kcal/mol,[24] which is consistent with the diffusion-controlled quenching observed. No exciplex emission is observed, however, and we have as yet no direct evidence for a common intermediate. The observed reactions are of particular interest in light of recent evidence, presented by Fukuzumi and Kochi,[25] in support of electron-transfer-assisted thermal Diels–Alder reactions. We are currently probing the more intimate mechanistic details of these photoadditions and are attempting the conversion of the products to various novel azo compounds.[26]

Supplementary Material Available: ^{1}H NMR spectra on [4 + 2] adducts of MTAD with 1-methyl-, 2-methyl-, 1-chloro-, and 1-carbomethoxynaphthalene (1 page). Ordering information is given on any current masthead page.

(24) Calculated with $E_{1/2}^{ox}$ = 1.71 V for naphthalene, and $E_{red}^{o'}$ = 0.025 V for MTAD. Both were measured at a Pt electrode in CH_2Cl_2 containing 0.1 M tetra-n-butylammonium perchlorate vs. SCE. We thank D. Kapp for these measurements.

(25) Fukuzumi, S.; Kochi, J. K. Tetrahedron 1982, 38, 1035.

(26) We have, for example, found that 1 undergoes di-π-methane rearrangement on triplet sensitization.

Ozonolysis of Methyl Vinyl Ether: Synthesis of 3-Methoxy-1,2-dioxolane and 3-Alkoxy-1,2,4-trioxolanes

Helmut Keul and Robert L. Kuczkowski*

*Department of Chemistry, University of Michigan
Ann Arbor, Michigan 48109*

Received March 29, 1984

Enol ethers have played an important role in the elucidation of cycloaddition chemistry so it is curious that their ozonolysis reactions have not been studied in a systematic manner.[1] For the few reported investigations, partial cleavage of the double bond was observed in several cases[2] as well as examples with complete cleavage.[2a-c,3] No stable peroxide intermediates were reported.

We have ozonized methyl vinyl ether in pentane and obtained a 9% yield of the secondary ozonide **1a**, which was previously

1 a, b

	a	b
R[1]	H	CH_3
R[2]	CH_3	C_2H_5
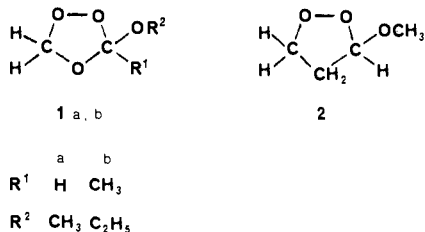
obtained[4] from the ozonolysis of styrene in methyl formate solvent. In addition, 3-methoxy-1,2-dioxolane (**2**), the simplest member

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

(2) (a) Hoffmann, R. W.; Schneider, J. Chem. Ber. 1967, 100, 3698. (b) Borowitz, I. J.; Rapp, R. D. J. Org. Chem. 1969, 34, 1370. (c) Gassman, P. G.; Creary, X. Tetrahedron Lett. 1972, 4407, 4411. (d) Clark, R. D.; Heathcock, C. H. J. Org. Chem. 1976, 41, 1396.

(3) (a) Strobel, M. P.; Morin, L.; Paquer, D. Tetrahedron Lett. 1980, 21, 523. (b) Schmidt, U.; Grafen, P. Liebigs Ann. Chem. 1962, 656, 97. (c) Thompson, Q. E. J. Org. Chem. 1962, 27, 4498.

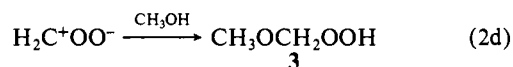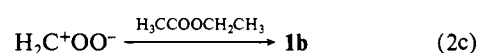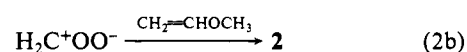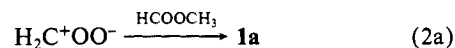(4) Keul, H.; Kuczkowski, R. L. J. Am. Chem. Soc. 1984, 106, 3383.

Table I. Absolute Yields from Ozonolysis of Methyl Vinyl Ether at −78 °C in Different Solvents[a]

run	solvent	% yield			
		1a	1b	2	3
1	pentane	9		68	
2	methyl formate	29		59	
3	methyl formate[b]	8		85	
4	ethyl acetate	2	11	52	
5	methanol				96

[a] 1:1 = mmol O_3:mmol alkene; See also ref 7. [b] 1:3 = mmol O_3:mmol alkene.

of the 3-alkoxy-1,2-dioxolane series,[5] was obtained in 68% yield.[7] This is the first known case of such dioxolane production during an ozonolysis.[9]

These products are in accord with the Criegee mechanism of ozonolysis[11] if the carbonyl oxide H_2COO is produced preferentially upon breakdown of the primary ozonide (reaction 1) and

$$\overbrace{H_2COOOCHOCH_3} \rightarrow H_2C^+OO^- + HCOOCH_3 \quad (1)$$

$$H_2C^+OO^- \xrightarrow{HCOOCH_3} \textbf{1a} \quad (2a)$$

$$H_2C^+OO^- \xrightarrow{CH_2=CHOCH_3} \textbf{2} \quad (2b)$$

$$H_2C^+OO^- \xrightarrow{H_3CCOOCH_2CH_3} \textbf{1b} \quad (2c)$$

$$H_2C^+OO^- \xrightarrow{CH_3OH} CH_3OCH_2OOH \quad (2d)$$
$$\textbf{3}$$
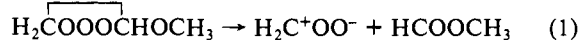
reacts competitively with the available ester and unreacted alkene (reactions 2a and 2b). The reaction yields imply that the primary ozonide decomposition is fast and they suggest that the dipolarophilicity of the alkene is greater than the ester.

In order to examine such a proposal further, ozonolyses were carried out in three other solvents: methanol, methyl formate, and ethyl acetate. The results are given in Table I. In methanol the high isolated yield of methoxymethyl hydroperoxide (**3**) is consistent with nearly exclusive cleavage of the primary ozonide in the direction of $H_2^+COO^-$ production (reactions 1 and 2d). In the ester solvents compared to pentane, higher ozonide yields occur

(5) CAS Online searching yielded no references to **2**. Two 3-methoxydioxolanes of spiro naphthalene derivatives[6a] and a dimethoxy derivative, viz., 3,5-dimethoxy-3,5-dimethyl-1,2-dioxolane,[6b] were retrieved in a search for the $\overline{C-C-O-O-C-O-C}$ skeleton.

(6) (a) Paquette, L. A.; Hertel, L. W.; Gleiter, R.; Boehm, M. C.; Beno, M. A.; Christoph, G. G. J. Am. Chem. Soc. 1981, 103, 7106. (b) Sato, T.; Yoshiie, S.; Imamura, T.; Hasegawa, K.; Miyahara, M.; Yamamura, S.; Ito, O. Bull. Chem. Soc. Jpn. 1977, 50, 2714.

(7) In a typical reaction 20 mmol of methyl vinyl ether was ozonized in 40 mL of solvent at −78 °C until O_3 passed the reaction vessel. Successive distillations at 20 mm and in a high vacuum separated volatile solvent and polymeric residues leaving a mixture of ozonide and dioxolane. The dioxolane could be isolated in 99% purity[8] by reducing the more reactive ozonide upon addition of the stoichiometric amount of triphenylphosphine followed by distillation. The dioxolane could be transformed into the isomeric methyl β-hydroxypropionate by treating it in methanol solution with Amberlyst-15 ion-exchange resin, a strongly acidic, macroreticular resin, suitable for nonaqueous catalysis.

(8) **Caution.** 3-Methoxy-1,2-dioxolane did not appear hazardous during the workup but normal precautions in handling peroxides should be followed. $\overline{C_αH(OCH_3)C_βH_2C_γH_2OO}$: ^{1}H NMR (360 MHz, CDCl$_3$) δ 2.56–2.63 (m, 1 H, H$_{β1}$), 2.75–2.83 (m, 1 H, H$_{β2}$), 3.41 (s, 3 H, CH$_3$), 3.92–3.99 (m, 1 H, H$_{γ1}$), 4.20–4.26 (m, 1 H, H$_{γ2}$), 5.20–5.22 (m, 1 H, H$_α$); ^{13}C NMR (CDCl$_3$) δ 42.40 (t, 134.11 Hz, C$_β$), 55.11 (q, 142.63 Hz, C$_{Me}$), 68.06 (t, 149.36 Hz, C$_γ$), 102.99 (d, 167.11 Hz, C$_α$); IR (CCl$_4$) 925 (vs) 955 (s) 990 (w), 1030 (w), 1100 (vs), 1110 (vs), 1190 (s), 1220 (w), 1270 (w), 1355 (s), 1450 (s), 1475 (w), 1745 (w), 1755 (sh), 2850 (s), 2890 (sh), 2910 (s), 2950 (s), 2980 (s), 3020 (s); GCMS (70 eV), m/e (relative intensity %) 104 (M$^+$, 5), 72 (11), 71 (100), 57 (14), 45 (12), 43 (40), 42 (37), 41 (15).

(9) Dioxolane production from decomposition of a secondary ozonide in the presence of BF_3·OEt_2 and alkenes has been reported.[10]

(10) (a) Miura, M.; Yoshida, M.; Nojima, M.; Kusabayashi, S. J. Chem. Soc., Chem. Commun. 1982, 397. (b) J. Am. Chem. Soc. 1983, 105, 6279.

(11) Criegee, R. Angew. Chem., Int. Ed. Engl. 1975, 14, 745; Angew. Chem. 1975, 87, 765.

due to the more effective trapping of $H_2C^+OO^-$ by the increased amount of ester (reactions 2a and 2c). However, the dioxolane product is still predominant which is indicative that the relative dipolarophilicities toward $H_2C^+OO^-$ are $CH_2=CHOCH_3$ > $HCOOCH_3$ > $CH_3COOCH_2CH_3$. Such an order is not unreasonable since esters are generally very poor dipolarophiles toward carbonyl oxides,[4] while electron-rich enol ethers have an extensive 1,3-dipolar cycloaddition chemistry.[12]

In order to explore whether the dioxolane might be formed by a reaction between starting alkene and ozonide (perhaps assisted by adventitious catalyst), 60 mmol of methyl vinyl ether in 50 mL of methyl formate was ozonized with 20 mmol of ozone. A workup of 25 mL of this reaction mixture showed no difference in the product composition (Table I, run 3) compared to the second half of the solution, which was analyzed 20 h later. The increased dioxolane yield compared to run 2 is consistent with the higher effective concentration of the starting alkene. The mutual stability of the dioxolane and ozonide observed under these conditions makes it unlikely that a catalyzed reaction between them leads to the dioxolane. Moreover, the high yields of dioxolanes and the change in product yields with solvent (Table I) are plausible for a kinetic scheme which derives these products from the cleavage fragments of the primary ozonide recombining with themselves, the solvent, or the initial alkene in a competitive manner. Experiments with labeled vinyl ethers are in progress to explore this reaction scheme further.

---

(12) Huisgen, R. *Angew. Chem., Int. Ed. Engl.* **1963**, *2*, 565, 633; *Angew. Chem.* **1963**, *75*, 604, 741.

Figure 1. ORTEP plot of **3** (Scheme I). The phenyl groups of which C301 and C401 are the ipso carbon atoms are not shown. Selected bond lengths in angstroms: Mo1–Mo2, 3.282; P1–Mo1, 2.398; P1–Mo2,, 2.417; Mo1–H1, 1.96; Mo2–H1, 1.78; P2–Mo1, 2.382. Angle Mo1–P1–Mo2, 86.0°.
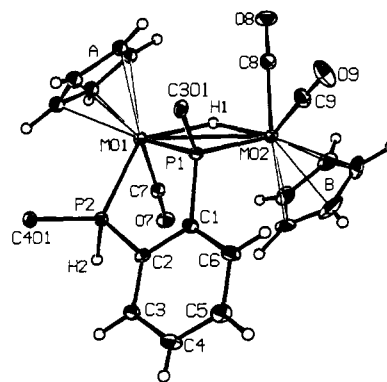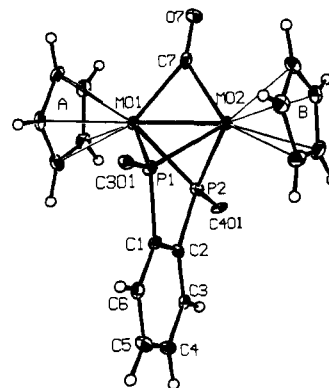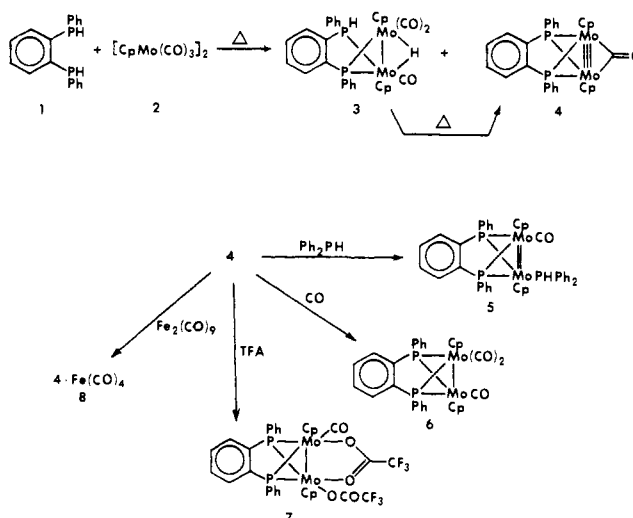

Figure 2. ORTEP plot of **4** (Scheme I). The phenyl groups of which C301 and C401 are the ipso carbon atoms are not shown. Selected bond lengths in angstroms: Mo1–Mo2, 2.532; P1–Mo1, 2.376; P2–Mo1, 2.385; P1–Mo2, 2.363; P2–Mo2, 2.368; C7–Mo1, 2.082; C7–Mo2, 2.099. Selected bond angles: Mo1–C7–Mo2, 74.5°; Mo1–P1–Mo2, 64.6°; Mo1–P2–Mo2, 64.4°.

Linked Bis(μ-phosphido) and Related Ligands for Metallic Clusters. 3. Synthesis and Chemistry of a Bis(μ-phosphido)(μ-carbonyl)dimolybdenum(*Mo*≡*Mo*) System[1]

Evan P. Kyba,* J. Douglas Mather, Karen L. Hassett, Jeffrey S. McKennis, and Raymond E. Davis*

Department of Chemistry
The University of Texas at Austin
Austin, Texas 78712

Received April 13, 1984

The chemistry of the $[CpMo(CO)_mX_n]_2$ system has generated considerable attention lately, due to the multifaceted bonding arrangements engendered by such molecules.[2] As part of our recent development of the chemistry of linked bis(bridging) di- and polymetal systems,[1,3a] we investigated the thermal reaction of the bis(secondary phosphine) **1**[3b–d] and $[CpMo(CO)_3]_2$ (**2**), which led to the isolation of two novel Mo_2 complexes. We describe these herein, along with some of the chemistry exhibited by these species (Scheme I).

---

(1) For the preceding paper in this series, see: Kyba, E. P.; Davis, R. E.; Hassett, K. L.; McKennis, J. S.; Sheikh, B. *Phosphorus Sulfur* **1983**, *18*, 275.

(2) For recent work, see inter alia: (a) D'Errico, J. J.; Messerle, L.; Curtis, M. D. *Inorg. Chem.* **1983**, *22*, 851–852. (b) Messerle, L.; Curtis, M. D. *J. Am. Chem. Soc.* **1982**, *104*, 889–891. (c) Green, M.; Orpen, A. G.; Schaverien, C. J.; Williams, I. D. *J. Chem. Soc., Chem. Commun.* **1983**, 181–183. (d) Alper, H.; Einstein, F. W. B.; Petrignani, J.-F.; Willis, A. C. *Organometallics* **1983**, *2*, 1422–1426. (e) Curtis, M. D.; Messerle, L.; Fotinos, N. A.; Gerlach, R. F. In "Reactivity of Metal–Metal Bonds"; Chisholm, M. H., Ed.; American Chemical Society: Washington, DC, 1981; ACS Symp. Ser. No. 155, Chapter 12.

(3) (a) McKennis, J. S.; Kyba, E. P. *Organometallic* **1983**, *2*, 1249–1251. (b) Kyba, E. P.; John, A. M.; Brown, S. B.; Hudson, C. W.; McPhaul, M. J.; Harding, A.; Larsen, K.; Niedzwiecki, S.; Davis, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 139–147. (c) Mann, F. G.; Mercer, A. J. H. *J. Chem. Soc., Perkin Trans. 1* **1972**, 2548–2555. (d) A much superior method for the synthesis of **1** has been developed: Kyba, E. P.; Rines, S. P., submitted for publication.

Scheme I

The reaction of equimolar quantities of **1** and **2** in degassed boiling mesitylene for 4 h gave **3** (56%), following workup and alumina chromatography (benzene eluent).[4] When the reaction was carried out for 12 h, **4** was isolated in 47% yield, following chromatography on alumina (CH_2Cl_2 eluent).[4] We also estab-

---

(4) Spectroscopic data as well as tables associated with the three X-ray structure determinations described in this paper are contained in a supplementary section (9 pages).