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# Epoxidation Reactions Catalyzed by Iron Porphyrins. Oxygen Transfer from Iodosylbenzene

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**Abstract:** The epoxidation of olefins by iodosylbenzene is catalyzed by synthetic iron porphyrins. With (chloro-5,10,15,20-tetraphenylporphyrinato)iron(III) (FeTPPCl), cyclohexadiene oxide was produced in 93% yield and with (chloro-5,10,15,20-tetra-*o*-tolylporphyrinato)iron(III) (FeTTPCl), cyclooctene oxide was produced in 84% yield. Cis olefins were found to be more reactive than trans olefins. Thus, whereas *cis*-stilbene was epoxidized by FeTPPCl/iodosylbenzene in 77% yield, *trans*-stilbene was unreactive under these conditions. The degree of cis/trans selectivity was a sensitive function of substitution of the porphyrin periphery. With (chloro-5,10,15,20-tetramesitylporphyrinato)iron(III), the relative reactivity of *cis*- and *trans*-cyclododecene was 8.92:1. Similarly, the less reactive cis double bond of *trans,trans,cis*-cyclododecatriene could be selectively epoxidized by this catalyst. Trans 1,2-disubstituted double bonds and 1,1-disubstituted double bonds showed similar reactivities. These results suggest an approach of the double bond from the side of the iron-bound oxygen and parallel to the porphyrin plane. A mechanism involving formation of and oxygen transfer from a reactive iron–oxo intermediate is proposed for this reaction. The preference for side-on approach of the olefin to the iron-bound oxygen has been attributed to a stereoelectronic effect involving parartially filled oxygen–iron $p\pi,d\pi$ antibonding orbitals.

The development of new strategies for the selective oxidation of hydrocarbons continues to be an important goal.[1] Whereas whole cell[2] and coupled enzyme systems[3] have been employed for some recent applications, synthetic catalysts based on biological models represent an area of considerable untapped potential. The wide range of oxidative transformations catalyzed by the heme-containing monooxygenase cytochrome P-450[4] suggests that simple metalloporphyrin complexes should also catalyze such reactions under appropriate conditions.

The mechanism of oxygen activation and transfer by cytochrome P-450 has been widely investigated. Although several aspects of the catalytic cycle for this enzyme are still controversial, the process outlined in Scheme I is consistent with existing data for most substrates.[4]

The finding that exogenous oxygen donors such as alkyl hydroperoxides,[5a–c] periodate,[5d] and iodosylbenzene[6] are effective oxygen sources for the enzyme in the absence of oxygen and a reducing agent has supported the view that oxygen is bound and reduced to a metal-bound peroxide at the active site. The active oxygen species can be reasonably formulated as a reactive iron(V)–oxo[7] complex (**1**) or some equivalent that is responsible for oxygen transfer to the substrate.[8]

To establish the minimal structural criteria for oxidative catalysis by heme proteins and to gain some insight into the role of higher valence states in oxygen transfer to organic substrates, we have sought to establish some precedents for these reactions with simple systems. We describe here oxygen transfer reactions from iodosylbenzene to olefins catalyzed by synthetic iron porphyrins.[9,10]

Scheme I

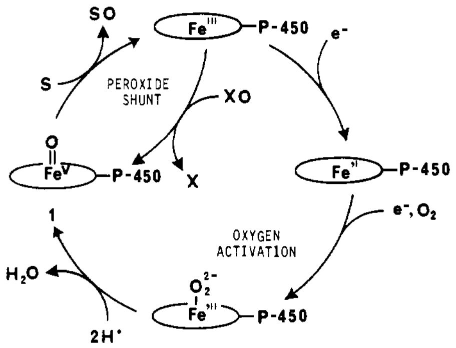
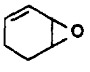
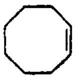
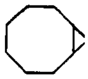
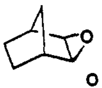
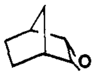
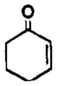
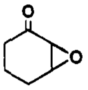
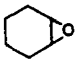
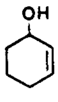
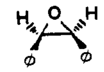


Table I. Epoxidations Catalyzed by Ferric Porphyrins

| | | | |
|---|---|---|---|
|  | FeTPPCl |  | 93% |
|  | FeTTPCl |  | 84% |
|  | FeTTPCl |   | 67%, 3% |
|  | FeTPPCl |  | 0%[b] |
|  | FeTPPCl |  ·  | 55%, 15% |
| | FeTTPCl | | 67%, 15% |
| | FePPIX-DME | | 22%, 5% |
|  | FeTPPCl |  | 77%[c] |

[a] Yield based on iodosylbenzene consumed. [b] On standing with iodosylbenzene alone, cyclohexenone produced small amounts of epoxide. [c] *trans*-Stilbene oxide was not produced.

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(2) Johnson, R. A. In "Oxidation in Organic Chemistry"; Trahanovsky, W. S., Ed.; Academic Press: New York, 1978; Vol. 5-C, pp 131–210.

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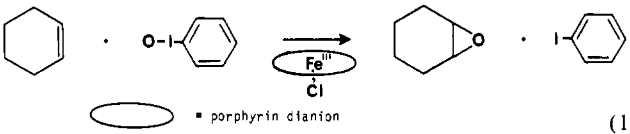
## Results and Discussion

**Epoxidation.** Iodosylbenzene was found to react readily with iron porphyrin in the presence of olefins to produce epoxides in good yield (eq 1). Yields for olefin epoxidation catalyzed by



(1)

(chlorotetraphenylporphyrinato)iron(III) (FeTPPCl) and (chlorotetra-*o*-tolylporphyrinato)iron(III) (FeTTPCl) are presented in Table I. In a typical reaction solid iodosylbenzene was added to a methylene chloride solution in the porphyrin catalyst at room temperature. Higher yields were obtained when the rate of addition of iodosylbenzene was slow and when the concentration of olefin was increased.

An examination of the yield of cyclohexene oxide from cyclohexene with FeTTPCl as the catalyst revealed that each successive equivalent of iodosylbenzene produced the same amount of product and that the visible spectrum of the catalyst was unchanged after 10 equiv of oxidant had been added.

Exposure of the reaction mixtures to air for short periods had a negligible effect on product distributions or yields. However, longer exposures to air or oxygen caused the initiation of free radical autoxidation processes. The effects were most evident for cyclohexene. When oxygen had been excluded from the reaction mixtures, negligible amounts of cyclohexenone were produced, whereas in the presence of air the amount of this product increased rapidly. (Acetonylacetonato)iron(III) was found to be ineffective as a catalyst for the epoxidation of cyclohexene with iodosylbenzene. After 12 h, the iodosylbenzene was consumed but only small amounts of allylic oxidation products were formed.

**Cis–Trans Selectivity.** Whereas *cis*-stilbene was found to react under these conditions to give good yields of *cis*-stilbene oxide, *trans*-stilbene was found to be relatively unreactive. This selectivity is remarkable since typical epoxidizing reagents such as peroxyacids have been shown to react with cis olefins only about two times faster than the corresponding trans olefins.[11] For *m*-chloroperoxybenzoic acid in methylene chloride at room temperature, *cis*- and *trans*-stilbene are epoxidized at equal rates. The reaction of a mixture of *cis*- and *trans*-stilbene with FeTPPCl/iodosylbenzene showed that the cis epoxide formed at least 15 times faster than the trans epoxide under these competitive conditions. This selectivity was inferred to result from nonbonded interactions between the phenyl groups of *trans*-stilbene and the pendant phenyl groups of the FeTPPCl catalyst. Significantly, ferriprotoporphyrin(IX) dimethyl ester (FePPIX–DME) reacted with a mixture of *cis*- and *trans*-stilbene to give low (5%) but equal yields of the two stereoisomeric epoxides. The lower selectivity observed here with the porphyrin catalyst is consistent with the smaller steric size of the methyl groups. The substituent methyl and vinyl groups of FePPIX–DME make this porphyrin relatively flat, whereas the phenyl groups of FeTPPCl are constrained to be nearly perpendicular to the porphyrin plane. Epoxidation of a mixture of *cis*- and *trans*-2-butene by FeTPPCl and iodosylbenzene indicated that the cis compound was 5.8 times more reactive at −5 °C than the trans compound. The relative reactivity of these stereoisomers with *m*-chloroperoxybenzoic acid has been determined to be 2.5:1.[11]

The selectivity for cis olefin epoxidation by FeTPPCl suggested that a family of shape-selective epoxidation catalysts could be developed by altering the steric environment of the porphyrin. The use of ortho-substituted phenylporphyrins to provide an encumbered pocket for oxygen binding is well established.[12] For the purpose of this study ortho methyl, benzo, and phenyl groups were chosen because CPK space-filling models indicated that the resulting steric hindrance would not be so severe as to prevent approach of the olefin to the iron. Table II presents results for the epoxidation of *cis*- and *trans*-cyclododecene in competitive oxidations using FeTPPCl, (chloro-5,10,15,20-tetrakis(1-naphthyl)porphyrinato)iron(III) (FeTNPCl), (chloro-5,10,15,20-tetrakis(*o*-phenylphenyl)porphyrinato)iron(III) (FeTPPPCl) and (chloro-5,10,15,20-tetramesitylporphyrinato)iron(III) (FeTMPCl). Results for FePPIX–DME and *m*-chloroperoxybenzoic acid are included for comparison. These data clearly show that the relative reactivity of the *cis*- and *trans*-alkenes was sensitive to the substitution on the porphyrin periphery. With the exception of FeTPPPCl, the reaction became more selective for the cis olefin as the steric bulk of the catalyst increased. With FeTMPCl, the ratio of cis to trans epoxide produced was 8.9:1. This variation in product ratio for each catalyst indicates that oxygen transfer must have taken place at or very close to the porphyrin as would be expected for an iron–oxo intermediate. The eight ortho methyl groups of FeTMPCl form shallow pockets that surround the porphyrin iron. Apparently, nonbonded interactions develop upon approach of a trans double bond to the iron–oxo group which are absent in the approach of cis olefins.

Table II. Epoxidation of *cis*- and *trans*-Cyclododecene by Ferric Porphyrins

| ferric porphyrin | cis/trans epoxide[a-c] | % yield[d] |
|---|---|---|
| FeTPPCl | 1.55 | 33 |
| FeTPPCl | 3.0 | 58 |
| FeTNPCl | 2.76 | 98[e] |
| FeTPPPCl | 1.52 | 55 |
| FeTMP | 8.92 | 51 |
| FePPIX–DME | 1.27 | 16 |
| mCPBA | 0.59 | no data |

[a] Alkene composition: 60% *trans*-cyclododecene, 30% *cis*-cyclododecene, and 10% cyclododecane. [b] The ratio of products produced were determined by GLPC and are corrected for the amount of each isomer present. [c] Typical amounts of reactants: iodosylbenzene, 0.590 mmol; ferric porphyrin, 0.05 mmol; alkene, 2.60 mmol. [d] Yields based on iodosylbenzene. [e] 5.20 mmol of alkene used.

In contrast to the cis double bonds of straight chain alkenes, the cis double bond of medium-sized cycloalkenes is known to be less reactive than the correspondig trans-double bonds toward peroxyacids.[13] The relativel reactivity of *cis*- and *trans*-cyclododecene toward *m*-chloroperoxybenzoic acid is 0.59:1. Consistent with the small steric size of its substituents, FePPIX–DME was the least selective catalyst.

The anomalous behavior of the ortho phenyl substituted catalyst FeTPPPCl can be understood if the steric hindrance of two or more ortho phenyl groups substantially decreases the rate of epoxidation on that particular face. This catalyst, as well as FeTTPCl, is expected to exist as a mixture of four rotational isomers.[14] Accordingly, most of the epoxidation would occur at the beta face of the $\alpha,\alpha,\alpha,\beta$-atropisomer, the major species. Examination of CPK models of the various atropisomers of this porphyrin indicates that the phenyl substituents project over the

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(9) (a) First presented at the Symposium on Biochemical and Clinical Aspects of Oxygen, Colorado State University, Pingree Park Campus, Sept 1978. (b) Groves, J. T.; Nemo, T E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032–3. (c) This paper has been abstracted from the Ph.D. thesis of T.E.N.

(10) See also: (a) Chang, C. K.; Kuo, M.-J. *J. Am. Chem Soc.* **1979**, *101*, 3413–15. (b) Lindsay Smith, J. R.; Sleath, P. R. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1009–15.

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Table III. Ferric Porphyrin-Iodosylbenzene Epoxidation of *trans,trans,cis*-1,5,9-Cyclododecatriene

| ferric porphyrin uncorrected | cis/trans epoxide | | % yield[c,d] |
|---|---|---|---|
| | *a* | *b* | |
| FeTPPCl | 0.5 | 1.0 | 43 |
| FeTTPCl | 1.3 | 2.6 | 40 |
| FeTNPCl | 1.0 | 2.0 | *e* |
| FeTPPPCl | 0.5 | 1.0 | 49 |
| FeTMPC | 5.2 | 10.4 | 50 |
| | 6.25 | 12.5 | 58[f] |
| mCPBA | 0.1 | | 80 |

[a] Actual amounts of epoxides formed determined by hydrogenation and then analysis by GLPC. [b] Corrected ratio of products accounting for two trans double bonds and one cis double bond. [c] Yields based on iodosylbenzene. Unreacted olefin could be recovered. [d] Typical amounts of reactants: iodosylbenzene, 4.55 mmol; ferric porphyrin, 0.213 mmol; alkene, 6.16-4.55 mmol. [e] Not determined. [f] Reaction in toluene at 0 °C.

Table IV. Ferric Porphyrin-Iodosylbenzene Epoxidation of (+)-Limonene[a]

| ferric porphyrin | A/B[b] | C/D[b] | (A + B/ C + D) | % yield[c] |
|---|---|---|---|---|
| FeTTPCl | 1.15 | 1.01 | 19.6 | 78 |
| FeTMPCl | 1.62 | 1.01 | 6.9 | 70 |
| mCPBA | 1.0 | 0.97 | 10.2 | no data |

[a] Typical amounts of reactants: iodosylbenzene, 0.533 mmol; ferric porphyrin, 0.053 mmol; (+)-limonene, 3.09 mmol. [b] Ratio of products determined by GLPC, stereoisomers were not identified. [c] Yields based on iodosylbenzene and include all epoxides.

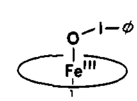
plane of the porphyrin. Such an arrangement would be expected to seriously deactivate the porphyrin faces with two or more ortho phenyl groups. Reaction would then hae to occur on the less hindered faces.

A potentially useful application of the selectivity for *cis*-alkene epoxidation observed here is the selective epoxidation of an inherently less reactive cis double bond in the presence of a trans double bond. Such a situation exists in *trans,trans,cis*-cyclododecatriene (CDT). Peroxyacid epoxidizing reagents are known to react preferentially with the trans double bonds in this molecule. Likewise, reagents such as osmium tetroxide, permanganate, and halocarbenes react preferentially with trans double bonds. Results for the epoxidation of CDT by the family of ortho-substituted iron porphyrins are shown in Table III. From these results it is apparent that the selectivity observed for the intermolecular competitive epoxidation of *cis*- and *trans*-cyclododecene has been observed here for the epoxidation of the cis double bond of CDT. For the hindered mesityl-substituted iron porphyrin, the ratio of cis to trans epoxide was 5.2:1. No other direct method for the preparation of this cis epoxide has been reported.

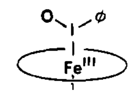
**Steric and Electronic Effects.** The epoxidation of limonene provided an opportunity to compare steric and electronic effects for this epoxidation reaction.[10b] As shown in Table IV, variations are observed both in the ratio of trisubstituted to disubstituted epoxide and in the ratio of stereoisomers of the trisubstituted epoxide. Epoxidations with peroxyacids are known to favor trisubstituted double bonds,[15] indeed this has been used as one of the criteria to establish the concerted, three-centered transition state generally accepted for this oxidant.[16,17] The FeTTPCl/iodosylbenzene system has an even larger preference for the trisubstituted double bond, suggesting that the iron porphyrin catalyzed epoxidation is more electrophilic in nature than is the peroxyacid reaction. The effect of nonbonded interactions is apparent with the FeTMPCl catalyst since the preference for epoxidation of the trisubstituted double bond has decreased to 6.9:1 relative to the disubstituted double bond. The results obtained from these epoxidation reactions indicate that steric and not electronic factors are primarily responsible for the observed changes in selectivity.[10b]

To probe the nature of the transition state for oxygen transfer from iron to the carbon-carbon double bond, the reactivity of methylenecyclohexane was compared to that of cycloheptene. It is expected that a transition state with significant charge development at one end of the double bond should favor reaction with a 1,1-disubstituted olefin over a 1,2-disubstituted olefin such as cycloheptene. In fact, FeTTPCl was found to react with cycloheptene 4.5 times *faster* in an intermolecular competitive situation than with methylenecyclohexene. Both olefins were equally reactive to *m*-chloroperoxybenzoic acid.

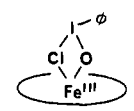
**Mechanism of Epoxidation.** The sensitivity of product ratios to the structure of the porphyrin, the observed greater reactivity of trisubstituted double bonds, and the unreactivity of cyclohexenone indicate that the epoxidizing intermediate in these reactions is an electrophilic porphyrin species. The most reasonable candidates are several iodosylbenzene-iron porphyrin adducts **2**-**4** or one of several possible highvalent iron-oxo species **5**-**7**. Of



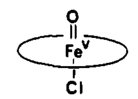
**2**



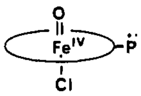
**3**



**4**



**5**



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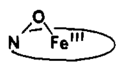

**7**

the iodosylbenzene adducts, structure **3** is unlikely since the chemistry of iodosyl compounds[17] and the iodine Mössbauer spectra of these compounds[18] indicate a large positive charge on iodine and, consequently, a substantial negative charge on oxygen. That iodosylbenzene contains a nucleophilic oxygen is supported by the slow spontaneous reaction of iodosylbenzene with electron-deficient olefins. Support for the intermediacy of an oxygen-bound 1:1 adduct derives from our isolation of such a species upon reaction of manganese(III) chloro-5,10,15,20-tetraphenylporphyrin with iodosylbenzene.[19] Similarly, hypervalent iodine intermediates such as Ph-I·-Cl and R-O-I·-O-R have been proposed in free radical chain reactions involving iodine compounds.[20] We have found that iodosylmesitylene reacts rapidly with iron porphyrins, even FeTMPCl, to give product distributions indistinguishable from those reactions using iodosylbenzene. Further, examination of the $^1H$ NMR spectrum of a mixture of excess isdosylmesitylene and FeTMPCl at -80 °C showed aromatic hydrogens for unreacted iodosylmesitylene and free iosomesitylene.[21] Iron-oxo complexes such as **5**-**7** have received a great deal of attention particularly as they relate to the putative oxidized intermediates of peroxidase[22] and cytochrome P-450.[23] We have recently reported that the oxidation of FeTMPCl with either iodosylbenzene and acid or *m*-chloroperoxybenzoic acid leads to a green, iron(IV)-porphyrin cation radical that is kinetically competent to carry out the epoxidations observed here.[24]

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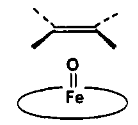
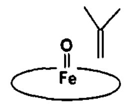
Thus, we conclude that iodosylbenzene has transferred an oxygen atom to the iron of the porphyrin to form a reactive iron–oxo intermediate similar to **6**.

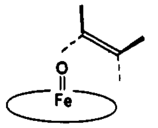
The mechanism of oxygen transfer from iron to the carbon–carbon double bond is less clear. Several reasonable geometries for the approach of a double bond to the iron–oxo group are depicted in **8–10**. Approach as in **8**, along the axis of the Fe–O bond, is unlikely since inspection of CPK models for this geometry reveals no nonbonded interactions between the olefin substituents and the porphyrin periphery. The sensitivity of the product distributions to relatively small changes in the porphyrin substituents noted above requires significant olefin–porphyrin interactions.



**8**

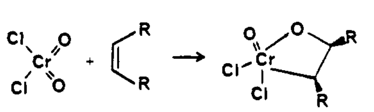


**9**



**10**

Geometry **9** should be particularly favorable for a 1,1-disubstituted alkene. Sharpless has proposed that olefin epoxidation by chromyl chloride follows such a path to produced an intermediate metallacycle, **11**.[25] Such a process is precedented in metal–carbene chemistry and is based on the interpretation that the coordinatively unsaturated and positive charged chromium atom is the initial point of attack by the electron-rich olefin. Interestingly, GVB molecular orbital calculations by Goddard[26] have led to the conclusion that an oxametallacycle path is favored but only as the result of stabilization by the second, nonreacting chromium–oxo group. The lower reactivity of methylene cyclohexane with respect to cycloheptene argues against the oxametallacycle path. It should be noted, however, that chromic acid oxidations of 1,1- and 1,2-disubstituted olefins proceed at similar rates.[27]

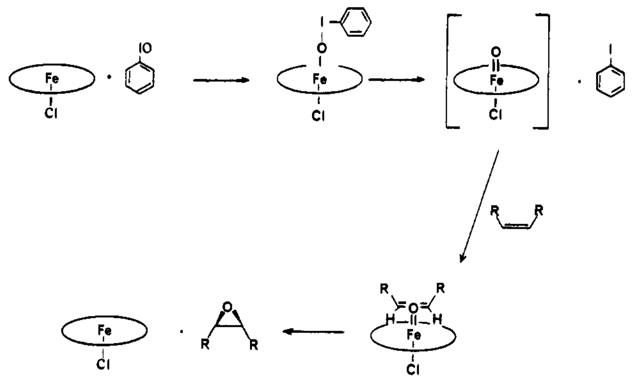


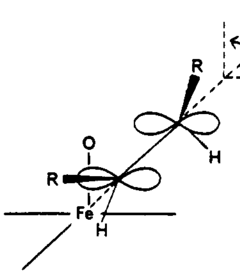
**11**

Approach of the double bond from the side and parallel to the plane of the porphyrin ring as in **10** adequately explains the observed results. Such a geometry could be accommodated by a *cis*-alkene but either the 1,1-disubstituted or trans 1,2-disubstituted cases would require one of the double-bond substitutents to encounter the porphyrin ring substituents.[28] Since the relative reactivity of *cis*- and *trans*-2-butene was found to be 5:1 and that of cycloheptene to methylenecyclohexane to be 4.5:1, the effect of one alkylporphyrin interaction must be less than 1 kcal/mol in the transition state for oxygen transfer. Thus, after accounting for these steric factors, methylenecyclohexane and cycloheptene have similar reactivities. Other reagents that react with 1,1- and 1,2-disubstituted alkene with similar rates are carbenes,[29] bromine,[30] and peroxyacids,[31] all of which are thought to have symmetrical transition states.

A mechanism for olefin epoxidation that is consistent with the observed results is shown in Scheme II. The apparent side-on approach (**10**) is best explained as the result of a stereoelectronic effect. The electronic structure expected for iron(IV) or iron(V) in an oxo porphyrin complex such as **5** or **6** will have two singly occupied $d_{xz}$ and $d_{yz}$ orbitals. Extended Hückel calculations by Hanson et al.[32] and Loew et al.[33] have indicated significant delocalization of these orbitals onto the oxo ligand. The resulting Fe–O($\pi$) antibonding orbitals are expected to be the point of nucleophilic attack by the substrate olefin. Favorable orbital overlap for such an approach can be obtained between the oxygen $p_x$ and $p_y$ orbitals and the olefin p orbitals with a geometry such as **12**.

Scheme II





**12**

If an angle $\alpha$ is specified as indicated in **12**, maximum overlap between the $\pi$ orbitals of the approaching olefin and those of the singly occupied $\pi$-antibonding orbitals of the iron–oxo group will occur for small values of $\alpha$. Decreasing the approach angle $\alpha$ will necessarily increase the steric involvement of the olefinic substituents nearest the porphyrin ring. This mode of metal-bound oxene addition is conceptually related to the addition of carbenes to olefins which has received detailed theoretical attention.[34]

The selectivity for cis olefin epoxidation observed here and the stereoelectronic requirement for side-on approach suggest a molecular rationale for the design of site-specific and even enantioselective catalysts. The preparation of catalysts with such designed molecular voids is under current investigation.

## Experimental Section

**General Data.** Analytical gas chromatography was done on Varian instrument Models 1200, 2400, or 3700 equipped with flame ionization detectors. Capillary gas chromatography was done on a Varian 3700 instrument. Peak areas were measured by electronic integration using a Hewlett-Packard 3380 A or Spectra Physics SP4100 reporter–integrator. Mass spectra were taken on a Finnigan 4021 gas chromatograph/mass spectrometer. NMR spectra were taken on a Varian T-60A, JEOL PS-100, or Brüker WM 360 NMR spectrometer. Chemical shift values are reported relative to $Me_4Si$. Infrared spectra were taken on a Beckman IR 4240 or Perkin-Elmer 457 or 727B instrument. Visible spectra were measured on a Varian Cary 219 spectrometer. Extinction coefficients were measured by dissolving an appropriate amount of the compound in 100 mL of solvent and then successively diluting this solution to achieve absorbance values of less than one for each hand.

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Methylene chloride was purified by distillation from phosphorus pentoxide. Elemental analyses were done by Galbraith Microanalytical Laboratories.

**Porphyrins.** Porphyrins and iron–porphyrin complexes were prepared according to published procedures or exactly as we have reported elsewhere.[35]

**(Chloro-5,10,15,20-tetrakis(*o*-phenylphenyl)porphyrinato)iron(III) (FeTPPPCl).** Propionic acid (400 mL) was refluxed under nitrogen for approximately 0.75 h. 2-Biphenylcarboxaldehyde (13.0 g, 71.4 mmol) and pyrrole (5 mL, 72.1 mmol) were added quickly, and approximately 15 s later the reaction flask was opened to the air. After 1 h at reflux and cooling overnight, purple crystals (2.36 g) formed which were removed by filtration. After treatment with DDQ and chromatography on silica gel (Woelm, activity 1) using dry methylene chloride, 1 g (6%) of porphyrin was isolated. This porphyrin (TPPPH$_2$) was only slightly soluble in halogenated solvents and toluene: $^1$H NMR (CDCl$_3$, 100 MHz) $\delta$ 8.59 (9 H, m), 8.08–6.35 (36 H, m), –3.06 (2 H, m).

Although TPPH$_2$ was insoluble in cold DMF, it was very soluble in refluxing DMF and the metalation took place smoothly by standard procedures.[36] FeTPPPCl was very soluble in most organic solvents: vis (CH$_2$Cl$_2$) $\lambda_{\max}$ 327 nm ($\epsilon$ 68 800 cm$^{-1}$ M$^{-1}$), 352 sh (39 600), 379 (46 800), 430 (108 600), 514 (13 800), 580 (4070), 668 (3200), 697 (3540). Anal. Calcd for C$_{68}$H$_{44}$N$_4$FeCl: C, 80.99; H, 4.40; N, 5.56. Found: C, 80.73; H, 4.51; N, 5.48.

**Iodosylbenzene and Iodosylmesitylene.** Iodosyl compounds were prepared either by the hydrolysis of the corresponding diacetates (Aldrich Chemical Co.) or dichlorides[37] with aqueous sodium hydroxide. Samples were stored at 5 °C and replaced every 3 months.

**Epoxidation Reactions. General Procedures.** Most reactions of iodosylbenzene with olefinic substrates catalyzed by ferric porphyrins were carried out in a 25-mL three-neck flask equipped with an addition tube containing the preweighed iodosylbenzene, a bubbler, serum cap, and stirring bar. All reactions were done under nitrogen, and the reaction mixture was purged with nitrogen for approximately 10 min before the addition of iodosylbenzene. Iodosylbenzene was slowly added to the solution of the ferric porphyrin and organic substrate at a rate to keep the amount of solid iodosylbenzene in the flask at a minimum. The maximum rate of addition depended on the substrate being oxidized.

Reaction mixtures were worked up by washing with aqueous sodium sulfite to ensure complete reduction of iososylbenzene. Gas chromatographic analysis (GLPC) was performed on aliquots withdrawn directly from the reaction mixture.

All starting alkenes were checked by gas chromatography or NMR spectroscopy to ensure that no oxidation products were present before reaction. This procedure was especially important for older samples of alkenes. Purification, when necessary, was accomplished by distillation from potassium or passage through a column of activity I alumina. Petroleum ether was used to elute the higher boiling hydrocarbons and then the petroleum ether removed under reduced pressure. Yields were determined, unless noted, by gas chromatography using internal standard methods. No reactions occurred with the absence of catalyst in the reactions checked under similar temperature and time of reactions. All of the reactions, except where noted, were done at ambient temperature.

**Reaction of Iodosylbenzene with Cyclohexene Catalyzed by FeTPPCl, FeTTPCl, and FePPIX–DME.** Iodosylbenzene (0.100 g, 0.455 mmol) was slowly added to a solution of cyclohexene (1 mL, 10 mmol) and FeTPPCl (0.0245 g, 0.347 mmol) in methylene chloride (4 mL). At the end of addition, cyclohexanone was added as an internal standard and the mixture was analyzed by GLPC (Carbowax 20 M, 100–150 °C at 1°/min). On the basis of iodosylbenzene, cyclohexene oxide (retention time 4.2 min) was produced in 55% yield and cyclohexen-3-ol (15.06 min) in 15% yield. Iodobenzene (17.4 min) was detected quantiatively. Cyclohexanone had a retention time of 7.83 min.

This reaction was repeated by using FeTPPCl and FePPIX–DME as catalysts. With minor variations the same procedure was used for cyclohexadiene, cyclooctene, and norbornene. Product epoxides were compared to authentic standards.[38]

**Reaction of Iodosylbenzene with *cis*- and *trans*-Stilbene Catalyzed by FeTPPCl and FePPIX–DME.** Iodosylbenzene (0.103 g, 0.469 mmol) was slowly added to a solution of *cis*-stilbene (0.202 g, 1.12 mmol; Aldrich Chemical Co.), and *trans*-stilbene (0.205 g, 1.14 mmol; J. T. Baker Chemical Co.) and FeTPPCl (0.024 g, 0.034 mmol) were dissolved in methylene chloride (5 mL). After complete addition, the mixture was stirred for 0.5 h and the methylene chloride removed under reduced pressure (water aspirator). Pentane (15 mL) was added to precipitate the FeTPPCl. The mixture was passed through a plug of glass wool and the pentane removed under reduced pressure (water aspirator). Analysis by NMR spectroscopy (CDCl$_3$) showed the presence of *cis*-stilbene oxide (singlet $\delta$ 4.25) and a trace of *trans*-stilbene oxide (single $\delta$ 3.85; 15:1). *trans*-Stilbene oxide was then added as an internal standard. *cis*-Stilbene oxide was produced in 26% yield based on iodosylbenzene. When this reaction was repeated by using FePPIX–DME as the catalyst, equal amounts of *cis*- and *trans*-stilbene oxides were formed. Total yields of epoxides was approximately 5% based on iodosylbenzene. The epoxidation of *cis*-stilbene alone by FeTPPCl under these conditions produced a 71% yield of *cis*-stilbene oxide at 65% conversion.

**Reaction of Iodosylbenzene with *cis*- and *trans*-2-Butene Catalyzed by FeTPPCl.** A solution of *trans*-2-butene (1.5 mL) and *cis*-2-butene (1.2 mL) in methylene chloride (10 mL) was prepared by distillation of the hydrocarbons into a graduated tube. Iodosylbenzene (0.100 g, 0.455 mmol) was slowly added to a solution of FeTPPCl (0.020 g, 0.028 mmol) in 2 mL of the above solution at –5 °C. Gas chromatographic analysis (Carbowax 20 M, 55 °C) showed the ratio of cis epoxide (3.78 min) to trans epoxide (2.92 min) formed to be 5.8, respectively, after correction for the relative amount of alkenes present. There was no isomerization of the epoxide products in the injection port of the gas chromatograph. Similar oxidation with *m*-chloroperoxybenzoic acid (1 h at 0 °C) gave a ratio of 2.5.

**Reaction of Iodosylbenzene with *cis*- and *trans*-Cyclododecene Catalyzed by Ferric Porphyrins.** Typically iodosylbenzene (0.130 g, 0.591 mmol) was slowly added to a solution of *cis*- and *trans*-cyclododecene (1:2, cis–trans) (0.50 mL, 2.60 mmol) in methylene chloride (5 mL) containing the ferric porphyrin (approximately 0.040 g). The cyclododecane mixture obtained from Aldrich Chemical Co. was contaminated with *trans*-cyclododecene oxide and other oxidized materials. Purification was achieved by passing the alkene through a column of activity I acidic alumina. The composition of the olefin was determined by GLPC (Carbowax 20 M, 100 °C) to be *cis*-cyclododecene (11.02 min), *trans*-cyclododecene (9.63 min), and cyclododecane (8.54 min).

The yields and ratios of epoxides formed were determined by GLPC (Carbowax 20 M, 150 °C). Adamantanone (15.4 min) was used as an internal standard. *cis*-Cyclododecene oxide had a retention time of 20 min, and *trans*-cyclododecene oxide had a retention time of 17.7 min. Authentic samples of *cis*- and *trans*-cyclododecene oxides were prepared by mCPBA epoxidation. The relative reactivity of *cis*- and *trans*-cyclododecene toward mCPBA was determined by adding mCPBA (0.110 g, 0.542 mmol) to a solution of *cis*- and *trans*-cyclododecene (0.50 mL, 2.60 mmol) in methylene chloride (5 mL).

**Reaction of *trans,trans,cis*-1,5,9-Cyclododecatriene with Iodosylbenzene Catalyzed by Ferric Porphyrins.** *trans,trans,cis*-1,5,9-Cyclododecatriene (1.00 g, 6.16 mmol; Aldrich Chemical Co.) and FeTPPCl (0.150 g, 0.213 mmol) were dissolved in methylene chloride (10 mL). Iodosylbenzene (1.00 g, 4.55 mmol) was slowly added. After complete addition the methylene chloride was removed under reduced pressure (aspirator) and pentane (20 mL) was added which precipitated the catalyst. Filtration, followed by removal of the pentane under reduced pressure, resulted in 1.86 g of a dark liquid. A sample of this material (0.380 g) was mixed with 2-adamantanone (internal standard) and analyzed by GLPC (Carbowax 20 M, 160 °C). Adamantanone had a retention time of 12.6 min. From this analysis it was determined that the yield of epoxides (20 min) was 47% based on iodosylbenzene. The remaining 1.48 g of reaction product was loaded on a 25 cm × 1 cm column of silica gel (Woelm, activity I) and eluted first with pentane to remove the unreacted triene and iodobenzene (1.15 g) and then 5% ether in pentane to remove the product epoxides (0.276 g) in 43% yield. The fractions were checked by GLPC.

The ratio of cis epoxide to trans epoxide was determined by hydrogenation in ethanol over 5% Pd/C. Typically, 0.10 g of epoxide mixture, 0.02 g of catalyst, and 6 mL of ethanol were hydrogenated at 1 atm and then analyzed by GLPC (Carbowax 20 M, 160 °C). The ratio of *trans*-cyclododecene oxide (14.7 min) to *cis*-cyclododecene oxide (16.5 min) was 2.1. Small amounts (5%) of cyclododecanone (17 min) and cyclododecanol (33 min) were also formed. The identical procedure was used for all ferric porphyrin catalysts. The epoxidation of a 10-fold excess of CDT by mCPBA produced a 10:1 mixture of the trans and cis epoxides, respectively.

**Reaction of Iodosylbenzene with a Mixture of Methylene Cyclohexane and Cycloheptene.** Iodosylbenzene (0.100 g, 0.455 mmol) was slowly added to a solution of cycloheptene (0.50 mL, 4.28 mmol), methylenecyclohexane (0.50 mL, 4.16 mmol), and FeTTPCl (0.035 g, 0.046 mmol) in methylene chloride (5 mL). The mixture was analyzed by GLPC

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(Carbowax 20 M, 100 °C for 10 min and then at 5°/min to 130 °C). Cycloheptanone (9.26 min) was used as an internal standard. The ratio of cycloheptene oxide to methylenecyclohexene oxide was 4.5:1. Similar oxidation of these olefins by mCPBA produced equal amounts of both epoxides.

**Reaction of Iodosylbenzene with (+)-Limonene Catalyzed by FeTMPCl and FeTTPCl.** Iodosylbenzene (0.117 g, 0.530 mmol) was added to a solution of (+)-limonene (0.50 mL, 3.09 mmol) and FeTTPCl (0.04 g, 0.053 mmol) in methylene chloride (5 mL). Analysis of GLPC (Carbowax 20 M, 110 °C) showed that the two epoxides were formed in a ratio of 19:1. Capillary GLPC (30 m SP-2250) showed the major peak to be a 1.15:1 mixture of the diastereomeric 1,2-oxides (larger peak eluted first). The 7,8-oxides were formed in equal amounts. The total yield of epoxides was 78% based on iodosylbenzene.

This reaction was repeated for FeTMPCl, and the total yield of epoxides was 69%. With mCPBA the ratio of 1,2-oxides to 7,8-oxides was 10:1.

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**Registry No.** FeTPPCl, 16456-81-8; FeTTPCl, 52155-50-7; FeTNPCl, 86456-39-5; FeTPPPCl, 86456-38-4; FeTMPC, 77439-21-5; FePPIX-DME, 15741-03-4; *cis*-CDT oxide, 42539-84-4; *trans*-CDT oxide, 40702-89-4; cyclohexene, 110-83-8; *cis*-stilbene, 645-49-8; *trans*-stilbene, 103-30-0; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; *cis*-cyclododecene, 1129-89-1; *trans*-cyclododecene, 1486-75-5; *trans*,*trans*,*cis*-1,5,9-cyclododecatriene, 706-31-0; methylenecyclohexane, 1192-37-6; cycloheptene, 628-92-2; (+)-limonene, 5989-27-5; 2-norbornene, 498-66-8; cyclooctene, 931-88-4; 1,3-cyclohexadiene, 592-57-4; 2-cyclohexen-1-one, 930-68-7; iodosylbenzene, 536-80-1; 1,3-cyclohexadiene oxide, 6705-51-7; cyclooctene oxide, 286-62-4; *exo*-norbornene oxide, 3146-39-2; cyclohexene oxide, 286-20-4; *cis*-2,3-diphenyloxirane, 1689-71-0; *cis*-cyclododecene oxide, 1502-29-0; *trans*-cyclododecene oxide, 4683-60-7; (+)-limonene oxide (isomer 1), 4680-24-4; (+)-limonene oxide (isomer 2), 6909-30-4; (+)-limonene oxide (isomer 3), 28098-67-1; (+)-limonene oxide (isomer 4), 28098-68-2.

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# Catalytic Asymmetric Epoxidations with Chiral Iron Porphyrins

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**Abstract:** Iron porphyrins have been modified to include optically active functionalities at the meso positions. Asymmetric epoxidations of prochiral olefins with these chiral iron porphyrins and iodosyl compounds have been investigated. Thus, 5$\alpha$,10$\beta$,15$\alpha$,20$\beta$-tetrakis(*o*-(*R*)-hydratropamidophenyl)porphyrin ($H_2T(\alpha,\beta,\alpha,\beta$-Hyd)PP) and 5$\alpha$,10$\beta$,15$\alpha$,20$\beta$-tetrakis(*o*-[(*S*)-2′-carboxymethyl-1,1′-binaphthyl-2-carboxamido]phenyl)porphyrin ($H_2T(\alpha,\beta,\alpha,\beta$-Binap)PP) were synthesized by the condensation of optically active acid chlorides with 5$\alpha$,10$\beta$,15$\alpha$,20$\beta$-tetrakis(*o*-aminophenyl)porphyrin. Subsequent insertion of iron into $H_2T(\alpha,\beta,\alpha,\beta$-Hyd)PP and $H_2T(\alpha,\beta,\alpha,\beta$-Binap)PP gave FeT($\alpha,\beta,\alpha,\beta$-Hyd)PPCl and FeT($\alpha,\beta,\alpha,\beta$-Binap)PPCl, respectively. Employing FeT($\alpha,\beta,\alpha,\beta$-Hyd)PPCl and iodosylbenzene, styrene was oxidized to (*R*)-(+)-styrene oxide in 31% ee. Similarly, FeT($\alpha,\beta,\alpha,\beta$-Binap)PPCl and iodosylmesitylene gave (*R*)-(+)-styrene oxide in 48% ee. Various substituted styrenes and aliphatic olefins were epoxidized with enantiomeric excesses varying between 0% for 1-methylcyclohexene oxide and 51% for *p*-chlorostyrene oxide.

Asymmetric syntheses have been the focus of considerable recent attention. Among the most interesting approaches to this general problem is the use of chiral catalysts capable of catalytic asymmetric induction. Impressive results have been achieved in the case of catalytic asymmetric reductions,[1] such as the Monsanto process for the production of L-DOPA from prochiral starting materials.[2]

By contrast, asymmetric epoxidation reactions have received little attention. Monoperoxycamphoric acid has been reported to epoxidize simple olefins such as styrene with a 7.8% enantiomeric excess (ee).[3] The highest degrees of asymmetric epoxidation of olefins without coordinating functional groups, in the range of 5–35% ee, have been reported recently by Mimoun with a chiral peroxomolybdenum(VI) reagent.[4] Significant asymmetric inductions (25% ee) were observed by Wynberg et al. for the epoxidation of $\alpha,\beta$-unsaturated ketones with basic hydrogen peroxide in the presence of a chiral phase-transfer catalyst.[5]

The first major advances in catalytic asymmetric epoxidation were reported by Sharpless[6] and Yamada,[7] who used chiral vanadium and molybdenum catalysts for the epoxidation of allylic alcohols by alkyl hydroperoxides. Very recently Sharpless has reported an improved, titanium tartarate catalytic system which gave spectacular enantiomeric excesses, greater than 95%, for a wide variety of allylic alcohols.[8] Molybdenum(VI)-catalyzed asymmetric oxidations give much lower optical yields (10–14%).[9]

Whole cell studies with *Corynebacterium equi* have been reported[10] in which 1-hexadecene was converted to (*R*)-(+)-1,2-epoxyhexadecane in 41% yield and 100% optical yield. Likewise, significant asymmetric induction for 1-octene epoxidation (80%) has been observed by May with the $\omega$-hydroxylating system of *P. oleovorans*.[11]

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