Supplementary Material Available: Tables and computer printout giving details of the structural study are available (39 pages). Ordering information is given on any current masthead page.

Intramolecular Oxygen Atom Transfer from a Carbonyl Oxide Moiety to a Methoxyvinyl Group

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Several recent studies have investigated the transfer of an oxygen atom from carbonyl oxide intermediates[1] as models for certain reactions catalyzed by monooxygenase enzymes.[2] Carbonyl oxides have for example been shown to function as nucleophilic oxygen-transfer agents in the oxygenation of sulfoxides and electron-deficient olefins.[1a,b] We report herein that under certain conditions, however, electron-rich olefins can also be efficiently oxidized.

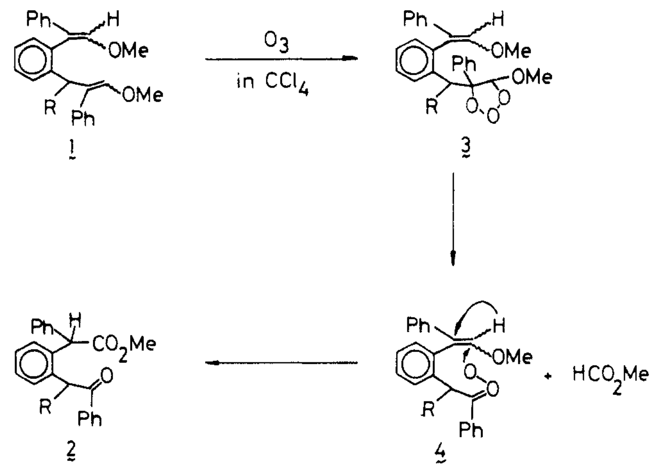
The reaction of diene **1a**[3] with 1 equiv of ozone in carbon tetrachloride at 0 °C afforded the keto ester **2a**[4] (62% yield) as the sole isolable product; unreacted starting material **1a** (35%) was also recovered. Treatment of **1a** with 2 mol equiv of ozone resulted in quantitative formation of the keto ester **2a**. Similar trends were observed for the reaction of diene **1b** (Scheme I).

To explain the exclusive formation of the keto ester **2**, two mechanisms can be postulated. On the one hand, selective attack of ozone at the less-hindered double bond of diene **1** would afford the primary ozonide **3** which could preferentially break down to the carbonyl oxide **4**.[5] Subsequent intramolecular oxygen atom transfer, followed by a 1,2-hydride migration, would produce the observed keto ester **2**. Examination of molecular models suggest that the terminal oxygen of the postulated carbonyl oxide moiety could adopt a favorable conformation for the intramolecular oxygen transfer to the adjacent methoxyvinyl group. Alternatively a direct intramolecular transfer of oxygen from the primary ozonide **3**, followed by a sequence similar to that outlined above, is plausible.

To differentiate between these mechanistic alternatives, the reaction of diene **1a** with 1 mol equiv of ozone was undertaken in methanol in the presence of 10 mol equiv of dimethyl sulfide. Although methanol readily scavanges carbonyl oxide to produce methoxy hydroperoxide, it is not known to interfere significantly with the intrinsic chemistry of primary ozonide.[1d,6] It was, therefore, anticipated that the product composition from the above reaction could provide an insight into the oxygen-transfer mechanism. The reaction product consisted of a mixture of keto ester **2a** (12%), keto olefin **6a** (24%),[7] and diketone **7a** (6%); some starting material (36%) was also recovered.[8] The formation of the keto olefin **6a** and the diketone **7a** with a concomitant decrease in the yield of the keto ester **2a** is more consistent with reaction proceeding via intramolecular oxygen transfer from the carbonyl oxide intermediate **4a**[9] rather than the 1,2,3-trioxane moiety in **3a**. In methanol, trapping of carbonyl oxide **4a** competes strongly with the oxygen-transfer process. Reduction of the hydroperoxide **5a**, thus formed, by dimethyl sulfide affords the keto olefin **6a**. Further reaction of the keto olefin **6a** ultimately leads to the formation of the diketone **7a** (Scheme II).

Since the formation of the keto ester **2a** is not completely suppressed in methanol, the intramolecular oxygen transfer must be extremely fast. Consistent with this, the ozonolysis of diene

Scheme I



a; R=H, b; R=Me

(1) (a) Pryor, W. A.; Govindan, C. K. *J. Am. Chem. Soc.* **1981**, *103*, 7681. (b) Sawaki, Y.; Kato, H.; Ogata, Y. *Ibid.* **1981**, *103*, 3832. (c) Hinrichs, T. A.; Ramachandran, V.; Murray, R. W. *Ibid.* **1979**, *101*, 1282. (d) Keay, R. F.; Hamilton, G. A. *Ibid.* **1975**, *97*, 6876. (e) Adam, W.; Haas, W.; Sieker, G. *Ibid.* **1984**, *106*, 5020. (f) Jeyaraman, R.; Murray, R. W. *Ibid.* **1984**, *106*, 2642. (g) Murray, R. W.; Jeyaraman, R. *J. Org. Chem.* **1985**, *50*, 2847.

(2) Hamilton, G. A. In *Molecular Mechanism of Oxygen Activation*; Hayaishi, O., Ed.; Academic Press: New York, 1974; p 405.

(3) The diolefin **1a** was an oil: ^{1}H NMR δ 3.30 (s, 2 H), 3.47 (s, 3 H), 3.63 (s, 3 H), 5.73 (s, 1 H), 5.97 (s, 1 H), 6.63–7.47 (m, 14 H); IR 1640 cm^{-1}. Anal. ($C_{25}H_{24}O_2$) C, H. The diolefin **1b** was a solid: mp 95 °C (from methanol); ^{1}H NMR δ 1.37 (d, J = 7.5 Hz, 3 H), 3.54 (s, 3 H), 3.63 (s, 3 H), 4.19 (q, J = 7.5 Hz, 1 H), 5.88 (s, 1 H), 5.91 (s, 1 H), 6.80–7.49 (m, 14 H); IR 1640 cm^{-1}; mass spectrum, *m/e* 370 (M$^+$). Anal. ($C_{26}H_{26}O_2$) C, H.

(4) The keto ester **2a** was an oil: ^{1}H NMR δ 3.63 (s, 3 H), 4.17 (s, 2 H), 5.10 (s, 1 H), 6.66–8.10 (m, 14 H); IR 1735, 1690 cm^{-1}; mass spectrum, *m/e* 344 (M$^+$). Anal. ($C_{23}H_{20}O_3$) C, H. The keto ester **2b** was a solid: mp 143 °C (from benzene–hexane); ^{1}H NMR δ 1.49 (d, J = 6.0 Hz, 3 H), 3.68 (s, 3 H), 4.67 (q, J = 6.0 Hz, 1 H), 5.46 (s, 1 H), 6.59–7.94 (m, 14 H); IR 1740, 1690 cm^{-1}; mass spectrum, *m/e* 358 (M$^+$). Anal. ($C_{24}H_{22}O_3$) C, H.

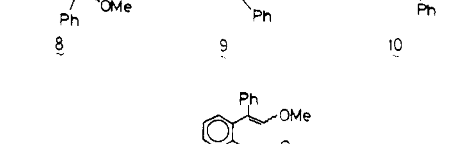
(5) (a) Keul, H.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1984**, *106*, 5370. (b) Keul, H.; Choi, H.; Kuczkowski, R. L. *J. Org. Chem.* **1985**, *50*, 3365. Kuczkowski and co-workers have demonstrated that the esters, produced by ozonolysis of vinyl ethers, are generally very poor dipolarophiles toward carbonyl oxides, and, consequently, the carbonyl oxides formed from the ozonolysis of vinyl ethers show their intrinsic characteristics.

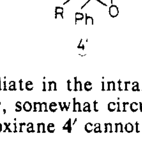
(6) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1978; Vol. 1; 1982; Vol. 2.

(7) The keto olefin **6a** was an oil: ^{1}H NMR δ 3.59 (s, 3 H), 3.95 (s, 2 H), 6.05 (s, 1 H), 6.81–7.83 (m, 14 H); IR 1690, 1640, 1240 cm^{-1}; mass spectrum, *m/e* 328 (M$^+$). Anal. ($C_{23}H_{20}O_2$) C, H. The keto olefin **6b** was an oil: ^{1}H NMR δ 1.19 (d, J = 6.0 Hz, 3 H), 3.63 (s, 3 H), 4.60 (q, J = 6.0 Hz, 1 H), 6.03 (s, 1 H), 6.65–7.78 (m, 14 H); IR 1690, 1640, 1240 cm^{-1}. Anal. ($C_{24}H_{22}O_2$) C, H.

(8) The reaction of diene **1a** in methanol in the absence of dimethyl sulfide resulted in the formation of a complex mixture of products. Although we failed to isolate the expected methoxy hydroperoxide **5a** in a pure state, the following facts may support the formation of **5a**. (a) The ^{1}H NMR spectra of the crude products showed the existence of some hydroperoxide [δ around 9.0 (br s, H–D exchange in D_2O] and (b) treatment of the products with excess of dimethyl sulfide gave keto olefin **6a** in 27% yield, together with **2a** (9%) and **7a** (18%); some starting material (22%) was also recovered.

(9) As an alternative intermediate in intramolecular oxygen transfer, the isomeric dioxirane **4′** would be considered.[1e–g] Since (a) the composition of the products obtained from the ozonolysis of diene **1** was a marked function of the solvent and (b) the ozonolysis of the relevant keto olefin **8** was found to proceed mainly by the carbonyl oxide **9** to provide 2,3-diphenylindene ozonide (**10**) in good yield (eq 1), we prefer to consider that the carbonyl oxide





4 is the more likely intermediate in the intramolecular oxygen transfer.[1g] These evidences are, however, somewhat circumstantial, and, therefore, a partial contribution of the dioxirane **4′** cannot be rigorously excluded.

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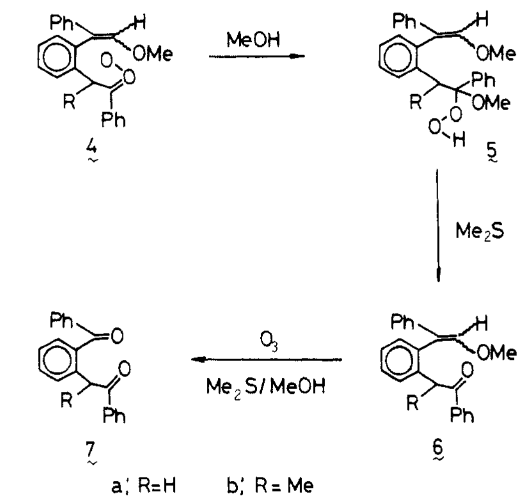
Scheme II



1a in carbon tetrachloride was not significantly perturbed by the presence of dimethyl sulfide or dimethyl sulfoxide which are well-known scavangers of carbonyl oxides.[1b,e]

From our preliminary work, it appears that, in favorable cases such as the intermediate **4**, the intramolecular oxygen transfer can be a highly efficient process. This is in marked contrast to the generally accepted view that carbonyl oxides are poor reagents for the epoxidation of electron-rich olefins.[1b,c] On the other hand, intermolecular oxygen transfer from nucleophilic carbonyl oxides is very slow and hence a variety of other processes including dimerization[6] and rearrangement[10] tend to predominate as, for example, in the ozonolysis of 1,1-diphenyl-2-methoxyethylene and 1-phenyl-2-methoxyethylene.[11]

Acknowledgment. We thank Dr. Kevin J. McCullough of Heriot-Watt University and Prof. Karl Griesbaum of Universität Karlsruhe for useful discussions.

(10) Sawaki, Y.; Ishiguro, K. *Tetrahedron Lett.* **1984**, *25*, 1487.
(11) The detail will be published elsewhere.

Structural Consequence of a Hydrophobic Environment on Phosphorus Dioxy Monoanions and the Potential Application to Structural Changes in Nucleic Acids

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As part of our research[1] on ionic interactions with phosphates we have begun to use $H_2PO_2^-$, phosphinate ion, to investigate structural changes in the $>PO_2^-$ group as a result of change in local environment.[2] The experimental probe is the one-bond P-H coupling constant, $^1J_{PH}$. One-bond C-H couplings are dependent primarily upon percent s character in the C-H bond and this determines the magnitude of the coupling constant.[3] The same principle appears dominant in $^1J_{PH}$. An increase or decrease in $^1J_{PH}$ in $H_2PO_2^-$ indicates more or less s character in the P-H bonds, caused by a smaller or larger O-P-O angle, respectively.

We have found previously that small metal cations increase $^1J_{PH}$ in $H_2PO_2^-$; guanidinium ions and large metal ions such as Ba^{2+} cause small changes in $^1J_{PH}$ whereas $^1J_{PH}$ increases substantially with metal cations with small ionic radii.[2] Therefore, we concluded that the effects are due to O-P-O angle contraction as would be expected from chelation. For complete association, ΔJ = 14 Hz for Li^+, 18 Hz for Mg^{2+}, and 26 Hz for Zn^{2+} but only 4.5 Hz for Ba^{2+} and no significant change for guanidinium ion which can associate to $H_2PO_2^-$ with no effect on bond angle.[2,4,5] In this paper we report results which appear to reflect the structural changes in $H_2PO_2^-$ as the environment becomes hydrophobic.

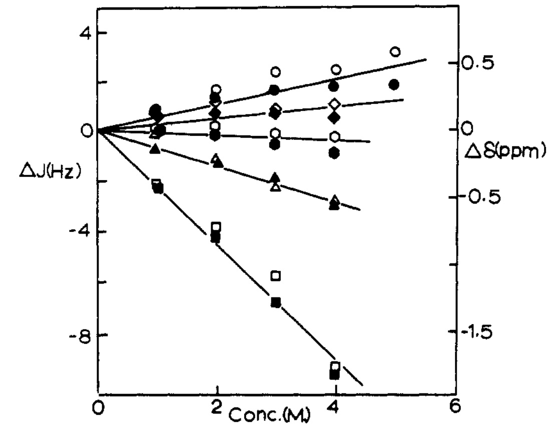

Figure 1. Correlations in change in coupling constant and change in chemical shift with the concentration of ammonium chlorides: ○ = NH_4Cl; ◇ = CH_3NH_3Cl; ○ = $(CH_3)_2NH_2Cl$; △ = $(CH_3)_3NHCl$; □ = $(CH_3)_4NCl$. The closed figures represent data for chemical shifts and the open figures represent data for coupling constants.

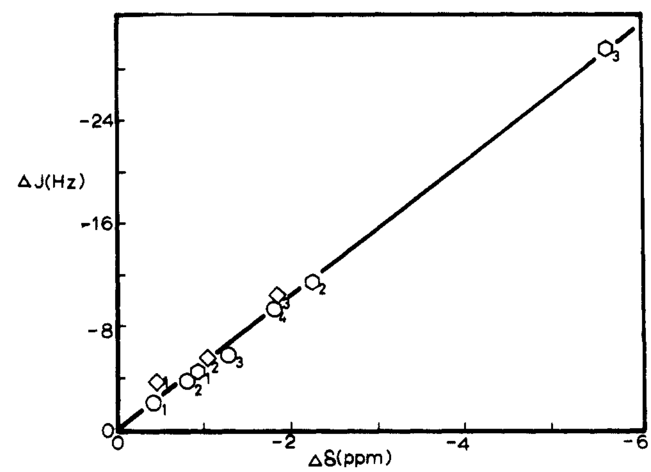

Figure 2. Correlation of chemical shift with coupling constant for tetraalkylammonium chlorides: ○ = $(CH_3)_4NCl$; ◇ = $(C_2H_5)_4NCl$; ○ = $(n\text{-}C_4H_9)_4NCl$. The subscripts represent the concentrations of tetraalkylammonium chlorides for each data point.

Samples were prepared by adding a weighed amount of ammonium salt to about 1 mL of D_2O plus 0.2 mL of stock $H_2PO_2^-$ (0.2 M) which had been prepared by neutralizing reagent grade H_2PO_2H with tetramethylammonium hydroxide. The sample was brought to a volume of 2 mL and the pH was taken to ensure that the solution was near pH 7.0. ^{31}P NMR spectra were taken on a Varian XL-200 spectrometer. The frequencies were obtained from the printout of the stored digital data. Couplings should be accurate to 0.1 Hz. With no added ammonium salts, $H_2PO_2^-$ (0.022 M) gives $^1J_{PH}$ = 518.4 Hz.

After observing a decrease in $^1J_{PH}$ on addition of tetramethylammonium chloride to aqueous solutions of $H_2PO_2^-$,[2] we investigated the effect of substitution of methyl groups by hydrogens with the results shown in Figure 1. The fanlike distribution of data demonstrates a progressive change in both coupling constants and chemical shifts which are correlated for each ammonium chloride. The more methylated ammonium ions decrease the coupling constant and shield the ^{31}P nucleus; $^+NH_4$ causes increases in the coupling constant and deshielding.[1]

(1) Haake, P.; Prigodich, R. V. *Inorg. Chem.* **1984**, *23*, 457 and references therein; **1985**, *24*, 89; *J. Org. Chem.* **1984**, *49*, 2090.
(2) Spitz, F. R.; Cabral, J.; Haake, P. *J. Am. Chem. Soc.* **1986**, *108*, 2802.
(3) Muller, N.; Pritchard, D. *J. Chem. Phys.* **1959**, *31*, 768, 1471.
(4) Haas, T. E.; Gillman, H. D. *Inorg. Chem.* **1968**, *7*, 2051.
(5) Springs, B.; Haake, P. *Bioorg. Chem.* **1977**, *6*, 181; *Tetrahedron Lett.* **1977**, 3223.

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