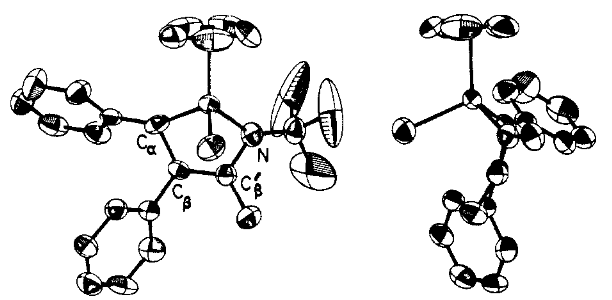

Figure 1. ORTEP plots (50% probability ellipsoids) of $CpTa(Me)(CPhCPhCMeN\ t\text{-}Bu)$ (3). Bond distances: Ta–C_α, 1.98 (1); Ta–N, 1.98 (1); C_α–C_β, 1.48 (2); C_β–C'_β, 1.39 (2); C'_β–N, 1.40 (1) Å. The methyl groups in the *tert*-butyl group have been deleted from the drawing on the right.

$(ArO)_2Zr(NRCHCHNR)$[11] and $Cp^*{}_2Zr(OCHCHO)$.[12] The ring folding in the latter has also been interpreted with the EHMO model.[12]

Compounds **1–3** have the requisite structures to be acetylene polymerization catalysts.[13] In fact, terminal acetylenes are readily polymerized by these and related compounds and these results will be communicated in due course.[14]

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE-8305235). J.R. thanks the Department of Chemistry for Paul Bagley and Walter R. Yates Fellowships and the U.S.-Spanish Joint Committee for Cultural and Educational Cooperation for a Fellowship.

Supplementary Material Available: Table of ^1H and ^{13}C NMR spectral data for **1–3**, tables of crystal and data collection statistics, fractional atomic coordinates, thermal parameters, bond distances, and bond angles, and ORTEP drawings for **2** and **3** (13 pages). Ordering information is given on any current masthead page.

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(11) Latesky, S. L.; McMullen, A. K.; Niccalai, G. P.; Rothwell, I. P.; Huffman, J. C. *Organometallics* **1985**, *4*, 1896.

(12) Hofmann, P.; Frede, M.; Stauffert, P.; Lasser, W.; Thewalt, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 712.

(13) Katz, T. J.; Hacker, S. M.; Kendrick, R. D.; Yannoni, C. S. *J. Am. Chem. Soc.* **1985**, *107*, 2182.

(14) Curtis, M. D.; Kwon, D.-K., unpublished results.

On the Mechanism of the Homogeneous Catalytic Hydrogenation Using Anion-Promoted Metal Clusters

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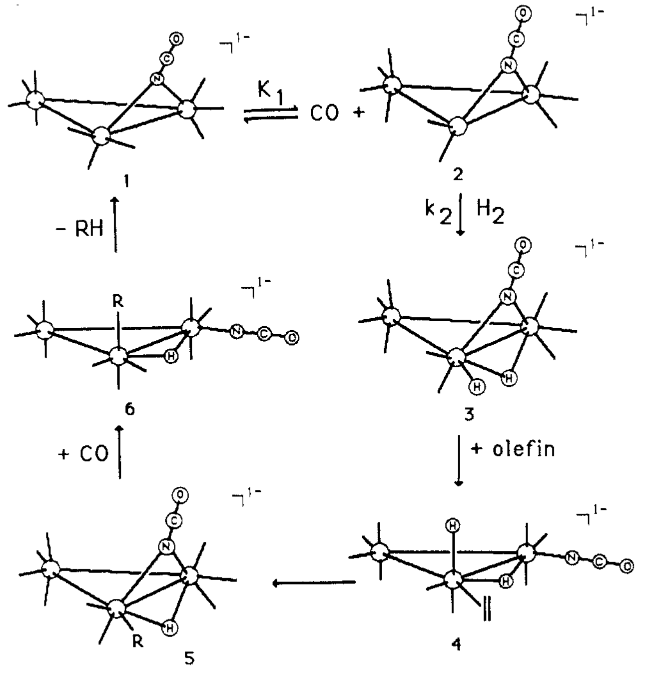
Received March 10, 1986

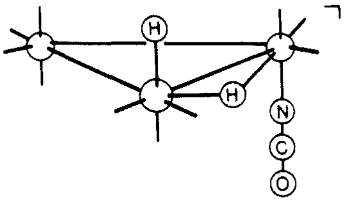
We recently reported[2] that anions, in particular isocyanate, were effective in converting normally unreactive $Ru_3(CO)_{12}$ into an active catalyst (5–6 turnovers/min under ambient conditions) for alkene hydrogenation. While both spectroscopic and kinetic evidence supported a catalytic cycle involving an intact ruthenium triangle, no intermediates were isolated. With the hope of isolating such species, we turned to the osmium system and have found a rich chemistry that is reported here.

The scenario posed in Scheme I was based upon the earlier studies which established that $[Ru_3(NCO)(CO)_{10}]^{1-}$ was the active catalyst. Using the compounds formulated in this scheme as targets, we initially synthesized the anionic osmium isocyanato clusters using the same reaction found successful in the ruthenium chemistry.[3] $PPN(N_3)$ (where PPN = bis(triphenylphosphine)iminium cation) quantitatively converts $Os_3(CO)_{12}$ to $PPN[Os_3(NCO)(CO)_{11}]$[4] in THF, and the infrared spectrum of this compound indicated all the ligands were terminally bound to the metals. During 3.5 h in refluxing THF, $[Os_3(NCO)(CO)_{11}]^{1-}$ smoothly converted into $[Os_3(NCO)(CO)_{10}]^{1-}$ (**1** in Scheme I). While this cluster could not be isolated as crystalline material, the infrared spectrum in the carbonyl region was nearly superimposable upon that of the structurally characterized cluster $[Os_3(NO)(CO)_{10}]^{1-}$.[5] The shift from 2248 to 2217 cm^{-1} for the isocyanate stretch in going from $[Os_3(NCO)(CO)_{11}]^{1-}$ to $[Os_3(NCO)(CO)_{10}]^{1-}$ is characteristic for the conversion of a terminal to bridging isocyanate ligand.[3] The only difference between $[Os_3(NCO)(CO)_{10}]^{1-}$ and the ruthenium analogue is the absence of the semitriply bridging carbonyl.

Scheme I



Molecular hydrogen reacts with $[Os_3(NCO)(CO)_{11}]^{1-}$ in a sealed tube at 50 psig and 52 °C to form $[H_2Os_3(NCO)(CO)_{10}]^{1-}$.[6] The independent synthesis of this cluster involves the straightforward extension of the known chemistry of $H_2Os_3(CO)_{10}$.[7-10] This neutral, unsaturated cluster reacts with PPN(NCO) to give $[H_2Os_3(NCO)(CO)_{10}]^{1-}$ whose structure[11] shown below is similar



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(1) Fellow of the Alfred P. Sloan Foundation 1983–1985.

(2) Zuffa, J. L.; Blohm, M. L.; Gladfelter, W. L. *J. Am. Chem. Soc.* **1986**, *108*, 552–553.

(3) Fjare, D. E.; Jensen, J. A.; Gladfelter, W. L. *Inorg. Chem.* **1983**, *22*, 1774–1780.

(4) Characterization of $PPN[Os_3(NCO)(CO)_{11}]$. Anal. Calcd: C, 39.51; H, 2.07; N, 1.92. Found: C, 39.55; H, 2.16; N, 1.83. IR(THF): ν_{NCO} 2248 cm^{-1} (br), ν_{CO} 2098 w, 2043 m, 2031 s, 2006 vs, 1994 m (sh), 1984 w (sh), 1961 m, 1938 w (sh) cm^{-1}.

(5) Johnson, B. F. G.; Lewis, J.; Mace, J. M.; Raithby, P. R.; Stevens, R. E.; Gladfelter, W. L. *Inorg. Chem.* **1984**, *23*, 1600–1603.

(6) Characterization of $PPN[H_2Os_3(NCO)(CO)_{10}]$. Anal. Calcd.: C, 39.39; H, 2.25; N, 1.95. Found: C, 39.53; H, 2.30; N, 1.88. IR(THF): ν_{NCO} 2252 cm^{-1} (br), ν_{CO} 2091 w, 2056 s, 2041 m, 2009 vs, 1994 vs, 1963 m, 1945 w, 1928 w (sh) cm^{-1}. ^1H NMR ($CDCl_3$): δ (−76 °C) −10.16 (d, J = 3.75 Hz, 1 H), −16.61 (d, J = 3.75 Hz, 1 H). 17% of a second isomer is observable in the ^1H NMR spectrum: (23 °C) −8.27 (s, 1 H), −16.20 (s, 1 H). Interconversion between the isomers is slow on the NMR time scale but fast on the laboratory time scale.

(7) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* **1975**, *88*, C21–C23.

(8) Shapley, J. R.; Keister, J. R.; Churchill, M. R.; DeBoer, B. G. *J. Am. Chem. Soc.* **1975**, *97*, 4145–4146.

(9) Keister, J. B.; Shapley, J. R. *Inorg. Chem.* **1982**, *21*, 3304–3310.

(10) Adams, R. D.; Golembeski, N. M. *Inorg. Chem.* **1979**, *18*, 1909–1912.

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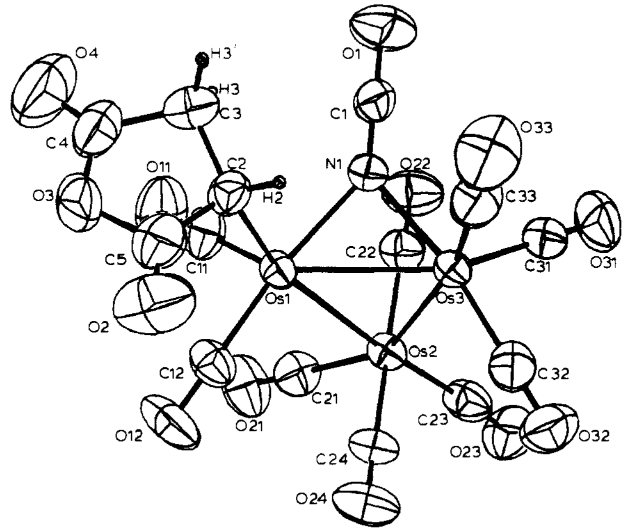

Figure 1. View of $[HOs_3(NCO)(succinoyl)(CO)_9]^{1-}$ showing the atom labels. The hydride ligand was not found, and its proposed location is given by the intercept of the Os1–C11 and Os3–C31 vectors. Selected distances (Å): Os1–Os2 = 2.838 (1); Os1–Os3 = 2.817 (1); Os2–Os3 = 2.844 (1); Os1–N1 = 2.133 (6); Os3–N1 = 2.152 (6); Os1–C2 = 2.200 (6); N1–C1 = 1.178 (9); C1–O1 = 1.191 (9); C2–C3 = 1.50 (1); C2–C5 = 1.45 (1). Selected angles (deg): Os1–C2–C3 = 114.0 (5); Os1–C2–C5 = 110.1 (5); Os1–N1–Os3 = 82.2 (2); Os1–N1–C1 = 142.6 (6); Os3–N1–C1 = 134.7 (6); N1–Os1–C2 = 83.5 (2); N1–Os1–C12 = 171.6 (3); N1–Os3–C32 = 170.0 (3); C22–Os2–C24 = 167.0 (3); N1–C1–O1 = 178 (1).

to the structurally characterized neutral analogue $H_2Os_3(CO)_{10}(CN\text{-}t\text{-}Bu)$.[10] This structure not only provides an example of a dihydride, but it also serves as a model for the possible structure of the alkyl-containing cluster, $[HOs_3(NCO)(R)(CO)_{10}]^{1-}$ (**6**).

If $[H_2Os_3(NCO)(CO)_{10}]^{1-}$ is heated in refluxing THF under N_2, a new, labile species containing a bridging isocyanate is formed. Since this reverts rapidly back to $[H_2Os_3(NCO)(CO)_{10}]^{1-}$ under a CO atmosphere, we suggest that the formula is $[H_2Os_3(NCO)(CO)_9]^{1-}$ (**3**).

The strategy for examining the olefin activation step was based on the successful study by Keister and Shapley of the reactivity of $H_2Os_3(CO)_{10}$.[12] By employing an α,β-unsaturated ester as the olefin they found that the metal alkyl was stabilized enough through a bridging interaction to allow isolation. The reaction of maleic anhydride[13] with $[H_2Os_3(NCO)(CO)_{10}]^{1-}$ occurs quantitatively at 25 °C in 5.5 h to give a new cluster containing a σ-bound succinoyl anhydride ligand.[14] *The structural characterization*[15] *(Figure 1) of this alkyl represents the first such characterization of a terminally bound alkyl ligand on a metal carbonyl cluster.* The hydride ligand, which was not directly observed, is almost certainly bridging Os1–Os3 forming a stable edge double-bridged trimer that is very common for ruthenium and osmium triangular clusters.[16] The CO inhibition of this olefin addition is consistent with the proposed intermediacy of $[H_2Os_3(NCO)(CO)_9]^{1-}$ (**3**). The formula of the alkyl–hydride cluster is similar to that of the dihydride and as such sheds some light on the possible structure of **3**. Since both the carbon atom C2 and the cluster itself are chiral centers, we examined the ^1H NMR spectrum for the presence of the other diastereomer. Both the aliphatic and hydride regions exhibited peaks due to the second diastereomer, and integration revealed a 6:1 ratio of the two diastereomers.

The mechanism of the olefin activation was further probed by studying the reaction of $[D_2Os_3(NCO)(CO)_{10}]^{1-}$ with maleic anhydride. The ^1H and ^2H NMR spectra indicated that only the position cis to the osmium was enriched. While cis stereochemistry is required for a migratory insertion of a coordinated olefin into a M–H bond,[17] other mechanisms do not necessarily occur stereospecifically. One such mechanism could involve hydride transfer from the anionic cluster to the Michael acceptor forming the enolate ion. If the enolate were long-lived enough to flip relative to the cluster, a mixture of both cis and trans isomers would be observed. This demonstration of the likely involvement of a coordinated olefin is the basis for the olefin–hydride structure **4**.

The final step proposed in Scheme I is the reductive elimination of the C–H bond. For the cluster $[HOs_3(NCO)(R)(CO)_9]^{1-}$ (**5**), where R = succinoyl anhydride, succinic anhydride is observed after 3 h at 75 °C in THF under a CO atmosphere (50 psig). The starting cluster, $[Os_3(NCO)(CO)_{11}]^{1-}$, is also recovered in 72% recrystallized yield from this reaction. While no intermediate CO adduct is observed in this reaction, a species such as **6** might be the immediate precursor to reductive elimination.

In summary, the osmium cluster chemistry presented here provides evidence for the intermediates proposed in Scheme I. While less active than the ruthenium system, these isocyanate-promoted osmium clusters also catalyze the hydrogenation of olefins.[18] Our current theory on the origin of the activating influence of the anions has two parts. First, the ability of the isocyanate to exist as a three-electron donor bridging or one-electron donor terminal ligand, depending on the cluster electron count, must help maintain similar relative energies of the intermediates. Second, the rate of initial CO dissociation may be increased by a transition-state stabilization analogous to the process defined as cis labilization by Brown and co-workers.[19] From their studies, the two best cis-labilizing ligands were found to be Cl^- and NCO^-. These catalytic studies along with the previous reports of CO substitution on $Ru_3(CO)_{12}$[20] underscore the importance of the halide or pseudohalide labilization process in metal carbonyl cluster chemistry.

Acknowledgment. This research was supported by the National Science Foundation (CHE-8410999).

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(11) The structure of $PPN[H_2Os_3(NCO)(CO)_{10}]$ was established unambiguously by a single-crystal X-ray crystallographic study which will be reported separately.

(12) Keister, J. B.; Shapley, J. R. *J. Am. Chem. Soc.* **1976**, *98*, 1056–1057.

(13) Dimethyl and diethyl fumarate, methyl and phenyl acrylate, and acrylonitrile undergo the same reaction.

(14) Characterization of $PPN[HOs_3(NCO)(CO)_9[\overline{CHCH_2C(O)OC}(O)]]$. Anal. Calcd: C, 39.95; H, 2.28; N, 1.86. Found: C, 39.81; H, 2.36; N, 1.97. IR(THF): ν_{NCO} 2216 cm^{-1}, ν_{CO} 2081 m, 2042 vs, 1997 vs, 1979 s (sh), 1950 w (sh), 1920 w cm^{-1}, $\nu_{CO(acyl)}$ 1820 w, 1757 w cm^{-1}. ^1H NMR ($CDCl_3$): (major diastereomer) δ −12.39 (s, 1 H), 2.90 (d, J = 7.7 Hz, 1 H), 3.19 (d, J = 18.8 Hz, 1 H), 3.73 (d of d, J = 7.8, 18.8 Hz, 1 H), (minor diastereomer) −12.75 (s, 1 H), 2.55 (d, J = 7.7 Hz, 1 H), 3.37 (d, J = 18.7 Hz, 1 H), 3.63 (d of d, J = 7.9, 19.1 Hz).

(15) X-ray diffraction data for $PPN[HOs_3(NCO)(CO)_9[\overline{CHCH_2C(O)OC}(O)]]$: crystal dimensions = 0.20 × 0.40 × 0.45 mm; crystal system = triclinic; space group = $P\bar{1}$; a = 14.725 (5) Å, b = 18.595 (5) Å, c = 9.868 (6) Å, α = 72.60 (4)°, β = 76.61 (4)°, γ = 86.33 (3)°; Z = 2; formula weight = 1503.4 g/mol; absorption coefficient = 77.3 cm^{-1}; diffractometer = Enraf-Nonius CAD4; radiation = graphite-monochromatized Mo Kα; scan range = 0–48°; reflections collected = 7830, 6591 with $F_o > 1.0\sigma(F_o)$; d(calcd) = 1.99 g/cm^{-3}; R = 0.038; R_w = 0.048.

(16) Bruce, M. I. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Elmsford, NY, 1982; Vol IV.

(17) James, B. R. *Homogeneous Catalysis*; Wiley: New York, 1973.

(18) The hydrogenation of maleic anhydride can be catalyzed by $PPN[Os_3(NCO)(CO)_{11}]$ at 60 °C and 50 psig of H_2. Three equivalents of maleic anhydride were converted to succinic anhydride after 24 h. Spectral data indicated the major species present at the end of the catalysis was $PPN[HOs_3(NCO)(CO)_9[\overline{CHCH_2C(O)OC}(O)]]$. Eight equivalents of 3,3-dimethylbutene were hydrogenated by $PPN[Os_3(NCO)(CO)_{11}]$ at 78 °C and 50 psig of H_2 in 24 h.

(19) Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 3380–3385. Atwood, J. D.; Brown, T. L. *J. Am. Chem. Soc.* **1976**, *98*, 3155–3159. Atwood, J. D.; Brown, T. L. *Ibid.* 3160–3166. Cohen, M. A.; Brown, T. L. *Inorg. Chem.* **1976**, *15*, 1417–1423. Lichtenberger, D. L.; Brown T. L. *J. Am. Chem. Soc.* **1978**, *100*, 366–373. Bellus, P. A.; Brown, T. L. *Inorg. Chem.* **1978**, *17*, 3726–3727.

(20) Lavigne, G.; Kaesz, H. D. *J. Am. Chem. Soc.* **1984**, *106*, 4647–4648. Anstock, M.; Taube, D.; Gross, D. C.; Ford, P. C. *J. Am. Chem. Soc.* **1984**, *106*, 3696–3697. Darensbourg, D. J.; Gray, R. L.; Pala, M. *Organometallics* **1984**, *3*, 1928–1930.

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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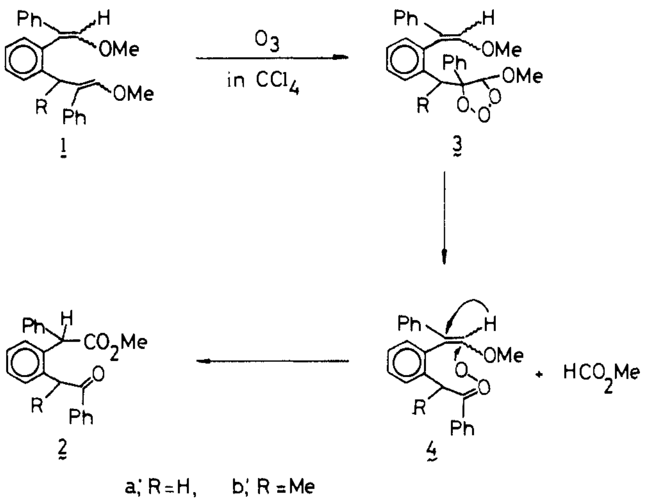
Several recent studies have investigated the transfer of an oxygen atom from carbonyl oxide intermediates[1] as models for certain reactions catalyzed by monooxygenase enzymes.[2] Carbonyl oxides have for example been shown to function as nucleophilic oxygen-transfer agents in the oxygenation of sulfoxides 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).

Scheme I



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

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(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.

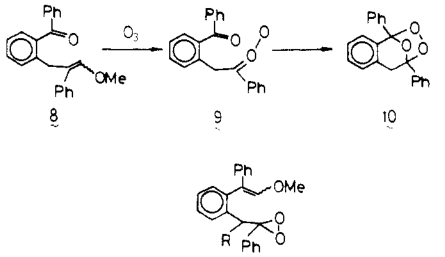
(5) (a) Keul, H.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1984**, *106*, 5370. (b) Keul, H.; Choi, H.; Kuczkowski, R. L. *J. Org. Chem.* **1985**, *50*, 3365. Kuczkowski and co-workers have demonstrated that the esters, produced by ozonolysis of vinyl ethers, are generally very poor dipolarophiles toward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

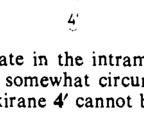
(7) The keto olefin **6a** was an oil: ^{1}H NMR δ 3.59 (s, 3 H), 3.95 (s, 2 H), 6.05 (s, 1 H), 6.81–7.83 (m, 14 H); IR 1690, 1640, 1240 cm^{-1}; mass spectrum, m/e 328 (M$^+$). Anal. ($C_{23}H_{20}O_2$) C, H. The keto olefin **6b** was an oil: ^{1}H NMR δ 1.19 (d, J = 6.0 Hz, 3 H), 3.63 (s, 3 H), 4.60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



(1)



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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