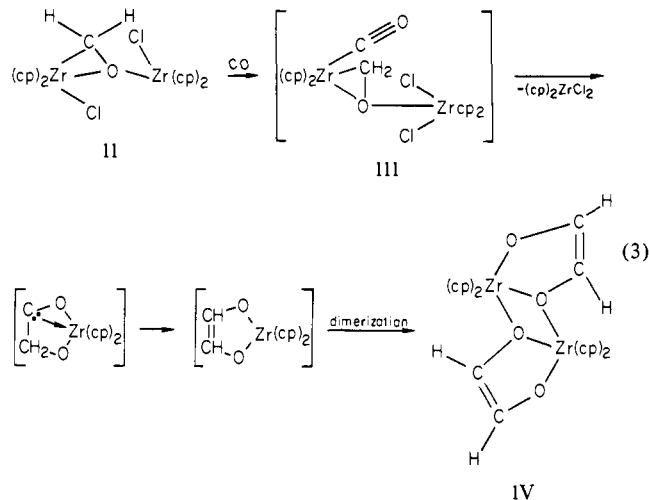


structure of II (Figure 1) was confirmed by X-ray diffraction methods.⁶ All cyclopentadienyl ligands are coordinated in a conventional η^5 mode. [Zr-cp distances (Å) are as follows: cp1-Zr1, 2.24 (1); cp2-Zr1, 2.21 (1); cp3-Zr2, 2.21 (1); cp4-Zr2, 2.20 (1) (Figure 1)], the oxymethylene bridge is η^2 -C,O bonded to Zr1 [Zr1-C21, 2.19 (1); Zr1-O, 2.13 (1) Å] with a Zr1-O-Zr2 angle of 166.9 (4)°. The distance Zr2...C21 = 3.07 (1) Å rules out any possible interaction of C21 with both zirconium atoms. The C-O bond distance [1.43 (2) Å] and the C-O stretching vibration (1015 cm^{-1}) are to be compared with the corresponding ones found in $(\text{cp})_2\text{V}(\eta^2\text{-CH}_2\text{O})$ [1.353 (10) Å, 1160 cm^{-1}],⁷ $\text{Os}(\text{CO})_2(\text{PPh}_3)_2(\eta^2\text{-CH}_2\text{O})$ [1.59 (1) Å, 1017 cm^{-1}],⁸ and $\text{Fe}(\text{CO})_2(\text{P}(\text{OMe})_3)_2(\eta^2\text{-CH}_2\text{O})$ [1.32 (2) Å, 1220 cm^{-1}].⁹ The oxymethylene ligand in complex II displays a bonding mode that strongly resembles that of formaldehyde bonded to vanadium in $(\text{cp})_2\text{V}(\eta^2\text{-CH}_2\text{O})$.⁷ Zr1, C11, C21, O, Zr2, and C12 atoms are close to being coplanar, the dihedral angle between Zr1, C11, C21, O, and Zr2, C12, O planes being 10.5 (8)°. Zr1, C11, C21, and O are nearly coplanar with a maximum deviation from the plane of 0.07 (1) Å. The two chloride ligands having trans configuration [the torsional angle Cl1-Zr1-Zr2-Cl2 is 169.5 (2)°], are bonded at unexpected different distances. Zr1-Cl1, 2.522 (4) Å, is significantly weaker than the corresponding Zr2-Cl2, 2.344 (3) Å. The ¹H NMR spectrum shows only one singlet for all cp ligands, suggesting an easy exchange in the roles of the two zirconium atoms in the equatorial plane.^{5,10}

Complex II can be formally viewed as a η^2 -formaldehyde complex $[\text{Zr}(\eta^2\text{-CH}_2\text{O})]$ with the oxygen interacting with a Lewis acid center, Zr2 in Figure 1.⁹ Lewis acids have been employed for converting a formaldehyde into an oxymethylene ligand, which is more appropriate for inserting carbon monoxide, as complex II does.^{7,9,11} Carbonylation of II is a slow reaction in THF solution at atmospheric pressure of CO and at room temperature.^{12,13} A simplified picture of how this reaction may occur is given in eq 3. The IR spectrum of the THF solution of II exposed to a carbon monoxide atmosphere showed a weak band at 1970 cm^{-1} and a band at 1605 cm^{-1} , whose intensity increased during the carbonylation. Carbon monoxide caused the loss of $(\text{cp})_2\text{ZrCl}_2$ from complex II. Analytical data and IR and mass spectra agree with the proposed formula for complex IV.¹²



Acknowledgment. We thank Dr. A. Stefani (ETH Zürich) for mass spectra and the Italian National Research Council for financial support.

Registry No. I, 37342-97-5; II, 83385-36-8; IV, 84750-99-2; CO, 630-08-0.

Supplementary Material Available: Tables of positional (SI) and thermal parameters (SII) for complex II and a listing of structure factor amplitudes (19 pages). Ordering information is given on any current masthead page.

Evidence for a Peroxide Intermediate in the 1,2-Cycloaddition of Singlet Oxygen to Adamantylideneadamantane: Nucleophilic Oxygen Atom Transfer to Sulfoxides

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Singlet oxygen (¹O₂) reacts with adamantylideneadamantane (1, Scheme I) to afford the unusually stable 1,2-dioxetane 3.^{1,2} Under certain conditions the photooxidation of 1 can yield the corresponding epoxide 4 in addition to 3.³ The mechanism for the formation of 3, and in particular 4, has been a subject of considerable controversy.⁴ Dewar⁵ and Bartlett^{3c} have suggested that epoxide 4 may be produced by reaction of an intermediate peroxide 2 with ¹O₂ with concomitant generation of ozone. On the other hand, free-radical processes have also been proposed for the formation of 4.^{3d}

We now provide evidence for a trappable intermediate in the reaction of ¹O₂ with 1. This species, which we suggest is perep-

(6) Crystals of $[(\text{cp})_2\text{ZrCl}]_2(\mu\text{-CH}_2\text{O})$ are monoclinic with $a = 10.775$ (2) Å, $b = 15.166$ (4) Å, $c = 13.687$ (3) Å, $\beta = 115.85$ (2)°, $U = 2012.8$ (9) Å³, space group $P2_1/n$, $Z = 4$, $\text{Mo K}\alpha$ 13.0 cm^{-1} . Of the 4052 independent reflections ($5 < 2\theta < 52^\circ$) measured on a Philips PW 1100 diffractometer using $\text{Mo K}\alpha$ radiation, 2065 were considered observed [$I > 3\sigma(I)$]. No absorption correction was applied. The structure was solved by heavy-atom methods and refined anisotropically to give a current $R = 0.058$. During the refinement all the cp rings were treated as rigid groups. All the hydrogen atoms were found from a difference Fourier synthesis and introduced in the refinement as fixed contributors with $B_{\text{iso}} = 6.3$ Å².

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(12) A THF (50 mL) solution of complex II (0.97 g) was exposed to a carbon monoxide atmosphere in the dark. After 1 day the IR spectrum of the solution showed two weak bands at 1970 and 1605 cm^{-1} . Five days later the band at 1970 cm^{-1} remained constant, while the intensity of the band at 1605 cm^{-1} had increased. The IR spectrum did not change further. Faster carbonylation can be carried out under 100 atm of carbon monoxide. The THF solution, concentrated and cooled at 0 °C, gave beautiful crystals of complex IV (0.30 g), $[(\text{cp})_2\text{Zr}]_2(\mu\text{-CH}_2\text{O})_2$. Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{O}_4\text{Zr}_2$: C, 51.61; H, 4.30. Found: C, 51.60; H, 4.37. The IR spectrum shows two sharp and strong bands (Nujol) at 1600 and 1225 cm^{-1} for the C=C and C-O bond vibrations. Complex IV showed mass spectral peaks at 556, 557, 558, 559, 560, 561, 562, 564 $[(\text{cp})_2\text{Zr}]_2(\mu\text{-CHO=CHO})_2$, 278, 279, 280, 282 $[\text{cp}_2\text{Zr}(\text{CHO=CHO})]$ whose positions and relative intensity are in agreement with the natural isotopic mixture of zirconium.

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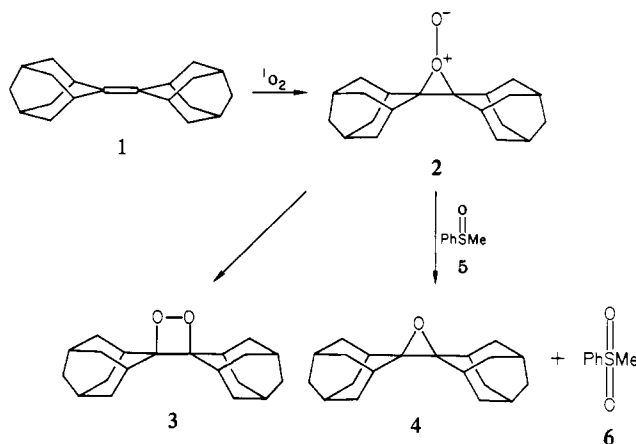
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Scheme I

Table I. Photooxygenation of Adamantylideneadamantane (1) in the Presence of Methyl Phenyl Sulfoxide (5)^a

| solvent | [1], mM | [5], mM | epoxide 4, % | dioxetane 3, % | epoxide 4 sulfone 6 |
|---------------------------------|---------|---------|--------------|----------------|---------------------|
| PhH | 4.0 | | 6 | 93 | |
| PhH | 5.1 | 8.3 | 97 | 3 | 1.0 |
| CCl ₄ | 4.0 | | 13 | 86 | |
| CCl ₄ | 4.0 | 8.6 | 100 | 0 | 1.0 |
| CH ₂ Cl ₂ | 4.0 | | 2 | 99 | |
| CH ₂ Cl ₂ | 4.0 | 8.0 | 26 | 75 | 1.0 |
| CH ₂ Cl ₂ | 4.0 | 77 | 92 | 8 | 1.0 |

^a Photooxygenations were conducted under oxygen at 10 °C with 1.7×10^{-4} M tetraphenylporphine and a 250-W high-pressure sodium lamp. Product yields were determined by gas chromatography with dioxetane 3 analyzed as its cleavage product, adamantane.

oxide 2, can be quantitatively trapped by nucleophilic oxygen atom transfer to sulfoxides to yield sulfones and epoxide 4.⁶ Our investigation was prompted by the view that the rearrangement of 2 to 3 might be sufficiently slowed by steric restrictions of the adamantyl groups to allow oxygen transfer to an acceptor.

Photooxygenation of 1 was carried out at 10 °C for 30 min in oxygenated solution (benzene, methylene chloride, or carbon tetrachloride) containing 1.7×10^{-4} M tetraphenylporphine as sensitizer, with use of a 250-W high-pressure sodium lamp. Irradiation of solutions of 1 under these conditions produced 86–99% yields of dioxetane 3 with the balance of the material, epoxide 4. These results are in accord with earlier observations.³ We now, however, report that in the presence of methyl phenyl sulfoxide (5) the reaction can be totally diverted to give cooxidation of 1 and 5 with formation of equimolar quantities of epoxide 4 and methyl phenyl sulfone (6, Table I).⁷ Almost complete inhibition of dioxetane formation is observed. It should also be noted that the 1:1 ratio of 4 and 6 indicates that the reaction pathway for epoxide production in the absence of 5 has also been suppressed.

We have shown that dioxetane 3 is stable under the photooxygenation conditions in the presence of 5. A free-radical inhibitor, 2,6-di-*tert*-butyl-*p*-cresol, at 4×10^{-4} M has no significant effect on the cooxidation of 5 and 1. Further, 4.2×10^{-2} M Dabco, a ¹O₂ quencher, totally inhibits the reaction. Control experiments showed that 5 is essentially inert toward ¹O₂ in the absence of 1.

Bartlett has demonstrated that a photochemically produced oxygen-biacetyl complex can effectively epoxidize olefins.⁸

(6) For the photooxidation of 7,7'-binorbornylidene, Bartlett has reported that yields of the corresponding epoxide could be significantly increased in the presence of tetracyanoethylene.^{8c} Although this observation was attributed to trapping of an intermediate perepoxide by TCNE, isolation of the cooxidation product derived from TCNE was not described.

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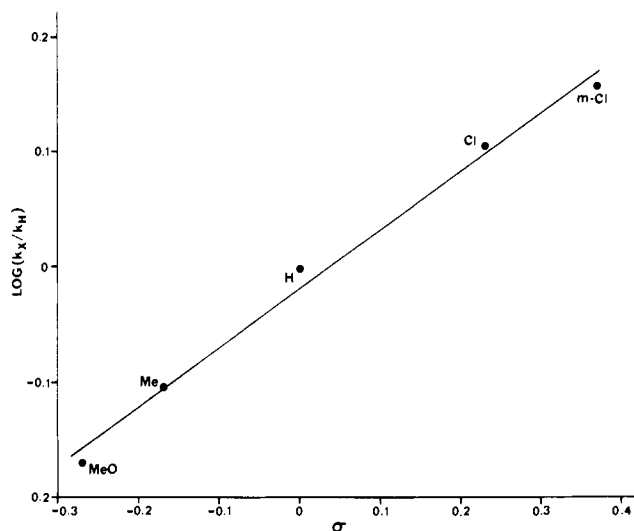



Figure 1. Hammett plot of the logarithm of the relative rates for the photosensitized cooxidation of X-C₆H₄SOMe in the presence of adamantylideneadamantane (1) vs. substituent constants σ . Substituents are para except where noted.

Table II. Nucleophilic Oxygen Atom Transfer to Sulfoxides

| oxygen atom donor | sulfoxide | solvent | Hammett ρ value | ref |
|---|--|---------------|----------------------|---------------|
|  | X-C ₆ H ₄ SOMe | benzene | +0.52 | present study |
| Me ₃ COO ⁻ | (X-C ₆ H ₄) ₂ SO | toluene | +1.4 ^a | <i>b</i> |
| PhC(=O)OO ⁻ | X-C ₆ H ₄ SOPh | dioxane-water | +0.71 | <i>c</i> |
| R ₂ C=C-O ⁻ (fluorenone oxide) | (X-C ₆ H ₄) ₂ SO | benzene | +0.26 | <i>d</i> |
| Me ₂ ⁺ SOO ⁻ | (X-C ₆ H ₄) ₂ SO | benzene | +0.25 | <i>e</i> |
| Me ₂ ⁺ S(=O)OO ⁻ | (X-C ₆ H ₄) ₂ SO | benzene | +0.23 | <i>e</i> |

^a For the reaction of disubstituted diphenyl sulfoxides with Me₃COO⁻, ρ was calculated from the relative rates at 40 °C given in this paper by plotting $\log k_{rel}$ vs. 2σ . ρ values given in ref *d* and *e* were calculated also in this way. ^b Curci, R.; DiFuria, F.; Modena, G. *J. Chem. Soc., Perkin Trans.* **2** 1978, 603. ^c Curci, R.; Modena, G. *Gazz. Chim. Ital.* **1964**, *94*, 1257. ^d Sawaki, Y.; Kato, H.; Ogata, Y. *J. Am. Chem. Soc.* **1981**, *103*, 3832. ^e Sawaki, Y.; Ogata, Y. *Ibid.* **1981**, *103*, 5947.

Further, epoxidations of olefins by carbonyl oxides are well documented.⁹ Therefore, one plausible explanation for the cooxidation of olefin 1 and sulfoxide 5 would involve the reversible formation of a persulfone (R₂⁺S(=O)OO⁻) from ¹O₂ and 5, which could epoxidize 1. To test this possibility, a photoepoxidation of a 3×10^{-2} M solution of norbornene in benzene in the presence of 4.5×10^{-3} M 5 was attempted for 2 h. Although this olefin was very reactive under Bartlett's conditions, no oxidation of either norbornene or 5 was found. This result is consistent with the observation of Ogata that an intermediate persulfone formed from Me₂SO and ¹O₂ was not effective in epoxidation of α -methylstyrene.¹⁰

The nucleophilic character of perepoxide 2 is illustrated by the results of an investigation of substituent effects on the trapping reaction. A series of competition experiments with substituted-phenyl methyl sulfoxides gave the following relative reactivities for the cooxidation of these sulfoxides during the photooxygenation

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of **1** in benzene: *m*-Cl, 1.4; *p*-Cl, 1.3; H, 1; *p*-Me, 0.79; *p*-OMe, 0.68. A Hammett plot of the logarithm of these rates against σ affords a ρ value of +0.52, $r = 0.995$ (Figure 1). These results are consistent with theoretical studies of Dewar¹¹ and Kearns,¹² which predicted that a perepoxide would be a very polar species with significant negative charge on the exocyclic oxygen atom. A comparison of **2** to other nucleophilic oxygen-transfer intermediates is shown in Table II.

Our observations on the reaction of perepoxide **2** with sulfoxides parallel to those of Foote,¹³ who recently reported the trapping of a persulfoxide ($\text{Et}_2^+\text{SOO}^-$) by sulfoxides. In benzene relative trapping abilities of 1:51:6 for Ph_2S , Ph_2SO , and Me_2SO were obtained, indicating the nucleophilic character of the persulfoxide in benzene.¹⁴ Similarly, we find that perepoxide **2** is trapped more effectively by sulfoxides than sulfides with relative reactivities for Ph_2S , Ph_2SO , and PhSOMe in benzene of 1:28:38.

While alternative explanations for the photosensitized co-oxidation of **1** and sulfoxides may be possible, we feel that our results are best accommodated by the proposed mechanism involving nucleophilic oxygen atom transfer from perepoxide **2** to sulfoxides. The unreactivity of norbornene under the reaction conditions together with the observed substituent effect tends to rule out a mechanism involving epoxidation of **1** by an intermediate persulfone.

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Rearrangement of 4,4-Diarylcyclohexadienones Induced by Attack of Methyl Metaphosphate at the Carbonyl Group

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In recent research, we have shown that monomeric methyl metaphosphate reacts with acetophenone in the presence of an appropriate base to yield the methyl ester of the enol phosphate of acetophenone. Metaphosphate ion reacts similarly.^{2,3} We have interpreted these reactions as proceeding by way of an attack of the metaphosphate on the carbonyl group of the ketone.⁴ We now report a reaction where the attack of methyl metaphosphate on a carbonyl group is essentially unambiguous. The rearrangement of 4,4-diarylcyclohexadienones, induced by methyl

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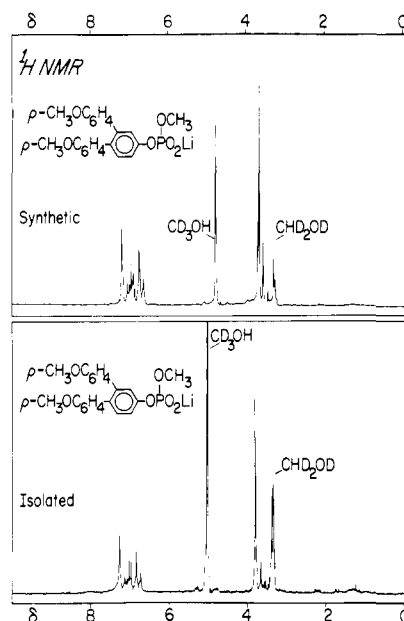
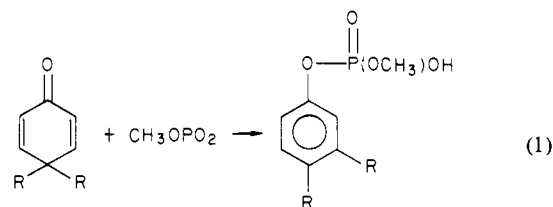
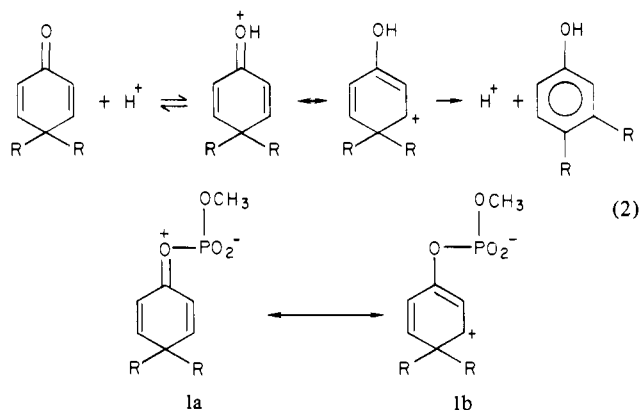


Figure 1. ¹H NMR spectra of synthetic lithium methyl 3,4-dianisylphenyl phosphosphate and of the product of the rearrangement of 4,4-dianisylcyclohexadienone induced by methyl metaphosphate.

metaphosphate, yields the methyl ester of the corresponding 3,4-diarylphenyl phosphate (eq 1).



The rearrangement of cyclohexadienones to the corresponding phenols⁶ is acid catalyzed and presumably takes place by a carbonium ion rearrangement (eq 2). In a parallel manner, an attack of methyl metaphosphates on the carbonyl group of the dienone will produce an intermediate, I, a and b, which is appropriate to a carbonium ion rearrangement.



For the reactions here reported, 30 mg of the methyl ester of *threo*- or *erythro*-(1,2-dibromo-1-phenylpropyl)phosphonate (II or III) and 0.1 mL of 2,2,6,6-tetramethylpiperidine (IV) were dissolved in 0.5 mL of purified dry chloroform, and 0.3 g of 4,4-dianisylcyclohexadienone was added. The mixture was sealed in a tube and heated at 72 °C for 14 h. We have previously shown that the Conant-Swan fragmentation⁷ of our bromophosphonates

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