crystal structure of the homologous α1-antitrypsin, and (iv) molecular dynamics simulations provides for the first time detailed insight in the *highly specific* binding of a sulfated polysaccharide (glycosaminoglycan) fragment with a protein at the molecular level. We feel that specific binding of other proteins with sulfated polysaccharides may also involve well-defined, relatively small complementary domains on both the carbohydrate polymer and the protein.

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Registry No. AT-III, 9000-94-6; heparin, 9005-49-6.

Nature of the Epoxidizing Species Generated by Reaction of Alkyl Hydroperoxides with Iron(III) Porphyrins. Oxidations of *cis*-Stilbene and (*Z*)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene by *t*-BuOOH in the Presence of [*meso*-Tetrakis(2,4,6-trimethylphenyl)porphinato]-, [*meso*-Tetrakis(2,6-dichlorophenyl)porphinato]-, and [*meso*-Tetrakis(2,6-dibromophenyl)porphinato]iron(III) Chloride

Gong-Xin He and Thomas C. Bruice*

Contribution from the Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California 93106. *Received August 30, 1990*

Abstract: The mechanism of the oxidation of alkenes by *t*-BuOOH in the presence of iron(III) tetraphenylporphyrins has been explored (CH_2Cl_2 sovent). The alkenes, *cis*-stilbene and (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (**1**-*Z*), have been chosen because they serve as traps for radical intermediates. The substituted iron(III) tetraphenylporphyrin catalysts employed are [*meso*-tetrakis(2,4,6-trimethylphenyl)porphinato]iron(III) chloride ((TMP)Fe^{III}(Cl)), [*meso*-tetrakis(2,6-dichlorophenyl)porphinato]iron(III) chloride ((Cl_8TPP)Fe^{III}(Cl)), and [*meso*-tetrakis(2,6-dibromophenyl)porphinato]iron(III) chloride ((Br_8TPP)Fe^{III}(Cl)). In separate experiments, azobisisobutyronitrile (AIBN) was used as a radical chain initiator for the oxidation of the alkenes by *t*-BuOOH. Oxidation of *cis*-stilbene with iron(III) porphyrins as catalysts provides *trans*-stilbene oxide as a major product along with diphenylacetaldehyde, deoxybenzoin (trace), and a compound assigned [^{1}H NMR, MS(CI)] the structure PhCH[OO(*t*-Bu)]CH[O(*t*-Bu)]Ph. We conclude that the reaction products are derived from initial combination of *t*-BuOO$^\bullet$, rather than ($^{+\bullet}$Porph)Fe^{IV}(O), with *cis*-stilbene. Oxidation of **1**-*Z* with iron(III) porphyrins as catalysts provides A (^{1}H NMR, MS(CI), FT-IR) as the major product. Other products are B (whose structure has not been determined), which contains intact one of the two *trans*-2,*trans*-3-diphenylcyclopropane groups, *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde, and deoxybenzoin. In A, one cyclopropyl group has undergone a cyclopropylcarbinyl to homoallylcarbinyl radical rearrangement (CPCRR) while the other has remained intact. The major product A arises from initial combination of *t*-BuOO$^\bullet$ with **1**-*Z* followed by CPCRR. Reaction sequences are suggested. The *cis*-epoxide of **1**-*Z* (**2**-*c*) is formed in 3.2% yield when (Cl_8TPP)Fe^{III}(Cl) is the catalyst. A trace of **2**-*c* is obtained with (TMP)Fe^{III}(Cl), but **2**-*c* could not be detected with (Br_8TPP)Fe^{III}(Cl). The *cis*-epoxide **2**-*c* most likely arises from the concerted reaction of **1**-*Z* with the iron(IV)–oxo porphyrin π cation radical ($^{+\bullet}Cl_8$TPP)Fe^{IV}(O)(Cl). The species ($^{+\bullet}Cl_8$TPP)Fe^{IV}(O)(Cl) may be the direct product of reaction of (Cl_8TPP)Fe^{III}(Cl) with *t*-BuOOH in a mechanism that involves heterolytic O–O bond breaking. Alternatively, ($^{+\bullet}Cl_8$TPP)Fe^{IV}(O)(Cl) may arise via (Cl_8TPP)Fe^{III}(Cl) + *t*-BuOOH $\rightarrow$ (Cl_8TPP)Fe^{IV}(O) + *t*-BuO$^\bullet$ followed by oxidation of (Cl_8TPP)Fe^{IV}(O) by *t*-BuOOH (or other). It is pointed out that (Cl_8TPP)Fe^{IV}(O), unlike (TMP)Fe^{IV}(O), accumulates in relatively high concentration and that *t*-BuOOH is present at 0.3 M.

Introduction

Iron(III) porphyrins have been established as effective catalysts for the epoxidation of norbornene (Nb) with *t*-BuOOH at high concentrations of alkene.[1,2] Epoxidation has been proposed to involve the reactions of eqs 1 and 2.[1] The mechanism of the reaction of eq 1 is suggested to involve an intermediate complex of iron(III) porphyrin and hydroperoxide that decomposes to products with O–O bond heterolysis and oxygen transfer to iron(III) porphyrin accompanied by its 2e$^-$ oxidation. The ratio of *endo*- to *exo*-norbornene epoxides (NbO) has been interpreted as showing that the epoxidations are carried out by a

$$t\text{-BuOOH} + (\text{Porph})\text{Fe}^{\text{III}}(\text{X}) \rightarrow t\text{-BuOH} + ({}^{+\bullet}\text{Porph})\text{Fe}^{\text{IV}}(\text{O})(\text{X}) \quad (1)$$

$$({}^{+\bullet}\text{Porph})\text{Fe}(\text{O})(\text{X}) + \text{Nb} \rightarrow (\text{Porph})\text{Fe}^{\text{III}}(\text{X}) + endo\text{-NbO}/exo\text{-NbO} \quad (2)$$

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[1] (a) Traylor, T. G.; Xu, F. *J. Am. Chem. Soc.* **1987**, *109*, 6201. (b) Traylor, T. G.; Fann, W-P.; Bandyopadyay, D. *J. Am. Chem. Soc.* **1989**, *111*, 8009.

[2] We have repeated Traylor's study with norbornene and found that we obtained similar yields of epoxide under the same conditions.

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$(^{+\bullet}\mathrm{Porph})\mathrm{Fe^{IV}(O)(X)}$ species.[1] The formation of both *endo*-NbO and *exo*-NbO was attributed to an initial 1e$^-$ oxidation of Nb to a cation radical ($\mathrm{Nb^{\bullet +}}$) as shown in eqs 3 and 4.[3] Homolytic

$$(^{+\bullet}\mathrm{Porph})\mathrm{Fe^{IV}(O)(X)} + \mathrm{Nb} \rightarrow (\mathrm{Porph})\mathrm{Fe^{IV}(O)} + \mathrm{Nb^{\bullet +}} + \mathrm{X^-} \tag{3}$$

$$(\mathrm{Porph})\mathrm{Fe^{IV}(O)} + \mathrm{Nb^{\bullet +}} + \mathrm{X^-} \rightarrow (\mathrm{Porph})\mathrm{Fe^{III}(X)} + endo\text{-}\mathrm{NbO}/exo\text{-}\mathrm{NbO} \tag{4}$$

O–O bond cleavage with 1e$^-$ oxidation of the iron(III) porphyrin (eq 5) was ruled out on the basis that the $(\mathrm{Porph})\mathrm{Fe^{IV}(O)}$ species is, at best, a very poor epoxidant for Nb. *tert*-Butyl hydroperoxide

$$t\text{-}\mathrm{BuOOH} + (\mathrm{Porph})\mathrm{Fe^{III}(X)} \rightarrow t\text{-}\mathrm{BuO^\bullet} + (\mathrm{Porph})\mathrm{Fe^{IV}(O)} + \mathrm{H^+} + \mathrm{X^-} \tag{5}$$

radical, which is known to be formed from *t*-BuOOH in the presence of iron(III) porphyrins (eqs 6 and 7), was also dismissed

$$(^{+\bullet}\mathrm{Porph})\mathrm{Fe^{IV}(O)(X)} + t\text{-}\mathrm{BuOOH} \rightarrow (\mathrm{Porph})\mathrm{Fe^{IV}(O)} + t\text{-}\mathrm{BuOO^\bullet} + \mathrm{H^+} + \mathrm{X^-} \qquad \text{(6)[6]}$$

$$(\mathrm{Porph})\mathrm{Fe^{IV}(O)} + t\text{-}\mathrm{BuOOH} \rightarrow (\mathrm{Porph})\mathrm{Fe^{III}(OH)} + t\text{-}\mathrm{BuOO^\bullet} \qquad \text{(7)[6,7]}$$

as the epoxidizing agent.[1] Other investigations,[8,9] however, provide significant evidence in favor of the homolytic mechanisms of eqs 5 and 7 and the involvement of ROO$^\bullet$ radicals as epoxidizing agents.

We now describe our detailed studies of the products formed on oxidation of *cis*-stilbene and (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (**1-*Z***) by *t*-BuOOH in the presence of [*meso*-tetrakis(2,4,6-trimethylphenyl)porphinato]iron(III) chloride ($\mathrm{(TMP)Fe^{III}(Cl)}$], [*meso*-tetrakis(2,6-dichlorophenyl)porphinato]iron(III) chloride ($\mathrm{(Cl_8TPP)Fe^{III}(Cl)}$), and [*meso*-tetrakis(2,6-dibromophenyl)porphinato]iron(III) chloride ($\mathrm{(Br_8TPP)Fe^{III}(Cl)}$).

Experimental Section

General Procedures. Melting points were determined on a Bristoline hot-stage microscope and are uncorrected. Infrared (IR) spectra were obtained in KBr on a Perkin-Elmer monochromator grating spectrometer (Model 1330) or in $\mathrm{CHCl_3}$ on a Bio-Rad Fourier transform spectrometer (Model FTS-60). Low-resolution mass spectra (LRMS) were recorded on a VG Analytical spectrometer (Model VGII-250) by electron impact (EI) and chemical ionization (CI) with $\mathrm{CH_4}$. ^{1}H NMR spectra were obtained in $\mathrm{CDCl_3}$ with Nicolet NT-300 and General Electric GN-500 spectrometers. Chemical shifts are reported in δ relative to $\mathrm{Me_4Si}$ with s, d, t, q, and m signifying singlet, doublet, triplet, quartet, and multiplet; coupling constants J are reported in hertz. For GC, a Varian Model 3700 with flame ionization detector using a 0.2 mm × 25 m WCOT vitreous $\mathrm{SiO_2}$ capillary column operating at ~80–200 °C (3 °C/min) was employed. Preparative thin-layer chromatography (TLC) was performed on glass-backed plates (20 × 20 cm) with 1.5-mm $\mathrm{Al_2O_3}$ 60-$\mathrm{F_{254}}$ (Merck). High-pressure liquid chromatography (HPLC) used two Perkin-Elmer Series 10 pumps. For analytic HPLC, a Hewlett-Packard variable-wavelength detector (Model HP1050) at 254 nm and integrator (Model 3392A) and, for semipreparative HPLC, an ISCO variable-wavelength absorbance detector (Model V[4]) at 254 nm and fraction collector (Model Retriever II) were used. Chromatographic conditions are given in the following order: column (col), solvent system (sys), solvent composition, and flow rate (mL/min) (as subscript). Altex columns: 4.6 × 250 mm, 5-μm RSil-CN (col A); 4.6 × 250 mm, 5-μm Lichrosorb SI-60 (col B); 4.6 × 250 mm, 5-μm Spherisorb alumina (col C); 10 × 150 mm, 10-μm RSil–CN (Col D); and Whatman column 10 × 500 mm, 10-μm Partisil $\mathrm{SiO_2}$ (col E). The columns eluted with the solvent systems hexane (sys A), hexane–$\mathrm{CH_2Cl_2}$ (sys B), hexane–EtOAc (sys C) were employed.

Materials. Methylene chloride was distilled over calcium hydride, degassed by three freeze–pump–thaw cycles, and stored in a $\mathrm{N_2}$ glovebox. *tert*-Butylhydroperoxide (*t*-BuOOH) was purchased from Aldrich, and the concentration was determined by iodometric titration.[10] *cis*-Stilbene, from Aldrich, was distilled and stored in the $\mathrm{N_2}$ glovebox. Azobisisobutyronitrile (AIBN) was purchased from Eastman Kodak Co. and used as received. HPLC–GC standards (Aldrich) were purified to homogeneity as established by HPLC or ^{1}H NMR. The possible epoxide products *cis*- and *trans*-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)oxirane (**2-*c*** and **2-*t***, respectively) were synthesized with published methods.[11] The porphyrin catalysts, [*meso*-tetrakis(2,4,6-trimethylphenyl)porphinato]iron(III) chloride ($\mathrm{(TMP)Fe^{III}(Cl)}$), [*meso*-tetrakis(2,6-dichlorophenyl)porphinato]iron(III) chloride ($\mathrm{(Cl_8TPP)Fe^{III}(Cl)}$), and [*meso*-tetrakis(2,6-dibromophenyl)porphinato]iron (III) chloride ($\mathrm{(Br_8TPP)Fe^{III}(Cl)}$), were available from previous studies.[4,11,12] (*Z*)- and (*E*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (**1-*Z*** and **1-*E***, respectively) were prepared by an improved procedure of Wittig condensation of [(*trans*-2,*trans*-3-diphenylcyclopropyl)methyl]triphenylphosphonium bromide and *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde, which were synthesized as previously reported.[11]

(*Z*)- and (*E*)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (1-*Z* and 1-*E*). An 18% sodium acetylide slurry (400 mg, 1.5 mmol of NaCCH) was washed with dry hexane (2 × 5 mL), and the remaining solid was dried over $\mathrm{N_2}$ stream. To the solid were added 740 mg of [(*trans*-2,*trans*-3-diphenylcyclopropyl)methyl]triphenylphosphonium bromide (1.35 mmol) and 5 mL of dry DMF at 0 °C. After the solution was stirred at 0 °C for 0.5 h, 300 mg of *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde (1.35 mmol) was added. The temperature was allowed to rise gradually to room temperature, and the color of the solution changed from orange to pale yellow. After being stirred for 1 h at room temperature, the reaction mixture was poured into cold water (100 mL) and extracted with $\mathrm{Et_2O}$ (4 × 50 mL). The combined organic solutions were dried ($\mathrm{MgSO_4}$) and concentrated in vacuo. The residue was purified by column chromatography ($\mathrm{Al_2O_3}$, neutral activity II, 100% $\mathrm{CCl_4}$) to give 470 mg of a **1-*Z***/**1-*E*** mixture (85%, **1-*Z***:**1-*E*** = 9). To the mixture, 100 mL of MeOH was added and the solution refluxed for 1 h. The solution was filtered while hot to remove insoluble white solid. The filtrate was concentrated, 50 mL of MeOH was added to the residue, and the solution was refluxed and filtered again while hot. The solid obtained on concentration of the filtrate was recrystallized twice from MeOH to provide 250 mg of **1-*Z*** as colorless prisms, and HPLC (col B, sys B, $9{:}1_2$) showed that **1-*Z*** contained less than 0.1% **1-*E***. Recrystallization of the white MeOH-insoluble solid from MeOH–$\mathrm{CHCl_3}$ (3:1) gave 25 mg of **1-*E*** as white needles, which contained <0.1% **1-*Z*** (HPLC, col B, sys B, $9{:}1_2$). The filtrate could be purified further by semipreparative HPLC (col F, sys C, $9{:}1_6$). **1:*Z***: mp 96–97 °C. **1-*E***: mp 204–205 °C. IR and ^{1}H NMR spectra are identical with those previously reported.[11]

Oxidation of *cis*-Stilbene. *cis*-Stilbene (44.5 μL, 0.25 mmol) was sealed in a 1-mL serum bottle with a stirring bar in a $\mathrm{N_2}$ glovebox. After the bottle was removed from the glovebox, *t*-BuOOH (71% in $\mathrm{H_2O}$ and *t*-BuOH, 3.2 μL, 0.025 mmol) and azobisisobutylronitrile (AIBN) (1 M in degassed $\mathrm{CH_2Cl_2}$, 25 μL, 0.025 mmol) or $\mathrm{(Porph)Fe^{III}(Cl)}$ (3 mM in $\mathrm{CH_2Cl_2}$, 25 μL, 0.075 μmol) were added with microsyringes. The solution was stirred at room temperature for 4 h in the dark, and then quenched with 1 M aqueous $\mathrm{Na_2SO_3}$. The organic phase was analyzed by HPLC and GC.

Oxidation of (*Z*)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (1-*Z*). **1-*Z*** (103 mg, 0.25 mmol), 40 μL of $\mathrm{CH_2Cl_2}$, and a stirring bar were sealed in a 1-mL serum bottle while in a $\mathrm{N_2}$ glovebox. Next, the bottle was removed from the box and *t*-BuOOH (71%, 3.2 μL, 0.025 mmol) and 25 μL of a solution of AIBN (1 M in $\mathrm{CH_2Cl_2}$, 0.025 mmol) or $\mathrm{(Porph)Fe^{III}(Cl)}$ (3 mM in $\mathrm{CH_2Cl_2}$, 0.075 μmol) were added. The resultant solution was stirred at room temperature for 4 h in the dark, and quenched with 1 M $\mathrm{Na_2SO_3(aq)}$. The organic phase was separated

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(3) It has been pointed out that 1e$^-$ oxidation of alkenes to provide carbocation radical intermediates cannot be the first step in epoxidations by $(^{+\bullet}\mathrm{Porph})\mathrm{Fe(O)(X)}$ or $\mathrm{(Porph)Cr^V(O)(X)}$ species[4] and that steric and electronic factors serve to explain the *endo*-NbO to *exo*-NbO ratio.[5]

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Table I. Product Yields (%) for the Oxidation of *cis*-Stilbene with *t*-BuOOH Catalyzed by AIBN or (Porph)Fe^{III}(Cl)[a]

catalyst			PhCHO	Ph_2CHCHO	$PhCH_2COPh$	 $PhCH(OR)CH(OR')Ph$
AIBN[b]	0.4	0.0	2.9	0.0	0.0	0.0
AIBN[c]	0.5	0.0	0.5	0.0	0.0	0.0
(TMP)Fe^{III}(Cl)	13.2	0.0	7.1	1.3	trace	4.6
(TMP)Fe^{III}(Cl)[d]	25.0	trace	5.0	5.3	0.7	5.8
(Cl_8TPP)Fe^{III}(Cl)	20.7	trace	4.5	1.3	trace	6.5
(Br_8TPP)Fe^{III}(Cl)[e]	8.3	trace	1.0	trace	0.0	trace

[a] Reactions employed 0.25 mmol of *cis*-stilbene, 0.025 mmol of *t*-BuOOH, and 0.025 mmol of AIBN or 0.075 μmol of (Porph)Fe^{III}(Cl) in 25 μL of CH_2Cl_2. Yields (%) are based on oxidant. [b] Key: 24 h. [c] Key: 24 h, 60 °C in 25 μL of CH_2ClCH_2Cl. [d] Key: 24 h. [e] A total of 0.0075 μmol of (Br_8TPP)Fe^{III}(Cl) was used. This is the saturated solution of the catalyst.

Table II. Product Yields (%) for the Oxidation of (*Z*)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (**1-*Z***) with *t*-BuOOH Catalyzed by AIBN or (Porph)Fe^{III}(Cl)[a]

catalyst	compd A	compd B	deoxybenzoin	aldehyde[b]	*cis*-epoxide
AIBN[c]	0.0	<1	0.5	0.0	0.0
(TMP)Fe^{III}(Cl)	7.5	<3	1.0	0.0	0.0
(TMP)Fe^{III}(Cl)[c]	24.3	<5	2.0	0.5	trace
(TMP)Fe^{III}(Cl)[d]	20.0	<5	2.0	trace	trace
(Cl_8TPP)Fe^{III}(Cl)	24.0	<5	2.0	1.8	3.2
(Br_8TPP)Fe^{III}(Cl)[e]	2.8	<3	1.0	trace	0.0

[a] Reactions employed 0.25 mmol of **1-*Z***, 0.025 mmol of *t*-BuOOH, and 0.025 mmol of AIBN or 0.075 μmol of (Porph)Fe^{III}(Cl) in 65 μL of CH_2Cl_2. Yields (%) are based on oxidant. [b] *trans*-2,*trans*-3-Diphenylcyclopropanecarboxaldehyde. [c] Key: 24 h. [d] Key: 24 h in 50 μL of CH_2Cl_2; **1-*Z*** could not dissolved completely at this condition. [e] Total of 0.0075 μmol of (Br_8TPP)Fe^{III}(Cl) was used. This is the saturated solution of the catalyst.

and analyzed by HPLC. The main products were isolated by TLC and semipreparative HPLC, and their structures were identified by ^{1}H NMR, MS, and FT-IR.

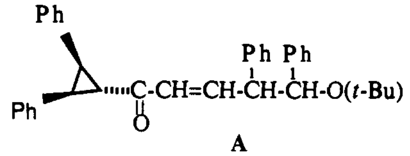
Results

Oxidation of *cis*-Stilbene. Identification of reaction products was carried out by HPLC with use of coinjection of mixtures of standards. Structural assignments were based on coelution on two different HPLC systems: col A, sys B, 25:1$_2$; col C, sys C, 49:1$_2$. Product quantitation by HPLC analysis (col A, sys A or sys B) involved integration of peaks after response factors were determined with authentic standards. The detection limit was 0.1%, but the limit for quantitation was 0.5%. The accuracy of the yield determination for diphenylacetaldehyde was inferior since both enolation and hydration of the aldehyde occurred under the HPLC conditions with both product mixtures and standards.[13] It should be noted that ^{1}H NMR showed that the standard used was pure and did not exhibit signs of contamination by enol or ketone hydrate in $CDCl_3$. It was also found that both *cis*-stilbene oxide and *trans*-stilbene oxide isomerized under the GC conditions employed. A GC analysis of a CH_2Cl_2 solution of pure *cis*-stilbene oxide provided 50% *cis*-stilbene oxide, 14% diphenylacetaldehyde, and 22% deoxybenzoin, while *trans*-stilbene oxide produced, on GC analysis, 3% *cis*-stilbene oxide, 21% diphenylacetaldehyde, and 70% deoxybenzoin on the basis of the integration area. On the other hand, the purity of the standard was checked by HPLC (col A, sys A) and ^{1}H NMR ($CDCl_3$).

Concentrations of (Porph)Fe^{III}(Cl), *t*-BuOOH, and *cis*-stilbene used in this study were similar to those used previously.[8c] As shown in Table I, the major product was *trans*-stilbene oxide; no or only a trace of *cis*-stilbene oxide was detected in any experiment. Similar results were obtained in reactions using azobisisobutyronitrile (AIBN) and (Porph)Fe^{III}(Cl), although the yields when using AIBN were found to be much lower than those from the reaction with (Porph)Fe^{III}(Cl). A trace amount of *trans*-stilbene (0.1–0.2%) was present in the *cis*-stilbene employed (HPLC; col B, sys B, 49:1$_2$). The concentration of *trans*-stilbene did not change during the course of the reaction. In addition to the stilbene oxide, benzaldehyde, diphenylacetaldehyde, and deoxybenzoin were found from the reaction mixture.

Analytical HPLC analysis (col A, sys B, 25:1$_2$) showed that there is an additional compound present in the product mixture from the reaction of *cis*-stilbene with *t*-BuOOH and (Porph)Fe^{III}(Cl), which is more polar (t_R = 30 min) than *trans*-stilbene oxide (t_R = 6 min) and deoxybenzoin (t_R = 22 min) under the HPLC conditions used. The compound decomposed to deoxybenzoin on a SiO_2 HPLC column (col B, sys C, 99:1$_1$). Through a short Al_2O_3 column (neutral activity V, 100% CH_2Cl_2), the polar compound changed to diphenylacetaldehyde as shown on HPLC (col A, sys B, 25:1$_2$). Since *meso*-hydrobenzoin could not be eluted from the HPLC column under the conditions used (col A, sys B, 25:1$_2$), the structure of the compound might be considered to be PhCH(OR)CH(OR′)Ph (R = R′ = *t*-Bu or R = *t*-BuO, R′ = *t*-Bu), which may decompose in different ways under the different conditions. However, attempted isolation of the putative PhCH(OR)CH(OR′)Ph with semipreparative HPLC (col D, sys B, 9:1$_6$) failed to provide a sample, and only a mixture containing about 90% deoxybenzoin was obtained even when the fraction of the compound was concentrated at a low temperature. ^{1}H NMR examination of the mixture showed two kinds of *tert*-butyl groups (δ 1.151 and 1.106), and LRMS(CI) spectrum of the mixture has *m*/*z* 57 and 73, which are diagnostic for butyl and butoxy cation, respectively.

Oxidation of (*Z*)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (1-*Z*). Products obtained from the oxidation of **1-*Z*** by *t*-BuOOH in the presence of AIBN, (TMP)Fe^{III}(Cl), (Cl_8TPP)Fe^{III}(Cl), and (Br_8TPP)Fe^{III}(Cl) in CH_2Cl_2 are presented in Table II. *trans*-Epoxide **2-*t*** and *trans*-alkene **1-*E*** could not be detected as products. The latter would result if an acyclic intermediate with free rotation about the central carbon–carbon bond were formed. Coinjection with standards showed that 3.2% *cis*-epoxide **2-*c*** (on the basis of *t*-BuOOH used) forms in the reaction using (Cl_8TPP)Fe^{III}(Cl). With the other catalytic agents, however, no or only a trace of *cis*-epoxide **2-*c*** was detected with HPLC (col A, sys B, 9:1$_2$). Isolation of previously unknown products was carried out for the reaction with (TMP)Fe^{III}(Cl) by use of the two following procedures. A polar component (compound A, t_R = 45 min, col A, sys B, 9:1$_2$) is the major product of the reaction. For separation of compound A, the reaction mixture was directly injected onto the semipreparative HPLC



A

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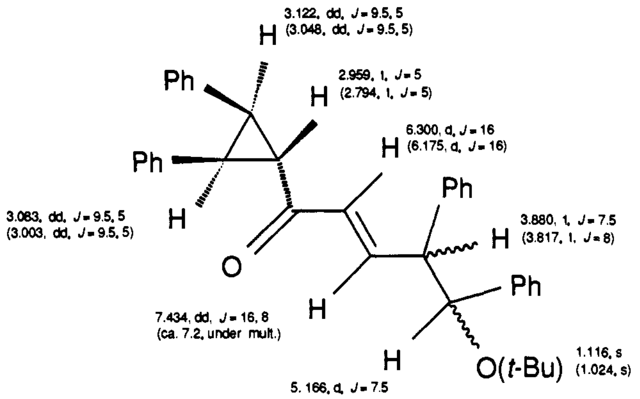


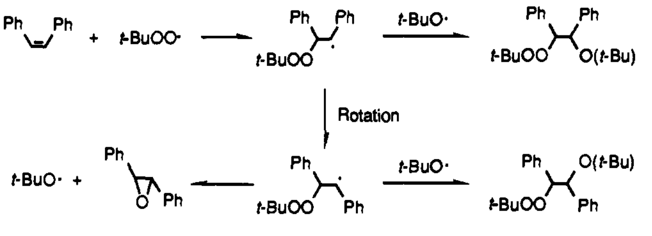
Figure 1. ^{1}H NMR data and structural assignments of the major product (compound A) of the oxidation of **1-*Z*** with (Porph)Fe^{III}(Cl) and *t*-BuOOH. Signals outside and inside parentheses belong to either isomer. Resonances for benzyl protons in the cyclopropyl ring are interchangeable. For all aromatic protons: δ 7.06–7.32, multiplet.

column (col D, sys B, 6:1$_6$). For isolation of less polar unknown components (t_R = 6–20 min, col A, sys B, 9:1$_2$), the reaction mixture was first loaded on a preparative TLC plate (Al_2O_3, 100% CCl_4) to remove the remainder of **1-*Z***, used in excess, and the catalyst. The fractions between the solvent line, containing most of **1-*Z***, and the starting line, containing (TMP)Fe^{III}(Cl), were cut and washed with CH_2Cl_2. After concentration at room temperature, the residue was separated by semipreparative HPLC (col D, sys B, 9:1$_6$).

Figure 1 shows the ^{1}H NMR data and structural assignment of the major product (compound A) of the reaction of **1-*Z*** with (porph)Fe^{III}(Cl) and *t*-BuOOH. Proton coupling relationships were established by a 2-D COSY experiment. Compound A is a racemic mixture of two diastereomers with respect to its two asymmetric carbons. Although these isomers could not be separated by HPLC, all protons in the compound except for the benzyl methine proton in –CH(Ph)O(*t*-Bu) show two sets of peaks representing the two diastereomers. For the benzyl methine proton in –CH(Ph)O(*t*-Bu), only one doublet is found but the integration value suggests that this signal accounts for both diasteomers (or the two expected doublets overlapping). The large coupling constant (J = 16 Hz) for two vinyl protons is consistent with a trans configuration, and their chemical shifts, δ 6.175 (6.300) and 7.434 (~7.2), suggest that the carbon–carbon double bond is α,β to a carbonyl group. The cyclopropyl ring protons appear as an ABX pattern, and the vicinal coupling constant is 9.5 Hz. The magnetic nonequivalence of the benzyl protons can be explained by the fact that the two protons are diastereotopic because of the asymmetric centers present in the compound. The highest observed m/z in the LRMS(CI) spectrum of the compound is 427, which comes from fragmentation of the compound by loss of a butoxy group, and fragment m/z = 337 (339) in the spectrum can be explained by further loss of a benzyl methine group. The spectrum also has m/z = 221 and 193, which are diagnostic for (diphenylcyclopropyl)carbonyl cation and diphenylcyclopropyl cation fragment, respectively. In compound A, one cyclopropyl group has undergone a cyclopropylcarbinyl to homoallylcarbinyl radical rearrangement (CPCRR), while the other has remained intact.[11] FT-IR ($CHCl_3$) shows a peak at 1650 cm^{-1} that is consistent with a vinylcyclopropyl ketone. Interestingly, compound A disappeared after the preparative TLC (Al_2O_3, 100% CCl_4), while the concentration of *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde increases as shown by periodic HPLC analysis (col A, sys B, 9:1$_2$). The yields of compound A for the reaction of Table II were calculated from the increase in yield of this aldehyde on the basis of the presumption that A was decomposing to this aldehyde under TLC conditions (vide infra). The aldehyde and deoxybenzoin, which are in the less polar component, were isolated after TLC separation by semipreparative HPLC (col D, sys B, 9:1$_6$) and identified by ^{1}H NMR and coinjection with a standard sample.

Compound B, which is one of the less polar components, has t_R = 11 min on HPLC (col A, sys B, 9:1$_2$). ^{1}H NMR shows that in compound B one cyclopropyl group has opened while the other has remained intact. The cyclopropyl group is connected with a methine group, and the two benzyl protons in the cyclopropyl ring are magnetically nonequivalent. Neither vinyl protons nor *tert*-butyl protons were found for compound B. Diphenylcyclopropyl and the (diphenylcyclopropyl)carbonyl cation are also observed from its LRMS(CI) spectrum, and the highest m/z is 356. Table II only gives the estimated yields for compound B from the integration area on the HPLC.

Scheme I



Discussion

The mechanism by which iron(III) porphyrins undergo oxidation by hydroperoxides (2e$^-$ oxidation of the metal porphyrin with heterolytic cleavage of the hydroperoxide O–O bond (eq 1) to provide $(^{+\bullet}$Porph)Fe^{IV}(O)(X) or 1e$^-$ oxidation of the metal porphyrin with homolytic cleavage of the hydroperoxide O–O bond (eq 5) to provide (Porph)Fe^{IV}(O)) is a topic of current research.[1,6–9,14,15] It is known that epoxidation of alkenes takes place at high concentrations of alkene in the presence of iron(III) porphyrins and that (Porph)Fe^{IV}(O) is at the very best a poor epoxidation agent.[1] A conclusion drawn from these observations is that the reaction of alkyl hydroperoxides with iron(III) porphyrins involves the 2e$^-$ heterolytic mechanism (eq 1) and that the epoxidant is $(^{+\bullet}$Porph)Fe^{IV}(O)(X).[1] The alternative is that the epoxidation agent is ROO$^\bullet$, which could be generated by a number of reactions that include the oxidation of ROOH by either (Porph)Fe^{IV}(O) or $(^{+\bullet}$Porph)Fe^{IV}(O)(X) (eqs 6 and 7).[8] The purpose of this investigation has been to provide some enlightenment to these perplexing questions.

We have chosen to use *t*-BuOOH as the hydroperoxide and the substituted iron(III) tetraphenylporphyrins (TMP)Fe^{III}(Cl), (Cl_8TPP)Fe^{III}(Cl), and (Br_8TPP)Fe^{III}(Cl) as catalysts. In certain experiments, azobisisobutyronitrile (AIBN) was used as a radical chain initiator with *t*-BuOOH. The alkenes employed are *cis*-stilbene and (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (**1-*Z***).

***cis*-Stilbene Oxidation Products.** Epoxidation of *cis*-stilbene by (Porph)Fe^{III}(Cl) and iodosylbenzene provides *cis*-stilbene oxide plus benzaldehyde, diphenylacetaldehyde, and deoxybenzoin.[16] Epoxidation of *cis*-stilbene by (TMP)Fe^{III}(Cl) and *t*-BuOOH provides *trans*-stilbene oxide as the major product, benzaldehyde, a small yield of diphenylacetaldehyde, and traces of deoxybenzoin (Table I). No *cis*-stilbene oxide could be detected. The low yield of products, recorded in Table I, with (Br_8TPP)Fe^{III}(Cl) is due to the concentration employed being one-tenth that of other (Porph)Fe^{III}(Cl) species due to its low solubility in CH_2Cl_2. When *cis*-stilbene oxide was allowed to react with *t*-BuOOH in the presence of (TMP)Fe^{III}(Cl), under the same conditions used in the oxidation of *cis*-stilbene, about 28% of the epoxide decomposed and benzaldehyde (trace), diphenylacetaldehyde (9.3%), and deoxybenzoin (1.1%) were found in the reaction mixture (material balance 82.4%). The same control experiment with *trans*-stilbene oxide resulted in only ~6% loss of the epoxide, and benzaldehyde (trace) and diphenylacetaldehyde (2.3%) were formed (material

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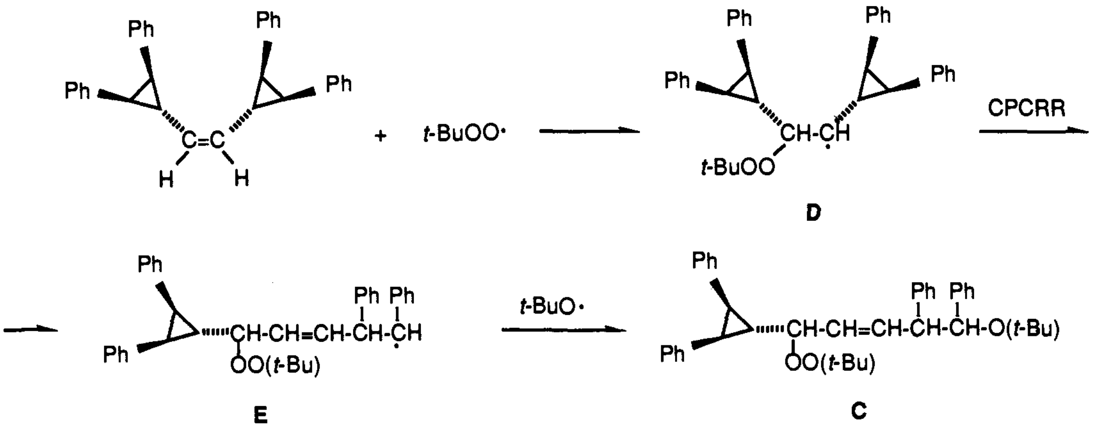
(14) (a) Traylor, T. G.; Ciccone, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 8413. (b) Traylor, T. G.; Xu, F. *J. Am. Chem. Soc.* **1990**, *112*, 178.

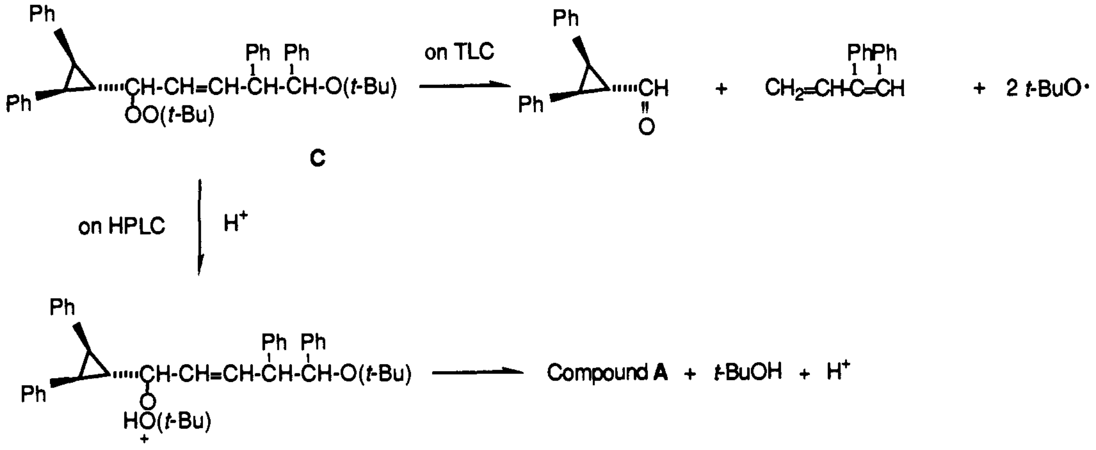
(15) (a) Lee, W. A.; Yuan, L.-C.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 4277. (b) Lindsay Smith, J.J.; Balasubramanian, P. N.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7411.

(16) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 158.

Scheme II

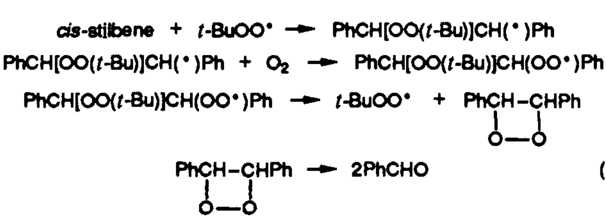


Scheme III



balance 96.3%). Thus, as pointed out by Labeque and Marnett,[8c] *trans*-stilbene oxide is produced directly in the oxidation of *cis*-stilbene by *t*-BuOOH in the presence of (Porph)Fe^{III}(Cl) (Scheme I).

In the reaction of *cis*-stilbene with (Porph)Fe^{III}(Cl) and iodosylbenzene, the yield of benzaldehyde was dependent upon the concentration of O_2. The mechanism of benzaldehyde formation was suggested to involve 1e$^-$ oxidation of *cis*-stilbene and reaction of O_2 with the resultant carbocation radical.[16] In the hydroperoxide reaction, the yield of benzaldehyde is independent of an O_2 atmosphere. Several explanations for this observation are available. The first consideration is that O_2 is not limiting since it is a product in the hydroperoxide reaction. A second consideration is that benzaldehyde could arise from a reaction of O_2 with a radical species formed by reaction of *t*-BuOO• with *cis*-stilbene. A possible reaction path is given in eq 8. Benzaldehyde may also arise from the oxidation of *cis*-stilbene oxide.[17]



$$\begin{aligned}&cis\text{-stilbene} + t\text{-BuOO}^\bullet \rightarrow \mathrm{PhCH[OO}(t\text{-Bu})]\mathrm{CH}(^\bullet)\mathrm{Ph}\\&\mathrm{PhCH[OO}(t\text{-Bu})]\mathrm{CH}(^\bullet)\mathrm{Ph} + O_2 \rightarrow \mathrm{PhCH[OO}(t\text{-Bu})]\mathrm{CH(OO}^\bullet)\mathrm{Ph}\\&\mathrm{PhCH[OO}(t\text{-Bu})]\mathrm{CH(OO}^\bullet)\mathrm{Ph} \rightarrow t\text{-BuOO}^\bullet + \underset{\mathrm{O{-}O}}{\mathrm{PhCH{-}CHPh}}\\&\underset{\mathrm{O{-}O}}{\mathrm{PhCH{-}CHPh}} \rightarrow 2\mathrm{PhCHO}\end{aligned} \tag{8}$$

The formation of *trans*-stilbene oxide in the hydroperoxide reaction establishes the occurrence of a nonconjugated intermediate with free rotation about the σ bond. Such a structure can be assigned to the adduct of *cis*-stilbene and *t*-BuOO• (Scheme I). Oxidations of *cis*-stilbene to *trans*-stilbene oxide via radical intermediates have been proposed previously.[18] Epoxidation through a radical chain process to convert *t*-BuOOH to *t*-BuOO•, by use of the initiator AIBN, resulted in the finding of much smaller product yields (Table I) than obtained with (Porph)Fe^{III}(Cl). At 60 °C, most of AIBN should have decomposed in the reaction time employed; however, the product yields were almost the same as obtained at room temperature. It is clear that an AIBN-initiated radical chain reaction for epoxidation is very inefficient. When (Porph)Fe^{III}(Cl) is employed as catalyst, the ROO• species is generated at a constant steady-state concentration.

Most important to the question of the reactivity of *t*-BuOO• with alkenes is our observation of the formation of the product of Table I labeled PhCH(OR)CH(OR')Ph. Since α,α'-di(*tert*-butoxy)bibenzyl, PhCH[O(*t*-Bu)]CH[O(*t*-Bu)]Ph, is known to be very stable,[19] it is reasonable to believe that the product is a peroxide that has a structure of PhCH[OO(*t*-Bu)]CH[O(*t*-Bu)]Ph. Such a structure is supported by the ^{1}H NMR and MS(CI) results. It should be noted that in the MS spectrum of the mixture containing PhCH[OO(*t*-Bu)]CH[O(*t*-Bu)]Ph from the reaction using *cis*-stilbene both butyl and butoxy cation have been observed, while the MS spectrum of compound A from **1**-*Z* (vide ante) exhibits only butyl cation (m/z = 57). Though an extensive effort was made at purification, the lability of the peroxide to decomposition to deoxybenzoin was an insurmountable barrier to its purification (See Results). The PhCH[OO(*t*-Bu)]CH[O(*t*-Bu)]Ph is proposed to be formed by the initial reaction of *t*-BuOO• with *cis*-stilbene. One of several possible sequences is shown in eq 9, followed by a mechanism shown in Scheme I.

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(17) Sawaki, Y.; Foote, C. S. *J. Org. Chem.* **1983**, *48*, 4934 and references cited therein.

(18) Yuan, L.-C.; Bruice, T. C. *J. Chem. Soc., Chem. Commun.* **1985**, 868.

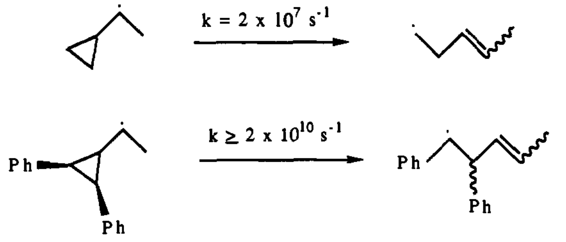
(19) α,α'-Di(*tert*-butoxy)bibenzyl is a crystalline solid and can even be distilled under reduced pressure. Goh, S. H.; Huang, R. L.; Ong, S. H.; Sieh, L. *J. Chem. Soc. C.* **1971**, 2282.

$$\text{(Porph)Fe}^{\text{III}}\text{(Cl)} + t\text{-BuOOH} \rightarrow \text{(Porph)Fe}^{\text{IV}}\text{(O)} + t\text{-BuO}^{\bullet} + \text{Cl}^{-} \quad (9)$$

$$\text{(Porph)Fe}^{\text{IV}}\text{(O)} + t\text{-BuOOH} \rightarrow \text{(Porph)Fe}^{\text{III}}\text{(OH)} + t\text{-BuOO}^{\bullet}$$

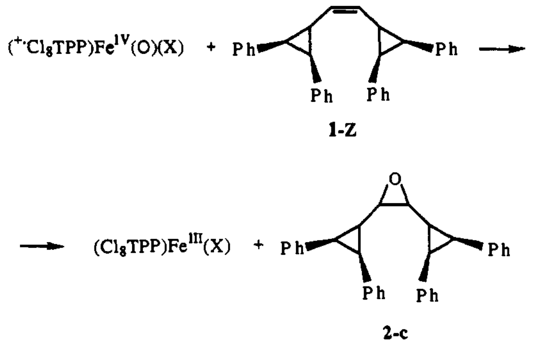
In conclusion, the formation of both *trans*-stilbene oxide and PhCH[OO(*t*-Bu)]CH[O(*t*-Bu)]Ph can only be explained by radical mechanisms. Perhaps, the best evidence for the *t*-BuOO$^{\bullet}$ initiation of epoxidation (eq 9) derives from the latter product.

Oxidation Products of (*Z*)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene. (*Z*) and (*E*)-1,2-(*trans*-2,*trans*-3-diphenylcyclopropyl)ethenes, **1**-*Z* and **1**-*E*, respectively, were designed and synthesized as radical traps to explore the chemistry of alkenes.[11] We showed, from competitive experiments, that the cyclopropylcarbinyl to homoallylcarbinyl radical rearrangement (CPCRR) with the *trans*-2,*trans*-3-diphenylcyclopropyl substituent exceeded the rate of the CPCRR with the cyclopropyl substituent by a minimum value of 10^3 (eq 10).[11] **1**-*Z* and its products can be detected to 0.1% by HPLC with UV monitoring due to the absorbance of the phenyl substituents. The combination of the rate constant for CPCRR with **1**-*Z* and detection limit allows the trapping of radical intermediates that proceed to product(s) with a first-order rate constant of 10^{12} s^{-1}.



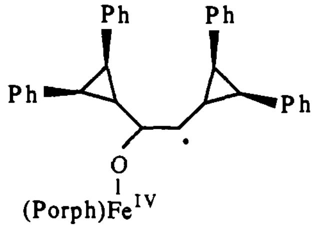
(10)

By use of the oxidant C_6F_5IO, **1**-*Z* is converted to its *cis*-epoxide in 89 and 95% yields in the presence of the catalysts (Cl_8TPP)Fe^{III}(Cl) and [*meso*-tetrakis(pentafluorophenyl)porphinato]iron(III) chloride ((F_{20}TPP)Fe^{III}(Cl)), respectively (eq 11).



(11)

Neither *trans*-alkene **1**-*E*, *trans*-epoxide **2**-*t*, nor any polar oxidation product could be found as ≥0,1% yield (detection limit).[11] A back of the envelope calculation shows that if the radical species (X) were to exist as an intermediate in epoxidation of **1**-*Z*, then the rate constant for partitioning of X to epoxide would be $\geq 2 \times 10^{11}$ s^{-1} when (Cl_8TPP)Fe^{III}(Cl) is catalyst and $\geq 2 \times 10^{12}$ s^{-1} when (F_{20}TPP)Fe^{III}(Cl) is the catalyst. Clearly, epoxidation by the hypervalent iron–oxo porphyrin species, generated from iodosylarene and these iron(III) porphyrins, does not involve a detectable covalent radical intermediate.

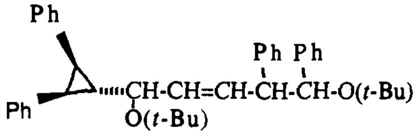


X

Oxidation of **1**-*Z* by *t*-BuOOH in the presence of AIBN, (TMP)Fe^{III}(Cl), (Cl_8TPP)Fe^{III}(Cl), and (Br_8TPP)Fe^{III}(Cl) does not provide *trans*-alkene (**1**-*E*) or *trans*-epoxide (**2**-*t*). This shows that the *trans*-2,*trans*-3-diphenylcyclopropyl substituent is able to trap the radical intermediate at a rate that is greater than its cis to trans isomerization. Product yields using (TMP)Fe^{III}(Cl) are less than with (Cl_8TPP)Fe^{III}(Cl). The *cis*-epoxide (**2**-*c*) could not be detected as a product with (Br_8TPP)Fe^{III}(Cl) and was obtained in trace concentration with (TMP)Fe^{III}(Cl). However, **2**-*c* was obtained in 3.2% yield in the reaction with (Cl_8TPP)Fe^{III}(Cl). However, **2**-*c* was obtained in 3.2% yield in the reaction with (Cl_8TPP)Fe^{III}(Cl). The *cis*-epoxide most likely arises from a concerted reaction of **1**-*Z* with iron(IV)–oxo porphyrin π cation radical ($^{+\bullet}$Cl$_8$TPP)Fe^{IV}(O)(X).[5,11] Changes in products have been reported in going from (TMP)Fe^{III}(Cl) to (Cl_8TPP)Fe^{III}(Cl) by Marnett[8c] and Traylor.[1,14b] However, in the latter study, CH_2Cl_2 was the solvent with (TMP)Fe^{III}(Cl) and a mixed solvent of CH_2Cl_2–CH_3OH–H_2O was used with (Cl_8TPP)Fe^{III}(Cl).

The major product (Table II) has been assigned the structure A (Figure 1). A is proposed to arise via the sequence of reactions shown in Scheme II. Attack of *t*-BuOO$^{\bullet}$ upon **1**-*Z* provides the radical D, which decomposes by CPCRR to yield E, which then combines with *t*-BuO$^{\bullet}$ to provide C. The major product A arises from C. C could not be established as being present in the reaction solution at completion of reaction. After the preparative TLC on alumina, *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde became the major product, while A disappeared as shown by HPLC. Compound A is rather stable, and a mechanism for its decomposition on the TLC to *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde is not obvious. Possibly, the more rational mechanism (Scheme III) would involve C as precursor of both *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde and A under TLC and HPLC conditions, respectively. In Scheme III, the coproduct of *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde is 1,2-diphenyl-1,3-butadiene. Though we have no unequivocal evidence for the presence of the latter in the resulting mixture, a very nonpolar compound (t_R = 6 min) has been observed on HPLC (col A, sys B, 9:1$_2$) that accompanies the increase of the aldehyde after the TLC separation. Attempts to isolate this nonpolar compound failed because of the presence of the large excess of **1**-*Z* employed in the reaction.

No product corresponding to the addition of *t*-BuO$^{\bullet}$ to the double bond of **1**-*Z* was found in the spent reaction solution. If *t*-BuO$^{\bullet}$ should add to **1**-*Z*, there would follow a CPCRR and the resultant radical would react with an additional *t*-BuO$^{\bullet}$ species to give a stable product (compound F) with a structure similar to C with *t*-BuO replacing *t*-BuOO. The greater reactivity of *t*-BuOO$^{\bullet}$ seen with **1**-*Z* and *cis*-stilbene, may be attributed to its lessened steric requirements and possibly to an α effect.



F

The direct formation of *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde can be explained by the oxidation of the double bond with molecular oxygen present in the reaction system. Deoxybenzoin should be the product of the direct oxidation of the *trans*-2,*trans*-3-diphenylcyclopropyl ring. The latter reaction may be initiated by hydrogen abstraction by *tert*-butoxy radicals,[20] resulting in cleavage of the carbon–carbon bond of the cyclopropyl ring. Both compounds could also arise from further decomposition of compound C under the reaction conditions.

Conclusions Concerning the Mechanisms of Epoxidation. The most obvious conclusion of this study is that *t*-BuOO$^{\bullet}$ adds to the double bonds of *cis*-stilbene and (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (**1**-*Z*) and that the intermediate carbon

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(20) Walling, C.; Fredricks, P. S. *J. Am. Chem. Soc.* **1962**, *84*, 3326.

radical species accounts for the major products isolated from reaction solutions that initially contained these alkenes plus (Porph)Fe^{III}(Cl) and *t*-BuOOH. *cis*-Stilbene oxide is not formed. In the case of **1**-*Z*, there is formed *cis*-epoxide in 3.2% yield when (Cl$_8$TPP)Fe^{III}(Cl) is employed as catalyst. *cis*-Epoxide is obtained in a trace quantity with (TMP)Fe^{III}(Cl) and not observed with (Br$_8$TPP)Fe^{III}(Cl).

Interpretation of the formation of the *cis*-epoxide of **1**-*Z* in 3.2% yield with (Cl$_8$TPP)Fe^{III}(Cl) follows. The molar ratios of reactants employed were **1**-*Z*:*t*-BuOOH:(Porph)Fe^{III}(Cl) = 10000:1000:3. Volume ratios were **1**-*Z*:*t*-BuOOH:CH$_2$Cl$_2$ = 32:1:8. The reaction solutions consist, therefore, of almost neat alkene containing about 0.3 M *t*-BuOOH. Reaction of (Cl$_8$TPP)Fe^{III}(Cl) with *t*-BuOOH has been proposed to form either ($^{+\bullet}$Cl$_8$TPP)Fe^{IV}(O)(Cl) (eq 1) or (Cl$_8$TPP)Fe^{IV}(O) (eq 2) (loc cit). On the basis of previous experience, it is expected that the reaction of ($^{+\bullet}$Cl$_8$TPP)Fe^{IV}(O)(Cl) with **1**-*Z* would provide the corresponding *cis*-epoxide.[5,11] One might then propose that our experimental results establish the reaction of eq 1. The small yield of the *cis*-epoxide of **1**-*Z* may then be attributed to the competition of *t*-BuOOH and **1**-*Z* for ($^{+\bullet}$Cl$_8$TPP)Fe^{IV}(O)(Cl). The lack of formation of the *cis*-epoxide of *cis*-stilbene could then be rationalized by the assumption that this alkene can not compete with *t*-BuOOH for ($^{+\bullet}$Cl$_8$TPP)Fe^{IV}(O)(Cl). The potentials (SCE) for the 1e$^-$ oxidation of *cis*-stilbene and **1**-*Z* have been determined to be (acetonitrile solvent) 1.64 and 1,47 V, respectively.[21] Thus, the potential for oxidation of *cis*-stilbene is 170 mV more positive than is the potential for oxidation of **1**-*Z*. One-electron oxidation potentials for alkenes are[4] a linear function of σ^+ and the log of the rate constants for epoxidation of alkenes by ($^{+\bullet}$Porph)Fe^{IV}(O)(Cl) is a linear function of σ^+.[22] From this, the assumption that **1**-*Z* is more easily epoxidized by ($^{+\bullet}$Cl$_8$TPP)Fe^{IV}(O)(Cl) than is *cis*-stilbene is rational. Under similar reaction conditions norbornene is epoxidized in a 10–20% yield,[1] though the potential for its 1e$^-$ oxidation is 1.9 V! However, norbornene is a special case. Thus, reaction of norbornene (5 M) with *t*-BuOOH (50 mM) and AIBN (50 mM) in CH$_2$Cl$_2$ at 25 °C for 24 h has been reported[8c] to produce norbornene oxide in 64% yield based on *t*-BuOOH. This shows that norbornene is epoxidized in the absence of iron porphyrin.

The question arises as to why the catalyst (Cl$_8$TPP)Fe^{III}(Cl) should yield **1**-*Z* epoxide while (TMP)Fe^{III}(Cl) or (Br$_8$TPP)Fe^{III}(Cl) does not. At the concentrations of *t*-BuOOH employed, the reactions taking place may be quite varied and complex. It is known that the iron(IV)–oxo porphyrin and iron(IV)–oxo porphyrin π-cation species formed from (Cl$_8$TPP)Fe^{III}(Cl) have unusually long lifetimes.[7,23,24] In competition with the oxidation of *t*-BuOOH to *t*-BuOO$^\bullet$ by (Cl$_8$TPP)Fe^{IV}(O) (eq 7), there may also be an oxidation of (Cl$_8$TPP)Fe^{IV}(O) to ($^{+\bullet}$Cl$_8$TPP)Fe^{IV}(O)(OH) by *t*-BuOOH (eq 12). The steady-state concentration

$$(\mathrm{Cl_9TPP})\mathrm{Fe^{IV}(O)} + t\text{-}\mathrm{BuOOH} \rightleftharpoons (\mathrm{Cl_8TPP})\mathrm{Fe^{IV}(O)}(t\text{-}\mathrm{BuOOH}) \quad (12)$$

$$(\mathrm{Cl_8TPP})\mathrm{Fe^{IV}(O)}(t\text{-}\mathrm{BuOOH}) \rightarrow (^{+\bullet}\mathrm{Cl_8TPP})\mathrm{Fe^{IV}(O)(OH)} + t\text{-}\mathrm{BuO}^\bullet$$

of *t*-BuO$^\bullet$ is expected to be high, allowing the reaction of eq 13.

$$(\mathrm{Cl_8TPP})\mathrm{Fe^{IV}(O)} + t\text{-}\mathrm{BuO}^\bullet \rightarrow (^{+\bullet}\mathrm{Cl_8TPP})\mathrm{Fe^{IV}(O)}(t\text{-}\mathrm{BuO}) \quad (13)$$

Acknowledgment. This study was supported by a grant from the National Institutes of Health. We express our gratitude to Dr. Andrei Blasko for assistance with 2-D ^{1}H NMR.

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(23) Dolphin, D.; Nakano, T. Maiona, T. E.; Kirk, T. K.; Farrell, R.; In *Lignin Enzymic and Microbial Degradation*; Odier, E., Ed.; INRA Publications: Paris, 1987; pp 157–162.

(24) Sugimoto, H.; Hung, H.-C.; Sawyer, D. T. *J. Am. Chem. Soc.* **1988**, *110*, 2465.