

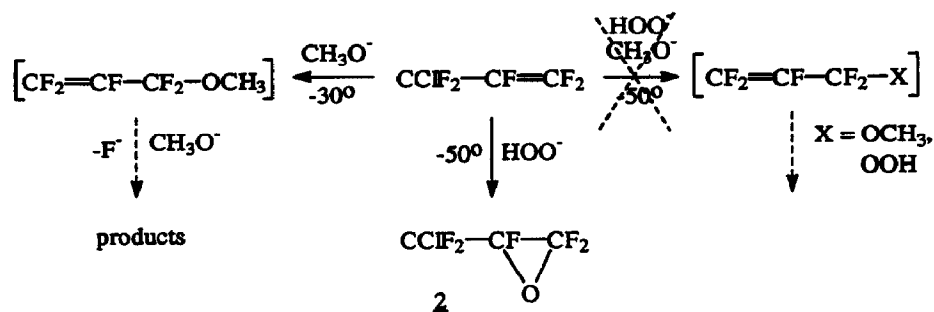
**3-CHLOROPENTAFLUOROPROPENE-1,2-OXIDE: PREPARATION AND REACTIONS
WITH SOME HETEROATOM NUCLEOPHILES AND ANTIMONY PENTAFLUORIDE****J. Kvičala^a and O. Paleta**Department of Organic Chemistry, University of Chemical Technology, Technická 5, 166 28 Prague 6,
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Summary: Nucleophilic epoxidation of 3-chloropentafluoro-1-propene at PTC conditions afforded 3-chloropentafluoropropene-1,2-oxide, which was reacted with some oxygen and nitrogen nucleophiles to 3-chloro-3,3-difluoropropionic acid derivatives. With antimony pentafluoride, mixture of fluorinated acetones was obtained.

The chemistry of hexafluoropropene-1,2-oxide (**1**) has been exhaustively studied and thoroughly reviewed¹. Consequently, synthetic applications include a wide scale of compounds as inert liquids, special polymers, heterocycles bearing CF₃ group and derived low-molecular synthons, *e.g.* hexafluoroacetone or trifluoropyruvic acid derivatives¹⁻³. On the other hand, only a scarce data can be found dealing with the chloro analogue of the epoxide **1**, *e.g.* 3-chloropentafluoropropene-1,2-oxide (**2**); the patents cover its preparation⁴ and ionic telomerization with perfluorinated acid fluorides⁵. We wish to report here our results concerning a convenient laboratory preparation of the title epoxide and its reactions with some common nucleophiles and, with antimony pentafluoride.

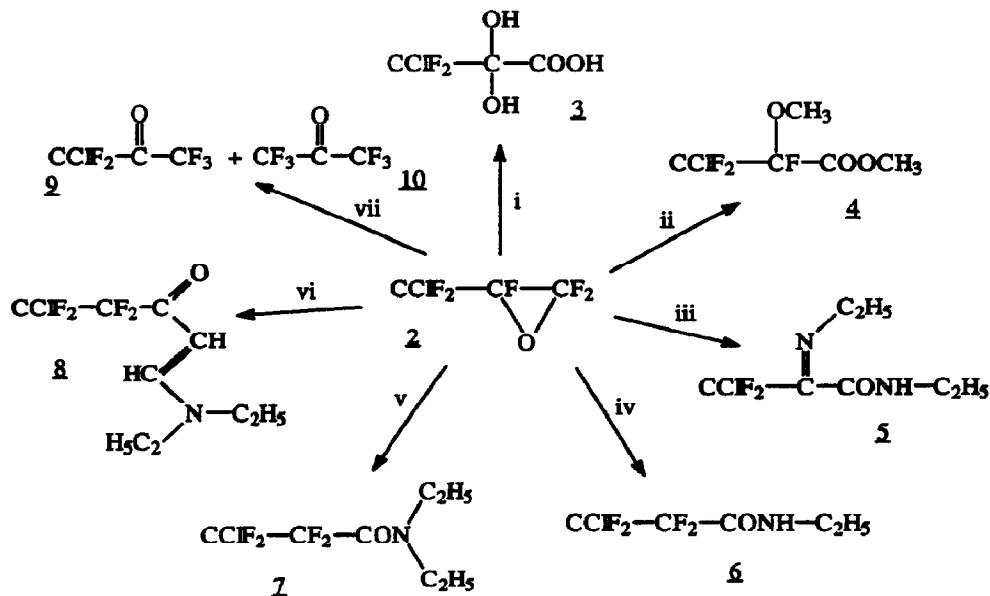
An electron-deficient double bond of fluoroalkenes, the common precursors of fluoroepoxides^{1,6}, can be oxidized by either a radical or a nucleophilic manner. The former method has been reported⁴ to afford only a low yield of the chlorofluoroepoxide **2**. In nucleophilic oxidations, temperatures between -30 °C and 0 °C and methanol or water as solvents have been mostly used^{1,2}, reaction conditions that enable according to our recent experience^{7,8} a S_N2' allylic rearrangement of starting 3-chloropentafluoro-1-propene (see Scheme 1). In further transformations of the unstable rearrangement product, hydrogen fluoride is evolved⁸ changing the reaction pH and stopping thus the epoxidation. To avoid this we applied the Bornengo's method⁹ (originally used for epoxide **1**) with respect to high yields reported⁹ and protection of both the starting compound and the product under the PTC conditions. Moreover, under the low temperatures used the side S_N2 reactions were suppressed effectively.

We found that quarternary ammonium salts used as phase transfer catalysts (tetrabutylammonium bromide, TBAB, and hexadecyltrimethylammonium bromide, HTMAB) differ significantly in their catalytic activity. TBAB-catalyzed reaction proceeded with negligible conversion when a 30% hydrogen peroxide was used as oxidation agent and only unchanged starting fluoroalkene was recovered from the reaction mixture. However, experiments with altering concentration of hydrogen peroxide revealed that the yield of the epoxide **2** up to 31% at 50%



conversion of the starting fluoroalkene could be achieved when the more concentrated 60% peroxide was used. On the other hand, the oxidation in the presence of the more efficient catalyst, HTMAB, allowed us to carry out the oxidation with 30% hydrogen peroxide and to avoid thus the bromination procedure as all unreacted fluoropropene was decomposed by side reactions, the yield of the target epoxide **2** being 46%.

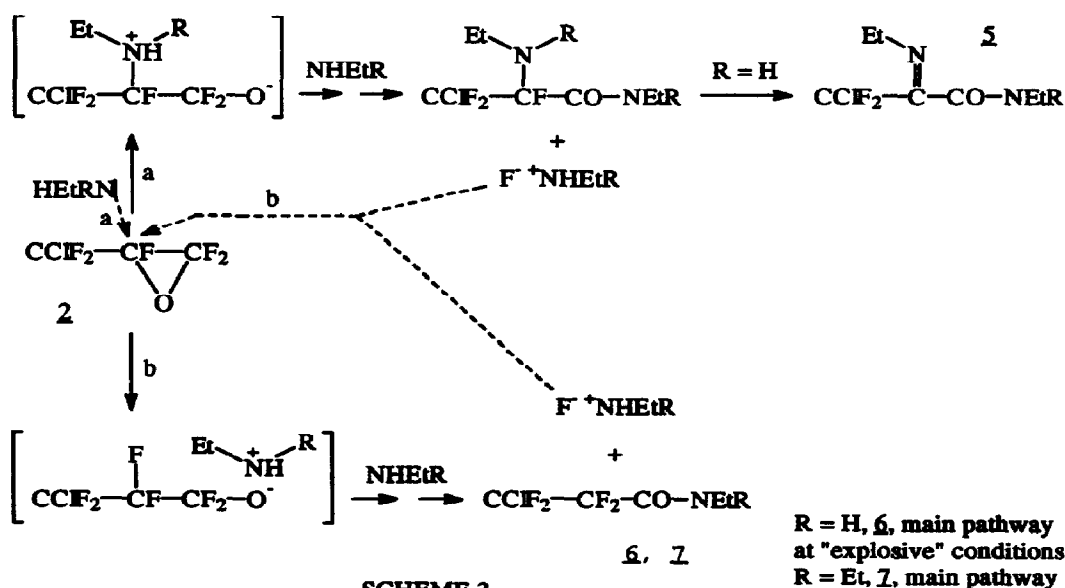
Easy access to epoxide **2** enabled us to study its reactivity with some common oxygen and nitrogen nucleophiles. We also performed a reaction with antimony pentafluoride as the representative electrophile. The reactions of epoxide **2** are depicted in Scheme 2.



i Water/dioxane; ii methanol; iii ethylamine/diethyl ether; iv ethylamine/diethyl ether, "explosive" conditions; v diethylamine/diethyl ether; vi triethylamine/benzene; vii antimony pentafluoride.

A reaction with water in dioxane either under an autogenic pressure in a glass ampoule (20 h at 25 °C) or in an open system equipped with a low-temperature condenser (3 days, room temp.) afforded hydrate of chlorodifluoropyruvic acid (3) in 77.7% and 62.3% isolated yields, resp. In a similar reaction with methanol in the sealed glass ampoule (6 hours, room temp.), epoxide 2 yielded 40.0% of methyl 3-chloro-2,3,3-trifluoro-2-methoxypropionate (4, b.p. 54-56 °C/2.5 kPa). Geminal fluoromethoxy grouping remained unchanged under the reaction conditions and hence can be employed in further synthetic transformations.

To examine a course of reactions of epoxide 2 with nitrogen nucleophiles, we choose the respective ethyl amines as the representatives of primary, secondary and tertiary amines. When epoxide 2 was gradually added to an excess of ethylamine, *i.e.* the basic and sterically unhindered amine, in diethyl ether at -25 °C, an immediate vigorous reaction occurred affording after a work-up 40.0% of distilled 3-chloro-N-ethyl-2-(ethylimino)-3,3-difluoropropionamide (5), which solidified in a refrigerator (m.p. 38-40 °C). An unstable intermediate formed by an attack of ethylamine molecule on the epoxide ring was further stabilized both by an elimination of hydrogen fluoride from an unstable aminofluoro grouping and by an aminolysis of the fluoroalkoxide group (See Scheme 3).



Attempts to carry out the reaction in a sealed ampoule resulted in an uncontrolled explosion. From the repeated experiment under "controlled explosion" conditions, surprisingly 3-chloro-N-ethyl-2,3,3,3-tetrafluoropropionamide (6, b.p. 92-95 °C/2.5 kPa) was obtained as a sole product in a yield of 32.5%. We assume that this product arose as a result of an attack of ethylammonium fluoride formed *in situ* on the epoxide ring followed by the usual transformation of fluoroalkoxide group to amide (see Scheme 3). This "rearrangement" reaction pathway is analogical to that of perfluoroepoxide 1 with either highly basic (as ethylene diamine¹⁰) or sterically hindered (as diethylamine¹¹) amines. We similarly obtained only a "rearranged" product - 3-chloro-N,N-diethyl-2,2,3,3-tetrafluoropropionamide (7, b.p. 85-86 °C/2.5 kPa) - in a yield of 55.6% from a reaction of epoxide 2 with diethylamine. Presumably, in a reaction environment containing both diethylamine and diethylammonium fluoride as reagents of comparable reactivity a steric hindrance of the nitrogen atom is a decisive factor in a reaction pathway selection (see Scheme 3).

Reaction of epoxide **2** with triethylamine in a sealed ampoule (room temp., 24 h) afforded 5-chloro-1-(diethylamino)-4,4,5,5-tetrafluoro-1-penten-3-one (**8**) in a 30.4% yield (b.p. 138-140 °C/50 Pa), which solidified on standing (m.p. 50-55 °C). The enaminketone was formed by a complex redox reaction between intermediate 3-chlorotetrafluoropropionyl fluoride and triethylamine in a close analogy to similar reaction¹² of fluoroepoxide **1**.

To examine a reactivity of epoxide **2** with electrophilic reagents we treated it with antimony pentafluoride (4 h, reflux) and obtained thus a mixture of chloropentafluoroacetone (**9**) and hexafluoroacetone (**10**) in a 72 : 28 ratio (based on ¹⁹F NMR), combined yield 81.1%. The latter compound was probably formed by subsequent fluorination of the former product, as antimony pentafluoride besides the strong electrophilic properties also acts as a powerful fluorination agent.

Structures of all products were confirmed by spectral methods (IR, ¹H and ¹⁹F NMR spectroscopy) and by elemental analyses.

The results of experiments support close resemblance of the title epoxide **2** to hexafluoropropene-1,2-oxide¹(**1**). In analogy to epoxide **1**, 3-chloropentafluoropropene-1,2-oxide can be used both in preparation of derived synthons (chlorodifluoropyruvates, chloropentafluoroacetone) and in the synthesis of biologically active compounds with chlorodifluoromethyl group.

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