloride, and sparingly soluble in methyl or ethyl alcohol. **1**: Found: C, 73.28; H, 7.46; N, 8.88. Calcd for $C_{76}H_{90}N_8O_8$: C, 73.40; H, 7.29; N, 9.01. UV-vis. ($CHCl_3$) λ/nm at 25 °C (ε/M^{-1} cm^{-1}),[19] 421 (3.5×10^5), 474 (3.1×10^3), 512 (2.2×10^4), 542 (3.1×10^3), 586 (6.9×10^3), 640 (5.6×10^2). The nitro groups show characteristic infrared absorptions: 760, 840, 1530 cm^{-1}. **1** is a mixture of four atropisomers. TLC on silica (toluene) show four spots; R_f values: **1a**, 0.28; **1b**, 0.65; **1c**, 0.74; **1d**, 0.88.

Separation of Four Isomers. The most polar isomer, the **1a** isomer, could be separated from the other three isomers by means of a skillful column-chromatographic technique. Before the isomer separation, the preferential isomerization was carried out by the utilization of adsorption.[20,21] Ten grams of the porphyrin **1** were dissolved in 2 dm^3 of toluene. The solution was then refluxed under Ar, and a 30-g portion of Merck alumina 90 was added nine times every three hours. After refluxing for 30 h, the solution was cooled to the ambient temperature. The isomerized product was then extracted from the alumina with a 1:1 chloroform–acetone mixed solvent. The solvent was removed by the use of a rotary evaporator, and the residue was redissolved in a minimum amount of chloroform (about 300 cm^3). The chloroform solution was poured onto a 5.5×60 cm column of Merck alumina 90 prepared as a slurry in chloroform. After all the material had been loaded, chloroform (about 2 dm^3) was passed through the column until the eluate became very pale. The **1a** isomer was then removed by the use of a 1:1 chloroform–acetone mixture, and the solvent was removed at a temperature lower than 40 °C. Five grams of the crude **1a** isomer obtained as has been described above was dissolved in 100 cm^3 of chloroform and again loaded onto a 3×60 cm column of Merck alumina 90 prepared as a slurry in chloroform. After the loading, the column was eluted with chloroform, and the eluate of the second brown band was collected. The solution was subsequently taken to dryness at room temperature. The residue was redissolved in 300 cm^3 of toluene. After it had then been placed in a 3×40 cm column of silicagel (Wako gel C-200) prepared as a slurry in toluene, toluene (about 2 dm^3) was passed through the column. The desired pure **1a** isomer was then removed by elution. The solution was concentrated to 40 cm^3 at the ambient temperature. The resulting purple brown crystals were filtered, washed with methyl alcohol, and dried in vacuo. Percentage yield: ca. 15%.

The other three isomers were separated in the usual way. Ten grams of **1**, the **1a** isomer of which had been removed in the above procedure, were dissolved in a minimum amount of toluene (about 600 cm^3). After the sample had then been placed in a 5.5×60 cm column of alumina (Woelm N-Super 1) prepared as a slurry in toluene, the column was eluted with toluene. The separation was followed by the TLC analysis of the eluate. The fractions of the three bands were separately collected and condensed for crystallization using a rotary evaporator at room temperature. The purple brown crystals were filtered, washed with methyl alcohol, and dried in vacuo. Yields: **1b**, 5.7 g, **1d**, 1.2 g. The **1c** isomer still contained a minor amount of the **1d** isomer at this stage of the separation. Several subsequent recrystallizations from toluene gave 0.9 g of the desired pure **1c** isomer.[22]

Measurement of Atropisomerism. The change in the isomer distribution was measured by the method of the literature[14] with the following modification. A 0.4-g portion of the porphyrin was dissolved in 300 cm^3 of toluene or chloroform. Under Ar, the solution was refluxed in a oil bath or photoirradiated with a high pressure mercury lamp (400 W, Riko. UVL-400HA) at the ambient temperature. A few cm^3 of the solution was sampled with a pipet at appropriate intervals and spotted on a 20×20 cm TLC plate (Merck silica gel 60). The four isomers were separated with toluene on the TLC plate. The quantity was measured by spectrometry after the extraction of each isomer from the TLC plate with chloroform. The relative abundance of the isomers was photometrically determined using the Soret-band.

Iron Insertion. A 0.4-g portion (0.32 mmol) of **1** was dissolved in a 100-cm^3 portion of a mixed solvent of 1:3 chloroform–acetic acid, after which the solution was purged with Ar to remove the O_2. Then, anhydrous $FeBr_2$ (0.34 g, 1.6 mmol), anhydrous sodium acetate (0.4 g, 4.9 mmol), and 2,6-lutidine (0.18 cm^3) were added to this solution of **1**. The resulting solution was stirred for 5 h at 50 °C. When **1a** was used, the solution was stirred for 1 h at 50 °C. After a 100-cm^3 portion of water was added to the resulting solution, the organic layer was separated and subsequently washed, first with water and then with a dilute sodium hydroxide solution. The crude iron complex of **1** was purified by silica-gel chromatography. The chloroform solution of the product was placed in a silica-gel column (Wako gel C-200) prepared as a slurry in chloroform. Afrer loading, the column was eluted with chloroform. The remaining porphyrin free base was first eluted, and then the desired iron complex of **1** was eluted. The second eluate was collected and then stirred together with 47% hydrobromic acid. The red-brown solution turned dark brown during stirring. After the organic layer had been separated, the solvent was removed by means of a evaporator. The iron complex **1**–FeBr was recrystallized from a benzene–heptane mixed solvent, and the resulting dark blue-purple crystals were dried in vacuo. Percentage yields: **1a**–FeBr, 64%; **1b**–FeBr, 59%; **1c**–FeBr, 65%; **1d**–FeBr, 74%. Found: C, 66.06; H, 6.57; N, 7.99; Br, 5.99. Calcd for $C_{76}H_{88}N_8O_8FeBr$: C, 66.28; H, 6.41; N, 8.14; Br, 5.80. UV-vis. (toluene) λ/nm: 360, 392, 422, 512, 588, 650.

In order to estimate the relative ease of iron insertion in relation to atropisomeric porphyrins, controlled metal-insertion experiments were carried out. In a typical experiment,[21] a porphyrin free base (0.08 mmol), 2,6-lutidine (0.4 mmol), and anhydrous $FeBr_2$ (0.4 mmol) were dissolved in 20 cm^3 of THF, and the reaction was carried out under Ar for 3 h at 30 °C. The products were separated by the use of a silica-gel column (Wako gel C-200) prepared as a slurry in chloroform. The silica-gel column was eluted by chloroform, and the second band was collected. The second eluate was stirred with 47% of hydrobromic acid. After the solvent had been removed, a bromo iron(III) complex was dried in vacuo and weighed. The insertion ratios were calculated relative to the total amount of porphyrin ligands.

Manganese Insertion. The porphyrin **1** (1.0 g), $MnBr_2 \cdot 4H_2O$ (1.0 g), anhydrous CH_3COONa (0.5 g), and pyridine (10 cm^3) were dissolved in 300 cm^3 of a mixed solvent of 1:3 chloroform–acetic acid under oxygen-free conditions. The resulting solution was stirred for 5 h at 50 °C. When the porphyrin **1a** was used, the manganese insertion was carried out for 5 h at room temperature. The solution was then brought to dryness, and the residue was redissolved in a minimum amount of chloroform. The chloroform solution was poured into the alumina column (Merck alumina 90) prepared as a slurry in chloroform. After loading, the column was eluted by chloroform. The porphyrin free base was eluted, and the desired manganese complex was adsorbed on alumina. Chloroform was passed through the column until the eluate was very pale. Then, a 2:1 chloroform–methanol mixed solvent was added, the desired manganese complex of **1** was removed. The eluate was stirred with 20% hydrobromic acid. After the solvent had been removed by the use of a rotary evaporator, the manganese porphyrin was recrystallized from dichloromethane–hexane; the dark green crystals thus obtained were dried in vacuo. Percentage yields: **1a**-MnBr, 40%; **1c**-MnBr, 18%; **1d**-MnBr, 20%. Found: C, 65.19; H, 6.23; N, 7.97; Br, 5.89. Calcd for $C_{76}H_{88}N_8O_8MnBr \cdot H_2O$: C, 65.46; H, 6.51; N, 8.04; Br, 5.73. UV-vis. (toluene) λ/nm: 376, 490, 588.

Measurement of the Stabilities of the Hydroxy Iron(III) Complexes. The hydroxy iron(III) porphyrins **1a**—**d**-FeOH were prepared from the corresponding bromo iron(III) complexes. The bromo iron(III) porphyrins **1a**—**d**-FeBr were treated with aqueous sodium hydroxide. The products (the hydroxy iron complex and the μ-oxo dimer) were purified by the use of an alumina column (Merck alumina 90), using toluene as an eluate, and were identified by spectroscopic methods. The thermal stabilities of the hydroxy iron(III) complexes were measured as follows. Chloroform solutions of **1a**—**d**-FeOH were refluxed for 8 h, and then the resulting material was analyzed by means of UV-vis. and ^{1}H NMR spectroscopy.[23] Other porphyrins, $TBPPH_2$ and $TMPPH_2$,[24] were used for comparison.

Oxygenation Reaction. In controlled experiments using iodosylbenzene as an oxidant, the reaction conditions were as follows. In a typical experiment of olefin epoxidation, **1**-FeBr or **1**-MnBr (0.010 mmol) and olefin (1.7 mmol) were dissolved in 5 cm^3 of dichloromethane. Iodosylbenzene (0.3 mmol) was added to this solution, and the resulting mixture was stirred for 3 h in an ice bath. All these operations were carried out under Ar. In the experiments on the hydroxylation of alkane,[25] **1**-FeBr (0.002 mmol), cyclohexane (2 mmol), and iodosylbenzene (0.060 mmol) were employed. The reaction was continued for 3 h at 15—17 °C. In both olefin epoxidation and alkane hydroxylation, the products were analyzed by means of GLC.

When hypochlorite was used as an oxidant, the reaction rates and the yields were also measured for comparison with those of the authentic catalyst, MnTPPBr.[4] All kinetic experiments in the metalloporphyrin–hypochlorite system were controlled, as will be described below.[17] The complex, **1**-FeBr or **1**-MnBr (0.0082 mmol), olefin (7.8 mmol, styrene, α-methylstyrene, cyclohexene, or cyclooctene), the internal standard reagent (*p*-dichlorobenzene or 1,3,5-trichlorobenzene), and the phase-transfer reagent (benzyldimethyltetradecylammonium chloride) were dissolved in 20 cm^3 of dichloromethane. When manganese complexes were used, 1-triphenylmethylimidazole (0.46 mmol) was added to the solution as the N-base ligand. Then, 15 cm^3 of the sodium hypochlorite solution (8.7 mmol) was layered over the organic phase. The epoxidation reaction was initiated by vigorous stirring, and the reaction temperature was maintained at 22 °C during olefin epoxidation. The products were periodically monitored by means of GLC.

Results

In contrast with 5,10,15,20-tetrakis(2-nitrophenyl)-porphyrin, which has hardly shown solubility to any organic solvent,[18] the pophyrin **1** is soluble in common organic solvents. Their iron and manganese complexes of **1** are also well soluble in organic solvents, such as chloroform, benzene, toluene, acetone, alcohol, and *N,N*-dimethylformamide. All the isomers of **1** show identical electronic absorption spectra, but their proton NMR patterns are substantially different from each other (See Table 1).

Atropisomerization. The results of atropisomerization are listed in Table 2. Each isomer is rather stable in refluxing chloroform (61 °C), but is gradually converted to other isomers in refluxing toluene (111 °C). Strong UV irradiation with a mercury lamp for 11 h gives no appreciable amount of other isomers. The time-dependency of the distribution of the isomer which was isomerized from the **1a** isomer to others in refluxing toluene or chloroform is shown in Fig. 5 or 6. The change in the isomer distribution in refluxing toluene has not been observed over 60 h refluxing. The results of this experiment are listed in Table 3.

The Stabilities of Hydroxy Iron(III) Complexes. The treatment of the bromo iron(III) complex of $TMPPH_2$ with sodium hydroxide quantitatively gave the μ-oxo dimer, while that of $TBPPH_2$ afforded a mixture of the hydroxy and μ-oxo compounds, the two species was separated by alumina column chromatography (relative weight of products; hydroxy/μ-oxo=5:1), as is shown in Scheme 2 and Table 4.

The purified hydroxy complex of $TBPPH_2$ was stable in organic solvents at room temperature (ca. 23 °C) for at least 6 d. At higher temperatures, however, the hydroxy complex of $TBPPH_2$ was

Table 1. Proton NMR Data of **1a**—**d**[a]

Assignment[b]	**1a**	**1b**	**1c**	**1d**
Internal pyrrole H	−2.97 (s, 2H)	−2.98 (s, 2H)	−2.98 (s, 2H)	−2.99 (s. 2H)
5-*t*-Butyl H	1.45 (s, 36H)	1.43 (s, 9H)	1.47 (s, 36H)	1.52 (s, 36H)
		1.48 (s, 18H)		
		1.52 (s, 9H)		
3-*t*-Butyl H	1.60 (s, 36H)	1.55 (s, 9H)	1.60 (s, 36H)	1.57 (s, 36H)
		1.58 (s, 18H)		
		1.62 (s, 9H)		
Ortho phenyl H	7.93 (d, 4H, J=2.1)	7.81 (m, 1H)	7.97 (d, 4H, J=0.5)	8.23 (d, 4H, J=1.8)
		8.06 (m, 2H)		
		8.17 (m, 1H)		
Para phenyl H	7.99 (d, 4H, J=2.1)	7.99 (m, 4H)	7.99 (d, 4H, J=0.5)	7.99 (d, 4H, J=1.8)
β-Pyrrole H	8.69 (s, 8H)	8.64 (s, 2H)	8.64 (s, 4H)	8.65 (s, 8H)
		8.66 (s, 2H)	8.68 (s, 4H)	
		8.68 (s, 2H)		
		8.69 (s, 2H)		

a) Chemical shifts in ppm relative to TMS, coupling constants J in Hz: solvent $CDCl_3$. b) The assignment of observed proton NMR signals is ably assisted by the use of the nuclear Overhauser method.

Table 2. Thermal and Photo-Induced Atropisomerization

Starting isomer	Solvent	Temp	Time	Conversion ratio[a]
		°C	h	%
1a	Toluene	111	11	90
	Chloroform	61	5	5
	Toluene (hν)[b]	18	11	5
1b	Toluene	111	11	30
1c	Toluene	111	11	40
	Chloroform	61	5	5
1d	Toluene	111	11	20
	Chloroform	61	11	0
	Toluene (hν)[b]	18	11	0

a) Original isomer is converted to others. Total percentage represents amount of other isomers converted. b) Photoirradiation with high-pressure mercury lamp (400W, Riko, UVL-400HA).

Table 3. Isomer Distribution of Atropisomerization in Toluene Refluxing

Reflux time	**1a**	**1b**	**1c**	**1d**
h	%	%	%	%
0	0.4	54.5	33.5	11.6
60	1.5	35.3	17.8	45.4
120	1.6	33.8	17.2	47.5

gradually converted to the μ-oxo dimer. After 8 h heating in toluene (60 °C), the hydroxy complex of $TBPPH_2$ was completely turned into the μ-oxo dimer.

The treatment of bromo iron(III) complexes of **1a**—**d** quantitatively converted them into hydroxy iron(III) complexes. These four hydroxy iron complexes are stable at 60 °C for at least 8 h.

Oxygenation Reaction. The yields of oxygenation reaction using iodosylbenzene are listed in Table 5.

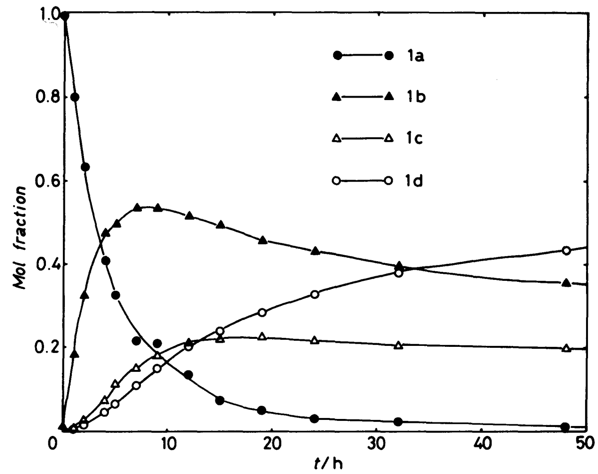


Fig. 5. Time course of isomerization reaction starting from **1a** in refluxing toluene (111 °C).

All the percentage yields are based on the iodosylbenzene consumed. These results show that manganese and iron complexes of the porphyrin **1** are efficient catalyst for both epoxidation and hydroxylation in iodosylbenzene systems.

For obtaining a further understanding of the catalytic activity of **1**-FeBr and **1**-MnBr, we developed olefin epoxidation in hypochlorite systems.

In the estimation of the oxygenation capabilities of the porphyrin catalyst, the oxygenation reaction with hypochlorite was continued until the porphyrins were decomposed by bleaching. The yields in these experiments are represented as "maximum yield in turnovers" in Table 6.[26]

The kinetic results (the reaction rates and the yields) of controlled experiments in hypochlorite systems are listed in Table 7. The reaction rates are represented by turnovers/sec, while the yields are represented by turnover numbers. The kinetic results of the epoxidation of olefin using MnTPPBr are also listed in Table 7.

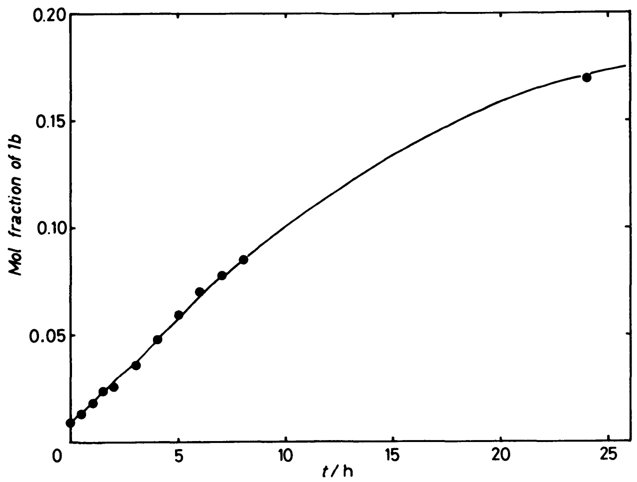
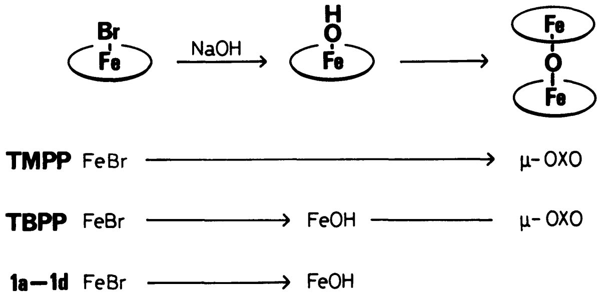


Fig. 6. Time course of isomerization reaction from **1a** to **1b** in refluxing chloroform (61 °C). Other isomers, **1c** and **1d**, were not detected in this experiment.

The epoxides are the main product in all the olefin oxygenation reactions except for the measurements of the "maximum yield in turnovers" using FeTPPCl. When MnTPPBr is used for a control experiment of styrene oxygenation, a notable amount of phenylacetaldehyde (15%) and a small amount of benzaldehyde are also detected. By the use of all the



Scheme 2. Interconversion from bromo iron(III) complexes to corresponding hydroxy iron(III) complexes or μ-oxo dimers.

Table 4. Spectroscopic Data of Hydroxy Iron Complexes and μ-Oxo Dimers[a)]

Compounds	UV-Vis. (λ/nm)						^{1}H NMR (δ/nm), in benzene-d_6			
							β-pyrrole H	ortho H	t-butyl H[b)]	para H
TBPPFe(OH)	336	418	576	617		(Toluene)	81.2		1.8 2.0	
TBPPFe μ-oxo	321	411	576	616	648	(Toluene)	13.9		1.3 1.7	
TMPPFe μ-oxo		410	572	612	648	(Toluene)	13.8	7.2	2.3 2.6	
1a-FeOH	342	419	579			($CHCl_3$)	78.4		1.6 1.9	8.5
1b-FeOH	338	417	579			($CHCl_3$)	82.3		1.7	8.4
1c-FeOH	340	418	576			($CHCl_3$)	79.9		1.7	8.3
1d-FeOH		418	575			($CHCl_3$)	79.5 82.5		1.7	8.1

a) The hydroxy iron complexes and μ-oxo dimers were identified in a way similar to that of Ref. 23. b) In the case of TMPPFe μ-oxo, the chemical shifts of methyl H are listed.

Table 5. Oxygenation Reactions Using Iodosylbenzene

Yield[a)]	Fe salt					Mn salt		
%	**1a**	**1b**	**1c**	**1d**	TPP	**1a**	**1d**	TPP
Cyclohexene								
Cyclohexene oxide	90	89	88	73	44	92	69	31
2-Cyclohexen-1-one	4	4	3	6	7	3	5	12
2-Cyclohexen-1-ol	6	7	9	14	26	5	21	12
Total	100	100	100	93	77	100	95	55
Cyclohexane								
Cyclohexanol	36	27	26	26	Trace	nd[b)]	nd	nd
Cyclohexanone	5	6	5	9	Trace	nd	nd	nd
Total	41	33	31	35	Trace	nd	nd	nd
Heptane								
Total[c)]	18	18	25	19	0.7	14	7	9

a) The yields are based on the iodosylbenzene consumed. b) Not determined. c) The products are mixtures of the seven oxygenated species.

Table 6. The Maximum Yields in Turnovers[26)]

Porphyrin	Styrene	α-Methylstyrene
MnTPPBr	5000	2900
1a-MnBr	23000	95000
1c-MnBr	7300	31000
1d-MnBr	21000	15000
FeTPPCl	300	400
1a-FeBr	4800	2400
1c-FeBr	1600	3500
1d-FeBr	4300	1800

Table 7. The Reaction Rates and Yields.
Reaction Rate (yield)

Porphyrin	Styrene	α-Methylstyrene	Cyclohexene	Cyclooctene
MnTPPBr[a)]	3.7 (690)	1.6 (820)	0.037 (50)	0.14 (120)
1a-MnBr[a)]	2.3 (730)	2.6 (900)	0.014 (310)	0.12 (250)
1c-MnBr[a)]	0.1 (640)	1.2 (850)	nd[b)]	nd
1d-MnBr[a)]	1.2 (620)	0.7 (840)	0.007 (190)	0.05 (60)
1a-FeBr	1.3 (620)	2.3 (790)	0.33 (210)	0.57 (290)
1c-FeBr	4.6 (860)	3.7 (870)	0.48 (570)	0.37 (760)
1d-FeBr	1.8 (490)	2.5 (850)	0.40 (600)	1.1 (850)

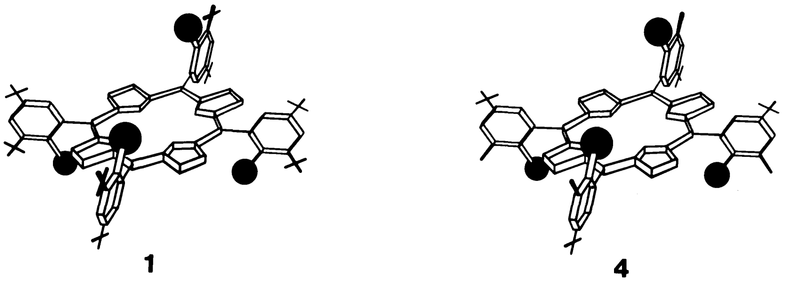
a) A 1-triphenylmethylimidazole was added to the solution. b) Not determined.

manganese and iron complexes of **1**, with the exception of **1a**–MnBr, however, the phenylacetaldehyde is not detected during controlled styrene epoxidation.

Discussion

Atropisomerization. The atropisomerization of various ortho-substituted tetraphenylporphyrins has been the subject of several recent studies.[13,14,27,28)] For example, when the methanol solution of the ααα*β* isomer of 5,10,15,20-tetrakis(2-hydroxyphenyl)porphyrin was allowed to stand for an hour at 23 °C, the other three isomers began to reappear.[27)] On the contrary, each isomer of **1a**—**d** is stable in refluxing chloroform (61 °C, See Fig. 6 and Table 3). When toluene solution is refluxed for 11 h (111 °C), each isomer of **1a**—**d** is gradually converted to other isomers. In this experiment, the total conversion ratio from the **1a** isomer is the largest, while that from **1d** is the smallest, among the four isomers (see Table 2). The conversion ratio from **1a** achieves ca. 50% after 3 h refluxing in toluene (111 °C). Hatano et al. investigated the gradual transition of one isomer to the other isomers using 5,10,15-20-tatrakis(2-cyanophenyl)porphyrin **3** at 40—60 °C.[14a)] The αααα isomer of the porphyrin **3** decreased to 50% when the chloroform solution was allowed to stand for 1.5 h at 50 °C[14a)] These results clearly show that the porphyrin **1** has a higher conformational stability than 5,10,15,20-tetrakis(2-hydroxyphenyl)porphyrin or the porphyrin **3**.

As a further comparative study, an analogous porphyrin, 5,10,15,20-tetrakis(5-*t*-butyl-3-methyl-2-nitrophenyl)porphyrin **4** (See Fig. 1 and 7), has been prepared by a method similar to that shown in Scheme 1,[15)] and its α*β*α*β* isomer has been separated (Fig. 7). Heating in chloroform (61 °C) or photoirradiation in a toluene solution for 11 h results in an easy isomerization of the α*β*α*β* isomer of **4**, with the conversion percentages of 50 and 20 respectively. In the case of the **1d** isomer, the conversion percentage is negligible upon heating in chloroform for 11 h or upon photoirradiation (see Table 2). Although both **1** and **4** are ortho-substituted by nitro groups, the conformational stability of **1** is considerably higher than that of **4**. The conformational stability toward the atropisomerization of the ortho-substituted tetraphenylporphyrins depend on the rotational barrier around the phenyl–porphyrin single bond—in other words, the activation energy to the atropisomerization. The four isomers of **1** apparently have higher activation energies than those of **4**. Judging from the CPK model of the porphyrin **1**, the plane of the nitro group is forced to be almost perpendicular to the phenyl ring by the steric bulk of neighboring *t*-butyl moiety. This steric interaction of *t*-butyl is what is called "the buttressing effect." In contrast, the CPK model of the porphyrin **4** suggests that the steric interaction between the nitro group and the neighboring methyl group is small. Therefore, the nitro group may be supposed to be conjugated with the phenyl ring π system. The planar structure of the



1 **4**

Fig. 7. The porphyrins **1** and **4**.

nitrophenyl group in **4** may cause easy isomerization. The high conformational stability of the porphyrin **1** is given by the strong buttressing effect of the adjacent *t*-butyl group, i.e., by the absence of the conjugation of the nitro group with the phenyl π system.

It has been reported that the four isomers of 5,10,15,20-tetrakis-(2-hydroxyphenyl)porphyrin,[27] 5,10,15,20-tetrakis(4-*t*-butyl-2-aminophenyl)porphyrin,[21] 5,10,15,20-tetrakis(2-aminophenyl)porphyrin,[14b] and "picket fence" porphyrin[14b] have been equilibrated in a statistical abundance ($\alpha\alpha\alpha\alpha$:$\alpha\alpha\alpha\beta$:$\alpha\alpha\beta\beta$:$\alpha\beta\alpha\beta$= 12.5:50:25:12.5). The isomer distribution of **1a**—**d** in the equilibrium state ($\alpha\alpha\alpha\alpha$:$\alpha\alpha\alpha\beta$:$\alpha\alpha\beta\beta$:$\alpha\beta\alpha\beta$=1.6: 33.8:17.2:47.5), however, is quite different from that of the statistical abundance. In the equilibrium state, **1d** is the dominant isomer. The amount of the **1a** isomer is much smaller, while the corresponding ratio of **1d** is considerably larger than that of the statistical abundance. In kinetic studies of isomerization, the $\alpha\alpha\alpha\beta$ isomer has been the key compound for the analyses of atropisomerization. Hence, the relative ratios are represented by the amounts of **1a**, **1c**, and **1d** in relation to that of **1b**; the results are listed in Table 8. For the sake of comparison, the relative ratios ($\alpha\alpha\alpha\alpha/\alpha\alpha\alpha\beta$, $\alpha\alpha\beta\beta/\alpha\alpha\alpha\beta$, $\alpha\beta\alpha\beta/\alpha\alpha\alpha\beta$) of the porphyrin **3** and the statistical abundance are also listed in Table 8. These results clearly show that the relative ratios toward **1b** ($\alpha\alpha\alpha\beta$) of the porphyrin **1** or **3** are rather different from those of the statistical abundance and that **1** and **3** porphyrins have similar tendencies. These findings on the isomer distribution in the porphyrin **1** indicate that the thermal stability of the porphyrin **1d** is higher than that of **1b**, while that of **1a** is lower than that of **1b**. In the course of the isomerization, the **1a** isomer is immediately changed into the other three isomers. After 3 h refluxing in toluene (111 °C), the conversion ratio from **1a** is achieved at ca. 50%. The relative ratio of **1d** has been constantly growing during refluxing (see Fig. 5). These results of the time-course experiment also show that the thermal stability of **1d** is higher than those of the other isomers, while that of **1a** is extremely low among the four isomers. The variation in the stabilities of **1a**—**d** is explained by an electrostatic repulsive model. In the porphyrin **1a**—**d**, the interactions between the two nitro groups projecting from the diagonal phenyl rings are supposed to be negligible. On the contrary, the two nitro groups projecting to the same side of the porphyrin plane from the adjacent phenyl rings may have large repulsive interactions. The **1a**, **1b**, **1c**, and **1d** isomers have four, two two, and no pairs of such large repulsive interactions respectively. Because of these repulsive interactions, the **1a** isomer has the lowest conformational stability. On the other hand, the **1d** isomer has the highest conformational stability because of the absence of the repulsion between nitro groups.

Table 8. Relative Ratios in the Equilibrium State

Porphyrin	$\dfrac{\alpha\alpha\alpha\alpha}{\alpha\alpha\alpha\beta}$	$\dfrac{\alpha\alpha\beta\beta}{\alpha\alpha\alpha\beta}$	$\dfrac{\alpha\beta\alpha\beta}{\alpha\alpha\alpha\beta}$
1	0.05	0.51	1.41
3	0.06	0.69	1.11
Statistical abundance	0.25	0.50	0.25

As has been mentioned above, ortho-substitution by nitro groups with the *t*-butyl moiety at the adjacent position seems to have a great influence on the conformational stability or on the isomer distribution of atropisomerization. At any rate, the extremely high conformational stability toward the isomerization of the porphyrin **1** pushed us to further investigations of the relationship between the shape of the porphyrin and its capability as oxygenation catalyst.

Iron Insertion and Stabilities of Hydroxy Iron(III) Complexes. The insertion ratio of each isomer of **1** in controlled experiments is listed in Table 9. In controlled experiments at 30 °C, the yield of **1a** is rather higher than that of the other three isomers. Therefore, the metal incorporation of **1a** need not maintain a high temperature for a long time. Although the yields of the other three isomers **1b**—**d** are very low at 30 °C, the metal insertion of these isomers can be carried out at high temperatures. After all, each isomer of the porphyrin **1a**—**d** is converted to the corresponding iron(III) complex, with a retention of the ligand conformation.

In recent years, several research groups have reported the formation of stable hydroxy iron(III) complexes by the use of such protected porphyrins as 5,10,15,20-tetrakis(2,4,6-trimethoxyphenyl)porphyrin or 5,10,15,20-tetramesitylporphyrin.[23,27,31] Iron(III) complexes of our protected porphyrins **1a**—**d** have also formed stable hydroxy iron(III) complexes. By contrast, simple unprotected porphyrins, e.g., 5,10,15,20-tetraphenylporphyrin or 2,3,7,8,12,13,17,18-octaethylporphyrin, from the hydroxy iron species in

Table 9. The Metal-Insertion Ratios in Controlled Experiments

Porphyrin	$\dfrac{\text{Ratio}^{a)}}{\%}$
1a	60
1b	Trace
1c	Trace
1d	Trace
$TMPPH_2$	80
$TBPPH_2$	60

a) The ratios are based on the porphyrin free base used.

solution; however, these are serious difficulties with the isolation of the species as stable compounds.[32]

The thermal stability of the hydroxy iron(III) complex against transformation into the μ-oxo dimer is supposed to be influenced by the protection of the porphyrin plane. Our results show that the steric bulk of $TBPPH_2$ is just enough for the stabilization of the hydroxy iron(III) species at room temperature, while that of $TMPPH_2$ is insufficient. Furthermore it is certain that ortho substituted nitro groups of **1a—d**, which give rise to great restrictions on the rotation about porphyrin-phenyl single bonds, afford additional thermal stability to the hydroxy iron(III) complexes of **1a—d**.

Oxygenation Reaction. In cyclohexene epoxidation by iodosylbenzene, **1**–FeBr, and **1**–MnBr, but not **1d**–FeBr and **1d**–MnBr, completely consumed the iodosylbenzene (see Table 5). The **1**–FeBr complex sufficiently catalyzed the hydroxylation of alkanes in comparison with FeTPPCl, which generated only a trace amount of the oxygenation products (see Table 5). Groves et al. investigated the influence of the ortho-position substitution of phenyl groups using FeTPPCl and FeTTPCl (TTP=5,10,15,20-tetrakis(2-tolyl)porphyrin)iodosylbenzene system.[33,34] In cyclohexene epoxidation, the total yield and the selectivity for epoxide production of the FeTTPCl catalyst (cyclohexene oxide 67%; 2-cyclohexen-1-ol 15%) were slightly higher than those of the FeTPPCl catalyst (cyclohexene oxide 55%, 2-cyclohexen-1-ol 15%).[33] In the experiment on cyclohexane hydroxylation, the total yields of the FeTTPCl system (cyclohexanol 22%, cyclohexanone 2.4%) were considerably higher than those of the FeTPPCl system (cyclohexanol 7.6%, cyclohexanone 0.5%).[34] These results show that ortho-substitution by the methyl group give rise to high yields in both epoxidation and hydroxylation reactions. The selectivity for epoxide production in cyclohexene oxygenation was also enhanced in the FeTTPCl system. In our **1**–FeBr system, these tendencies are extremely remarkable (see Table 9). Our results indicate that the ortho-substitution of the phenyl moiety by the nitro group is effective and better than the ortho-substitution by the methyl group. Although the yields based on the porphyrin catalyst in these experiments are very small (within 30 turnovers), these results clearly show that the iron and manganese complexes of **1** have quite high catalytic activities compared with FeTPP or MnTPP in metalloporphyrin-iodosylbenzene systems.

The hypochlorite is a cheap, convenient oxygen source for olefin-epoxidation reactions; hence, the manganese porphyrin–hypochlorite systems have been well established for olefin-epoxidation reactions.[7–9] We recently reported a successful olefin epoxidation in iron porphyrin–hypochlorite systems.[17] In order to gain a better understanding of catalysis by our protected metalloporphyrin **1**, the maximum yields in turnovers, the reaction retes, and the yields of the olefin-epoxidation reactions were measured by the use of hypochlorite as an oxidant. The maximum yields in tunovers of manganese complexes of **1a—d** are considerably larger than those of MnTPP, while those of the iron complexes **1**–FeBr are comparable to those of MnTPP (see Table 6). In styrene are α-methylstyrene epoxidation, the reaction rates and the yields of **1**–FeBr or **1**–MnBr are almost the same as those of MnTPP (see Table 7). In cyclohexene and cyclooctene epoxidation, however, the reaction rates and the yields by the use of **1**–FeBr are higher than those of MnTPP and the respective manganese complexes of **1a** and **1d**. These results clearly show that the manganese and iron complexes of the protected porphyrin **1** are useful catalysts for the epoxidation using hypochlorine. In all cases of styrene epoxidation catalyzed by **1**–FeBr or **1**–MnBr except for that catalyzed by **1a**–MnBr, a phenylacetaldehyde is not produced. Thus, the catalytic system of the protected porphyrin **1** has a high selectivity for the epoxide production in styrene oxygenation reactions.

The reaction rates are slightly different among the three isomers (see Table 7). When manganese complexes are used for olefin epoxidation, the orders of the reaction rates in controlled measurements are **1a**>**1d**>**1c** (in styrene epoxidation), **1a**>**1c**>**1d** (in α-methylstyrene epoxidation), and **1a**>**1d** (in cyclohexene and cyclooctene epoxidation). In each reaction, the reaction rates of the **1a** isomer (**1a**–MnBr) are the highest among the isomers. As for the controlled experiments using iron complexes, the orders of the reaction rates are **1c**>**1d**>**1a** (in styrene, α-methylstyrene, and cyclohexene epoxidation) and **1d**>**1a**>**1c** (in cyclooctene epoxidation). When manganese complexes are used, the reaction rates of **1a** are always higher than those of **1d**. When iron complexes are used, however, the reaction rates of **1a** are always lower than those of **1d**. These results indicate that the shape of the porphyrin catalyst might influence the reaction rates in olefin epoxidation, and that the mechanism of olefin epoxidation may be different between manganese and iron complexes.

These kinetic results can be explained by our speculative mechanisms as follows. The isomer **1d** is symmetrical and has two topological identical faces ("half-crowded sites" in Fig. 8). On the contrary, the steric environments of the upper and lower sides of the isomer **1a** are quite different. The porphyrin **1a** has a steric bulk on one side of the porphyrin plane formed by four nitro groups ("crowded site" in Fig. 8), yet leaves the other side comparatively unemcumbered ("open site" in Fig. 8). In the MnBr or FeBr complexes of **1a**, Br is expected to ligate on the "open site" (see Scheme 3-(1)).[35] Employing a N-base such

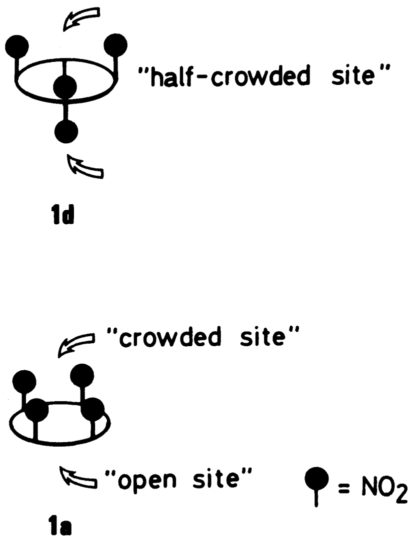
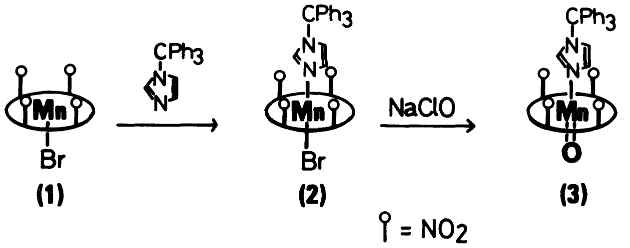


Fig. 8. The reaction site of **1a** and **1d**.



Scheme 3. The speculative oxygenation mechanism of **1a**–MnBr system.

as 1-triphenylmethylimidazole with **1a**–MnBr probably allows the coordination of the N-base on the "crowded site" (see Scheme 3-(2)). The high-valent manganese oxo complex which is illustrated in Scheme 3-(3) may be produced by hypochlorite, and it seems that the oxygenation reaction is carried out on the "open site" in **1a**–MnBr with the N-base system. The oxygenation reaction of **1d**–MnBr and the N-base, however, is done on the "half-crowded site." The analysis of products in styrene oxygenation provides similar information about the reaction site of **1a**–MnBr with the N-base. The ratios of the products in styrene oxygenation are shown in Table 10. In the experiments using **1c**–MnBr and **1d**–MnBr, which oxygenated the olefin on the "half-crowded site," a phenylacetaldehyde cannot be detected. A notable amount of phenylacetaldehyde was, however, produced in the MnTPPBr (15%), MnTBPPBr (11%), and **1a**–MnBr (11%) systems. These results indicated that the reaction site of **1a**–MnBr with the N-base may be the "open site," which is a steric environment similar to that of the reaction site of MnTBPPBr with the N-base. The electronic factors do not influence the rates of oxygenation. In fact, the manganese complexes of **1a**—**d** have similar electronic structures, judging from their identical UV-vis spectra.' The reaction rates of the oxygenation reaction using **1**-MnBr and the N-base are only influenced by the steric environments of the reaction site. The epoxidation reaction on an "oprn site" seems to be more reactive than the reaction on a "crowded site" or on a "half-crowded site." Therefore, the reaction rates of **1a**–MnBr with N-base are always higher than those of **1d**–MnBr with the N-base.

When iron complexes of **1a** are used in the absence of the N-base,[36] the reaction mechanism of epoxidation is different from that of the manganese complex of **1a**. In the **1a**–MnBr and N-base system, the axial ligand Br is ligated on the same side ("open site") in the resting state because the "crowded site" is occupied by the N-base. On the contrary, the axial ligand displacement by X (Br^- or other anion in a water solution) may occur on both sides of the porphyrin plane during the oxygenation-reaction cycles in the **1a**–FeBr system.[37] Because of the easy dissociation and scrumbling of the axial ligand, the oxygenation reaction of **1a**–FeBr may take place on both an "open site" and a "crowded site," the average reaction rate of **1a**–FeBr is deduced comparison with the case in which the oxygenation is performed only on an "open site." Accordingly, the reaction rates of **1a**–FeBr are lower than those of **1d**–FeBr whose reaction site is "half-crowded site."

When iron complexes of **1** are used in styrene oxygenation, no phenylacetaldehyde could be detected in any isomer system (see Table 10). In the absence of the N-base, styrene oxygenation catalyzed by **1a**–MnBr or MnTBPPBr afforded no phenylacetaldehyde. These results indicated that phenylacetaldehyde production is affected not only by the reaction site ("open site" or "crowded site"),[38] but also by the N-base. Taking all these findings together, we proposed the speculative mechanism shown in Scheme 3.

At the present stage, we cannot explain completely

Table 10. The Ratios of Products in the Styrene Oxygenation

Catalyst	Styrene oxide	Phenyl-acetaldehyde	Benzal-dehyde
MnTPPBr+N-base[a)]	84	15	1
MnTBPPBr+N-base	87	11	2
1a–MnBr+N-base	88	11	1
1c–MnBr+N-base	96	0	4
1d–MnBr+N-base	99	0	1
MnTBPPBr	95	0	5
1a–MnBr	100	0	0
1a–FeBr	99	0	1
1c–FeBr	99	0	1
1d–FeBr	97	0	3

a) N-base=1-triphenylmethylimidazole.

the relationship between the reaction rates of oxygenation and the shape of the porphyrin catalysts. Spectroscopic measurements were not useful for the specification of the chemical species in each step; further efforts to get kinetic information still continue in our laboratory. However, it has been proved that our protected porphyrins, **1**–FeBr and **1**–MnBr, show sufficient catalytic activity against olefin epoxidation and alkane hydroxylation.

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 61470041) from the Ministry of Education, Science and Culture.

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25) In heptane epoxidation, the experiment was carried out as follows: The porphyrin (0.010 mmol) and the heptane (6.8 mmol) were dissolved in 4 cm^3 of CH$_2$Cl$_2$. Then, 0.30 mmol of iodosylbenzene was added, and the reaction was performed for 3 h in an ice bath.

26) In a typical experiment, **1a**–MnBr (0.0019 mmol), 1-triphenylmethylimidazole (0.19 mmol), a phase-transfer reagent, and an internal standard reagent (*p*-dichlorobenzene) were dissolved in 40 cm^3 of CH$_2$Cl$_2$. Then, 30 cm^3 of α-methylstyrene (230 mmol) and 160 cm^3 of the sodium hypochlorite solution (280 mmol) were added. The resulting two-phase mixture was stirred for 1 d at room temperature. The products (α-methylstyrene oxide and 2-phenylpropionaldehyde) were analyzed by GLC. The total yield of the products, based on the porphyrin catalyst, is represented as the "maximum yield in turnovers."

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