structures of products **1-4** are based on the ^1H NMR peaks of 12-H/14-H and observations of NOEs (ca. 40%) between CHO/cisoid CH_2 in **1** and **3** and between CHO/12-H in **2** and **4**.

Bovine opsin was incubated as a suspension with a 5-fold excess of pure chromophores **1-4** at pH 7.0 (67 mM phosphate buffer, 25 °C, 20 h in the dark), the suspension was centrifuged, and the pellets were washed five times with hexane at -20 °C to remove excess and decomposed chromophore, and then were solubilized in 2% digitonin.[19,20] As shown in Table I, *all four chromophores yield pigments*. Furthermore, as expected, since the 11-ene is cis locked, the absorption spectra or the orange color of pigment solution did not change when irradiated for 8 h with a 100-W tungsten lamp [>500 nm (filter cutoff)] at 4 °C; namely, *the four pigments are not bleached when exposed to light of wavelengths corresponding to their absorption maxima.*

When the CH_2Cl_2 denaturation-extraction procedure[21] was applied to the 11-*cis*-**1**-derived pigment, in the dark, and also after irradiation with a 100-W tungsten lamp (2 h, 4 °C), the high-pressure LC traces of extracted chromophores were similar; they consisted of 88% of isomer **1** and 12% of a mixture of other isomers. This experiment again shows the nonbleachable nature of the pigment.[22]

The following experiments provide support that the chromophores occupy the same opsin binding site as with natural 11-*cis*-retinal. The hexane-washed pigments were reincubated for a further period with 11-*cis*-retinal, which should bind to the unoccupied binding sites to give rhodopsin, λ_{max} 500 nm. Because of the overlap of the λ_{max} of natural and unnatural rhodopsins, the additional binding was checked by measuring the increase in the 480-500-nm absorption upon reincubation, and subsequent decrease when the pigment was irradiated (only natural rhodopsin is bleached). After 3 h, i.e., when reincubation was complete, the absorbance values showed that reincubation of **1**-, **2**-, **3**-, and **4**-derived pigments produced only 8, 10, 3, and 30%[23] of additional natural rhodopsin.

It is remarkable that in addition to the 11-cis analogue **1**, the 11,13-*dicis*-**2**, 9,11-*dicis*-**3**, and 9,11,13-*tricis*-**4** compounds with 7-membered rings and multiple cis bonds[24] all afford visual pigment analogues. This suggests that the side-chain binding site is rather nondiscriminating as was the case with the ring binding site.[25] The close similarity in the CD curves (Table I) of the four pigments with that of natural rhodopsin, 340 nm (+12.6)/490 nm (+11.7) (in 2% digitonin),[26] should be noted. Since the heptatrienylidene chromophore is constrained into a nonplanar shape, it is likely that a chirally twisted chromophore plays an important role in the CD. Comparisons with the CD spectra of other artificial rhodopsins should clarify the origin of the extrema of natural pigments.[27]

The current studies show that *retinals with fixed 11-cis geometry block the bleaching of visual pigments*; namely, *an 11-cis to 11-trans isomerization is a prerequisite for visual transduction.*

Acknowledgment. We thank the National Institutes of Health (Grant EY 01253) and Hoffmann-La Roche Inc. for financial support. We acknowledge the assistance of John D. Carriker.

(19) Bridges, C. D. B. *Vision Res.* **1977**, *17*, 301.

(20) All four pigments were unstable in Triton X-100 at room temperature in the dark. In 2% digitonin (pH 7.0, 6.7 mM phosphate buffer), only a 10% decrease in λ_{max} intensities was seen when left for 66 h (4 °C) in the dark; in the form of suspension or pellets, the pigments were stable in the dark at 4 °C for at least 3 days. The pigments, however, are not stable to 0.1 M NH_2OH; e.g., with the pigment derived from **1**, half of it was bleached after 30 min, and all had bleached after 24 h in the dark.

(21) (a) Crouch, R.; Purvin, V.; Nakanishi, K.; Ebrey, T. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 1538. (b) Pilkiewicz, F. G.; Pettei, M. J.; Yudd, A. P.; Nakanishi, K. *Exp. Eye Res.* **1979**, *24*, 421.

(22) Bathorhodopsin, the crucial intermediate leading to visual transduction, was not formed from the pigment derived from "11-*cis*"-**1**, as shown by both continuous irradiation at 77 K and flash experiments at 10 °C: Mao, B.; Tsuda, M.; Ebrey, T. G.; Akita, H.; Balogh-Nair, V.; Nakanishi, K., submitted elsewhere for publication.

(23) The binding conditions may not have been optimum for the 9,11,13-tricis chromophore **4**.

(24) Other rhodopsins containing multiple cis bonds in the chromophore are the following. 9,13-Dicis, ref 21. (a) 7,11-Dicis: Kini, A.; Matsumoto, H.; Liu, R. S. H. *J. Am. Chem. Soc.* **1979**, *101*, 5078. 7-Cis, 7,9-dicis, 7,11-dicis, 7,13-dicis, and 7,9,13-tricis: DeGrip, W. J.; Liu, R. S. H.; Ramamurthy, V.; Asato, A. *Nature (London)* **1976**, *262*, 416. Matsumoto, H.; Yoshizawa, T. *Vision Res.* **1978**, *18*, 607.

(25) Nakanishi, K.; Yudd, A. P.; Crouch, R. K.; Olson, G.; Cheung, H.-C.; Govindjee, R.; Ebrey, T. G.; Patel, D. J. *J. Am. Chem. Soc.* **1975**, *98*, 236. Blatchly, R. A.; Carriker, J. D.; Balogh-Nair, V.; Nakanishi, K. *Ibid.* **1980**, *102*, 2495.

(26) Waddell, W. H.; Yudd, A. P.; Nakanishi, K. *J. Am. Chem. Soc.* **1976**, *98*, 238.

(27) Two mechanisms have been proposed. (a) Twisted chromophore: Sperling, W.; Rafferty, C. N. *Nature (London)* **1969**, *224*, 591. Burke, M. J.; Pratt, D. C.; Faulkner, R. R.; Moscowitz, A. *Exp. Eye Res.* **1973**, *17*, 557. Ebrey, T. G.; Yoshizawa, T. *Ibid.* **1973**, *17*, 545. (b) Dipole-dipole interaction: Johnston, E. M.; Zand, R. *Biochem. Biophys. Res. Commun.* **1972**, *47*, 712. Kropf, A.; Whittenberger, P.; Goff, S. P.; Waggoner, A. S. *Exp. Eye Res.* **1973**, *17*, 591. Waggoner, A. S.; Stryer, L. *Biochemistry* **1971**, *10*, 3250.

(28) Fellow in Cancer Research supported by Grant DRG-162F of the Damon Runyon-Walter Winchell Cancer Fund.

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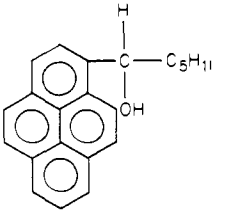
Enhanced Optical Activity Associated with Chiral 1-(1-Hydroxyhexyl)pyrene Excimer Formation

Sir:

Chiroptical techniques are powerful methods for the study of optically active molecules. The relatively new technique of circularly polarized luminescence (CPL) spectroscopy has proved to be exceedingly useful in the study of molecular excited states.[1,2] Although the photophysical processes for excimer formation have been elucidated for some time,[3] investigation of the stereochemistry of optically active excimers has only been initiated recently. Thus, appreciable differences have been found in the kinetic and thermodynamic parameters of excimer formation between the enantiomerically pure *N*-[4-(1-pyrene)butanoyl]-D-tryptophan methyl ester, pyr-D-Trp, and its racemate, *N*-[4-(1-pyrene)butanoyl]-DL-tryptophan methyl ester, pyr-DL-Trp, in methanol and those for pyr-D-Trp between (*R*)-(-)-2-octanol and (*S*)-(+)-2-octanol.[4] In the present work, CPL spectra of (+)-**1**-(1-hydroxyhexyl)pyrene, (+)-**1**, and its enantiomer, (-)-1-(1-hydroxyhexyl)pyrene, (-)-**1**, have been determined in methanol



1(+) or **1**(-)

at different concentrations. Dramatically enhanced optical activities associated with the excimer formation of (+)-**1** and (-)-**1** have been observed (eq 1 and 2).

$$(+)\text{-}\mathbf{1} \xrightarrow{h\nu} (+)\text{-}\mathbf{1}^* + (+)\text{-}\mathbf{1} \rightleftharpoons (+)\text{-}\mathbf{1}^*(+)\text{-}\mathbf{1} \quad (1)$$

$$(-)\text{-}\mathbf{1} \xrightarrow{h\nu} (-)\text{-}\mathbf{1}^* + (-)\text{-}\mathbf{1} \rightleftharpoons (-)\text{-}\mathbf{1}^*(-)\text{-}\mathbf{1} \quad (2)$$

(1) Richardson, F. S.; Riehl, J. P. *Chem. Rev.* **1977**, *77*, 773.

(2) Steinberg, I. In "Biochemical Fluorescence: Concepts"; Chen, R. F.; Edelhoch, H., Ed.; Marcel Dekker: New York, 1975; Vol. 1.

(3) Birks, J. B. "Photophysics of Aromatic Molecules", Interscience: New York, 1973. Birks, J. B., Ed. "Organic Molecular Photophysics"; Interscience: New York, 1973. Birks, J. B. *Rep. Prog. Phys.* **1973**, *38*, 903.

(4) Tran, C. D.; Fendler, J. H. *J. Am. Chem. Soc.* **1980**, *102*, 2923.

0002-7863/80/1502-6372$01.00/0

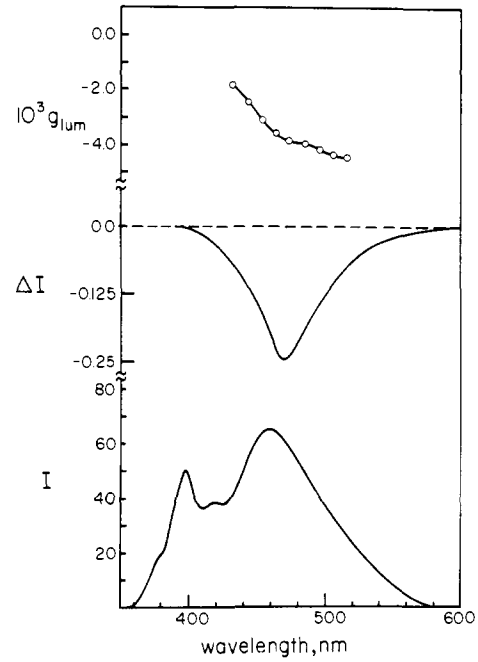


Figure 1. Total luminescence (bottom), circularly polarized luminescence (middle), and wavelength dependence of g_{lum} (top) for a 3.65×10^{-3} M solution of (+)-1-(1-hydroxyhexyl)pyrene, (+)-**1**, in methanol. Both I and ΔI are expressed in arbitrary units, and all data were recorded at 25 °C in degassed solutions. The CPL spectra of the (−) isomer, (−)-**1**, is the mirror image of the CPL spectra of the (+) isomer at identical concentrations.

1-(1-Hydroxyhexyl)pyrene was prepared from 1-pyrenecarboxyaldehyde by the Grignard reaction by using $C_5H_{11}MgBr$ in THF/benzene. The recrystallized product was reacted with phthalic anhydride to yield the acid phthalate of 1-(1-hydroxyhexyl)pyrene.[5] Resolution of this compound was carried out via the brucine salt. (+)-**1** and (−)-**1** were obtained by $LiAlH_4$ reduction of the enantiomeric acid phthalates.[6]

Increasing the concentrations of (+)-**1** or (−)-**1**[7] in methanol resulted in the appearance of excimers, (+)-**1***(+)-**1** or (−)-**1***-(−)-**1**, characterized by blue structureless emission bands centered at 460 nm (Figure 1). The bands were found to be partially circularly polarized.[7] Significantly, the magnitude of the CPL is appreciably larger than that commonly observed for aromatic molecules.[1] The CPL experiment measures two observables; the total luminescence intensity, I, and the circularly polarized luminescence, ΔI. Since these quantities are measured in arbitrary units, one commonly calculates their ratio, the luminescence dissymmetry factor,[1] g_{lum} (eq 3). I_L and I_R refer to the emitted

$$g_{lum} = \frac{2(\Delta I)}{I} = \frac{I_L - I_R}{\frac{1}{2}(I_L + I_R)} \quad (3)$$

intensities of left- and right-circularly polarized light, respectively. The value of g_{lum} was found to vary markedly with the initial concentration of **1**. Concentration dependence of g_{lum} is shown in Figure 2. No CPL was observed at concentrations of **1** less than 10^{-4} M. The g_{lum} factor due to the singlet excited state of (+)-**1** or (−)-**1** must therefore be less than 10^{-5}. The data in Figure 2 clearly show how the CPL effect is proportional to the extent of excimer formation. Decreasing the stoichiometric concentration of (+)-**1** or (−)-**1** "titrates out" the CPL. Degassing the solutions of (+)-**1** or (−)-**1** resulted in an approximate 4-fold increase in total luminescence relative to oxygen-saturated solutions, and to an increased concentration of excimer (as evidenced by an increase in excimer emission). The CPL intensity increased by an approximate 4-fold amount also, with the g_{lum} of a degassed solution being approximately 1.15 times that of an air-saturated solution. All band maxima remained unchanged.

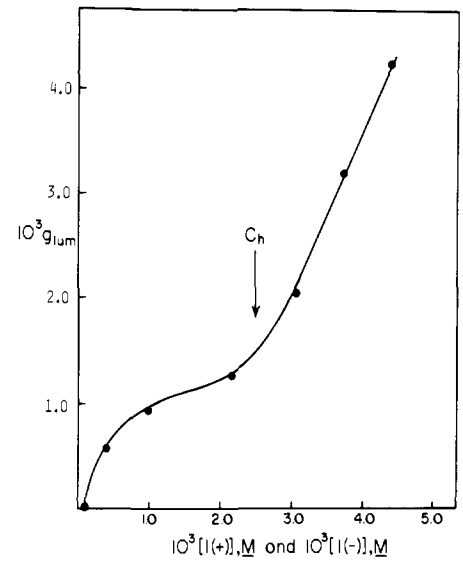


Figure 2. Dependence of g_{lum} on the molar concentration of (+)-**1** (●) at 470 nm. The absolute values associated with each g_{lum} factor have been plotted. The arrow indicates C_h, the concentration at which equal amounts of monomers, (+)-**1***, and excimers, (+)-**1***(+)-**1**, coexist.

At sufficiently high concentrations of (+)-**1** or (−)-**1**, values of g_{lum}, and hence the degrees of optical activities, increase as the wavelength increases.[8] Variation in g_{lum} can arise from[9] (a) different intensity mechanisms between total luminescence and CPL processes, (b) the presence of more than one emitting species which have different chiroptical properties, and (c) emission of two different excited states which have different chiroptical properties and whose emission bands overlap. While we have no evidence at the present time to favor one origin over another, case (b) probably represents the most plausible explanation for the observed trend in g_{lum}.

It is well established that when monomeric aromatic systems are attached to a single chiral center, the g_{lum} value associated with the emission is equal to zero.[1] However, numerous investigations have demonstrated that CPL can be detected in tryptophan- and tyrosine-containing proteins and that this optical activity is due solely to the helical coiling of the protein chain[2] (configurational effect). In the present study, we have shown that monomeric excited states (+)-**1*** and (−)-**1*** do not exhibit measurable chirality, inspite of an observable ground state CD.[10]

(5) Magnesium metal (3.4 g, 0.14 mol) in 100 mL of dry THF was stirred with a solution of 1-bromopentane (25.3 g, 0.168 mol) in 50 mL of dry THF for 30 min. 1-Pyrenecarboxyaldehyde (25.0 g, 0.108 mol) in 150 mL of dry THF was added dropwise, refluxed for 15 min, allowed to stand for 3 h at 25 °C, and added to 500 mL of cold saturated NH_4Cl. The product was extracted with 500 mL of ether. Recrystallization (hexene) yielded 13 g (40%) of racemic **1**. A solution of **1** (12.4 g, 0.0410 mol) and phthalic anhydride (6.00 g, 0.041 mol) in 90 mL of dry pyridine was heated at 90 °C for 12 h and added to 250 g of crushed ice and 125 mL of concentrated HCl. After the ice had melted, the mixture was extracted with ether (3 × 100 mL). The combined ether extracts were washed with water and extracted by 3% $NaHCO_3$ (3 × 200 mL). The organic phase was dried, and the ether was removed to yield 12.0 g (64.9%) of the acid phthalate of **1**, **2**.

(6) **2** was resolved by brucine. The resolved (+) and (−) brucine salts of **2**, (+)-**3** and (−)-**3**, were reduced with $LiAlH_4$. Typically, $LiAlH_4$ (0.057 g, 1.5 mmol) in ethyl ether was stirred with (+)-**3** or (−)-**3** (0.371 g, 0.822 mmol) in ethyl ether for 6 h at room temperature. Addition of water (15 mL, dropwise) hydrolyzed the $LiAlH_4$, and (+)-**1** or (−)-**1** was recovered from the ether (yield 0.204 g, 82%). (+)-**1** and (−)-**1** were characterized by their absorption, IR, and ^1H NMR spectra. Optical rotations of (+)-**1** are the following: $[\alpha]^{25}_D$ +96.7° (*c* 0.0092, MeOH); $[\alpha]^{25}_{578}$ +96.7° (*c* 0.0092, MeOH); $[\alpha]^{25}_{546}$ +112° (*c* 0.0092, MeOH); $[\alpha]^{25}_{436}$ +237° (*c* 0.0092, MeOH). (−)-**1**: $[\alpha]^{25}_D$ −83° (*c* 0.0092, MeOH); $[\alpha]^{25}_{578}$ −85.9° (*c* 0.0092, MeOH); $[\alpha]^{25}_{546}$ −100° (*c* 0.0092, MeOH); $[\alpha]^{25}_{436}$ −209° (*c* 0.0092, MeOH).

(7) Total emission intensities and CPL spectra were measured simultaneously on apparatus described previously: Brittain, H. G. *J. Am. Chem. Soc.* **1980**, *102* 3693.

(8) These values were computed at wavelength regions where monomer emission is insignificant.

(9) Brittain, H. G.; Richardson, F. S. *J. Phys. Chem.* **1976**, *80*, 2590.

Conversely, excimers (+)-**1***(+)-**1** and (−)-**1***(−)-**1** are highly chiral. The large magnitude of the CPL that we have found for the chiral excimers implies that the optical activity is also configurational in nature. We believe that these observations indicate that the excimers have a definite preferred orientation of pyrene rings.

In a previous study, solvent-induced CPL was observed on dissolving an achiral fluorescein dye in (*R*)-α-phenethylamine in spite of the lack of detectable CD.[9] Attention has been focused on enhanced optical activities associated with excimer formation in the present work. These investigations indicate the power of the CPL technique and open the door to stereoselective photosynthesis via suitable chiral sensitizers.

Acknowledgment. Support of this work by the Research Corporation (H.B.) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society (J.H.F.), is gratefully acknowledged.

(10) Absorbance dissymmetry factors, g_{abs}[11] values, of 2.8×10^{-5} and 3.5×10^{-5} have been calculated from the CD spectra of (−)-**1** [or (+)-**1**] at 340 and 325 nm, respectively.

(11) $g_{abs} = \Delta\epsilon/\epsilon$; where $\Delta\epsilon = \theta/32.92Cz$,[12] θ = the ellipticity in degrees, determined in the CD experiments with a Jasco J-20 spectrometer, C = the molar concentration of (+)-**1** or (−)-**1**, and z = the path length of the cell in cm.

(12) Charney, E. "The Molecular Bases of Optical Activity, Optical Rotatory Dispersion and Circular Dichroism"; Wiley: New York, 1979; p 352.

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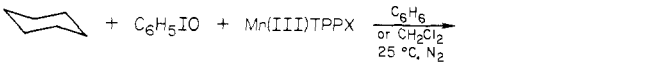
Alkane Activation and Functionalization under Mild Conditions by a Homogeneous Manganese(III) Porphyrin–Iodosylbenzene Oxidizing System

Sir:

Two areas of intense current research interest, the activation of alkanes[1,2] and the role of metalloporphyrins in biological oxidation processes, provided the impetus for our work described below. Although there has been considerable effort recently devoted to the development of alkane activation and functionalization reactions and to the development of catalysts for these processes, there are still very few alkane reactions that are preparatively or industrially useful.[2] The lack of progress in this area is primarily a consequence of the facts that alkane C–C and C–H bonds are very inert and the few species that do attack these bonds do so with little selectivity. In contrast, Nature has evolved monooxygenase enzymatic systems such as cytochrome P-450 that are capable of catalyzing alkane hydroxylation with great selectivity.[3] Many studies have implicated that high-valent oxometalloporphyrin species are key oxidizing intermediates in the catalytic cycles of several heme-containing oxygenase enzymes.[4,5] Very recently model studies have demonstrated both biomimetic oxidation of alkenes and alkanes by oxoiodine(III) derivatives catalyzed by synthetic iron(III) porphyrin species[6,7] and epoxidation of olefins by an isolated and fairly well characterized (oxoporphinato)chromium(V) complex.[8] We have discovered and investigated a class of manganese(III) porphyrin catalyzed alkane functionalization reactions. In this communication, we report the stoichiometric replacement of unactivated alkane C–H bonds with C–Cl, C–Br, C–I, and C–N bonds at room temperature and the isolation of a high-valent manganese porphyrin species that displays alkane C–H bond cleavage reactivity.

The reaction of (tetraphenylporphinato)manganese(III) derivatives, Mn(III)TPPX,[9] X = Cl^-, Br^-, I^-, N_3^-, with iodosylbenzene and cyclohexane in rigorously purified benzene or chlorocarbon solvents under a nitrogen atmosphere produced high yields of cyclohexyl–X compounds on the basis of Mn(III)TPPX, in addition to alcohol, ketone, and products derived from attack on the solvent (eq 1, Table I).



X = Cl^-, Br^-, I^-, and N_3^-

The yields of the cyclohexyl halides or cyclohexyl azide based on MnTPPX were 96–99% when ≥5 equiv of iodosylbenzene per equiv of MnTPPX were used. The production of alcohol from iodosylbenzene was catalytic in manganese porphyrin if a sufficient molar excess of iodosylbenzene over MnTPPX was used. The reaction of MnTPPCl with iodosylbenzene in cyclohexane–benzene gave the same product distribution when run under intense illumination by laboratory lights or in absolute darkness, implicating that the functionalization reactions were neither photocatalytic nor photochemical processes. For the reactions in Table I, the equivalents of oxidant unlike the equivalents of halide or azide ion were not quantitatively accounted for by all the observed products. Several control experiments established that the ca. 50% of the reactant iodosylbenzene oxidant unaccounted for was utilized to oxidize either the porphyrin ligand or the solvent. Benzene solvent was oxidized in large part at first to phenol, which was subsequently oxidized at a much greater rate to as yet unidentified higher oxidation products. The iodination reaction is of interest in that production of alkyl iodides by the reaction of molecular iodine with alkanes is unfavorable thermodynamically. The production of cyclohexyl azide is the first example of the direct replacement of an unactivated alkane C–H bond by a C–N bond in a thermal process at room temperature in an appreciable yield.

Several lines of evidence implicate the intermediacy of alkyl radicals in these reactions. First, the reactions all produced low but definite yields of dicyclohexyl.[10] Second, the chlorination reaction produced a reasonable yield of cyclohexylbenzene when run in benzene as solvent. Third, the bromination reactions when run in dichloromethane gave cyclohexyl chloride, and the chlorination reactions run in this solvent gave >100% yield of this

(1) Reviews on alkane activation: (a) Parshall, G. W. *Acc. Chem. Res.* **1975**, *8*, 113. (b) Shilov, A. E.; Shteinman, A. A. *Coord. Chem. Rev.* **1977**, *24*, 97. (c) Webster, D. E. *Adv. Organomet. Chem.* **1977**, *15*, 147. (d) Shilov, A. E. *Pure Appl. Chem.* **1978**, *50*, 725.

(2) Discussion of preparatively or industrially useful alkane C–H cleavage reactions: (a) Carruthers, W. "Some Modern Methods of Organic Synthesis", Cambridge University Press: Cambridge, Great Britain, 1971; Chapter 4. (b) Hucknall, D. J. "Selective Oxidation of Hydrocarbons", Academic Press, London, 1974; Chapters 4 and 5. (c) McMahon, K. S. In "Encyclopedia of Chemical Processing and Design"; McKetta, J. J.; Cunningham, W. A., Eds.; Marcel Dekker: New York, 1976; Vol. 1, pp 216–240. (d) Luedeke, V. D. *Ibid.* 1977; Vol. 2, pp 128–146, and references cited in each.

(3) (a) Gunsalus, I. C.; Meeks, J. R.; Lipscomb, J. D.; Debrunner, P.; Münck, E. In "Molecular Mechanisms of Oxygen Activation"; Hayaishi, O., Ed., Academic Press: New York, 1974; Chapter 14. (b) Orrenius, S.; Ernster, L. *Ibid.* 1974, Chapter 6.

(4) Yamazaki, I. In "Molecular Mechanisms of Oxygen Activation", Hayaishi, O., Ed.; Academic Press: New York, 1974; Chapter 13.

(5) Groves, J. T. *Adv. Inorg. Biochem.* **1979**, *1*, 119.

(6) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032.

(7) Chang, C. K.; Kuo, M.-S. *J. Am. Chem. Soc.* **1979**, *101*, 3413.

(8) Groves, J. T.; Kruper, W. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7613.

(9) Mn(III)TPP(OAc) was prepared by the method of Adler et al.; cf.: Adler, A. D.; Longo, F. R.; Kampas, F.; Kim, J. *J. Inorg. Nucl. Chem.* **1970**, *32*, 2443. Mn(III)TPPX, X = Cl^-, Br^-, I^-, N_3^-, was made by ligand exchange with Mn(III)TPP(OAc) by the procedure used by Ogoshi et al. on the corresponding iron complexes; cf.: Ogoshi, H.; Watanabe, E.; Yoshida, Z.; Kincaid, J.; Nakamoto, K. *J. Am. Chem. Soc.* **1973**, *95*, 2845.

(10) Although efforts were made to detect cyclohexene resulting from disproportionation of cyclohexyl radicals, separation of cyclohexene from solvent cyclohexane proved very difficult by GC. Furthermore, control experiments established that alkenes were more reactive than alkanes in the Mn(III)TPP–iodosylbenzene oxidizing system.

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