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Remarkable Effects of Metal Ions and Axial Bases on Catalytic and Asymmetric Oxidation of Simple Olefins with a "Twin-coronet" Porphyrin

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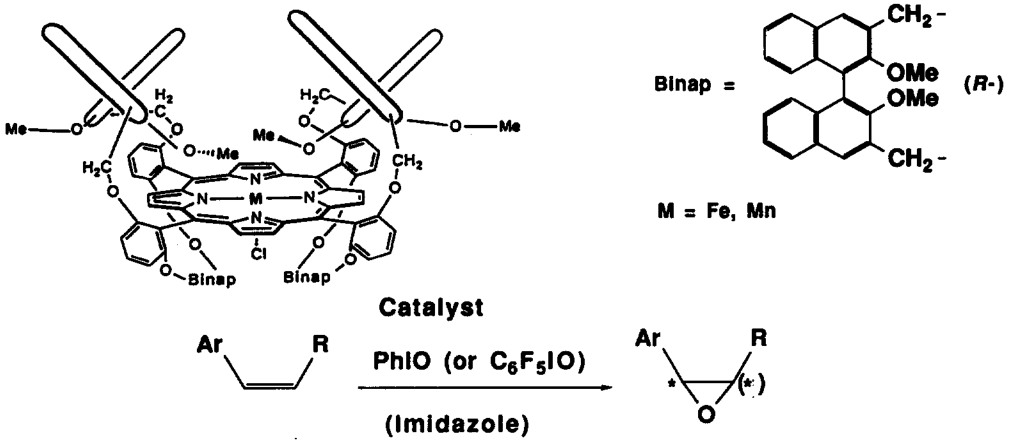
Abstract: Effect of central metals and oxidants on the catalytic and asymmetric epoxidation of simple olefins was evaluated with a chiral binaphthalene-linked twin-coronet porphyrin catalyst, whose Mn derivative gave superior ees of resultant epoxide than the corresponding Fe derivative.

Extensive efforts have been made to design catalytic systems in asymmetric oxidation of simple olefins, which do not bear a hydroxyl group at their allylic position and are not suitable substrates for coordinating to chiral titanium tartrate catalysts to realize their efficient asymmetric oxidation.[1] Asymmetric oxidation of olefins is the chemistry of their prochiral face selection, and in this context, this subject is also interested as *molecular recognition without the aid of hydrogen bonding*. Among many catalytic and asymmetric oxidation systems, especially those with porphyrin-based chiral catalysts, there have never been pointed out the effect of central metal ions on asymmetric oxidation. Comparison of the reactions between two metalloporphyrins, Fe and Mn, has been appeared, while the obtained results were ambiguous.[2]

We have synthesized chiral "twin-coronet" porphyrins, which are robust enough to analyze and estimate reactions in excellent accuracy, because they showed the same oxidation rate and product enatioselectivity as the initial ones even after several hundreds turnover numbers of oxidation.[1a,3] And the catalysts have been shown to oxidize olefins in satisfactorily good enantiomeric excesses to be discussed. Thus, our catalytic system is suitable for the precise analysis of reaction conditions. In this report, we show the Mn derivative of the catalyst exhibits higher enantioselectivity than the corresponding Fe one on the oxidation of simple olefins.

First, we compared the effect of the central metal ions between Fe and Mn under the following standard conditions: A catalyst (1 μmol), PhIO (100 μmol), an olefin (500 μmol), and a GLC standard was dissolved in dichloromethane (1.0 mL) under argon at 0°C and the mixture was stirred at a constant speed. When the oxidation reaction stopped, the products were isolated by flush-column chromatography and analyzed by ^{1}H NMR. We used the Fe and Mn derivatives of (*R*)-binaphthalene-linked "twin-coronet" porphyrins as catalysts. In the oxidation of styrene and 2-nitro styrene, the Mn catalyst did not give any improvement



on the product ee. On the other hand, *cis*-β-methylstyrene and the analogous cyclic olefins gave higher ees in the Mn-catalyst reaction. The maximum increase (19 to 61%ee) in their enantioselectivity was observed in the reaction of *cis*-β-methylstyrene.

The absolute configuration of the epoxides is same between the two metal ions through the reaction. Every epoxide was accompanied by the corresponding carbonyl compound, which was established to be given through the 1,2-proton migration in the corresponding radical intermediate after the single-electron transfer from the olefin to the putative high-valent metalloporphyrin. Since the ratio of epoxide/carbonyl compound almost resembled in all runs regardless of the kind of metal ions, two porphyrin catalysts are expected to give the products through the similar reaction mechanism. But the rate of product formation considerably decreased in the reaction catalyzed by the Mn porphyrin. Thus, the improvement of the ees in the Mn catalyzed reaction would caused by the slight change of the transition state in the oxygen transfer stage closer to the product in the sense of the Hammond postulate.

Next, manganese porphyrins generally favor the formation of the corresponding monoimidazole complex than the diimidazole ones in the presence of the base, and the formation constants are reasonably higher than that of the diimidazole ones. According to the present manganese porphyrin, its formation constants with 1-methylimidazole were photometrically determined to be K_1=6700 M^{-1} and K_2<<1 M^{-1} at 0 °C in CH_2Cl_2.[4] This implies the Mn complex can selectively form its monoimidazole complex in the wide range of the imidazole concentration. Through the selective formation of the monoimidazole complex, the Mn ion could be pulled out of the porphyrin plane, and the resultant oxometal complex will require more proximal position to the porphyrin plane at their oxygen-atom transfer to olefins. The catalytic oxidation of the two olefins was done in the presence of 1-methylimidazole or 4'-(imidazol-1-yl)acetophenone (4~5 × 10^{-2} M) (Table 2). The velocity of the product formation was almost the same between the two metalloporphyrins. Against our expectation, however, decrease in the epoxide ee was observed. To increase oxygen-atom

Table 1. Comparison of catalytic epoxidation of simple olefins on the effect of central metal ions, Fe and Mn.[a]

substrate	catalyst M	reaction time, h	turnover no.[b] epoxide	carbonyl	ee, %[c]	confign.[d]
	Fe	3.5	50	5	22	*S*
	Mn	9	67	12	16	*S*
	Fe	3	26	tr[e]	80	(*S*)
	Mn	9	22	tr[e]	66	(*S*)
	Fe	4.5	48	2	24	n.d.[e]
	Mn	5	40	2	37	n.d.[e]
	Fe	2	38	3	19	*1S,2R*
	Mn	4	28	3	**61**	*1S,2R*
	Fe	3	34	7	18	*1S,2R*
	Mn	22	20	7	**40**	*1S,2R*
	Fe	2	22	4	20	*1S,2R*
	Mn	23	11	4	**44**	*1S,2R*

[a] All reactions were done under the standard reaction conditions depicted in the text. [b] Turnover numbers were based on the amount of the catalyst applied. [c] Determined by means of ^1H NMR with $Eu(hfc)_3$ as a chiral shift reagent. [d] The absolute configuration of styrene oxide was determined by the comparison of the spectroscopic behavior on ^1H NMR with the authentic sample. Configuration in parentheses were deduced from analogy with the the spectroscopic behavior of the (*S*)-styrene oxide. The major configurations of *cis*-β-methylstyrene oxide and the other epoxides of cyclic olefins were determined by the measurement of their optical rotations. see ref. 7. [e] tr: trace, n.d.: not determined.

Table 2. Effect of Oxidant and Axial Ligands on the Epoxide Ee.[a]

substrate	catalyst M	oxidant	ligand[b,c]	reaction time, h	turnover no. epoxide	carbonyl	ee, %[d]	confign.[d]
	Mn	PhIO	-	9	67	12	16	*S*
	Mn	PhIO	MeIm	7	45	1	0	-
	Mn	C_6F_5IO	-	3	62	7	0	-
	Mn	C_6F_5IO	MeIm	5	53	5	12	*S*
	Mn	C_6F_5IO	AcPIm	6[e]	67	3	**23**	*S*
	Mn	PhIO	-	4	28	3	61	*1S,2R*
	Mn	PhIO	AcPIm	6.5	27	3	46	*1S,2R*
	Mn	C_6F_5IO	-	1	23	3	47	*1S,2R*
	Mn	C_6F_5IO	AcPIm	3	9	1	**70**	*1S,2R*

[a] All reaction conditions were the same as described in Table 1 except otherwise noted. [b] [MeIm] = 4×10^{-2} M. [AcPIm] = 5×10^{-2} M. [c] MeIm: 1-methylimidazole, AcPIm: 4'-(imidazol-1-yl)acetophenone. [d] Enantiomeric excesses and the absolute configuration of the epoxide was determined as described in Table 1. [e] At -20°C.

transfer rate from an oxidant to the Mn ion, we applied C_6F_5IO as a stronger one than PhIO. Utilization of imidazole bases or C_6F_5IO is only affordable in the reaction with the Mn porphyrin catalyst.[5] The combination of C_6F_5IO and 4'-(imidazol-1-yl)acetophenone gave better ees without decrease of the reaction rate. Through this fine tuning of the oxidation conditions, the ees of styrene oxide and *cis*-β-methylstyrene oxide were improved to be 23 and 70%ee, respectively.[6] If one use the iron derivative as the substitution to the Mn porphyrin, addition of imidazole to the reaction mixture completely inhibits the oxidation reaction,[4] and use of C_6F_5IO instead of PhIO caused very rapid degradation of the Fe catalyst, whose porphyrin ring is electron-rich and susceptible to get electrophilic attack.

Thus, we showed that the Mn porphyrin catalyst is superior than the iron one, especially for β-substituted styrene derivatives, if the porphyrin is appropriately designed and its combination with C_6F_5IO-imidazole derivatives will further improvement on the resultant ees.

References and Notes

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$$\mathrm{MnP} \overset{\mathrm{Im},\ K_1}{\rightleftharpoons} \mathrm{(Im)MnP} \overset{\mathrm{Im},\ K_2}{\rightleftharpoons} \mathrm{(Im)_2MnP}$$

At the same concentration of the imidazole, the iron catalyst formed diimidazole complex.

5 If one use the iron derivative as the substitution to the Mn porphyrin, addition of imidazole to the reaction mixture completely inhibits the oxidation reaction, and use of C_6F_5IO instead of PhIO caused very rapid degradation of the Fe catalyst, whose porphyrin ring is electron-rich and susceptible to electrophilic attack. This is the first example which examined the oxidation with C_6F_5IO-Mn porphyrin system. Concerning to the reaction with C_6F_5IO and a highly electron-deficient porphyrin, see, Collman, J. P.; Kodadek, T.; Raybuck, S. A.; Braumann, J. I.; Papazian, L. M.; *J. Am. Chem. Soc.* **1985**, *107*, 4343.

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