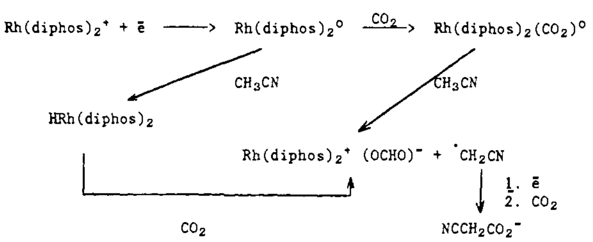
Scheme I



A glass cell was employed in which the anode and cathode compartments were separated by a medium glass frit. The working electrode was a 12-cm^2 mercury pool and the counter electrode was a 10-cm^2 platinum foil. The electrolysis solution was 60 mL of a 0.1 M solution of tetraethylammonium perchlorate in dry acetonitrile. To the catholyte was added 1.0 g of the rhodium complex. Before the electrolysis was started, the catholyte was saturated with CO_2. CO_2 was continually bubbled through the catholyte during the electrolysis. A current of 100 mA was passed through the cell. In the presence of the rhodium complex, the potential of the mercury pool (referenced to a silver wire electrode) varied from an initial value of approximately −1.55 V to a final potential of −1.45 V. In the absence of the rhodium complex, direct electroreduction of CO_2 was observed at −2.23 V. Hence, the presence of the rhodium complex caused a lowering in the reduction potential of CO_2 by approximately 700 mV (not as much lowering as in ref 1 but still significant).

The results of these constant-current electrolyses are shown in Table I. As can be seen, the CO_2 reduction product observed is the formate anion.[7] A small yield of cyanoacetate is also formed (characterized as the methyl ester by GC-mass spectral analysis) suggesting the presence of $(-)CH_2CN$ which was trapped by CO_2. No succinonitrile was detected. It should also be noted that in experiments in which more than 4*F*/mol of rhodium complex were passed, the quantities of formate obtained are greater than the initial molar quantities of $Rh(diphos)_2^+$, hence the reaction is electrocatalytic. The current efficiencies for the production of the formate anion varied between 42% for shorter electrolysis times and 22% for longer electrolytic experiments. The organometallic compounds isolated from the catholyte by sequential extractions with toluene and tetrahydrofuran were $HRh(diphos)_2$ and $Rh(diphos)_2^+$, respectively (60% combined yield). There is no evidence of reaction of CO_2 and $Rh(diphos)_2Cl$ prior to electrolysis.

While no mechanistic studies have been carried out, Scheme I contains our proposals for the mechanistic pathways involved. The electrogenerated species is able to react via two pathways, with CO_2 to generate a $Rh-CO_2$ species or with acetonitrile to produce the hydride (eq 2b). On the basis of the voltammetric results shown in Figure 1, we propose that while hydride formation does take place (as evinced by the isolation of the hydride from the catholyte), the predominant reaction pathway of the electrogenerated species is with CO_2. The rhodium–CO_2 species may then abstract a hydrogen atom from acetonitrile to give the ionic metalloformate derivative thereby regenerating the starting rhodium cation. The proposed metalloformate has been prepared by the interaction of $HRh(diphos)_2$[3] with CO_2 and been shown[8] to be ionized in acetonitrile by ^{31}P NMR spectroscopy and voltammetry. The reaction of $HRh(diphos)_2$ with CO_2 in acetonitrile is a slow reaction and would account for the isolation of the hydride from the catholyte. This last fact could also be a contributing factor to our declining current efficiencies on longer reaction times. This mechanism is supported by the fact that repeating the electrolysis in benzonitrile provides current efficiencies for formate production that are 50% of those obtained in acetonitrile, therefore implicating acetonitrile as the source of the hydrogen atom in the product formate.

Work is continuing in an effort to improve the observed current efficiencies and to extend the lifetime of our electrocatalytic system. We also plan to expand our experiments to include the analogous iridium system.

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[7] The formate anion was characterized by esterifying it to its methyl ester followed by gas chromatographic analysis using the internal standard method for quantitative analysis.

[8] The ^{31}P NMR spectrum[9] and cyclic voltammetric behavior of the rhodium formate is identical with that of $Rh(diphos)_2Cl$, which is known to be a 1:1 electrolyte in acetonitrile.

[9] $^{31}P\{^1H\}$ spectrum: δ -56.86 (relative to H_3PO_4), J_{Rh-P} = 134 Hz.

Photochemical Cycloaddition of *N*-Methyltriazolinedione to Naphthalene

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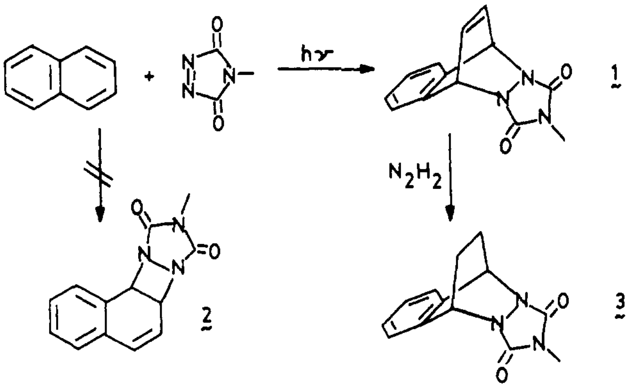
Additions of triazolinediones to organic molecules have led, inter alia, to a wide variety of 1,2-diazenes.[2] The derived azo compounds are of interest as potential biradical precursors and as routes to novel molecules. In contrast to an abundance of information on the thermal chemistry of triazolinediones, little attention has been paid to the photoadditions of these compounds.[3,4] We now wish to describe the novel photochemical addition of 4-methyltriazoline-3,5-dione (MTAD) to naphthalenes.

Visible irradiation of deaerated solutions of MTAD and naphthalene (15 mM each in CCl_4 or CH_2Cl_2; 1000-W incandescent bulb) for ca. 6 h gives, after solvent removal, a crystalline product. Although the product is thermally and acid labile, flash chromatography on silica gel gives reasonably pure material in ca. 40% yield. Spectroscopic[5] and chemical evidence are consistent with the [4 + 2] structure **1**. In particular, the ^1H NMR spectrum (200 MHz) shows characteristic aa′bb′ multiplets in the aromatic and olefinic/bridgehead regions, similar to other benzobicyclo[2.2.2]octenes.[6] Moreover, only seven signals appear in the ^{13}C NMR spectrum,[5] ruling out less symmetric structures such as **2**. Low-temperature irradiation and subsequent ^1H NMR (both at −78 °C) showed no evidence for the intermediacy of **2**. Adduct **1** can be reduced to **3**, which also exhibits appropriate spectra.[7]



To probe the generality of this reaction, the photoaddition of MTAD to a number of other aromatic compounds was attempted. We find no evidence for photochemical addition of MTAD to

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[1] Recipient of a Camille and Henry Dreyfus Foundation Grant for Newly Appointed Young Faculty in Chemistry.

[2] Adam, W.; DeLucchi, O. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 762.

[3] Amey, R. L.; Smart, B. E. *J. Org. Chem.* **1981**, *46*, 4090.

[4] Warmhoff, H.; Wald, K. *Chem. Ber.* **1977**, *110*, 1699.

[5] Compound **1** ^1H NMR (200 MHz, $CDCl_3$) Ar AA′BB′ δ_A 7.34, δ_B 7.23 (J_{AB} = 5.4, $J_{AB'}$ = 1.2, $J_{BB'}$ = 6.0 Hz), olefin/bridgehead AA′BB′ δ_A 5.82, δ_B 6.82 (J_{AB} = 4.2, $J_{AB'}$ = 1.6, $J_{BB'}$ = 5.3 Hz), δ 2.9 (s, 3 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 158.0, 136.8, 134.5, 127.6, 123.5, 56.8, 25.3; IR (KBr) 1760, 1710, 1700 cm^{-1}; MS (30 eV), *m/e* calcd 241.0852, measured 241.0852, base peak 128.

[6] Tori, K.; Takano, Y.; Kitahonoki, K. *Chem. Ber.* **1964**, *97*, 2798.

[7] Compound **3** ^1H NMR (200 MHz, $CDCl_3$) δ 7.25 (m, 4 H), 5.25 (br s, 2 H), 2.90 (s, 3 H), 2.35 (m, 2 H), 1.65 (m, 2 H); MS (30 eV), *m/e* calcd 243.1009, measured 243.1008.

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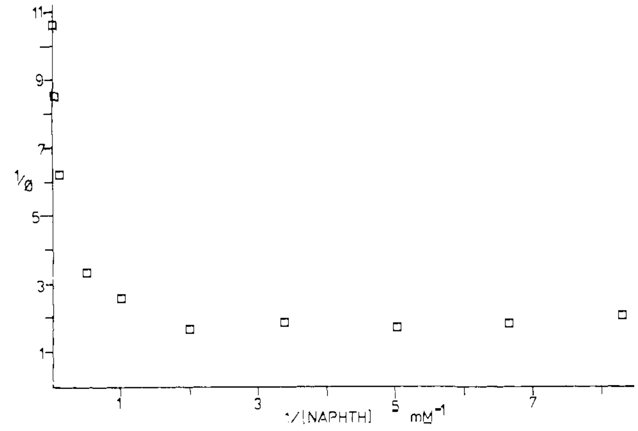


Figure 1. Naphthalene concentration dependence of quantum yield for formation of **1**. Measurements were made at 514 nm in deaerated CCl_4; [MTAD] = 0.6 mM. Each ϕ is the average of three runs, and all numbers are ±10% of the value shown.

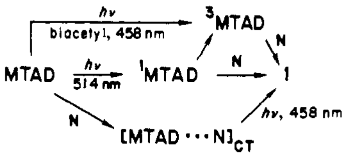
simple substituted benzenes including benzene, toluene, hexamethylbenzene, anisole, 1,4-dimethoxybenzene, 1,4-dibromobenzene, and hexachlorobenzene. The reaction appears to be general for a wide variety of substituted naphthalenes, however. For example, photoadducts of MTAD with 1-methyl-, 2-methyl-, 1-chloro-, and 1-carbethoxynaphthalene can be isolated by chromatography. Interestingly, the 1-substituted isomers give predominantly (>90% by NMR crude mixtures) the 5,8-photoadducts, but 2-methylnaphthalene gives a ca. 1:1 mixture of 5,8- and 1,4-addition. Spectral information is given in the supplementary material. Speculations concerning relative reactivity and regiochemistry are hampered by possible differences in thermal lability of the adducts (vide infra). These points are under current investigation.

Only a handful of triazolinedione Diels–Alder adducts with simple aromatic compounds have been reported.[8-10] Although the Diels–Alder addition of MTAD to anthracene is facile,[10] thermal cycloadditions of triazolinediones to lower benzologues appear to be limited to strained cyclophanes.[8,9] Askani and Schneider[11] have recently reported unsuccessful attempts to generate triazolinedione–benzene and azodicarboxylate–benzene cycloadducts. Similar attempts in our laboratories have also failed. On gentle heating, adduct **1** readily undergoes quantitative cycloreversion to MTAD and naphthalene ($t_{1/2} \cong 45$ min at 40 °C in benzene). It is thus not unreasonable that Diels–Alder adducts between monocyclic aromatic compounds and triazolinediones are extremely labile and difficult to isolate.

To obtain more quantitative information on these novel additions, we have centered our attention on the naphthalene–MTAD photoreaction. The quantum yields were obtained with an Ar^+ laser; absorbed power was measured with a Scientech laser power meter calibrated with Reinecke's salt[12] actinometry. Product assay was complicated by the lability of the adduct. Both naphthalene and MTAD disappearance could be measured by UV–vis spectroscopy, however. Careful integration of the ^1H NMR spectra of several samples with internal standards showed that disappearance quantum yields paralleled formation of **1**.

A plot of ϕ_{add}^{-1} vs. $[N]^{-1}$ (N = naphthalene) is shown in Figure 1. Interestingly, increasing [N] first increases ϕ_{add} (to a maximum of 0.6 at 0.5 mM [N]), then decreases it to a limiting value of 0.09 (extrapolated to [N] = ∞). The quantum yields are independent of [MTAD], ruling out possible chain mechanisms. Although MTAD undergoes unimolecular photodecomposition,[4,13] control experiments showed this to be a minor contributor to the overall quantum yield, even at the lowest [N] studied. The reaction can also be triplet sensitized. Irradiation of a solution of MTAD, naphthalene, and biacetyl, under conditions where only biacetyl absorbs, gives product with $\phi_{add} = 0.63$.[14]

Scheme I



The concentration dependence shown in Figure 1 suggests that both singlet and triplet excited MTAD give product. The fraction of singlet reaction can be gauged by reference to the approximately diffusion controlled quenching of ^{1}MTAD fluorescence by naphthalene. Stern–Volmer treatment of the quenching data, with use of a ^{1}MTAD lifetime of 77 ns[16] measured in CCl_4, gives a quenching rate constant of 2×10^{10} M^{-1} s^{-1}.[17] The significant efficiency of photoaddition at high [N] indicates that ^{1}MTAD gives product. For example, the Stern–Volmer equation shows that at 50 mM [N], 98% of ^{1}MTAD is quenched. The ϕ_{add} at this naphthalene concentration is 10%, however. On the other hand, ϕ_{add} at low [N] is too high for only ^{1}MTAD reaction, and triplet reaction must be invoked. For example, at [N] = 0.2 mM, 22% ^{1}MTAD is quenched at diffusion control, but $\phi_{add} = 60\%$. Dalton and Snyder[18,19] have predicted similarly curved double-reciprocal plots for bimolecular reactions occurring through two sequentially formed excited states. Our results are consistent with reaction via mainly ^{3}MTAD at low [N]. At high concentrations, naphthalene intercepts ^{1}MTAD prior to intersystem crossing and leads to product, albeit less efficiently.

At higher concentrations (>100 mM), naphthalene forms a ground-state charge-transfer (CT) complex with MTAD. The complex shows a broad electronic absorption ($\lambda_{max} \sim 400$ nm), whose concentration dependence, treated by a modified Benesi–Hildebrand[20] scheme, indicates a small complexation constant of ca. 0.4 M^{-1}. This observation is similar to recent reports of triazolinedione CT complexes with other electron-rich aromatic compounds.[21,22] At the concentrations of starting materials used for the 514-nm irradiations above, the concentration of CT complex is negligible. However, irradiation (457.9 nm) of only the charge-transfer absorption in the complex formed at higher [N] leads to product ($\phi_{add} = 0.09$, [N] = 500 mM, [MTAD] = 0.6 mM).

The above results are summarized in Scheme I. It is tempting to speculate that ^{1}MTAD reaction and CT irradiation lead to a common excited-state complex or contact radical ion pair. Application of the Weller equation[23] indicates that electron transfer from naphthalene to ^{1}MTAD should be exothermic by ca. 3

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[8] Murad, A. F.; Kleinschroth, J.; Hopf, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 389. Kleinschroth, J.; Hopf, H. *Ibid.* **1982**, *21*, 469.

[9] Gassman, P. G.; Bailey, T. F.; Hoye, R. C. *J. Org. Chem.* **1980**, *45*, 2923.

[10] Burrage, M. E.; Cookson, R. C.; Gupte, S. S.; Stevens, I. D. R. *J. Chem. Soc. Perkin Trans. 2* **1975**, 1325.

[11] Askani, R.; Schneider, W. *Chem. Ber.* **1983**, *116*, 2355.

[12] Wegner, E. E.; Adamson, A. W. *J. Am. Chem. Soc.* **1966**, *88*, 394.

[13] Pirkle, W. H.; Stickler, J. C. *J. Am. Chem. Soc.* **1970**, *92*, 7497.

[14] Irradiated with 457.9-nm laser line; [N] = 1 mM, [MTAD] = 0.6 mM, [biacetyl] = 50 mM in CCl_4. Although the triplet energy of MTAD is not known, it is expected to lie around 40 kcal/mol.[15]

[15] Poicus, A. V.; Yardley, J. T. *J. Chem. Phys.* **1974**, *61*, 2779.

[16] We thank M. Olken, C. Verschoor, J. Eisenhart, and Professor Ellis for assistance in making this measurement. This value is somewhat larger than the 43 ns previously reported,[15] although we have found that the singlet lifetime is quite sensitive to adventitious quenching.

[17] A diffusion rate constant of 1.1×10^{10} M^{-1} s^{-1} has been calculated for CCl_4 at 25 °C: Murov, S. "Handbook of Photochemistry"; Marcel Dekker: New York, 1973.

[18] Dalton, J. C.; Snyder, J. J. *Mol. Photochem.* **1974**, *6*, 291.

[19] A similar interpretation was given by: Das, P. K.; Muller, A. J.; Griffin, G. W.; Gould, I. R.; Tungs, C.-H.; Turro, N. J. *Photochem. Photobiol.* **1984**, *39*, 281.

[20] Foster, R. "Organic Charge-Transfer Complexes"; Academic Press: London, 1969.

[21] Konovalov, A. I.; Brecus, I. P.; Sharagin, I. A.; Kiselev, V. D. *Zh. Org. Khim.* **1979**, *15*, 361.

[22] Hall, J. H. *J. Org. Chem.* **1983**, *48*, 1708.

[23] Weller, A. In "The Exciplex"; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975; Chapter 2.

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]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the Americal Chemical Society, the Camille and Henry Dreyfus Foundation, the University of Wisconsin Alumni Research Foundation, and the National Science Foundation (CHE 81173180) for support of this work. We also are grateful to Mike Reibe for technical assistance and Professor Art Ellis for helpful discussions.

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.

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(24) Calculated with $E_{1/2}^{\mathrm{ox}}$ = 1.71 V for naphthalene, and $E_{\mathrm{red}}^{\circ\prime}$ = 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

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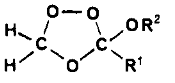
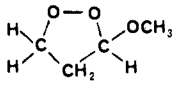
Enol ethers have played an important role in the elucidation of cycloaddition chemistry so it is curious that their ozonolysis reactions have not been studied in a systematic manner.[1] For the few reported investigations, partial cleavage of the double bond was observed in several cases[2] as well as 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



2

	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 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]

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

		% yield			
run	solvent	**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.

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

$$\mathrm{H_2\overline{COOOC}HOCH_3 \rightarrow H_2C^{+}OO^{-} + HCOOCH_3} \tag{1}$$

$$\mathrm{H_2C^{+}OO^{-} \xrightarrow{HCOOCH_3} \mathbf{1a}} \tag{2a}$$

$$\mathrm{H_2C^{+}OO^{-} \xrightarrow{CH_2{=}CHOCH_3} \mathbf{2}} \tag{2b}$$

$$\mathrm{H_2C^{+}OO^{-} \xrightarrow{H_3CCOOCH_2CH_3} \mathbf{1b}} \tag{2c}$$

$$\mathrm{H_2C^{+}OO^{-} \xrightarrow{CH_3OH} \underset{\mathbf{3}}{CH_3OCH_2OOH}} \tag{2d}$$

reacts competitively with the available ester and unreacted alkene (reactions 2a and 2b). The reaction yields *i*mply 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

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(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.

(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 $\overline{\mathrm{C{-}C{-}O{-}O{-}C}}\mathrm{{-}O{-}C}$ 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. $\overline{\mathrm{C_{\alpha}H(OCH_3)C_{\beta}H_2C_{\gamma}H_2OO}}$: ^{1}H NMR (360 MHz, $CDCl_3$) δ 2.56–2.63 (m, 1 H, H_{β_1}), 2.75–2.83 (m, 1 H, H_{β_2}), 3.41 (s, 3 H, CH_3), 3.92–3.99 (m, 1 H, H_{γ_1}), 4.20–4.26 (m, 1 H, H_{γ_2}), 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.

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