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.

Acknowledgment. Support from National Science Foundation Grant CHE 83-17451 is gratefully acknowledged.

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(12) Isoporphyrins exhibit characteristic long-wavelength bands; values for the ferric isoporphyrin complex are 344, 450, 805, and 881 nm.[11]

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

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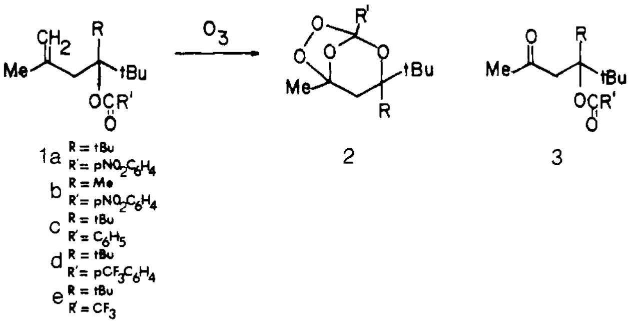
The Criegee mechanism for ozonolysis of alkenes has won general acceptance. Much recent attention has focused on the chemistry of the key carbonyl oxide intermediate, a reactive 1,3-dipolar species.[1] Additions of carbonyl oxides to aldehydes and, to a lesser extent, ketones have been well established 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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(3) Stable, peroxidic products have been obtained from ozonolysis of certain benzofurans. Although these might be alkoxy ozonides resulting from intramolecular carbonyl oxide-ester reaction, the structures have not been established unambiguously. See: (a) Bernatek, E.; Ledaal, T.; Stensvik, S. *Acta Chem. Scand.* **1961**, *15*, 429. (b) Bernatek, E.; Bo, I. *Acta Chem. Scand.* **1959**, *13*, 337 and references therein.

(4) **2a** (3,3-bis(1,1-dimethylethyl)-1-(4-nitrophenyl)-5-methyl-2,6,7,8-tetraoxabicyclo[3.2.1]octane): ^{1}H 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): ^{1}H 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): ^{1}H 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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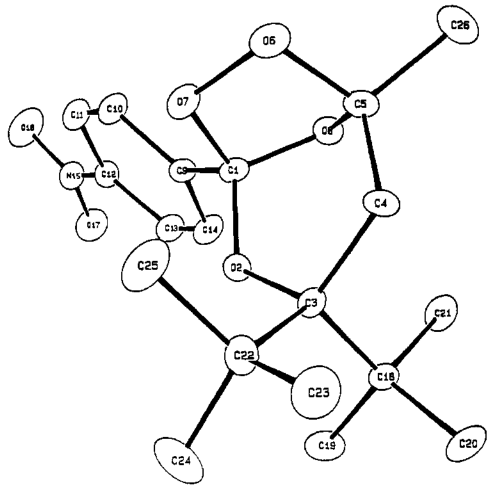

Figure 1. X-ray structure of **2a**. Hydrogen atoms have been omitted for clarity. Selected bond distances (in angstroms): C1–O2 = 1.378 (2), C3–O2 = 1.478 (2), C1–O7 = 1.434 (2), O6–O7 = 1.465 (2), O6–C5 = 1.449 (2). Bond angles: C1–O2–C3 = 119.9 (1)°, C18–C3–C22 = 117.9 (1)°.

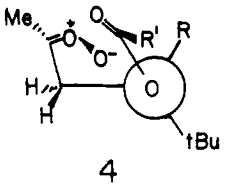

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Figure 2. Conformation of **4**, viewed in Newman projection along the ester oxygen–alkyl bond. When R = Me, a clockwise rotation about this bond is favorable, removing the ester C═O from proximity to the carbonyl oxide.

the dioxane ring of **2a** exists in an envelope conformation with O8 lying 0.81 Å out of the least-squares plane calculated for C1–O2–C3–C4–C5. The flattened ring minimizes transannular interactions of the *gem*-di-*tert*-butyl system with the epoxy or peroxy bridges. The five-membered ring adopts a half-chair conformation with C5 situated 0.26 Å below, and O8 0.46 Å above, the C1–O7–O6 plane. At C1, the axial peroxy bridge sets up an anomeric effect with O2. Indeed, strong differentiation of bond lengths to this center (C1–O2, 1.378 (2) Å, C3–O2, 1.478 (2) Å) confirm this interaction, as established for alkyl pyranosides.[6]

The formation of **2a** is considered to involve cycloaddition of the carbonyl oxide moiety with the ester group within **4a** (Figure 2), which is produced on fragmentation of the primary ozonide of **1a**. Thus, ozonolysis of **1a**, followed by addition of dimethyl sulfide at −70 °C, leads to a 1:1 mixture of **2a** and **3a** in essentially quantitative yield. Since **2a** does not react with dimethyl sulfide, this result requires reductive diversion of a percursor of **2a** to give **3a**. From the Criegee mechanism, only the carbonyl oxide **4a** satisfies this role. Examination of molecular models indicates that only the syn geometry of carbonyl oxide **4** is suitably disposed for intramolecular cycloaddition. Moreover, it is clear that the steric effect of the *gem*-di-*tert*-butyl segment operates to enforce a conformation of **4a** which places the reactive groups in close proximity. In this light, it was of interest to examine a less sterically biased analogue. Ozonolysis of **1b** gave none of the ozonide **2b**. Instead, subsequent reduction (Me_2S) of the crude reaction mixture led to ketone **3b** as the only isolable product. Apparently, replacement of a *tert*-butyl group by methyl allows greater conformational flexibility in the carbonyl oxide **4b**, so that intramolecular cyclization is no longer favored. Indeed, rotation about the ester alkyl oxygen bond (toward R = CH_3 in Figure 2) moves the ester group out of alignment with the carbonyl oxide, so that intermolecular reaction of the carbonyl oxide with, for example, the cognate formaldehyde, can compete successfully.

Preliminary studies indicate a strong electronic influence on the cyclization. Ozonolysis of benzoate ester **1c** gave quite cleanly the ketone **3c**—no ozonide product was detected. Since **4c** is subject to the same steric constraints as **4a**, the change in products reflects the decreased dipolarophilicity of the benzoate carbonyl group as compared to the *p*-nitrobenzoate.[7] Activation by an electron-withdrawing group is again manifested in **1d**, which leads to a 1:1 mixture of **2d**[4] and **3d**. The reaction of trifluoroacetate **1e** gives a complex mixture of products, from which **2e**[4] can be isolated in 18% yield. Thus, these early experiments establish rather strict steric and electronic requirements for the intramolecular carbonyl oxide–ester cycloaddition.

Acknowledgment. W.B. thanks the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this work.

Supplementary Material Available: Tables of positional parameters, thermal parameters, interatomic distances, interatomic angles, and dihedral angles for non-hydrogen atoms (7 pages). Ordering information is given on any current masthead page.

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(5) Data were collected from a 0.3 × 0.3 × 0.4 mm crystal with an Enraf-Nonius CAD4 diffractometer. $C_{19}H_{27}NO_6$ crystallizes from methanol in space group $P2_1/c$, $a = 7.624$ (1) Å, $b = 12.778$ (3) Å, $c = 19.210$ (7) Å, $\beta = 92.50$ (2)°, $V = 1869$ (2) Å^3, $z = 4$, $d_{calcd} = 1.296$. The structure was solved (1881 reflections, $I > 2\sigma$) by direct methods and refined to $R = 0.042$ ($R_w = 0.056$).

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An Example of Axial Selectivity in Nucleophilic Additions to Cyclohexanones and Cyclohexenones

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Controlling the stereochemistry of additions of carbanions to cyclic ketones remains an important contemporary problem. The concept that steric effects control such reactions leads to the normal introduction of nucleophiles in an equatorial orientation in the case of six-membered ring ketones.[1,2] A recent interesting variation using a bulky aluminum alkyl directed the nucleophile in an axial fashion due to the preference to place the even bulkier aluminum alkoxide equatorially.[3] On the other hand, orbital distortion arguments[4] and consideration of torsional effects[5] associated with the addition suggest that there may exist an intrinsic bias for axial attack—a bias which is frequently overwhelmed by

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(1) For some recent examples of enhancing equatorial attack, see: Mac Donald, T. L.; Still, W. C. *J. Am. Chem. Soc.* **1975**, *97*, 5280. Ashby, E. C.; Noding, S. A. *J. Org. Chem.* **1979**, *44*, 4371. Weidmann, B.; Maycock, C. D.; Seebach, D. *Helv. Chim. Acta* **1981**, *64*, 1552. Reetz, M. T. *Top. Curr. Chem.* **1982**, *106*, 1.

(2) For an exception in the case of a 1,3-dioxan-5-one, see: Kobayashi, Y. M.; Lambrecht, J.; Jochims, J. C.; Burkert, U. *Chem. Ber.* **1978**, *111*, 3442.

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