Anal. Calcd for $C_{30}H_{38}N_3Cl_3 \cdot 2.5H_2O$: C, 60.86; H, 7.27; N, 7.10; Cl, 18.01. Found: C, 60.70; H, 6.93; N, 7.04; Cl, 18.14.

1,2-Bis(4-propylpyridinium-1-yl)-3-chloro-7-propylindolizine dichloride (20): ^1H NMR (D_2O) δ 8.77 (2, dd, J = 6.7, 2.3), 8.69 (2, dd), 8.21 (1, d, J = 7.8), 7.94 (4, dd), 7.23 (1, br s), 7.01 (1, dd, J = 1.8); ^1H NMR ($CDCl_3$) δ 10.27 (4, m), 8.08 (1, d), 7.92 (4, d), 6.95 (1, d), 6.90 (1, s), 2.90 (4, t), 2.61 (2, t), 1.76 (6, m), 1.04 (9, m); ^{13}C NMR ($CDCl_3$) δ 194.5, 194.0, 166.0, 165.1, 148.5, 141.0, 128.1, 127.2, 122.4, 121.9, 117.3, 111.9, 98.5, 38.0, 37.2, 37.0, 23.2, 22.3, 13.8.

1,2-Bis(pyridinium-1-yl)-3-chloroindolizine Diiodide. A solution of **4** (0.50 g, 1.3 mmol) in water was added to LiI (0.84 g, 6.3 mmol) in water resulting in a color change from yellow to orange. Extraction with $CHCl_3$ and removal of the solvent under vacuum gave a crystalline solid, mp 281–283 °C dec: ^1H NMR ($CDCl_3$) superimposable with that of **4**.

Anal. Calcd for $C_{18}H_{14}N_3ClI_2 \cdot H_2O$: C, 37.30; H, 2.78; N, 7.25. Found: C, 37.29; H, 2.57; N, 7.26.

1,2-Bis(4-*tert*-butylpyridinium-1-yl)-3-chloro-7-*tert*-butylindolizine Diiodide. To a stirred solution of 0.927 g (1.57 mmol) of the corresponding chloride **5** in 60 mL of water was added 2.6 g of potassium iodide (15.9 mmol) in 30 mL of water. A bright yellow precipitate formed immediately. The product was extracted from solution with methylene chloride. The organic layer was dried over magnesium sulfate and evaporated to dryness on a rotary evaporator to give 1.060 g (1.38 mmol, 86.8%) of the bright yellow solid (mp >300 °C); ^1H NMR ($CDCl_3$) δ 1.38 (s, 9), 1.54 (s, 18), 7.09 (s, 1), 7.19 (d, 1), 7.24 (d, 1), 8.20 (m, 4), 10.20 (m, 4).

Anal. Calcd for $C_{30}H_{38}N_3ClI_2 \cdot H_2O$: C, 47.04; H, 5.49; N, 5.49; I, 33.16. Found: C, 46.93; H, 5.28; N, 5.47; I, 33.30.

1,2-Bis(4-*tert*-butyl-4-cyanodihydropyridin-1-yl)-3-chloro-7-*tert*-butylindolizine (19). To a stirred solution of 0.791 g of **5** (1.34 mmol) in 50 mL of methanol was added 0.30 g of sodium cyanide (6.1 mmol) in 10 mL of methanol. The solution immediately turned from yellow to orange. After 1 h, a white precipitate formed and was filtered and washed with additional methanol. The solid was crystallized twice from anhydrous ether to give 0.312 g (0.59 mmol, 43.5%) of the product, mp 170–172 °C; IR ($CHCl_3$) 2900, 1680, 1605, 1520, 1480, 1370, 1320, 1025, 925; UV–vis (CH_3CN) 263 (4.42), 348 (3.66); ^1H NMR ($CDCl_3$) δ 1.07 (s, 9), 1.10 (s, 9), 1.30 (s, 9), 4.67 (d, 2, J = 8.1), 4.70 (d, 2, J = 7.7), 6.11 (d, 2, J = 7.9), 6.21 (d, 2, J = 8.1), 6.76 (dd, 1, J = 7.4, 1.6), 7.09 (d, 1, J 0.5), 7.82 (d, 1, J = 7.6); mass spectrum (chemical ionization) 500 (0.21), 475 (0.75), 465 (0.28).

Anal. Calcd for $C_{32}H_{38}N_5Cl$: C, 72.80; H, 7.20; N, 13.27; Cl, 6.73. Found: C, 72.98; H, 7.20; N, 13.28; Cl, 6.77.

1,2-Bis(piperidin-1-yl)-5,6,7,8-tetrahydroindolizine (17) and 3,4-Bis(piperidin-1-yl)dihydroindolizine (18). A mixture of **4** (0.500 g, 1.26 mmol) and 50 mg of PtO_2 in 20 mL of ethanol was placed under H_2 (48 psi) and shaken at room temperature for 36 h. The resulting light-yellow solution was filtered and the solvent was removed to yield 380 mg of a yellow oil containing many compounds by TLC. Column chromatography (silica gel; 95% $CHCl_3$, 5% CH_3OH) yielded 132 mg of the product mixture in a ratio of fully saturated to partially reduced compound of 0.39 (by NMR and mass spectroscopy): ^1H NMR ($CDCl_3$) δ 6.97 (s), 3.35–3.95 (br m), 3.15 (br m), 1.4–2.2 (br m); ^{13}C NMR ($CDCl_3$) δ 110.4, 106.0, 56.2, 53.2, 52.3, 51.4, 47.5, 45.6, 44.3, 37.1, 26.7, 26.0, 24.3, 23.6, 22.3; LRMS, m/e (relative intensity) 291 (2.9), 288 (7.7), 287 (37.4), 204 (12.1), 193 (22.5), 124 (18.2), 97 (base), 84 (61.2), 69 (33.4).

Acknowledgment. This research was supported initially by the Committee on Research, University of California, Berkeley, and subsequently by National Science Foundation Grant Number CHE82-05696. The X-ray structure was determined by Fred Hollander of the Department of Chemistry, University of California, Berkeley.

Registry No. **3**·Cl, 97351-56-9; **3**·BPh_4, 86289-25-0; **4**, 86289-23-8; **4**·2I, 97351-60-5; **5**, 97351-57-0; **5**(cation)·2I, 97374-06-6; **8**, 97351-58-1; **17**, 86289-26-1; **18**, 86289-27-2; **19**, 97351-61-6; **20**, 97351-59-2; TCCP, 6262-42-6; tetrabromocyclopropene, 6262-43-7; pyridine, 110-86-1; 4-*tert*-butylpyridine, 3978-81-2.

Supplementary Material Available: Crystallographic data, bond lengths and angles, and thermal parameters for **3** (24 pages). Ordering information is given on any current masthead page. Structure factor tables are available from the authors.

Ozonolysis of Enol Ethers. Formation of 3-Alkoxy-1,2-dioxolanes by Concerted Addition of a Carbonyl Oxide to an Enol Ether

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Received April 18, 1985

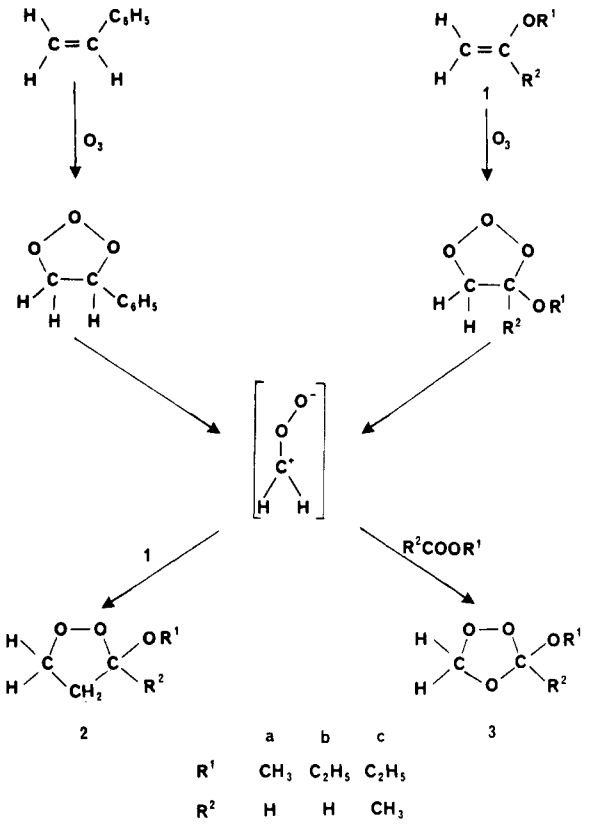
The ozonolyses of methyl vinyl ether, ethyl vinyl ether, and ethyl isopropenyl ether were studied in a variety of solvents. Alkoxy-1,2,4-trioxolanes and alkoxy-1,2-dioxolanes were the main products in pentane and ester solvents. These products arose from the carbonyl oxide (H_2COO) produced upon ozonolysis undergoing 1,3-cycloaddition reactions with esters and activated olefins (enol ethers). From additional trapping experiments, the following relative dipolarophilicities toward the carbonyl oxide were inferred: aldehydes > enol ethers > esters ≃ ketones. Ozonolysis of stereolabeled ethyl vinyl-2-d_1 ether gave ethoxy-1,2-dioxolane with retention of the alkene configuration at the –CHDCH(OEt)– linkage. This is the first example where stereospecificity, implying concertedness, has been directly observed for a reaction of a carbonyl oxide with a substrate. These results are consistent with the Criegee mechanism and extend it to the ozonolysis of enol ethers.

In previous papers, we reported the synthesis of 3-methoxy-1,2,4-trioxolane (**3a**) from the ozonolysis of styrene in methyl formate[1] or the ozonolysis of methyl vinyl ether (**1a**).[2] The latter reaction also produced unexpectedly high yields of 3-methoxy-1,2-dioxolane (**2a**). It was postulated that the synthesis of alkoxy-1,2,4-trioxolanes **3** and alkoxy-1,2-dioxolanes **2** could be rationalized by cycloaddition reactions of the carbonyl oxide (H_2COO) which is produced upon breakdown of a primary ozonide (Scheme I). This would extend the Criegee ozonolysis mechanism[3] to include cycloaddition of a car-

(1) Keul, H.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1984**, *106*, 3383.
(2) Keul, H.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1984**, *106*, 5370.
(3) (a) Criegee, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 745. (b) Bailey, P. S. "Ozonation in Organic Chemistry"; Academic Press: New York, 1978; Vol. 1; 1982; Vol. 2.

0022-3263/85/1950-3365$01.50/0

Scheme I



bonyl oxide to esters and activated alkenes, specifically enol ethers.[4]

The formation of dioxolane **2a** was the first example of a cycloaddition between a carbonyl oxide and an alkene during an ozonolysis.[5] This motivated us to examine further such dioxolane formation and extend it to the ozonolysis of two additional enol ethers **1b** and **1c**. Additional trapping experiments of the carbonyl oxide were conducted to provide further confirmation of the Criegee mechanism and to obtain insight on the relative dipolarophilicity of enol ethers compared to aldehydes, ketones, and esters. Trapping of the enol ethers opened the possibility to investigate the stereochemistry of the dioxolane formation by using deuterium-labeled alkenes and thereby to test for the first time the concertedness of a carbonyl oxide cycloaddition reaction in the classical way as recently discussed by Huisgen.[7] Concertedness in carbonyl oxide (2 + 3)-cycloaddition reactions has heretofore been inferred from a variety of less direct analyses.[8] Evidence for nonconcerted reactivity also exists at least for some conditions.[8f] The results of these studies are reported here as well as characterization of the novel 1,2-dioxolanes,

(4) (a) See ref 1 and 2 for additional discussion on the lack of participation of esters in ozonolysis reactions heretofore and for the few previous reports on the ozonolysis of enol ethers. We have recently become aware of another report[4b] describing a methoxy-1,2,4-trioxolane from ozonolysis of (methoxymethylene)-Meldrums acids. (b) Schank, K.; Schuhknecht, C. *Chem. Ber.* **1982**, *115*, 2000.

(5) Nonconcerted dioxolane production from decomposition of a secondary ozonide in the presence of BF_3·OEt_2 and phenylalkenes[6] is a related process.

(6) (a) Miura, M.; Yoshida, M.; Nojima, M.; Kusabauashi, S. *J. Chem. Soc., Chem. Commun.* **1983**, 397; (b) *J. Am. Chem. Soc.* **1983**, *105*, 6279.

(7) Huisgen, R. "1,3-Dipolar Cycloaddition Chemistry"; Padwa, A., Ed.; Wiley: New York, 1984; Chapter 1, p 61.

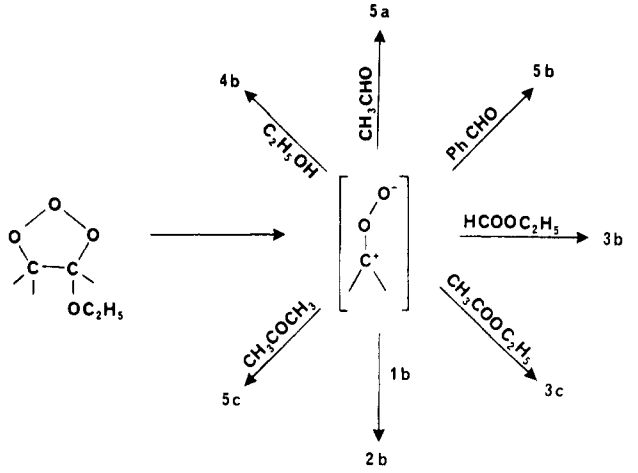
(8) (a) Bailey, P. S.; Ferrell, T. M. *J. Am. Chem. Soc.* **1978**, *100*, 894. (b) Lattimer, R. P.; Kuczkowski, R. L.; Gillies, C. W. *Ibid.* **1974**, *96*, 348. (c) Choe, J.-I.; Painter, M. K.; Kuczkowski, R. L. *Ibid.* **1984**, *106*, 2891. (d) Nangia, P. S.; Benson, S. W. *Ibid.* **1980**, *102*, 3105. (e) Cremer, D. *Ibid.* **1981**, *103*, 3619, 3627. (f) See ref 8c for a discussion of nonconcerted reactivity and relevant references.

Table I. Ozonolysis of Methyl Vinyl Ether (1a), Ethyl Vinyl Ether (1b), and Ethyl Isopropenyl Ether (1c) in Various Solvents at −78 °C

run[a]	olefin	solvent	products and yields, %		
1	**1a**	methanol	**4a**, 96		
2	**1a**	pentane	**2a**, 68	**3a**, 9	
3	**1a**	methyl formate	**2a**, 59	**3a**, 29	
4	**1a**	ethyl acetate	**2a**, 52	**3a**, 2	**3c**, 11
5	**1b**	ethanol	**4b**, 95		
6	**1b**	pentane	**2b**, 78	**3b**, 7	
7	**1b**	ethyl formate	**2b**, 53	**3b**, 20	
8	**1b**	pentane/acetaldehyde	**2b**, 20	**3b**, 30	**5a**, 15
9	**1b**	pentane/benzaldehyde	**2b**, 23	**3b**, 2	**5b**, 60
10	**1b**	acetone	**2b**, 22	**3b**, 2	**5c**, 2
11	**1c**	ethanol	**4b**, 94		
12	**1c**	pentane	**2c**, 63	**3c**, 3	
13	**1c**	ethylacetate	**2c**, 56	**3c**, 5	

[a] Starting materials: run 1, 9.93 mmol of **1a**, 20 mL of MeOH; run 2, 20.8 mmol of **1a**, 40 mL of n-C_5H_{12}; run 3, 19.1 mmol of **1a**, 40 mL of $HCOOCH_3$; run 4, 19.5 mmol of **1a**, 40 mL of MeCOOEt; run 5, 21.1 mmol of **1b**, 40 mL of EtOH; run 6, 20.5 mmol of **1b**, 40 mL of n-C_5H_{12}; run 7, 21.6 mmol of **1b**, 40 mL of HCOOEt; run 8, 10.5 mmol of **1b**, 35.8 mmol of CH_3CHO, 20 mL of C_5H_{12}; run 9, 20.0 mmol of **1b**, 40 mmol of C_6H_5CHO, 40 mL of C_5H_{12}; run 10, 20.0 mmol of **1b**, 40 mL of $(CH_3)_2CO$; run 11, 11.7 mmol of **1c**, 20 mL of EtOH; run 12, 20.0 mmol of **1c**, 40 mL of C_5H_{12}; run 13, 17.7 mmol of **1c**, 40 mL of MeCOOEt.

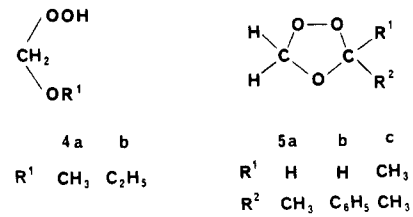
Scheme II



analysis of their NMR spectra, and observations on their decomposition. Some of the previously reported reactions of **1a**[2] are also repeated here for completeness and to facilitate comparisons between the enol ethers **1b** and **1c**.

Results and Discussion

Ozonolysis of Enol Ethers. Ozonolyses were carried out in various solvents and in the presence of added aldehydes. Reactions were conducted at −78 °C and reaction products were isolated by distillative workup at 25 °C. The results are shown in Table I where the isolated yields of various products **2**–**5** are given.



The changes in reaction yields in various solvents can be rationalized in the framework of trapping reactions of

the H_2COO moiety with the solvent, starting alkene, or an added aldehyde. The reactions of the carbonyl oxide resulting from the ozonolysis of **1b** are illustrated in Scheme II.

Ozonolysis of **1a–c** in an alcohol solvent with the same alkoxy group as the enol ether to simplify the analysis gave high yields of the corresponding alkoxy hydroperoxides **4a** and **4b**. This is consistent with essentially exclusive cleavage of the primary ozonide in the direction of H_2COO production. Ozonolysis of **1a–c** in pentane solvent gave high yields of the corresponding dioxolanes **2a–c** and low yields of the trioxolanes **3a–c**. Ozonolysis of **1a–c** in ester solvents chosen to be the same as the ester resulting from the breakdown of the primary ozonide showed the expected increase in the trioxolanes **3a–c** due to the higher concentration of the ester. The fact that the dioxolanes **2a–c** still were the predominant product is evidence for a greater dipolarophilicity for the enol ether compared to the ester. Ozonolysis of **1a** in ethyl acetate also produces the dioxolane **2a** as the major product with **3a** and **3c** the minor products. The lower overall ozonide yields in an acetate solvent—runs 4 and 13—compared to those using formates as the solvent—runs 3 and 7—indicate a lower dipolarophilicity for acetate compared to the formate esters. The product distribution from the ozonolysis of **1b** in acetone or in pentane in the presence of acetaldehyde or benzaldehyde indicates that the dipolarophilicity of enol ethers is greater than ketones but less than aldehydes. The large decrease in overall yields in acetone or pentane/acetaldehyde mixtures has no obvious explanation except that precedents exist in other ozonolysis reactions for repression of the usual ozonolysis products when the concentration of an aldehyde or ketone becomes high.[9]

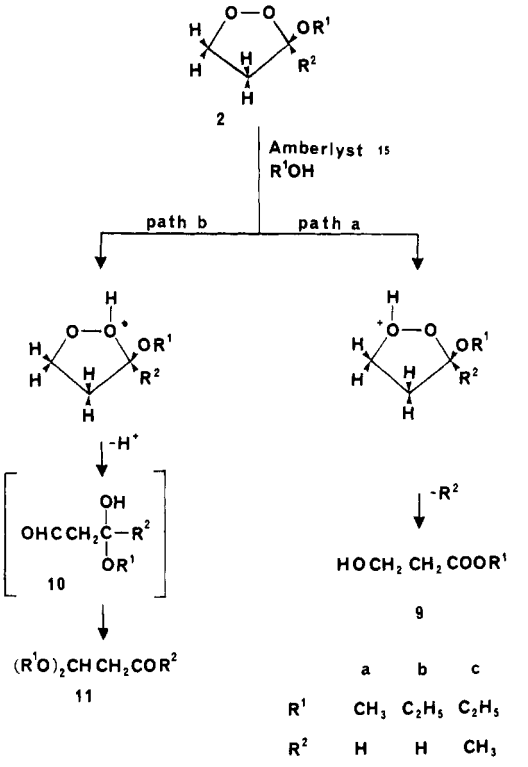
These observations focus on the relative dipolarophilicities of the 2π reactant. They help to rationalize why dioxolanes are formed upon ozonolysis of alkoxy-1-alkenes but not from alkyl-1-alkenes. The formation of the alkoxydioxolane and -trioxolane from the enol ether arises from the favorable presence of the carbonyl oxide, the activated alkene (good dipolarophile), and the ester (poor dipolarophile). Of course other reaction kinetics including ozone addition to the alkene, primary ozonide decomposition, and solvent cage effects must also be conducive to dioxolane and trioxolane formation. In the ozonolysis of an alkyl-1-alkene, the high dipolarophilicity of the aldehydes produced in situ and the reduced dipolarophilicity of the alkene toward the carbonyl oxide lead to the predominance of ozonide products.

Synthesis of 2a by an Intramolecular Cyclization. As part of the characterization of the alkoxydioxolanes, **2a** was synthesized by a different approach. From the synthesis of bicyclic endoperoxides it is known that *trans*-3-bromocyclopentane hydroperoxide reacts with silver acetate to give an intramolecular cyclization product 1,2-dioxabicyclo[2.2.1]heptane.[10] In analogy to this reaction **2a** was obtained in high yield by reacting 3-

$$BrCH_2CH_2CH{=}CH_2 \xrightarrow[CH_3OH]{O_3} BrCH_2CH_2CH(OCH_3)OOH \xrightarrow{Ag_2O} \mathbf{2a}$$

bromo-1-methoxypropyl hydroperoxide, obtained from ozonolysis of 4-bromo-1-butene in methanol, with silver oxide in methylene chloride at room temperature.

Scheme III. Acid-Catalyzed Rearrangement of 3-Alkoxy-1,2-dioxolanes



Decomposition Reactions of 3-Alkoxy-1,2-dioxolanes. The dioxolanes described in this paper are very stable for weeks in neutral solutions at 25 °C. When kept neat at this temperature, they decompose in several days. Two categories of decomposition products were observed and studied qualitatively. One group of products arose from cleavage of the O–O and either the C(3)–C(4) or C(4)–C(5) bonds of the dioxolanes. This is characteristic of a thermal or photochemical decomposition of peroxides. The decomposition products in this category included acetaldehyde, formaldehyde and traces of ethylene oxide from **2a–c**, methyl formate and methyl acetate from **2a**, and ethyl formate and ethyl acetate from **2b** and **2c**. After removal of these highly volatile products, analysis of the residue showed a complex reaction mixture in which only methyl β-hydroxypropionate from **2a** and ethyl β-hydroxypropionate from **2b** could be identified as major products. In those products the carbon skeleton of the dioxolane system is retained. This is characteristic of an acid-catalyzed rearrangement.

In order to study the acid-catalyzed decomposition, solutions of the dioxolanes **2a–c** in an alcohol containing the same alkoxy group found in the dioxolane were treated with Amberlyst-15 ion exchange resin, a strongly acidic, macroreticular resin suitable for nonaqueous catalysis. In the case of the 3-alkoxy-1,2-dioxolanes the course of the reaction depends on the substituents at C(3) and C(5). When R^2 (at C(3)) = H, protonation occurs at O-1 (Scheme III, path a) leading to the corresponding β-hydroxypropionate **9**. When R^2 = methyl, path b is predominant with protonation at O-2. In this case C(5) is oxidized leading to **10** and subsequently to the β-keto acetal **11**.

Recent thermolysis studies[6b,11a] of 1,2-dioxolanes reported fragmentation and rearrangement to give ketones

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(10) Porter, N. A.; Gilmore, D. W. *J. Am. Chem. Soc.* **1977**, *99*, 3503.

(11) (a) Adam, W.; Duran, N. *J. Am. Chem. Soc.* **1977**, *99*, 2729. (b) Keul, H.; Griesbaum, K. *Can. J. Chem.* **1980**, *58*, 2049; (c) *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 716; *Angew. Chem.* **1975**, *87*, 748. (d) Wilson, R. M.; Rekers, J. W. *J. Am. Chem. Soc.* **1981**, *103*, 206.

Table II. ^{1}H NMR Data for Deuterium-Labeled Ethyl Vinyl Ethers 7a–e[a]

ethyl vinyl ether	δ 6.45 m J, Hz	δ 4.16 m J, Hz	δ 3.96 m J, Hz
7a	*b*	*b*	s
7b	t[c] 2.1 d 6.8	*b*	d 6.8
7c	d 14.3	d 14.3	*b*
7d	*b*	t 2.1	*b*
7e	*b*	d 1.9 t 2.1	d 1.9 t 0.9
1b	d 14.4 d 6.8	d 14.4 d 1.9	d 6.8 d 1.9

[a] In $CDCl_3$. The ethoxy resonances: δ 1.29 (t, J = 7.0 Hz), 3.74 (q, J = 7.0 Hz). [b] Intensity ≤4% relative to ethoxy protons. [c] The triplet splittings arise from deuterium coupling.

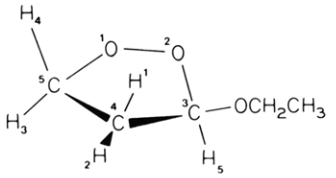
and epoxides as major products presumably via a 1-oxatrimethylene diradical. The volatile products observed from the alkoxy dioxolanes are consistent with these studies although the production of ethyl formate from **2c** requires an involved rearrangement scheme. The acid-catalyzed rearrangements of the alkoxydioxolanes parallel well-known reactions of peroxides. For example, methoxy hydroperoxides of the form $RHC(OCH_3)OOH$ are known to give methyl carboxylates by an intramolecular redox reaction.[11b,c] β-Hydroxy ketones which are analogous to the product obtained by path a, Scheme III, have been observed[6b] in the Fe^{2+} catalyzed decomposition of 1,2-dioxolanes. The three-carbon bridge cleavage observed upon protic acid decomposition of bicyclic endoperoxides[11d] is also similar to the reaction scheme proposed here.

Stereochemistry of 1,2-Dioxolane Formation. In order to probe the stereochemistry of the cycloaddition between the carbonyl oxide and enol ether, several stereolabeled ethyl vinyl ether species were synthesized, **7a–e**. Procedures analogous to those starting with methoxyacetylene were employed[12] substituting ethoxyacetylene **6a** due to its availability. Reduction of **6a** or **6b** (Scheme IV) with $LiAlH_4$ or $LiAlD_4$ and decomposition of the adduct with either H_2O or D_2O gave the vinyl ethers **7a–e**. Their NMR data are given in Table II and discussed in the Experimental Section.

Ozonolysis of **7a–d** in pentane followed by the destruction of the 3-ethoxy-1,2,4-trioxolanes (Scheme IV) yielded the dioxolanes **8a–h**. Analysis of their NMR spectra showed that each of the starting olefins **7a–d** gave two dioxolanes differing only in the stereochemical orientation of the hydrogen and deuterium at C-5 of the dioxolane ring. The stereochemistry of the H,D substituents at C(3) and C(4) was the same as in the starting vinyl ether. From inspection of the relative intensities of the different protons attached to C(5) (Table III) we concluded that pairs of isomeric dioxolanes **8a** and **8b** or **8c** and **8d** were produced in a ratio of 45/55 from **7a** or **7b**, respectively. Similarly **8e** and **8f** or **8g** and **8h** were obtained in a ratio of 45/55 from **7c** or **7d**, respectively.

The retention of alkene stereochemistry at C(3) and C(4) in the dioxolanes is consistent with a concerted 1,3-dipolar cycloaddition between the carbonyl oxide and the enol ether. Since indirect evidence for the concerted reactions of carbonyl oxides with other dipolarophiles exists[8] as well as for stereoselective reactions of enol ethers with other 1,3 dipoles,[13] this stereospecificity is not unexpected. On the other hand, the incomplete randomization of the

Table III. ^{1}H NMR Intensities for the Dioxolane Produced from Ozonolysis of Deuterium-Labeled Ethyl Vinyl Ether[a]



ethyl vinyl ether	H-1, δ	H-2, δ	H-3, δ	H-4, δ	H-5, δ
	2.59	2.76	3.94	4.24	5.32
7a	*b*	106	43	57	*b*
7b	*b*	102	45	55	98
7c	105	*b*	56	44	103
7d	99	*b*	55	45	*b*

[a] In pentane at −78 °C. [b] Intensity as in starting material, ≤4%.

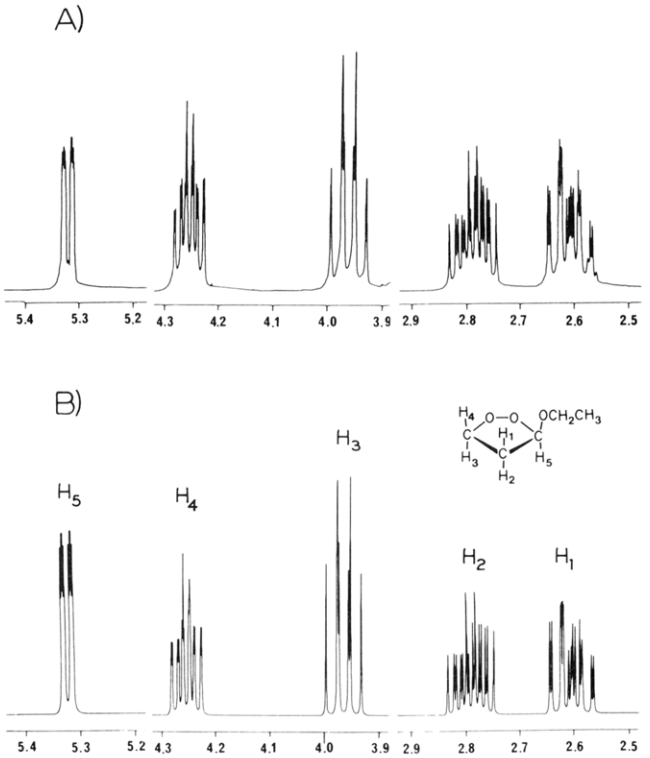


Figure 1. ^{1}H NMR signals due to ring protons H-1–H-5 of 3-ethoxy-1,2-dioxolane (**2b**): (A) experimental spectrum; (B) simulated spectrum.

stereochemistry at C(5) of the dioxolanes suggests a small stereoselectivity arising from the HDCOO moiety. This is suggestive of some preferential syn-anti isomerism in the carbonyl oxide formation and stereoselectivity in its subsequent reaction with the enol ether. A framework for introducing such stereoselectivity during ozonolysis reactions has already been discussed for reactions of alkyl-substituted alkenes and carbonyl oxides,[8a,b,14] although it has not previously been observed for reactions between HDCOO[15] and carbonyl compounds. This aspect of the reactivity of the carbonyl oxide is under investigation and will be described more fully in a subsequent report.[16]

^{1}H NMR Analysis of 3-Alkoxy-1,2-dioxolanes. The assignment and coupling constant analysis of the dioxolane

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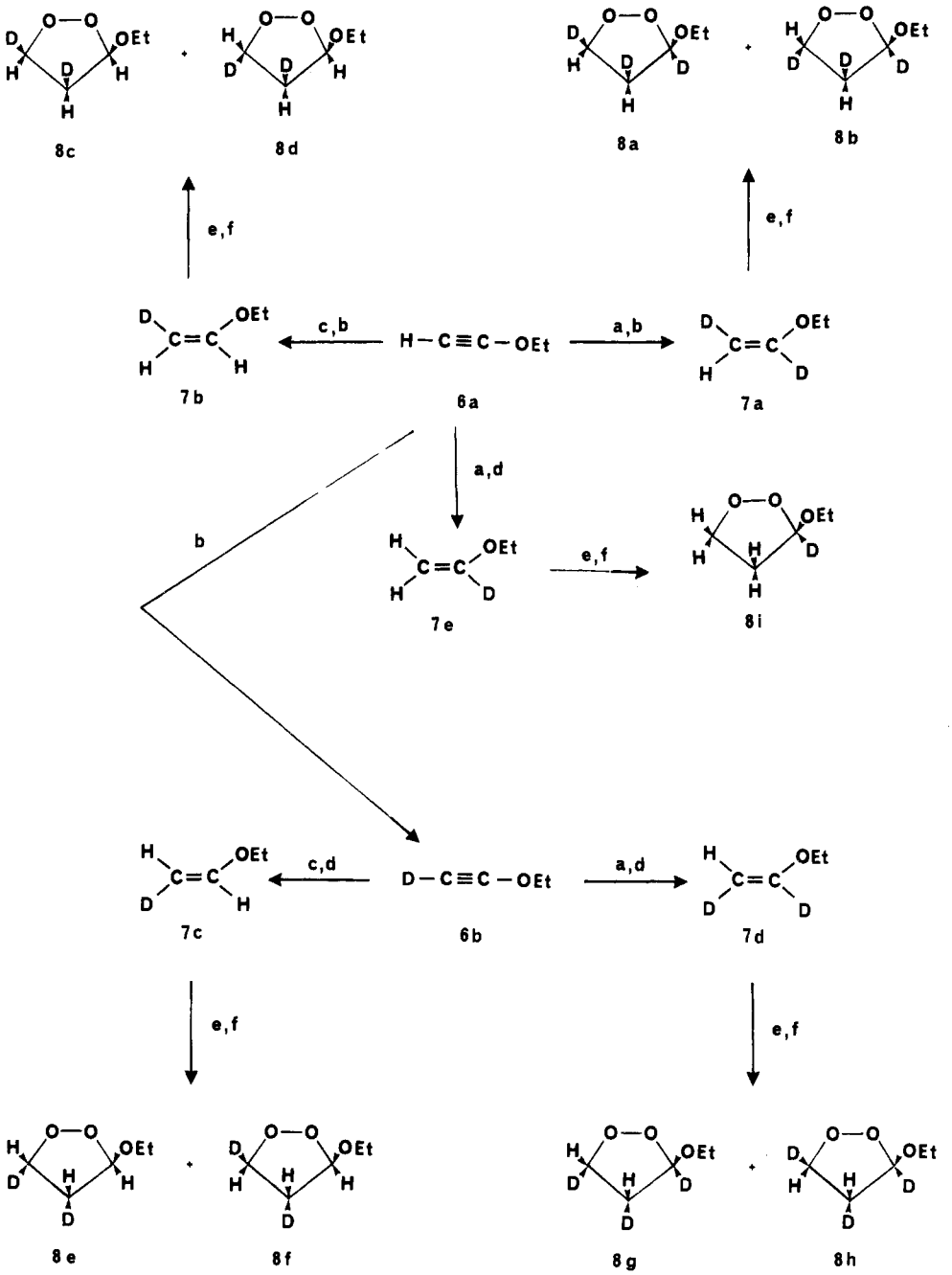
Scheme IV[a]



[a] (a) $LiAlD_4$/diglyme; (b) D_2O; (c) $LiAlH_4$/diglyme; (d) H_2O; (e) O_3/pentane; (f) Ph_3P.

^1H NMR spectra required some effort. The analysis of the spectra for **2b** (Figure 1) is representative of the methodology. The unlabeled dioxolane shows a complex ABMNX pattern with the chemical shift assignment presented in Table III. From the ozonolysis of **7c** and **7d** it was concluded that the proton cis to the ethoxy group became H-1 in the dioxolane. The proton trans to the ethoxy group must then be H-2, as confirmed by the ozonolysis of **7a** and **7b**. From comparison of the spectra of **8i** with that of the unlabeled **2b** all couplings associated with H-5 could be identified. With the program PANIC[17] the spectra of all three dioxolanes **2a–c** could then be simulated in good agreement with the experimental spectra. The resultant coupling constants are given in the Experimental Section. Efforts to unambiguously assign H-3 and H-4 by chemical shifts and coupling constants to H-1, H-2, and H-5 were not completely satisfactory. Difference NOE techniques were employed to resolve this problem[18] and the observed effects are given in Table IV

Table IV. {^1H:^1H} Nuclear Overhauser Enhancement Data for 3-Methoxy-1,2-dioxolane (2a)

irradiated[a]	obsd[a] – NOE[b]
H-1	H-2, H-4
H-2	H-1, H-3, H-5
H-3	H-2, H-4
H-4	H-1, H-3
H-5	H-2
OCH_3	H-5

[a] The numbering is the same as shown in Table III for **2b**. [b] All observed NOE's had a S/N ratio >4 in the difference spectra and ranged from 3% to 24% relative to the area of a nonenhanced proton resonance.

(17) PANIC (parameter adjustment in NMR by iteration calculation) is the spectra simulation program included in the operating system of the WM-360 NMR spectrometer provided by Bruker Co.

Table V. ^{13}C NMR Data for 3-Ethoxy-1,2-dioxolanes 8a–i in $CDCl_3$[a]

dioxolanes		C(3)	C(4)	C(5)	OCH_2	CH_3
8a + 8b	δ, m	101.41, t	41.93, d, t	67.75, d, t	63.46, t	14.84, q
	J_{CH}		133.2	150.3	143.3	126.9
	J_{CD}	26.5	20.7	22.6		
8c + 8d	δ, m	101.57, d	41.93, d, t	67.52, d, t	63.28, t	14.69, q
	J_{CH}	168.6	133.0	153.1	141.1	126.7
	J_{CD}		20.8	22.5		
8e + 8f	δ, m	101.71, d	42.07, d, t	67.70, d, t	63.51, t	14.86, q
	J_{CH}	166.2	134.9	150.2	143.0	127.2
	J_{CD}		20.2	22.4		
8g + 8h	δ, m	101.25, t	41.79, d, t	67.55, d, t	63.24, t	14.70, q
	J_{CH}		134.3	147.3	142.0	126.2
	J_{CD}	25.8	20.4	22.5		
8i	δ, m	101.73, t	42.48, t	68.05, t	63.48, t	14.85, q
	J_{CH}	168.5	134.2	147.7	142.1	127.6

[a] Coupling constants in Hz, chemical shift in ppm.

for **2a**.[19] These results, which are readily transferable to **2b** and **2c**, confirm the stereo assignment illustrated in Table III.

Experimental Section

Conventional vacuum line techniques were employed with some reactants and for product isolation. A Welsbach Model T-408 ozonator was employed. Mass spectra were obtained with a Finnegan Model 4021 GC/MS. Infrared spectra were taken with a Beckman IR 4240.

NMR spectra were taken with a Bruker WM-360 spectrometer with the exception of the NOE experiments reported in Table IV. These studies were performed on a Bruker AM-300 system by the FT difference method. Proton relaxation measurements were made on a carefully degassed sample with the inversion recovery (180°–τ–90°–*T*) sequence. A PAPS sequence was used to obtain the data. A 28.4° observation pulse and irradiation periods of 1–2 times the average T_1's were used. Acquisition times were 4 s with no relaxation delay between the end of acquisition and the start of the next irradiation. The FID with the decoupler off resonance was subtracted from a FID with the decoupler set on a given resonance.

Caution: No evidence of fast decomposition occurred during the workup and characterization of these potentially hazardous materials but the normal precautions in handling peroxides should be observed.

Materials. All solvents were dried by standard methods. Methyl vinyl ether (**1a**, Matheson) and ethyl vinyl ether (**1b**, Aldrich) were used without further purification. Ethyl isopropenyl ether (**1c**) was synthesized according to the literature.[20] The synthesis of specific labeled ethyl vinyl ether was carried out by analogy to the method of Dombroski[12] starting with ethoxyacetylene (Alfa), $LiAlD_4$, 98 atom % D (Aldrich), and D_2O, 99.8 atom % D (Aldrich).

Ozonolysis Procedure. Most of the ozonolyses of **1a–c** in different solvents (Table I) proceeded very similarly. Approximately 10–20 mmol of alkene in 20–40 mL of solvent (exact amounts in Table I) was ozonized at −78 °C until ozone passed the reaction vessel. Fast warmup to room temperature (25 °C) and successive distillations at 20 torr (water aspirator) and in a high vacuum separated solvent and polymeric residues from the hydroperoxides, dioxolanes, and trioxolanes. Yields were determined by weighing combined with the NMR analysis of mixtures. Methoxymethyl hydroperoxide,[21] ethoxymethyl hydroperoxide,[22] and trioxolane products were confirmed from literature data. Isolation and characterization of the new dioxolanes is discussed subsequently.

Ozonolysis of 1b in Pentane/Acetaldehyde or Acetone. The workup of runs 10 and 12 differed from the above. For both runs, the solvent was removed by distillation at 25 °C and 100 torr. For run 10, the remaining product was distilled at 25 °C on a high vacuum line into a trap at −196 °C. ^1H NMR analysis of the distillate showed a complex reaction mixture containing propylene ozonide, acetaldehyde, acetic acid, 1,3,5-trimethyl-2,4,6-trioxane, and ethyl formate but no dioxolane **2** or trioxolane **3**. Redistillation of this mixture gave 276 mg of product containing acetaldehyde, ethyl formate, and propylene ozonide[23] in a ratio of 3:2:5 corresponding to a yield of 15% for propylene ozonide. For run 12, the residue was distilled at 25 °C on a high vacuum line into traps at −40 and −196 °C. The fraction at −196 °C (880 mg) contained 95% acetone, 2.5% **5c**,[9a] and 2.5% ethyl formate. The fraction at −40 °C (330 mg) was consistent with 88% **2b** and 12% **3b**. This corresponds to a yield of 22% **2b**, 2% **3b**, and 2% **5c**.

Isolation of 2a–c. Approximately 1 g of the mixture obtained from either run 2, 6, or 12 (Table I) in 8 mL of methylene chloride was treated with the stoichiometric amount of triphenylphosphine in 2 mL of methylene chloride to completely reduce the trioxolane. Methylene chloride was removed with a water aspirator and the dioxolane was distilled at room temperature on a high vacuum line. Elemental analyses of the dioxolanes were not possible due to their slow decomposition to volatile materials. The spectral analyses along with the intramolecular cyclization synthesis of **2a** and the analysis of decomposition products described herein were adequate to establish purity (<99%) and structure.

3-Methoxy-1,2-dioxolane (2a). The IR, MS, and ^{13}C NMR have been reported.[2] ^1H NMR (360 MHz, $CDCl_3$) ABMNX system δ 2.60 (H-1), 2.79 (H-2), 3.96 (H-3), 4.24 (H-4), 5.21 (H-5) (J_{12} = 12.8, J_{13} = 7.4, J_{14} = 7.6, J_{15} = 1.3, J_{23} = 8.7, J_{24} = 4.4, J_{25} = 5.7, J_{34} = 7.4, J_{35} = 0, J_{45} = 0.8 Hz), OMe group 3.41 (s). **3-Ethoxy-1,2-dioxolane (2b)**: ^1H NMR ($CDCl_3$) ABMNX system δ 2.59 (H-1), 2.76 (H-2), 3.94 (H-3), 4.24 (H-4), 5.32 (H-5) (J_{12} = 12.6, J_{13} = 7.5, J_{14} = 7.9, J_{15} = 1.5, J_{23} = 8.5, J_{24} = 4.3, J_{25} = 5.7, J_{34} = 7.2, J_{35} = 0, J_{45} = 0.8 Hz), ETO group 1.23 (t, J = 7.1 Hz, 3 H), 3.50 (dq, J = 9.5, 7.1 Hz, 1 H), 3.82 (dq, J = 9.5, 7.1 Hz, 1 H); ^{13}C NMR ($CDCl_{13}$) δ 14.85 (q, J = 127.6 Hz CH_3 from EtO group), 42.48 (t, J = 134.2 Hz, C-4), 63.48 (t, J = 142.1 Hz, CH_2 from EtO group), 68.05 (t, J = 147.7 Hz, C-5), 101.73 (t, J = 168.5 Hz, C-3); IR (CCl_4) 3000 (vs), 2950 (s), 2920 (s), 2895 (vs), 1450 (s), 1410 (w), 1380 (s), 1340 (vs), 1285 (s), 1215 (w), 1145 (vs), 1110 (vs), 1085 (vs), 1045 (w), 980 (s), 935 (vs), 915 (s), 905 (s) cm^{-1}; GC-MS (70 eV), *m/e* (relative intensity) 118 (M^+, 9), 85 (100), 73 (25), 58 (34), 57 (76), 47 (11), 45 (32), 44 (14), 43 (44). **3-Ethoxy-3-methyl-1,2-dioxolane (2c)**: ^1H NMR (360 MHz, $CDCl_3$) ABMN system δ 2.51 (H-1), 2.75 (H-2), 4.13 (H-3), 4.28 (H-4) (J_{12} = 12.2, J_{13} = 8.6, J_{14} = 5.3, J_{23} = 6.8, J_{24} = 7.7, J_{34} = 7.1 Hz), EtO group 1.20 (t, J = 7.0 Hz, 3 H), 3.53 (dq, J = 9.2, 7.0 Hz, 1 H), 3.66 (dq, J = 9.2, 7.0 Hz, 1 H), methyl group 1.52 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 15.32 (q, J = 126.0 Hz, CH_3 from

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EtO group), 18.67 (q, J = 128.2 Hz, CH_3 from Me group), 47.26 (t, J = 134.2 Hz, C-4), 57.10 (t, J = 146 Hz, CH_2 from EtO group), 69.41 (t, J = 151.4 Hz, C-5), 105.90 (s, C-3); IR (CCl_4) 2990 (s), 2945 (s), 2890 (s), 1770 (vw), 1725 (vw), 1450 (w), 1395 (w), 1385 (s), 1305 (w), 1210 (s), 1165 (vs), 1125 (s), 1105 (s), 1065 (vs), 960 (w), 905 (w), 865 (s) cm^{-1}; GC-MS (70 eV), m/e (relative intensity) 132 (M^+, 6), 99 (100), 87 (61), 72 (25), 71 (29), 61 (8), 57 (11), 43 (88), 42 (13).

Synthesis of 2a from 3-Bromo-1-methoxypropyl Hydroperoxide (12) with Silver Oxide. 4-Bromo-1-butene, 270 g (20 mmol), was ozonized in 30 mL of methanol. The methanol was removed by using a water aspirator and the residual volatile products were removed on a vacuum line. The residue (3.30 g, 90%) **12** was dissolved in 50 mL of dichloromethane and treated with 5 g of silver oxide while cooling with an ice bath. After it was stirred for 12 h at 25 °C the reaction mixture was filtered, dichloromethane was removed, and the product was distilled at high vacuum. A yield of 1.67 g (16 mmol, 80%) of **2a** was obtained.

Synthesis of Deuterium-Labeled Ethyl Vinyl Ethers 7a-e. To lithium aluminum hydride or deuteride (2.5 g, 66 mmol or 60 mmol) in 60 mL of diglyme 7 g (100 mmol) of ethoxyacetylene (**6a**) or ethoxyacetylene-d_1 (**6b**) was added dropwise. Intermittent cooling maintained the temperature between 35 and 40 °C. After an additional hour at room temperature deuterium oxide or water was added dropwise, while the reaction temperature was maintained between 20 and 30 °C. The reaction product was distilled under vacuum into a trap at -196 °C. Redistillation yielded the corresponding ethyl vinyl ethers **7a-e** in yields between 3 and 3.7 g or 42-51%. The product was allowed to stand over calcium hydride for 12 h and was then stored at -16 °C under argon. ^1H NMR spectra of the labeled ethyl vinyl ethers are given in Table II. The stereospecificity in the products was nearly 100%.

Ozonolysis of Deuterated Ethyl Vinyl Ether. 7a-e, 500 mg (6.75 or 6.85 mmol), in 10 mL of pentane was ozonized at -78 °C. After the reaction mixture was degassed and warmed to 0 °C, it was treated with a solution of 178 mg (0.68 mmol) of triphenylphosphine and stirred 2 h at 25 °C. The solvent was removed with a water aspirator and the dioxolanes **8a-i** were isolated by high-vacuum distillation. The results of the ^1H NMR spectra are shown in Table III. Table V gives the ^{13}C NMR data for the labeled dioxolanes.

Decomposition Reactions of 3-Alkoxy-1,2-dioxolanes 2a-c. Approximately 300 mg of the respective dioxolane was stored in an evacuated sample bulb at 25 °C for 2 weeks. At that time, **2a** and **2b** were completely decomposed while appreciable amounts of **2c** still remained. The volatile products were then distilled at room temperature on a vacuum line into a trap at -196 °C leaving an involatile residue (200 mg) which contained as the major product methyl β-hydroxypropionate[25] (**9a**) from **2a**, ethyl β-hydroxypropionate[26] (**9b**) from **2b** and undecomposed starting material from **2c**. The volatile products were acetaldehyde, methyl formate, and methyl acetate (4:5:1) from **2a** and acetaldehyde, ethyl formate, and ethyl acetate from **2b** and **2c** in a ratio of 4:4.5:1.5 and 6.5:2:1.5, respectively. There was also evidence for formaldehyde and traces of ethylene oxide. Acid-catalyzed rearrangements were carried out by dissolving 1-6 mmol of **2a-c** in approximately 5 mL of dry methanol and ethanol and treating this overnight (stirring) with 200-500 mg of Amberlyst 15. After separation of the Amberlyst, the alcohol was removed by distillation at 20 torr. The product was distilled in a high vacuum and identified as methyl β-hydroxypropionate[25] (**9a**, 53%) from **2a**, ethyl β-hydroxypropionate[26] (**9b**, 66%) from **2b** and 1,1-diethoxybutan-3-one[27] (**11c**, 76%) from **2c**.

Acknowledgment. This work was supported by Grant CHE-8303615 from the National Science Foundation, Washington, DC. We are pleased to acknowledge helpful discussions with Prof. S. Ege on dioxolane decomposition and Prof. M. Koreeda on the dioxolane NMR. The assistance of Frank Parker in obtaining difference NOE data was invaluable.

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Stereochemistry in the 1,3-Dipolar Cycloaddition Reactions of Formaldehyde Oxide-d_1 (HDCOO)

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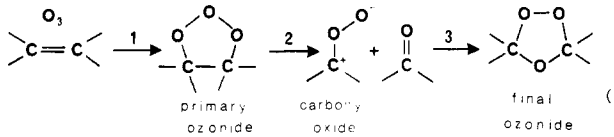
Received April 18, 1985

Ozonolysis of *E,Z* pairs of ethyl vinyl-2-d_1 ether, ethyl vinyl-1,2-d_2 ether, styrene-β-d_1, and 1-hexene-1-d_1 were investigated in pentane and ester solvents and in the presence of added acetaldehyde and benzaldehyde. Different amounts of H,D stereoselectivity were found at C(5) in the resultant 1,2,4-trioxolanes and 1,2-dioxolanes. The deuterium atoms at C(5) in the predominant trioxolane isomers had the same configuration as in the starting alkenes but the opposite configuration in the predominant dioxolane isomers. The stereoselectivity was associated with syn-anti isomerism in the carbonyl oxide HDCOO. It was analyzed, in the context of the Criegee mechanism, as arising from competing transition states in the decomposition of the primary ozonide and in the recombination of the carbonyl oxide with a dipolarophile. It was shown that syn-anti equilibration was not important and that the stereodirective influence of the dipolarophile reacting with HDCOO decreases in the order ester > acetaldehyde > benzaldehyde.

The carbonyl oxide produced during ozonolysis of an alkene (eq 1) is an intriguing 1,3-dipole which has played



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a central role in the mechanism of ozonolysis since the 1950's.[1] It has a sufficient lifetime, especially in polar media, to escape the initial solvent cage and react with a variety of dipolarophiles. However, low steady-state concentrations have precluded its spectroscopic detection. In spite of this fleeting existence a good deal has been inferred

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0022-3263/85/1950-3371$01.50/0