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.

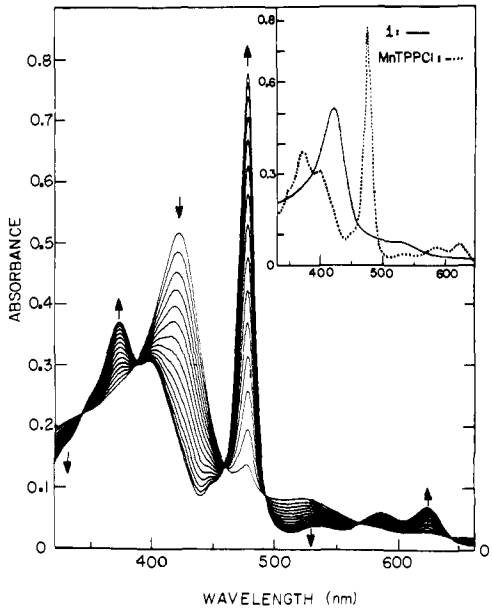

Figure 1. Conversion of a ca. 0.7 mM solution of **1** in cyclohexane–benzene solution back to $[Mn(III)TPP]^+$. The arrows indicate the progression of the reaction. Spectra were directly recorded on a spectrometer for publication, not traced. (inset) Visible spectra of Mn(III)TPPCl and **1**.

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.

(11) Reviews of radical rearrangements, including the neophyl radical rearrangement: (a) Wilt, J. W. In "Free Radicals", Kochi, J. K., Ed.; Wiley: New York, 1973, Vol. 1, Chapter 8. (b) Walling, C. In "Molecular Rearrangements", DeMayo, P., Ed.; Interscience: New York, 1963; Vol. 1, Chapter 7.

(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.

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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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

(1) (a) Groves, J. T. *Adv. Inorg. Biochem.* **1979**, *1*, 119. (b) Coon, M. J.; White, R. E. In "Metal Ion Activation of Dioxygen"; Spiro, T. G., Ed.; Wiley: New York, 1980; in press. (c) Yamazaki, I. In "Molecular Mechanisms of Oxygen Activation"; Hayaishi, O., Ed.; Academic Press: New York, 1974; p 535.

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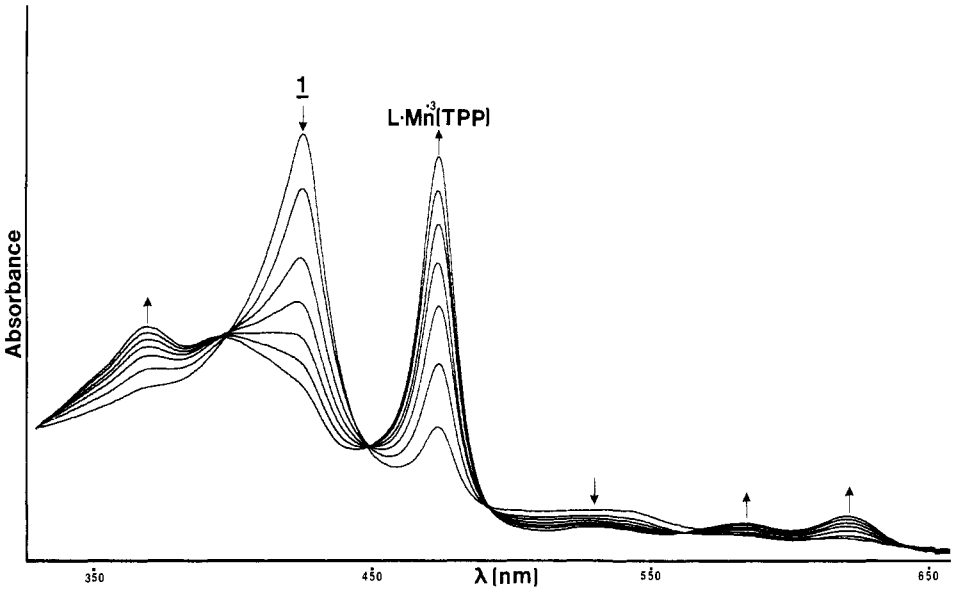
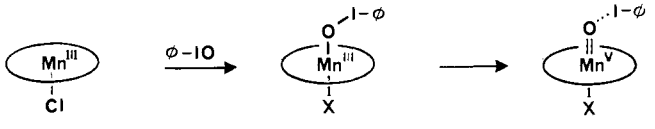


Figure 1. Visible absorption spectrum of **1** decomposing to L·Mn^{III}TPP in THF.

chloro(tetraphenylporphinato)iron(III) (TPPFe^{III}Cl) efficiently catalyzed the epoxidation of olefins with iodosylbenzene as an oxygen source[2] and that TPPCr^{III}Cl was converted to a reactive oxochromium(V) intermediate under similar conditions.[3] Here we report the isolation of a (porphinato)maganese(V) complex which hydroxylates and halogenates alkanes and epoxidizes olefins in both catalytic and stoichiometric reactions.

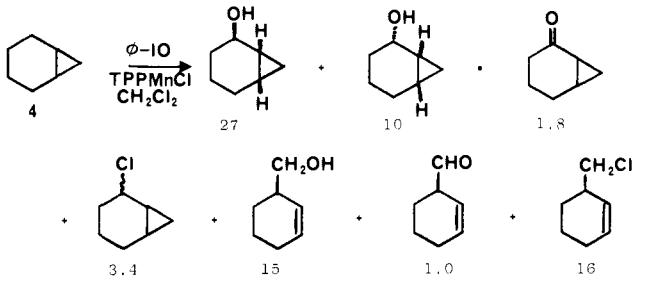
Chloroaqua(tetraphenylporphinato)manganese(III)[4] (TPP-Mn^{III}Cl) was dissolved in dry methylene chloride under nitrogen and oxidized with excess iodosylbenzene for 1 min at room temperature. The resulting orange-brown solution was filtered into a receiver at −78 °C and treated with *tert*-butylamine. Dilution of this solution with hexane at −40 °C caused a black, microcrystalline solid (**1**) to precipitate in 85% yield. Solid **1**, when dissolved in methylene chloride or THF, gave the same visible spectrum as a 1:1 mixture of TPPMn^{III}Cl and iodosylbenzene, and it decomposed rapidly at room temperature to give TPP-Mn^{III}Cl (Figure 1). Decomposition of **1** in the presence of norbornene gave a quantitiative yield of norbornene oxide and equivalent amounts of iodobenzene.

Two likely compositions of **1** are a TPPMn^{III} iodosylbenzene adduct (**2**) and an oxo–TPPMn^{V} complex (**3**) which has occluded iodobenzene.[5] Several lines of evidence favor the oxo-



manganese(V) structure **3**.[6] Magnetic susceptibility measurements on solid **1** by the Faraday method gave a value of 2.9 μ_B. This value is consistent with a high-spin, d^2 electronic structure expected for **3** and is much too small for a high-spin manganese(III) adduct such as **2**. The blue-shifted visible spectrum of

Scheme I



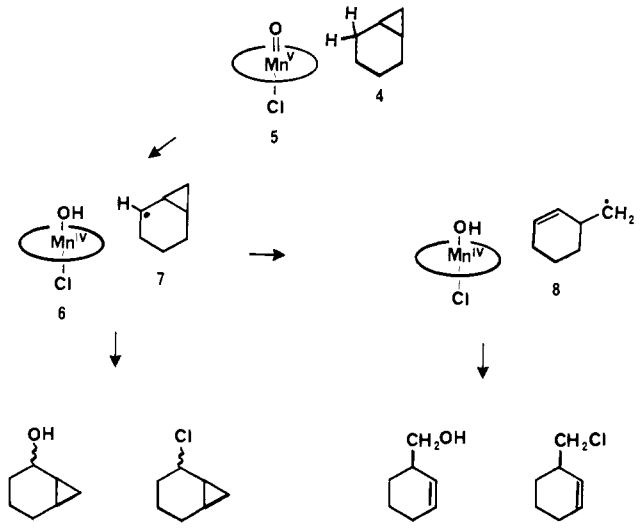
1 (Figure 1) is nearly identical with the corresponding oxochromium(V) complex we have recently reported.[3,7] In addition, the generation of **1** in the presence of $H_2{}^{18}O$ and norbornene gave norbornene oxide with 80% incorporation of the label. Since iodosylbenzene does not exchange oxygen with water under these conditions, exchange of a labile oxo ligand in an intermediate such as **3** is indicated.[8]

Complex **1** is a powerful oxidant for hydrocarbons in stoichiometric reactions, and catalytic oxidations with excess iodosylbenzene gave significantly better yields than iron or chromium porphyrin catalysts. Oxidation of cyclohexane with iodosylbenzene catalyzed by TPPMn^{III}Cl in methylene chloride gave a 2.5:1 mixture of cyclohexanol and cyclohexyl *chloride* in a combined yield of 70%, based on iodosylbenzene. Treatment of adamantane under similar conditions gave 1-adamantanol (5.2), 2-adamantanol(1.6), 1-adamantyl chloride (1.0), and 2-adamantyl chloride (1.1) in 80% yield. In dibromomethane or bromotrichloromethane solvent, the corresponding alkyl *bromides* became the major products. Small amounts of ketone were also produced in these oxidations.

To probe the nature of these oxygen and halogen transfer reactions, we have examined the oxidation of norcarane (**4**). Typical free-radical reactions, such as the tri-*n*-butyltin hydride induced dehalogenation of 2-chloronorcarane, are known to produce ring-opened methylcyclohexenyl derivatives.[9a] In con-

(2) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032.
(3) Groves, J. T.; Kruper, W. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7613.
(4) Kobayashi, H.; Yanagawa, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 450.
(5) (a) Metalloporphyrin complexes are known to occlude toluene: Kirner, J. F.; Reed, C. A.; Scheidt, W. R. *J. Am. Chem. Soc.* **1977** *99*, 1093. (b) Dimeric structures should also be considered for **1** since the IR spectrum does not show a prominent Mn=O peak.
(6) (a) For a leading reference to the few known manganese(V) compounds, see: Jasinski, J. P.; Holt, S. L. *Inorg. Chem.* **1975**, *14*, 1267. (b) The intermediacy of Mn(IV) and possibly Mn(V) upon oxidation of Mn(III) hematoporphyrin IX (in alkaline aqueous solution) has been reported: Loach, P. A.; Calvin, M. *Biochemistry* **1963**, *2*, 361.
(7) Spectral transients which are also observed in the reaction of iron porphyrins and with iodosylbenzene may be the related iron oxides. (a) Presented at the ACS/CSJ Chemical Congress, Honolulu, April 1979. (b) Groves, J. T.; Kruper, W. J.; Nemo, T. E.; Myers, R. S. *J. Mol. Catal.* **1980**, *7*, 169. (c) Chang, C. K.; Kuo, M.-S. *J. Am. Chem. Soc.* **1979**, *101*, 3413. (d) Chin, D.-H.; Balch, A. L.; LaMar, G. N. *Ibid.* **1980**, *102*, 1446.
(8) (a) Murmann, R. K. *J. Am. Chem. Soc.* **1974**, *96*, 7836. (b) Sharpless, K. B.; Townsend, J. M.; Williams, D. R. *Ibid.* **1972**, *94*, 295.
(9) (a) Friedrich, E. C.; Holmstead, R. L. *J. Org. Chem.* **1976**, *37*, 2550. (b) Friedrich, E. C.; Jassawalla, J. D. C. *Ibid.* **1979**, *44*, 4224.

Scheme II



trast, cationic processes such as solvolyses or lead tetraacetate oxidation give cycloheptenyl rearrangement products.[9b] The products of the oxidation of norcarane with iodosylbenzene catalyzed by $TPPMn^{III}Cl$ are shown in Scheme I.

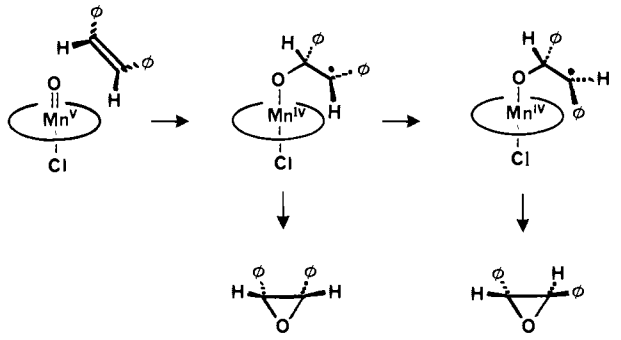
It is apparent that both oxygenated and chlorinated products characteristic of a free-radical reaction are obtained. A mechanism consistent with these observations is presented in Scheme II.

Hydrogen abstraction by the intermediate oxomanganese(V) complex **5** would give a chlorohydroxymanganese(IV) species (**6**) and a norcaranyl free radical (**7**). Ligand transfer from **6** to **7** could occur by homolytic displacement on the ligand or via a transient alkyl manganese species.[10] In either case, the radical **7** must be long-lived enough to rearrange to the cyclohexenylmethyl radical **8** and to abstract halogen from the solvent. Aliphatic chlorination is also observed in benzene with $TPPMn^{III}Cl$ as the catalyst, showing that transfer of chlorine from the metal competes with oxygen transfer even when the solvent is not involved.[11]

Another indication of the stepwise radical nature of the reaction of $TPPMn^{III}Cl$/PhIO with hydrocarbons is apparent in the epoxidation of olefins. Oxidation of *trans*-stilbene under these conditions gave only *trans*-stilbene oxide in 53% yield. In contrast, *cis*-stilbene gave a 1.6:1 mixture of *trans*- and *cis*-epoxide, respectively, in 88% overall yield. Chloro(tetra-*o*-tolylporphinato)manganese(III) ($TTPMn^{III}Cl$) gave mostly *cis*-epoxide (2.8:1) in 87% yield. Thus, this epoxidation occurs with loss of stereochemistry at the double bond, and the distribution of products is sensitive to the substitution pattern on the porphyrin periphery. Addition of a manganese(V) intermediate to the carbon–carbon double bond to give a freely rotating free-radical intermediate is consistent with these observations (Scheme III).[12]

The lack of stereospecificity in olefin epoxidation and the relative abundance of evidence for free radicals in the reactions of alkanes with oxomanganese(V) complexes contrast with results we have obtained for the closely related iron and chromium porphyrins.[2,3] We suggest that the triplet ground state expected for a high-spin d^2 Mn(V)=O ion has affected the degree of concertedness of these reactions. The isolation and reactions of **1** suggest that the olefin oxygenation with $O_2/NaBH_4$/$TPPMn^{III}Cl$ recently reported by Tabushi[13] may proceed through a similar oxomanganese(V) species. The role of such high oxidation state oxometalloporphinates in metalloenzyme function and the use of these catalysts in synthetic oxidation reactions are under continued study in our laboratories.

Scheme III



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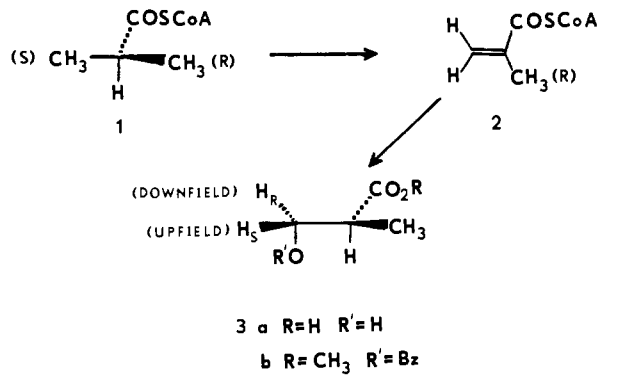
Application of Tritium NMR Spectroscopy in the Determination of the Stereochemistry of Dehydrogenation of Isobutyryl CoA in *Pseudomonas putida*

Sir:

The principal catabolic pathway of L-valine proceeds via the metabolite isobutyryl CoA (**1**).[1] Dehydrogenation of **1** by a flavin-dependent[2] short-chain acyl CoA dehydrogenase[3] produces



methacrylyl CoA (**2**). In rats[4] and in *Pseudomonas putida* (ATCC 21244),[5] hydrogens are eliminated from C-2 and from

(10) (a) For an excellent review, see: Kochi, J. K. *Free Radicals* **1973**, *1*, 591. (b) Organochromium intermediates have been suggested in the oxidation of olefins by chromyl chloride: Sharpless, K. B.; Teranishi, A. Y. Bäckvall, J. E. *J. Am. Chem. Soc.* **1977**, *99*, 3120.

(11) The yield of chloride is consistent with the amount of catalyst used. A more detailed account of ligand transfer oxidation will appear elsewhere.

(12) (a) The possibility of a four-membered oxametallacyclic intermediate should also be considered. (b) Kobayashi, Y. *Tetrahedron Lett.* **1972**, 5093. (c) Ryang, H. S.; Foote, C. S. *J. Am. Chem. Soc.* **1980**, *102*, 2130.

(13) Tabushi, I.; Koga, N. *J. Am. Chem. Soc.* **1979**, *101*, 6456.

(1) (a) Bender, D. A. "Amino Acid Metabolism", Wiley: New York, 1975; pp 132–142. (b) Tanaka, K.; Armitage, I. M.; Ramsdell, H. S.; Hsia, Y. E.; Lipsky, S. R.; Rosenburg, L. E. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 3692–3696.

(2) (a) Brown, L. E.; Hamilton, G. A. *J. Am. Chem. Soc.* **1972**, *92*, 7225–7227. (b) Hamilton, G. A. *Prog. Bioorg. Chem.* **1971**, *1*, 83–157.

(3) (a) Beinert, H. *Methods Enzymol.* **1962**, *5*, 546–557. (b) Thorpe, C.; Mattews, R. G.; Williams, C. H. *Biochemistry* **1979**, *18*, 331–337. (c) Frerman, F. E.; Kim, J. P.; Huhta, K.; McKean, M. C. *J. Biol. Chem.* **1980**, *255*, 2195–2198.

(4) Amster, J.; Tanaka, K. *J. Biol. Chem.* **1980**, *255*, 119–120.

(5) Aberhart, D. J. *Bioorg. Chem.* **1977**, *6*, 191–201.

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