158 © 1993 The Chemical Society of Japan *Bull. Chem. Soc. Jpn.*, **66**, 158—166(1993) [Vol. 66, No. 1

Asymmetric Epoxidation of Simple Olefins by Chiral Bitetralin-Linked "Twin-Coronet" Porphyrin Catalysts

Yoshinori NARUTA,* Nobuo ISHIHARA, Fumito TANI, and Kazuhiro MARUYAMA*
Department of Chemistry, Faculty of Science, Kyoto University, Sakyo-ku, Kyoto 606-01

(Received May 27, 1992)

Catalytic and asymmetric epoxidation of styrenes and related aryl substituted olefins with the iron complexes of chiral bitetralin (Bitet)-linked "twin-coronet" porphyrins was performed with iodosylbenzene as an oxidant. Among two topological isomers of the catalyst, the eclipsed one (**5b**) showed higher enantioselectivity than the staggered (**6b**). With **5b**, the resulting epoxides, except for the olefins bearing an electron-donating substituent, were obtained in good to excellent enantioselectivity (54—96% ee), especially for the styrenes with electron-withdrawing substituent(s). Being different from other porphyrin-based chiral catalysts, the catalyst **5b** is robust enough under the applied oxidation conditions to exhibit chiral epoxidation with the same ee and the same rate as those of the initial period of the reaction even after about 500 turnovers. The Bitet catalyst is superior in the epoxide enantioselectivity than the corresponding chiral binaphthalene (Binap)-linked catalyst (**3b**). In the reactions with the catalysts **3b** and **5b**, good correlation in epoxide ees was observed. Increase of the epoxide ee in the reaction with the Bitet catalyst was elucidated by the shape and size of the reaction cavities of the Bitet were tighter than those of the latter. The observed ees of the substituted styrene oxides showed good correlation with $\Sigma\sigma^+$ values of their substituent(s). In the reaction with the electron-deficient olefins, π–π^* interaction between the HOMO of the electron-rich Bitet auxiliary ring and the LUMO of the electron-deficient aryl ring of the substrate are pointed out as the key for the realization of high ees. Some nitrostyrenes, however, gave rather lower ees in spite of rather higher degree of their electron deficiency. This deviation was elucidated by the mismatching of their frontier orbitals.

Catalytic and asymmetric oxidation is not a fully developed area among other asymmetric reactions, e.g., reduction and C–C bond formation, regardless of its usefulness and importance in organic synthesis.[1] This results from the severe requirements for catalysts in oxidation reaction: Chiral catalysts or ligands should be robust enough under the applied oxidation conditions and have to survive after numerous turnovers. These requirements limit kinds of applicable ligands to a great extent.

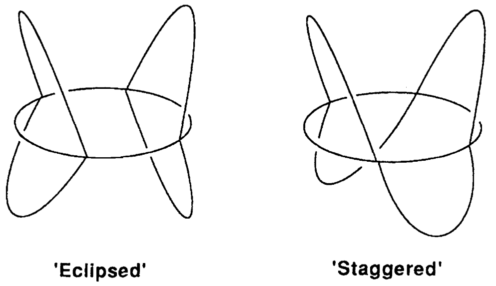
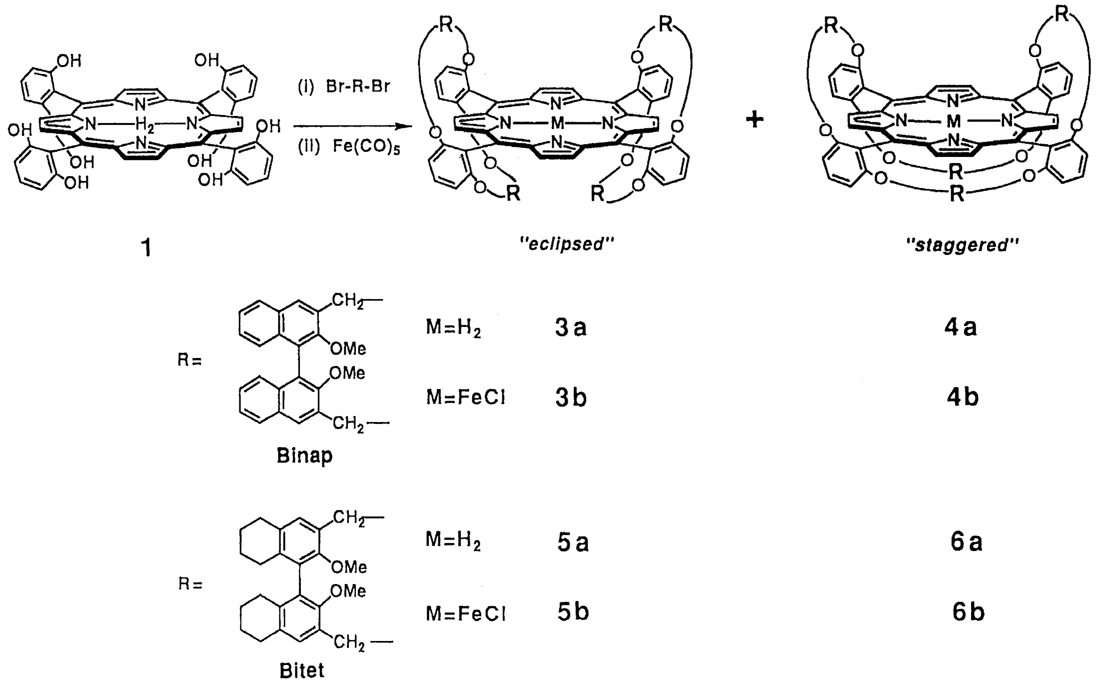


Fig. 1. Schematic drawing of topological isomers of "twin-coronet" porphyrins.

Chiral porphyrins are interested as model compounds of cytochrome P-450 monooxygenase. Although several chiral porphyrins have been synthesized and used in the catalytic asymmetric oxidation,[2] these studies have never shown how the porphyrin catalyst differentiated the prochiral faces of substrates. In one case,[2d] it has been explained only by unclear steric interaction between a substrate and the auxiliary group on the porphyrin catalyst. In order to design an efficient catalyst both in view of enantioselectivity and the catalytic turnover numbers, detailed analysis of the catalytic reaction is inevitable. For this end, we have designed and synthesized chiral porphyrin catalysts **3** and **4**, "twin-coronet" porphyrins, bearing four chiral binaphthalene (Binap) auxiliaries on both faces of the porphyrin plane through eight ethereal linkages to fulfill the requirements mentioned above (Fig. 1).[3] The four bulky binaphthalene groups were efficiently connected to the porphyrin ring by Williamson reaction in one pot and made four chiral pockets over both faces of the porphyrin plane. By the difference of the binding mode of the auxiliary, there are two topological isomers, 'eclipsed' **3** and 'staggered' **4**, both of which have D_2 symmetry (Fig. 2). The methoxyl groups inside the cavity, which are very close to the metal center of the porphyrins, are expected to function as those to regulate the direction of substrate approach in cooperation with rigid binaphthalene walls above the periphery of the porphyrin ring. Catalytic monooxygenation of olefins and sulfides with the eclipsed isomer of the iron twin-coronet porphyrins gave the corresponding epoxides and sulfoxides,[4] respectively, in moderate to good enantioselectivity and the electron-deficient substrates gave in higher ees than the electron-rich ones. We concluded the epoxidation of styrene derivatives (and also monooxidation of sulfides) proceeded through single-electron transfer process. To improve their enantioselectivity, it is necessary that steric environment of the reaction cavity should be tunable by replacing with an appropriate appendage. Metalloporphyrin residue should be electronically equivalent for the fair evaluation of the steric factor of appendage on the enantioselectivity. In this context, the bitetralin (Bitet)-linked



Scheme 1.

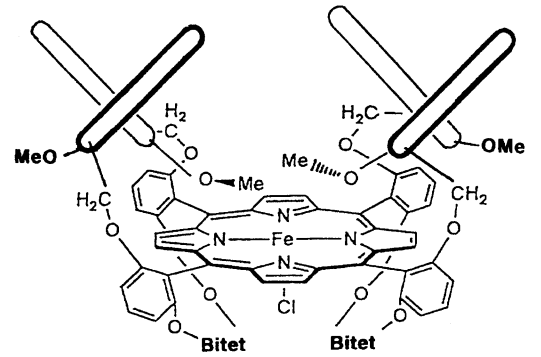


Fig. 2. Chiral "twin-coronet" porphyrin **5b** (eclipsed form).

twin-coronet porphyrin is a very good model compound (Fig. 2).

Recently, we have shown that the relating bitetralin (Bitet)-linked porphyrin catalyst exhibited superior enantioselectivity than the corresponding Binap analogs in our preliminary report.[3c)] Aim of this report is to give the solid base concerning the mode of prochiral-face recognition of simple olefins in catalytic and asymmetric epoxidation, and we reveal detailed result of the asymmetric epoxidation with the catalyst.

Results and Discussion

Improvement of Catalyst Synthesis. The Bitet "twin-coronet" porphyrins **5a** and **6a** were synthesized by means of the coupling reaction of *meso*-tetrakis(2, 6-dihydroxyphenyl)porphyrin (**1**) and (*R*)- or (*S*)-3,3′-bis(bromomethyl)-2,2′-dimethoxy-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′- binaphthalene (**2**) (Scheme 1). In our preliminary synthesis,[3b)] their total yields were in the range of 0.7—3% with poor reproducibility. To improve their synthetic efficiency, we tried various reaction conditions. The octahydroxyporphyrin **1** is very unstable under basic conditions, especially in the presence of homogeneous bases such as pyridine or DBU. Furthermore, when the porphyrin was dissolved in the basic solution, its polymerization was accelerated by trace amount of oxygen to give the corresponding polymer that was insoluble in most of organic solvents. Other solid bases, Na_2CO_3 or Cs_2CO_3, were ineffectual to the coupling.

Reaction temperature was another important factor to affect their yields. From CPK model, the dihedral angle of the two phenyl rings of bitetralin is restricted in 70—100° by the steric interaction between their saturated tetramethylene chains and is more restricted than the corresponding Binap molecule.[3b)] The lack of the flexibility of this appendage implies that the condensation reaction requires higher temperature. In consequence, the reaction was performed in an autoclave under high-purity argon atmosphere at 110°C for 6 d. An acetone-THF mixture and K_2CO_3 were used as a solvent and a base, respectively, and a small amount of zinc mossy was added for prevention of oxidative polymerization of the octahydroxyporphyrin by trace amount of remaining oxygen. Under these optimized conditions, the yields of **5a** and **6a** were improved to be 2—3% and 2.5—6%, respectively.

The two isomers of the free base twin-coronet porphyrins showed their CD signals at the wavelength corresponding to their Soret- and Q bands (Fig. 3). The spectra of the two enantiomers were mirror images in each other, and this implies the absence of their racemi-

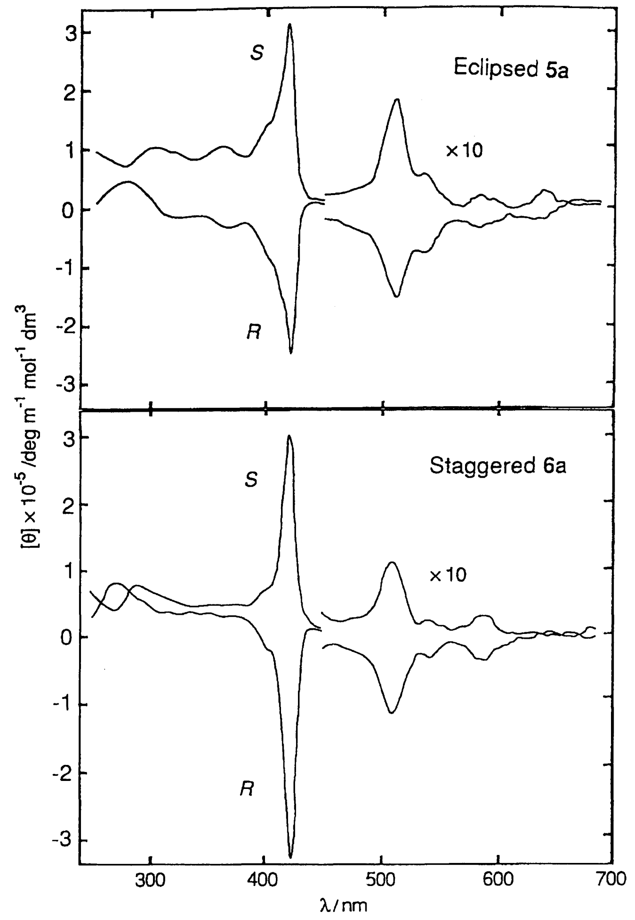


Fig. 3. CD spectra of free base Bitet porphyrins **5a** and **6a**.

zation of the auxiliary molecule in the coupling stage. These spectra were very similar to those of the corresponding Binap-linked porphyrins and their porphyrin ring is somewhat distorted by the conjunction of the optically active appendages.

The resultant free base porphyrins, **5a** and **6a**, were converted to the corresponding iron(III) complexes, **5b** and **6b**, respectively, with $Fe(CO)_5$–I_2.

Catalytic Epoxidation. For evaluation of these catalysts and the reaction mode, we systematically performed catalytic epoxidation of various styrene derivatives in the presence of the iron Bitet porphyrins, **5b** or **6b**, with iodosylbenzene as an oxidant (Chart 1). As standard reaction conditions, PhIO (100 equiv to the amount of the catalyst) was added to a dichloromethane solution of an olefin (500 equiv) and the catalyst at 0°C under argon atmosphere. At appropriate intervals, aliquots taken from the reaction mixture were quenched by a slight excess of PPh_3 and analyzed by GLC. When increase in the amount of oxidized product(s) was no longer observed, the products were isolated by flush column chromatography. In some instances, the corresponding arylacetaldehyde or aryl ketone were obtained as side products. Enantiomeric excess for the resulting epoxide was determined by ^1H NMR spectroscopy performed in the presence of a chiral shift reagent, tris[3-(heptafluoropropyl)hydroxymethylene]-*d*-camphorato]europium(III), $Eu(hfc)_3$. Results were summarized in Table 1 in comparison with the turnover numbers and ees observed in the reaction with the corresponding Binap catalysts. Without any iron porphyrin catalysts, the styrene derivatives were hardly oxygenated by iodosylbenzene under the applied conditions. When epoxide yield in the reaction of styrene did not increase, by the addition of another 100 equiv of PhIO, the epoxidation started in the similar velocity with the initial one and the ee of the resultant epoxide was almost same as that observed after the initial addition of PhIO within technical errors (±2%). The repeated addition of PhIO (overall 1200 equiv) and styrene during 24 h gave styrene oxide in 485 turnovers and 58% ee (Run 3). After such repeated catalytic cycles, both the observed yield and the ee were unaffected in comparison with those run under the standard reaction conditions. This implies the Bitet catalyst is sufficiently robust under the present oxidation conditions in comparison with most of the reported catalysts. Lack of the catalyst degradation process will allow the following mechanistic analysis. Total chemical yields of oxidized products based on the amount of PhIO applied were 10—44%, which depended upon the substrate. Disproportionation of iodosylbenzene to poorly reactive iodylbenzene and iodobenzene will take place as a major competitive reaction in the case of less reactive styrenes bearing electron-withdrawing group(s). Consequently, the epoxide yield based on the amount of applied PhIO decreased.

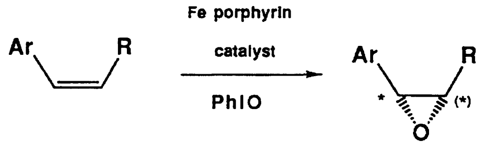
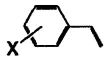
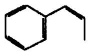
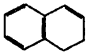
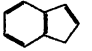


Chart 1.

Enantioselectivity of the eclipsed catalyst **5b** was higher than that of the staggered (Runs 2 vs. 4, and 5 vs. 6) as observed in the corresponding Binap analogs. Since there were no distinctive differences between the two diastereoisomers on UV-vis and CD spectra, the reason for their difference on enantioselectivity is unclear, but slight structural change of the chiral cavity above the active center during the formation of the putative high-valent iron complex would affect the degree of the prochiral-face recognition. Thus, we employed the eclipsed isomer **5b** in the most of catalytic oxidation.

Mode of Prochiral-Face Recognition. Absolute configuration of the resultant epoxide is worth while to mention. The (*R*)-catalyst gave (*S*)- or (1*S*, 2*R*)-epoxides and (*S*)-catalyst provided (*R*)-product. Thus, the configurational correlation between the catalysts and products is observed in all runs and is useful for the

Table 1. Asymmetric Epoxidation Catalyzed by Iron "Twin-Coronet" Porphyrins

Run	Olefin	Catalyst	Reaction time/h	Turnover no.[a,b] Epoxide	Carbonyl compound	Ee/%[b,c]	Config.[d]
	 X=						
1	H	(*S*)-**5b**	3(3.5)	28(49)	0(5)	56(20)	*R*
2	H	(*R*)-**5b**	8(3.5)	84(50)	0(5)	54(22)	*S*
3[c]	H	(*R*)-**5b**	24	485	0	58	*S*
4	H	(*R*)-**6b**	7	44	0	28	*S*
5	2-NO_2	(*R*)-**5b**	3(3)	17(26)	0(tr)	89(80)	(*S*)
6	2-NO_2	(*R*)-**6b**	3(3)	10(26)	0(tr)	43(54)	(*S*)
7	3-NO_2	(*R*)-**5b**	2(2)	26(57)	0(tr)	74(60)	(*S*)
8	4-NO_2	(*R*)-**5b**	3(2)	21(38)	0(tr)	67(54)	(*S*)
9	2,4-$(NO_2)_2$	(*R*)-**5b**	2(3)	11(20)	0(tr)	76(68)	(*S*)
10	3,5-$(NO_2)_2$	(*R*)-**5b**	4(2)	36(20)	0(tr)	96(74)	(*S*)
11	F_5	(*S*)-**5b**	3(2)	10(36)	0(tr)	83(74)	(*R*)
12	4-Br	(*R*)-**5b**	3(2)	31(31)	8(5)	51(28)	(*S*)
13	4-Me	(*R*)-**5b**	3(5)	30(48)	11(12)	27(11)	(*S*)
14	2-OCH_3	(*S*)-**5b**	3(2.5)	0(32)	35(16)	—(0)	—
15	3-OCH_3	(*R*)-**5b**	2(2.5)	33(35)	0(6)	73(45)	(*S*)
16		(*R*)-**5b**	3(2)	17(38)	0(3)	63(19)	1*S*,2*R*
17		(*R*)-**5b**	3(2)	29(11)	-[f](4)	56(20)	1*S*,2*R*
18		(*R*)-**5b**	3(2)	51(34)	20(7)	70(18)	1*S*,2*R*

a) Mol product/mol catalyst, determined by GLC. b) Numbers in parentheses were obtained in the reaction with the corresponding Binap catalysts, eclipsed **3b** or staggered **4b**. c) Enantiomeric excesses (±2%) were determined by ^1H NMR spectroscopy performed in the presence of a chiral shift reagent, $Eu(hfc)_3$. d) Major configurations of the epoxides of styrene and pentafluorostyrene were determined by comparison with the corresponding authentic optically pure oxides. Others in parentheses were deduced on the analogy with the spectroscopic behavior of (*R*)-styrene oxide. For Runs 16—18, the configuration of their major enantiomers was determined by the measurement of their optical rotation, see Ref. 13. e) A 50 equiv-portion of PhIO to the amount of the catalyst was added at one-hour intervals by keeping the concentration of styrene constant. f) Not determined.

judgment of their relative arrangement at the oxo-transfer stage. In the following discussion, we mention on the reaction of the (*S*)-catalyst. There are three options in their transition-state geometries (Fig. 4). Among them, the geometry A or C is responsible for (*R*)-epoxide formation from the (*S*)-Bitet catalyst, though the latter can easily be excluded by anticipated severe steric repulsion between the aromatic ring of a styrene derivative and the auxiliary bitetralin. The remaining geometry B will lead (*S*)-epoxide with the reverse configuration and is not the major pathway in these reactions. Thus, for the preferential formation of (*R*)-epoxide, it should be taken path A where a substrate and the auxiliary π system can be in parallel and very proximal array. Such conformation has also been considered in the Binap-catalyzed reaction. Discussion of the possibility of π–π^* interaction expected between them is given in the next section.

We compared the ees of substituted styrene oxides between the two catalysts (Runs 1, 5, and 7—15). Every reaction with the Bitet catalyst **5b** exhibited higher enantioselectivity than those with the corresponding Binap one in the range of 8—52%. The increased steric bulkiness of the auxiliary Bitet groups would cause this remarkable improvement on ees, because larger dihedral angle (70—110°) between their two aromatic rings in the bitetralin auxiliary than the binaphthalene one could make the cavity tighter and geometry B in Fig. 4 less favorable. In this comparison, we postulate that the steric effect arising from the bulkiness of the catalyst auxiliary will affect in similar extent on all the styrene derivative, because the steric bulkiness around their C–C double bond is almost equivalent in each styrenes. Such a sterical effect on epoxide ees arising from the shape of their chiral cavity is further enhanced in the reaction of β-substituted styrene derivatives or relating olefins (Runs 16—18). Since they have bulky groups at their olefinic terminus, the geometry B at their oxo-transfer stage is less advantageous than in the reaction of other β-free styrene derivatives, because the steric repulsion between the auxiliary MeO groups in the cavity and the β-substituent of the aryl-substituted olefins

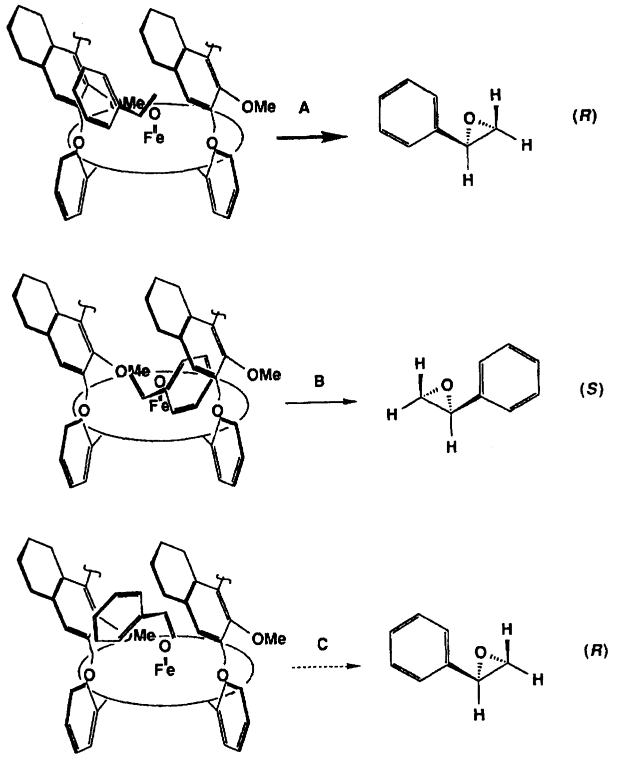


Fig. 4. Possible geometries of styrene in the cavity over the catalyst ((*S*)-**5b**) in the transition state of oxygen transfer. Partial structure of the catalyst is shown for clarity.

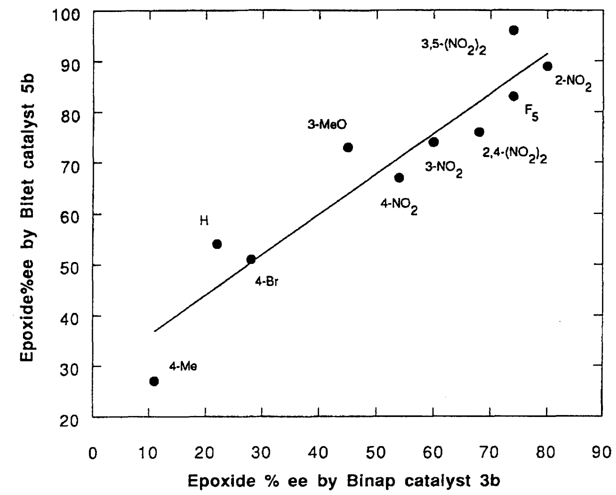


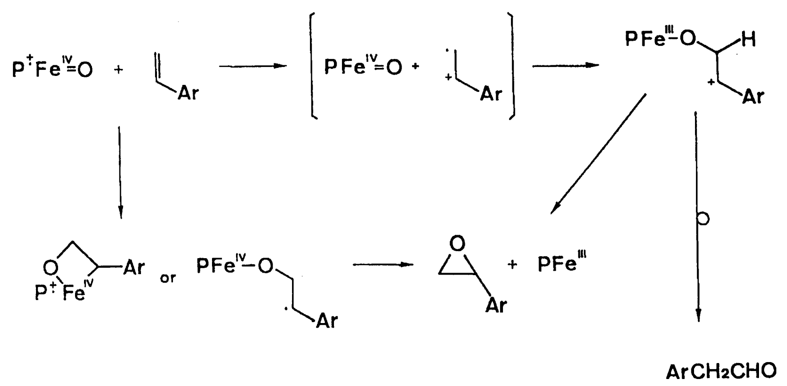
Fig. 5. Correlation of enantiomeric excesses between the reactions catalyzed by the eclipsed isomers of the Binap **3b** and the Bitet catalysts **5b**.

at the geometry should become more severe. Thus, the difference of the resultant ees between the two catalysts reached to 36—52% in the reaction of β-substituted styrene derivatives.

We consider the electronic character of this reaction. The Bitet catalyst as well as the Binap one also showed excellent ees in the reaction of electron-deficient styrene derivatives: The best enantioselectivity reached 96% ee in the reaction of 3,5-dinitro derivative. This is the highest ee value ever recorded in such a simple olefin without modification by any bulky substituent at the olefinic double bond. The plot of ees obtained separately by these sterically different catalysts is shown in Fig. 5. In the comparison of the two catalysts, the mode of asymmetric oxidation resembles between them: Electron-deficient olefins gave better ees than the electron rich ones. Alignment of the olefins, however, in the order of their ees is subtly different between the two catalysts: by the Binap catalyst, 2-NO$_2$>3,5-(NO$_2$)$_2$≈F$_5$>2,4-(NO$_2$)$_2$>3-NO$_2$>4-NO$_2$, while by the Bitet, 3,5-(NO$_2$)≫2-NO$_2$>F$_5$>2,4-(NO$_2$)$_2$≈3-NO$_2$>4-NO$_2$. This implies the two catalysts are different in the mode of their prochiral-face recognition.

In our previous study with the Binap catalyst, the epoxide ees also showed good correlation with $\Sigma\sigma^+$ value of substituent(s) on the phenyl ring of styrene derivatives except for some electron-deficient olefins. This implies the epoxidation proceeded initially through the formation of cationic or positively polarized intermediate by single-electron transfer from olefins to the putative high-valent iron porphyrin intermediate followed by the succeeding oxo-transfer (Scheme 2). This mechanism is also supported by the formation of the corresponding arylacetaldehydes or aryl ketones as side procucts, which are expected to arise by proton migration from the corresponding benzylic cation or the equivalent intermediate. This scheme is also applicable to the present oxidation.

If only the electron deficiency of substrates causes higher enantioselectivity, it can be explained simply by the Hammond postulate, because the epoxidation by an iron porphyrin catalyst is electrophilic and electron-deficient olefins become less reactive and more selective, i. e. they will give larger free energy difference ($\Delta\Delta G^{\neq}$) between the two enantiomers. In this mechanistic elucidation, resultant ees should monotonously correlate to the degree of electron-deficiency of olefins, if one can postulate that steric factor is equivalent in each olefin. So, we plotted $\Delta\Delta G^{\neq}$ vs. substituent $\Sigma\sigma^+$ (Fig. 6). Most of the olefins showed linear correlation, while three nitro substituted styrenes, 3-NO$_2$, 4-NO$_2$, and 2,4-(NO$_2$)$_2$, showed large deviation from this correlated line, irrespective their relatively large $\Sigma\sigma^+$ values. Especially, the difference between 3,5-(NO$_2$)$_2$ and 2,4-(NO$_2$)$_2$ became to be 20%, regardless of their similar $\Sigma\sigma^+$ values. These results indicate that the behavior of the all styrene derivatives can not be elucidated only by the Hammond postulate. Thus, such large differences in the ees can not be explained simply by the overall electronic character of olefins. If one tries to attribute the observed difference only to the steric effect between nitro group(s) and the auxiliary bitetralin, all data should systematically be explained without any discrepancy in each other. As seen from geometries A or B in Fig. 5, substituents at the para position of the



Scheme 2.

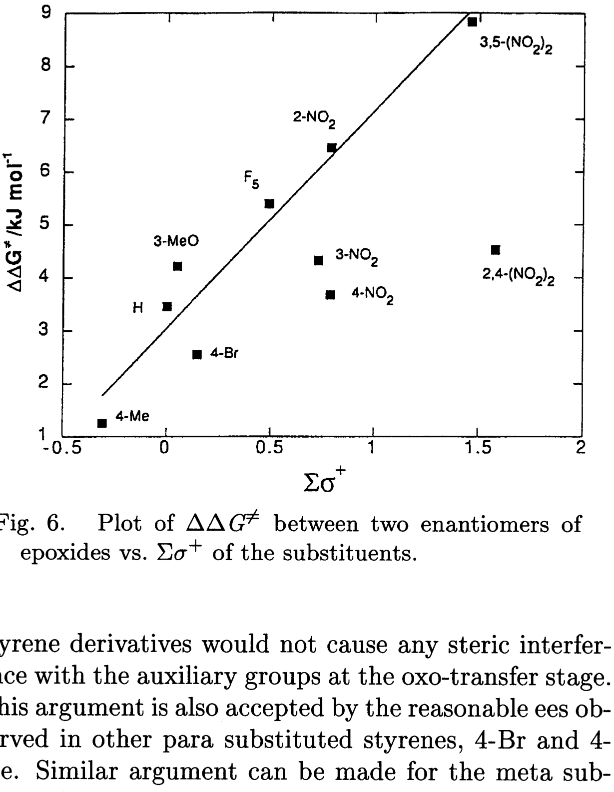


Fig. 6. Plot of $\Delta\Delta G^{\neq}$ between two enantiomers of epoxides vs. $\Sigma\sigma^{+}$ of the substituents.

styrene derivatives would not cause any steric interference with the auxiliary groups at the oxo-transfer stage. This argument is also accepted by the reasonable ees observed in other para substituted styrenes, 4-Br and 4-Me. Similar argument can be made for the meta substituted styrenes. On the other hand, the substitution at the ortho position of the styrenes could potentially and much sensitively affect to the resultant ees because of their proximity to the C–C double bond. The epoxidation of 2-nitrostyrene, however, did not show any unusualness. Thus, the unexpectedly low ee values of the several nitrostyrenes can not be explained only by the steric effect.

π–π^* Interaction between a Substrate and the Auxiliary. According to the discussion described above, we consider the electronic interaction between the two aromatic rings of the styrene derivative and the bitetralin residue. In the geometry A, parallel orientation of the two aromatic rings can be allowed to develop an effective π–π^* interaction. Moreover, the aromatic ring of the bitetralin is sufficiently electron-rich, and it will be a most probable candidate for an electron donor toward electron-deficient substrate π-systems. Thus, consideration of the frontier-orbital interaction in the donor-acceptor combination is very rational. We performed CNDO/2 MO calculations for the typical styrene derivatives and a substituted biphenylylene as an electronically analogous model compound **7** of the chiral bitetralin auxiliary (Fig. 7). LUMOs of several typical nitrostyrenes[6] and HOMO of the auxiliary biaryl[7] were indicated, and the former orbitals are overlapped with the latter to take most likely geometry at the transition state of their oxo-transfer. Their symmetry and degree of orbital electron population were compared. The auxiliary model compound **7** has higher population of electron at C-1 and C-2 with the same orbital symmetry. The LUMO of 2-nitro- and 3,5-dinitrostyrenes can overlap with **7** at the 3,6- and 2,5-positions of phenyl ring of the styrenes, respectively, keeping the symmetry without sign inversion. These styrenes have matched orbital symmetries with that of the auxiliary and can make maximum π–π^* interaction at the oxo-transfer geometry. Actually, these olefins gave good ees among electron-deficient ones. On the other hand, the rest of the listed olefins, 3-NO_2, 4-NO_2, and 2,4-$(NO_2)_2$ derivatives, have mismatched orbital symmetries with that of the auxiliary, e.g. LUMO of the 3-NO_2 derivative as well as 2,4-$(NO_2)_2$ ones has nodes at C-1/C-2 and C-4/C-5. They will weaken the expected frontier-orbital interaction with the donor molecule **7**. Analogously, 4-nitrostyrene has large electron population at C-2, C-3, C-5, and C-6, and the presence of a node between each adjacent two carbons can make the efficient interaction with the auxiliary π system unfavorable. Thus, these three olefins gave similarly low ees in their epoxidation regardless of their electron deficiency.

Finally, subtle differences in enantioselectivity among the electron-deficient olefins between the Bitet and the Binap catalysts could be due to the different symmetry of their frontier orbitals. Figure 8 shows their HOMOs of the corresponding model compounds, **7** and **8**, whose positions with large electron population and their symmetry are completely different. This implies that a substrate having matched LUMO with these auxiliary HOMOs will be different.

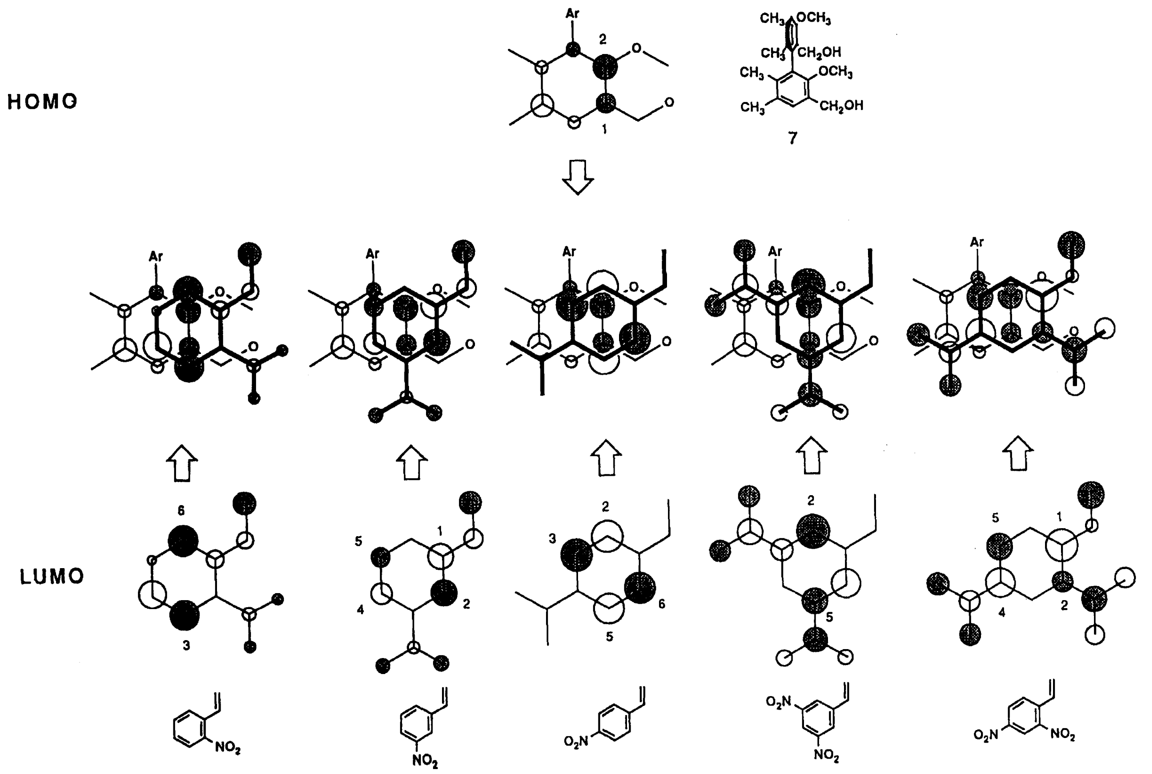


Fig. 7. Investigation of the frontier-orbital symmetries between nitro styrenes and a model compound **7** of the Bitet auxiliary.

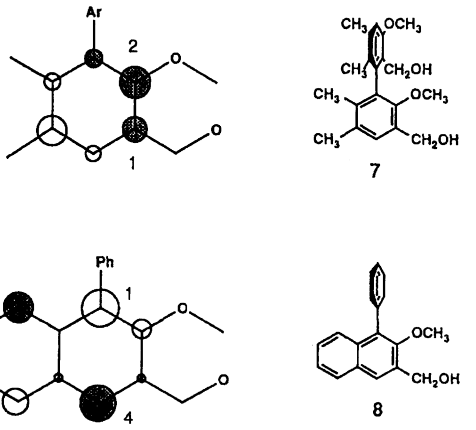


Fig. 8. Comparison of HOMOs of the two model compounds, **7** and **8**, analogous to the bitetralin and the binaphthalene auxiliaries, respectively.

Concluding Remarks. The bitetralin-modified twin-coronet porphyrins catalyzed the epoxidation of styrene derivatives in superior enantioselectivity without catalyst degradation than the porphyrin-based catalysts ever reported. The highest ee (96%) was attained in the reaction of 3,5-dinitrostyene. This is a remarkable value in consideration of its simple structure. We confirmed the ee was dependent upon the electronic character of the substrate. In all reactions of various styrene derivatives except for that with the staggered catalyst, higher ees than those with Binap catalyzed ones were observed. Increase of the ees was attributed to the shape of the reaction cavity consisted of chiral aryl auxiliaries. Electron-deficient styrene derivatives gave higher ees, while several nitrostyrenes, whose aromatic ring was sufficiently electron-deficient, showed unexpectedly lower ones. This substrate selectivity was rationally explained by the presence of auxiliary-substrate π–π^* interaction at their oxo-transfer stage, and matching of their frontier-orbital symmetry is essential for maximization of their interaction to fix a substrate tightly on the catalyst at a desired geometry for prochiral-face recognition. As seen in our previous paper, the proposed mode of substrate prochiral-face recognition has further been approved through the detailed analysis in this study with an electronically different auxiliary. These results suggest that the π–π^* interaction of frontier orbitals between a substrate and a catalyst is one of the effective mode as well as the steric one in enantioselective reaction, where hydrogen bonding is unavailable. Since this interaction is tunable by the introduction of appropriate substituents onto the catalyst and predictable by consideration of their frontier-orbitals, it will give an useful guideline for the design of the asymmetric catalyst.

Experimental

Experimental protocols are same as our previous paper.[3b] For the epoxies of which ees were too high to determine by ^{1}H NMR, they were determined by HPLC with a chiral stationary-phase column. Following substituted styrenes were obtained from the corresponding benzaldehyde through Knaevenagel condensation and thermal decarboxylation of the resultant cinnamic acid derivatives; 2-NO_2, 3-NO_2, 4-NO_2, 3,5-$(NO_2)_2$, and 2-MeO.$^{8)}$ 2,4-Dinitrostyrene was prepared by nitration of 2-phenylethanol and succeeding dehydration by modification of the described procedure.$^{9)}$ 4-Methylstyrene$^{10)}$ and pentafluorostyrene$^{11)}$ were prepared from the corresponding benzaldehydes through methylation by MeMgI and succeeding dehydration with $KHSO_4$ and P_2O_5, respectively. 4-Bromo-and 3-methoxystyrenes were obtained from the corresponding acetophenones through $NaBH_4$ reduction/dehydration. *cis*-2-Methylstyrene was obtained by partial hydrogenation of 1-phenyl-1-propyne.$^{12)}$ Other olefins were commercially available and were used after distillation.

(*S*)- and (*R*)-3,3′-Bis(bromomethyl)-2,2′-dimethyl-5,5′,6,6′, 7,7′,8,8′-octahydro-1,1′-binaphthalene (2). These dibromides were prepared from optically active 1,1′-binaphthalene-2,2′-diol as reported.

H_2[(*R*)- Bitet$(OMe)_2]_4$TPP- Eclipsed (5a) and -Staggered (6a). A suspension of finely ground K_2CO_3 (1.0 g) and zinc mossy (10 mg) in an acetone (40ml)-THF (40 ml) solution containing **1** (120 mg, 0.161 mmol) and (*R*)-**2** (384 mg, 0.776 mmol) was bubbled with high-purity argon in an stainless-steel autoclave and was stirred for 6 d at 110°C (bath temperature). The suspension was filtered and extracted with dichloromethane. The organic layer was evaporated and the resulting residue was dissolved again in dichloromethane. The solution was washed successively with 0.5 M HCl ($1\,M=1\ mol\,dm^{-3}$), water, and brine, and then dried over anhydrous Na_2SO_4. The resultant dichloromethane solution was evaporated and the residue was separated by flush-column chromatography on silica gel (eluted successively by benzene and dichloromethane). The first fraction was purified through activated alumina (eluted by methanol-free dichloromethane) to give **5a** (10.3 mg, 3.0%).

The second fraction was purified by flush chromatography on silica gel (eluted by benzene). The resulting first fraction was purified through activated alumina (eluted by methanol-free dichloromethane) to give **6a** (18.8 mg, 5.5 %). Physical and spectroscopic data of **5a** and **6a** were same as the reported ones.$^{3b)}$

Catalytic Epoxidation of Olefins by Fe(Cl)[(*R*)-Bitet$(OMe)_2]_4$TPP, (5b) or (6b). To a mixture of the catalyst **5b** or **6b** (1.0 μmol), an olefin (500 μmol), and a GLC internal standard (tridecane or 1-chlorooctane, 50 μmol) in deaerated dry dichloromethane (1 ml) was added freshly prepared iodosylbenzene (22 mg, 100 μmol). The reaction mixture was stirred constantly under argon atmosphere at 0 °C. The reaction mixture (5 μl) was taken at appropriate intervals and quenched with a dichloromethane solution of triphenylphosphine ($1.3\times10^{-6}\ mol\,dm^{-3}$, 45 μl). When the substrate was nitrostyrene derivatives, the mixture was not quenched. Formation of reaction product(s) was monitored by GLC. When the increase of the product yield stopped, products were isolated by flush-column chromatography on silica gel, and were identified by ^{1}H NMR spectroscopy. The ees were determined by ^{1}H NMR with a chiral shift reagent, Eu$(hfc)_3$. When ees of the resultant epoxides were too high to determine by means of ^{1}H NMR (Run 10), HPLC with a chiral stationary phase column was used for the quantitative analysis. To examine the durability and efficiency of the catalyst, PhIO (a 50 equiv-portion, overall 1200 equiv to the amount of the catalyst) was added at every one-hour for 24 h by keeping the amount of styrene constant (450 equiv to the catalyst). The monitoring of the reaction course and the workup were done as described above.

We are grateful to Professor Sho Takahashi, Institute for Chemical Research, for the loan of a CD spectrometer.

References

1) Review: *Chem. Br.*, **1987**, 259.

2) Typical examples: a) J.T. Groves and R. S. Myers, *J. Am. Chem. Soc.*, **105**, 5791(1983); b) D. Mansuy, P. Battioni, J. -P. Renaud, and P. Guerin, *J. Chem. Soc., Chem. Commun.*, **1985**, 155; c) S. O'Mally and T. Kodadek, *J. Am. Chem. Soc.*, **111**, 9116 (1989); d) J.T. Groves and P. Viski, *J. Org. Chem.*, **55**, 368 (1990); e) R.L. Halterman and S. -T. Jan, *J. Org. Chem.*, **56**, 5253 (1991); f) Ph. Maillard, J. L. Guerquin-Keern, and M. Momenteau, *Tetrahedron Lett.*, **32**, 4901 (1991); g) K. Konishi, K. Oda, K. Nishida, T. Aida, and S. Inoue, *J. Am. Chem. Soc.*, **114**, 1313 (1992).

3) a) Y. Naruta, F. Tani, and K. Maruyama, *Chem. Lett.*, **1989**, 1269; b) Y. Naruta, F. Tani, N. Ishihara, and K. Maruyama, *J. Am. Chem. Soc.*, **113**, 6865 (1991); c) Y. Naruta, N. Ishihara, F. Tani, and K. Maruyama, *Chem. Lett.*, **1991**, 1933.

4) Y. Naruta, F. Tani, and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, **1990**, 1378; Y. Naruta, F. Tani, and K. Maruyama, *Tetrahedron: Asymmetry*, **2**, 533 (1991).

5) G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

6) Since the 1st LUMOs of mononitrostyrenes show large electron population mainly on their nitro group, their 2nd LUMOs were taken into consideration for their frontier-orbital interaction in this discussion. As the dinitrostyrenes, however, have sufficient electron density on their aromatic carbons at their 1st LUMOs, these orbitals were used for the orbital symmetry analysis.

7) The HOMO of the biaryl molecule **7** was estimated by changing the dihedral angle of two aryl rings between 65—120°, the calculated electronic population and the symmetry were not affected by the dihedral angle in this range. In Figs. 7 and 8, results at 90° were indicated.

8) R. H. Wiley and N.R. Smith, *Org. Synth.*, Coll. Vol. 4, 731 (1963).

9) J. R. Gandler and T. Yokoyama, *J. Am. Chem. Soc.*, **106**, 130 (1984).

10) W. S. Emerson, *Chem. Rev.*, **45**, 347 (1949).

11) G.G. Furin, G. F. Grebenshchikova, A. Y. Lvova, V.W. Ulasov, and G. G. Yakobson, "Synthesis of Fluoroorganic Compounds," ed by I. L. Knunyants and G. G. Yakobson, Springer, Berlin (1985), p. 130.

12) C. A. Brown and V. K. Ahuja, *J. Chem. Soc., Chem. Commun.*, **1973**, 553.

13) B. Witkop and C. M. Foltz, *J. Am. Chem. Soc.*, **79**, 197 (1957); M. M. Akhtar, P.R. Boyd, and F. G. Hamilton, *J. Chem. Soc., Perkin Trans. 1*, **1979**, 2437 ; M. Imuta and

H. Ziffer, *J. Org. Chem.*, **43**, 4540 (1978); D. R. Boyd, N.D. Sharma, and A. E. Smith, *J. Chem. Soc., Perkin Trans. 1*, **1982**, 2767.