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.

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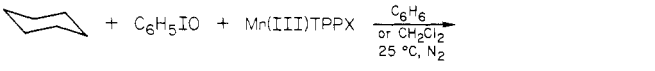
Alkane Activation and Functionalization under Mild Conditions by a Homogeneous Manganese(III) Porphyrin–Iodosylbenzene Oxidizing System

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).



(1)

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

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(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.

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(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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Table I. Product Yields for Cyclohexane Functionalization[a]

MnTPPX, X =	solv	mol ratio, C_6H_5IO/ MnTPPX	% yield[b] RX	ROH	c-$C_6H_{10}O$	RR	C_6H_5R	C_6H_5OH	C_6H_5I
Cl	C_6H_6	8.9	98 (11)	237 (26)	48 (5)	5 (0.5)	20 (2)	<1	(>92)
Br	CH_2Cl_2	6.0	99 (17)	193 (32)	<20 (3)	4 (0.7)			(>92)
Br	CH_2Cl_2	9.5	99 (10)	243 (26)	<20 (3)	4 (0.7)			(>95)
Br	C_6H_6	0.5	20 (41)	6 (13)	<3	<0.2	c	c	(102)
Br	C_6H_6	0.98	42 (43)	7.4 (7.6)	<3	<0.2	c	c	(94)
Br	C_6H_6	2.1	74 (35)	13 (6)	<7	<0.2	c	c	(87)
I	C_6H_6	6.1	>95	d	d	d	d	d	d
N_3	C_6H_6	5.3	>95 (18)	120 (23)	43 (8)	<1	<2	<1	(>91)

[a] All reactions were run, worked up, and analyzed similarly. Reactant ratios were varied, but cyclohexane was always present in excess. In a typical reaction, 5 mL of a degassed 5.4 mM solution of Mn(III)TPPX in rigorously purified cyclohexane–benzene solvent (cyclohexane 0.95 M in benzene) was added by syringe to a 25-mL Schlenk flask equipped with a $^1/_4$-inch magnetic stirring bar and containing 35.6 g (1.62×10^{-4} mol) of iodosylbenzene. The reaction was stirred for 5 h under nitrogen, quenched by addition of 1 mL of 10% aqueous sodium bisulfite, and the internal standard added; then the organic phase was analyzed directly by GC or GC MS. Control experiments showed no reaction if either MnTPPX or C_6H_5IO was omitted. [b] Yields based on MnTPPX, yields in parentheses based on C_6H_5IO. [c] Below detectable limit (<<1%). [d] Values not determined.

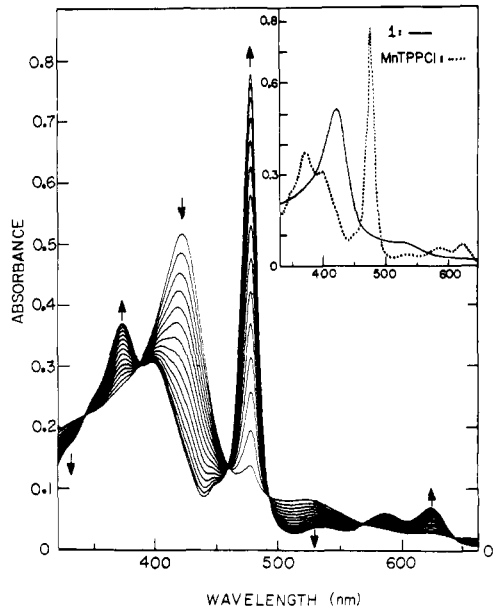

Figure 1. Conversion of a ca. 0.7 mM solution of **1** in cyclohexane–benzene solution back to $[Mn(III)TPP]^+$. The arrows indicate the progression of the reaction. Spectra were directly recorded on a spectrometer for publication, not traced. (inset) Visible spectra of Mn(III)TPPCl and **1**.

product, indicating chlorine atom abstraction from solvent. Fourth, the chlorination of *tert*-butylbenzene produced the following four principal products (yields in a typical reaction based on product C_6H_5I taken as 100%): β,β-dimethylbenzeneethanol (neophyl alcohol) (18%), (2-chloro-1,1-dimethylethyl)benzene (34%), α,α-dimethylbenzeneethanol (2.8%), and (2-chloro-2-methylpropyl)benzene (4.2%). The former two products were derived from intermediate unrearranged neophyl radicals, and the latter two products were derived from benzyldimethylcarbinyl radicals produced upon 1,2-phenyl migration in the neophyl radical.[11] This product distribution argues for the presence of fairly long-lived free alkyl radicals[12] as precursors to both halide and alcohol products and against the involvement of any appreciable percentage of carbonium ion intermediates in at least the halogenation reactions.

Stirring the green solutions of MnTPPCl or MnTPPBr in benzene, dichloromethane, or acetonitrile solvents under nitrogen with a large (≥10-fold M) excess of iodosylbenzene produces a dark yellow-brown solution of a higher valent MnTPP complex (**1**). This complex, although stable in the solid state at 25 °C for a period of at least days, is rapidly reduced back to $[Mn(III)TPP]^+$ in minutes when dissolved in aromatic or chlorocarbon solvents. The spectra of Mn(III)TPPCl and **1** are illustrated in the Figure 1 inset. If the reaction time of MnTPPX with the excess of iodosylbenzene is maintained only for a period 2–2.5 times as long as the time needed to completely remove the green color and no longer, then the degree of oxidative attack on the porphyrin ligand is insufficient to have a measurable effect on the visible absorption spectra, and the reduction of **1** back to $[Mn(III)TPP]^+$ is a dramatic one-to-one interconversion producing visible spectra with six isosbestic points, 344, 388, 460, 492, 512, and 641 nm (Figure 1). If, however, the reaction is allowed to run longer, partial oxidative degradation of the porphyrin results in loss of the isosbestic points.

Two lines of evidence suggest that **1** is the species responsible for the alkane C–H bond activation process. First, the production of **1** in all reactions is faster than the production of the oxidized organic products, and, second, if **1** is isolated, weighed, then dissolved in cyclohexane–benzene or cyclohexane–dichloromethane under nitrogen, the distribution and yields of the oxidized organic products are in close accord with those in Table I.

Efforts directed at the purification and further characterization of **1** as well as studies aimed at elucidating the scope and complete mechanism of these reactions are in progress.

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(12) The rate, k, for the 1,2-phenyl shift in the neophyl radical is undoubtedly $<10^5$ s^{-1} in alkane solvents at 25 °C; cf.: Whitesides, G. M.; Panek, E. J.; Stedronsky, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 232, and references cited therein.

Hydrocarbon Oxidations with Oxometalloporphinates. Isolation and Reactions of a (Porphinato)manganese(V) Complex

Sir:

The role of protoporphyrin IX in biological oxygenation reactions[1] has understandably focused attention on synthetic metalloporphinates as oxidation catalysts. We recently reported that

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