3-Methoxy-6-pyrrolidino-1,2,4,5-tetrazine (19): red crystals from diethyl ether and petroleum ether, mp 74–75 °C; ^{1}H NMR (Me_2SO-d_6, 360 MHz) δ 2.01 (m, 4 H, CH_2), 3.57 (m, 4 H, NCH_2), 4.05 (s, 3 H, OCH_3). Anal. Calcd for $C_7H_{11}N_5O$: C, 46.40; H, 6.12; N, 38.65. Found: C, 46.48; H, 6.25; N, 38.91.

3-(Methylamino)-6-(methylthio)-1,2,4,5-tetrazine (20): red crystals from methanol, mp 85–86 °C; ^{1}H NMR (Me_2SO-d_6, 360 MHz) δ 2.61 (s, 3 H, SCH_3), 2.98 (d, ^3J = 5 Hz, 3 H, NCH_3), 8.30 (br s, 1 H, NH). Anal. Calcd for $C_4H_7N_5S$: C, 30.56; H, 4.49; N, 44.55. Found: C, 30.76; H, 4.55; N, 44.85.

3-(Methylthio)-6-pyrrolidino-1,2,4,5-tetrazine (22): red crystals from diethyl ether and petroleum ether, mp 79–80 °C; ^{1}H NMR (Me_2SO-d_6, 360 MHz) δ 2.01 (m, 4 H, CH_2), 2.62 (s, 3 H, SCH_3), 3.59 (m, 4 H, NCH_2). Anal. Calcd for $C_7H_{11}N_5S$: C, 42.62; H, 5.62; N, 35.50. Found: C, 42.61; H, 5.52; N, 35.23.

PE Spectra. The $He^{I\alpha}$ PE spectra were measured on a PS 18 instrument (Perkin-Elmer) and calibrated with reference to the 15.75-eV argon line.

Cyclic Voltammograms. Cyclic voltammetric studies were carried out on deoxygenated acetonitrile[38] solutions containing the *s*-tetrazine sample (0.4–0.8 mM) and tetraethylammonium tetrafluoroborate (0.1 M)[4] at 298 °C. The cyclic voltammograms of these solutions were obtained by using a Bruker Universal Modular Polarograph E 310 attached to an electrochemical cell equipped with a glassy carbon electrode as working electrode, a standard Ag/Ag^+ reference electrode, and a platinum counter electrode and were scanned at a current of 0.1–0.5 mA and a sweep rate of about 100 mV s^{-1}. $E_{1/2}$ values are corrected relative to ferrocene, $E_{1/2}$ = 0.0906 V.

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(38) Purified according to Kiesele H. *Anal. Chem.* **1980**, *52*, 2230.

Catalytic Homogeneous Functionalization of Adamantane. Influence of Electronic and Structural Features of the Metalloporphyrin Catalyst on Atom Transfer Selectivity (Oxygenation versus Azidification/Halogenation)

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Upon treatment of the two-phase systems, Mn tetraarylporphyrin, and alkane (organic phase)/Na^+X^- (aqueous phase), with iodosylarenes, both alcohols and alkyl azides (or halides), X^- = halide or azide, are formed from the alkane substrates. The Mn porphyrin functions as a catalyst for alkane oxygenation and a phase transfer catalyst for X^-. Catalytic functionalization of the exemplary caged alkane, adamantane, by a variety of these two-phase systems as function of the reaction conditions has been examined. The results reported here allow, for the first time, an assessment of the relationship between the electronic and structural features of the metalloporphyrin catalysts and their selectivity with respect to the replacement of unactivated alkane carbon–hydrogen bonds with oxygen versus non-oxygen (halide or azide) functional groups. Of the first-row transition metal metalloporphyrins, only those of manganese are active for both the cleavage of unactivated alkane C–H bonds and replacement of these bonds by halogen or nitrogen-based groups. The oxygen donors that give the highest yields of these non-oxygenated products are the iodosylarenes. Examination of adamantane functionalization by iodosylarenes catalyzed by eight different manganese tetraphenylporphyrin derivatives, whose porphyrin ligands vary widely in electron-donating ability, establishes that the relative tertiary–secondary C–H cleavage selectivities are minimally affected by such electronic effects. In contrast, the selectivity for incorporation of the non-oxygen versus oxygen functions is substantially affected by the electron-donating ability of the catalyst porphyrin rings. The more electron withdrawing the porphyrin ring, and consequently the more anodic the potential of the ligated, S = 2, manganese(III) ion, the lower the selectivity for incorporation of the non-oxygen functions. Functionalization of adamantane catalyzed by the most electron poor manganese porphyrin complex, $Mn^{III}(F_{20}TPP)X$, is effectively selective for oxygenation. All the metalloporphyrins examined here eventually succumb to deactivation by irreversible oxidative degradation of the organic porphyrin ligand.

Introduction

A number of studies addressing the homogeneous catalytic oxygenation and functionalization of hydrocarbons by metalloporphyrins have been published in recent years. These studies have been stimulated both by attempts to delineate the complex mechanism(s) of hydrocarbon oxidation by cytochrome P-450 and to develop new and practical methods for the selective catalytic oxygenation of organic substrates.[1-4] The catalytic incorporation of oxygen functions, eq 1, and the stoichiometric incorporation of halogen and nitrogen functions, eq 2 into alkanes

$$RH + DO \xrightarrow{Mn^{III}(Por)X} ROH + D \quad (1)$$

$$RH + DO + Mn^{III}(Por)X \rightarrow RX + D + Mn^{III}(Por)OH \quad (2)$$

RH = alkane; X^- = Br^-, Cl^-, N_3^-, NO_2^-, etc.;
DO= oxygen donor (e.g. iodosylarene)

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Table I. Hydroxylation/Chlorination of Adamantane in Benzene by Transition Metal Tetraphenylporphyrin Complexes as a Function of the Metal[a]

catalyst	oxygen donor[b]	product yields,[c,d] %					total yield,[d,e] %	tertiary/secondary[d,f]	% X[d,g]	R-X/R-O[d,h]
		1-OH	2-OH	2(O)	1-Cl	2-Cl				
Mn(TPP)Cl	PhIO	12.9	0.2	4.6	3.3	2.7	23.7	6.5	25	0.3
	PFIB	12.6	1.9	1.9	3.4	2.9	22.7	7.2	28	0.4
Fe(TPP)Cl	PhIO	17.7	2.9	0.8	0	0	21.4	14.4	0	0
	PFIB	10.9	1.1	0.5	1.5	0	14.0	23.3	11	0.1
Co(TPP)Cl	PhIO	1.7	0.5	0.5	0	0	2.7	5.1	0	0
	PFIB	2.1	0.5	0.4	2.6	0.4	6.0	10.8	50	1.0
Cr(TPP)Cl	PhIO	2.2	0.5	3.1	1.1	0.2	7.1	2.6	18	0.2
	PFIB	1.5	0.4	1.3	2.9	1.4	7.5	4.3	57	1.3

[a] Reaction conditions given in the Experimental Section; mole ratios of substrate:oxygen donor:metalloporphyrin catalyst = 40:10:1. [b] PhIO = iodosylbenzene; PFIB = pentafluoroiodosylbenzene. [c] 1-OH and 1-Cl are the 1-adamantyl alcohol and chloride respectively; 2-OH and 2-Cl are the 2-adamantyl alcohol and chloride respectively; 2(O) is 2-adamantanone. Yields based on the oxygen donor. [d] The second $2e^-$ equivalent required in the conversion of alkane to ketone has specifically not been taken into account in these calculations. [e] Moles of all oxidation products/moles of oxygen donor. [f] Ratio of tertiary to secondary C–H cleavage products statistically corrected (values given are per C–H). Both R–O and R–Cl products (tertiary or secondary) are taken together in these calculations. [g] Percentage incorporation of Cl = [(moles 1-Cl + 2-Cl)/total moles of all products] × 100. [h] (Moles 1-Cl + 2-Cl)/[moles 1-OH + 2OH + 2(O)].

facilitated by metalloporphyrins was achieved some time ago.[1,2] The term "non-oxygen functions" used in this paper refers to the halide and azide functional groups only. Of the extensively investigated first-row transition metal metalloporphyrins, those of manganese are the most effective for incorporation of non-oxygen functions.[4] Subsequent work coupling the oxo transfer and unactivated C–H bond cleavage processes catalyzed by the metalloporphyrins with phase transfer catalysis led to systems for the catalytic incorporation of the halide and nitrogen functions.[4] These latter systems are constituted by an organic solvent, S, containing the metalloporphyrin catalyst, M^{III}(Por)X, and, as a second liquid phase, an aqueous solution of the inorganic moiety to be incorporated into the organic substrate, X, as an inexpensive inorganic salt (e.g. $Na^+N_3^-{}_{aq}$ for catalytic azidification). The oxygen donor oxidant, DO, depending on its polarity, can reside in the organic phase (e.g. tertiary amine *N*-oxides, *m*-chloroperoxybenzoic acid), in the aqueous phase (e.g. OCl^-, $HOOSO_2^-K^+$, etc.), or, in the case of the minimally soluble polymeric iodosylarenes, ArIO, as a third phase.[5] These two (or three) phase systems invariably lead to oxygenation in competition with halogenation or azidification. Although some aspects of the mechanism and other features of multiphase systems for the catalytic incorporation of non-oxygen functions into unactivated C–H bonds are known, several others are not.[4]

$$S,\ M^{III}(Por)X//H_2O,\ NaX//ArIO$$

Several recent studies have done much to define the product selectivities and regioselectivities displayed in alkane hydroxylation as a function of the electronic and structural features of the tetraarylmetalloporphyrin catalysts.[1i,j] In contrast, very little is currently known about how such features of these intensely examined catalysts affect their selectivity for the incorporation of oxygen versus non-oxygen functions into alkanes and other organic compounds. This study is the first that addresses the effect altering the electronic and structural features of tetraarylporphyrin ligand has on the selectivities displayed by the Mn complexes with respect to transfer of oxygen versus non-oxygen moieties and C–H bond cleavage (tertiary versus secondary). The features that would optimize the azidification versus oxygenation of C–H bonds are of particular interest. The highly symmetrical hydrocarbon adamantane was chosen for the present investigation for two reasons: its nitrogenated analogues are of interest as pharmaceuticals[6] and energetic materials[7] and its high symmetry dictates relatively simple product distributions and ready analysis of products. Also addressed here is the oxidative stability of Mn tetraarylporphyrin complexes under catalytic alkane functionalization conditions, as a function of the substituents on the porphyrin ring.

Results

A number of multiphase metalloporphyrin-based systems for the functionalization of adamantane have been examined. Most of the data are presented in Tables I–III. In each table are given the following: (1) product distributions, (2) total yield of all products based on oxidant, (3) selectivities for tertiary versus secondary C–H cleavage (on a per C–H basis), and (4) selectivities for incorporation of oxygen functions (alcohol and ketone) versus non-oxygen functions (halide or azide). All reactions in the tables in this paper employ conditions of relatively low turnover (10

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(2) Recent reviews on metalloporphyrin catalyzed oxygenation: (a) Meunier, B. *Bull. Soc. Chim. Fr.* **1986**, *4*, 578. (b) Hill, C. L. *Advances in Oxygenated Processes*; Baumstark, A. L., Ed.; Vol I, in press. (c) Mansuy, D. *Pure Appl. Chem.* **1987**, *59*, 759.

(3) Representative recent papers on modelling of reactivity features of cytochrome P-450. See also ref 1. (a) McMurry, T. J.; Groves, J. T. *Cytochrome P-450*; Ortiz, de Montellano, P. R., Ed.; Plenum: New York, 1986; Chapter 1 and references cited therein. (b) Castellino, A. J.; Bruice, T. C. *J. Am. Chem. Soc.* **1988**, *110*, 1313. (c) Castellino, A. J.; Bruice, T. C. *Ibid.* **1988**, *110*, 158. (d) Groves, J. T.; Watanabe, Y. *Inorg. Chem.* **1987**, *26*, 785. (e) Groves, J. T.; Watanabe, Y. *J. Am. Chem. Soc.* **1986**, *108*, 7836. (f) Collman, J. P.; Hampton, P. D.; Brauman, J. I. *Ibid.* **1986**, *108*, 7861. (g) Traylor, T. G.; Nakano, T.; Miksztal, A. R.; Dunlap, B. E. *Ibid.* **1987**, *109*, 3625.

(4) (a) Hill, C. L.; Smegal, J. A. *Nouv. J. Chim.* **1982**, *6*, 287. (b) Hill, C. L.; Smegal, J. A.; Henly, T. J. *J. Org. Chem.* **1983**, *48*, 3277.

(5) Schardt, B. C.; Hill, C. L. *Inorg. Chem.* **1983**, *22*, 1563.

(6) For example, see: (a) Schinazi, R. F.; Prusoff, W. H. *Pediatr. Clin. North. Am.* **1983**, *30*, 77. (b) Nafta, I.; Turcanu, A. G.; Braun, I.; Companetz, W.; Simionescu, A.; Birt, E.; Florea, V. *W.H.O.* **1970**, *42*, 423 and references cited in each.

(7) For example, see: (a) *Opportunities in Chemistry*, Pimentel, G. C., Principal Ed.; National Academy: Washington, DC, 1985; pp 230–232. (b) Sollott, G. P.; Gilbert, E. E. *J. Org. Chem.* **1980**, *45*, 5405.

Table II. Product Distributions and Selectivities for the Catalytic Oxygenation and Azidification (or Halogenation) of Adamantane Using Mn^{III}TPPX Derivatives and Iodosylbenzene as a Function of the Solvent[a]

catalyst	solvent	product yields,[b,c] %							total yield,[c,d] %	tertiary/ secondary[c,e]	% X[c,f]	R–X/ R–C[e,g]
		1-OH	2-OH	2(O)	1-Cl	2-Cl	1-X	2-X				
Mn(TPP)N_3	C_6H_6	9.1	0.2	4.4	0	0	11.1	4.5	29.3	6.7	53	1.1
	CH_2Cl_2	26.9	2.5	0.1	0.7	0.6	15.3	8.6	53.4	11.3	45	0.8
	$CHCl_3$	11.7	1.2	0.6	7.3	2.0	2.0	3.2	18.7	8.2	28	0.4
	CCl_4	11.8	0.6	1.4	18.4	7.3	0.6	0.5	14.9	14.9	7	0.1
	PhCl	12.4	1.4	3.0	0	0	7.3	5.0	29.1	6.3	42	0.7
	C_6F_6	14.0	3.2	3.6	0	0	2.4	2.3	25.5	5.4	18	0.2
Mn(TPP)Br	C_6H_6	8.8	0.3	2.9	0	0	12.4	9.5	33.9	5.0	65	1.8
	CH_2Cl_2	15.0	1.4	0.3	0.3	0.1	11.6	5.8	34.1	10.6	51	1.0
	$CHCl_3$	8.9	0.2	0.6	2.0	1.2	12.0	5.0	26.7	10.8	64	1.8
	CCl_4	5.1	1.1	1.4	8.2	1.8	0.9	2.7	11.2	3.5	32	0.5
	PhCl	12.4	4.6	3.1	0.1	0.1	8.4	6.8	35.3	4.3	43	0.8
	C_6F_6	7.9	0	2.2	0	0	2.2	2.8	15.1	6.1	33	0.5
Mn(TPP)Cl	C_6H_6	12.9	0.2	4.6	3.3	2.7			23.7	6.5	25	0.3
	CH_2Cl_2	30.5	1.7	0.9	5.7	3.2			42.0	18.7	21	0.3
	$CHCl_3$	12.3	1.2	0.4	4.9	1.4			20.2	17.2	31	0.5
	CCl_4	12.3	1.6	1.8	11.2	6.1			33.0	7.4	52	1.1
	PhCl	16.6	5.1	3.3	2.0	2.3			29.3	5.2	15	0.2
	C_6F_6	11.9	3.0	1.6	0.7	1.5			18.7	6.2	12	0.1

[a] Reaction conditions given in the Experimental Section; mole ratios of substrate:oxygen donor:metalloporphyrin catalyst = 40:10:1. [b] 1-OH, 1-Cl, and 1-X are the 1-adamantyl alcohol, chloride (from solvent), and halide (from axial ligand, X), respectively; 2-OH, 2-Cl, and 2-X are the 2-adamantyl alcohol, chloride (from solvent), and halide, respectively; 2(O) is 2-adamantanone. Yields based on the iodosylbenzene. [c] The second $2e^-$ equivalent required in the conversion of alkane to ketone has specifically not been taken into account in these calculations. Calculation of product yields for the bromination and azidification reactions exclude products derived from the solvent (the chlorides). Calculation of product yields for the chlorination reactions include the contribution to the yields of the chlorinated products, 1-Cl and 2-Cl, derived from chlorine abstraction from the solvent (where applicable). [d] Moles of all oxidation products (excluding, again, the chlorides derived from solvent)/moles of iodosylbenzene. [e] Ratio of tertiary to secondary C–H cleavage products statistically corrected (values given per C–H). Both R–O and R–X products (tertiary or secondary) are taken together in these calculations. [f] Percentage incorporation of X = [(moles 1-X + 2-X)/total moles of all products (excluding, again, the chlorides derived from the solvent)] × 100. [g] (Moles 1-X + 2-X)/[moles 1-OH + 2OH + 2(O)].

equiv of oxygen donor per equivalent of metalloporphyrin catalyst) to minimize further oxidation of initial products and to minimize chemistry or catalysis resulting from transition metal containing species derived from metalloporphyrin oxidative degradation. The collective yields of adamantane derived products in these reactions rarely exceed 50% based on the oxygen donor oxidant (five turnovers of metalloporphyrin catalyst). The yields for functionalization of other alkanes under similar conditions are considerably higher.[4] The oxidizing equivalents not accounted for in these reactions are largely represented by the formation of the iodoxyarenes, $ArIO_2$, and porphyrin ligand degradation products. The stability of all the adamantane derived products in the tables were examined under the catalytic functionalization conditions themselves. All but 2-adamantanol exhibited minimal or small losses, and these losses, in all cases, were reproducible. The 2-adamantanol was further oxidized principally to 2-adamantanone, and the degree of this oxidation of this initial product varied greatly with the particular system. The greatest conversion of the secondary alcohol to the ketone under the reaction conditions was approximately 50%. All the following oxo transfer oxidants were examined in context with the catalytic incorporation of non-oxygen functions in these two (or three) phase systems: sodium hypochlorite, *m*-chloroperoxybenzoic acid, sodium bromate, periodate, *tert*-butylhydroperoxide, hydrogen peroxide, and iodosylarenes (iodosylbenzene = PhIO or pentafluoroiodosylbenzene = PFIB). As the iodosylarenes gave substantially higher yields than the other oxygen donor oxidants for this functionalization chemistry, these agents were the principal ones used in this study.

An important point should be explicitly made here, a point that has really not been discussed in any detail in the catalytic hydrocarbon (alkane and alkene) oxygenation literature. This point involves the way yields are reported in these reactions and the percent conversion of such processes, where percent conversion = moles of product(s) derived from substrate/moles of reactant substrate. For reactions in general, product yields are usually based on substrate, or better, on substrate consumed. However, in all but two of the 25 or so papers in the literature surveyed by the authors that address the homogeneous oxygenation of *alkanes* catalyzed by metalloporphyrins or related complexes, the yields given are not based on alkane. The yields in a majority of the cases are based on oxidant, and several papers report yields based on catalyst. One of the two papers that does give yields based on substrate alkane is the special case of an intramolecular reaction. The fact that yields are reported in these nonconventional ways in this growing group of papers on catalytic alkane oxygenation reflect the fact that the products of these reactions, usually alcohols and/or ketones, are far more reactive than the alkanes themselves. As a consequence, it is customary to run such reactions under pseudo-first-order conditions (large excess of alkane) to simplify the product distributions and enable more mechanistic inferences to be drawn. Likewise the average percent conversion in these 25 or so papers is 1 or 2%. No catalytic process, be it homogeneous or heterogeneous in nature, for the high conversion–high selectivity transformation of alkanes has yet been reported, although some in current development by our group look promising in this regard.

Table I summarizes yields for competitive oxygenation and chlorination of adamantane with PhIO and PFIB and four representative first-row transition-metal tetraphenylporphyrin catalysts in three-phase systems. The only complexes that are really effective for alkane functionalization by iodosylarenes are those based on iron and manganese, with those of manganese being the only ones effective for transfer of the non-oxygen functions. Table II summarizes the product distributions and selectivities for oxygenation versus halogenation or azidification, with halo (or azido) (tetraphenylporphinato)manganese(III)

Table III. Selectivities in the Catalytic Bromination and Azidification of Adamantane by a Variety of Mn Tetraarylporphyrins[a]

catalyst[b]	oxygen donor[c]	product yields,[d,e] % 1-OH	2-OH	2(O)	1-X	2-X	total yield,[e,f] %	tertiary/secondary[e,g]	% X[e,h]	R–X/R–O[e,i]
A. Bromination (X = Br)										
Mn(TPP)Br	PhIO	8.8	0.3	2.9	12.4	9.5	33.9	5.0	65	1.8
	PFIB	10.7	0.1	1.3	7.5	7.7	27.3	6.0	56	1.3
Mn(*p*-FTPP)Br	PhIO	14.5	0.5	5.1	11.0	5.1	36.2	7.1	44	0.8
	PFIB	11.4	0.7	2.8	6.6	6.0	27.5	5.7	46	0.9
Mn(*m*-FTPP)Br	PhIO	11.0	1.3	1.7	10.0	9.1	33.1	5.2	58	1.4
	PFIB	13.7	0.5	1.9	5.2	6.5	27.8	6.4	42	0.7
Mn(*o*-FTPP)Br	PhIO	24.4	4.4	3.3	5.3	4.4	41.8	7.4	23	0.3
	PFIB	25.4	3.5	1.9	4.9	4.8	40.5	8.9	24	0.3
Mn(*p*-CF_3TPP)Br	PhIO	19.7	1.5	4.0	7.4	5.1	37.7	7.7	33	0.5
	PFIB	18.3	3.0	3.6	4.9	4.7	34.5	6.2	28	0.4
Mn(2,6-F_2TPP)Br	PhIO	27.2	5.5	2.2	4.4	3.6	42.9	8.4	19	0.2
	PFIB	28.8	4.7	1.9	3.5	3.7	42.6	9.4	17	0.2
Mn(F_{20}TPP)Br	PhIO	34.0	7.1	1.9	<0.1	1.1	44.2	10.1	3	0.03
	PFIB	39.6	7.5	1.4	1.8	1.4	51.7	12.1	6	0.1
Mn(*p*-MeOTPP)Br	PhIO	11.9	1.0	3.6	7.8	5.6	29.9	5.8	45	0.8
	PFIB	7.8	0.4	1.8	5.9	6.7	22.6	4.6	56	1.3
B. Azidification (X = N_3)										
Mn(TPP)N_3	PhIO	9.1	0.2	4.4	11.1	4.5	29.3	6.7	53	1.1
	PFIB	9.5	0.1	1.6	7.7	6.0	24.9	6.7	55	1.2
Mn(*p*-FTPP)N_3	PhIO	19.8	4.7	7.0	10.4	2.7	44.6	6.3	29	0.4
	PFIB	13.7	1.1	2.3	6.5	4.6	28.2	7.6	39	0.7
Mn(*m*-FTPP)N_3	PhIO	10.5	0.6	3.5	8.5	4.3	27.4	6.8	47	0.9
	PFIB	11.2	2.1	2.5	7.1	5.8	28.7	5.3	45	0.8
Mn(*o*-FTPP)N_3	PhIO	26.1	4.8	3.2	3.6	2.9	40.6	8.2	16	0.2
	PFIB	28.4	6.8	2.3	2.4	2.7	42.6	8.0	12	0.1
Mn(*p*-CF_3TPP)N_3	PhIO	15.0	1.7	4.1	8.1	4.4	33.3	6.8	38	0.6
	PFIB	20.0	2.6	2.9	4.9	3.7	34.1	8.1	25	0.3
Mn(2,6-F_2TPP)N_3	PhIO	21.6	3.9	1.8	1.6	2.3	31.2	8.7	13	0.1
	PFIB	25.0	4.3	2.5	2.1	3.6	37.5	7.8	15	0.2
Mn(F_{20}TPP)N_3	PhIO	32.6	7.9	1.0	<0.1	1.2	42.8	9.7	3	0.03
	PFIB	42.2	9.1	1.2	0.5	1.9	54.9	10.5	4	0.05
Mn(*p*-MeOTPP)N_3	PhIO	8.2	1.2	2.4	9.2	5.0	26.0	6.1	55	1.2
	PFIB	8.8	0.8	1.5	6.7	5.0	22.8	6.4	51	1.1

[a] Reaction conditions given in the Experimental Section; mole ratios of substrate:oxygen donor:metalloporphyrin catalyst = 40:10:1. [b] Catalysts defined in text. [c] PhIO = iodosylbenzene; PFIB = pentafluoroiodosylbenzene. [d] 1-OH and 1-X are the 1-adamantyl alcohol and halide respectively; 2-OH and 2-X are the 2-adamantyl alcohol, and halide, respectively; 2(O) is 2-admantanone. Yields based on the oxygen donor. [e] The second $2e^-$ equivalent required in the conversion of alkane to ketone has specifically not been taken into account in these calculations. [f] Moles of all oxidation products/moles of oxygen donor. [g] Ratio of tertiary to secondary C–H cleavage products statistically corrected (values given are per C–H). Both R–O and R–X products (tertiary or secondary) are taken together in these calculations. [h] Percentage incorporation of X = [(moles 1-X + 2-X)/total moles of all products] × 100. [i] (Moles 1-X + 2-X)/[moles 1-OH + 2OH + 2(O)].

complexes as catalysts and iodosylbenzene as the oxygen donor in six representative solvents. Although the chlorinated solvents can and usually do donate chlorine to alkyl radicals derived from the alkane substrate (see Discussion below), including the 1-adamantyl and 2-adamantyl radicals generated in the systems addressed here, fluorine transfer is not seen in the reactions using hexafluorobenzene as the solvent. The data in Table II and other experiments indicate that benzene is one solvent of choice for this chemistry, as it dissolves reasonably well a variety of metalloporphyrin derivatives, it is highly resistant to oxidation (although trace amounts of biphenyl are formed in some reactions), and, unlike the chlorinated solvents, it does not lead to adventitious chloride incorporation into the substrate hydrocarbon during the catalytic functionalization process. For these reasons, benzene was the solvent used for all reactions in Tables I and III.

Table III summarizes the results of adamantane functionalization with both PhIO and PFIB by a variety of substituted (tetraarylporphinato)manganese(III) derivatives as catalysts. The manganese complexes of the following dianionic tetraphenylporphyrin ligands were prepared and evaluated in this study (the abbreviation used henceforth for each ligand is given in parentheses after the name): tetraphenylporphyrin (TPP), tetrakis(*p*-fluorophenyl)porphyrin (*p*-FTPP), tetrakis(*m*-fluorophenyl)porphyrin (*m*-FTPP), tetrakis(*o*-fluorophenyl)porphyrin (*o*-FTPP), tetrakis[*p*-(trifluoromethyl)phenyl]porphyrin (*p*-CF_3TPPP), tetrakis(2,6-difluorophenyl)porphyrin (2,6-F_2TPP), tetrakis(pentafluorophenyl)porphyrin, (F_{20}-TPP), and tetrakis(*p*-methoxyphenyl)porphyrin (*p*-MeOTPP). Several points are noted from the data in Table III. First, the fluorinated manganese tetraphenylporphyrin derivatives, all more electron withdrawing than Mn^{III}TPPX, lead to slightly but reproducibly higher total yields in both the bromination/oxygenation and the azidification/oxygenation reactions with either iodosylarene oxygen donor. The complexes Mn^{III}(*p*-CF_3TPP)X, Mn^{III}(2,6-F_2TPP)X, and Mn^{III}(F_{20}TPP)X, X = Br or N_3, are the most electron deficient and lead to the highest total yields of adamantane functionalization products. A second and related point is that the total yields for both the bromination/oxygenation and the azidification/oxygenation reactions with either iodosylarene oxygen donor are lower with the more electron rich Mn^{III}(*p*-MeOTPP)X complex than with Mn^{III}TPPX, X = Br or N_3.

The third and fourth points concern the C–H cleavage and the oxygen versus non-oxygen function incorporation selectivities manifested in observed product distributions, which, given a point made previously, reflect principally kinetic control. An examination of the relative apparent kinetic selectivities for cleavage of tertiary versus secondary C–H bonds in Table III shows that alteration of the electron-withdrawing (-donating) characteristics of the

porphyrin rings has remarkably little effect on these selectivities. The tertiary/secondary values are similar to those observed before by us[1e,f,4] and others[1a-d,g-j] in related systems and are in accord with hydrogen atom abstraction as the substrate oxidizing step in the mechanism (see Discussion). In contrast to the insensitivity of the relative C–H bond reactivities, the selectivities for incorporation of the non-oxygen, versus oxygen functions, in both cases examined here, bromination/hydroxylation and azidification/hydroxylation, are quite sensitive to the degree of electron-withdrawing (-donating) character of the porphyrin ligand. Whereas more than 50%, and in some cases substantially more than 50%, of the products are nonoxygenates (adamantyl bromides or azides), using as the catalysts the manganese complexes of the relatively electron rich porphyrin ligands, Mn^{III}(TPP)X and Mn^{III}(*p*-MeOTPP)X, X = Br or N_3, this is not the case with the other manganese complexes. The percentage of nonoxygenates decreases in direct proportion to the number and the electronegativity of the substituents on the meso-aryl rings for both the bromination/hydroxylation and azidification/hydroxylation reactions. For bromination/hydroxylation using PFIB as the oxidant, the following order is observed (for Por in Mn^{III}(Por)Br): TPP ~*p*-MeOTPP (highest selectivities for bromide relative to alcohol and ketone) > *p*-FTPP > *m*-FTPP > *p*-CF_3TPP > *o*-FTPP > 2,6-F_2TPP > F_{20}TPP (lowest selectivity for bromide relative to alcohol and ketone). For azidification/hydroxylation using PhIO as the oxidant, the following order is observed (for Por in Mn^{III}(Por)N_3): *p*-MeOTPP (highest selectivity for azide relative to alcohol and ketone) > TPP > *m*-FTPP > *p*-CF_3TPP > *p*-FTPP > *o*-FTPP > 2,6-F_2TPP > F_{20}TPP (lowest selectivity for azide relative to alcohol and ketone). For the same process using PFIB as the oxidant, the following order is observed: TPP (highest selectivity for azide relative to alcohol and ketone) > *p*-MeOTPP > *m*-FTPP > *p*-FTPP > *p*-CF_3TPP > 2,6-F_2TPP > *o*-FTPP > F_{20}TPP (lowest selectivity for azide relative to alcohol and ketone). When Mn^{III}(F_{20}TPP)X is used as the catalyst, generation of the bromide or azide products has nearly been eliminated and the processes are selective for oxygenation.

In addition to the experiments discussed above and those enumerated in the tables, the stability along with the secondary/tertiary C–H cleavage and C–X versus C–O incorporation selectivities of each of the eight manganese tetraarylporphyrin catalysts as a function of age (number of turnovers) during azidification/oxygenation of adamantane were studied extensively. Specifically, each of the above criteria were assessed after consumption of 10, 20, 50, and 100 equiv of oxygen donor. Although the Mn^{III}(Por)N_3, Por = 2,6-F_2TPP and F_{20}TPP, showed an apparently slightly higher resistance to oxidative degradation, all eight metalloporphyrins were largely inactivated after consumption of 50 equiv of oxidant. The secondary/tertiary C–H cleavage and C–X versus C–O incorporation selectivities changed little as long as the metalloporphyrin catalysts were largely intact.

Discussion

In the early stages of development of metalloporphyrin-based oxo transfer and hydrocarbon oxidation processes several years ago, we reported fairly thorough studies of the mechanism and the structure–reactivity relationships exhibited by the Mn^{III}TPPX, X = halide or pseudohalide/PhIO systems for the catalytic incorporation of oxygen functions and the stoichiometric incorporation of the non-oxygen functions, halide, or pseudohalide.[1e,f,8]

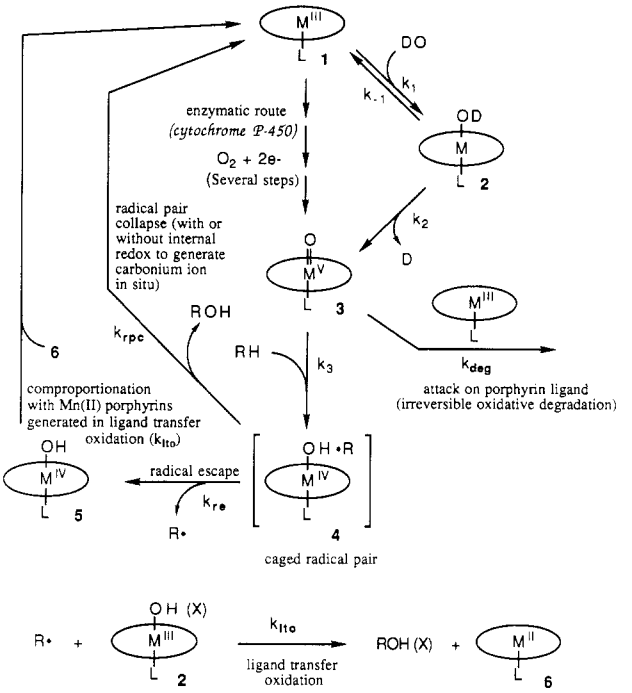

Figure 1. Principal pathways in the metalloporphyrin-catalyzed functionalization of alkanes by oxygen donors, DO. All pathways appear to be applicable for the manganese tetraarylporphyrin-catalyzed processes, M = Mn, when the iodosylarenes, PhIO and PFIB, are used as the oxygen donors. The oval in all cases represents the metalloporphyrin dianion ligand. Steps k_1, k_2, k_3, k_{re}, for radical escape, and k_{lto}, for ligand transfer oxidation, coupled with axial ligand exchange, X^- for OH^-, etc., in the *S* = 2, Mn^{III} complexes, **2**, facilitate the catalytic incorporation of the non-oxygen functions, X = N_3, Br, and Cl, into alkanes.

This work on the parent alkane functionalization systems included the isolation and characterization (including several X-ray crystal structures) of high-valent MnTPP species, derived from these MnTPP/PhIO systems.[8] The salient mechanistic features of the multiphase systems for the catalytic incorporation of the non-oxygen functions reported in this paper are addressed by the data in these early papers on the parent system and by the data presented in this paper. Figure 1 represents several of the principal processes.

It is a combination of two processes involving the manganese porphyrin catalysts, both of whose rates are dictated primarily by d orbital occupancy, that best explain the results in the systems reported here. In order to address these two processes, the other processes in Figure 1 first need brief elaboration. At present time, based on the work of other groups, the processes of oxygen-donor binding to the metalloporphyrin, k_1, generation of the oxometal species, **3**, k_2, subsequent hydrogen atom abstraction from substrate by this species, k_3, followed by radical pair collapse, k_{rpc}, appear to be operable for systems where M = Fe.[1d,i] Our early work[1e,8] indicated that these processes, in addition to radical escape k_{re}, and ligand transfer oxidation, k_{lto}, are operable for the manganese systems. It is the latter two processes that lead to the incorporation of non-oxygen functions into the hydrocarbon substrates. The electronic structural properties,

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principally the d orbital occupancy, of the formal hydroxymetal(IV) species in the caged radical pair, **4**, dictates whether or not any radical will escape. In contrast to the Fe systems where this hydroxymetal(IV) species has an electronic structure well suited for ready radical coupling to form the alcohol product directly, k_{rpc}, this hydroxymetal(IV) species in the Mn systems is far more stable, allowing radical escape to compete with direct alcohol production, $k_{re} \geq k_{rpc}$. Several (tetraarylporphyrinato)manganese(IV) derivatives that we independently synthesized and characterized as representations of the manganese porphyrin moiety in **4**, have all, in fact, turned out to be minimally distorted, $S = 3/2$, Mn^{IV}–neutral porphyrin species,[8] complexes that would be expected to be relatively slow in undergoing k_{rpc}. Several lines of evidence from studies on the parent system including product distribution, kinetics, and rearrangement studies[1e] established the intermediacy of freely diffusing alkyl radicals in the stoichiometric incorporation of halogen and nitrogen into alkanes. In the systems reported here for the catalytic incorporation of these non-oxygen functional groups, further evidence for the intermediacy of freely diffusing radicals comes from the production of alkyl chlorides from substrate alkane by chlorine abstraction from chlorinated solvents and the fact that the hexafluorobenzene does not produce even small amounts alkyl fluorides derived from alkane.

Once the alkyl radicals escape the cage, **4**, in the manganese systems, they must undergo ligand transfer oxidation at rates competitive with oxidation and the usual bimolecular radical processes, coupling and disproportionation. The same factors that allowed the radicals to escape the cage, **4**, in the first place, $k_{re} > k_{rpc}$, are those that prohibit ligand transfer oxidation of radicals by freely diffusing $S = 3/2$, Mn^{IV}–neutral porphyrin species from being appreciable in these reactions. In contrast to the Mn^{IV} porphyrins, the Mn^{III} porphyrins are clearly, from our previous work[8,9] and that of others,[10,11] all tetragonally distorted $S = 2$ species and, as such, should exhibit high ligand transfer oxidation rate constants, k_{lto} in Figure 1.

The other process dictated largely by d orbital occupancy that facilitates the catalytic incorporation of non-oxygen functions reported here is the rate of axial ligand exchange. For k_{lto} in Figure 1 to be the product determining step, the hydroxide axial ligands on the manganese(IV) species resulting from radical escape, k_{re}, must be able to exchange with the great excess of X^- present in the second liquid (aqueous) phase ($X^- = Br$, N_3, etc.). Not surprisingly, the $S = 3/2$, Mn^{IV} porphyrins do not exchange their axial ligands rapidly.[4,8] They do, however, undergo reduction by the Mn^{II} species generated by ligand transfer oxidation, k_{lto} in Figure 1, to make 2 equiv of the labile $S = 2$, Mn^{III} species.[1e] Thus both the rapid ligand exchange rates *and* the facile ligand transfer oxidation processes exhibited by the latter complexes are critical to the successful catalytic incorporation of halogen and nitrogen functions into the alkanes.

The tertiary to secondary cleavage ratios, in this chemistry are dictated by the intrinsic kinetic selectivity for this process, k_3, provided that k_3 is the only pathway generating hydrocarbon radicals in this chemistry. If hydrogen abstraction by X•, e.g. Br•, were important, then the observed tertiary/secondary values would be substantially higher. It appears reasonable at the present time that in these multiphase systems, only k_3 is important in generating the radicals. The tertiary/secondary values that are observed in the tables are indicative of fairly high energy and nonselective radical abstraction. These kinetic selectivities certainly rule out any appreciable degree of carbonium ion–hydride abstraction character in the transition state of C–H cleavage process. Pure carbonium ion–hydride abstraction transition states have been estimated to display tertiary/secondary values in the range of 10^4 to 1.[12] The data presented in this paper indicate that attempts to control the C–H cleavage selectivities in the halogen or nitrogen incorporation processes by altering the substituents on the porphyrin rings is not likely to be useful. Control of these selectivities in the non-oxygen functionalization processes by steric modification of porphyrin ligands, the techniques used successfully by both the Suslick[1j] and the Nappa[1i] groups for the hydroxylation processes, are likely to be more effective.

The final point to be discussed is that of catalyst stability. The major limitation of metalloporphyrin-catalyzed hydrocarbon functionalization reactions is the ready oxidative degradation of the porphyrin ligand, k_{deg} in Figure 1. Several recent studies have indicated that metalloporphyrins with sufficiently large substituents on the ortho positions of the meso-aryl rings, e.g. chloride, methyl, or larger group, to preclude μ-oxo dimer formation and several intermolecular ligand oxidation processes are demonstrably more resistant to oxidative degradation than those metalloporphyrins that do not have such substituents.[13] It is clear from the work here, however, that placing substituents on the rings, such as fluorides, that change the electronic and redox features of the complexes and can, in fact, alter the chemistry as seen above but do not preclude dimer formation and various intermolecular reactions, do not impart demonstrable oxidative stability to the catalysts.

Experimental Section

Methods. Elemental analyses were performed by Atlantic Microlabs. Visible spectra were recorded on a Hewlett-Packard (H/P) 8451A spectrophotometer. Gas chromatographic analyses were carried out with either a H/P Model 5710A or a Model 5890 gas chromatograph, each equipped with H/P 3390A reporting integrators. OV-101 (12 m) or a 50-m 5% phenyl methyl silicone fused silica capillary columns with nitrogen as the carrier gas were used in these analyses. Yields were determined by using the internal standard method. The identities of the products were verified by co-injection with authentic samples and by gas chromatographic–mass spectrometric (GC/MS) analysis. Infrared spectra were recorded on a Perkin-Elmer (P/E) 983 spectrophotometer as KBr pellets. ^1H NMR spectra were obtained using a Nicolet Model 360-NB spectrometer operating at 361.0 MHz with a probe temperature of 25 °C. Mass spectra were obtained on a VG Analytical 70S high-resolution mass spectrometer using electron impact ionization with an accelerating voltage of 8 kV.

Materials. The solvents benzene, dichloromethane, chloroform, carbon tetrachloride, and chlorobenzene were Burdick and Jackson glass-distilled grade and were used as received. Hexa-

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fluorobenzene (Lancaster) was fractionally distilled before used. Adamantane (Aldrich) was used without further purification. Water was deionized and fractionally distilled from $KMnO_4$. All other reagents were commercial samples and used as received. The porphyrins, TPP,[14] *p*-FTPP,[14] *m*-FTPP,[14] *o*-FTPP,[14] *p*-CF_3TPP,[15] 2,6-F_2TPP,[16] *p*-CH_3OTPP,[16] and F_{20}TPP,[17] were made by literature methods. These complexes were then metalated by the method of Alder,[18] and the axial ligands, were exchanged by the method used by Ogoshi on the corresponding iron complexes.[19] These compounds after recrystallization, all gave satisfactory elemental analysis and electronic absorption spectra. Pentafluoroiodosylbenzene (PFIB),[20] and iodosylbenzene (PhIO),[21] prepared by literature methods, were titrated iodometrically and shown to be ≥99% pure. Both iodosylarenes were stored under argon at −25 °C.

Functionalization Reactions. The reactions were conducted and analyzed by similar procedures in all cases. In a typical reaction, 2×10^{-4} mol of iodosylarene (10 equiv based on metalloporphyrin catalyst) were added to a magnetically stirred degassed solution of 14.2 mg (2×10^{-5} mol) of $Mn^{III}TPPN_3$ in 5 mL of degassed benzene containing 8×10^{-4} mol of adamantane substrate, and, as a second liquid phase, 3.0 mL of saturated aqueous sodium halide (azide), under an Ar atmosphere contained in a 25- or 50-mL Schlenk flask. All reactions were carried out at 22 °C. After a reaction time of 3 h, the marginally soluble polymeric oxygen donor (PhIO or PFIB) had been consumed. Internal standard was added, and the contents of the reaction vessel analyzed immediately by GC and GC/MS.

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Notes

Determination of the Enantiomeric Purity of Chiral Allyl Alcohols and Allyl Ethers by ^{195}Pt NMR Spectroscopy

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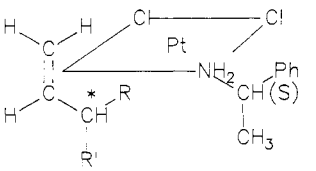
NMR methods have been widely used for determining the enantiomeric purity of organic compounds.[1] A possible approach is to convert an enantiomeric mixture to a diastereoisomeric pair with an appropriate chiral derivatizing agent and then to measure the resonances of the diastereotopic groups, most commonly by ^1H and ^{19}F NMR, and, occasionally, by ^{13}C and ^{31}P NMR.[1] No cases have been reported in which the enantiomeric purity was determined by detecting the ^{195}Pt NMR resonances of diastereoisomeric platinum(II) complexes.

In this paper we show how ^{195}Pt NMR measurements on the diastereoisomeric complexes *cis*-dichloro[(*S*)-α-methylbenzylamine][CH_2=CHCH(R)R′]Pt(II), **1**, (R = OH, OMe; R′ = alkyl or aryl) (Figure 1) can be used to determine the enantiomeric purity of chiral allyl alcohols and allyl ethers. The complexes were prepared by adding the unsaturated alcohol or ether to *cis*-dichloro[(*S*)-α-methylbenzylamine](ethylene)platinum(II)[2] in $CHCl_3$ solution. On standing at room temperature for a few minutes, the unsaturated compound replaces the coordinated ethylene, and this reaction is driven to completion by removing ethylene.



R = OH, OMe; R' = alkyl or aryl

complex 1

Figure 1. Complexes *cis*-dichloro[(*S*)-α-methylbenzylamine]-[CH_2=CHCH(R)R′]platinum(II).

The complex *cis*-dichloro[(*S*)-α-methylbenzylamine]-[CH_2=CHCH(OH)Me]platinum(II), **1a**, forms four diastereoisomers, which arise from the chiral center in the alcohol and binding of the two prochiral faces of the double bond (Figure 2). The ^{195}Pt NMR spectrum (^{195}Pt $I = 1/2$, natural abundance 33.8%) of **1a** shows four well-resolved resonances due to these diastereoisomers at −2689, −2711, −2720, and −2740 ppm relative to Na_2PtCl_6 (Figure 3). In contrast, the analogous complex containing the *R* antipode of the same alcohol (optical purity >98%) shows only the resonances at −2689 and −2740 ppm (Figure 3), which must be assigned to the two epimers containing the *R* antipode. Thus the absorptions at −2711 and −2720 ppm are due to the two epimers containing the S antipode.

In addition, when complex **1a** is prepared by using an excess of the ethylene complex with respect to racemic α-methyl allyl alcohol (molar ratio 1.5:1), the sum of the areas of the two peaks produced by the *R* antipode at −2689 and −2740 ppm equals the sum of the areas of the

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