We are currently extending the methodology to the synthesis of prostaglandin and brefeldin intermediates. Experimental and theoretical studies are also in progress to explore the characteristics and synthetic potentials of boat forms of the dioxane and related ring systems.

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Detection of High-Valent Intermediates in the Chlorine(I) Oxidation of (Porphinato)manganese(III) Complexes

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Recent years have seen a growing fascination with transition-metal complexes that effect efficient oxygen transfer from an oxo ligand source to organic substrates such as alkanes and alkenes. The hypochlorite system set forth by Meunier and co-workers[1] is intriguing for its economic implications as well as those of general structure–reactivity relationships. This system is biphasic in nature with an aqueous phase containing hypochlorite ion (OCl^-) in the form of commercial bleach and an organic phase consisting of the (tetraphenylporphinato)manganese(III) catalyst (Mn(TPP)X; X = Cl^-, Br^-, or OAc^-) and an alkene substrate in CH_2Cl_2. A phase-transfer catalyst is employed to shuttle OCl^- from the aqueous to the organic phase where it oxidizes Mn(TPP)X to produce a putative high-valent, oxomanganese intermediate (such high-valent oxo complexes are known for Cr(IV) and Cr(V) and have been suggested for analogous Fe(IV) and Mn(V) derivatives).[2] This oxomanganese intermediate in turn oxidizes the alkene to an epoxide. Montanari and co-workers[3] have recently shown that the functionality of such a system does not require that the aqueous phase be at the pH of commercial bleach (i.e , pH 12.8). In fact, it was demonstrated that if the pH is lowered to approximately 9.5, the system turns over more rapidly, even in the absence of the phase-transfer catalyst. This suggests that a neutral chlorine(I) compound is crossing the phase boundary and serves to generate the high-oxidation-state manganese complex. It has been postulated that this neutral chlorine(I) species is HOCl.[3]

In the gas phase, HOCl is in equilibrium with its anhydride, chlorine monoxide (Cl_2O), and water. Relatively large concentrations of Cl_2O can be produced in organic solution (i.e., on the order of 1.5 M in CCl_4).[4,5] It is thus conceivable that Cl_2O is present and acts as the oxidant in the organic phase of the manganese porphyrin catalytic system. Accordingly, we have employed Cl_2O in CCl_4 solution as an oxidant for Mn(TPP)Cl.

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(4) Cady, G. H. *Inorganic Synthesis*; Moeller, T., Ed.; McGraw-Hill: New York, 1957; Vol. V.

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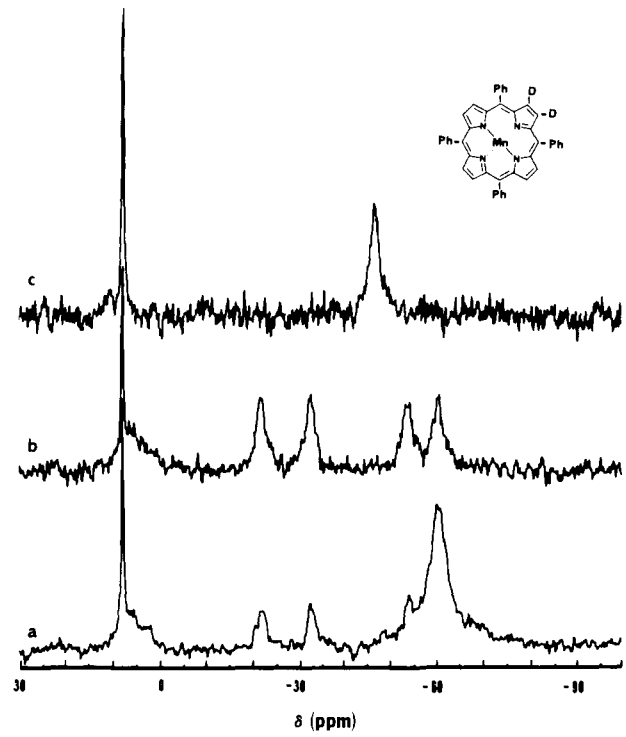

Figure 1. 55-MHz ^2H NMR acquired at −80 °C, $CHClF_2$ solvent. The sharp signal at 7.44 ppm is due to natural abundance $CDClF_2$. (a) Mn(TPP-d_8)Cl treated with Cl_2O at −165 °C and warmed to −80 °C. (b) Sample further warmed to −60 °C and cooled back to −80 °C. (c) Mn(TPP-d_8)X regenerated by addition of cyclohexene to the sample.

Oxidations were carried out at temperatures ranging from −165 to −78 °C in the absence of a substrate in an effort to generate the high-oxidation-state manganese intermediate at concentrations suitable for examination by ^2H NMR spectroscopy. Inasmuch as the low gyromagnetic ratio of the deuterium nucleus results in much narrower NMR lines (relative to proton line widths) for paramagnetic molecules, we have employed (tetraphenylporphinato)manganese(III) deuteriated at the β-pyrrole positions [Mn(TPP-d_8)Cl].[6]

Upon treatment of Mn(TPP-d_8)Cl at low temperature in CH_2Cl_2 or $CHClF_2$ with a CCl_4 solution of Cl_2O or HOCl, a red-brown color is immediately observed. This solution was subsequently examined by low-temperature NMR spectroscopy. The deuterium NMR spectra in Figure 1 (acquired at 55 MHz) indicate the presence of two high-valent species that can be produced concurrently or exclusively. Mixing Mn(TPP-d_8)Cl and Cl_2O in $CHClF_2$ at −165 °C followed by careful warming to −78 °C affords an oxidized (porphinato)manganese complex with a single β-pyrrole NMR signal at −60 ppm. When the solution is warmed to −60 °C in the presence of excess Cl_2O, the first product is quantitatively converted to a second product with no further color change. This second species consistently exhibits four upfield β-pyrrole deuteron NMR peaks of equal area over a range of temperatures, thus suggesting formation of a species that has lost the 4-fold symmetry of the Mn(TPP)X molecule. Conversion of the symmetric to the asymmetric product is irreversible upon cooling the solution back to −80 °C. Through the addition of Cl_2O as a CCl_4 solution to Mn(TPP-d_8)Cl at −78 °C a mixture of the symmetric and asymmetric products is obtained. Although treatment of the product mixture with a limited amount of cyclohexene at −78 °C shows preferential reduction of the symmetric species, both components of the mixture react with cyclohexene to regenerate the Mn(TPP-d_8)X complex with little degradation of the porphyrin. Titration of Mn(TPP-d_8)Cl with Cl_2O indicates that approximately a 2:1 mole ratio (Cl_2O:Mn) is required for formation of the asymmetric species.

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Liquid helium temperature ESR spectroscopy of both oxidized species is indicative of highly anisotropic $S = {}^3/_2$ electronic systems. The general spectral features are typical of high-spin (porphinato)manganese(IV) complexes[7] with signals at $g = 4.0$ and 2.0 for the symmetric species. The asymmetric species exhibits a perturbed spectrum with signals at $g = 6.8$, 4.0, and 2.0. Signals in the $g = 2$ region display six hyperfine lines as a result of splitting by ^{55}Mn in both spectra.

Detectable ESR signals and large NMR chemical shift values for pyrrole deuterons of both symmetric and asymmetric products are consistent with isolated paramagnetic manganese centers. This behavior is to be contrasted with previously characterized μ-oxo(porphinato)manganese(IV) complexes that are magnetically coupled and ESR silent from 4 to 300 K.[8] The strong resemblance between their ESR spectra indicates that conversion of the axially symmetric product to the asymmetric product is not the result of further oxidation of the manganese center. Rather, the appearance of the asymmetric species is concluded to be the consequence of a coordinative interaction between the Mn(IV) complex and the second molar equivalent of Cl_2O or oxidation of a pyrrole nitrogen atom with subsequent coordination of O^{2-} or OCl^-. It has been suggested that the reactive form of highly oxidized hemes may involve oxygen atom insertion between the metal ion and a pyrrole nitrogen atom.[9] An (octaethylporphinato)nickel complex with this structure was recently synthesized and characterized in the solid state by X-ray diffraction.[10] A Mn–pyrrole nitrogen atom linkage through a Cl_2O, OCl^-, or O^{2-} ligand or chlorine(I) attack at a porphyrin methine carbon (producing an isoporphyrin) could account for the observed loss of Mn(TPP) symmetry. Amazingly, the symmetry-breaking porphyrin modification is highly reversible in terms of oxidation and reduction, as demonstrated in Figure 1. Although the preparation and characterization of a redox-reversible ferric isoporphyrin has been reported, its thermal stability is greater than that of the Mn(IV) species observed in this study.[11] The possibility of isoporphyrin formation was nevertheless investigated via ^{13}C NMR spectroscopy of the aysmmetric product containing 60% ^{13}C at the methine carbon. Two methine signals of equal intensity were observed at −14.1 and −63.7 ppm ($T = 193$ K). This result indicates that the asymmetric product bears a vertical plane of symmetry containing two pyrrole nitrogen atoms and the Mn(IV) ion. In addition, the molecule displays no fluxional behavior up to −10 °C, and its visible spectrum at about −50 °C is atypical of isoporphyins (λ_{max} at 406 and 520 nm)[12] and is reminiscent of the dimeric Mn(IV) complexes. Overall, these observations suggest a covalent interaction between the second equivalent of Cl_2O (or a product of its reduction) and a pyrrole nitrogen atom or between two β-pyrrole carbon atoms.[13]

The asymmetry of the high-valent (porphinato)manganese(IV) complex generated by Cl_2O or HOCl oxidation is novel and may provide insight into the mechanism of the catalytic hypochlorite–alkene epoxidation system. Furthermore, the low-temperature observations provide the first experimental evidence for involvement of pyrrole residues in facile transfer of oxidation equivalents.

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Intramolecular Carbonyl Oxide–Ester Cycloaddition. Structure of a Novel Alkoxy Ozonide

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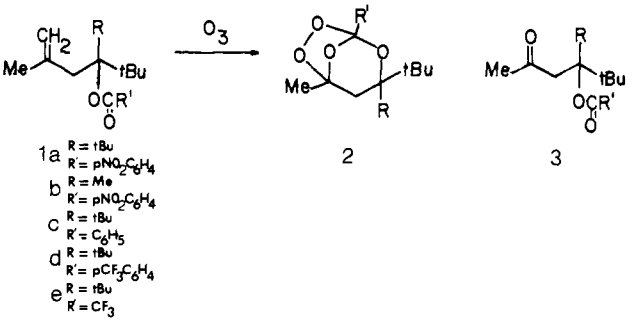
The Criegee mechanism for ozonolysis of alkenes has won general acceptance. Much recent attention has focused on the chemistry of the key carbonyl oxide intermediate, a reactive 1,3-dipolar species.[1] Additions of carbonyl oxides to aldehydes and, to a lesser extent, ketones have been well established for both intermolecular and intramolecular cases.[2] The poor dipolarophilicity of esters was thought to preclude their reaction with carbonyl oxides, but Keul and Kuczkowski have recently shown that, under favorable conditions, intermolecular additions can occur, albeit in low yield.[1a,c] To our knowledge, the corresponding intramolecular reaction has not yet been demonstrated.[3] We report here the first example of intramolecular addition of a carbonyl oxide to a remote ester group, confirmed by X-ray structural determination of the novel alkoxy ozonide product.

Treatment of homoallylic esters **1a** with ozone in dichloromethane at −70 °C, followed by warming to room temperature, allows isolation of the beautifully crystalline bicyclic ozonide **2a** in 86% yield. This compound appears to be quite stable, melting



without decomposition at 123–124.5 °C. A solution of **2a** in CH_2Cl_2 remains unchanged even on prolonged treatment with dimethyl sulfide at room temperature, while quantitative reduction to ketone **3a** is effected with triphenylphosphine. Although **2a** does not appear to be hazardous, normal precautions in handling peroxidic compounds should be followed.

This chemical evidence, taken with spectral and analytical data,[4] was sufficient to assign the structure for **2a**, which was confirmed by single-crystal X-ray diffraction.[5] As illustrated in Figure 1,

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(4) **2a** (3,3-bis(1,1-dimethylethyl)-1-(4-nitrophenyl)-5-methyl-2,6,7,8-tetraoxabicyclo[3.2.1]octane): ^1H NMR δ 8.27 (d, $J = 9$ Hz, 2 H), 7.90 (d, $J = 9$ Hz, 2 H), 2.37 (AB quartet, 2 H), 1.75 (s, 3 H), 1.20 (s, 9 H), 1.08 (s, 9 H); ^{13}C NMR δ 149.0 (s), 139.8 (s), 127.9 (d), 123.4 (d), 115.4 (s), 106.8 (s), 84.9 (s), 43.3 (s), 42.3 (s), 36.8 (t), 29.9 (q), 28.9 (q), 21.3 (q); IR ν 1524, 1349, 1314, 1220, 1063 cm^{-1}; Anal. ($C_{19}H_{27}NO_6$) C, H, N. **2d** (3,3-bis(1,1-dimethylethyl)-5-methyl-1-[4-(trifluoromethyl)phenyl]-2,6,7,8-tetraoxabicyclo[3.2.1], octane): ^1H NMR δ 7.79 (m, 4 H), 2.35 (AB quartet), 1.72 (s, 3 H), 1.18 (s, 9 H), 1.07 (s, 9 H); IR ν 1319, 1131, 1074 cm^{-1}. **2e** (3,3-bis(1,1-dimethylethyl)-5-methyl-1-(trifluoromethyl)-2,6,7,8-tetraoxabicyclo[3.2.1]octane): ^1H NMR δ 2.36 (AB quartet, 2 H), 1.70 (s, 3 H), 1.11 (s, 9 H), 1.09 (s, 9 H); IR ν 1211, 1196, 1135, 1109 cm^{-1}.

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