12 (R = tBu) (5.13 g) as a yellow oil. The product was flash chromatographed (2:1, hexane/EtOAc, 15 × 5 cm), yielding 3.6 g of 17 (R = tBu) (70%) as a pale yellow oil, a mixture of diastereomers that could be separated by MPLC (silica gel) 15% EtOAc, 85% hexane, first compound eluted 4.5–5.6 h, second compound 5.6–6.5 h (some overlap still occurred). ^{1}H NMR ($CDCl_3$, 250 MHz) first diastereomer (as a racemate) eluted by silica gel, material obtained as a solid (purity: 95% by NMR, HPLC): δ 7.44–7.31 (m, 5 H), 5.24–5.04 (m, 2 H), 4.97 and 4.89 (d, J = 7, 1 H, exch), 4.83–4.69 (m) and 4.47–4.34 (m, including a doublet at 4.39, J = 5) and 4.18 (d, J = 5, 3 H), 3.61–3.50 (m, 1 H), 3.31–3.19 (m, 1 H), 2.63–2.55 (m, 2 H), 2.31–2.18 (m, 1 H), 2.05–1.80 (m, 2 H), 1.52–1.46 (m, includes a large singlet at 1.48) and 1.21 (d, J = 7, 12 H). ^{1}H NMR ($CDCl_3$, 250 MHz) second diastereomer (as a racemate) eluted on silica gel, material obtained as an oil, contaminated with ca. 10% of 1st diastereomer: δ 7.42–7.24 (m, 5 H), 5.18–5.04 (m, 2.5 H, 0.5 H exch), 4.84 (d, J = 8, 0.5 H, exch), 4.78–4.67 and 4.67–4.50 (m, 1 H), 4.26 and 4.12 (d, J = 5, 1 H), 3.63–3.51 (m, 1 H), 3.31–3.20 (m, 1 H), 2.71–2.57 (m, 2 H), 2.29 and 2.23 (s, 1 H), 2.00–1.78 (m, 2 H), 1.61–1.38 (m) and 1.15 (d, J = 7, 12 H). MS (m/e): 411 (M^+, 8), 355 (9), 311 (24), 202 (16), 91 (100).

Determination of the Ease of Epimerization of the Alanine α-CH in Z-Ben-Ala-OtBu. Either of the diastereomers separated in the above procedure could be used in the epimerization experiments. HPLC was used to detect formation of the other diastereomer under the reaction conditions. The following conditions gave no detectable epimerization (detection limit is ca. 0.5%; all conditions are 18 h and 50 °C unless otherwise specified): CH_3OH alone or containing HOAc or Et_3N or both; DMSO containing HOAc and Et_3N; Et_3N. The following experiments gave no detectible epimerization over 24 h at 25 °C: CH_2Cl_2 containing HOAc; CH_2Cl_2 containing H-Ala-OMe; CH_2Cl_2 containing 1:1 HOAc and H-Ala-OMe. In CH_2Cl_2 containing dichloroacetic acid at 25 °C for 24 h, 14% epimerization was observed, and addition of 1 equiv of H-Val-OMe raised the level of epimerization to 22%.

Cbz-Ben-Ala-Phe-OMe (17c). In a glovebag filled with N_2 was mixed BF_3·OEt_2 (0.1 mL), glacial HOAc (ca. 0.8 mL), and CH_2Cl_2 (8 mL). Solid Cbz-Ben-Ala-OtBu, **17**, X = tBu (49 mg, 0.12 mmol), was added in one portion with stirring at room temperature, and the mixture allowed to stand for 45 min. The crude reaction mixture was poured into a solution of EtOAc (30 mL) and washed with phosphate buffer saturated with NaCl (pH 7, 3 × 5 mL), $NaHCO_3$ solution (3 × 5 mL), and brine (1 × 5 mL). The resulting organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude product mixture was dissolved in THF (2 mL), and 1-hydroxybenzotriazole (18 mg, 0.12 mmol) was added with stirring. After all HOBt had dissolved, the solution was chilled to 0 °C, and DCC (25 mg, 0.12 mmol) was added with stirring. After the mixture was stirred for 1 h, the free base of H-L-Phe-OMe (26 mg, 0.12 mmol) in THF (0.5 mL) was added. The solution was maintained at 0 °C for 1 h more and at room temperature for 12 h. Solid dicyclohexylurea was removed by filtration, and the DCU was washed with THF. The combined THF solutions were concentrated, and the crude mixture was flash chromatographed on silica gel (1:1 gradient to 1:2, hexane/EtOAc). The impure product was dissolved in EtOAc (25 mL) and washed with $NaHCO_3$ solution (3 × 5 mL) and brine (1 × 5 mL) providing **17C**, X = Phe-OMe (25 mg, 42%), as a white solid (mp 80 °C with decomposition), purity 97% by HPLC. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.46–7.06 (m, 10 H), 6.82 and 6.12 (d, J = 9, combined 1 H), 5.22–4.64 (m, 4 H), 4.40–4.03 (m, 2 H), 3.74 and 3.69 (s, 3 H), 3.72–3.35 (m, 2 H), 3.33–3.03 (m, 3 H), 2.70–2.48 (m, 2 H), 2.28–2.13 (m, 1 H), 2.05–1.05 (m, 14 H). MS (m/e): 516 (M^+, 13), 311 (33), 310 (71), 91 (100).

Cbz-Gly-Ben-Ala-OtBu (18). To a solution of Cbz-Ben-Ala-OtBu **17A** (100 mg, 0.243 mmol) in CH_3OH (2 mL) and glacial HOAc (28 μL) under an atmosphere of N_2 was added Pd/C (15 mg). The N_2 was displaced with H_2, and a positive pressure of H_2 was maintained with a H_2-filled balloon while the reaction mixture was stirred vigorously. Within 30 min the reaction was complete and purged with N_2. The crude reaction mixture was filtered through a pad of Celite, and the celite pad was washed with CH_3OH until the washes gave a negative ninhydrin test. The combined filtered reaction mixture and washes were concentrated, and HOAc was removed by azeotropic distillation with toluene, yielding a yellow oil. This oil was dissolved in CH_2Cl_2 (2 mL) to which was added Cbz-Gly-OSu (74 mg, 0.24 mmol) and diisopropylethylamine (31 mg, 0.24 mmol) with stirring. This solution was stirred at room temperature for 18 h. The crude reaction mixture was diluted with EtOAc (10 mL), washed with $KHSO_4$ solution (3 × 2 mL), $NaHCO_3$ solution (2 × 2 mL), and brine (1 × 2 mL), dried over $MgSO_4$, filtered, and concentrated, yielding **18** (105 mg, 92%) as an oil, purity 90% by HPLC. ^{1}H NMR ($CDCl_3$, 250 MHz): δ 7.34 (s, 5 H), 5.79–5.62 (m, 1 H), 5.31–5.05 (m, 3 H), 4.80–4.48 (m, 2 H), 4.03–3.79 (m, 3 H), 3.65–3.48 (m, 1 H), 3.33–3.18 (m, 1 H), 2.86–2.60 (m, 2 H), 2.38–2.19 (m, 1 H), 1.95–1.78 (m, 2 H with a s at δ 1.90), and 1.49–1.34 (m, 12 H). MS (m/e): 468 (M^+, 3), 267 (20), 159 (24), 91 (100).

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Stereochemical Effects in the Ozonolysis of (*E*)- and (*Z*)-1-Ethoxypropene

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The ozonolysis of (*E*)-1-ethoxypropene (or (*Z*)-1-ethoxypropene) gave cis and trans pairs of 1,2-dioxolanes, 1,2,4-trioxolanes (ozonides), and 1,2,4,5-tetroxanes. Ozonolysis of mixtures of the *E* and *Z* alkenes led to variation in the dioxolane stereoisomer ratios but not in the trioxolane ratios. Ozonolysis in the presence of added alcohol or aldehydes produced hydroperoxides or ozonides, respectively, from the methyl-substituted carbonyl oxide. The results are consistent with a Criegee ozonolysis mechanism if the two alkenes produce different relative amounts of the syn and anti carbonyl oxide (CH_3HCOO), which recombine at different rates with dipolarophiles.

Introduction

It was recently reported[1] that the ozonolysis of methyl vinyl ether gave 3-methoxy-1,2-dioxolane in 68% yield, along with small amounts of the normal ozonide or 1,2,4-trioxolane. The unexpected dioxolane could be explained by a Criegee mechanism involving reaction of a carbonyl

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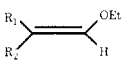
oxide with the starting alkene (Scheme I). This was the first example of a cycloaddition between a carbonyl oxide and alkene during an ozonolysis.[2] The stereochemistry of the reaction was explored by ozonizing stereolabeled HDC=CHOEt.[5] The cycloaddition across the double bond was found to be stereospecific, but incomplete randomization of the H–D stereochemistry occurred at C-5 of the dioxolane as well as the trioxolane. This indicated the stereoselective formation of syn and anti HDCOO carbonyl oxides during the primary ozonide decomposition (cycloreversion).

In order to further explore the ozonolysis of enol ethers and to study the stereochemical effects involved in the reaction, we undertook the ozonolysis of (*E*)- and (*Z*)-1-ethoxypropene, **1a** and **1b**. The findings described here



1a: $R_1 = H; R_2 = CH_3$
1b: $R_1 = CH_3; R_2 = H$

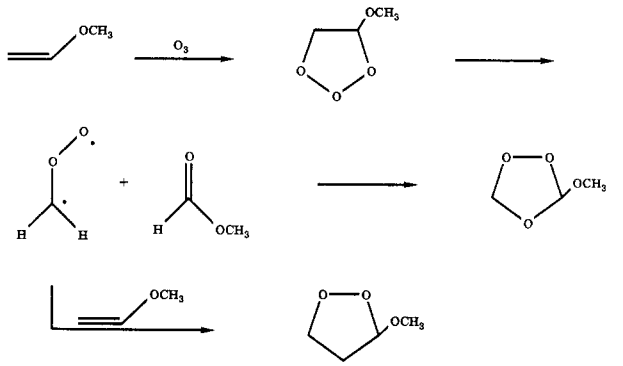
2a: $R_1 = CH_3; R_2 = H$
2b: $R_1 = H; R_2 = CH_3$

indicate that cis–trans pairs of the 1,2-dioxolanes and the trioxolanes were formed as well as dimers (1,2,4,5-tetroxanes) of the carbonyl oxide CH_3HCOO. An intriguing variability in the cis/trans ratios of the dioxolanes was observed as different mixtures of the *E* and *Z* alkenes were ozonized, but no variation was detected in the trioxolane stereochemistry. This paradoxical finding could be rationalized if each alkene produces a different syn/anti carbonyl oxide (CH_3HCOO) ratio and if each carbonyl oxide has a different reactivity toward various dipolarophiles. This paper also reports on additional trapping reactions of the carbonyl oxide produced during the ozonolysis.

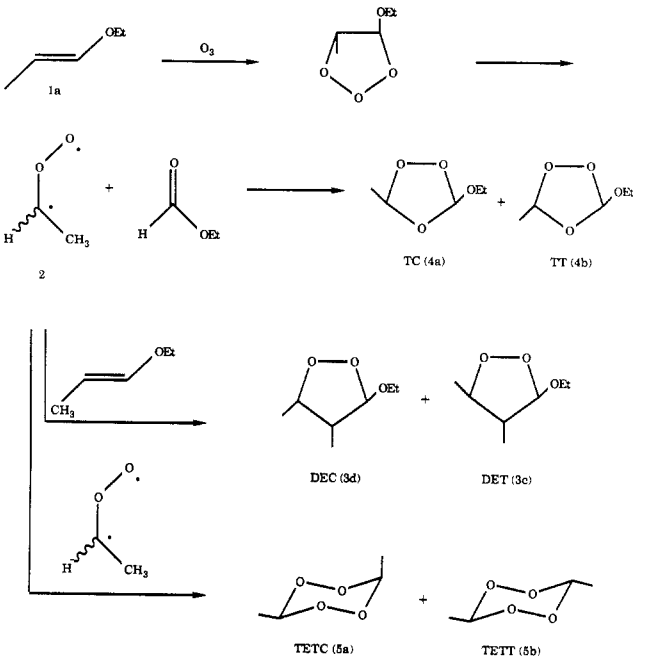
Results and Discussion

The reaction of (*E*)-1-ethoxypropene with ozone was initially studied in the solvent pentane. This results in two dioxolanes called DET (**3c**; *d*ioxolane, *E* starting alkene, *t*rans methyls) and DEC (**3d**), two trioxolanes, TC (**4a**; *t*rioxolane, *c*is methyl) and TT (**4b**), and a tetroxane TETT (**5b**; tetroxane, trans methyls; only this isomer was seen in pentane). In ether (cf. below), the cis tetroxane isomer TETC (**5a**) was also obtained according to Scheme II. (*Z*)-1-Ethoxypropene reacts in an analogous manner to form two new dioxolanes DZT (**3a**) and DZC (**3b**) as well as the same trioxolanes and tetroxanes. The yields of these products are given in Table I as runs 1 and 6. These yields are quite low as the major product was polymeric residues. The yield of ethyl formate was high (~85%), implying that little ethyl formate or unreacted alkene was incorporated in the residue. No evidence for any 4-ethoxy-1,2-dioxolanes or 3-ethoxy-1,2-dioxolanes with loss of the alkene stereochemistry at C-3 and C-4 (cf. next paragraph) were observed; their yields must be at least 10 times smaller than the observed dioxolanes. The absence of the latter product implies that isomerization of the alkene under reaction conditions is not a significant factor.

Scheme I



Scheme II

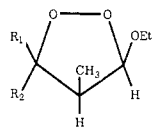


NMR Analysis. The stereochemistries of the four dioxolanes were determined by NOE experiments on the ring protons (Table II). Of the two dioxolanes (**3c**, **3d**) obtained from the *E* alkene, the DET isomer must have the three protons (H-3, H-4, H-5) in the down, up, down configuration (**3c**) since no protons show NOE effects. The other isomer DEC must have the three protons in the down, up, up configuration (**3d**) since irradiation of H-4 affects H-5 and vice versa. For the dioxolanes obtained from the *Z* alkene, the DZC isomer must have all three protons on the same side (**3b**) since irradiation of H-4 affects both H-3 and H-5 and vice versa. The other isomer DZT has H-5 trans to H-4 (**3a**) since irradiation of H-4 affects only H-3 and vice versa.

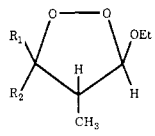
NOE was not helpful in the determination of the trioxolane stereochemistry. No effect was seen upon irradiation of any proton. Stereochemical assignment was made on the basis of the chemical shift, coupling constants, and analogies to other ozonides.[6] A key observation is the presence of a long-range coupling between the trans protons H-3 and H-5 similar to the observation first documented in propylene ozonide.[6]

The energies of activation to ring inversion of 3,6-dimethyl-1,2,4,5-tetroxane were determined by use of variable-temperature NMR spectroscopy. In the methine

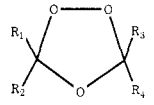
(1) Keul, H.; Kuczkowski, R. L. *J. Am. Chem. Soc.* **1984**, *106*, 5370.
(2) Nonconcerted dioxolane production from decomposition of a secondary ozonide in the presence of BF_3·OEt_2 and phenylalkenes is a related process.[3] An intramolecular variant of the cycloaddition reaction has recently been observed.[4]
(3) Yoshida, M.; Miura, M.; Nojima, M.; Kusabayashi, S. *J. Am. Chem. Soc.* **1983**, *105*, 6279.
(4) Bunnelle, W. H.; Schlemper, E. O. *J. Am. Chem. Soc.* **1987**, *109*, 612.
(5) Keul, H.; Kuczkowski, R. L. *J. Org. Chem.* **1985**, *50*, 3371.
(6) Choe, J.-I.; Choi, H.-S.; Kuczkowski, R. L. *Magn. Reson. Chem.* **1986**, *24*, 1044.



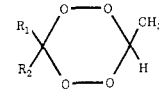
3a: R_1 = H; R_2 = CH_3 (DZT)
3b: R_1 = CH_3; R_2 = H (DZC)



3c: R_1 = CH_3; R_2 = H (DET)
3d: R_1 = H; R_2 = CH_3 (DEC)



4a: R_1 = CH_3; R_2 = H; R_3 = OEt; R_4 = H (TC)
4b: R_1 = H; R_2 = CH_3; R_3 = OEt; R_4 = H (TT)
4c: R_1 = CH_3; R_2 = H; R_3 = CH_3; R_4 = H
4d: R_1 = H; R_2 = CH_3; R_3 = CH_3; R_4 = H
4e: R_1 = CH_3; R_2 = H; R_3 = CD_3; R_4 = CD_3
4f: R_1 = CH_3; R_2 = H; R_3 = $(CH_3)_2HC$; R_4 = H
4g: R_1 = H; R_2 = CH_3; R_3 = $(CH_3)_2HC$; R_4 = H
4h: R_1 = CH_3; R_2 = H; R_3 = $(CH_3)_3C$; R_4 = H
4i: R_1 = H; R_2 = CH_3; R_3 = $(CH_3)_3C$; R_4 = H



5a: R_1 = CH_3; R_2 = H (TETC)
5b: R_1 = H; R_2 = CH_3 (TETT)

region, a quartet was observed for one isomer, which remained unchanged from −70 to +55 °C. A pair of equal intensity quartets was observed for the other isomer, which coalesced at 55 °C, corresponding to an activation energy of 15.6 kcal mol^{-1}. This spectrum was assigned to the cis isomer (**5a**). The lack of further splitting for the trans isomer indicates that the equilibrium distribution of the diaxial and diequatorial conformers favors essentially one of them.

Medium Effects. The effect of solvent polarity on the product yield and stereochemistry is seen in Table I. As the polarity of the solvent increases, the amount of trioxolane decreases. Presumably, the in-cage recombination of the carbonyl oxide and ester formed in step 2 of the Criegee reaction is decreased by increased break up of the solvent cage in the polar solvents. The changes in dioxolane and tetroxane yields are less systematic. One noteworthy case is run 2 in ether where the predominant product is tetroxane, and the cis and trans isomers (TETC, **5a**; TETT, **5b**) could be identified. In the other solvents, the amounts of tetroxane **5a** were too low to definitely establish a yield. The ether results might be attributed to a stabilization of the carbonyl oxide by complexation with the lone pairs of the solvent, as first suggested in other ozonolyses.[7] This could increase the opportunity to form tetroxanes (as found) and might alter the cis/trans ratios of the products if syn–anti equilibration also occurs. Some evidence for stereo changes are found in the ozonides but not in the dioxolanes.

It is apparent that the overall yields vary in a complex fashion with changes in solvent. Nevertheless, the dioxolane stereochemistry is relatively insensitive to changes in the polarity of the solvent (Table I). No change is observed in the cis/trans ratio of the dioxolanes from the *E* alkene in pentane and $CHClF_2$. A small change in the stereochemistry from the *Z* alkene occurs as the polarity of the solvent is increased. The DZC/DZT ratio is 29/71 in pentane and 21/78 in $CHClF_2$.

Trapping Reagents. In order to determine the cleavage direction of the primary ozonide, both the *E* and the *Z* alkenes were ozonized in methanol, which effectively traps the carbonyl oxide. Both alkenes formed the same product, 1-methoxyethyl hydroperoxide (**6**) in yields of 75–80% arising from the methyl carbonyl oxide (CH_3HCOO). No product was observed for the other cleavage direction.

Additional trapping experiments were conducted to provide information on the syn/anti stereochemistry of the carbonyl oxide. Both alkenes were separately ozonized in a variety of solvent systems, which included acetone-d_6, ethyl formate, and pentane containing aldehydes (Table III). As expected, the yield of ozonides increased in ethyl formate (run 11). In the other experiments, the trioxolanes expected from the cycloaddition of methylcarbonyl oxide (CH_3HCOO) with the aldehyde or ketone were observed as products. The stereochemistry of the trioxolanes did not differ markedly between the *E* or *Z* starting alkene.

As the size of the added aldehyde increased from acetaldehyde to pivaldehyde, the cis/trans ratio of the cross ozonides increased from 37/63 to 61/39, independent of alkene stereochemistry. This increase in the cis ozonide upon addition of bulkier added aldehydes has been seen previously.[8] In that case, a *tert*-butyl-substituted carbonyl oxide was the dipolarophile, but the same trend was observed in the cis/trans ratio of the ozonides.

Ozonolysis of *E*/*Z* Alkene Mixtures. The information obtained from the aldehyde trapping experiments might imply that similar methylcarbonyl oxide syn/anti ratios are obtained from the two alkenes since the stereochemistry in the 1,2,4-trioxolanes does not change markedly with alkene configuration. If this is correct, the stereochemical ratios for the dioxolanes and trioxolanes should be the same whether a single isomer or a mixture of the two alkenes is ozonized. Inspection of the results in Table IV shows that this was observed for the trioxolanes but was not for the dioxolanes. For example, with 100% *Z* isomer, a 29/71 DZC/DZT ratio was obtained. With 51% *Z* the ratio increased to 49/51 and with 6% *Z* it was 67/33. This suggests that different syn/anti carbonyl oxide ratios are obtained from the two alkenes. These results also indicate that the *E* alkene reacts faster with ozone than the *Z* alkene since at 12% *Z*, 0.58 mmol of DZC and 0.36 mmol of DZT are formed, which gives a calculated yield of 133% based on the initial amount of *Z* alkene.

The diversity in the dioxolane and trioxolane stereochemical ratios is obviously paradoxical. To resolve this, the stereochemical factors that affect an ozonolysis reaction need to be examined in the context of the Criegee mechanism.[9] Assuming that the cycloaddition of ozonide to the alkene (step 1) is stereospecific,[9a] stereochemistry enters at two other steps. The cycloreversion of the primary ozonide (step 2) can form a syn or anti carbonyl oxide, and the reaction of the carbonyl oxide with a dipolarophile endo or exo (step 3) can lead to cis and trans isomers in the 5-membered ring. Related considerations are whether syn–anti interconversion can occur and whether step 3 is concerted.

Upon review of the dioxolane results, it is noteworthy that the stereochemistry is unaffected by solvent changes while the stereochemistry at C-5 of the dioxolane (but not at C-3 and C-4) varies with the composition of the *E*,*Z* alkene mixture. From the variability at C-5, it is reasonable to postulate that each alkene produces a different syn–anti carbonyl oxide ratio and that equilibration between them does not occur. Also, step 3 is concerted (stereospecific addition between C-3 and C-4), and the variability at C-5 results from various stereo interactions between the substituent on the carbonyl oxide and the dipolarophile. For example, the four configurations that

(7) (a) Bauld, N.; Thompson, J. A.; Hudson, C. E.; Bailey, P. S. *J. Am. Chem. Soc.* **1968**, *90*, 1822. (b) Bailey, P. S. *Ozonation in Organic Chemistry*; Academic Press: New York, 1978; Vol. 1, p 91.

(8) Murray, R. W.; Williams, G. J. *J. Org. Chem.* **1969**, *34*, 1891.

(9) (a) Kuczkowski, R. L. *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; Wiley: New York, 1984; Chapter 11. (b) Kuczkowski, R. L. *Acc. Chem. Res.* **1983**, *16*, 42.

Table I. Yields (in Percent) of Dioxolanes, Trioxolanes, and Tetroxane from Ozonolysis of (*Z*)- or (*E*)-1-Ethoxypropene

run	solvent	alkene	DZC (3b)	DZT (3a)	DEC (3d)	DET (3c)	TC (4a)	TT (4b)	TETT (5b)
1	pentane	*Z*	8	20			4	1	3
2	ether	*Z*	5	12			1	1	16[a]
3	$CDCl_3$	*Z*	6	19			0	1	4
4	CH_2Cl_2	*Z*	12	34			0	2	7
5	$CHClF_2$	*Z*	5	18			0	1	3
6	pentane	*E*			13	14	2	<1	4
7	$CHClF_2$	*E*			10	11	0	0	1

[a] 5% of **5a** and 11% of **5b**.

Table II. Nuclear Overhauser Effects for the Dioxolanes

	affected			
irradiated	DZC (3b)	DZT (3a)	DEC (3d)	DET (3c)
H-3	H-4	H-4		
H-4	H-3, H-5	H-3	H-5	
H-5	H-4		H-4	

Table III. Ozonolysis in Reactive Solvents: Formation of Hydroperoxides and Cross Trioxolanes

run	solvent	alkene	product	% yield (cis/trans)
1	CH_3OH	*E*	**6**	77
2	CH_3OH	*Z*	**6**	75
3	CH_3CHO/pentane (>1.0 M)	*E*	**4c/4d**	30 (37/63)
4	CH_3CHO/pentane (<0.1 M)	*E*	**4c/4d**	30 (32/68)
5	CH_3CHO/pentane (>1.0 M)	*Z*	**4c/4d**	32 (41/59)
6	CH_3CHO/pentane (<0.1 M)	*Z*	**4c/4d**	15 (37/63)
7	$(CH_3)_2HCCHO$/pentane	*E*	**4f/4g**	*a* (55/45)
8	$(CH_3)_2HCCHO$/pentane	*Z*	**4f/4g**	*a* (51/49)
9	$(CH_3)_3CHO$/pentane	*E*	**4h/4i**	45 (61/39)
10	$(CH_3)_3CHO$/pentane	*Z*	**4h/4i**	93 (60/40)
11	CH_3CH_2OCHO/pentane	*Z*	**4a/4b**	7 (100/0)
12	$(CD_3)_2CO$	*Z*	**4e**	10

[a] Yield not determined.

Table IV. Cis/Trans Ratios of Products as *Z*/*E* Ratio of Alkene Mixture Was Varied[a]

Z/*E*	DZC (3b)/DZT (3a)	DEC (3d)/DET (3c)	TC (4a)/TT (4b)	TETT (5b)
100:0 (9.82)	30:70 (1.42)	0:0 (0)	80:20 (0.49)	100[b] (0.17)
100:0 (9.58)	30:70 (1.31)	0:0 (0)	80:20 (0.41)	100 (0.12)
100:0 (12.77)	28:72 (1.92)	0:0 (0)	80:20 (0.76)	100 (0.20)
96:4 (8.17)	27:73 (1.65)	100:0 (0.06)	75:25 (0.71)	100 (0.20)
88:12 (8.98)	29:31 (1.22)	100:0 (0.12)	75:25 (0.63)	100 (0.17)
88:12 (13.41)	35:65 (1.24)	100:0 (0.29)	75:25 (0.59)	100 (0.16)
88:12 (8.65)	30:70 (1.45)	100:0 (0.15)	75:25 (0.71)	100 (0.16)
83:17 (6.19)	32:68 (0.74)	71:29 (0.14)	76:24 (0.38)	100 (0.10)
63:37 (6.01)	44:56 (0.55)	61:39 (0.31)	75:25 (0.32)	100 (0.13)
51:49 (8.59)	49:51 (0.90)	72:28 (0.53)	76:24 (0.41)	100 (0.13)
46:54 (12.93)	56:44 (1.17)	60:40 (0.95)	75:25 (0.59)	100 (0.33)
12:88 (11.74)	62:38 (0.94)	60:40 (1.96)	74:26 (0.47)	100 (0.15)
12:88 (2.28)	64:36 (0.14)	53:47 (0.40)	75:25 (0.12)	100 (0.07)
6:94 (1.90)	67:33 (0.03)	54:46 (0.24)	71:29 (0.07)	100 (0.04)
0:100 (2.81)	0:0 (0)	45:55 (0.40)	71:29 (0.07)	100 (0.06)
0:100 (1.43)	0:0 (0)	48:52 (0.21)	75:25 (0.04)	100 (0.02)
0:100 (0.43)	0:0 (0)	50:50 (0.04)	75:25 (0.02)	0 (0)

[a] Pentane solvent, the values in parentheses after the ratios are total millimoles of reactants or products. [b] Only the trans isomer was found.

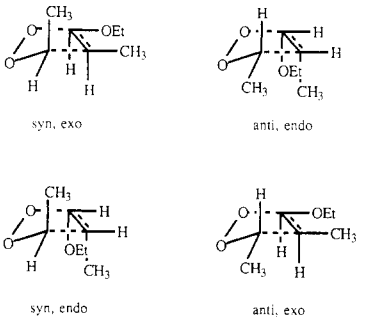


Figure 1. Possible transition states for the recombination of a syn or anti carbonyl oxide with (*Z*)-1-ethoxypropene.

arise from recombination with the *Z* alkene are illustrated in Figure 1. An envelope transition state is chosen on the basis of orbital alignment arguments[9a] and more detailed energy calculations.[10] It is seen that the carbonyl oxide could be syn or anti and the cycloaddition endo or exo. It appears difficult to estimate a priori the lowest energy transition state. We note that the absence of syn–anti equilibration, and concertedness in the reaction of a carbonyl oxide with an alkene has also been inferred in the reaction of stereolabeled HDC=CHOEt with ozone.[5,11]

With consideration of the trioxolane results, it is seen that the cross ozonide stereochemistry in the presence of added aldehyde is essentially independent of the alkene configuration. This apparently also holds for the normal ozonide (in the absence of aldehyde, Table I), although the low yields make some runs ambiguous. The data suggests that the stereochemistry varies with solvent (Table I) and with aldehyde concentration (Table III). Three possibilities may explain the independence of the trioxolane stereochemistry on the *E*/*Z* ratio of the starting alkene mixture. One possibility is that the reaction between the carbonyl oxide and the aldehyde (or ester) is nonconcerted and kinetic control of the stereochemistry is lost in this step. This prospect has been considered in some other studies.[12] However, results with a similar system are difficult to reconcile with a nonconcerted path. In the reaction of HDC=CHOEt with ozone and with acetaldehyde used as a trap for syn and anti HDCOO, a 76/24 cis/trans ratio for the trioxolanes was obtained from the *Z* alkene while a 25/75 ratio was obtained from the *E* alkene.[5] Since a change in the mechanism on adding a methyl to the carbonyl oxide seems surprising, the nonconcerted hypothesis is unappealing. Nevertheless this prospect cannot be rejected with the present data.

A second possibility is that syn–anti equilibration of the carbonyl oxide occurs, catalyzed just before reaction by the ester or added aldehyde, in the solvent cage. Upon equilibration, the carbonyl oxide does not escape the solvent cage and impact on the dioxolane stereochemistry.

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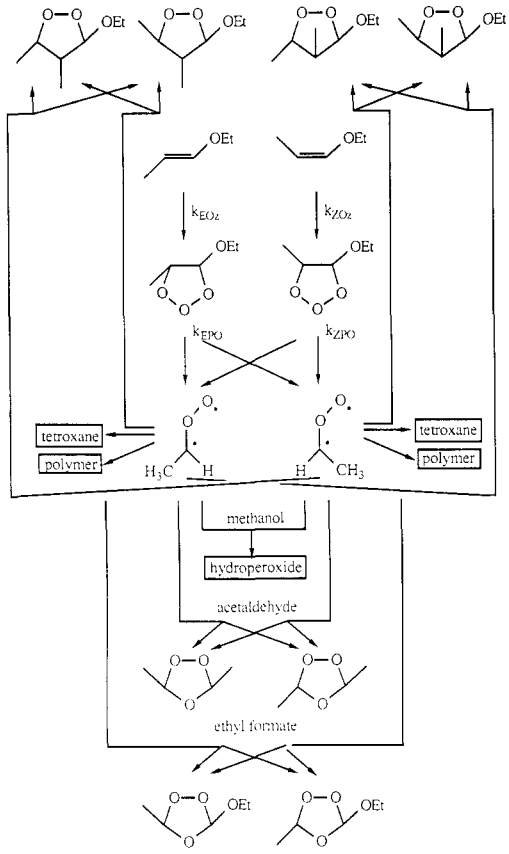

Figure 2. Schematic diagram of the kinetic network that was modeled.

In effect, this is indistinguishable from the nonconcerted proposal just discussed. One can again question whether an H_2COO carbonyl oxide should behave differently than CH_3HCOO. Theoretical data[13,14] suggest that methyl substitution stabilizes a carbonyl oxide and that the barrier to syn–anti equilibration is very high in the absence of some catalysis. Experimental data[15] also indicates that the H_2COO is more reactive (perhaps 2×) than CH_3HCOO toward aldehydes. These differences do not readily seem to account for the observed chemistry.

A third possibility is that the dioxolane and trioxolane stereochemistry arise as the inevitable consequence of the syn and anti carbonyl oxides competitively reacting via several paths. In order to examine whether a complex kinetic network might be compatible with the data, a computer program (cf. the Experimental Section) was written to model the reaction system in Scheme II as extended in Figure 2. Sets of rate constants were found that could account for the stereochemical trends as the *E*/*Z* ratio of the alkene was varied, although quantitative agreement across the board was not precise. One set of relative rate constants is given in Table V, which led to the calculated dioxolane ratios in Figure 3 and the calculated yields in Table V. The rate constants were chosen to give large amounts of polymer, followed by dioxolanes, etc. The cycloaddition with ozone was chosen to be about 6 times faster for the *E* alkene compared to the *Z* alkene, but experimental work at low fraction ozonolysis in methanol suggests this difference may be smaller, perhaps 2 times as fast. More subtle details involve the relative

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Table V. Reaction Rate Constants for the Carbonyl Oxide Reactions in Scheme III

carbonyl oxide	dipolarophile	endo/exo[a]	product (% yield)[b]	rate constant[c]
anti	*E*	endo	DET (12)	0.020
syn	*E*	exo	DET	0.020
anti	*E*	exo	DEC (10)	0.200
syn	*E*	endo	DEC	0.007
anti	*Z*	endo	DZC (7)	0.006
syn	*Z*	endo	DZT	0.030
anti	*Z*	exo	DZT (15)	0.020
syn	*Z*	exo	DZC	0.040
anti	ethyl formate	endo	TC (1)	0.010
syn	ethyl formate	exo	TC	0.002
anti	ethyl formate	exo	TT (4)	0.002
syn	ethyl formate	endo	TT	0.001
anti	anti, syn		TETT (4)	0.050
syn	anti, syn		TETT (46)	0.050
anti			polymer	0.025
syn			polymer	0.025

[a] Endo/exo relative to ethoxy group of alkenes in dioxolane formation. [b] The yields for TC, TT, TETT, and polymer are the average of the values from the *Z* and *E* alkene. [c] Only relative values are meaningful. Other constants were $k_{E_{os}} = 0.0125$, $k_{Z_{os}} = 0.0020$, $k_{E_{po}} = 0.1250$, $k_{Z_{po}} = 0.0125$. The rate constant for polymer formation is pseudo-first-order.

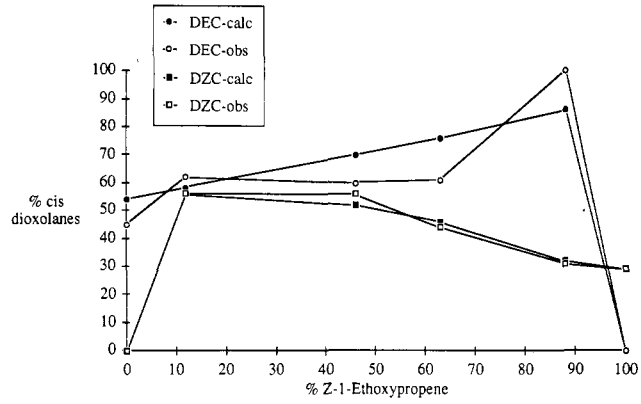

Figure 3. Observed and calculated 1,2-dioxolane stereochemical ratios as the composition of the (*E*)- and (*Z*)-1-ethoxypropene starting mixture is varied.

amounts and reactivities of the syn and anti carbonyl oxides. For example, the *E* alkene forms approximately a 4/1 syn/anti ratio while the ratio reverses to 1/4 from the *Z* alkene. Moreover, the anti carbonyl oxide reacts faster with the *E* alkene while the opposite is found for the syn isomer. The rate constants are such that the insensitivity in the trioxolane stereochemistry is associated with predominantly syn carbonyl oxide remaining toward the end of the reaction when ozonide formation becomes competitive due to low alkene and higher formate concentrations.

In order to rationalize the formation of appreciable amounts of cross trioxolanes in the presence of added aldehydes and their stereochemistry, it was necessary to fix the relative reaction rate constants as shown in the bottom section of Table V where the anti carbonyl oxide rate constants are at least 500 larger than the syn carbonyl oxide. The calculated yields with added acetaldehyde are somewhat higher than the experimental values. The calculated stereochemistry of the cross trioxolanes follows trends seen in the experimental data; both the *E* and the *Z* alkene form more trans trioxolane.

It is not surprising that the rate constants for the anti carbonyl oxide are larger than those for the syn carbonyl oxide. The syn carbonyl oxide is calculated to be 3.3–4.1 kcal more stable than the anti carbonyl oxide.[13] Also, the

transition states for the anti carbonyl oxide[10] reacting with acetaldehyde were calculated to be 1–2 kcal lower in energy than the syn. This translates into a large difference in activation energies consistent with the relative rate constants in Table V for the syn and anti carbonyl oxides reacting with acetaldehyde. This large difference in rates for the formation of cross trioxolanes is not paralleled in the rate constants of the dioxolanes. The dioxolanes have gauche interactions between the two methyls at C-4 and C-5 and an anomeric effect due to the ethoxy group at C-3, which need to be considered. For example, the anti carbonyl oxide always has a gauche interaction, which may tend to equalize the reactivities of the syn and the anti carbonyl oxides. Neither of these effects is present in the reaction of a carbonyl oxide with acetaldehyde.

If the concentration of the added aldehyde is increased, the kinetic scheme predicts that the stereochemistry of the cross trioxolanes should reverse as the reaction of the syn carbonyl oxide with the aldehyde is expressed in the products. The results in Table III do not reflect this, perhaps because the trioxolane yields are usually less than 45%. In other systems, it is interesting that as the concentration of the added aldehyde increases the yield of ozonides decreases and in some cases is suppressed.[8,12,16] A reverse in stereochemistry is also usually not observed, perhaps due to this decrease in yields.

In summary, the observed stereochemistry of the cross trioxolanes is due mainly to the difference in the energies of activation of syn and anti carbonyl oxides rather than the syn/anti carbonyl oxide ratio. As long as some anti carbonyl oxide is present, its reactions will dominate the stereochemistry of the products at lower aldehyde concentration.

What can be garnered of lasting value from the computer modeling? Of course, the analysis is not unique since some 20 parameters are manipulated to fit eight reaction products. Hence, while the rate constants in Table V might provide information on relative dipolarophilicities or subtle stereochemical competitions, it seems unduly speculative to make very much of such comparisons at this point. The usefulness of the scheme is more academic than practical. It confirms that subtle competitions in the reaction network can account for the general product trends as reaction mixtures are varied. An essential element of the model is that different syn/anti carbonyl oxide ratios are produced from each alkene and that they react at different rates with various dipolarophiles. This reversal in the syn/anti ratios on changing the alkene configuration is consistent with the results from the HDC=CHOEt isomers. Unfortunately, the preferred configuration of the carbonyl oxide produced from a given alkene isomer cannot be confidently inferred, and that aspect remains ambiguous. However, the sensitivity of the dioxolane stereochemistry to the E/Z mixture of the starting alkene while the trioxolane stereochemistry is invariant does not seem anomalous. In summary, there appears to be no compelling reason to view the ozonolysis of enol ethers as distinctly different from other alkenes, save for the low ozonide and high dioxolane yields.

Experimental Section

The ozonolyses were performed with a Welsbach ozone generator. NMR spectra were obtained with a Bruker AM-300 or a Bruker WM-360 spectrometer. Chemical shifts were referenced to internal TMS in $CDCl_3$. High-resolution mass spectra were obtained from a VG Analytical 70-250-S mass spectrometer by using a direct probe, electron impact at 70 eV. Elemental analyses were not done as the new dioxolane and ozonides were not stable and decomposed when isolated at room temperature after a few hours.

Materials. (*E*)- and (*Z*)-1-ethoxypropene were obtained from Adams Chemical Co. The separation of the two isomers, originally 71.3% *Z*, was accomplished with a Perkin–Elmer Microstill M-131 spinning band column. Solvents were purified and dried by standard methods. Acetaldehyde and 2-methylpropanal were distilled before use in trapping experiments.

Ozonolysis Procedure. Most of the ozonolyses proceeded in the same manner. Between 0.4 and 12 mmol of alkene in 1–10 mL of solvent were ozonized at −78 °C until completion. Completion was determined upon passage of ozone through the reaction vessel or after a calculated amount of ozone was added based on alkene present (taking into account alkene consumption by reaction with carbonyl oxide). No difference in yields was observed for the two procedures. The solvent was stripped off with a rotary evaporator. When the solvent was $CDCl_3$, however, the alkene was ozonized at −63 °C. The products were separated from an involatile, peroxidic residue with use of a trap-to-trap distillation on a vacuum line from room temperature to −41, −78, and −196 °C traps. Dioxolanes were collected in the −41 °C trap, trioxolanes in the −78 °C trap. Yields were determined by NMR analysis using benzene as an internal standard. **CAUTION**: Two explosions occurred during the workup after ozonolysis of mixtures of the 1-ethoxypropene isomers in pentane.

***cis*-4-Methyl-*trans*-5-methyl-3-ethoxy-1,2-dioxolane (3a)**: ^{1}H NMR ($CDCl_3$) δ 5.11 (d, J = 4.6 Hz, 1 H, H-3), 4.03 (dq, J = 9.1, 5.8 Hz, 1 H, H-5), 3.83 (dq, J = 9.6, 7.1 Hz, 1 H, CH_2), 3.47 (dq, J = 9.6, 7.1 Hz, 1 H, CH_2), 2.40 (ddq, J = 4.6, 9.1, 6.9 Hz, 1 H, H-4), 1.27 (d, J = 5.8 Hz, 3 H, CH_3 (C-5)), 1.22 (t, J = 7.1 Hz, 3 H, OCH_2CH_3), 1.10 (d, J = 6.9 Hz, 3 H, CH_3 (C-4)); ^{13}C NMR ($CDCl_3$) δ 103.7 (d, $J_{C[H]}$ = 169 Hz), 80.0 (d, $J_{C[H]}$ = 148 Hz), 63.4 (t, $J_{C[H]}$ = 141 Hz), 54.5 (d $J_{C[H]}$ = 134 Hz), 16.9 (q, $J_{C[H]}$ = 133 Hz), 14.8 (q, $J_{C[H]}$ = 129 Hz), 9.8 (q, $J_{C[H]}$ = 128 Hz); EIMS, exact mass calcd for $C_7H_{14}O_3$ 146.0942, obsd 146.0944.

***cis*-4-Methyl-*cis*-5-methyl-3-ethoxy-1,2-dioxolane (3b)**: ^{1}H NMR ($CDCl_3$) δ 5.14 (d, J = 5.5 Hz, 1 H, H-3), 4.39 (ddq, J = 0.5, 6.6, 6.3 Hz, 1 H, H-5), 3.83 (dq, J = 9.7, 7.1 Hz, 1 H, CH_2), 3.45 (dq, J = 9.7, 7.1 Hz, 1 H, CH_2), 2.96 (ddq, J = 5.5, 6.6, 7.4 Hz, 1 H, H-4), 1.22 (t, J = 7.1 Hz, 3 H, OCH_2CH_3), 1.20 (d, J = 6.3 Hz, 3 H, CH_3 (C-5)), 1.05 (d, J = 7.4 Hz, 3 H, CH_3 (C-4)). The low yields and instability precluded further characterization of this isomer.

***trans*-4-Methyl-*cis*-5-methyl-3-ethoxy-1,2-dioxolane (3c)**: ^{1}H NMR ($CDCl_3$) δ 4.86 (d, J = 2.2 Hz, 1 H, H-3), 3.87 (dq, J = 8.0, 6.1 Hz, 1 H, H-5), 3.82 (dq, J = 9.7, 7.1 Hz, 1 H, CH_2), 3.45 (dq, J = 9.7, 7.1 Hz, 1 H, CH_2), 2.42 (ddq, J = 2.2, 8.0, 7.0 Hz, 1 H, H-4), 1.30 (d, J = 6.1 Hz, 3 H, CH_3 (C-5)), 1.24 (t, J = 7.1 Hz, 3 H, OCH_2CH_3), 1.18 (d, J = 7.0 Hz, 3 H, CH_3 (C-4)); ^{13}C NMR ($CDCl_3$) δ 110.3 (d, $J_{C[H]}$ = 166 Hz), 83.9 (d, $J_{C[H]}$ = 152 Hz), 64.0 (t, $J_{C[H]}$ = 144 Hz), 56.7 (d, $J_{C[H]}$ = 133 Hz), 15.4 (q, $J_{C[H]}$ 128 Hz), 14.3 (q, $J_{C[H]}$ = 127 Hz), 14.0 (q, $J_{C[H]}$ = 127 Hz).

***trans*-4-Methyl-*trans*-5-methyl-3-ethoxy-1,2-dioxolane (3d)**: ^{1}H NMR ($CDCl_3$) δ 4.90 (d, J = 1.3 Hz, 1 H, H-3), 4.56 (dq, J = 5.8, 6.2 Hz, 1 H, H-5), 3.81 (dq, J = 9.5, 7.1 Hz, 1 H, CH_2), 3.45 (dq, J = 9.5, 7.1 Hz, 1 H, CH_2), 2.85 (ddq, J = 1.3, 5.8, 7.3 Hz, 1 H, H-4), 1.23 (t, J = 7.1 Hz, 3 H, OCH_2CH_3), 1.20 (d, J = 6.2 Hz, 3 H, CH_3 (C-5)), 1.08 (d, J = 7.3 Hz, 3 H, CH_3 (C-4)); ^{13}C NMR ($CDCl_3$) δ 108.6 (d, $J_{C[H]}$ = 164 Hz), 77.9 (d, $J_{C[H]}$ = 133 Hz), 63.6 (t, $J_{C[H]}$ = 142 Hz), 52.5 (d, $J_{C[H]}$ = 134 Hz), 14.8 (q, $J_{C[H]}$ = 128 Hz), 13.2 (q, $J_{C[H]}$ = 127 Hz), 11.1 (q, $J_{C[H]}$ = 124 Hz).

***cis*-3-Ethoxy-5-methyl-1,2,4-trioxolane (4a)**: ^{1}H NMR ($CDCl_3$) δ 6.04 (s, 1 H, H-3), 5.26 (q, J = 5.0 Hz, 1 H, H-5), 3.74 (q, J = 7.1 Hz, 1 H, OCH_2CH_3), 3.71 (q, J = 7.1 Hz, 1 H, OCH_2CH_3), 1.52 (dd, J = 5.0, 0.4 Hz, 3 H, CH_3 (C-5)), 1.26 (t, J = 7.1 Hz, 3 H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 112.7, 101.6, 60.3, 14.9, 14.7.

***trans*-3-Ethoxy-5-methyl-1,2,4-trioxolane (4b)**: ^{1}H NMR ($CDCl_3$) δ 6.05 (s, 1 H, H-3), 5.67 (dq, J = 0.4, 5.0 Hz, 1 H, H-5), 3.74 (q, J = 7.1 Hz, 1 H, OCH_2CH_3), 3.73 (q, J = 7.1 Hz, 1 H, OCH_2CH_3), 1.41 (d, J = 5.0 Hz, 3 H, CH_3 (C-5)), 1.26 (t, J = 7.1 Hz, 3 H, OCH_2CH_3); ^{13}C NMR ($CDCl_3$) δ 113.1, 104.2, 60.8, 17.7, 14.9.

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***trans*-3,6-Dimethyl-1,2,4,5-tetroxane (5b).** The diperoxidic character was determined by the reaction with triphenylphosphine. The reaction was done in a degassed, sealed tube. It was found that one tetroxane reacted with two Ph_3P to form two Ph_3PO and two acetaldehydes: ^1H NMR ($CDCl_3$) δ 5.99 (q, J = 5.5 Hz, 2 H, H-3), 1.28 (d, J = 5.5 Hz, 6 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 105.5 (dq, $J_{C[H]}$ = 179, 5 Hz), 15.0 (q, $J_{C[H]}$ = 130 Hz).

***cis*-3,6-Dimethyl-1,2,4,5-tetroxane (5a):** ^1H NMR ($CDCl_3$) δ 6.03 (q, J = 5.5 Hz, 1 H, H-3), 5.69 (d, J = 5.5 Hz, 1 H, H-6), 1.73 (d, J = 5.5 Hz, 3 H, CH_3 (C-6)), 1.06 (d, J = 5.5 Hz, 3 H, CH_3 (C-3)).

1-Methoxyethyl Hydroperoxide (6). Ten millimoles of alkene was ozonized in 20 mL of methanol at −78 °C. The solvent was stripped off, and the hydroperoxide was isolated without further purification in 75% yield. Its ^{1}NMR spectrum was slightly different from that reported in the literature:[17] ^{1}NMR ($CDCl_3$) δ 9.60 (s, 1 H), 4.96 (q, J = 5.6 Hz, 1 H), 3.50 (s, 3 H), 1.35 (d, J = 5.6 Hz, 3 H).

Trapping Experiments. Between 0.5 and 3 mmol of alkene and 0.5–1 mmol of aldehyde were ozonized in 5 mL of pentane. The resulting trioxolanes were isolated and weighed. They were identified by their ^{1}H NMR data in comparison to literature values.[18]

Computer Simulation. The program was written in FORTRAN-77 for a PDP-11/23 system and used numerical methods to approximate the kinetic reactions in Figure 3.[15] This scheme consists of unimolecular and bimolecular processes. Input to the calculation consisted of the initial concentration of the alkenes (and any added acetaldehyde or methanol) and relative values for the various rate constants. The product yields were then slowly changed for each iteration (typically < 0.1%). The algorithm contained several nested loops so that a systematic variation of reactant concentrations and rate constants could be explored. A flow diagram and listing of the program are available as supplementary material.

Acknowledgment. We are grateful to Professor Arthur Ashe for help in purification problems, Dr. H.-S. Choi for assistance in ozonolysis procedures, and Dr. K. W. Hillig II for advice on the computer programming.

Supplementary Material Available: Flow diagram and listing for the FORTRAN program called Rates, calculating the product yields (14 pages). Ordering information is given on any current masthead page.

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Free-Radical Selenosulfonation of Vinylcyclopropanes, a Cyclopropylidene, and Cyclopropylacetylene. Relative Rates of Chain-Transfer, Ring-Opening, and Inversion in Radical Intermediates

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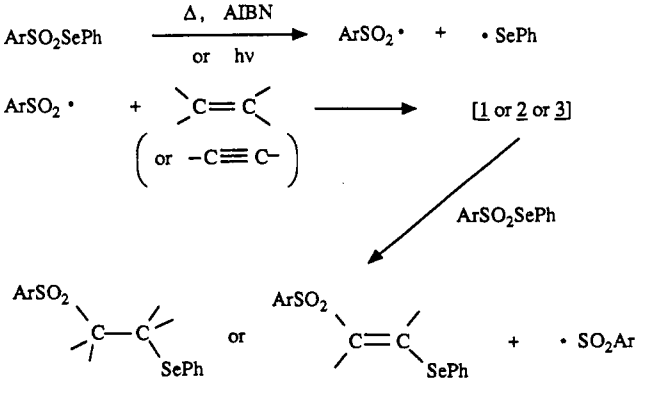
The free-radical selenosulfonation of vinylcyclopropanes **4a–e** and cyclopropylidene **9** was accompanied by ring-opening to afford 1,5- and 1,3-adducts **7a–e** and **11**, respectively, whereas cyclopropylacetylene (**13**) gave predominantly 1,2-addition to afford **15**. The relative rates of ring-opening, chain-transfer, and β-sulfonylvinyl radical inversion were inferred from the nature of the products. Selenoxide elimination of the products provided access to synthetically useful unsaturated sulfones. Thus, high yields of the dienyl sulfones **8a–e** and **12** and of the cyclopropylacetylenic sulfone **17** were obtained.

Selenosulfonates ($ArSO_2SePh$) undergo free-radical 1,2-additions to olefins,[1] acetylenes,[2] and allenes.[3] These processes[4] are synthetically useful[5] and proceed via the β-sulfonylalkyl, -vinyl, and -allyl radical intermediates **1–3**, respectively, which then react with a second molecule of the selenosulfonate in a chain-transfer step to afford the corresponding 1,2-adduct (Scheme I).

Scheme I



It has been reported that the additions to acyclic olefins are not stereospecific,[1a] whereas those to cyclohexene[1b] or

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