The Rate-Limiting Step in the One-Electron Oxidation of an Alkene by Oxo[*meso*-tetrakis(2,6-dibromophenyl)porphinato]-chromium(V) Is the Formation of a Charge-Transfer Complex†

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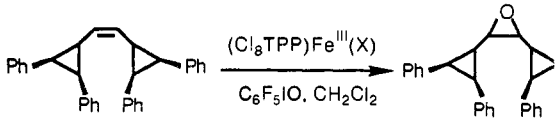
Abstract: We have proposed, in previous studies, that the rate-limiting step in the oxidation of alkenes by hypervalent metal–oxo porphyrin species is the formation of a charge-transfer (CT) complex. The CT complex then partitions, dependent upon the alkene and the metal, to various oxidation products as epoxide and carbocation radical. In this paper we provide evidence that a carbocation radical intermediate is formed on oxidation of (*Z*)-1,3-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (**1-*Z***) by $(Br_8TPP)Cr^V(O)(X)$. We also show that formation of carbocation radical is not rate-limiting. Oxidation of **1-*Z*** by $(Br_8TPP)Cr^V(O)(X)$ in the presence of the nonoxidative electrolyte $(n\text{-}Bu)_4NBF_4$ provides as the major product a mixture of the two isomeric (3*E*,5*E*)-1,8-dichloro-1,2,7,8-tetraphenylocta-3,5-diene (referred to as *trans,trans*-diene) and (3*E*,5*Z*)-1,8-dichloro-1,2,7,8-tetraphenylocta-3,5-diene (referred to as *trans,cis*-diene). Detailed ^1H NMR decoupling and 2-D COSY provided the assigned structures for *trans,trans*-diene and *trans,cis*-diene. The same diene mixture is obtained as the major product (and same ratio of the configurational isomers) on $1e^-$ oxidation of **1-*Z*** by controlled-potential bulk electrolysis (CPBE) in CH_2Cl_2 using the nonoxidative $(n\text{-}Bu)_4NBF_4$ as the supporting electrolyte. This shows that the oxidation of **1-*Z*** by $(Br_8TPP)Cr^V(O)(X)$ provides both *trans,trans*-diene and *trans,cis*-diene by way of an intermediate carbocation radical. The diene products arise from carbocation radical by opening one cyclopropyl ring via a cyclopropylcarbinyl to homoallylcarbinyl radical rearrangement, while the other cyclopropyl ring opens in a cyclopropylcarbinyl to homoallylcarbinyl carbocation rearrangement. In contrast to the oxidation of **1-*Z*** by $(Br_8TPP)Cr^V(O)(X)$ in the presence of the nonoxidative electrolyte $(n\text{-}Bu)_4NBF_4$, which provides the mixture of dienes plus $(Br_8TPP)Cr^{IV}(O)$, oxidation of **1-*Z*** by $(Br_8TPP)Cr^V(O)(X)$ in the presence of the cooxidant $(n\text{-}Bu)_4NClO_4$ provides *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde as a major product plus the immediate product $(Br_8TPP)Cr^{III}(X)$. Since the second-order rate constants are much the same for the reaction of **1-*Z*** with $(Br_8TPP)Cr^V(O)(X)$ in the presence of $(n\text{-}Bu)_4NBF_4$ or $(n\text{-}Bu)_4NClO_4$, it is concluded that the rate-limiting step for reaction of **1-*Z*** with $(Br_8TPP)Cr^V(O)(X)$ precedes and is separate from the product-forming reactions. The intermediate in the formation of a carbocation radical on $1e^-$ oxidation of an alkene is most reasonably a CT complex.

Introduction

A number of intermediates have been proposed in the epoxidation of alkenes by hypervalent oxo–metalloporphyrins in both chemical and enzymatic systems.[1] As shown in Chart I, they are metallaoxetane (I),[1a-d] carbon radical (II),[1e-h] carbocation (III),[1i-l,2a] and carbocation radical (IV).[1k,l] Additionally, the mechanism of epoxidation has also been considered to involve a concerted insertion of oxygen (V).[1m-p] Research from this laboratory has been directed toward establishing the presence or absence of intermediates I to IV along the reaction path for alkene epoxidation by hypervalent oxo–metalloporphyrins.[2]

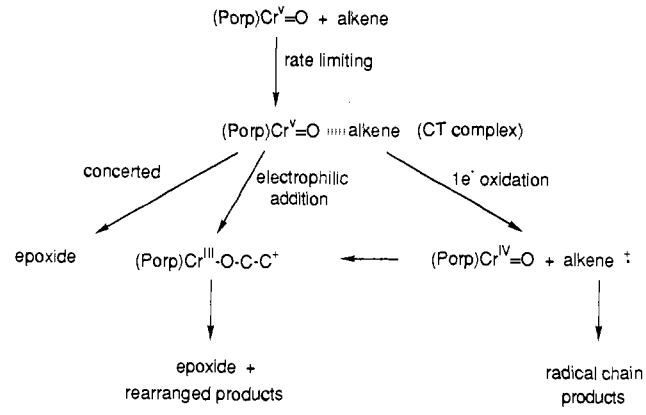
It has been established, by product and molecular modeling studies with sterically hindered metalloporphyrins, that epoxidation via 2 + 2 cycloaddition of alkene and metallo–oxo species followed by a concerted reductive elimination from the resultant metallaoxetane (I) is not a tenable mechanism.[2f,g,3] The alkene radical trap (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (**1-*Z***) undergoes the epoxidation of eq 1 to provide *cis*-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)oxirane (**2-*c***) in 95% yield.[2b,c] It could be shown that if the radical species II served as an intermediate its collapse to **2-*c*** would have to be associated with a rate constant of $\sim 10^{13}$ M^{-1} s^{-1}. This excludes the radical II as an intermediate in the epoxidation of eq 1. Also, the carbocation



1-Z **2-c**

radical IV was shown to be an unlikely intermediate in the epoxidation of eq 1. From a combination of kinetic and electrochemical studies, we have shown that the carbocation radical of

Scheme I



IV cannot be formed *in the rate-limiting step* in the oxidation of alkenes by oxo[*meso*-tetrakis(2,6-dibromophenyl)porphinato]-

† Abbreviations used: porp, a generic porphyrin dianion; Cl_8TPP, dianion of *meso*-tetrakis(2,6-dichlorophenyl)porphyrin; Br_8TPP, dianion of *meso*-tetrakis(2,6-dibromophenyl)porphyrin; TMP, dianion of *meso*-tetramesitylporphyrin.

(1) (a) Collman, J. P.; Brauman, J. I.; Meunier, B.; Raybuck, S. A.; Kodadek, T. *Proc. Natl. Acad. Sci. U.S.A.* **1984**, *81*, 3245. (b) Collman, J. P.; Brauman, J. I.; Meunier, B.; Hayashi, T.; Kodadek, T.; Raybuck, S. A. *J. Am. Chem. Soc.* **1985**, *107*, 2000. (c) Collman, J. P.; Kodadek, T.; Raybuck, S. A.; Brauman, J. I.; Papazian, L. M. *J. Am. Chem. Soc.* **1985**, *107*, 4343. (d) Collman, J. P.; Kodadek, T.; Brauman, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 2588. (e) Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6375. (f) Bortolini, O.; Meunier, B. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1009. (g) Fontecave, M.; Mansuy, D. *J. Chem. Soc., Chem. Commun.* **1984**, 879. (h) Groves, J. T.; Stern, M. K. *J. Am. Chem. Soc.* **1988**, *110*, 8628. (i) Groves, J. T.; Myers, R. S. *J. Am. Chem. Soc.* **1983**, *105*, 5791. (j) Linsay-Smith, J. R.; Sleath, P. R. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1967. (k) Traylor, T. G.; Nakano, T., Dunlap, B. E.; Traylor, P. S.; Dolphin, D. *J. Am. Chem. Soc.* **1986**, *108*, 2782. (l) Traylor, T. G.; Miksztal, A. R. *J. Am. Chem. Soc.* **1987**, *109*, 2770. (m) Watabe, T.; Akamatsu, K. *Biochem. Pharmacal.* **1974**, *23*, 1079. (n) Watabe, T.; Ueno, Y.; Imazumi, J. *Biochem. Pharmacal.* **1971**, *20*, 912. (o) Ortiz de Montellano, P. R.; Mangold, B. L. K.; Wheeler, C.; Kunze, K. L.; Reich, N. O. *J. Biol. Chem.* **1983**, *258*, 4208. (p) Hanzlik, R. P.; Shearer, G. O. *Biochem. Pharmacol.* **1971**, *20*, 912.

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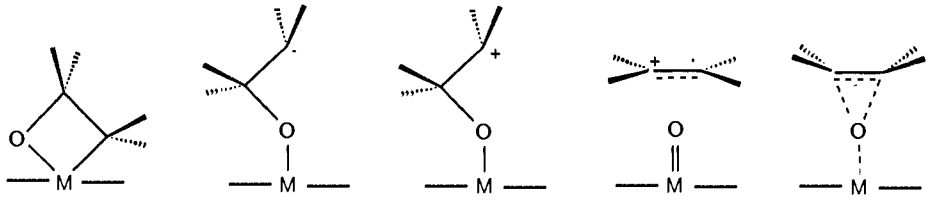
Chart I



I II III IV V

chromium(V) {$(Br_8TPP)Cr^V(O)(X)$}. Furthermore, IV cannot be an intermediate in epoxidations by $(Br_8TPP)Cr^V(O)(X)$ if the $1e^-$ oxidation potential of the alkenes exceeds ~1.7 V (SCE).[2d,e]

We proposed the unified mechanism of Scheme I to account for (i) the various products formed on reaction of alkenes with oxo[*meso*-tetrakis(2,4,6-trimethylphenyl)porphinato]iron(IV) π-cation radical {$(^{+\bullet}TMP)Fe^{IV}(O)$} and oxo[*meso*-tetrakis(2,6-dibromophenyl)porphinato]chromium(V) {$(Br_8TPP)Cr^V(O)(X)$} and (ii) the sensitivity of the log of the second-order rate constants for such reactions to the electron density of the alkene ($E_{1/2}$ and σ^+). The rate-limiting step is proposed to be charge-transfer complex formation.[2e] We also showed that for electron-rich alkenes $1e^-$ oxidation is possible, and carbocation radical (IV) might be an intermediate on the reaction path.[2e] Traylor and co-workers proposed that epoxidation with $(^{+\bullet}porp)Fe^{IV}(O)(X)$ proceeds via rate-limiting formation of iron(IV)–oxoporphyrin + alkene-derived cation radical.[1k] The basis for their proposal included kinetic[4] and trapping studies[11] using the easily oxidized hexamethyl Dewar benzene and 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*endo*,*endo*-dimethanonaphthalene. They used a mixed solvent (CH_2Cl_2/CH_3OH/H_2O = 80:18:2) for the kinetic study[4] and showed that the more polar the solvent is the more carbocation radical intermediate can be trapped.[11] In this paper we show unequivocal evidence for the formation of carbocation radical intermediate in the oxidation of **1-*Z*** by $(Br_8TPP)Cr^V(O)(X)$. Importantly, we also show that the carbocation radical intermediate is not formed in the rate-limiting step.

Experimental Section

Materials. Methylene chloride was purified as described previously.[2d] Tetrabutylammonium perchlorate $(n\text{-Bu})_4NClO_4$, and tetrabutylammonium tetrafluoroborate, $(n\text{-Bu})_4NBF_4$, were purchased from Aldrich and used as received. (*Z*)- and (*E*)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (**1-*Z***and **1-*E***, respectively) were synthesized as previously reported.[2c,5] The possible products *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde, *cis*- and *trans*-1,2-bis(*trans*-2,-*trans*-3-diphenylcyclopropyl)oxirane (**2-*c*** and **2-*t***, respectively) were prepared according to the published methods.[2c] Other standard samples for HPLC analysis were available commercially. Oxo[*meso*-tetrakis-(2,6-dibromophenyl)porphinato]chromium(IV) was available from a previous study.[2e,6]

Instrumentation. ^1H NMR spectra were obtained in $CDCl_3$ with a General Electric GN-500 spectrometer. Low-resolution and high-resolution mass spectra (LRMS and HRMS) were recorded on a VG Analytical spectrometer (Model VGII-250) by electron impact (EI) and chemical ionization (CI) with CH_4. UV–vis spectral measurements and repetitive scan experiments were carried out on an OLIS modified Cary-14 spectrophotometer (thermostated at 30 °C) interfaced to a Zenith computer equipped with OLIS data acquisition and processing software (On-Line Instruments, Inc.). High-pressure liquid chromatography (HPLC) was performed by using two Perkin-Elmer Series 10 Pumps. For analytic HPLC, a Hewlett-Packard variable wavelength detector (Model HP1050) at 254 nm, integrator (Model 3392A), and an Altex column 5 × 250 nm 5 μm RSil-CN eluted with a mixing solvent: hexane/CH_2Cl_2 = 9/1 at 2 mL/min were used. For semipreparative HPLC an ISCO variable wavelength absorbance detector (Model V^4) at 254 nm, fraction collector (Model Retriever II), and an Altex column 10 × 250 mm 10 μm RSil-CN eluted with a mixing solvent: hexane/CH_2Cl_2 = 9/1 at 6 mL/min were used. Cyclic voltammetry and controlled-potential bulk electrolysis (CPBE) were carried out as previously reported.[2e,6] The potentiostat used was a Bioanalytical Systems Model CV-27 Voltograph (West Lafayette, IN) and a Cypress Systems Model CYSY-1 Computer-Controlled Electroanalysis System (Lawrence, KS). A Pt flag electrode separated from the analyte compartment by a fine porosity frit was used as the auxiliary electrode. A Ag/AgCl electrode standardized to 0.00 V vs SCE was used as the reference electrode. Controlled-potential bulk electrolytic oxidation of $(Br_8TPP)Cr^{IV}(O)$ (**3**) → $(Br_8TPP)Cr^V(O)(X)$ (**4**) was carried out using a platinum gauze electrode (20 × 30 mm, 100 mesh, Aldrich) as the working electrode for 10 min at 1.06 V, and completion of the oxidation was confirmed by coulomb counting. The platinum gauze electrode and auxiliary electrode were cleaned by scanning (±Lim = 0.0–1.5 V) for 15 min in 10% HNO_3 (aqueous) solution prior to each electrolytic preparation of $(Br_8TPP)Cr^V(O)(X)$.

Kinetic Studies and Product Analysis. Solutions of $(Br_8TPP)Cr^V(O)(X)$ (**4**) used in the kinetic studies were prepared by dissolving $(n\text{-Bu})_4NClO_4$ or $(n\text{-Bu})_4NBF_4$ (0.10 M) and **3** (7.6 × 10^{-5} M) in 3.0 mL of CH_2Cl_2. After controlled-potential bulk electrolysis (CPBE) under Ar blowing a 0.2-mL aliquot of the resultant $(Br_8TPP)Cr^V(O)(X)$ solution was placed in a 1.0-cm cuvette and diluted with 1.8 mL of CH_2Cl_2. The alkene (800-fold molar excess) was then added neat, and the ensuing disappearance of $(Br_8TPP)Cr^V(O)(X)$ was monitored with time by repetitive scanning (500–350 nm) at 30 °C.

Reactions for product analysis were carried out at higher concentrations of $(Br_8TPP)Cr^V(O)(X)$ (2.3 × 10^{-4} M) and alkene (2.4 × 10^{-2} M). To a vial containing the alkene (20 mg) there was added 2 mL of the $(Br_8TPP)Cr^V(O)(X)$ solution obtained from CPBE. The reaction vial was sealed and stirred at room temperature in the dark for 24 h. After precipitating electrolyte and chromium porphyrin species by the addition of 15 mL of hexane, the precipitate was removed by filtration, and the filtrate was concentrated at room temperature. The residue so obtained was analyzed by HPLC. Structural assignments were based on co-elution with authentic standards. The product quantitation by HPLC analysis involved integration of peaks after determining response factors with authentic standards. For the unknown product isolation was carried out using semipreparative HPLC, and the structure was identified by ^1H NMR and MS.

Electrochemical Study of 1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene. Controlled-potential peak bulk electrolysis (CPBE) of (*Z*)-1,2-bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (**1-*Z***) was carried out in CH_2Cl_2 at 1.50 V using $(n\text{-Bu})_4NBF_4$ as the electrolyte ([**1-*Z***] = 2.0 × 10^{-3} M and $[(n\text{-Bu})_4NBF_4]$ = 0.1 M) with the same cell and instrument used for electrochemical oxidation of $(Br_8TPP)Cr^{IV}(O)$. The electrolysis was followed by coulomb counting and stopped when ~10% of **1-*Z*** was consumed. The products were analyzed and separated by HPLC. The same conditions, except for the working electrode (a Pt microdisk electrode, 10-μm diameter, used in LSV), were also employed in a linear sweep voltammetry (LSV) study using a Cypress Systems Model CYSY-1 computer-controlled electroanalysis system by changing the sweep rate, ν = 200–2500 mv/s, and the concentration of alkene, C = 4.0 × 10^{-3}–8.0 × 10^{-3} M.

Results and Discussion

As previously reported,[6] oxidation of (*Z*)-1,2-bis(*trans*-2,-*trans*-3-diphenylcyclopropyl)ethene (**1-*Z***) with $(Br_8TPP)Cr^V(O)(X)$ gave *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde as a major product (50%). No epoxide was obtained from the reaction although HPLC showed that some nonpolar products

(2) (a) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 158. (b) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 1313. (c) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 7512. (d) Garrison, J. M.; Bruice, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 191. (e) Garrison, J. M.; Ostovic, D.; Bruice, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 4960. (f) Ostovic, D.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 6906. (g) Ostovic, D.; Bruice, T. C. *J. Am. Chem. Soc.* **1989**, *111*, 6511.

(3) Traylor, T. G.; Miksztal, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 7443.

(4) Traylor, T. G.; Xu, F. *J. Am. Chem. Soc.* **1988**, *110*, 1953.

(5) He, G.-X.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, *113*, 2747.

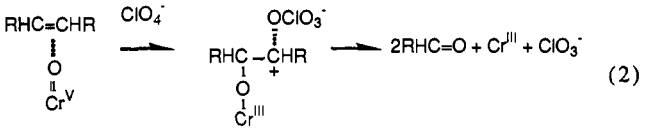
(6) He, G.-X.; Mei, H.-Y.; Bruice, T. C. *J. Am. Chem. Soc.* **1991**, *113*, 5645.

Table I. Second-Order Rate Constants (k_1) and Product Yields for the Oxidation of (Z)-1,2-Bis(*trans*-2,*trans*-3-diphenylcyclopropyl)ethene (**1-Z**) with $(Br_8TPP)Cr^V(O)(X)$

run	k_1 (M^{-1} s^{-1})	products[a] (yields, %)
1[b]	0.18	*trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde (50)[c]
2[d]	0.14	*trans*,*trans*-diene, *trans*,*cis*-diene (~60 in total)[e] *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde (6)
3[f]		no oxidation product

[a] Yields (%) are based on the oxidant. [b] $(n\text{-Bu})_4NClO_4$ was used as the supporting electrolyte. [c] Several very nonpolar products (total yields ~30%) have been found from HPLC. [d] $(n\text{-Bu})_4NBF_4$ was used as the supporting electrolyte. [e] The yield was estimated from HPLC, provided, its ϵ_{254} is twice the ϵ_{254} of *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde (see text). [f] In the absence of $(Br_8TPP)Cr^V(O)(X)$.

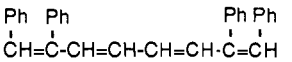
(unknown structure) formed. In these experiments, $(Br_8TPP)Cr^V(O)(X)$ was produced electrochemically from $(Br_8TPP)Cr^{IV}(O)$ in CH_2Cl_2 using tetrabutylammonium perchlorate $(n\text{-Bu})_4NClO_4$ as a supporting electrolyte. We explained the result by a cooxidation of **1-Z** by $(Br_8TPP)Cr^V(O)(X)$ and ClO_4^- as shown in eq 2.[6] A similar cooxidation of alkenes has been reported



(2)

by Kochi et al. for the system of $O{=}Cr^V(salen)^+$ and pyridine *N*-oxide.[7] In order to test the feasibility of a cooxidation mechanism we used tetrabutylammonium tetrafluoroborate $(n\text{-Bu})_4NBF_4$ as the supporting electrolyte in place of $(n\text{-Bu})_4NClO_4$. As shown in Table I, the oxidation of **1-Z** with $(Br_8TPP)Cr^V(O)(X)$ using $(n\text{-Bu})_4NBF_4$ in place of $(n\text{-Bu})_4NClO_4$ reduced the yield of *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde from 50% to 6%, and a new compound formed as the major product. No epoxide and traces of a few nonpolar products of unknown structure were found by HPLC. The new compound ("diene" in Table I, vide infra) is less polar (t_R = 12 min) than *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde (t_R = 18 min), *cis*-epoxide (**2-c**) (t_R = 29 min), and *trans*-epoxide (**2-t**) (t_R = 15 min) under the HPLC conditions used. It has an extinction coefficient (ϵ_{254}) larger than that of *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde. Thus, if one assumes that the "diene" has the same ϵ_{254} as does *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde the calculated yield of the "diene", by HPLC, would be 120%.

Structure of the "Diene" Product Obtained by Oxidation of 1-Z by $(Br_8TPP)Cr^V(O)(X)$. In Figure 1 there is provided the ^1H NMR spectrum for the "diene" product. The cyclopropane–proton signals which appear at δ = 2.65 and 2.55 ppm for C*H* and C(Ph)*H*, respectively, for **1-Z**[2c] are not seen in the spectrum of the "diene". The ^1H NMR signals of the "diene" can be divided into two groups, H_a, H_b, H_c, and H_d vs $H_{a'}$, $H_{a''}$, $H_{b'}$, $H_{b''}$, $H_{c'}$, $H_{c''}$, $H_{d'}$, and $H_{d''}$ (Figure 1) which have no coupling relationship. The integration ratio of the two groups of ^1H NMR signals were constant for samples from different batches of reactions. It is reasonable to conclude that these two sets of signals belong to two compounds which have very similar structures and could not be separated by HPLC under the conditions used.[8] Detailed decoupling experiments and the 2-D COSY technique provided the structural assignments shown in Figure 2. *trans*,*trans*-Diene is highly symmetric, and coupling constants are as follows: H_a–H_b, j = 9.5 Hz; H_b–H_c, j = 6.5 Hz; H_c–H_d, j = 12 Hz. For *trans*-,*cis*-diene the coupling constants are as follows: $H_{a'}$–$H_{b'}$, j = 9 Hz; H_b–$H_{c'}$, j = 7 Hz; $H_{c'}$–$H_{d'}$, j = 14 Hz; $H_{d'}$–$H_{d''}$, j = 8 Hz; $H_{d''}$–$H_{c''}$, j = 6.5 Hz; $H_{c''}$–$H_{b''}$, j = 6.5 Hz; $H_{b''}$–$H_{a''}$, j = 10 Hz.[9] Further splitting of the peaks can be seen for almost all signals due to the presence of the unsymmetric center in the molecules. A similar splitting pattern has also been found in the ^1H NMR spectrum of the ring-opened product from reaction of **1-Z** with *t*-BuOOH and $(TMP)Fe^{III}(Cl)$ in CH_2Cl_2.[5] From the spectrum the ratio of the two isomers was calculated as *trans*,*trans*-diene/*trans*,*cis*-diene = 1.7. With the assumption that ϵ_{254} of the mixture is two times the ϵ_{254} of *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde, the total yield for the mixture of the two isomers can be estimated from HPLC (Table I). The highest observed m/e in the LRMS(CI) spectrum of the mixture of dienes of 410 (base peak) arises from their fragmentation by loss of two HCl. Laser desorption arises from their fragmentation by loss of two HCl. Laser desorption MS also gives the highest m/e = 411 ($M - 2HCl + H^+$).[10] Such fragmentation under MS conditions is not unreasonable since it results in a product having a large conjugated system (**5**). HRMS(CI) for this fragment gives



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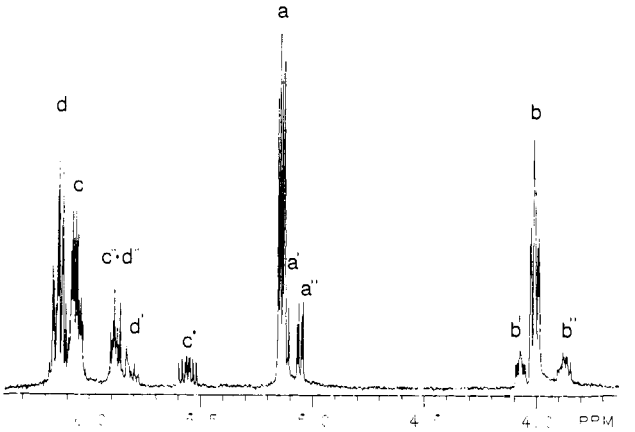
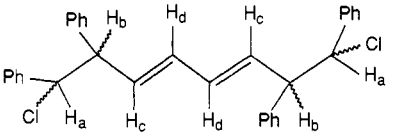
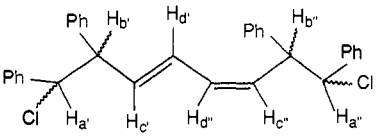


Figure 1. The 500-MHz ^1H NMR spectrum ($CDCl_3$) of the major product (diene mixture) of the oxidation of **1-Z** with $(Br_8TPP)Cr^V(O)(X)$ in CH_2Cl_2 using $(n\text{-Bu})_4NBF_4$ as the electrolyte. For all aromatic protons: δ 6.95–7.32 ppm (multiplet) and no signal in the region of $\delta \leq 3.8$ ppm.



(3E, 5E)-1,8-dichloro-1,2,7,8-tetraphenylocta-3,5-diene
(*trans*, *trans*-diene)



(3E, 5Z)-1,8-dichloro-1,2,7,8-tetraphenylocta-3,5-diene
(*trans*, *cis*-diene)

Figure 2. Structure and ^1H NMR spectrum assignments of the major product (diene mixture) of the oxidation of **1-Z** with $(Br_8TPP)Cr^V(O)(X)$ in CH_2Cl_2 using $(n\text{-Bu})_4NBF_4$ as the electrolyte.

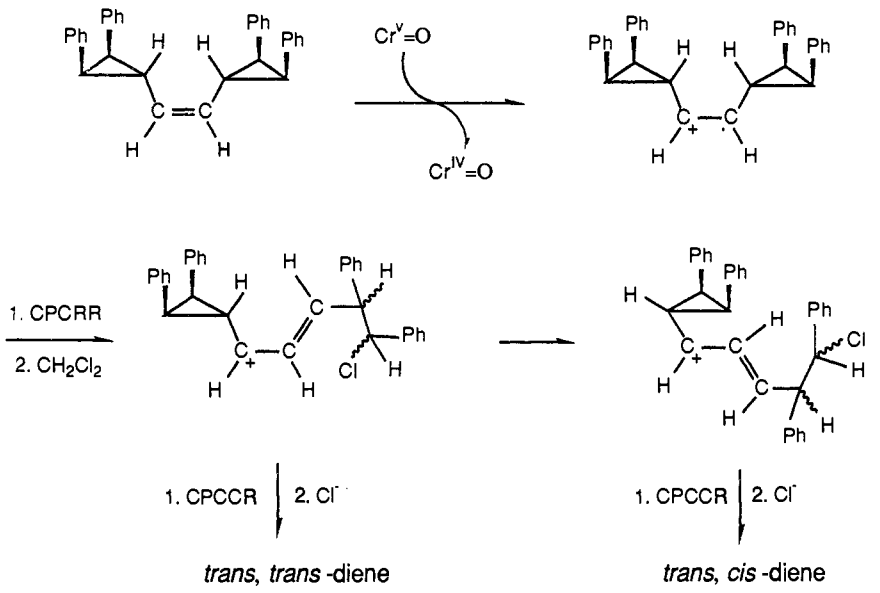
(7) Samsel, E. G.; Srinivasan, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1985**, *107*, 7606.

(8) Two peaks (t_R = 42.6 and t_R = 44.6 min) with the integration ratio $A_{44.6}/A_{42.6}$ = 1.8 can be separated by HPLC using an Altex column 5 × 250 mm 5 μm RSil-CN eluted with a mixing solvent: hexane/CH_2Cl_2 = 25/1 at 2 mL/min.

(9) The accuracy of the coupling constants for $H_{c'}$, $H_{c''}$, and $H_{d''}$ was inferior since the signals are too weak and complicated.

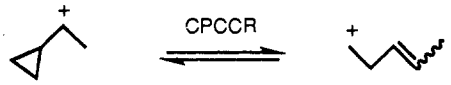
(10) Laser desorption mass spectral analysis was performed by Prof. Charles L. Wilkins at the Department of Chemistry, University of California, Riverside.

Scheme II



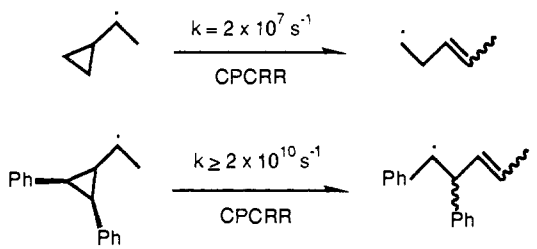
a molecular formula of $C_{32}H_{26}$ (calcd, 410.2034; found, 410.2007), which is consistent with the structure of **5**. From **5**, fragmentation of m/e = 410 gives m/e = 333 and 319 from loss of Ph and $PhCH_2$, respectively. Clusters centered at m/e = 243 (245), 231, 219 (217), and 205 indicates the presence of four continuous CH groups. Fragments of m/e = 193, 181, and 167, which are diagnostic for diphenylcyclopropyl, diphenylethyl, and diphenylmethyl cations, respectively, may come from the further fragmentation of the compound.

Mechanism of Formation of *trans,trans*-Diene and *trans,cis*-Diene involves the opening of both cyclopropane rings of **1-*Z*** following the oxidation by $(Br_8TPP)Cr^V(O)(X)$. The best explanation for the formation of the two nonoxygen containing dienes is through a carbocation radical intermediate. One ring opens by way of a cyclopropylcarbinyl to homoallylcarbinyl radical rearrangement (CPCRR), while the other ring opens in a cyclopropylcarbinyl to homoallylcarbinyl cation rearrangement (CPCCR) (eq 3). The cyclopropylcarbinyl to homoallylcarbinyl radical rearrangement (CPCRR) has been extensively studied.[11,12]



(3)

By comparison of the rate of an intramolecular reaction involving competition between cyclopropyl and *trans*-2,*trans*-3-diphenylcyclopropyl substituents, we showed that the 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 4).[2c] The cyclopropylcarbinyl to homoallyl cation



(4)

rearrangement (CPCCR) is a well-known mechanism.[13] Since cyclopropylcarbinyl cations are quite stable[13,14] and the CPCCR is reversible,[15] substituents on the cyclopropyl ring will control the position of equilibrium and the rate of ring opening.[13,16] The two phenyl groups in the *trans*-2,*trans*-3-diphenylcyclopropyl substituent are parallel to each other and bisect the plane defined by the cyclopropane carbon atoms.[2c] The phenyl groups are not in resonance with the cyclopropyl ring, and electrostatic repulsion between the π-systems of the two phenyl groups would raise the ground-state energy of the cyclopropyl ring in the CPCCR. Also, cyclopropyl ring opening with the *trans*-2,*trans*-3-diphenylcyclopropyl substituent will provide a benzylic carbocation. Thus, both electronic and steric factors should make ring-opening of *trans*-2,*trans*-3-diphenylcyclopropylcarbinyl cation much more facile than the ring-opening of cyclopropylcarbinyl cation since the latter would provide a primary carbocation. The mechanism for the formation of the *trans,trans*-diene and *trans,cis*-diene via CPCRR and CPCCR rearrangements is shown in Scheme II. Although it is unclear how the CPCRR and CPCCR effect the kinetic behavior of the other, the structure of the products show that the rearrangement of each ring occurs independently. As depicted in Scheme II, one of the cyclopropane rings may open first in a fast CPCRR followed by a relatively slow CPCCR of the other cyclopropane ring. The stereochemistry of the diene products are consistent with the reactions of Scheme II. It should be noted that CPCRR from a radical intermediate from **1-*Z*** provides product with only a trans configuration.[5] The mechanism and products for the oxidation of **1-*Z*** with $(Br_8TPP)Cr^V(O)(X)$ in the presence of different electrolytes are summarized in Scheme III.

The identity of the substituent Cl in the diene could not be established by MS, but it is strongly suggested by the ^1H NMR chemical shifts of the protons H_a, $H_{a'}$, and $H_{a''}$. Both Cl• and Cl^- may come from the solvent CH_2Cl_2. Abstraction of Cl• from CH_2Cl_2 by radical intermediates has been reported for oxidation reaction catalyzed by metalloporphyrin.[17] Chloride anions may be introduced in the reaction system by oxidation of the solvent by either or both $(Br_8TPP)Cr^V(O)(X)$ or electrolysis.[18]

(11) (a) Beckwith, A. L. J.; Ingold, K. U. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic: New York, 1980; pp 227–250. (b) Ortiz de Montellano, P. R.; Stearns, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 3415.

(12) (a) Newcomb, M.; Glenn, A. C. *J. Am. Chem. Soc.* **1989**, *111*, 275. (b) Bullock, R. M.; Samsel, E. G. *J. Am. Chem. Soc.* **1990**, *112*, 6886. (c) Lemieux, R. P.; Beak, P. *J. Org. Chem.* **1990**, *55*, 5454.

(13) (a) H. Richey In *Carbonium Ions*; Olah, G., Schleyer, P. v. R., Eds.; Wiley: New York, 1972; Vol. 3, pp 1201–1294. (b) Sarel, S.; Yovell, J.; Sarel-Imber, M. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 577.

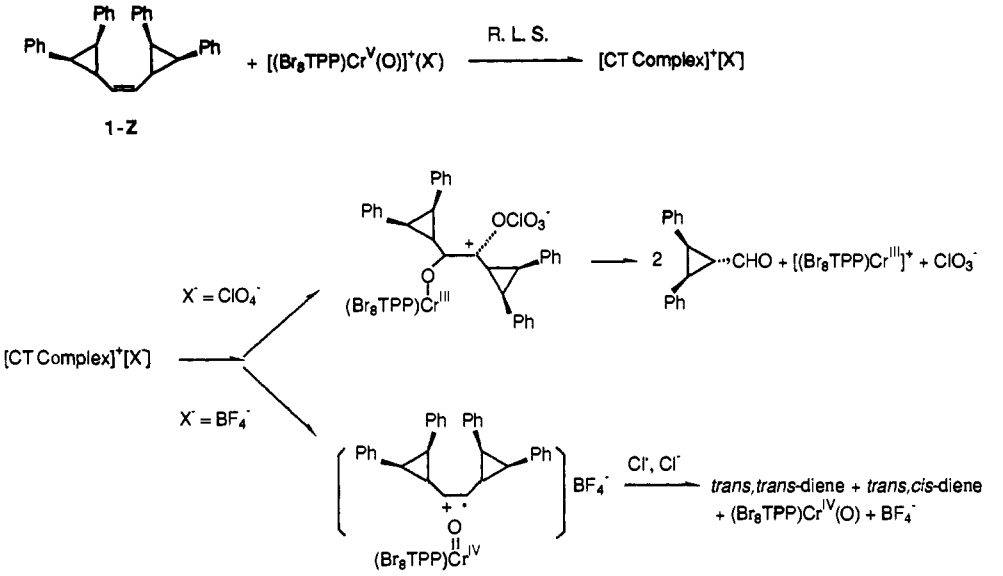
(14) Childs, R. F.; Kostyk, M. D.; Lock, C. J. L.; Mahendran, M. *J. Am. Chem. Soc.* **1990**, *112*, 8912 and references cited therein.

(15) (a) Hehre, W. J.; Hiberty, P. C. *J. Am. Chem. Soc.* **1972**, *94*, 5917. (b)Falkenberg-Andersen, C.; Ranganayakulu, K.; Schmitz, L. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1984**, *106*, 178.

(16) Majerski, Z.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1971**, *93*, 665.

(17) Hill, C. L.; Scharde, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 6374.

Scheme III



The formation of a small amount of *trans*-2,*trans*-3-diphenylcyclopropanecarboxaldehyde from the reaction using $(n\text{-Bu})_4NBF_4$ (Table I, run 2) may be explained by a mechanism through a cationic intermediate (Scheme I), which may form directly from the CT complex or from the recombination of the Cr(IV)–oxoporphyrin + alkene-derived carbocation radical pair. The life time of a radical pair solvent cage has been estimated at ca. 10^{-11} s,[19] and the rate constant of CPCRR for the *trans*-2,*trans*-3-diphenylcyclopropyl substituent measured is $\geq 2 \times 10^{10}$ s^{-1}.[2c]

Electrochemical Evidence for the Formation of *trans*,*trans*-Diene and *trans*,*cis*-Diene by Rearrangement of a Carbocation Radical. The most important evidence for the rearrangement mechanism of Scheme II is derived from the electrochemical $1e^-$ oxidation of **1-*Z***. Thus, $1e^-$ oxidation of **1-*Z*** by controlled-potential bulk electrolysis (CPBE) in CH_2Cl_2 using $(n\text{-Bu})_4NBF_4$ as the supporting electrolyte provided the same diene mixture (and same ratio of the configuration isomers) as major product as that obtained when $(Br_8TPP)Cr^V(O)(X)$ is the oxidant. Faraday efficiency for the electrolysis is ~40% when the oxidation is stopped at the point that only <10% of the alkene has been electrolyzed. Further electrolysis, however, may decrease the efficiency and increase the nonpolar components in the product mixture, which can be explained by the further electrolysis of the diene product. Linear sweep voltammetry (LSV) study of the alkene also supports these conclusions. Although LSV with **1-*Z*** failed since the electrode surface was poisoned by the active intermediate from the oxidation of the alkene, especially, at the low sweep rate, such a study with the *trans* isomer **1-*E*** gave a reasonable result with $\delta E_p/\delta \log(\nu)$ = 26.4 mV/decade and $\delta E_p/\delta \log(C)$ = 2.7 mV/decade (one-electron oxidation potentials $E_{1/2}$ = 1.45 and 1.35 V for **1-*Z*** and **1-*E***, respectively, in CH_2Cl_2 vs SCE). The result is consistent with a first-order EC mechanism (eq 5) which follows the expressions $\delta E_p/\delta \log(\nu)$ = 29.5 mV/decade and $\delta E_p/\delta \log(C)$ = 0 mV/decade.[20,21] The reaction kinetics for the homogeneous rearrangement could not be obtained by LSV because they are too fast.[22]

$$\text{alkene} \rightleftharpoons \text{alkene}^{\bullet+} + e^- \qquad \text{alkene}^{\bullet+} \rightarrow \text{product} \qquad (5)$$

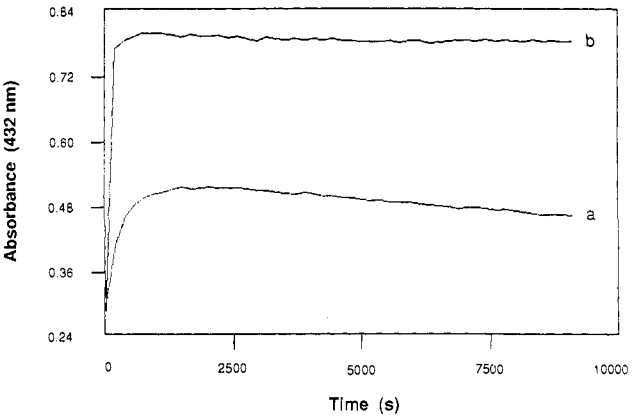


Figure 3. Plots of absorbance at 432 nm vs time for the reaction system of **1-*Z*** (6.1×10^{-3} M) and $(Br_8TPP)Cr^V(O)(X)$ (7.6×10^{-6} M) in CH_2Cl_2 at 30 °C: (a) $(n\text{-Bu})_4NClO_4$ (0.1 M) and (b) $(n\text{-Bu})_4NBF_4$ (0.1 M).

The Rate-Limiting Step in the Reaction of 1-*Z* with $(Br_8TPP)Cr^V(O)(X)$. The reactions of eq 6 are known to be involved in the reaction of an alkene with a $(porp)Cr^V(O)$ species in CH_2Cl_2.[2e] The slowest reaction step is 6a, while the com-

$$(porp)Cr^V(O)(X) + \text{alkene} \rightarrow (porp)Cr^{III}(X) + \text{oxidized alkene} \qquad (6a)$$

$$(porp)Cr^V(O)(X) + (Porp)Cr^{III}(X) \rightleftharpoons (porp)Cr^{IV}(O) + (porp)Cr^{IV}(X)_2 \qquad (6b)$$

$$(porp)Cr^V(O)(X) + e^- \rightarrow (porp)Cr^{IV}(O) + X^- \qquad (6c)$$

proportionation reaction 6b is very rapid. The spontaneous decomposition (solvent oxidation, etc.) of 6c is only important in determining product yields for those alkenes with $E_{1/2} > +2.0$ V (one-electron oxidation potentials, SCE). The Cr(IV) species may form mainly as a product of the comproportionation reaction 6b, which can be followed by UV–vis measurement at λ_{max} = 432 nm. Figure 3 gives the concentration changes of the Cr(IV) species in the oxidation of **1-*Z*** with $(Br_8TPP)Cr^V(O)(X)$ using $(n\text{-Bu})_4NClO_4$ and $(n\text{-Bu})_4NBF_4$ as electrolytes. It is clear that the reaction using $(n\text{-Bu})_4NBF_4$ produces more Cr(IV) species than that when using $(n\text{-Bu})_4NClO_4$. This observation is consistent with the mechanism in Scheme III. Using $(n\text{-Bu})_4NClO_4$ gives

(18) Cl^- may also come from a trace impurity present in $(n\text{-Bu})_4NBF_4$ since addition of $AgNO_3$ to a CH_2Cl_2 solution of the electrolyte produces a white precipitate.

(19) Noyes, R. M. *J. Am. Chem. Soc.* **1955**, *77*, 2042.

(20) (a) Aalstad, B.; Parker, V. D. *J. Electroanal. Chem.* **1980**, *112*, 163. (b) Parker, V. D. *Acta Chem. Scand.* **1981**, *B35*, 373. (c) Eliason, R.; Parker, V. D. *J. Electroanal. Chem.* **1984**, *165*, 21.

(21) (a) Parker, V. D. *Electroanal. Chem.* **1986**, *14*, 1. (b) Hammerich, O.; Svensmark, B.; Parker, V. D. In *Organic Electrochemistry*; Baizer, M. M., Lund, H., Eds.; Marcel Dekker, Inc.: New York, 1983; pp 77–150.

(22) Tanko, J. M.; Drumright, R. E. *J. Am. Chem. Soc.* **1990**, *112*, 5362.

trans-2,*trans*-3-diphenylcyclopropanecarboxaldehyde as the major product and produces Cr(III) from Cr(V) directly. Using $(n\text{-}Bu)_4NBF_4$, however, the major reaction stops at Cr(IV) because of the rearrangement of the cation radical intermediate to give the nonoxygen containing diene.

The second-order rate constants (k_1) for the reaction of **1-*Z*** with $(Br_8TPP)Cr^V(O)(X)$, which were determined by following the disappearance of $(Br_8TPP)Cr^V(O)(X)$ at its λ_{max} of 409 nm, are shown in Table I. The second-order rate constants are much the same when using $(n\text{-}Bu)_4NClO_4$ and $(n\text{-}Bu)_4NBF_4$ as electrolyte. For *cis*-stilbene, the second-order rate constants (k_1) of the reaction are 0.073 and 0.089 using $(n\text{-}Bu)_4NClO_4$ and $(n\text{-}Bu)_4NBF_4$, respectively. Thus, for **1-*Z***, though the products differ in the presence of $(n\text{-}Bu)_4NClO_4$ and $(n\text{-}Bu)_4NBF_4$ the calculated second-order rate constants for the reaction of **1-*Z*** with $(Br_8TPP)Cr^V(O)(X)$ do not change. As pointed by Kochi et al.,[7] in a reported study of the oxidation of alkenes with $O{=}Cr^V(salen)^+$, the rate-limiting step for oxidation precedes and is separate from the product-forming step. For the oxidation with $(Br_8TPP)Cr^V(O)(X)$, therefore, the formation of a carbocation radical intermediate on oxidation of electron-rich alkenes has been established, but carbocation radical is not formed in the rate-limiting step. This is as we proposed in our unified mechanism of Scheme I. It should be noted that the log of the second-order rate constants (k_1) for the oxidation of both *cis*-stilbene and **1-*Z*** by $(Br_8TPP)Cr^V(O)(X)$ fits the linear free-energy plot of log k_1 vs $E_{1/2}$ established with 16 alkenes in previous studies.[2e,6] The slope of the linear free-energy plot is much too small to support a rate-limiting step which involves rate limiting $1e^-$ transfer but is in accord with rate-limiting charge-transfer complex formation.[2e,6]

Relationship to Previous Studies Using Other Oxidants and Catalysts. Epoxidation of **1-*Z*** with C_6F_5IO and $(Cl_8TPP)Mn^{III}(OH)$ in CH_2Cl_2 gave the *cis*-epoxide (**2-*c***) as the major product (84%) and two nonpolar minor products.[2c] MS suggests that the two minor products are steric isomers, in which no oxygen is contained and one cyclopropyl ring is opened while the other remains intact. We explained the result by a mechanism through a carbocation radical intermediate, with one *trans*,*trans*-diphenylcyclopropyl ring undergoing CPCRR and the second remaining intact such that the carbocation center did not result in a CPCCR. The difference between the present study where both CPCRR and CPCCR of *trans*,*trans*-diphenylcyclopropyl ring occur and the result with $(Cl_8TPP)Mn^{III}(OH) + C_6F_5IO$ can be understood as follows. In the present study a large excess of $(n\text{-}Bu)_4NBF_4$ (0.1 M) has been used as the supporting electrolyte such that the system is much more polar and favors the CPCCR. The difference in concentrations of the nucleophilic Cl^- ion may also be of importance since combination of Cl^- with the carbocation center should be competitive with CPCCR. In the present study we show that a change in supporting electrolyte results in different major products. Product-forming reactions also differ dependent upon the hypervalent metal–oxo porphyrin (Fe, Mn, or Cr) and the structure of the alkene. Recently, a study of stereoselectivity of the epoxidation with metalloporphyrins showed that for some very electron-rich alkenes ($E_{1/2} \leq 1.1$ V) the rate-limiting step may shift from CT complex formation to electron transfer.[6] For instance, cis versus trans selectivity could not be found for the oxidation of *trans*-*p*,*p*′-dimethoxystilbene ($E_{1/2} = 1.05$ V), but it is very obvious for *trans*-stilbene ($E_{1/2} = 1.51$ V).

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Registry No. 1-*Z*, 112711-98-5; **3**, 134818-46-5; **4** ($X = BF_4^-$), 136954-54-6; **4** ($X = ClO_4^-$), 134818-44-3; 1,8-dichloro-1,2,7,8-tetraphenyl-3,5-octadiene, 136954-53-5; *trans*-2,*trans*-3-diphenylcyclopropane, 64200-26-6.

Supplementary Material Available: A complete 500-MHz ^1H NMR spectrum ($CDCl_3$) of the *trans*,*trans*-diene and *trans*,*cis*-diene mixture (1 page). Ordering information is given on any current masthead page.