A New Phase-Transfer Porphyrin Catalyst for the Olefin Epoxidation

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Synopsis. A new type of amphiphilic porphyrin has been synthesized and its manganese(III) complex has been used as a catalyst for the epoxidation of olefin. Catalytic oxygenation in a two-phase (CH_2Cl_2/H_2O) system has been undertaken in the absence of a phase-transfer reagent, such as benzyldimethyltetradecylammonium chloride.

During the last several years, efficient catalytic systems for the epoxidation of olefin in a two-phase (CH_2Cl_2/H_2O) system have been reported.[1,2] These synthetic model systems for the cytochrome P-450 have had several constituent elements. These elements included a hydrophobic Mn(III) porphyrin, an imidazole (or pyridine), a hypochlorite solution as an oxidant, and a phase-transfer reagent which catalyzed the transfer of an oxygen atom from hypochlorite to olefin (See Fig. 1).[3] In order to simplify the two-phase catalytic system, we developed a porphyrin catalyst toward a new amphiphilic manganese(III) salt (abb. Mn srf. **6**, Fig. 2) which had the function of a phase-transfer reagent as well as an epoxidation capability. We report here on the preparation of a new phase-transfer porphyrin catalyst (Mn srf. **6**) and its epoxidation of styrene and cyclohexene.

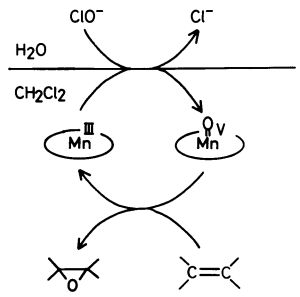


Fig. 1. The two-phase (CH_2Cl_2/H_2O) catalytic system for the olefin epoxidation.

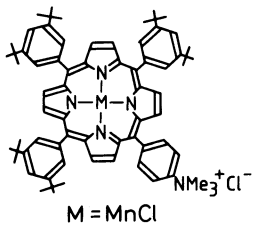
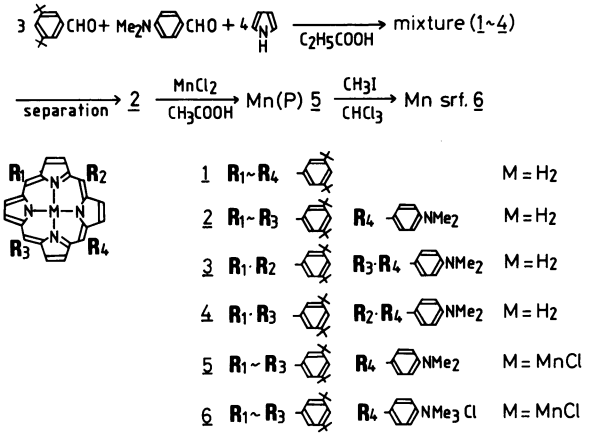


Fig. 2. Mn srf. **6**.



Scheme. The synthetic procedure to Mn srf. **6**.

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The synthetic procedure to Mn srf. **6** followed that of previous work[4] and is shown in the scheme.

5,10,15-Tris(3,5-di-*t*-butylphenyl)-20-(4-dimethylaminophenyl)-21*H*,23*H*-porphyrin 2. The porphyrin **2** was synthesized by Rothemund condensation. 3,5-di-*t*-butylbenzaldehyde (76 g, 0.35 mol), 4-dimethylaminobenzaldehyde (18 g, 0.12 mol), and pyrrole (33 g, 0.49 mol) in propionic acid (1 dm^3) were heated under reflux for 2 h. Propionic acid was removed by distillation to give a mixture of porphyrins **1**—**4**. The crude mixture was dissolved in chloroform and chromatographed on an alumina (Merck Alumina 90) column with chloroform as an eluent. The porphyrins **1**—**4** were eluted and other by-products tended to be absorbed on the alumina. After the solvent was removed, the mixture of porphyrins was redissolved in benzene/hexane (1:4). The solution was poured onto a silica gel (Wako gel C-200) column prepared as a slurry in hexane. After all the material was loaded, 1:2 benzene/hexane was added. The porphyrin **1** was eluted, and the mixed solvent was passed through the column until the eluate became very pale. Then, benzene was added and the desired porphyrin **2** was eluted. The solvent was removed and dried in vacuo. Yield: 15.5 g (13%). Anal. Calcd for $C_{70}H_{83}N_5$: C, 84.54; H, 8.41; N, 7.04. Found: C, 84.24; H, 8.24; N, 7.27. ^{1}H NMR ($CDCl_3$) δ=−2.5 (2H, s, internal pyrrole H), 1.4 (54H, s, *t*-butyl H), 3.1 (6H, s, N-CH_3), 6.9—7.9 (21H, m, phenyl H), 8.7 (8H, s, β-pyrrole H).

Mn Insertion to Porphyrin 2. The porphyrin **2** (2.0 g, 2.2 mol), anhydrous $MnCl_2$ (2.0 g), CH_3COONa (2.0 g), and pyridine (20 cm^3) were dissolved in 260 cm^3 of mixed solvent ($CHCl_3/CH_3COOH$ 3:10). The solution was heated under reflux for 4 h. A Mn (III) complex **5** was extracted with $CHCl_3$ and the crude material was purified by alumina column ($CHCl_3$). The eluate was stirred with 10% hydrochloric acid. The solvent was then evaporated. Yield: 2.1 g (91%).

Preparation of the Mn srf. 6. Mn porphyrin **5** (1.0 g) was treated with methyl iodide (30 cm^3) in $CHCl_3$ under reflux for 5 h. The product was purified by chromatography as an alumina column ($CHCl_3$) eluting with 2:1 $CHCl_3/CH_3OH$. After the eluate was stirred with 10% hydrochloric acid, the solvent was removed by the evaporator. Yield: 0.4 g (37%): Anal. Calcd for $C_{71}H_{84}N_5MnCl_2$: C, 75.25; H, 7.47; N, 6.18. Found: C, 75.40; H, 7.46; N, 6.09. UV-vis. ($CHCl_3$) λ/nm ($\varepsilon/M^{-1}cm^{-1}$)[5]: 381 ($4.9\times10^4$),

Table 1. Products of a Styrene Oxidation Reaction

Product	Yield/%[15]	(Yield/turnover)
Styrene oxide	44	(64)
Phenylacetaldehyde	24	(37)
Benzaldehyde	2	(5)
Total	70	(106)

Table 2. Products of a Cyclohexene Oxidation Reaction

Product	Yield/%[15]	(Yield/turnover)
Cyclohexene oxide	58	(90)
2-Cyclohexen-1-one	6	(9)
2-Cyclohexen-1-ol	4	(6)
Total	68	(105)

Table 3. Dependence of the Reaction Rate on the Olefin Concentration

Styrene concentration/M[5]	Reaction rate[13]
0.06	5.6
0.24	3.7
0.41	1.8

Table 4. Dependence of the Reaction Rate on the Catalyst Concentration

Mn srf. **6** concentration/mM[5]	Reaction rate[13]
0.19	1.2
0.27	8.0
0.37	8.0

406 (4.4×10⁴), 482 (7.9×10⁴), 589 (9.1×10³), 627 (1.3×10⁴).

Epoxidation Reaction. All experiments were carried out as follows. Mn srf. **6** (0.018 mmol), 4′-(imidazol-1-yl) acetophenone (65 times as many as mol of Mn srf. **6**), styrene (8 mmol, or cyclohexene), and *p*-dichlorobenzene (or cyclohexanone) as an internal standard were dissolved in 50 cm³ of dichloromethane. Then 50 cm³ of the sodium hypochlorite solution (2.9 mmol) was layed over the organic phase. The epoxidation reaction was initiated by stirring vigorously, and was carried out in an ice bath. The products were monitored by gas chromatography. A dependence of the reaction rate on the olefin concentration or on the Mn srf. **6** concentration was evidenced by control experiments. In an analysis of the kinetic experiments, the olefin concentration or the concentration of **6** was changed as listed in Table 3 or 4. Other conditions were maintained as mentioned above.

Results and Discussion

Mn srf. **6** was soluble in most organic solvents such as benzene, chloroform, *N,N*-dimethylformamide, ethanol and acetone etc. Mn srf. **6** was not soluble in water, but was soluble in an ethanol/water (1:5) mixed solvent. Soret bands were blue-shifted about 10 nm in methanol and ethanol/water compared with those in $CHCl_3$.[6]

The results of 2 h-oxidation of styrene and of cyclohexene are listed in Tables 1 and 2. In each reaction, epoxides were the main products. A certain amount of phenylacetaldehyde and a small amount of benzaldehyde[7] were also detected during styrene oxidation.[8] Styrene oxidation using Mn srf. **6** reached a maximum turnover number of 1200,[9] compared with that of 240[10] using a Mn complex of **1** and a phase-transfer reagent (benzyldimethyltetradecylammonium chloride). This result shows that Mn srf. **6** is superior to the Mn complex of **1** as a stable catalyst in an oxygenation reaction.[11,12]

The dependence of the reaction rate on the styrene concentration showed that a higher concentration led to a lower reaction rate (See Table 3). The catalyst concentration dependence indicated that the reaction rate changed from 8[13] (under a higher concentration, such as 0.27 and 0.37 mM) to 1.2 (under a lower concentration, such as 0.19 mM (See Table 4)).

This catalytic system using Mn srf. **6** showed a unique behavior regarding the dependence of the reaction rate on the substrate concentration or on the catalyst concentration in comparison with those of other Mn(III) porphyrin catalytic systems.[2,14] The kinetic behavior of an epoxidation reaction using Mn srf. **6** could not be completely fitted by a Michaels–Menten equation, which was proposed by Collman et al.[2] At the present stage, we cannot rationalize these characteristic concentration dependencies of the reaction rate. However, our Mn srf. **6** system efficiently put olefin epoxidation into practice without using a phase-transfer reagent.

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5) M=mol dm⁻³.

6) UV-vis (CH_3OH) λ/nm (ε/$M^{-1}cm^{-1}$): 384 (5.1×10⁴), 402 (5.2×10⁴), 422 (4.8×10⁴), 471 (7.2×10⁴), 572 (1.0×10⁴), 610 (1.0×10⁴). (C_2H_5OH/H_2O 1:5): 378 (4.0×10⁴), 398 (4.0×10⁴), 469 (4.7×10⁴), 588 (7.0×10³), 630 (8.8×10³).

7) Benzaldehyde was identified by gas chromatography

and ^{1}H NMR.

8) Styrene oxidation using MnTPP and a phase-transfer reagent produced less amount of phenylacetaldehyde (11%) than using Mn srf. **6** (24%).

9) Mn srf. **6** was not bleached in this reaction.

10) Mn complex of **1** was almost bleached.

11) We ascertained that the reaction rate of styrene oxidation using Mn srf. **6** was more than ten times as large as that using a Mn complex of **1** and a phase-transfer reagent.

12) The reaction rates of epoxidation at 22 °C using Mn srf. **6** or MnTPP are as follows: styrene, 18 (Mn srf. **6**), 220 (MnTPP); cyclohexene, 2.0 (Mn srf. **6**), 2.2 (MnTPP); cyclooctene, 7.8 (Mn srf. **6**), 8.4 (MnTPP). All experiments were carried out as follows. Mn porphyrin (0.0081 mmol), 1-triphenylmethylimidazole (0.46 mmol), substrate (7.8 mmol), and a internal standard were dissolved in 20 cm^3 of CH_2Cl_2. In case of MnTPP, a phase-transfer reagent was added in CH_2Cl_2. Then, 15 cm^3 of the sodium hypochlorite solution (8.7 mmol) was added and the reaction was started by stirring.

13) The reaction rates are represented by the turnover numbers per minute.

14) M. W. Nee and T. C. Bruice, *J. Am. Chem. Soc.*, **104**, 6123 (1981).

15) Yields are based on the sodium hypochlorite consumed.