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SHORT COMMUNICATION

Photolytic Preparation of Fluoroepoxides

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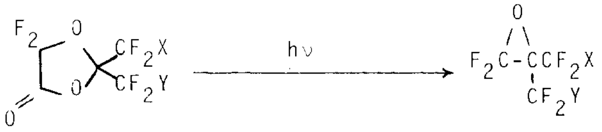
Most methods of producing fluoroepoxides involve the oxidation of fluoroolefins with oxygen, hydrogen peroxide, ozone, or other sources of oxygen atoms with only a few procedures having the distinction of not starting from the fluoroalkenes [1]. This paper reports on the photolysis of the recently described 2,2-di-(fluoroalkyl)-5,5-difluoro-1,3-dioxolan-4-ones [2] which leads to fluoroisobutylene epoxides, thus providing a novel method for making fluoroepoxides.



(I) X=Y=F
(II) X=Y=Cl
(III) X=F,Y=H
(IV) X=Y=H

The ultraviolet irradiation of 2,2-di(trifluoromethyl)-5,5-difluoro-1,3-dioxolan-4-one yielded the following data on the materials present after photolysis for 26 hours at 60-65° (percentage data obtained by glpc techniques)-16% perfluoroethane, 16% 1,2-epoxy-2-trifluoromethyl-1,1,3,3,3-

pentafluoropropane [1] (I), 18% carbonyl fluoride, 16% carbon dioxide and 22% 1,3-dioxolan-4-one. The infrared spectra for all products were identical to those of authentic samples. Carbonyl fluoride, carbon monoxide, carbon dioxide, and perfluoro-1,3-dioxolane have been reported from the only other photolytic reaction of perfluorolactones; in this case, perfluoro-β-oxa-δ-valerolactone [3]. Similarly, the excitation of hydrocarbon lactones by ultraviolet light was followed by bond cleavage involving loss of carbon monoxide or dioxide but epoxide formation has not been described [4-7].

The yields of 1,2-epoxy-2-chlorodifluoromethyl-3-chloro-1,1,3,3-tetrafluoropropane (II), 1,2-epoxy-2-trifluoromethyl-1,1,3,3 -tetrafluoropropane (III), and 1,2-epoxy-2-difluoromethyl-1,1,3,3-tetrafluoropropane (IV) were about 13% from the corresponding 2,2-di(fluoroalkyl-5,5-difluoro-1,3-dioxolan-4-ones. A previous report [8] has appeared on the formation of (II) from difluorocarbene and 1,3-dichloro-1,1,3,3-tetrafluoroacetone but neither analytical nor spectral verification were cited. The infrared spectra of the new fluoroepoxides contained a strong band at about 6.6 μ in accord with the characteristic absorption band for similar known epoxides [9,10]. In addition, the expected ^{19}F NMR pattern at about 108 $\emptyset^*$ for the terminal difluoroepoxides was noted [9,11].

EXPERIMENTAL

Product analyses and separations were carried out on a Perkin-Elmer Model 154 gas chromatograph employing a 12 ft by 3/8 inch column packed with 33% FS-1265 on Chrom P.

TABLE I

Analytical and Spectral Data for New Fluoroepoxides

Compd.	IR[a]	%C		%F		Ø*	Group	Coupling (Hz)
		Calc	Found	Calc	Found			
II	6.65	19.3	19.0	45.8	45.0	106.4	CF_2	m
						57.1	CF_2Cl	m
III	6.61	24.2	24.1	67.2	66.9	109.1,111.6	CF_2	AB,[b] J=49.2
						69.2	CF_3	m
						126.8	CF_2H[c]	m, J=52.1
IV	6.61	26.7	26.7	63.3	63.2	110.8	CF_2	m
						127.0	CF_2H[d]	m, J=52.8

[a] epoxide ring (μ) [b].complex [c] 4.09 τ (t[b], J= 52.1, $CF_2\underline{H}$)

[d] 4.04 τ (t, J= 52.8, $CF_2\underline{H}$)

The infrared spectra were recorded on a Perkin-Elmer 21 and the ^{19}F NMR spectra were measured on a Varian V-4300-2 spectrometer at 40.0 MHz utilizing fluorotrichloromethane as internal standard and solvent. Table I tabulates the analytical and spectral data.

1,2-Epoxy-2-difluoromethyl-1,1,3,3-tetrafluoropropane (IV)

Irradiation of 1.3 g (0.0053 m) of 2,2-di(difluoromethyl)-5,5-difluoro-1,3-dioxolan-4-one in a 500 ml quartz bulb equipped with a Fisher-Porter Teflon valve was carried out using a 140 watt Hanovia mercury vapor arc ultraviolet lamp. After 20 h at 40°, the products were cooled and allowed to vaporize into two evacuated traps connected in series in a standard vacuum line, cooled to -40° and -196°, respectively, as the temperature of the reactor rose from -196° to 25°. From the gases produced, 0.003 m each of 1,1,2,2-tetrafluoroethane and carbonyl fluoride were identified. Finally, 0.11 g (0.006 m) of (IV) (nc) was found. All product separations were achieved by glpc techniques.

The preparation of (I), (II), and (III) (nc) were performed in a similar manner.

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