(1.2), 57 (0.8), 47 (15.2), 46 (44.4), 45 (40.7), 44 (100), 33 (0.3), 32 (3.7), 31 (40.7), 30 (37.0), 29 (85.2), 28 (40.7). It seems reasonable to propose that the peaks at 184, 138, 92, and 46 arise from $(H_2COO^+)_n$ fragments and that the fragment at 110 might arise from the $(HFCOO)(H_2COO)^+$ ion. However, vinyl fluoride has the same mass as H_2COO suggesting other possibilities.

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Registry No. **1**, 60553-18-6; **2**, 289-14-5; **3a**, 54892-65-8; **3b**, 54892-64-7; **4**, 54943-69-0; **5**, 557-99-3; **6**, 1514-42-7; **7**, 462-51-1; **8**, 70879-14-0; C_2H_3F, 75-02-5; HCOF, 1493-02-3; H_2CO, 50-00-0; HCOOH, 64-18-6; CO_2, 124-38-9; SiF_4, 7783-61-1.

Ozonolysis of Ethylene, Vinyl Fluoride, and 1,2-Difluoroethylene: Isotopic Labeling Experiments

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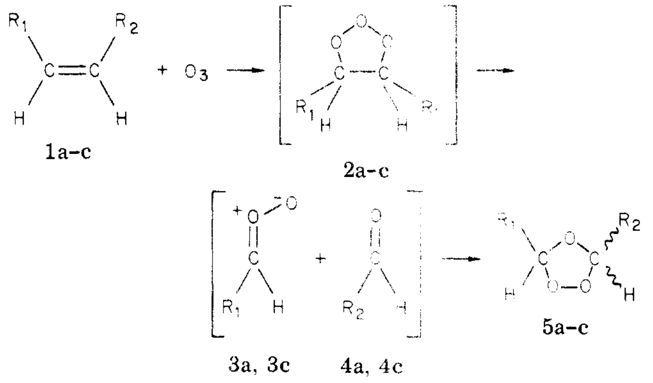
The condensed phase, low-temperature ozonolyses of ethylene, vinyl fluoride, and 1,2-difluoroethylene were investigated. Five trapping experiments are reported involving mixtures of these alkenes with an added aldehyde (formaldehyde or formyl fluoride). Four experiments are discussed where cross ozonide formation could be followed involving an isotopically enriched alkene or two different alkenes. These results indicate that the various synthetic routes to vinyl fluoride ozonide are consistent with a Criegee cleavage mechanism. It is likely that vinyl fluoride, upon ozonolysis, cleaves predominantly to H_2COO and HCOF, but that some production of HFCOO and H_2CO also occurs. Isotopic data suggest that the small amounts of *cis*-1,2-difluorooxirane produced upon ozonolysis of C_2H_3F (neat) may arise from trace amounts of $1,2\text{-}C_2H_2F_2$ present initially or produced during the ozonolysis.

Studies of the ozonolysis of C_2H_4,[1] C_2H_3F,[2] and $1,2\text{-}C_2H_2F_2$[3] at low temperatures in solution or solid phases have been previously reported. These reports analyzed the production of secondary ozonides in terms of the Criegee cleavage mechanism. The expected products from this mechanism for the three alkenes are outlined in Scheme I.[4-6]

Isotopic labeling experiments involving C_2H_4 and added aldehydes were shown to be consistent with the Criegee scheme.[1] Results for $1,2\text{-}C_2H_2F_2$ demonstrated that the secondary ozonide (**5c**) was formed along with HCOF, *cis*-1,2-difluorooxirane (**6**), and traces of *cis*-1,2,3-trifluorocyclopropane.[3] Mixtures of 1,2-difluoroethylene-d_0 and -d_2 were employed to show that **6** was formed without carbon–carbon bond cleavage. However, the isotopic content of the ozonide (**5c**) was not determined.

The ozonolysis of C_2H_3F has led to the three ozonides expected from Scheme I.[2] The total cross ozonide yields (relative to normal ozonide) were about 3% for ozonolysis in CH_3Cl solvent but rose to about 9% when no solvent was employed. HCOF and peroxidic solids were other major products along with trace amounts of CH_3COF. Trace amounts of **6** and $FC(O)CH_2F$ (**7**) were also observed when C_2H_3F was ozonized neat. **5b** was unstable and readily decomposed, giving a complex mixture which included small amounts of $(CH_2F)_2O$ (**8**) and $HC(O)OCH_2F$ (**9**).

Scheme I



a, $R_1 = R_2 = H$; b, $R_1 = H$, $R_2 = F$; c, $R_1 = R_2 = F$

Although the observation of both cross ozonides from C_2H_3F is consistent with Scheme I, the other two unexpected difluoro species raise the question whether another process could lead to **5c**. Consequently, a series of isotopic labeling experiments were conducted to study (1) the process of fluorinated ozonide formation, (2) the direction of cleavage of **2b** obtained from C_2H_3F, (3) the mechanism of formation of **6** from C_2H_3F, and (4) the decomposition of **5b** to produce **8** and **9**.

Results

Table I lists the results of five trapping experiments with added aldehydes and four experiments involving two chemically different and/or isotopically distinct alkenes where cross ozonide formation could be followed. The general procedure was to effect a crude separation of ozonolysis products by trap-to-trap distillation[2b] and then to further separate and isolate the components of the −95 °C trap by VPC. Mass and microwave spectra of these components afforded relative isotopic information of each component but not accurate relative or absolute yields of

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[1] (a) C. W. Gillies and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **94**, 6337 (1972); (b) C. W. Gillies, R. P. Lattimer, and R. L. Kuczkowski, *ibid.*, **96**, 1536 (1974).

[2] (a) R. P. Lattimer, U. Mazur, and R. L. Kuczkowski, *J. Am. Chem. Soc.*, **98**, 4012 (1976); (b) U. Mazur, A. Lopata, R. P. Lattimer, and R. L. Kuczkowski, *J. Org. Chem.*, preceding paper in this issue.

[3] C. W. Gillies, *J. Am. Chem. Soc.*, **99**, 7239 (1977); **97**, 1276 (1975).

[4] R. Criegee, *Angew. Chem., Int. Ed. Engl.*, 14, 745 (1975).

[5] For **1a**, the species expected are **2a** → **3a**, **4a** → **5a**. For **1b**, they are **2b** → **3a**, **3c**, **4a**, **4c** → **5a**–**c**. For **1c**, they are **2c** → **3c**, **4c** → **5c**. Note that **3a** is H_2COO and **3c** is HFCOO.

[6] (a) A diradical form for **3** has been identified as reflecting more accurately its ground electronic state.[6b] The chemistry does not provide a ready distinction between the diradical and zwitterionic representations and so in this paper we will retain the widely used Criegee zwitterionic form for the carbonyl oxide **3**. (b) W. R. Wadt and W. A. Goddard III, *J. Am. Chem. Soc.*, **97**, 3004 (1975); L. B. Harding and W. A. Goddard III, *J. Am. Chem. Soc.*, **100**, 7180 (1978).

Table I. Ozonolysis of Alkenes in the Presence of Added Aldehydes or Alkene–Alkene Mixtures

		reactants			products, % d			
reaction	temp, °C	alkene (mmol)	alkene or aldehyde (mmol, % d)	O_3, mmol	$\overline{CHFOOCH_2O}$ **5b**	$\overline{CH_2OOCH_2O}$ **5a**	$\overline{CHFOOCHFO}$ **5c**	*cis*-$\overline{CHFOCHF}$ **6**
1	−126	CH_2=CHF (25.8 (neat))	DCOF (2.55, >99.5 d_1)	2.50	d_0 57.9 ± 2.0 d_1 42.1 ± 2.0	d_0 99.5 ± 1.0 d_1 0.5 ± 1.0	d_0 42.8 ± 0.8 d_1 57.2 ± 0.8	d_0 99.2 ± 0.4 d_1 0.8 ± 0.4
2	−95	CH_2=CHF (4.32 in 26.5 mmol of CH_3Cl)	DCOF (4.92, >99.5 d_1)	2.52	d_0 29.8 ± 2.4 d_1 70.2 ± 2.6		d_0 19.6 ± 1.4 d_1 80.4 ± 1.4	
3	−95	*cis*-CHF=CHF (25.3 (neat))	DCOF (2.51, >99.5 d_1)	2.56			d_0 41.9 ± 2.0 d_1 58.1 ± 2.0	d_0 99.8 ± 0.4 d_1 0.2 ± 0.4
4	−95	CH_2=CH_2 (3.34 in 26 mmol of CH_3Cl)	HCOF (3.24, no enrich)	1.76	2[a]	98		
5	−45	*trans*-CHF=CHF (1.7 in 10 mmol of isobutane)	H_2CO (1.0, 55–60 ^{18}O)	0.90	ether-^{18}O 55 ± 15			
6	−95	*cis*-CHF=CHF (13.6 (neat))	*cis*-CDF=CDF (4.0, d_0 0.0 ± 0.4, d_1 5.3 ± 0.4, d_2 94.7 ± 0.4)	3.41			d_0 47.4 ± 2.8 d_1 41.0 ± 2.8 d_2 11.5 ± 2.0	d_0 75.0 ± 0.6 d_1 3.0 ± 0.6 d_2 22.0 ± 0.6
7	−95	*cis*-CHF=CHF (1.3 in 20 mmol of CH_3Cl)	CH_2=CH_2 (1.3, no enrich)[b]	1.25	5[a]	54	14	27
8	−126	CH_2=CHF (12.9 (neat))	*cis*-CDF=CDF (10.4, d_1 5.3 ± 0.4, d_2 94.7 ± 0.4)	2.43	d_0 76.9 ± 2.4 d_1 23.1 ± 2.4	d_0 99.2 ± 1.2 d_1 0.8 ± 1.0	d_0 0.1 ± 2.4 d_1 58.5 ± 2.4 d_2 41.4 ± 2.4	d_0 4.5 ± 2 d_1 3.9 ± 2 d_2 91.6 ± 2
9	−126	CH_2=CHF (18.2 (neat))	CD_2=CDF (3.3, d_0 0.5 ± 1.5, d_1 9.5 ± 1.0, d_2 40.6 ± 4.0, d_3 49.4 ± 4.0)	3.48	d_0 68.6 ± 0.8 d_1 18.7 ± 0.8 d_2 9.8 ± 1.4 d_3 2.9 ± 1.0			d_0 72 ± 8 d_1 3 ± 2 d_2 25 ± 5

[a] Approximate relative yields based on the products listed (Experimental Section). [b] With CHDCHD (~98% d_2), the vinyl fluoride ozonide product had enrichment of ~98% d_1.

the overall reaction. Some stoichiometric data is available from previous studies.[2,3] Kinetic isotope effects in the reaction or mass spectral analysis have been ignored. In spite of these limitations, the data nevertheless provides several significant insights into the reaction processes.

Inspection of Table I indicates that all the ozonides expected from Scheme I were observed. Consequently, the discussion will largely proceed with Scheme I as a premise for analysis. The production of ozonides will be considered first and subsequently the formation of **6–9**.

Reactions 3–7 of Table I involve symmetric alkenes which via Scheme I produce a single carbonyl oxide, either **3a** or **3c**. Since **3a** is readily trapped by added aldehydes such as $H_2C^{18}O$ or CH_3CHO,[1] reaction 4 indicates that it has a lower reactivity toward HCOF than internally generated H_2CO. H_2CO also is a good trap for **3c** since reaction 5 indicates that $H_2C^{18}O$ traps it as well or better than HCOF. The ^{18}O label was observed predominantly in the ether site of **5b** as expected for Scheme I. Reaction 3 indicates that DCOF readily competes with reaction generated HCOF to produce **5c** and lends further credence for the viability of a HFCOO Criegee intermediate. The large amount of d_1 cross ozonide formed in reaction 6 indicates that extensive scrambling of carbon occurs. In this reaction, the isotopic distribution in **5c** approaches the statistical values (61% d_0, 34% d_1, 5% d_2) predicted from Scheme I for complete scrambling of fragments **3** and **4** before recombination.[7] Reaction 7 illustrates another route to **5b** consistent with Scheme I. Presumably, **5b** production arises principally from reaction of HFCOO and H_2CO.

In summary, reactions 4, 5, and 7 provide synthetic routes to **5b** which are consistent with Scheme I and avoid the direct ozonolysis of C_2H_3F. Reactions 3–7 provide support for both Criegee intermediates, **3a** and **3c**. Both intermediates can react with either HCOF or H_2CO to form secondary ozonides. The relative reactivity of H_2CO seems to be greater than HCOF toward either **3a** or **3c**.

Reviewing next the ozonolysis of the unsymmetrical alkene C_2H_3F, the prior report[2] showed that the three ozonides expected from Scheme I are produced although the yields of cross ozonides (especially **5c** in solvent) were small. This suggested the production of both **3a** and **3c** although the lack of data on the relative reactivity of the fragments with carbonyls precluded any unambiguous inference regarding a preferred direction of cleavage for the primary ozonide **2**. The isotopic data from reactions 1, 2, 8, and 9 now provide additional evidence on this point.

Reactions 1 and 2 in which extensive deuteration is observed in ozonides **5b** and **5c** provide evidence that the primary ozonide of C_2H_3F cleaves to produce both possible zwitterions. Considering reaction 1 and assuming that the source of HCOF leading to **5c**-d_0 arises solely from Criegee cleavage of the primary ozonide, the observed ratio of d_0/d_1 = 42.8:57.2 for **5c** would indicate extensive production of HCOF and H_2COO unassociated or weakly associated in solution. At least a 73% cleavage in this direction would be necessary to produce the required quantity of HCOF. Combining this with the relative yield of cross ozonides (~8%),[2] an upper limit of 92% is indicated for this cleavage pathway. Considering the same data for reaction 2 (solvent), a similar analysis places limits between 48 and 97% for production of HCOF and H_2COO. However, the amount of **5b**-d_1 suggests the lower limit for this pathway

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[7] Unpublished data in our labs (G. Fong and R. L. Kuczkowski, private communication) suggest that an inverse secondary isotope effect might occur in reaction 6. This could contribute to values of d_1 and d_2 ozonides larger than statistical.

should be 70.2%. These conclusions are not entirely unambiguous, since assumptions about relative reactivities and isotope effects are implied, but the experiments are reasonably persuasive in indicating a preferential production of H_2COO from **2** on the order of 75–90%.

The results from reactions 8 and 9 are consistent with this analysis. The deuterium content in **5b** from reaction 9 is essentially the statistical values (d_0, d_1, d_2, d_3 in ratios 73:18:8:1) expected for Criegee cleavage of the primary ozonide followed by complete out-of-cage scrambling before recombination to **5b**. This data does not provide information on the direction of cleavage except somewhat indirectly. Given the cleavage of **2b** to preferentially produce H_2COO, the apparent higher reactivity of H_2COO toward H_2CO over HCOF and the extensive out of cage scrambling, then the usually low yield[2] of ethylene ozonide from C_2H_3F is also supportive of preferential cleavage to H_2COO and HCOF. A sizable quantity of solid peroxidic material is obtained upon ozonolysis of C_2H_3F (but absent with C_2H_4 or 1,2-$C_2H_2F_2$) and contains some $(H_2COO)_n$ with n = 2–4. This also readily incorporates into this reaction scheme.

Reaction 8 is complicated by possible differences in reactivity, since two different alkenes were employed. A plausible interpretation assumes that C_2H_3F ozonizes more readily than 1,2-$C_2H_2F_2$. The faster ozonolysis of C_2H_3F then leads to production of quantities of HCOF that could give rise to the preferences for **5b**-d_0 and **5c**-d_1. The relative yields of the two ozonides might further support this analysis, but they were unavailable.

In summary, the data dealing with C_2H_4, C_2H_3F, and 1,2-$C_2H_2F_2$ are supportive of Scheme I as a viable mechanism leading to the ozonide formation. It is plausible to conclude that the primary ozonide of C_2H_3F preferentially cleaves (75–95%) to the H_2COO species, but evidence supports some HFCOO production also. For C_2H_3F and 1,2-$C_2H_2F_2$, substantial out-of-cage reaction of zwitterions and carbonyls is evident. There is some evidence that H_2CO is more effective than HCOF toward trapping the H_2COO species.

The preferential cleavage of the primary ozonide of C_2H_3F to give H_2COO is consistent with trapping experiments for other unsymmetrically substituted alkenes which indicated that electron-withdrawing groups are less likely to appear in the carbonyl oxide cleavage product.[8,9] This was rationalized in terms of electronic effects in the transition state whereby electron-releasing groups favor the zwitterion formation on the carbon atom to which they are attached. In the case of monochloro olefins,[10] the production of the acyl chloride and RHCOO species was essentially quantitative.

The apparent lower reactivity of HFCO compared to H_2CO toward H_2COO is not as readily correlated into a consistent picture. Its higher IR frequency (1837 cm^{-1} vs. 1744 cm^{-1}), shorter CO bond distance (1.181 Å[11] vs. 1.206 Å[12]), and slightly smaller dipole moment (2.02 D[13] vs. 2.35 D[14]) might suggest a lower reactivity. Conversely, Criegee has pointed out[4] that electron-withdrawing groups can sometimes activate a carbonyl by enhancing its dipolarophilicity. The frontier molecular orbital model for 1,3-dipolar cycloadditions[15] would indicate similar reactivities for HFCO and H_2CO if the addition step is dominated by the LUMO on H_2COO, since the aldehydes have nearly identical π ionization energies.[16]

The isotopic data also provides some insight on the pathways leading to **6**–**9**. Small amounts (~0.4%) of **6** were isolated during the ozonolysis of C_2H_3F neat. The results of reactions 1, 3, and 6 exclude the production of **6** from decomposition of **5c** due to their different enrichments. This possibility was also previously rejected by Gillies.[3,17] Processes involving HCOF, such as addition by fluorocarbene, are excluded by reaction 1. Reaction 9 eliminates mechanisms that derive the two CHF moieties in **6** randomly from different C_2H_3F species. Such pathways would lead to ratios of 72:26:2 for the d_0, d_1, and d_2 species of **6**. The low d_1 enrichment in **6** (reaction 9) is rather more consistent with noncleavage of the CC atoms in the original C_2H_3F. Therefore, the most attractive interpretation is that some fluorination of C_2H_3F to 1,2-$C_2H_2F_2$ occurs followed by epoxidation.[18] Difluoroethylene was not observed in the recovered starting material; however, it would be difficult to detect due to the large excess of C_2H_3F.

Although **7** is an isomer of **6**, its detection in trace amounts appears unusual since it is apparently not observed during ozonolysis of CHF=CHF. Hence, fluorination of C_2H_3F to 1,2-$C_2H_2F_2$ followed by oxidation to **7** would have to involve an oxidant like H_2COO but not HFCOO or O_3. Alternatively, it could arise from a fluorination process involving CH_3COF. The fluorinating agents leading to **6** and **7** might be trace amounts of F radicals, HF, or possibly a reactive HFCOO.

The small amounts of **8** and **9** obtained upon decomposition of liquid **5b** constitute a curious phenomenon repeated many times. It apparently is unrelated to the ozonolysis mechanism.[2] Two reported syntheses of **8** involve HF and $(CH_2O)_n$.[19] Since HF (as evidenced by SiF_4 production), H_2CO, HCOOH, and possibly HCOF are likely species upon decomposition of **5b**, it is attractive to speculate that these species are involved in production of **8** and **9** perhaps via the unstable intermediate CH_2FOH.[19b] Thus, the reaction of HF with CH_2O would lead to unstable CH_2FOH, which could further react to give the ether or formate. Attempts to confirm this possibility with mixtures of HF, H_2CO, and HCOOH were unsuccessful, but these similations were probably a poor reflection of the actual reaction conditions and concentrations.

However, results of one isotopically labeled decomposition are consistent with the above proposal. Decomposition of **5b** from reaction 1 (see Experimental Section) indicated deuteration in **9** but not in **8**. The deuterium is presumably at the aldehydic carbon in **9**. These results could be rationalized by the CH_2FOH intermediate. Via this process, CH_2F moieties are undeuterated since CH_2O

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[16] K. Wittel, *J. Electron Spectrosc. Relat. Phenom.*, 8, 245 (1976).

[17] It should also be noted that the relative amounts of **5c** and **6** from C_2H_3F are markedly different than from 1,2-$C_2H_2F_2$.[2,3] This supports the inference that the major source of **5c** is not from adventitious amounts of 1,2-$C_2H_2F_2$ but arises from C_2H_3F via Scheme I.

[18] A noncleavage pathway should lead to enrichments in **6** in a range 85:2:13 to 85:6:9 for d_0, d_1, d_2, in qualitative agreement with the results of reaction 9. Systematic experimental errors and possible isotope effects probably give rise to the poor quantitative agreement. However, the secondary isotope effect on the epoxidation of CHFCHF is apparently small based on the results for **6** from reaction 6 and the extensive data of Gillies.[3]

[19] (a) V. Weinmayer, *J. Org. Chem.*, **28**, 492 (1963); (b) G. A. Olah and G. D. Mateescu, *J. Am. Chem. Soc.*, **93**, 781 (1971).

produced from **5b** should be undeuterated. This would lead to undeuterated **8**, while reaction of CH_2FOH (or CH_2FOD) with any HCOF and HCOOH (perhaps derived in part from HCOF) containing deuteriums would produce enrichment in **9** at the aldehydic site. While this rationalization is attractive, the proposed pathway needs further testing before being considered on firm ground.

Experimental Section

Reference 2 should be consulted regarding ozonolysis procedures, reaction workup, and instrumental details. With exceptions noted below, the procedure generally consisted of ozonolysis followed by trap-to-trap distillation (usually -63, -95, and -196 °C). The mixture isolated in a -95 °C trap was then separated by gas chromatography. These products were subsequently mass analyzed by mass or microwave spectroscopy.

Mass Spectrometry. Percent enrichments were determined from molecular ions using the procedure outlined by Gillies.[3] Where possible, the enrichments were also checked with other fragments. The reported uncertainties are two standard deviations from the analysis of at least five spectra.

Microwave Spectroscopy. Isotopic enrichments of C_2H_3F, **6** from reactions 8 and 9, and **5b** from reaction 5 were determined by relative peak intensity measurements of identical rotational transitions.[20] These intensities were then corrected for rotational constants, line frequencies, and dipole moment matrix elements. Possible effects of absorption line half-widths, power saturation, and differences in vibrational partition functions were ignored. These effects and the weakness and richness of some spectra could lead to uncertainties of 10–20%, which are included in the reported data.

Vinyl Fluoride. Deuterated samples were obtained by reacting 20–25 mmol of C_2H_3F with 21 mL of 3 M NaOD at 125–130 °C in a small bomb (ca. 100 mL). The isotopic analysis was done by MW spectroscopy, since the spectra of the various deuterated species were previously measured[21] or could be predicted from the structure. Over a period of 1–2 weeks, this reaction produces first the α-d_1 species, followed by an increase in the *cis*- and *trans*-1,2-d_2 species, and finally the d_3. Consequently, the sample employed in reaction 9 contains almost 100% deuteration at the α-carbon site in the partially deuterated species.

***cis*-1,2-$C_2H_2F_2$** and the trans isomer were obtained from Peninsular Chemical. The cis isomer was exchanged with deuterium by a procedure described previously[3] and similar to that employed with C_2H_3F. Exchange was complete after 2 days and was monitored by mass spectrometry. Isomeric purity after exchange was not precisely evaluated but the IR indicated substantial cis isomer.

Formyl fluoride was prepared with HCOOH, KHF_2, and benzoyl chloride.[22] DCOOD (98% d_2, Merck) was substituted in order to obtain DCOF. Deuterium content was analyzed by IR and MS.

$H_2C^{18}O$ was synthesized by exchange of $H_2{}^{18}O$ with H_2CO.[1b] The enrichment was estimated by IR.

Product Analysis. The reaction conditions and products are listed in Table I. With the exceptions noted above, analysis and isotopic enrichment were estimated from mass spectra and do not need further discussion except for the following points.

Reaction 4. Attempts to insert HCOF into C_2H_4 were repeated several times in CH_3Cl (-95 °C), in isobutane (-126 °C), and neat. The latter reaction twice exploded during ozonolysis. The other reactions were followed by distillation into -95 and -196 °C traps. A mass spectrum of the -95 °C trap indicated only **5a** in isobutane and **5a** along with minor amounts of **5b** in CH_3Cl. The amount of **5b** was crudely estimated based on the mass spectral intensities. It could not be observed by IR.

Reaction 5. Experiments to insert H_2CO into *trans*-1,2-$C_2H_2F_2$ were performed before the GC separation scheme had been worked out. A reaction was followed by distillation through traps at -45, -78, and -196 °C. The -78 °C trap was then sampled by MW spectroscopy with a positive indication of **5b**. When $H_2C^{18}O$ (55–60%, ^{18}O) was employed, the spectrum of ordinary **5b** was observed along with slightly more intense transitions for the species enriched at the ether site. Rough intensity comparisons led to the enrichment listed for reaction 5. No species could be assigned corresponding to enrichment at the peroxy site. It is difficult to assign bounds for either the total amount of **5b** produced or the extent of ^{18}O incorporation at the ether site. It appears safe to conclude from the rough signal intensities that at least 50% of the ozonide produced was **5b** and that ^{18}O enrichment in **5b** was predominantly at the ether site. A preliminary report of this MW assignment work has been given.[2] The results will be more fully discussed in a future report dealing with the MW spectrum and structure of **5b**.

Reaction 7. The data in Table I are the relative yields from a typical run. They were estimated from VPC of the -95 °C trap. By this procedure, the estimate for **5b** is a lower limit and could be in error by as much as a factor of 10. The relative yields of **5a** and **5c** should be more reliable. Obviously it is difficult to reliably infer the relative reactivity of the two alkenes without more carefully attending to the reaction stoichiometry, the possibility of sweeping one alkene preferentially from the reactor, and other difficulties associated with competitive measurements for heterogeneous reactions.[23] In some reactions, 1,2-$C_2H_2D_2$ was employed, which produced samples of **5b** with high d_1 content. These samples were employed to assign the MW spectrum of the *cis*-d_1 isomer of **5b**.[2a]

Isotopic Content of 6. This was estimated by MS for reactions 1, 3, and 6. However, similar estimates for reactions 8 and 9 did not agree well with checks made by MW spectroscopy. The MW analysis was less ambiguous and these data are reported in Table I. **8** elutes from the GC close to **6** and contributes peaks at *m/e* 81 and 82. It was suspected as the origin of the spurious MS analysis.

Isotopic Content of 8 and 9. Small amounts were isolated from the decomposition of **5b** in reaction 1. The MS clearly showed that **8** was undeuterated, while **9** contained about 50 ± 10% deuterium based on the parent fragment region. The lack of evidence for any deuterium in the CH_2F fragment (*m/e* 33) suggested that the enrichment was mainly at the aldehydic site.

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Registry No. 5a, 289-14-5; **5b**, 60553-18-6; *cis*-**5c**, 54892-64-7; *trans*-**5c**, 54892-65-8; **6**, 54943-69-0; *cis*-CHF=CHF, 1630-77-9; CH_2=CH_2, 74-85-1; *trans*-CHF=CHF, 1630-78-0; DCOF, 558-04-3; HCOF, 1493-02-3; H_2CO, 50-00-0; *cis*-CDF=CDF, 5999-46-2; CD_2=CDF, 683-75-0; CH_2=CHF, 75-02-5.

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