Ozonolysis of *cis*- and *trans*-1,2-Difluoroethylene: Isolation and Characterization of *trans*-1,2-Difluoroethylene Oxide and *cis,trans*-1,2,3-Trifluorocyclopropane

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Abstract: The reaction of ozone with *cis*- and *trans*-1,2-difluoroethylene was studied in chlorotrifluoromethane, dichlorodifluoromethane, and 1,1,2-trichloro-1,2,2-trifluoroethane. Two previously unknown compounds were observed, *trans*-1,2-difluoroethylene oxide and *cis,trans*-1,2,3-trifluorocyclopropane. It is shown that epoxide formation is largely but not completely stereospecific for both olefin isomers. Epoxide formation is discussed in terms of partial and complete cleavage mechanisms. Cyclopropane formation likely occurs by a concerted addition of fluorocarbene to the olefin. Examination of ozonide cis/trans ratios shows little dependence on solvent, temperature, and ozone/olefin concentrations.

In recent years there has been increased interest in solution reaction of ozone with fluorinated ethylenes. It is found that the ozonolyses of fluorinated ethylenes with fluorines substituted on both sides of the double bond yield different products than with substitution on one side. Studies of the ozonolyses of 1,1-difluoroethylene[1,2] and vinyl fluoride[3] show ozonides and aldehydes are major products. These two systems parallel the chemistry of simple alkenes[4] and ozonide formation is consistent with the Criegee mechanism.[5] Unlike vinyl fluoride and 1,1-difluoroethylene, epoxides are a major product in the ozonolyses of perfluoroethylene, trifluoroethylene, and *cis*- and *trans*-1,2-difluoroethylene.[2,6,7]

Two studies have identified perfluoroethylene oxide and carbonyl fluoride as the major products in the ozonolysis of perfluoroethylene.[2,6] Under certain reaction conditions one study found small amounts of perfluorocyclopropane and perfluoroethylene ozonide.[6] The ozonolysis of trifluoroethylene yields trifluoroethylene ozonide, trifluoroethylene oxide, carbonyl fluoride and formyl fluoride.[2] *trans*-1,2-Difluoroethylene ozonide is formed in lower yield. Studies of the reaction of ozone with *cis*- and *trans*-1,2-difluoroethylene show formyl fluoride, *cis*-1,2-difluoroethylene oxide and 1,2-difluoroethylene ozonide are major products.[7] The ozonide isomers were formed in a 10/90 cis/trans ratio. A trace amount of the *cis,cis*-1,2,3-trifluorocyclopropane was also obtained from the cis olefin reactions in methyl chloride and dichlorodifluoromethane.

The mechanism of ozonide formation does not appear to differ for the 1,2-difluoroethylenes and trifluoroethylene. Aldehyde-trapping experiments using formaldehyde with both isomers of 1,2-difluoroethylene show the intermediacy of fluorocarbonyl oxide and argue strongly for the Criegee mechanism.[3,8] The formation of *trans*-1,2-difluoroethylene ozonide in trifluoroethylene ozonolyses is also in agreement with the Criegee mechanism.

The results for epoxidation in *cis*- and *trans*-1,2-difluoroethylene, trifluoroethylene, and perfluoroethylene ozonolyses are fairly consistent with both partial and complete cleavage mechanisms.[6,9] Deuterium-labeling experiments show the carbon–carbon bond is not broken in epoxide formation.[7] The observed stereoselectivity can also be satisfactorily rationalized by the two mechanisms.[7]

Very little is known about the mechanism of cyclopropane formation in fluorinated ethylene ozonolyses. Gozzo and Camaggi have suggested that difluorocarbonyl oxide generated via the Criegee mechanism decomposes to difluorocarbene plus molecular oxygen.[6] Addition of the carbene to olefin produces perfluorocyclopropane. The identification of only *cis,cis*-1,2,3-trifluorocyclopropane in the ozonolysis of only the cis olefin made it impossible to study the stereochemistry of this process.[7]

In this paper, it is shown that the reaction of ozone with *cis*- and *trans*-1,2-difluoroethylene under new reaction conditions yields previously unknown epoxide and cyclopropane isomers. The mechanism of epoxide, cyclopropane, and ozonide formation is discussed in order to rationalize the new stereochemical data.

Experimental Section

Materials. *cis*- and *trans*-1,2-difluoroethylene (from PCR, Inc.) were purified by preparative gas chromatography. A 20 ft × 0.125 in. stainless-steel column packed with 23% didecyl phthalate on 45/60 Firebrick was used. The typical flow rates of helium were 40 mL/min and the column temperature was 22 °C. the relative retention times for the two isomers were 1.0 and 1.5 for the trans and cis olefins, respectively. The isomeric purity of the two isomers was estimated to be no less than 99.8% by comparing peak areas on the gas chromatograph. Often samples were passed through the gas chromatograph several times to achieve this high purity. The purified samples were then stored under vacuum at −196 °C.

The ozone used in this work was prepared by using a Welsbach T-23 ozonator. Oxygen dried by a trap cooled to dry ice temperature was used to produce a few percent ozone in an oxygen stream. The ozone was prepared from oxygen by adsorbing it on silica gel at −78 °C and purging the system with helium to remove any traces of oxygen.[10] The ozone concentration in the helium stream was determined iodiometrically and controlled by raising the gel temperature to −30 °C.

$CF_2ClCFCl_2$ (Freon 113, 98% Eastman Kodak) and CF_2Cl_2 (Freon 12) and CF_3Cl (Freon 13, both from Matheson Co. CP grade) were used without further purification.

Instrumental. A conventional 8400 C Hewlett-Packard Stark-modulated microwave spectrometer was used to examine the microwave spectrum of some of the products. Typical pressures used were 50 mtorr with the microwave cell temperature maintained at approximately −60 °C.

Mass spectra were obtained by using a Hitachi Perkin-Elmer RMU-6E mass spectrometer by expanding the sample directly into the source to minimize decomposition by contact with the gas handling system. Mass spectra of both *trans*-1,2-difluoroethylene oxide and *cis,trans*-1,2,3-trifluorocyclopropane were obtained at an ionization voltage of 70

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eV and the source temperature at 60 °C.

The gas-phase infrared spectra were recorded by using a Hitachi Perkin-Elmer 298 and 621 spectrometers. A 10-cm gas cell with sodium chloride windows secured with Viton O-rings was used to contain samples at various pressures. The cell windows were frequently polished with Fe_2O_3 in methanol to remove impurity bands that would increase with use of the infrared cell.

^1H and ^{19}F NMR spectra were obtained by using a 60-MHz Hitachi Perkin-Elmer R-600 spectrometer at R.P.I. and Bruker CXP 200- and 270-MHz spectrometers at the NSF NMR facility at Yale University.

The preparative gas chromatograph used was a Aerograph Autoprep 700.

Ozonolyses Procedure. (1) Ozonolyses of *cis*- and *trans*-1,2-Difluoroethylene in CF_3Cl. Typically 3 mmol of olefin was dissolved in 2 mL of CF_3Cl at −95 °C. The olefin was ozonized to 100% completion using flow rates of 0.10–0.15 mmol of O_3/min. Immediately after the completion of each ozonolysis, the volatile material in the reactor was allowed to warm and was trap-to-trap distilled through −140 and −196 °C traps. The contents of the −196 °C trap were examined by gas-phase infrared spectroscopy and contained only CF_3Cl and a small amount of unreacted ozone, silicon tetrafluoride, and formyl fluoride.

The contents of the −140 °C trap were purified further by another trap-to-trap distillation through traps cooled to −95, −116, and −196 °C. The contents of the −95 °C trap were found to be *cis*-1,2-difluoroethylene oxide, *cis*- and *trans*-1,2-difluoroethylene ozonide, and small amounts of *cis,cis*-1,2,3-trifluorocyclopropane and formic acid. As previously mentioned the cis,cis cyclopropane is formed only in the ozonolysis of the cis olefin. The −116 °C trap contained *trans*-1,2-difluoroethylene oxide, *cis,trans*-1,2,3-trifluorocyclopropane, and small amounts of the cis epoxide. The −196 °C trap contained mostly formyl fluoride and small amounts of silicon tetrafluoride.

The contents of each trap were further purified by preparative gas chromatography by using gas-phase injection and a 17 ft × 0.25 in. Teflon column packed with 10% Halocarbon oil on 40–60 mesh chromosorb T at 22 °C. All eluted components were collected in glass U traps cooled to −196 °C. The relative retention times for each component using a flow rate of 40 mL of He/min were 1.0 for formyl fluoride and silicon tetrafluoride, 1.4 for *trans*-1,2-difluoroethylene oxide, 2.1 for *cis*-1,2-difluoroethylene oxide and *cis,trans*-1,2,3-trifluorocyclopropane, 3.0 for formic acid, 3.6 for *trans*-1,2-difluoroethylene ozonide, 4.6 for *cis*-1,2-difluoroethylene ozonide, and 7.6 for *cis,cis*-1,2,3-trifluorocyclopropane. The cis epoxide and cis,trans cyclopropane were further purified by using the didecyl phthalate column previously mentioned under the same conditions. The relative retention times were 1.0 for the cis epoxide and 1.5 for the cis,trans cyclopropane. The formyl fluoride and silicon tetrafluoride were separated by a subsequent trap-to-trap distillation. Yields were determined manometrically after a second pass through the gas chromatograph to achieve maximum purity.

Each reaction left a liquid residue at the bottom of the reaction flask. This material is likely peroxidic in nature because of its slow reaction with aqueous KI. This material appears to be similar to what was formed at −78 °C in previous studies.[7]

(2) Ozonolyses of *cis*- and *trans*-1,2-Difluoroethylene in $CF_2ClCFCl_2$. The reaction was carried out by flowing ozone in helium and olefin via separate inlets into 10–15 mL of $CF_2ClCFCl_2$ at 0 °C. Typically 3 mmol of olefin and flow rates of 0.10–0.15 mmol of O_3/min were used to ozonize to 100% completion. Both material left behind in the solvent and bubbled out into 1 L bulbs placed in line directly after the reactor were recovered and analyzed.

The material that remained dissolved in the solvent was purified by gas chromatography using liquid injections on to the Halocarbon oil column under similar conditions as discussed earlier. $CF_2ClCFCl_2$ has a retention time of 7.0 on this column. Hence, *cis,cis*-1,2,3-trifluorocyclopropane could not be separated from the broad peak of the solvent. The material bubbled out of the solvent into the bulbs consisted of formyl fluoride and very small amounts of silicon tetrafluoride and unreacted olefin. Yields were again determined manometrically.

(3) Ozonolysis of *trans*-1,2-Difluoroethylene in CF_2Cl_2. A 3-mmol sample of olefin was dissolved in 2 mL of CF_2Cl_2 at −78 °C. Ozone flow rates were 0.10–0.15 mmol/min and the reaction was carried to 100% completion. Immediately after termination of the reaction the volatile material left in the reactor was trap-to-trap distilled through traps maintained at −116 and −196 °C. The −196 °C trap was examined by gas-phase infrared spectroscopy and was shown to consist of formyl fluoride, CF_2Cl_2, and small amounts of unreacted ozone.

The contents of the −116 °C trap were further purified by a trap-to-trap distillation through −95 and −116 traps. The −95 °C trap was analyzed as previously discussed by using the Halocarbon oil column. The contents of the −116 °C trap were purified by using the didecyl phthalate column. The relative retention times were 1.0 for dichlorodifluoromethane, 2.0 for the trans epoxide 3.5 for the cis epoxide, and 5.1 for the cis,trans cyclopropane. Yields were determined manometrically for each species.

The reaction was carried out by using ozone flow rates of 0.25–0.30 mmol of O_3/min to 60% completion at −78 °C using CF_2Cl_2 solvent. The workup was carried out as discussed above. The ozonolysis of trans olefin was carried out in this manner to duplicate reaction conditions in earlier studies.[7] This was done to determine whether or not the trans epoxide and/or the cis,trans cyclopropane were formed but not isolated in the earlier studies.

Product Characterization. Formyl fluoride was identified by its known gas-phase infrared spectrum[11] and microwave spectrum.[12]

Silicon tetrafluoride was identified by its known gas-phase IR spectrum[13] and formic acid by comparison to the gas-phase IR of 98% reagent grade HCOOH from Aldrich.

cis-1,2-Difluoroethylene oxide was identified by its known ^1H NMR spectrum and gas-phase IR spectrum.[7]

cis- and *trans*-1,2-difluoroethylene ozonide were identified by their known gas-phase IR spectra.[7] In addition the cis ozonide was characterized by its previously unknown ^1H and ^{19}F NMR spectra. The chemical shifts in $(CO_3)_2CO$ for ^1H and ^{19}F are 7.37 ppm (Me_4Si internal reference) and 80.24 ppm ($CFCl_3$ internal reference), respectively. The ^1H and ^{19}F spectra were identical as expected for an AA′XX′ spin system. They consist of eight-line spectra in which two lines of one quartet overlap with the intense doublet. This assignment is consistent with the intensities expected for a ten-line spectrum. A computer NMR fitting program, LAOCN3,[14] was used to fit the experimental spectrum and obtain coupling constants. The complete analysis yielded the following coupling constants: J_{HF}(gem) = 86.7 Hz, J_{HF}(trans) = 2.2 Hz, J_{FF}(cis) = 6.0 Hz, and J_{HH}(cis) = 0.7 Hz. The coupling constant assignments were obtained by comparison to other fluorinated ozonides.[1-3,7] The ^1H and ^{19}F chemical shifts compare well to the trans isomer which are 7.60 ppm[15] in $(CD_3)_2CO$ (Me_4Si internal reference) and 83.7 ppm[7] in $CDCl_3$ ($CFCl_3$ internal reference), respectively.

cis,cis-1,2,3-Trifluorocyclopropane was identified by its known strong symmetric top microwave spectrum.[16] In addition its previously unknown gas-phase IR spectrum was obtained by using a maximum pressure of 5 torr. The important bands (cm^{-1}) with the prominent Q branch listed are as follows: 3058 (m), 1481 (m), 1429 (m), 1336 (m), 1241 (s), 1155 (m), 1076 (m), 952 (s), 730 (m), and 660 (m). The band at 1481 cm^{-1} is likely the ring breathing mode which is the characteristic band of fluorinated epoxides and cyclopropanes. The frequency of this band compares well to the bands found in c-$C_2F_4CH_2$, *trans*-c-$CFHCFHCH_2$, and *cis*-c-$CFHCFHCH_2$ which are 1526, 1460, and 1445 cm^{-1}, respectively.[17,18] The cis,cis cyclopropane was also characterized by ^1H NMR spectroscopy. The chemical shift was 4.25 ppm in $CDCl_3$ (Me_4Si internal reference). The spectrum shows the symmetry of a AA′A″XX′X″ spin system but was too weak to carry out a complete spectral analysis.

trans-1,2-Difluoroethylene oxide was characterized by ^1H and ^{19}F NMR, gas-phase IR, and mass spectral means. The ^1H and ^{19}F NMR spectra were identical and consisted of ten transitions located centrosymmetrically at 35.6, 36.4, 39.1, 50.9, and 52.0 Hz from the center. The chemical shifts in $CDCl_3$ for ^1H and ^{19}F NMR are 5.61 ppm (Me_4Si internal reference) and 158.02 ppm ($CFCl_3$ internal reference), respectively. These values of chemical shifts compare well to the cis isomer which are 5.45 ppm[19] (^1H in $CDCl_3$, Me_4Si internal reference) and 165 ppm[7] (^{19}F in $(CD_3)_2CO$, $CFCl_3$ internal reference). It also compares well to the ^1H chemical shift of trifluoroethylene oxide which is 5.81 ppm in $CDCl_3$[2] (Me_4Si internal reference). Analysis of the spectrum as a ten-line AA′XX′ spin system gave the following couplings constants: J_{HF}(gem) = 82.0 Hz, J_{HF}(cis) = −3.9 Hz, J_{FF}(trans) = 15.5 Hz, and J_{HH}(trans) = 1.0 Hz. The coupling constant assignments were obtained by comparison to related fluorinated epoxides.[2,7]

The gas-phase infrared spectrum was recorded by using pressures of 5–70 torr. The major bands (cm^{-1}) with the prominent Q branch listed

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Table I. Product Yields (%) from the Ozonolysis of *cis*- and *trans*-1,2-Difluoroethylene[a, b]

	cis epoxide	trans epoxide	ozonide	cis/trans ratio	HFCO	cyclopropane	
						cis,cis	cis,trans
			(1) −95 °C, CF_3Cl				
cis olefin	12	0.4	16[c]	5/95[d]	30	0.3	0.1
trans olefin	0.5	10	6[c]	6/94[d]	33		0.5
			(2) 0 °C, $CF_2ClCFCl_2$				
cis olefin	5		6	8/92	45		
trans olefin	0.3	0.5	3	12/88	50		0.3
			(3) −78 °C, CF_2Cl_2				
trans olefin	0.5	10	5	6/94	not determined[f]		0.5
			(4) −78 °C, CF_2Cl_2[g]				
trans olefin	0.4	7	13	7/93	not determined[f]		

[a] Yield values are averages taken from several reactions and are based upon total ozone consumed. [b] SiF_4 and HCOOH yields varied but did not exceed 1% in any of the reactions. [c] Yield of both isomers. [d] Determined by gas chromatography using total peak areas over several injections. [e] A slashed line indicates that these products were not detected by gas chromatography. [f] The HFCO could not be separated from the CF_2Cl_2 to adequately determine yields. [g] The reaction was carried out using ozone flow rates similar to ref 7.

are as follows: 3060 (s, singlet), 2160 (w, doublet), 1651 (w, doublet), 1477 (s, doublet), 1391 (m, triplet), 1268 (m, doublet), 1135 (vs, doublet), 1097 (vs, triplet), 951 (s, doublet), and 829 (s, triplet). No decomposition of the sample was noted in the IR cell. The band at 1477 cm^{-1} is ascribed to be the ring breathing mode. This band compares well to 1460 cm^{-1} which is assigned to the ring breathing mode in the cis epoxide.[7]

The mass spectrum yielded the following fragmentation pattern: *m/e* 29 (100, HCO^+), 32 (88.6, CHF^+), 33 (42.9, CH_2F^+), 44 (12.9, C_2HF^+), 47(4.3, CFO^+), 49 (5.7, ???), 51 (10.0, CHF_2^+), 55 (44.3, ???), 60 (8.68 C_2HFO^+) and 80 (8.6, $C_2H_2F_2O^+$). This pattern is similar to what is found with the cis isomer run on the same spectrometer and under similar conditions.

cis,trans-1,2,3-Trifluorocyclopropane was characterized by gas-phase IR, mass, and ^1H NMR spectrometry. The gas-phase IR spectrum obtained by using pressures no greater than 10 torr gave the following bands (cm^{-1}) with the prominent Q branch listed: 3060 (m, singlet), 1478 (w, singlet), 1332 (m, doublet), 1290 (m, singlet), 1201 (s, triplet), 1148 (vs, doublet), 1120 (s, singlet), 949 (m, doublet), 812 (m, doublet), and 639 (m, doublet). The weak feature of the spectrum at 1478 cm^{-1} is likely the ring breathing mode. It compares well to molecules already discussed. The mass spectrum gave the following fragmentation pattern: *m/e* 32 (12.2, CHF^+), 33 (4.2, CH_2F^+), 45 (8.4, $C_2H_2F^+$), 46 (10.0, $C_2H_3F^+$), 51 (37.1, CHF_2^+) 55 (9.4, C_3F^+), 58 (3.8, $C_3H_3F^+$), 69 (17.8, CF_3^+), 71 (12.7, $CH_2F_3^+$), 74 (4.7, $C_3F_2^+$), 75 (6.6, $C_3HF_2^+$), 77 (7.5, $C_3H_3F_2^+$), 95 (100, $C_3H_2F_3^+$), and 96 (9.4, $C_3H_3F_3^+$). The fragmentation pattern is similar to other fluorinated cyclopropanes; the M − 1 is also the base peak in *cis,cis*-c-$C_3H_3F_3$, *cis*-c-$CFHCFHCH_2$, and *trans*-c-$CFHCFHCH_2$.[7,18]

The ^1H NMR spectrum in $CDCl_3$ (Me_4Si internal reference) gave two complicated but symmetrical patterns centered at 4.73 and 5.02 ppm. Analysis of the spectrum shows the trans proton is located at 5.02 ppm and consists of an 18-line system. The two equivalent cis protons are located at 4.73 ppm and have a characteristic ten-line AA'XX' spectrum split by the trans CHF group to give a total of 40 lines. The chemical shift assignment is consistent with *trans*-1,2-difluoroethylene oxide and *trans*-1,2-difluorocyclopropane in that trans protons are shifted downfield with respect to cis protons.[20] The chemical shifts are also consistent with the cis,cis cyclopropane. LAOCN3 was used to fit the spectrum. The coupling constants for the cis protons were as follows: $J_{HF}(gem) = 56.4$ Hz, $J_{HF}(trans) = -0.2$, $J_{HH}(cis) = 6.4$ Hz, $J_{FF}(cis) = 21.5$ Hz, $J_{HF}(cis) = 15.8$ Hz, and $J_{HH}(trans) = 1.5$ Hz. Analysis of the trans proton gave the following coupling constants: $J_{HF}(gem) = 56.8$ Hz, $J_{HH}(trans) = 1.5$ Hz, and $J_{HF}(cis) = 18.9$ Hz. The assignment of the coupling constants was also made by comparison to similar fluorinated cyclopropanes.[21,22]

Results and Discussion

Epoxide Formation. As previously mentioned, initial studies of the ozonolyses of *cis*- and *trans*-1,2-difluoroethylene show that only the cis epoxide is formed.[7] This result was consistent with two stereoselective mechanisms for epoxide formation.[6,9] It was ruled out that olefin isomerization occurred during the ozonolysis. Epoxide isomerization seemed unlikely because possible cleavage products of the epoxide such as 2,2-difluoroacetaldehyde and fluoroacetyl fluoride were not found in the ozonolyses.[7]

Trifluoroethylene oxide and perfluoroethylene oxide are exceedingly volatile products in the ozonolysis of trifluoroethylene and perfluoroethylene, respectively.[2,6] The volatility of these epoxides suggests *trans*-1,2-difluoroethylene oxide may pass a −95 °C trap which means it would be difficult to separate this product from the solvents used in the previous studies of 1,2-difluoroethylene ozonolyses. Hence, it is possible the trans epoxide was formed in those ozonolyses but was not identified due to separation problems involving the solvents.

The ozonolysis of *trans*-1,2-difluoroethylene at 0 °C in $CF_2ClCFCl_2$ provided the first evidence for the presence of the trans epoxide. Under these conditions, the trans epoxide was obtained in low yield (see Table I) by using the Halocarbon oil column to separate the epoxide from the solvent as described in the Experimental Section. The trans epoxide is more easily obtained in much higher yields by ozonizing *trans*-1,2-difluoroethylene in CF_3Cl at −95 °C. It is possible to separate the epoxide from CF_3Cl by a trap-to-trap distillation.

Once the trans epoxide was well characterized, the reaction conditions were extended to −78 °C in CF_2Cl_2 solvent but again with use of the same ozone flow conditions as with CF_3Cl and $CF_2ClCFCl_2$. It was found by carrying out a series of trap-to-trap distillations at −116 °C, one continues to remove CF_2Cl_2 to enrich the mixture with trans epoxide. Eventually a gas-phase IR spectrum was obtained which showed the trans epoxide is present with CF_2Cl_2. The trans epoxide may be removed completely from the CF_2Cl_2 by gas chromatography using a didecyl phthalate column. An ozonolysis was performed at −78 °C in CF_2Cl_2 by using the higher ozone flow rates reported earlier. Results show that the trans epoxide is still formed but in lower yield. The effect is consistent with results by Gozzo and Camaggi for perfluoroethylene.[6] They found that with increasing ozone flow rates (higher ozone/olefin molar ratios), the yield of perfluoroethylene oxide decreased.

Examination of the product yields in Table I shows that epoxide formation is not completely stereospecific. For each reaction listed there is approximately 0.5% of the other epoxide isomer formed. This is a real effect because the isomeric purity of the olefins is at least 99.8%. If the other epoxide isomer was coming exclusively from the olefin impurity, the yield of the epoxide would only be about 0.02% (assuming 10% epoxide yields). However, contrary to the earlier study,[7] the cis and trans olefins produce mainly cis epoxide and trans epoxide, respectively. This result is relevant to the two epoxide mechanisms discussed in the previous study.

The partial cleavage mechanism rationalizes the formation of epoxides in sterically hindered 1-olefins.[9] The terminal oxygen atom of the ozone molecule attacks the olefin to give a 1:1 molar

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(20) The comparison of the trans epoxide to the cis epoxide has already been discussed. The chemical shifts of *trans*-c-$CFHCFHCH_2$ and *cis*-c-$CFHCFHCH_2$ are 4.7 and 4.3 ppm, respectively.[18]

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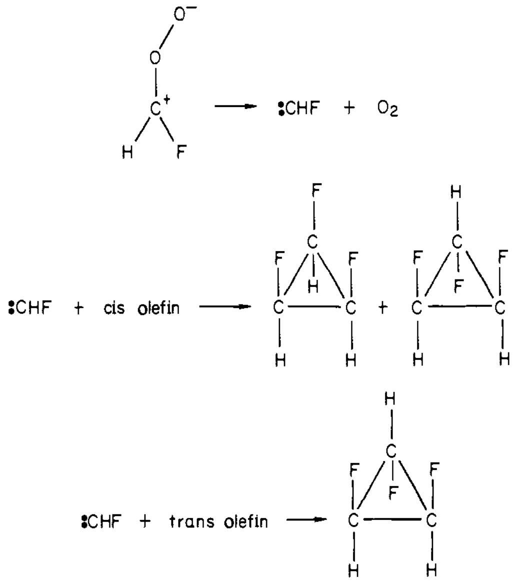
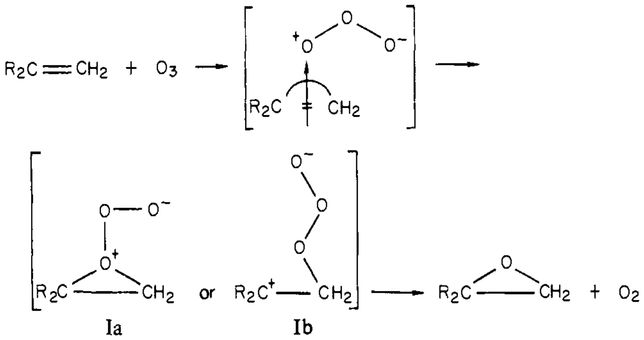
Scheme I



ratio of epoxide and molecular oxygen. Murray and Suzui found that *cis-* and *trans*-1-(1-naphthyl)-phenyl-1-propene give epoxides stereospecifically with retention of configuration.[23] Ia was favored as the intermediate but Ib cannot be eliminated if ring closure is faster than carbon–carbon bond rotation. Wadt and Goddard find Ia is unreasonable from the standpoint of a generalized valence bond (GVB) diagram.[24] They favor the appropriate GVB representation of Ib.

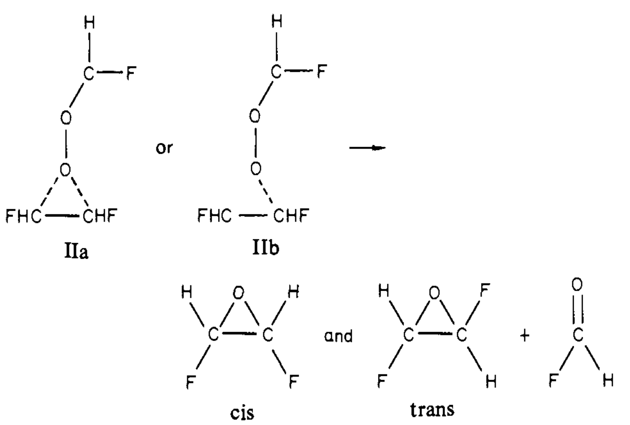


In the case of *cis-* and *trans*-1,2-difluoroethylene the present results show the epoxidation reactions proceed largely stereospecifically with retention of configuration. Either form of intermediate I is consistent with these results. However, only Ib explains the fact that a small amount of cis epoxide is formed from the trans olefin and vice versa. In this case rotation of carbon–carbon bond must be faster than ring closure to give epoxide and molecular oxygen.

The partial cleavage mechanism was postulated to explain epoxidation in sterically hindered 1-olefins, and it may not be applicable to fluorinated ethylenes. Gozzo and Camaggi have suggested that epoxidation in the ozonolysis of perfluoroethylene involves the reaction of difluorocarbonyl oxide, CF_2O_2, with perfluoroethylene to give epoxide and carbonyl fluoride.[6] The difluorocarbonyl oxide is generated via the Criegee mechanism. Ozone attacks the olefin to give an unstable primary ozonide, CF_2CF_2OOO, which decomposes to carbonyl oxide and carbonyl fluoride.

Support for the carbonyl oxide epoxidation comes from a number of experimental results. Recently, it was found that carbonyl oxide produced from singlet oxygen oxidation of diazo compounds epoxidized certain olefins.[25] In the perfluoroethylene ozonolysis, a variety of ozone/olefin concentrations did not give 1:1 molar ratios of epoxide to molecular oxygen. While perfluoroethylene ozonide is formed in small amounts only at ozone/olefin molar ratios approaching 1:1, recent evidence in our laboratory shows that if perfluoroethylene is ozonized in the presence of formyl fluoride, trifluoroethylene ozonide is produced.[26] Hence it is likely difluorocarbonyl oxide is present as an intermediate in perfluoroethylene ozonolyses.

The new results for *cis-* and *trans*-1,2-difluoroethylene ozonolyses do not distinguish between the two mechanisms. As with the partial cleavage scheme, the terminal oxygen of the carbonyl oxide can epoxidize the cis and trans olefins stereospecifically via intermediates IIa or IIB. Only IIb explains the formation of small amounts of the cis epoxide from the trans olefin and trans epoxide from the cis olefin. Here rotation about the carbon–carbon bond may procede ring closure.



Cyclopropane Formation. Gozzo and Camaggi suggested in the ozonolyses of perfluoroethylene that perfluorocyclopropane is formed from the addition of difluorocarbene to the olefin.[6] The difluorocarbene is produced via loss of molecular oxygen from the difluorocarbonyl oxide. In initial studies of the ozonolysis of *cis-* and *trans*-1,2-difluoroethylene, *cis,cis*-1,2,3-trifluorocyclopropane was a trace product with the cis olefin.[7] Deuterium-labeling experiments show that decomposition of the cis epoxide to fluorocarbene is unlikely. They are consistent with fluorocarbonyl oxide acting as either a free fluorocarbene source by decomposition of the carbonyl oxide to fluorocarbene and molecular oxygen or carbenoid in the addition to the olefin. With the exception of the above two studies, cyclopropanes have not been found as products in ozonolysis reactions. The stereochemistry of carbene addition can not be studied in the perfluoroethylene ozonolysis. It was also not possible to obtain stereochemical results in the 1,2-difluoroethylene ozonolyses because the cis,cis cyclopropane was found only in the cis olefin reaction.

The synthesis of *cis,trans*-1,2,3-trifluorocyclopropane is needed to study the stereochemistry of cyclopropane formation in 1,2-difluoroethylene ozonolyses. As discussed in the Experimental Section, this compound was found in low yield under most reaction conditions. The cis,trans cyclopropane was not isolated in earlier studies because it could not be separated from the solvents as was the case for the trans epoxide. In addition unlike the trans epoxide, it is formed in much lower yield (see Table I).

A concerted addition of fluorocarbene to *cis*-1,2-difluoroethylene will produce both the cis,cis and cis,trans isomers of 1,2,3-trifluorocyclopropane. The trans olefin isomer will give only the cis,trans cyclopropane for the same concerted process. These additions are shown in Scheme I. It is found that the cis,trans cyclopropane is produced by the ozonolysis of both the cis and trans olefins whereas the cis,cis cyclopropane is formed only from the cis olefin (see Table I). This is evidence for a concerted addition of fluorocarbene to the trans olefin since the cis,cis isomer was not observed.

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It seems likely that the fluorocarbene addition to the cis olefin is also a concerted process. Yields of both cyclopropane isomers are reported in Table I for the ozonolysis of the cis olefin in CF_3Cl. While they suggest a preference for the cis,cis isomer, the presence of an unknown compound which could not be completely separated from the cis,cis cyclopropane makes the results less certain. It is clear that more of the cis,trans cyclopropane is produced from the trans olefin than from the cis olefin. Syn stereochemistry has been noted previously in the addition of fluorocarbene to olefins.[27]

Ozonide Formation. Orbital symmetry arguments were used in earlier studies to rationalize the low cis/trans ozonide ratio observed in the ozonolysis of *cis*- and *trans*-1,2-difluoroethylene.[7,28] It was pointed out that dipole–dipole interactions may largely determine the transition state leading to final ozonide.[7] This means syn and anti fluorocarbonyl oxides preferentially form trans final ozonide. Hence, experimental conditions which may vary the syn/anti carbonyl oxide ratio will not vary the final ozonide cis/trans ratio.[7] Recent theoretical calculations are in agreement with this reasoning.[29]

Experimentally the cis/trans ozonide ratio is not very solvent dependent.[7] In addition the same ratio is obtained for the ozonolysis of vinyl fluoride where *cis*- and *trans*-1,2-difluoroethylene ozonide are obtained as cross ozonides.[3] Similarly an upper limit of 10/90 is placed upon this ratio in the ozonolysis of trifluoroethylene.[2]

The present work determines the cis/trans ozonide ratio in several new solvents over a wide temperature range and different ozone/olefin concentrations. As shown in Table I, the ratio does not vary much in CF_3Cl at −95 °C and $CF_2ClCFCl_2$ at 0 °C for both the cis and trans olefin isomers. Furthermore, the ratio is not dependent upon different ozone/olefin concentrations for the trans olefin in CF_2Cl_2 at −78 °C. These results provide additional support for the orbital symmetry arguments presented previously.

Overall ozonide yields follow earlier reports.[7] The cis olefin produces more ozonide in CF_3Cl and $CF_2ClCFCl_2$ solvents. The higher ozonide yield for the trans olefin in CF_2Cl_2 at larger ozone/olefin concentrations is consistent with perfluoroethylene ozonolyses.[6] In that case the highest ozone/olefin concentration (1:1 molar ratio) produced small amounts of perfluoroethylene ozonide.[6]

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Electron Transfer Induced Reactions. Electrochemically Stimulated Aromatic Nucleophilic Substitution in Organic Solvents

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Abstract: The main difference between organic solvents and solvents such as liquid ammonia as far as electrochemically induced aromatic nucleophilic substitution is concerned regards the role of H-atom abstraction from the solvent. This reaction and electron transfer at the electrode and in the solution are major side reactions competing with nucleophilic attack on the aryl radical. The resulting four-cornered competition is analyzed in the context of cyclic voltammetry and preparative scale electrolysis. In most cases, the experimental conditions can be adjusted so that the competition only involves nucleophilic attack, heterogeneous electron transfer, and H-atom abstraction. This allows a quantitative evaluation of the role of the latter reaction. Experimentally, a detailed investigation of the substitution of 9-haloanthracenes by cyanide and thiophenoxide ions has been made. Other systems for which preparative scale results were previously gathered are analyzed in the same context. A general mechanistic picture of the $S_{RN}1$ reaction can thus be drawn which is applicable to the case of electrochemical inducement but also to the other modes of stimulation. In homogeneously induced reactions, the side reactions act as termination steps in the chain mechanism. One consequence of the existence of the competing reactions, particularly H-atom abstraction, is the requirement of a rather high reactivity of the nucleophile toward aryl radicals for a good substitution yield to be reached. The positive counterpart of these negative aspects is that the very existence of side reactions that can be independently characterized allows the mechanism and reactivity patterns of the nucleophilic attack to be investigated. Proofs of the $S_{RN}1$ as opposed to an $S_{RN}2$ mechanism are discussed in this context as well as the nucleophile–aryl radical reactivity data so far obtained by electrochemical means.

Aromatic nucleophilic substitution occurring along an $S_{RN}1$ mechanism[2] can be stimulated in various ways involving all the introduction in the reaction medium or the in-situ generation of one-electron reducing agents: photostimulation,[2] addition of alkali metals dissolved in liquid ammonia,[2] injection of electrons from an electrode,[3] and addition of the anion radical of the substituted product.[4] The electrochemical approach to $S_{RN}1$ aromatic nucleophilic substitution[3] has provided a kinetically based demonstration of the validity of the $S_{RN}1$ mechanism originally proposed on the basis of qualitative arguments.[2] This demonstration con-

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