# Epoxides of 1,1-dichloro-2,2-difluoroethylene and chlorotrifluoroethylene

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The major products from the photochemically initiated oxidation of 1,1-dichloro-2,2-difluoroethylene and chlorotrifluoroethylene in the liquid phase are the corresponding epoxides and acyl halides. The epoxides have been isolated in pure form and characterized.

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Halogenated derivatives of ethylene are susceptible to direct oxidation by molecular oxygen because of the electronegativity of the substituents and this represents a potential method for preparation of the corresponding epoxides. However, a variety of oxidation products may be obtained depending on the structure of the olefin and the reaction conditions. For example, dibromofluoroethylene reacts readily with oxygen to give the acyl bromide (1). Similarly, the major product in the photochemically initiated oxidation of chlorotrifluoroethylene is reported (2) to be the acyl fluoride, although the epoxide (3) has been isolated in substantial yield from direct oxidation of the olefin at its boiling point. More recently, it has been shown (4–6) that the photochemical and γ-ray initiated oxidation of tetrafluoroethylene yields primarily the epoxide and carbonyl fluoride.

The oxidation of 1,1-dichloro-2,2-difluoroethylene and chlorotrifluoroethylene by molecular oxygen at temperatures of $-60$ to $+20$ °C is slow, but the reaction can be accelerated appreciably by ultraviolet (u.v.) irradiation, particularly in the shorter wavelength region of 2000–3000 Å where significant absorption by the olefin occurs (7). The most convenient preparative method for the epoxides has been found to be irradiation of the olefin under reflux at atmospheric pressure, while bubbling dry oxygen through the liquid. The progress of the reaction may be followed by means of the infrared (i.r.) absorption bands of the mono and dichloro olefins at 1792 and 1740 $\text{cm}^{-1}$ respectively.

With both olefins, at least 90% of the oxidation products are volatile and consist of the epoxide and acyl halides. Liquid peroxides occur in both cases but represent less than 5% of the total products. With chlorotrifluoroethylene, a small quantity of solid precipitates during the reaction and was shown to be polychlorotrifluoroethylene by i.r. analysis. In a typical photo-oxidation of 1,1-dichloro-2,2-difluoroethylene, approximately 40% of the volatile product is the epoxide, 50% is chlorodifluoroacetyl chloride, and 10% is dichlorofluoroacetyl fluoride. In the case of chlorotrifluoroethylene, the epoxide constitutes approximately 60% of the volatile product, the remainder being chlorodifluoroacetyl fluoride.

Isolation of the epoxides from the acyl halides proved to be difficult. Fractional distillation, gas–liquid chromatographic and adsorption methods were unsuccessful, resulting in either little or no separation of the components, or decomposition of the epoxides. Two procedures were employed. For the 1,1-dichloro-2,2-difluoroethylene oxide, the acyl halides were removed by successive extraction of a heptane solution with ice water and the epoxide recovered by nitrogen stripping of the heptane at ambient temperature. With the chlorotrifluoroethylene oxide, the acyl fluoride was separated by gas scrubbing with water and a dilute sodium hydroxide solution at 0 °C, using nitrogen as a carrier gas. In both cases the purity of the epoxide was at least 98% in terms of residual acyl halide and olefin as determined by i.r. analysis. However, aqueous treatments resulted in considerable decomposition of the epoxides, the yields of purified material being 10–30%.

As 1,1-dichloro-2,2-difluoroethylene oxide has not been described previously and information on chlorotrifluoroethylene oxide is limited, the epoxides were characterized and their physical properties determined. The data are given in Table I and the i.r. spectra of the two derivatives are shown in Fig. 1. The mass spectra did not show parent ions but the fragmentation patterns were consistent with the epoxide structures.

Both epoxides have limited thermal and hydrolytic stability. For example, a small sample of 1,1-dichloro-2,2-difluoroethylene oxide isom-

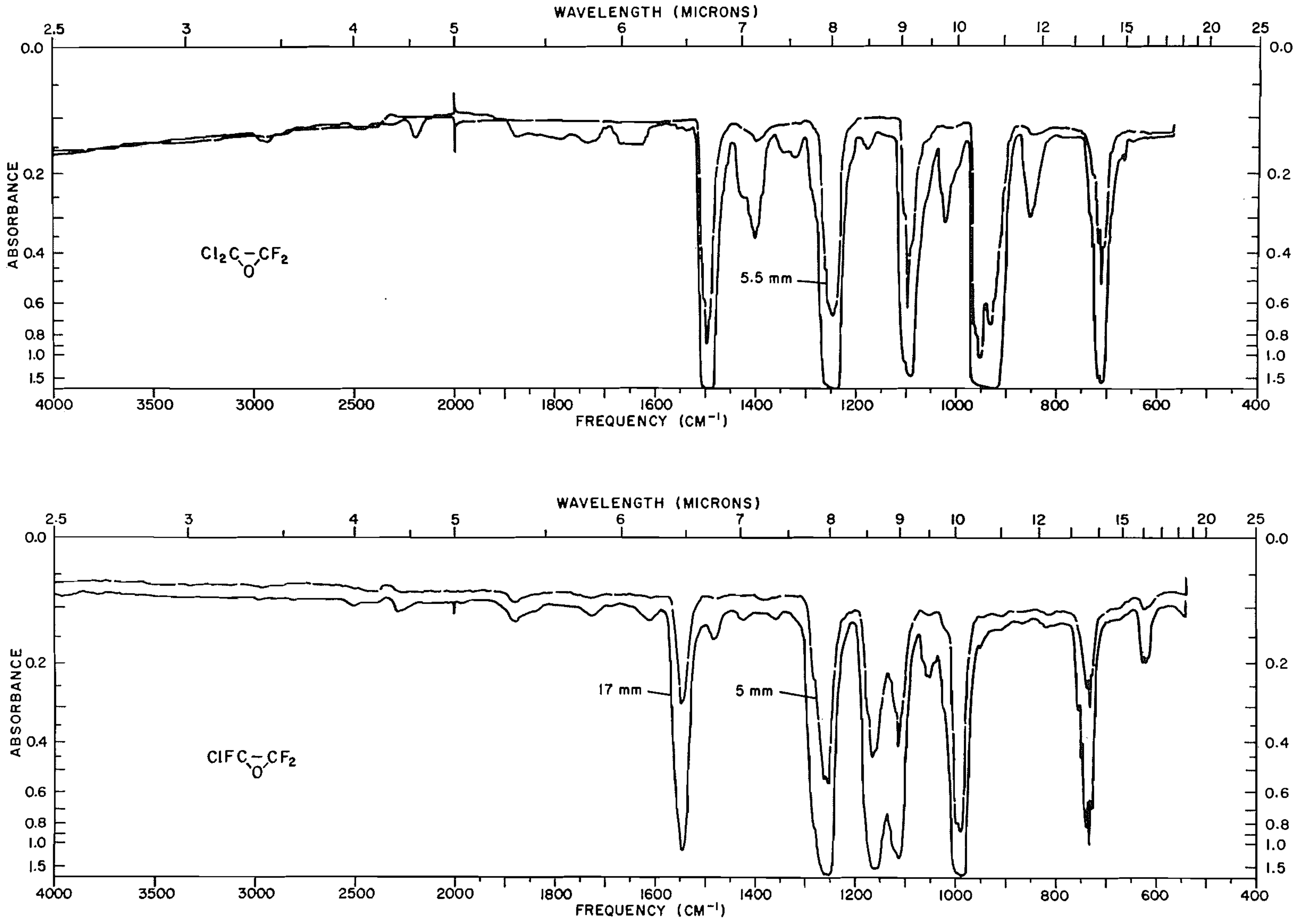
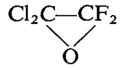
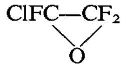


FIG. 1. Infrared absorption spectra of 1,1-dichloro-2,2-difluoroethylene oxide and chlorotrifluoroethylene oxide; 10 cm gas cell.

TABLE I
Characterization of epoxides

| | | Epoxide | |
|---|---|---|---|
| | |  |  |
| Molecular weight* | Calcd. | 149 | 132.5 |
| | Found | 147 | 132 |
| Elemental analysis† C | Calcd. | 16.11 | 18.11 |
| C | Found | 16.14 | 18.15 |
| Cl | Calcd. | 47.65 | 26.79 |
| Cl | Found | 45.71 | 26.73 |
| F | Calcd. | 25.50 | 43.02 |
| F | Found | 25.75 | 42.80 |
| Mass spectrum | | No parent ion | No parent ion |
| Characteristic i.r. absorption band | | 1500 $cm^{-1}$ | 1545 $cm^{-1}$(1550 $cm^{-1}$)‡ |
| Boiling point, micro, (°C) | | +20.2 ± 0.5 | −22.0 ± 0.5 (−19)‡ |
| Freezing point | | −93.5 ± 0.6 | −130.2 ± 0.8 |

*By vapor density.
†Performed by Swarzkopf Microanalytical Laboratory, New York.
‡From ref. 3.

erized almost entirely to dichlorofluoroacetyl fluoride on standing at 10 °C for 3 days. This rearrangement reaction, involving fluorine migration, is probably catalyzed by traces of moisture or acid and a similar process occurs with chlorotrifluoroethylene oxide. With the latter it has been shown, also, that contact with an excess of water results in complete hydrolysis to oxalic acid and hydrogen halides as indicated by Meyer (8).

## Experimental

### *Materials*

The 1,1-dichloro-2,2-difluoroethylene (99% pure) was obtained from Peninsula Chemresearch Inc., and chlorotrifluoroethylene (99% pure) was obtained from Matheson Company. In both cases, the materials were given a bulb to bulb distillation or distilled into the reaction flask to eliminate the inhibitor. Dry oxygen (99.65% purity) was obtained from Linde Company.

### *Photo-oxidation Reaction*

A 3-necked quartz flask (250 ml) was equipped with a dry-ice reflux condenser and gas inlet and outlet tubes. Exit locations were protected from moisture ingress by tubes containing Drierite. Approximately 100 g of the required olefin were condensed in the flask and allowed to reflux. Oxygen, dried by passing through a bed of Linde 13X molecular sieve, was bubbled through the liquid olefin at a rate of 6–9 l/h. A Westinghouse H44-4AB medium pressure mercury lamp (100 W) was used as the ultraviolet (u.v). source and a roughly collimated beam covering the flask area was obtained with a quartz lens. Progress of the reaction was followed by vaporizing small samples of the liquid reaction mixture into an evacuated 10 cm gas cell with KBr windows and measuring the optical density of the olefin absorption band ($Cl_2C{=}CF_2$, 1740 $cm^{-1}$; $ClFC{=}CF_2$, 1792 $cm^{-1}$). On complete consumption of the olefin, the volatile products, consisting of the epoxide and acyl halide, were vacuum distilled into a second container. The peroxide content of the liquid residue could be determined by iodine titration.

### *Isolation of Epoxide*

For 1,1-dichloro-2,2-difluoroethylene oxide, the volatile reaction product was dissolved in a 10–20 fold excess of cold heptane, extracted 4 times with ice water and once with dilute sodium hydroxide solution (0.1 *N*) at 0 °C. The heptane solution was dried over anhydrous magnesium sulfate and the epoxide recovered by stripping with dry nitrogen at room temperature. The product was given a final bulb-to-bulb distillation at low temperature to remove traces of heptane.

For chlorotrifluoroethylene oxide, a flask containing the volatile reaction product was connected to a gas scrubbing system consisting of two aqueous washes and a sodium hydroxide wash (0.1 *N*), the scrubbers being maintained at 0 °C. The reaction product was maintained 5–10° below its boiling point and the vapor carried through the train by a stream of nitrogen. It was found necessary to use small quantities of the reaction mixture (10–15 ml) to limit acid build-up in the scrubbers which accelerates decomposition of the epoxide. The vapor stream was dried with a bed of Drierite and the product condensed in a dry-ice – acetone trap, protected by a liquid nitrogen trap. This technique can also be applied to separation of the epoxide from the reaction product of 1,1-dichloro-2,2-difluoroethylene. The purified epoxides were stored at −80 °C.

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# Synthesis of some methylated tetroses and pentoses

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Oxidation of 2,3-di-*O*-methyl-D-glucitol (≡ 4,5-di-*O*-methyl-L-gulitol) and 2,3-di-*O*-methyl-D-mannitol (≡ 4,5-di-*O*-methyl-D-mannitol) with an excess of periodate gave 2,3-di-*O*-methyl-L-threose and 2,3-di-*O*-methyl-D-erythrose, each characterized as the 2,4-dinitrophenylhydrazone. Borohydride reduction of the sugars gave 2,3-di-*O*-methyl-L-threitol and 2,3-di-*O*-methylerythritol characterized as their di-*p*-nitrobenzoates. Oxidation of the hexitols with 1 mole of periodate gave 3,4-di-*O*-methyl-L-xylose characterized as methyl 3,4-di-*O*-methyl-α-L-xylopyranoside and 3,4-di-*O*-methyl-D-arabinose identified as 3,4-di-*O*-methyl-D-arabonamide. 2-*O*-Methyl-D-erythritol (≡ 3-*O*-methyl-L-erythritol) and 1-*O*-methyl-D-threitol (≡ 4-*O*-methyl-D-threitol) were also prepared and characterized as the tri-*p*-nitrobenzoates.

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Complex polysaccharides on methylation and hydrolysis may give isomeric methylated sugars, the separation and identification of which can be difficult. Sequential periodate oxidation and borohydride reduction of such mixtures may facilitate the process (1–3), particularly when partially methylated pentoses and tetroses are available as reference compounds. A previous paper (4) has described the 2,4-di-*O*-methyl-D- (and L-) tetroses and the present paper reports some mono- and di-*O*-methyltetroses and two di-*O*-methylpentoses (Table I).

Oxidation of 2,3-di-*O*-methyl-D-glucitol and 2,3-di-*O*-methyl-D-mannitol with an excess of periodate yielded respectively 2,3-di-*O*-methyl-L-threose and 2,3-di-*O*-methyl-D-erythrose, characterized as their 2,4-dinitrophenylhydrazones. Each tetrose was reduced to the glycitol and characterized as the *p*-nitrobenzoate. Oxidation of the two hexitols with one mole of periodate (5–8) gave high yields of 3,4-di-*O*-methyl-D-arabinose and 3,4-di-*O*-methyl-L-xylose, indicating a preferential attack of the C-5, C-6 bond.

4-*O*-Methyl-D-threose (9) was prepared by periodate oxidation of methyl 6-*O*-methyl-αβ-D-galactofuranosides. These furanosides form very readily and pure samples of the α-D- and β-D-furanosides were separated by cellulose-column chromatography and characterized. The periodate oxidation required about 50 h for completion in agreement with the findings of Jackson and Hudson (10) but longer than the time reported by Richards (9). The dialdehyde obtained was subjected to methanolysis in an attempt to reduce the extensive decomposition which has been reported on hydrolysis (9). In spite of some decomposition, the 4-*O*-methyl-D-threose was isolated as the dimethylacetal but could only be characterized through the threitol.

Similar difficulties were encountered in the attempted preparation of 2-*O*-methyl-D-erythrose from methyl 4-*O*-methyl-α-D-mannoside. The dialdehyde was resistant to hydrolysis or methanolysis and it was eventually reduced with borohydride before hydrolysis to give directly 2-*O*-methyl-D-erythritol.

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