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It was shown previously that perfluoro-1-butene (I) and perfluoro-2-butene (II) form α -oxides in high yield. Olefin (I) undergoes epoxidation with alkaline H₂O₂ to give 1,2epoxyperfluorobutane (III) [1] and olefin (II) upon treatment with sodium hypochlorite yields 2,3-epoxyperfluorobutane (IV) [2].

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In this work epoxidation of the β -chlorinated heptafluorobutenes 2-chloroheptafluoro-1butene (V) and 2-chloroheptafluoro-2-butene (VI),* is described. Replacement of the β -F atoms of (I) and (II) by Cl polarizes the multiple bonds of (V) and (VI) due to the smaller +M-effect of Cl compared to F and nucleophilic attack on these olefins is facilitated. Thus, (V) reacts readily with 30% H₂O₂ in alkaline solution and gives 1,2-epoxy-2-chloroheptafluorobutane (VII) in 65% yield.

> $CF_{3}CF_{2}CCl = CF_{2} \xrightarrow{H_{2}O_{2}} CF_{3}CF_{2}CCl - CF_{2} \xrightarrow{\Theta} CF_{3}CF_{2}CCl - CF_{2} + OH^{\Theta}$ (V)

Epoxidation of the internal olefin (VI) with aqueous alkaline NaOCl solution in the presence of MeCN yields, together with 2,3-epoxy-2-chloroheptafluorobutane (VIII), 1,1,1trifluoro-2,2-dichloroethane (IX). Moreover, during reaction CO and CF₃H are evolved, the formation of which is associated with further transformations of the epoxidation products. One can assume that by-products are formed by reaction of oxide (VIII) with chloride ion to give 3,3-dichlorohexafluoro-2-butanone which in aqueous alkaline medium undergoes the haloform reaction. However, oxide (VIII) turned out to be resistant to the action of NaCl in both aqueous alkaline media and in aprotic solvents.

$$(\text{VIII}) \xrightarrow{\text{Cl}^{\odot}} \left[\text{CF}_{3}\text{CFCCl}_{2}\text{CF}_{3} \right] \rightarrow \text{CF}_{3}\text{COCCl}_{2}\text{CF}_{3}$$

Epoxidation of (VI) can be represented by the following scheme



 $\overline{*(V)}$ and (VI) were obtained as in [3, 4].

1196

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$$(X) - \begin{bmatrix} +H^{\bigoplus} & HCCI_2CF_3 & (XI) \\ \hline \\ -CI^{\bigoplus} & : CCICF_3 & \frac{Na^{\oplus}}{H_2O} & CO + CF_3H + HCO_2Na + NaCI \end{bmatrix}$$

Previously epoxidation of internal perfluoroolefins was postulated to go through an intermediate cyclic π -complex [5]. This is improbable for olefin (VI) since hypochlorite ion in this case attacks at the CF group. Carbanion (IX) originally formed undergoes a) Cl⁻ expulsion and formation of α -oxide (VIII) and b) intramolecular rearrangement to 1,1-di-chloro-2,2,2-trifluoroethyl anion (X) which in the presence of water gives 1,1,1-trifluoro-2,2-dichloroethane (XI), and by Cl⁻ elimination, chlorotrifluoromethylcarbene. The latter forms with water formate, chloride, trifluoromethyl anion, and CO. The presence of CF₃H and CO in the reaction products confirms the scheme proposed and agrees with the data of [6].

Upon epoxidation of (VI) with $Ca(OCl)_2$ in aprotic solvent (MeCN) the yield of (VIII) increases to 54%. Formation of a small amount of alkane (XI) in this case is apparently explained by the presence in the oxidant of $Ca(OH)_2$ and traces of moisture, since reaction by route b) is the most probable in the presence of protons in the reaction medium.

Some reactions of (VII) and (VIII) were investigated in order to explain the difference in their behavior from the perfluorinated analogs studied in [1, 2]. In the presence of Lewis bases (alkaline metal fluorides in the dipolar aprotic solvent triethylamine) under mild conditions (VII) is isomerized to 2-chloroperfluorobutanoyl fluoride (XIII)

$$\begin{array}{c} \text{GF}_3\text{CF}_2\text{CCI} \longrightarrow \text{GF}_2\\ F \xrightarrow{\bigcirc} & \bigoplus \\ m \text{ onoglyme} [\text{GF}_3\text{CF}_2\text{CFCICF}_2\text{O}^{\ominus}] \xrightarrow{} & \bigoplus \\ -F^{\ominus} & \text{GF}_3\text{CF}_2\text{CFCICOF} \\ (\text{XII}) & (\text{XIII}) \end{array}$$

(VII

Shift of the electron density on the epoxide ring of (VII) toward the difluoromethylene group facilitates attack of F⁻ at the β -position of (VII). The intermediate alkoxy anion (XII) formed easily rearranges to (XIII) and substitution of the Cl atom by F is not observed. Synthesis of perfluorobutanoyl fluoride (XIV) succeeds only under rigid conditions (170°C) by the action of excess CsF on (VII) and (XIII) in dipolar aprotic solvent. Moreover, together with formation of (XIV) decomposition of the initial (VII) and (XIII) with formation of gaseous products is observed.

(VII), (XIII)
$$\xrightarrow{\text{CSF}}_{170^{\circ}}$$
 CF₃CF₂CCF₂COF (~20%)
(XIV)

It is known that oxide (VII), unlike (III), under the action of fluorides (KF, CsF) in tetraglyme even at ~ 20 °C is transformed practically completely into oligomeric products. Oxide (III) under the same conditions gives dimer (XV) and isomer (XIV)

The dimer of oxide (VII) is the main product upon action of KF in tetraglyme at increased temperature. Apparently, the presence of the chlorine atom in the β -position of the intermediate alkoxy anion (XII) stabilizes the latter, so that it is more likely to attack (VII) than isomerize into (XIII)

the intermediate alkoxy anion (XIII) (VII) than isomerize into (XIII) (VII) $\xrightarrow{\text{KF}, \text{tetraglyme}}_{100^{\circ}}$ [CF₃CF₂CFClCF₂O[©]] $\xrightarrow{(\text{VII})}$ CF₃CF₂CFClCF₂OCClCF₂CF₃ + oligomer (XII) (XVI)

Isomerization of oxide (VIII) under the action of KF or CsF in monoglyme or MeCN is observed only at reflux and in diglyme or tetraglyme at $\sim 20^{\circ}$ C

$$(\text{VIII}) \xrightarrow{\text{CsF, MeCN}} \begin{bmatrix} \text{CF}_3\text{CFCFCICF}_3 \\ \downarrow \\ \text{O}^{\ominus} \end{bmatrix} \xrightarrow{-\mathbf{F}^{\ominus}} \begin{array}{c} \text{CF}_3\text{COCFCICF}_3 \\ (\text{XVII}) \end{bmatrix}$$

δı98,1 δs 3,1 d, δs 46,2
δ ₁ 2,1 m, δ ₃ 59,4 m, δ ₈ -103, δ ₈ 43,6 6 δ ₈ 43,6 7,0 1

.

61,02	56,78 57,20	56,89 57,20
16,52	<u>15,18</u> 15,27	<u>15,36</u> 15,27
22,26 22,17	20,58 20,64	20,46
1670 (C=C)	1455 0	1785 (C=0)
$J_{12} = 1,25, J_{13} = 24,5, J_{23} = 5,0$ $J_{12} = 12,0, J_{13} = 9,0, J_{23} = 8,5$	$J_{23} = 16,0$ $J_{12} = 11,0$	$J_{12}=4,7$ $J_{12}=4,5, J_{13}=45,0,$ $J_{23}=6,2$
61 98,0 dq, 62 94,5 dq. 53 43,9 qq 61 100,5 dq, 62 96,4 dq. 63 56,1 sept.	δ ₁ 89,2 s, δ ₂ =90,8 d, δ ₃ 8,1 q δ ₁ 90,9 q, δ ₂ 92,1 q, δ ₃ 18,9 s	8, 85,4 d 8, 90,4 dq, 82 84,4 dq, 8, 22,5 qq.
ы Ы	ы, Ю	
t cr. 3 2 (VI)	CF4CH-CCICF3 (VIII)	

*Internal standard CF₃COOH. **PMR spectrum: δ_2 , 6.4 ppm (q, internal standard TMS).

For reaction of oxide (VII) with Et_3N the most probable mechanism, as in the case of (III), is nucleophilic substitution of an F atom on the CF₂ group followed by opening of the ammonium salt epoxide ring by fluoride ion [7]

$$(VII) \xrightarrow{Et_3N} \begin{bmatrix} \uparrow \\ NEt \\ I \\ CF_3 CF_2 CCI - CF \\ F^{\textcircled{O}} & O \end{bmatrix} \rightarrow (XIII) + Et_3N$$

Compound (VIII), unlike internal perfluorinated α -oxides [2] and oxide (VII), does not react with Et₃N even under severe conditions (in a sealed ampul, several hours, 100°C). An explanation is that nucleophilic substitution of the Cl in (VIII) by Et₃N is preferable to substitution of F due to the lower stability of the C-Cl bond and its higher polarizability [8]. Therefore, the action of Et₃N on (VIII) causes elimination of Cl⁻, which however does not cause isomerization of the intermediate ammonium salt.

It was established that in the presence of catalytic amounts of SbF_5 or $SbCl_5$ oxide (VII) is transformed into 1-chloroheptafluor-2-butanone (XVIII) in high yield

$$(VII) \xrightarrow{SbF_5} CF_3 CF_2 COCF_2 CI$$

$$(XVIII)$$

Isomerization of internal fluoroolefin oxides under the action of SbF_5 proceeds only under severe conditions ($\geq 150^{\circ}C$) [2]. It was established that oxide (VIII) reacts with catalytic amounts of SbF_5 in an open system at $\sim 20^{\circ}C$ to give 3-chloroheptafluoro-2-butanone (XVII) in high yield. The more facile reaction of (VIII) with SbF_5 can be explained by increase of alkalinity of the epoxide ring oxygen in (VIII) due to the weaker electron accepting effect of the Cl atom [9].

$$(VIII) \xrightarrow{SbF_5} (XVII)$$

Increasing the SbF_5 amount in reactions with (VII) and (VIII) results in formation of perfluoro-2-butanone (XIX) which at equimolar reagent ratio becomes the only product.

Spectral and analytical data of the obtained compounds are shown in Table 1.

EXPERIMENTAL

 $^{19}{\rm F}$ NMR spectra were taken on a Perkin-Elmer R-32 (84.6 MHz) and a Tesla BS-567A (94.1 MHz) spectrometers and PMR spectra on a Tesla BS-567A (100 MHz) instrument with CF₃COOH (external standard), C₆F₆ (internal standard), and TMS (internal standard) respectively. IR spectra were obtained on a Specord UV-VIS instrument in CCl₄ or thin layers. Mass spectra were taken on a VG-70-70E instrument. The mass spectrum of (XI) is shown for 35 Cl. Gasliquid chromatography was carried out on a LKhM-72 chromatograph with catharometer as detector and helium as carrier gas on a steel column (6000 × 4 mm) with 5% SKTFT-100 on Chromosorb G.

<u>1,2-Epoxy-2-chloroheptafluorobutane (VII)</u>. Into a flask cooled by a mixture of dry ice and isopropyl alcohol 80 ml of ethanol was placed, and at -15 to -20°C 250 ml of 30% H_2O_2 and 270 g (1.2 moles) of 2-chloroheptafluoro-1-butene (V) were added dropwise. Then a solution of 140 g (2.5 moles) of KOH in 120 ml H_2O was added dropwise with vigorous stirring for 5 h and the mixture was stirred at this temperature for 2 h, then the lower layer was separated, washed with water, and dried with MgSO₄. By distillation 182 g (65%) of oxide (VII) with bp of 34-35°C was obtained.

Reaction of 1,2-Epoxy-2-chloroheptafluorobutane (VII) with Fluorides of Alkaline Metals. a) To a suspension of 3.5 g (0.06 mole) of roasted KF in 5 ml of monoglyme (distilled from Na), 14 g (0.06 mole) of 1,2-epoxy-2-chloroheptafluorobutane (VII) was added dropwise with stirring and the mixture was refluxed with stirring for 33 h, then distilled. There was obtained 11.5 g (82%) of 2-chlorohexafluorobutanoyl fluoride (XIII) with bp of 35°C. b) To a suspension of 4.8 g (0.08 mole) of roasted KF in 8 ml tetraglyme with stirring 22 g (0.096 mole) of oxide (VII) was added dropwise over 3 h and the mixture was stirred for another 1 h and distilled. There was obtained 7.5 g of a product with bp of 40-220°C and 10.5 g of a product with bp of 100-180°C (10 mm). After a second distillation of fraction I 4.2 g (9.5%) of dimer (XVI) with bp of 121° C was isolated.

<u>1-Chloroheptafluoro-2-butanone (XVIII)</u>. a) To 15 g (0.64 mole) of oxide (VII) 0.4 ml of SbF₅ was added dropwise (an exotherm was observed). The reaction mixture was boiled for 10 min, ketone (XVIII) was distilled off, and redistilled from conc. H_2SO_4 . There was obtained 11.0 g (75%) of ketone (XVIII) with bp of 32°C. The IR and ¹⁹F NMR spectra were identical with those of [1].

b) A mixture of 33 g (0.14 mole) of 1,2-epoxy-2-chloroheptafluorobutane (VII) and 10 g (0.03 mole) of SbCl₅ in a steel autoclave of 250 ml capacity were shaken for 8 h at 150-160°C. By distillation there was obtained 23 g (71%) of ketone (XVIII).

<u>Reaction of 1,2-Epoxy-2-chloroheptafluorobutane (VII) with Et_3N .</u> To 20 g (86 mmoles) of oxide (VII) 0.4 ml of anhydrous Et_3N was added dropwise with stirring and the mixture was refluxed with stirring for 5 h, then distilled. There was obtained 15 g (75%) of 2-chloroperfluorobutanoyl fluoride (XIII) with bp 35°C.

<u>Heptafluorobutanoyl fluoride (XIV).</u> a) A mixture of 6.0 g (40 mmoles) of CsF in 5 ml anhydrous monoglyme and 5.0 g (20 mmole) of 2-chloroperfluorobutanoyl fluoride (XIII) in a 100 ml steel autoclave was shaken for 16 h at 170°C. Then the autoclave was cooled to ~20°C and the reaction products were condensed into a receiver (-78°C). There was obtained 0.9 g (20%) of fluoroanhydride (XIV) which was identified with a known sample by GLC.

b) From 4.5 g (19 mmoles) of oxide (VII) and 3.0 g (19 mmoles) of CsF in 4 ml of monoglyme 0.5 g (12%) of fluoroanhydride (XIV) was obtained by the same method.

2-Chloroheptafluoro-2-butene (VI) was obtained as in [4] from 1,2,2-trichloroheptafluorobutane [10]. Its bp was 31-32°C and the Z:E ratio was 1:4 according to GLC and ¹⁹F NMR.

<u>2,3-Epoxy-2-chloroheptafluorobutane (VIII).</u> a) To 240 ml of NaOCl solution, obtained according to [2], and 30 ml of MeCN 44 g (203 mmoles) of olefin (VI) was added dropwise with stirring over 3 h. The mixture was stirred for 1.5 h, the lower layer was separated, washed with water, dried with MgSO₄, and distilled. There was obtained 30.0 g of a substance with bp 25-33°C, which contained, according to GLC and ¹⁹F NMR data, 2,3-epoxy-2-chlorohepta-fluorobutane (VIII) (~55%, Z:E = 1:4) and 1,1,1-trifluoro-2,2-dichloroethane (XI) (~45%). Mass spectrum of (XI), m/z (rel. intensity, %): 152 (M⁺, C₂HF₃Cl₂⁺, 15), 133 (C₂HF₂Cl₂⁺, 32), 117 (C₂HF₃Cl⁺, 9), 98 (C₂HF₂Cl⁺, 7), 83 (CHCl₂⁺, 100), 69 (CF₃⁺, 26), 48 (CHCl⁺, 11). Compound (XI) was decomposed by NaOH solution. The remaining oxide (VIII) was separated, dried with MgSO₄, and distilled. There was obtained 14.5 g (31%) of oxide (VIII) with bp of 29-31°C.

b) To a suspension of 25.0 g (338 mmoles) of $Ca(OCl)_2$ in 60 ml of anhydrous MeCN 36 g (166 mmoles) of olefin (VI) was added dropwise with vigorous stirring. The mixture was stirred for another 2 h and the solid precipitate was filtered off. The filtrate was washed with water, the lower layer was separated, dried with MgSO₄, and distilled. There was obtained 25 g of a product with bp of 25-33°C, which contained, according to GLC and ¹⁹F NMR data, ~83% of 2,3-epoxy-2-chloroheptafluorobutane (VIII) (Z:E = 1:4) and ~17% of 1,1,1-trifluoro-2,2-dichloroethane (XI).

<u>Reaction of 2,3-Epoxy-2-chloroheptafluorobutane (VIII) with SbF₅.</u> To 10.0 g (43 mmoles) of 2,3-epoxy-2-chloroheptafluorobutane (VIII) 0.4 ml of SbF₅ was added dropwise, upon which evolution of heat was observed. The mixture was refluxed for 0.5 h and distilled. There was obtained 8.6 g (86%) of 3-chloro-heptafluoro-2-butanone (XVII) with bp of 31-32°C.

Reaction of 2,3-Epoxy-2-chloroheptafluorobutane (VIII) with CsF. a) To a suspension of 0.5 g (3 mmoles) of roasted CsF in 6 ml diglyme distilled from Na, 8.5 g (36 mmoles) of 2,3-epoxy-2-chloroheptafluorobutane (VIII) was added dropwise. The mixture was stirred for 20 h at \sim 20°C and distilled. There was obtained 4.2 g (50%) of ketone (XVII) with bp of 30-32°C.

b) To a suspension of 0.5 g (3 mmoles) of CsF in 6 ml of anhydrous MeCN 7.2 g (31 mmoles) of oxide (VIII) was added dropwise. The mixture was boiled with stirring for 36 h and dis-

tilled. There was obtained 5.7 g (79%) of 3-chloroheptafluoro-2-butanone (XVII) with bp of 31-32°C.

CONCLUSIONS

1. Nucleophilic epoxidation of heptafluorobutenes containing a chlorine atom in position 2 was carried out.

2. Chemical transformations of 2-chloroheptafluorobutene oxides in the presence of acids and Lewis bases were studied. 2-Chloro-2,3-epoxyheptafluorobutane isomerizes easily to 3-chloroheptafluoro-2-butanone under the action of catalytic amounts of SbF_5 and MF (M = Cs, K)e but it is resistant to the action of Et_3N . Catalytic action of F and Et_3N on 2-chloro-1,2-epoxyheptafluorobutane leads to 2-chlorohexafluorobutanoyl fluoride and SbF_5 and SbCl₅ give 1-chloroheptafluoro-2-butanone. Under the action of an equimolar amount of SbF_5 on 2-chloro-1,2-epoxy- and 2-chloro-2,3-epoxyheptafluorobutane, octafluoro-2-butanone is formed.

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2-ACETYL-SUBSTITUTED POLYFLUORINATED $\beta\text{-KETO}$ esters in reaction with amines

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Diacetylacetic ester (I) forms with NH_3 an ammonium salt [1], which at 20°C is unstable and decomposes to the starting compounds. On the other hand, acetylpropionylacetic ester gives with NH_3 the products of "acidic" splitting: acetoacetic ester, propionylacetic ester, acet- and propionamides [2]. Treatment of (I) with hydrazine leads, depending on the conditions, to the ethyl ester of 3,5-dimethylpyrazole-4-carboxylic acids [3] or to 3-methyl-5pyrazolone [4]. There are no data available on the reactions of 2-acyl- β -keto esters with other amines and of 2-R_RCO-substituted acetoacetic esters (II) with NH-nucleophiles.

We studied in the present work the reactions of (II) with NH_3 and bifunctional amines: ethylenediamine, o-phenylenediamine, hydrazine, and phenylhydrazine. It was found that in protic (95% EtOH) and aprotic media (abs. Et_2O) (IIa, d) react with NH_3 at -20-20°C regioselectively at the C² center to form an amide of fluorocarboxylic acid (III).

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