of the Eu^{III} aquo ion ($EuCl_3$) illustrated in Figure 8A, which is quasi-reversible. The reversible behavior gained upon complexation by the macrocycle is also observed in the Eu[2.2.1]- and Eu[2.2.2]cryptates and in similar Eu macrocyclic amine complexes.[26,27] The reduction potential of EuHAM is shifted approximately −270 mV relative to the potential for the aquo ion. This potential shift can be used to calculate the relative complex stability in the two oxidation states.[26] The measured shift corresponds to a stabilization by a factor of $10^{4.6}$ of Eu(III) relative to Eu(II) in the macrocycle. This contrasts with the positive shifts of 200 and 420 mV observed for the Eu[2.2.1]- and Eu[2.2.2]-cryptate complexes, respectively. These positive shifts were attributed largely to a better fit of Eu(II) in the cryptate cavities.[26] This suggests that the cavity size of the HAM ligand is much better suited to the +3 state than the +2 state. The ionic radius of Eu(II) is slightly larger (0.08 Å for 10-coordinate complexes) than that of La(III).[24]

Conclusion. The GdHAM complex shows significant promise as an MRI contrast agent because of its high relaxivity and kinetic stability. Both the GdHAM crystal structure and the EuHAM luminescent lifetime measurements indicate three to four open coordination sites for water. The hydrogen bonds to two coordinated acetate oxygens in the solid state provide an estimate for the closest approach of an outer-sphere water proton of 4.1–4.2 Å. The cavity size of the macrocycle appears to be slightly too large for Gd(III) based on a comparison of Ln–N bond lengths to acyclic analogues. This observation, in conjunction with the Eu(III)/Eu(II) redox potential, suggests that the optimum metal ion size for the HAM cavity is somewhere between the radii of Gd(III) and Eu(II). While the structural and dynamic properties responsible for the high relaxivity and stability of this complex need to be more completely defined, the concept of designing planar macrocyclic ligands for Gd(III) clearly shows potential for producing improved MRI contrast agents.

Acknowledgment. We are grateful to Dr. D. Smith for the use of the spin-lock NMR spectrometer, Drs. P. M. Killough and C. D. Tait for assistance with the luminescence lifetime measurements, Dr. C. J. Burns for help with the X-ray crystallography, and Dr. J. H. Hall for assistance with molecular modeling calculations. We appreciate helpful discussions with Dr. C. B. Storm, our colleagues at the Center for Non-Invasive Diagnosis, and the Medical Radioisotopes group at LANL. P.H.S. would like to acknowledge postdoctoral funding from the Director of the Laboratory.

Registry No. $[GdHAM(OAc)_2]Cl\cdot4H_2O$, 122114-27-6; $[EuHAM(OAc)_2]Cl\cdot4H_2O$, 122093-05-4.

Supplementary Material Available: Figure S1 showing the emission spectrum of EuHAM in aqueous solution, Table S2 listing the anisotropic thermal parameters for non-hydrogen atoms, and Table S3 listing the calculated positional and thermal parameters for hydrogen atoms (3 pages); Table S1 listing calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

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Alkene Epoxidations Catalyzed by Iron(III), Manganese(III), and Chromium(III) Porphyrins. Effects of Metal and Porphyrin Substituents on Selectivity and Regiochemistry of Epoxidation

Teddy G. Traylor* and Andrew R. Miksztal

Contribution from the Department of Chemistry, D-006, University of California, San Diego, La Jolla, California 92093. *Received February 3, 1989*

Abstract: The products of epoxidation of norbornene, cyclohexene, and adamantylideneadamantane with pentafluoroiodobenzene using as catalysts variously substituted tetraphenylporphyrin complexes of chloroiron(III), chloromanganese(III), and chlorochromium(III) have been determined. All catalysts afforded the epoxide from adamantylideneadamantane, suggesting that the metallacycle intermediate, impossible in this case, is not required for epoxidation. The ratios of *exo-* to *endo-*epoxynorbornanes obtained from norbornene varied from about 10^3 for electropositively substituted Cr(III) complexes gradually through the Mn(III) and Fe(III) series to a value of about 6 for electronegatively substituted iron(III) porphyrins. Mechanisms ranging from limiting electrophilic addition to limiting electron transfer are proposed to account for these changes. The electronegatively substituted iron porphyrins show a greater tendency toward epoxidation rather than allylic oxidation and show more selectivity for *cis*-alkenes.

The epoxidation of alkenes remains an important synthetic process. Recent development of metal-catalyzed epoxidations has encouraged further attempts to develop more selective and more commercially attractive epoxidation reactions.[1]

Among the transition-metal catalysts for oxygen transfer the metalloporphyrins offer some attractive advantages.[2-9] They provide a strong four-coordinate ligand, which can be very stable toward destruction and has a potential for elaboration to provide

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chemo-, regio-, and stereoselectivity. It is therefore of some interest to study the mechanisms by which metalloporphyrins transfer an oxygen atom to an alkene, eq 1 and 2. Understanding this process

$$RH + XO \xrightarrow{M^+Porph} ROH + X \quad (1)$$


(2)

would not only aid in catalyst design but would provide mechanistic information, which would be valuable in understanding other metal–ligand systems carrying out oxygen transfer.

In this paper we explore three aspects of the epoxidation reaction: (1) the effect of variation in the metal, Fe(III), Mn(III), Cr(III), on product ratios in epoxidation; (2) the effect of variations in electronic and steric environment of the porphyrin on product ratios; (3) the effects of metal and porphyrin changes on the catalyst stability. The results provide some information that is helpful in designing specific synthetic oxidation processes and helps to further define the mechanisms of epoxidation.

Experimental Section

Materials. Norbornene (Aldrich, 99%) was twice distilled under argon. Methylene chloride solutions of purified norbornene were passed twice through columns of activated neutral alumina and used immediately. Analysis by gas chromatography showed that the purified norbornene solution was free of any oxidation products or impurities. *exo*-2,3-Epoxynorbornane (98%), norcamphor (97%), cyclohexene-4-carboxaldehyde (99%), *exo*-norborneol (98%), and *endo*-norborneol (96%) were from Aldrich and used as received. *endo*-Epoxynorbornane was isolated from a hemin-catalyzed epoxidation by preparatory GLC and identified by NMR spectroscopy. Cyclohexene (Aldrich, 99%, stabilized with 0.01% di-*tert*-butyl-4-methylphenol) was purified by passing through activated alumina and used immediately. Analysis by gas chromatography showed that the purified cyclohexene was free of any oxidation products or impurities. Cyclohexene oxide (98%), cyclohexen-3-one (97%), and cyclohexen-3-ol (96%) were from Aldrich and used as received. Adamantylideneadamantane was a gift from Professor R. S. Brown[10] and used as received. Pentafluoroiodobenzene (PFIB) was prepared in a manner similar to that for iodobenzene[11] by stirring finely ground perfluoroiodobenzene bis(trifluoromethyl)acetate[12] with saturated aqueous sodium bicarbonate solution for 20 h. The powder was removed by filtration, washed with water, and dried over P_2O_5 under vacuum (<1 Torr). (EXPLODES![13]) *m*-Chloroperbenzoic acid (technical grade, Aldrich, MCPBA) was purified by literature methods[14] and recrystallized from CH_2Cl_2. Titration by iodometric assay indicated >99% purity. Mesitaldehyde (98%), 2,6-dichlorobenzaldehyde (99%), 2-chloro-6-nitrobenzaldehyde (99%), 2,4,6-trimethoxybenzaldehyde (98%), and 4-tolualdehyde (97%) were from Aldrich and used as received. Pyrrole (Aldrich, 98%) was stirred over and distilled from CaH_2 under argon and used immediately. 2,4,6-Collidine (Aldrich, 99%) was stirred over and distilled from CaH_2 under reduced pressure. Zinc acetate dihydrate (Aldrich, 98%) was dehydrated under high vacuum at 120 °C for 20 h. Iron(II) bromide (Alfa, anhydrous), manganese(II) chloride (Aldrich, 99%), and chromium(II) chloride (Aldrich, 95%) were used as received. Alumina (E. Merck, neutral) was activated by heating to 400 °C for 20 h. Methylene chloride (Fisher, ACS grade) was stirred over and distilled from CaH_2. Dimethylformamide (DMF), methanol, and propionic acid (Fisher, ACS grade) were used as received.

Porphyrins. Tetramesitylporphyrin[15] ($H_2(2,4,6\text{-}CH_3)PP$) and tetrakis(2,6-dichlorophenyl)porphyrin[16] ($H_2(2,6\text{-}Cl)PP$) were prepared by the Rothemund method,[15] except that pyridine was replaced by 2,4,6-collidine as solvent. Tetrakis(2-chloro-6-nitrophenyl)porphyrin[17] ($H_2(2\text{-}Cl,6\text{-}NO_2)PP$)[16] was prepared by condensation of pyrrole and aldehyde with $Zn(OAc)_2$ in refluxing 2,4,6-collidine with stirring under argon.[18] Tetrakis(2,4,6-trimethoxyphenyl)porphyrin ($H_2(2,4,6\text{-}OCH_3)PP$) and tetra-4-tolylporphyrin ($H_2(4\text{-}CH_3)PP$) were prepared by condensation of pyrrole and respective aldehyde in refluxing propionic acid.[19] The above porphyrins were isolated and purified as previously described. Tetraphenylporphyrin (chlorin-free) (H_2TPP), tetrakis(4-bromophenyl)porphyrin ($H_2(4\text{-}Br)PP$), tetrakis(4-cyanophenyl)porphyrin ($H_2(4\text{-}CN)PP$), tetrakis(4-methoxyphenyl)porphyrin ($H_2(4\text{-}OCH_3)PP$), tetrakis(2-bromophenyl)porphyrin ($H_2(2\text{-}Br)PP$), tetrakis(2-nitrophenyl)porphyrin ($H_2(2\text{-}NO_2)PP$), and tetra-2-tolylporphyrin ($H_2(2\text{-}CH_3)PP$) were from Mid-Century Chemicals and used as received. Tetrakis(pentafluorophenyl)porphyrin ($H_2(F_5)PP$) was from Aldrich and used as received.

Metalation Reactions. The iron porphyrin chloride,[20] manganese porphyrin chloride,[21] and chromium porphyrin chloride[22] complexes were prepared by refluxing the porphyrin with the respective metal salt in degassed DMF under argon.[23] The reactions were determined to be complete when a diluted aliquot in CH_2Cl_2 indicated by visible spectroscopy that there was no free porphyrin remaining. Isolation, purification, and conversion to the chloride complexes were by literature methods.[20-22]

Instruments. Samples were analyzed on a Varian 3700 gas–liquid chromatograph equipped with a 10% Carbowax 20M 80/100 Suppelcoport column. In the temperature program, the initial temperature of 65 °C was held for 3 min, ramped at 5 °C/min to a final temperature of 195 °C, and held there for 25 min. Typical retention times were the following: norbornene, 1.5 min; *endo*-epoxynorbornane, 8.7 min; *exo*-epoxynorbornane, 10.1 min; cyclohexene-4-carboxaldehyde, 11.7 min; pentafluoroiodobenzene, 12.2 min; and norcamphor, 13.4 min. The Carbowax column used for GLC analysis was required to be in excellent condition to accurately and reproducibly quantitate the small amounts of *endo*-epoxynorbornane formed in the reactions catalyzed with metalloporphyrins and in the reaction of norbornene with MCPBA. UV–visible spectra were recorded on a Kontron Uvikon 810 spectrophotometer.

Oxidation Procedures. The conditions for a typical oxidation reaction catalyzed by a metalloporphyrin were as follows: a CH_2Cl_2 solution of $Fe(2,6\text{-}Cl)PPCl$ (110 μL of 1.0 mM) was added to a small test tube and carefully evaporated to dryness. Purified norbornene (or cyclohexene) (110 μL of 1 M in CH_2Cl_2) was added and the contents thoroughly mixed to redissolve the catalyst. An aliquot (10 μL) was removed and diluted 50-fold with CH_2Cl_2, and its UV–visible spectrum was recorded. Freshly prepared PFIB (2.0 mg, 0.0064 mmol) was added in one portion to the remaining solution and the contents shaken until all the oxidant dissolved or the catalyst was bleached. At the end of reaction, aliquots were removed for GLC and UV–visible analyses. Each metalloporphyrin-catalyzed oxidation reaction was repreated at least two or three times.

For the oxidation of norbornene with MCPBA the conditions were as follows: MCPBA (1.1 mg, 0.0064 mmol) was added to a CH_2Cl_2 solution of norbornene (0.10 mL, 1.0 M, 0.1 mmol) in a small test tube, capped, and shaken for 1 min. The oxidant dissolved immediately. An aliquot was removed and analyzed by GLC. The average *exo*-epoxynorbornane/*endo*-epoxynorbornane value for three runs was 690 ± 50. A similar procedure was used to prepare the epoxide from adamantylideneadamantane.[24]

Cyclohexene Oxidations. The conditions for a typical oxidation reaction catalyzed by a metalloporphyrin were as follows: a CH_2Cl_2 solution of $Fe(2,6\text{-}Cl)PPCl$ (1.0 mM) containing cyclohexene (1 M) was added to a small test tube. Freshly prepared PFIB (sufficient for 0.064 M concentration if dissolved) was added in one portion to the solution, the test tube capped, and the contents shaken until the oxidant completely dissolved. At the end of reaction, aliquots were removed for GLC and UV–visible analyses.

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Table I. Yields of Products from the Oxidation of Norbornene with Pentafluoroiodobenzene Using Various Iron(III) Tetraphenylporphyrin Chlorides as Catalysts[a]

		yield, %				
substituent[b]	exo/endo[c]	epoxide[d]	aldehyde[d,e]	ketone[d,f]	% Soret[g]	hemir remaining[h]
4-OCH_3	77 (1)	28	1.2	0.3	0	
4-CH_3	71 (2)	45	2.4	0.4	0	
H	55 (1)	54	3.4	0.4	0	
4-Br	44 (2)	53	3.6	0.6	40	*N*-alkyl
4-CN	35 (1)	51	3.8	0.7	70	*N*-alkyl
2-CH_3	17 (1)	71	2.8	0.6	100	*N*-alkyl
2-Br	15 (1)	75	2.8	0.8	100	FeOH
2-NO_2	15 (1)	73	2.9	0.8	97	FeOH
2,4,6-CH_3	24	77	0.4	0.3	100	*N*-alkyl
2,4,6-OCH_3	20 (1)	60	4.0	0.6	69	*N*-alkyl
F_5	20 (1)	70	6.9	1.9	100	FeOH
2,6-Cl	9 (0.5)	82	1.0	0.6	100	FeOH
2-Cl, 6-NO_2	6 (0.4)	~80	1.4		100	FeCl
N-alkylhemin[i]	3.5 (0.1)	77	0.8	0.7	100	*N*-alkyl
[4-OCH_3][a]	86 (2)	35	1.5	0.3	40	*N*-alkyl
[4-CH_3][a]	72 (1)	50	3.2	0.5	50	*N*-alkyl
[H][a]	56 (2)	56	4.4	0.6	40	*N*-alkyl
[4-Br][a]	46 (2)	60	4.5	0.7	80	*N*-alkyl
[4-CN][a]	43 (2)	56	3.8	0.8	60	*N*-alkyl

[a] Conditions: norbornene, 1.0 M; catalyst, 10^{-3} M; PFIB, 0.064 M, insoluble in CH_2Cl_2. PFIB dissolved in 1–11 min depending upon hemin structure. The last five entries (substituents in brackets) were carried out with 0.016 M PFIB. [b] The substitutents are Y in the TPP derivatives, $[Y_nC_6H_{5-n}]_4$PorphFeCl. [c] These are the ratios of the GLC integrations for *exo*- and *endo*-epoxynorbornane, previously identified with authentic samples. Standard deviations are given in parentheses. [d] Percent yields based upon integrations of the product vs that of F_5PhI, corrected for response factors. For the epoxides the yields are the totals of exo and endo products. [e] Cyclohexene-4-carboxaldehyde, identified previously. [f] Norcamphor, previously identified. [g] This is an estimate of the amount of hemin remaining after the reaction. It is somewhat inaccurate as a result of the changes in the hemin. [h] The structure of the remaining hemin was assigned (tentatively) based upon the UV–visible spectrum. [i] This *N*-alkylhemin was formed during the the oxidation of 4,4-dimethyl-1-pentene catalyzed by Fe(2,6-Cl)PPCl. See ref 25 for synthesis and isolation.

Table II. Yields of Products from the Oxidation of Norbornene with Pentafluoroiodobenzene Catalyzed by $Cr^{III}Cl$ and $Mn^{III}Cl$ Complexes of Various Tetraphenylporphyrins[a]

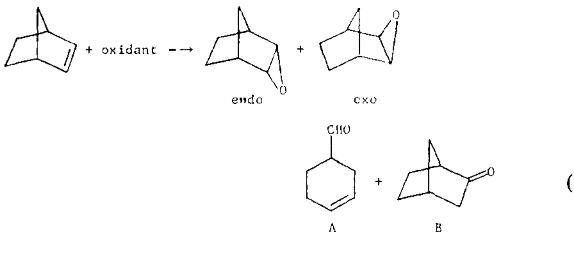
		yield, %			
substituent[b]	exo/endo	epoxide	aldehyde	ketone	% Soret
Cr(H)	~1000	32	0.6	0.2	0
Cr(F_5)	422 (41)	75	2.4	0.4	100
Cr(2,6-Cl)	362 (43)	74	1.1	0.3	83
Mn(4-OCH_3)	395 (26)	79	0.3	0.2	63
Mn(H)	351 (20)	82	0.3	0.2	69
Mn(4-Br)	324 (13)	82	0.3	0.2	70
Mn(2-CH_3)	250 (5)	77	0.3	0.2	83
Mn(2-Br)	126 (2)	82	0.5	0.4	84
Mn(2-NO_2)	93 (4)	76	0.6	0.7	89
Mn(F_5)	166 (6)	80	1.2	0.8	100
Mn(2,4,6-CH_3)	53 (3)	82	0.4	0.3	84
Mn(2,6-Cl)	35 (2)	83	0.4	1.2	89

[a] Conditions: exactly as in Table I, using 0.064 M PFIB (insoluble). See Table I for definitions of column readings. [b] The metal and substituents on the phenyl groups are given as in Table I.

Adamantylideneadamantane Oxidation. The conditions for a typical adamantylideneadamantane oxidation reaction catalyzed by a metalloporphyrin were as follows: a CH_2Cl_2 solution of Fe(2,6-Cl)PPCl (1.5 mM) containing adamantylideneadamantane (0.075 M) was added to a small test tube. Freshly prepared PFIB (sufficient for 0.032 M) was added in one portion to the solution, the test tube capped, and the contents shaken until the oxidant completely dissolved. At the end of reaction, aliquots were removed for GLC and UV–visible analyses.

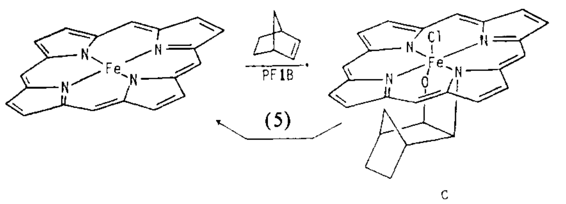
Results and Discussion

The reactions with norbornene produced four products in nearly all cases as previously reported for iron porphyrins (eq 3).[7] The product distributions obtained with 0.001 M catalyst and the equivalent of 0.064 or 0.016 M oxidant (PFIB) as a suspension at room temperature along with approximate percentages of metalloporphyrin survival are shown in Table I. Table II gives the results for similar studies of the manganese and chromium porphyrins.



(3)

As indicated in the last column and in our previous study,[25] the iron porphyrins reversibly form *N*-alkylporphyrins, with the reversal to the iron porphyrin being slower for more electron-rich porphyrins (eq 4). We found no evidence for this *N*-alkylporphyrin formation in the manganese or chromium porphyrins. The formation of *N*-alkylmetalloporphyrins has some important consequences. First, it makes the estimate of porphyrin survival difficult to ascertain since the extinction coefficients are not known for most of the *N*-alkylmetalloporphyrins. Second, the *N*-alkylhemins seem to be more stable toward destruction than are the metalloporphyrins from which they are derived although hemin destruction is competitive with *N*-alkylhemin formation early on.[25]



(4)

It can be seen in Table I that a lower ratio of *exo*-epoxide/*endo*-epoxide is obtained with the 2,6-chloro-*N*-alkylhemin than with the hemin itself. Because in most cases the hemin is converted essentially completely to the *N*-alkylhemin early in the reaction and remains as such until the oxidant disappears,[25] it is likely that the products are derived from catalysis by the *N*-alkylhemin (eq 6). This complicates comparisons between Fe and the other metals. If the hemin and *N*-alkylhemins respond in similar ways to electronic and steric effects, then our comparisons are still valid.

Another consequence of the *N*-alkylation is a misleading estimate of stabilities of the various hemins toward oxidative destruction. For example, the survival of tetramesitylhemin shown

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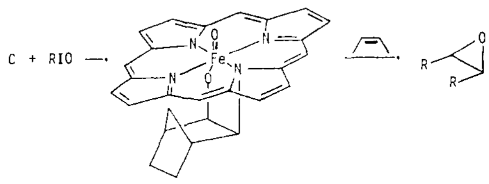


(6)

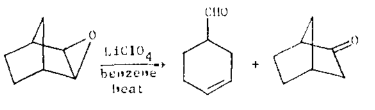
in Table I is probably a consequence of its being converted to *N*-alkylhemin during the catalytic reaction, only to return to hemin at the end of the reaction. It is encouraging that, as the hemin is made even more electronegative by halogenation of the pyrrole positions, extent of N-alkylation decreases while the resistance of the porphyrin toward oxidative destruction increases.[26]

With these reservations in mind we can examine the consequences of electronic and steric changes on the product distributions. Clearly the *exo*-epoxide/*endo*-epoxide ratio decreases as the electron density in the porphyrin decreases among the para-substituted hemins.[27] The oxidation potential for the Fe^{II}/Fe^{III} couple has been shown to correlate with the Hammett σ_Y in this series.[28] We plot in Figure 1 the log (exo/endo) versus $4\sigma_Y$ to obtain a reasonable linear correlation. We previously noticed that the approximately isosteric tetramesitylhemin and tetra-2,6-dichlorohemin also showed a marked electronic effect[7] (Table I). Interestingly, a similar plot for the manganese porphyrins shows a similar correlation (Figure 2) even though the ratios are much larger. The chromium porphyrins also show an increase in the exo/endo ratio with electron donation from the porphyrin (Table II).

The change of exo/endo ratio with the changes from Fe to Mn to Cr might also be explained in a qualitative way in terms of electron density at the metal centers. The oxidation potentials for the $TPPMPyr_2$ species are in the range of −0.7, −0.3, +0.1 V (vs SCE) for Cr(II), Mn(II), and Fe(II),[28] indicating that the electron deficiency at the metal increases in that order for these species. This is in keeping with the results of the porphyrin variation studies. The exo/endo ratio increases markedly from the iron to manganese to chromium porphyrins and is at least as large for Cr^{III}(TPP)Cl as the ratio obtained in the MCPBA uncatalyzed oxidation.

Both Tables I and II reveal an effect of ortho substituents, the exo/endo ratio decreasing with ortho substitution when the electronic effects do not vary much (e.g., phenyl vs mesityl substituents on the porphyrin).

The amounts of the two rearrangement products, norcamphor and cyclohexene-4-carboxaldehyde, do not correlate with the exo/endo ratios in any of these studies. The fact that small amounts of these products are found in MCPBA oxidations and that Lewis acids rearrange the *exo*-epoxide to these products[29] adds a further complexity of these results (eq 7). We have shown that this rearrangement is not catalyzed by the hemin or the oxidation intermediates by carrying out the catalytic epoxidation of cyclohexene in the presence of norbornene epoxide.[30] Neither norcamphor nor cyclohexene-4-carboxaldehyde were produced. Therefore, at least in the metalloporphyrin-catalyzed reaction, the rearrangements appear to accompany epoxidation.



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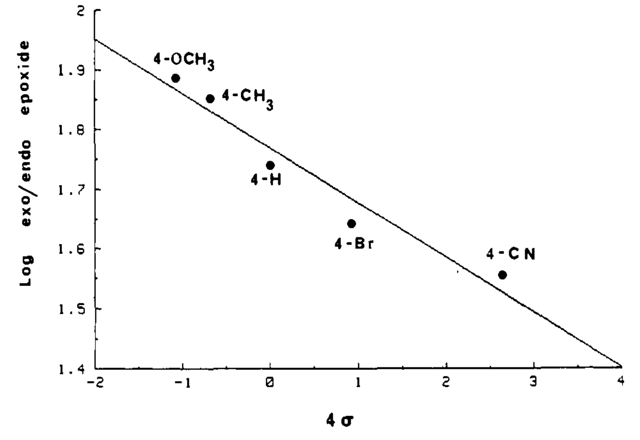


Figure 1. Plot of log (exo/endo) versus the Hammett σ_Y constants for the iron(III) porphyrin catalyzed epoxidations of norbornene. The data are from Table I.

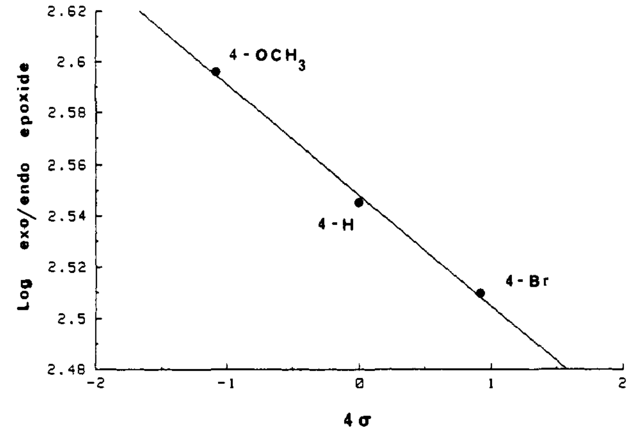
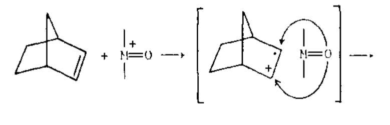


Figure 2. Plot of log (exo/endo) versus the Hammett σ_Y constants for the Mn(III) porphyrin catalyzed epoxidation of norbornene.

We have suggested that the extraordinarily low (~6–9) *exo*-epoxide/*endo*-epoxide ratios compared to those of other electrophilic or electrocyclic reactions on norbornene require a process involving fast bond formation, and we have adopted the electron-transfer mechanism[31] to accommodate these results. A correlation of epoxidation rates with ionization potential agrees with, but does not confirm, this mechanism (eq 8 and 9).[32] This mechanism could also be viewed as an early transition state for electrophilic attack in which little bond formation occurs at the transition state (eq 10 and 11).



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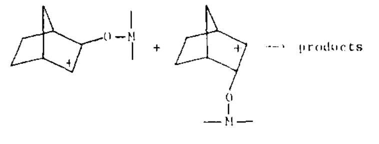

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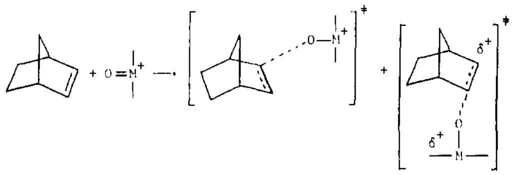

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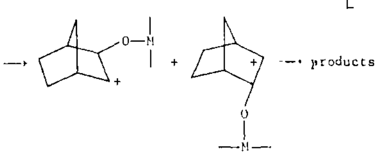

(11)

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(27) (a) We have determined the exo/endo ratios using a variety of solvents and oxidants (RIO, H_2O_2, *t*-BuOOH) and found that the exo/endo ratio shows little sensitivity to these changes.[7,27b] (b) Fann, W. P., unpublished results.

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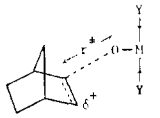
Table III. Oxidation of Adamantylideneadamantane Catalyzed by Iron, Manganese, and Chromium Tetrakis(2,6-dichlorophenyl)porphyrin Chlorides with Pentafluoroiodobenzene[a]

catalyst	yield epoxide,[b,c] %
iron	24
manganese	10
chromium	10

[a] The reaction conditions were as follows: catalyst, 1.5 mM; adamantylideneadamantane, 0.075 M; PFIB, 0.032 M, insoluble, in CH_2Cl_2. [b] Yields are based on pentafluoroiodobenzene produced. In the absence of catalyst no reaction occurs during the same time period. When cyclohexene was included, it was found to react 4 times faster than does adamantyladamantylidene. Response factors were experimentally determined. [c] Other possible products were hydroxylated adamantylideneadamantane.

As the electron density increases in going through the series electronegative porphyriniron(III), electropositive porphyriniron(III), electronegative porphyrinmanganese(III), electropositive porphyrinmanganese(III), electronegative porphyrinchromium(III), and electropositive porphyrinchromium(III), the extent of bond formation at the transition state increases (i.e., $r^‡$ decreases) and the steric differentiation between the exo and endo faces (exo/endo ~ 1000) resembles that of the uncatalyzed MCPBA epoxidation (exo/endo = 690).

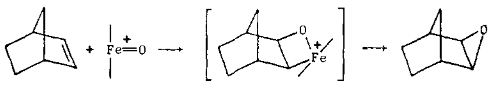


This predicts that a proximal base on the metal should increase the exo/endo ratio. However, addition of 0.1 M 1-methylimidazole to the reaction using the Fe(III) 2,6-DCPP catalyst did not change the exo/endo ratio.[27b] This effect requires further study.

Since the rearrangements occur after the C–O bond-making step, there is no reason for the extent of rearrangement to correlate with the exo/endo ratio according to this mechanism. It also follows that rearrangement does not require the electron-transfer step.

We conclude that the iron(III) electronegative porphyrin catalyzed epoxidations of norbornene are "limiting"[33] electron-transfer processes, and the chromium(III) electropositive porphyrin catalyzed epoxidations are essentially limiting electrophilic addition mechanisms. Consistent with this change in transition-state geometry is the observation (Tables I and II) that the iron porphyrins are more sensitive to electronic effects whereas the manganese porphyrins are more sensitive to steric effects.

The iron(III)-catalyzed reactions, giving low exo/endo product ratios, cannot be explained by the electrocyclic mechanism shown in eq 12. All electrocyclic reactions give very large (>1000) exo/endo ratios of products with norbornene.[7] The chromium(III) porphyrin and some of the manganese(III) porphyrin catalyzed reactions are not as clear. Large exo/endo ratios were obtained. For this reason we have investigated the epoxidation of adamantylideneadamantane with which the formation of the oxametallacycle intermediate is sterically impossible (eq 13). Table III lists the yields of epoxide with three catalysts. While a larger yield was obtained with the iron catalyst, it is clear that all three metalloporphyrins are capable of epoxidizing this alkene. The lower yields with Mn and Cr are understandable in terms of their greater tendency to hydroxylate, discussed below, as well as their requiring more productlike transition states. We therefore conclude that iron, manganese, and chromium porphyrin catalyzed epoxidations of this alkene proceed through the carbocation mechanism (eq 8) rather than the oxametallacycle pathway[8] (eq 12).



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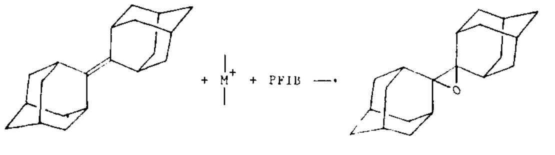

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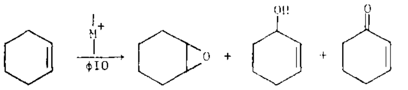
Table IV. Oxidation Products Obtained upon Oxidation of Cyclohexene with Catalysis by Iron(III), Manganese(III), and Chromium(III) Complexes of Tetrakis(2,6-dichlorophenyl)porphyrin and Tetraphenylporphyrin[a]

catalyst	yield, % epoxide	yield, % alcohol	yield, % ketone	remaining Soret, %	time min
Fe(2,6-Cl)[b]	76	2.8	0.9	100	0.8
Mn((2,6-Cl)[b]	69	7.6	6.2	80	2.5
Cr(2,6-Cl)[b]	23	27	10	100	12
Fe(TPP)[c,d]	55	15	0		
Mn(TPP)[c,e]	40	23	6		
Cr(TPP)[c,f]	4	75	21		

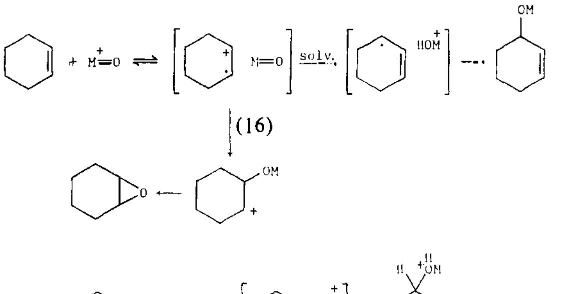
[a] All complexes were MPorphCl. [b] Conditions: catalyst, 1 mM; cyclohexene, 1 M; PFIB, 0.064 M, insoluble, in CH_2Cl_2. The yields are based upon pentafluoroiodobenzene obtained and are corrected for measured response factors. [c] Iodobenzene was the oxidant, and yields were based on iodobenzene produced. [d] Reference 2a. [e] Reference 35. [f] Reference 34.

Hydroxylation versus Epoxidation. Groves et al.[2a,34] and Fontecave and Mansuy[35] have observed that metalloporphyrin-catalyzed cyclohexene epoxidation is accompanied by large amounts of allylic hydroxylation and subsequent formation of ketone (eq 14). In order to determine the distribution of these products obtained with more electronegative metalloporphyrins, we have studied this epoxidation using the tetra-2,6-dichloroporphyrin. The results are compared with those reported for tetraphenylporphyrin in Table IV. It can be seen that the *o*-chloro substitution brings about greater selectivity toward epoxidation with all three metals while maintaining the greater selectivity of the iron porphyrin catalyst.



(14)

These results are consistent with those reported for norbornene, the more electronegative metalloporphyrins giving better selectivity toward epoxidation. There are two possible rationales for these results, a single electron-transfer mechanism in which proton loss leads to cyclohexenyl radical (eq 15) or a competition between electron-transfer epoxidation (eq 16) and hydrogen atom abstraction (eq 17). The competition between direct hydrogen abstraction and direct (ET) epoxidation (eq 16) is more likely to show the dependence upon electron density at the metal than is the single mechanism. The radical abstraction is also more



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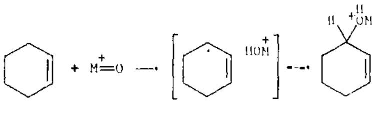

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[33] For a discussion of the "limiting" concept and references, see: *Mechanism and Theory in Organic Chemistry*, 3rd ed.; Lowry, T. H., Richardson, K. S., Eds.; Harper and Row Publishing Co.: New York, p 328.

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consistent with the deuterium scrambling and isotope effects reported by Groves et al.[36] Although this matter is not completely settled, our results are in agreement with the mechanism proposed by Groves[37] for cyclohexene oxidation.

Synthetic Applications. We have not discussed here the use of pyrrole-halogenated metalloporphyrins such as octabromooctachlorohemin.[26] Being more electronegative than any of those discussed here, these types of metalloporphyrins further extend the selectivity for epoxidation, show mechanisms that are more ET limiting, and are more resistant to destruction than any of those discussed here. We can therefore select metalloporphyrin catalysts to obtain desired products. For example, to epoxidize cyclohexene and similar alkenes, we would use the most electronegative iron(III) porphyrin available (Table I). To obtain cyclohexen-3-ol, we would use the most electropositive chromium porphyrin and carry the reaction to low conversion. At high conversion under these conditions almost pure cyclohexen-3-one would be obtained.

To obtain pure *exo*-norbornene epoxide, the (TPP)Cr(III) catalyzed reaction (exo/endo > 1000) is preferable even to MCPBA epoxidation (exo/endo = 690). On the other hand, we can obtain 20% *endo*-epoxide with the most electronegative iron porphyrins or electronegative *N*-alkyliron porphyrins. Although a separation is required, this one-step, high overall yield process is the easiest route to this epoxide.

As we have previously indicated,[32] the electronegative iron porphyrins also provide high selectivity for dienes over monoenes and for *cis*-alkenes over *trans*-alkenes. We also see little loss of stereospecificity with electronegative iron porphyrins whereas other iron porphyrins and manganese porphyrin catalyzed epoxidations give some loss of stereospecificity.

A comparison of kinetic properties of these metalloporphyrins that further delineates their differences will be reported elsewhere.

Acknowledgment. We are grateful to Professor R. S. Brown for a gift of adamantylideneadamantane and to the National Science Foundation (Grant CHE 87-21364) for financial support.

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Intramolecular Energy Transfer in a Chromophore–Quencher Complex

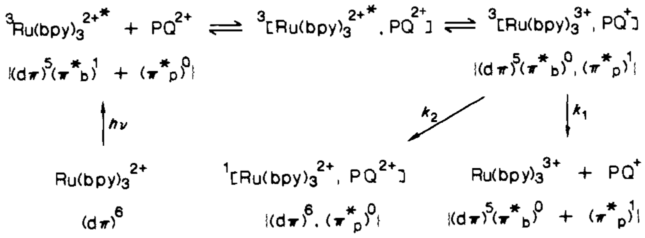
Stephen Boyde, Geoffroy F. Strouse, Wayne E. Jones, Jr., and Thomas J. Meyer*

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. *Received December 27, 1988*

Abstract: Metal-to-ligand charge-transfer excitation of the complex $[Ru(bpyCH_2OCH_2An)_3]^{2+}$ ($bpyCH_2OCH_2An$ is 4-[(9-anthrylmethoxy)methyl]-4'-methyl-2,2'-bipyridine is followed by rapid (<5 ns), efficient intramolecular energy transfer to one of the chemically attached anthryl groups, to give the anthryl triplet, $-^3An$. It has a lifetime of 6 μs in CH_3CN at 295 K. Oxidative quenching of $[(bpyCH_2OCH_2An)_2Ru^{II}(bpyCH_2OCH_2{}^3An)]^{2+*}$ by PQ^{2+} (PQ^{2+} is paraquat) occurs initially at $-^3An$ with $k(295\ K, CH_3CN) = 2.2 \times 10^9\ M^{-1}\ s^{-1}$. The oxidative quenching step is followed by rapid intramolecular electron transfer to give $[(bpyCH_2OCH_2An)_2Ru^{III}(bpyCH_2OCH_2An)]^{3+}$.

Photoconversion processes based on the electron-transfer quenching of molecular excited states are well established.[1-5] In this area a considerable effort has been expended in the search for molecules that have suitable excited-state lifetime and electron-transfer properties. Among the most versatile examples are polypyridyl complexes such as $[Ru(bpy)_3]^{2+}$ (bpy is 2,2'-bipyridine) where the ground-state electronic configuration is $(d\pi)^6$ and the relevant excited states are metal-to-ligand charge transfer (MLCT) in character.[5-10] An example of a photoconversion sequence based on the oxidative quenching of $[Ru(bpy)_3]^{2+*}$ by PQ^{2+} (PQ^{2+} is 1,1'-dimethyl-4,4'-bipyridinium dication) is shown in Scheme I.[1b]

Scheme I



In the electronic configurations shown in Scheme I, π^*_b and π^*_p are the lowest lying π^* levels of bpy and PQ^{2+}. The dominant

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