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SYNTHESIS OF PERFLUOROBENZYL KETONES AND RESEARCH OF THEIR REACTIVITY

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Abstract: 1,2-Epoxyperfluoro-3-phenylpropane was obtained by liquid phase oxidation of perfluoroallylbenzene. Under the action of SbF_5 or HSO_3F the epoxide was transformed into perfluoromethylbenzyl ketone and fluorosulfonyloxidifluoromethylheptafluorobenzyl ketone respectively. The methods of preparation of perfluorovinyl ethers based on the ketones obtained as starting materials have been studied.

Keywords: 1,2-Epoxyperfluoro-3-phenylpropane, perfluoromethylbenzyl ketone, fluorosulfonyloxidifluoromethylheptafluorobenzyl ketone.

The unique chemical and thermal stability of perfluorinated rubbers of saturated row is determined by high $\text{BTE} \cdot 107 \text{Г} \cdot 121 \text{ Kkal/mol BTE}$ value of C-F-bond [1]. At the same time this property of organofluorine compounds doesn't allow to cure perfluorinated rubbers by methods traditionally used for vulcanization of nonfluorinated or partially fluorinated rubbers [2].

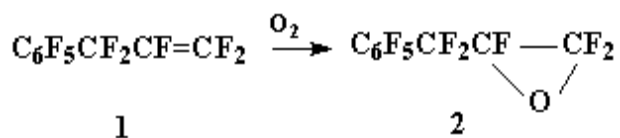
One of the possible solutions of this problem is a preparing perfluorinated rubber with incorporated monomer bearing a functional group, which is capable to interact with nucleophilic agents. Thus the copolymer of perfluorophenylglycidyl ether with HFPO can be cured under the action of bis-phenol A di-K-salt (N_2 , 200 $^\circ\text{C}$ /3 days) [3].

It could be expected that the introduction of fluoroalkyl substituent into aromatic ring entering the structure of perfluorinated monomers of alkyl aromatic row would increase the electrophilicity of pentafluorophenyl group, and the curing of rubbers containing monomers of such structure under the action of bifunctional nucleophiles could be achieved under more mild conditions.

In order to prepare perfluorovinyl ethers containing perfluorobenzyl group we have attempted to synthesize perfluorobenzyl ketones (**4**, **6**).

The ketones **4** and **6** were synthesized according to the scheme comprising liquid phase oxidation of perfluoroallylbenzene (**1**) [4] (scheme 1)

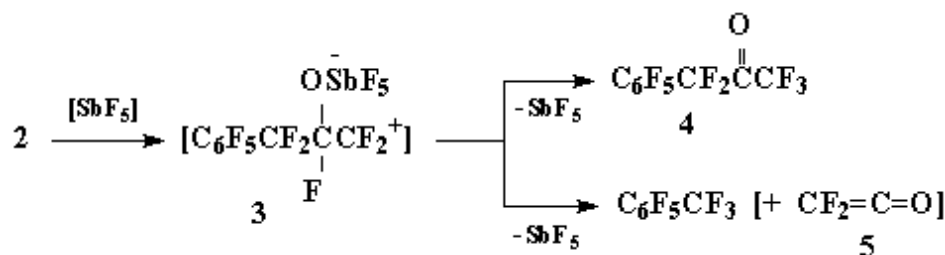
B Scheme 1



and consecutive electrophilic isomerization of perfluoroallylbenzene oxide (**2**) formed under the action of SbF_5 affording the ketone **4** (scheme 2) or HSO_3F that led to the formation of ketone **6** (scheme 3).

In the presence of catalytic amounts of SbF_5 (mol. ratio 2: SbF_5 = 60:1) oxide **2** forms a mixture of ketone **4** and perfluorotoluene (mol. ratio 9:1) as a result of exothermic reaction:

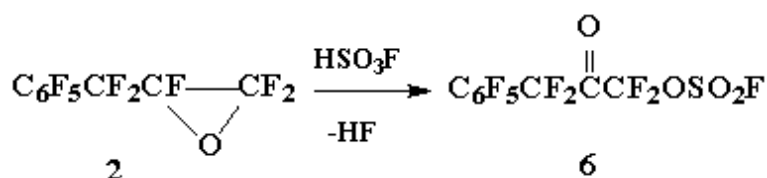
Scheme 2



Taking into consideration the negligible amount of SbF_5 taken into reaction with respect to the quantity of perfluorotoluene obtained - the formation of toluene can be explained by the scheme of decay of intermediate carbocation **3**, which comprises the elimination of stable perfluorobenzyl cation with simultaneous capture of fluoride ion from O^\pm -position and generation of difluoroketene (**5**).

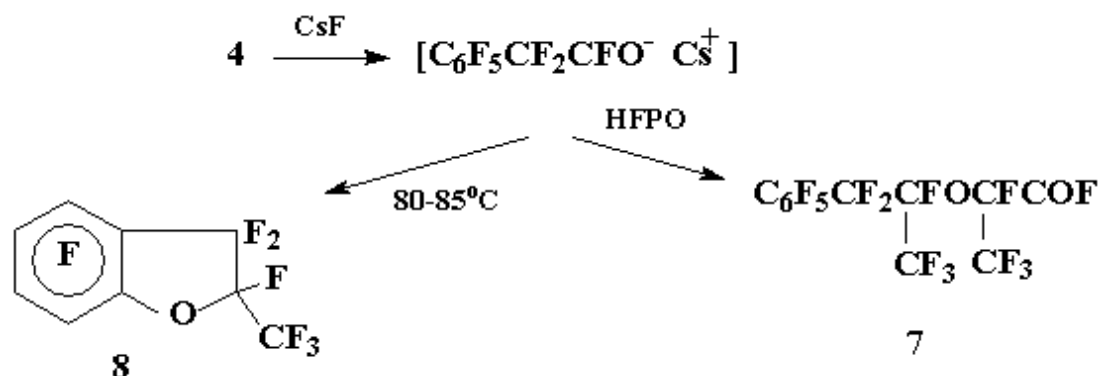
The reaction of oxide **2** with HSO_3F affording fluorosulfonyloxyketone **6** occurs under relatively mild conditions (100B°C/1.5 h) whereas the analogous reaction of HFPO demands heating up to 200Г· 220 B°C [5].

Scheme 3



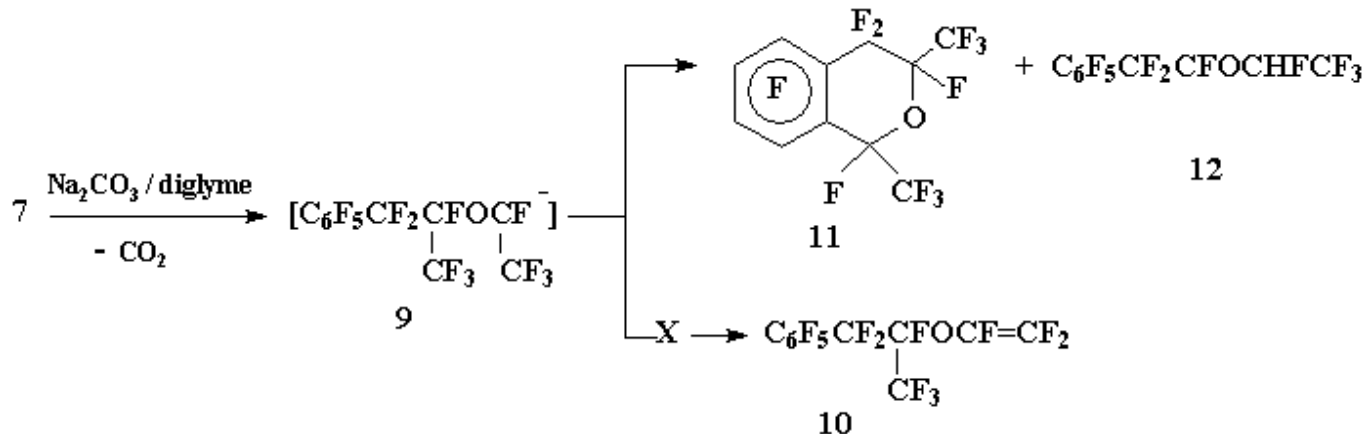
The ketone **4**, alike other perfluorinated ketones, forms water soluble hydrate. In the presence of catalytic amounts of CsF at 0Г· 15B°C it adds smoothly to HFPO with the formation of monoadduct (**7**). At the same time under more severe conditions вЂ“ 80Г·85B°C вЂ“ ketone **4** undergoes intramolecular cyclization catalyzed by CsF that leads to perfluoro-2-methylbenzofuran (**8**):

Scheme 4



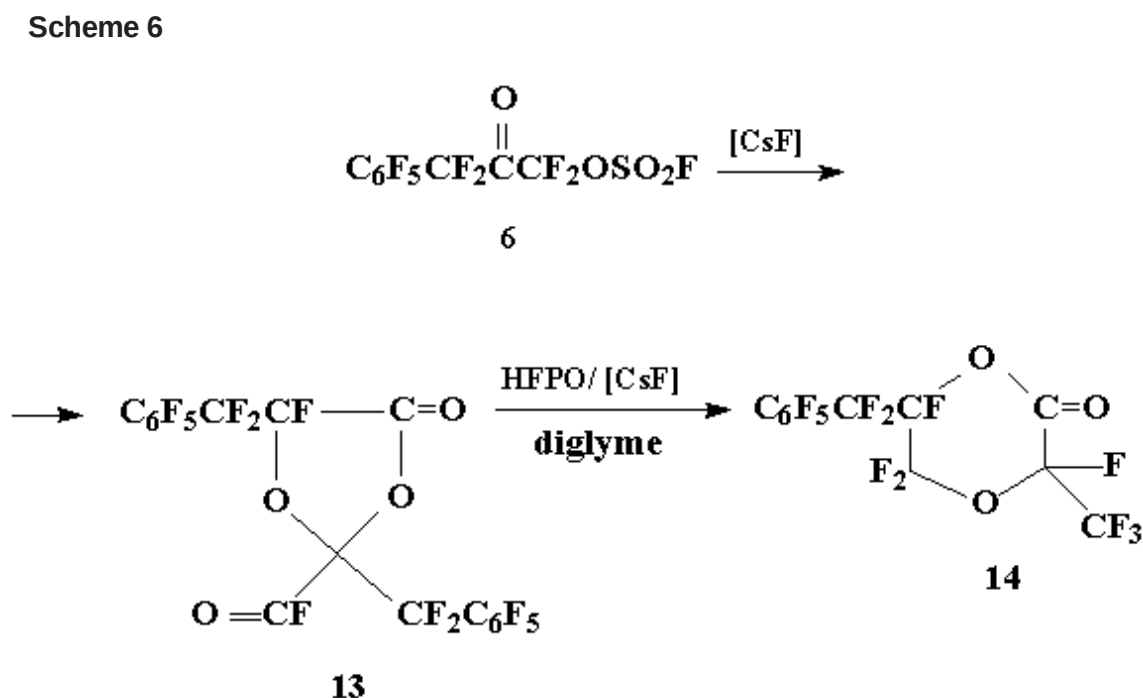
The attempt to obtain trifluorovinyl ether (**10**) by defluorocarbonylation of acyl fluoride **7** under the action of Na_2CO_3 in diglyme led to the formation of perfluoro-1,3-dimethyl-2-chromane (**11**) as the main reaction product as a result of nucleophilic substitution of fluorine atom in o-position of aromatic ring by carbanion (**9**), generated in the course of reaction, and to OI-(1,2,2,2-tetrafluoroethoxy)perfluoropropyl benzyne (**12**):

Scheme 5



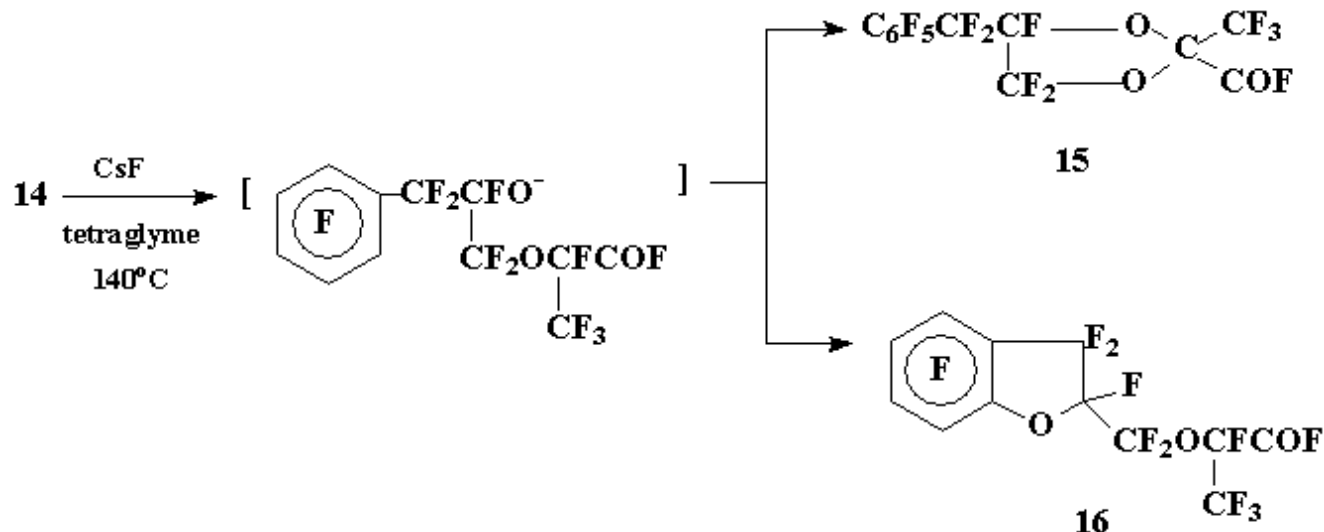
The alternative route of preparing fluorinated olefine based on oxide **2** as starting material could be a chain of transformations analogous to the scheme that was used for the synthesis of perfluoro-2-methylene-4-methyl-1,3-dioxolane [6aΓ· c]. This approach comprises the conversion of ketone **6** into the dimer of O±-ketoacyl fluoride (**13**), the preparation of cycloadduct of (**13**) with HFPO, the isomerization of 2-oxo-1,4-dioxane (**14**) obtained in the presence of CsF into 2-fluoroformyl-1,3-dioxolane (**15**) and saponification of **15** with aq. Na_2CO_3 with subsequent pyrolysis of carboxylate formed.

4-Oxo-1,3-dioxolane **13** was obtained by degradation of fluorosulfonyloxyketone **6** under the action of CsF; the subsequent reaction of **13** with HFPO/[CsF] resulted in formation of 2-oxo-1,4-dioxane **14** (about the formation of homodimers of perfluorinated O±-oxoacyl fluorides and their cycloadducts with HFPO see also [7Γ· 9]):



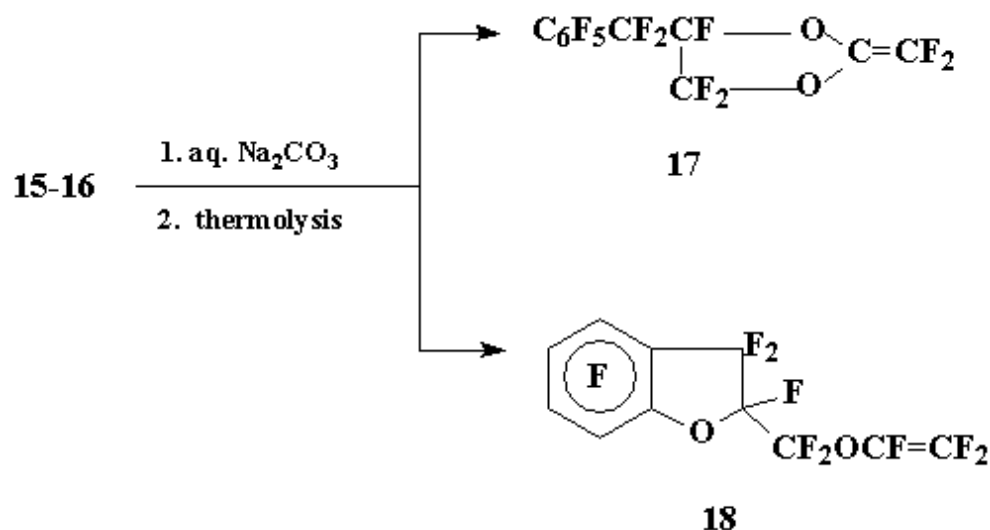
As it turned out the isomerization of dioxane **14** under the conditions described in [6] led to the formation of undivided mixture of the target 2-fluoroformyl-1,3-dioxolane **15** and perfluoro-2-benzofurylmethoxypropionyl fluoride (**16**) with the dominance of the latter (**16**:**15** = 5:4). In this case as well as in the above examples the nucleophilic substitution of fluorine in the aromatic ring appeared to be a dominating direction of the process:

Scheme 7



The mixture of acyl fluorides **15-16** was worked up with aq. Na₂CO₃; the subsequent pyrolysis of sodium carboxylates obtained afforded a mixture of trifluorovinyl ether (**17**) and 2-methylene-1,3-dioxolane (**18**), that were characterized with ¹⁹F NMR spectra:

Scheme 8



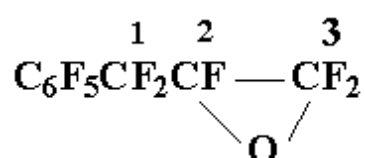
Thus we have shown that the transformations of perfluorobenzyl ketones and their derivatives that proceed with the intermediate generation of alkoxy- or cabanions are inevitably accompanied by formation of products of intramolecular nucleophilic substitution that is most probably connected with increased electrophilicity of aromatic ring in the perfluorobenzyl group structure.

Experimental

¹⁹F NMR spectra were recorded using a Bruker AVANCE-300 spectrometer at 282 MHz; the external standard was CDCl₃ or D₂O. Chemical shifts in ¹⁹F spectra are given in ppm vs. CF₃COOH. Mass-spectrum were recorded VG ANALYTICAL 70-70E (70 eV) and Finnigan Polaris/GCQ Plus (70 eV) instruments.

Preparation of perfluoroallylbenzyl oxide 2

The mixture of 39 g (0,13 mol) perfluoroallylbenzene and 150 ml of Freon 113 was loaded in to 200 ml stainless steel reactor. The oxygen was fed in the reaction vessel at 140Г· 150 B°C until its consumption ceased. The rectification of the reaction mixture gave 29 g (70 %) of oxide **2**, b.p. 51Г· 52 B°C/15 Torr.

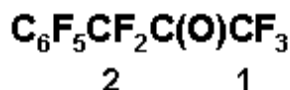


Found %: C 35,10;F 60,20. C₉F₁₀O. Calc. %: C 34,40;F 60,50.

¹⁹F NMR spectrum: AB-pattern with centra at 31.0 and 33.0 (2F³) (J_{AB} = 265 Hz); 72,3 (1F²); AB-pattern with centra at 20,0 and 28,1 (2F¹); 60,7 (2 o-F) 68,3 (1p-F), 81,5 (2 m-F).

Preparation of perfluoromethylbenzylketone 4

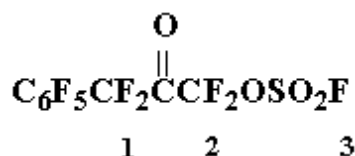
The oxide **2** (56 g, 178 mmol) was added drop wise to 0.7 g SbF₅, sustaining the temperature of the reaction mixture < 40Γ· 45B°C, the mixture was stirred vigorously 10 min more; according to ¹⁹F NMR data the mixture contained 90 % of ketone **4** and 10 % of perfluorotoluene. The reaction mixture was worked up with 4 ml of dry sulfolane, heated when stirred up to 105Γ· 110B°C, the liquid part of the reaction mixture was decanted from tarry deposit, filtered and distilled to give 7 g of fraction (125Γ· 135 B°C) that contained **4**:C₆F₅CF₃ = 1:1 and 42 g of fraction that contained **4**:C₆F₅CF₃ = 10:1; the yield of ketone **4** 75 %. The analytical sample of **4** was isolated by further rectification, b.p. 141Γ· 142,5B°C. Found %: F 59,94. C₉F₁₀O. Calc. %: F 60,51.



¹⁹F NMR spectrum: - 1,3 (3F¹); 23,8 (2F²); 63,0 (2 o-F); 72,0 (1 p-F); 85,0 (2 m-F).

Preparation of fluorosulfonyloxidifluoromethylheptafluorobenzylketone 6

The mixture of oxide **2** (13.3 g, 42 mmol) and HSO_3F (8,5 g, 85 mmol) was heated in a steel tube, protected from air moisture, at 100 B°C/1.5 h, then the reaction mixture was poured on to crashed ice, the organic layer was washed with ice water, dried with SOCl_2 (the reaction mixture was kept under reflux until gas evolution ceased), the excess of SOCl_2 was distilled off, the distillation of residue gave 9 g (52 %) of ketone **6**, b.p. 80°- 83 °C/7-8 Torr. Found %: C 28,10; F 47,86; S 7,73. $\text{C}_9\text{F}_{10}\text{O}_4\text{S}$. Calc. %: C 27,41; F 48,22; S 8,12.



¹⁹F NMR spectrum: - 126,0 (1F³); 1,1 (2F²); 23,2 (2F¹); 63,0 (2 o-F); 71,0 (1 p-F); 84,0 (2 m-F).

Preparation of acyl fluoride 7

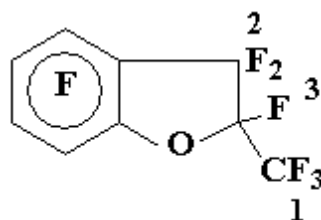
HFPO (5 g, 30 mmol) was gradually added to a mixture of ketone **4** (9,5 g, 30 mmol), CsF (0.5 g) and 2 ml diglyme at 0B°C, stirred at 0F· 15B°C/15 min, warmed up to ~25B°C, the low layer was separated and distilled to give 11.4 g of a fraction (52F· 74 °C/12 Torr), that contained ~95 % acyl fluoride **7** (a mixture of diastereo isomers): the yield of **7** 75 %. Further rectification gave the analytical sample, b.p. 69F·74 °C/12 Torr (mixture of diastereomers). Found %: C 29,98; F 63,46. C₁₂F₁₆O₂. Calc. %: C 30,00;F 63,33.

¹⁹F NMR spectrum: бт"102,6 (1F¹); 1,0 + 2,3 (3F⁴); 6,3 + 6,4 (3F²); a group of signals 27,0Г· 32,0 (2F⁶); 48,8 + 51,5 (1F³); 61,7 (2 o-F); 65,0 (1F⁵); 72,0 (1 рвт"Ф); 85,5 (2 m-F).



Preparation of benzofuran 8

Ketone **4** (4.5 g, 14 mmol) was added drop wise to a mixture of CsF (0.7 g) and 4 ml tetraglyme, when the exothermic reaction was over the solution obtained was stirred at 80Γ· 85 °C until sedimentation ceased, the products volatile at 70 °C/1-2 Torr were evacuated into receiver (-78B°C), the condensate obtained was distilled to give 3.9 g (86 %) of benzofuran **8**, b.p. 74Γ· 76 °C/70 Torr. Found %: C 34,71;F 59,61.C₉F₁₀O. Calc. %: C 34,39;F 60,51.



¹⁹F NMR spectrum: 5,30 + 5,35 (3F¹); AB-pattern with centra 25,2 Pë 31,2, J_{AB} = 235 Hz (2 F²); 57,0 (1F³); 64,5 + 68,7 (2 o-F); 83,6 + 84,4 (2 m-F).

The reaction of acyl fluoride **7** with Na₂CO₃

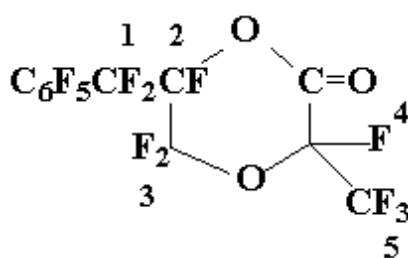
The acyl fluoride **7** (5.4 g, 11 mmol) was gradually added to a mixture of Na₂CO₃ (1.2 g, 12 mmol) Pë 15 ml of diglyme at 65Γ· 70 °C, the reaction mixture was stirred at 140 B°C until gas evolution ceased, washed with dilute aq. HCl, the organic layer (4 g) was separated and distilled over H₂SO₄ to give 3.3 g of a mixture chromane **11** and hydride **12** (**11**:**12** = 4:1) (ChMS).

Mass-spectrum **11** (m/z, reference): 414 [M]⁺ 20; 395 [M-F]⁺ 18; 367 [M-COF]⁺ 10; 345 [M-CF₃]⁺ 100; 326 [C₁₀F₁₀O]⁺ 2; 317 [C₉F₁₁]⁺ 8; 295 [C₉F₉O]⁺ 2; 276 [C₉F₈O]⁺ 8; 267 [C₉F₇O]⁺ 18; 248 [C₈F₈]⁺ 15; 245 [C₈F₇O]⁺ 17; 229 [C₈F₇]⁺ 12; 226 [C₈F₆O]⁺ 8; 217 [C₇F₇]⁺ 6; 198 [C₇F₆]⁺ 30; 179 [C₇F₅]⁺ 20; 167 [C₆F₅]⁺ 2; 160 [C₇F₄]⁺ 4; 148 [C₆F₄]⁺ 5; 141 [C₇F₃]⁺ 5; 129 [C₆F₃]⁺ 3; 124 [C₄F₄]⁺ 5; 117 [C₅F₃]⁺ 5; 110 [C₆F₂]⁺ 2; 98 [C₅F₂]⁺ 2; 93 [C₃F₃]⁺ 5; 79 [C₅F]⁺ 2; 69 [CF₃]⁺ 31.

Mass-spectrum **12** (m/z, reference): 434 [M]⁺ 7; 318 [C₉HF₁₁]⁺ 1;B 267 [C₉F₇O]⁺ 5; 217 [C₇F₇]⁺ 100; 198 [C₇F]⁺ 2; 167 [C₆F₅]⁺ 2; 101 [C₂HF₄]⁺ 10; 69 [CF₃]⁺ 8; 51[CHF₂]⁺ 3.

Preparation of 4-oxo-1,3-dioxolane **13** and 2-oxo-1,4-dioxane **14**

Ketone **6** (18,3 g, 46 mmol) was added drop wise to a mixture of CsF (0.8 g) and 3 ml of diglyme and stirred until gas evolution ceased (formation of dioxolane **13** as a mixture of isomers was registered according to ¹⁹F NMR data: 27,0 + 29,0 (2F_{CF₂}); 41,2 + 44,2 (1F_{CF}); 59,5 + 61,5 (4F o-F); 68,5 + 70,0 (2F p-F); 83,5 (4F m-F) (a signal of COF-group hadnвЂ™t been registered). The reaction mixture was loaded in to stainless steel autoclave (50 ml), the autoclave was cooled in liquid N₂, evacuated, HFPO (8.3 g, 50 mmol) was condensed in to autoclave, the reaction mixture was shaken at ~25B°C/48 h and distilled to give 15 g (71 %) of dioxane **14** (a mixture of isomers), b.p. 64Γ· 70°C/2Γ· 2,5 Torr. Found %: C 32,40; F 56,54. C₁₂F₁₄O₃. Calc. %: C 31,44;F 58,08.



¹⁹F NMR spectrum: 24,0 + 30,0 (2F¹); 46,8 + 48,0 (1F²); a group of signals 4,0Γ· 16,9 (2F³ + 3F⁵); 35,0 + 39,2 (1F⁴); 61,5 + 63,0 (2 o-F); 70,8 + 72,0 (1 p-F); 85,0 (2 m-F).

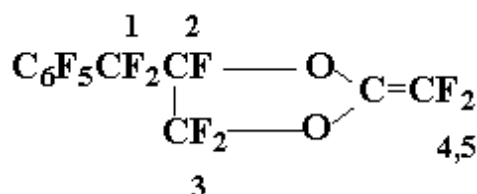
The isomerization of 2-oxo-1,4-dioxane **14** under the action of CsF

The mixture of dioxane **14** (14,8 g, 32 mmol), CsF (0,4 g) and 2 ml tetraglyme was stirred at 140°C/2 h, subsequent distillation afforded a mixture of isomers **15-16** (12.0 g), b.p. 41Γ· 46 °C/1,5Γ· 2 Torr.

Found %: C 32,11; F 57,28. $C_{12}F_{14}O_3$. Calc. %: C 31,44; F 58,08. Molecular ion 458 $[M]^+$ is present in mass-spectra of both isomers.

The preparation of vinyl ether **17** and olefine **18**

The mixture of acyl fluorides **15F**·**16** was worked up with aq. Na_2CO_3 , the aqueous solution was extracted with ether, the solvent was evaporated, the residue was dried over P_2O_5 (100B°C, 1F· 2 Torr). The pyrolysis of a mixture of salts obtained (5.7 g) afforded 3.9 g of a mixture that contained mainly the olefins **17F**·**18**. Further distillation gave 3.4 g (73 %) of a mixture **17**:**18** = 3:1 (ChMS, ^{19}F NMR), b.p. 83F· 84°C/17 Torr. Found %: 33,58; F 58,48. $C_{11}F_{12}O_2$. Calc. %: C 33,67; F 58,16. Mass-spectrum: 392 $[M]^+$ (2 isomers).



^{19}F NMR spectrum of methylenedioxolane **17**: AB-pattern with centrum 29,2 and 32,9 ($2F^1$, $J_{AB} = 292$ Hz); 49,5 ($1F^2$); AB-pattern with centra 7,4 Pë 10,45 ($2F^3$, $J_{AB} = 139$ Hz); AB-pattern with centra 51,6 Pë 53,1 ($1F^4 + 1F^5$, $J_{AB} = 128$ Hz); 62,1 (2 o-F); 72,1 (1 p-F); 85,6 (2 m-F).

^{19}F NMR spectrum of vinyl ether **18**: AB-pattern with centums 25,1 and 31,0 ($2F^1$, $J_{AB} = 264$ Hz); 57,3 ($1F^2$); 9,2 (centrum of multiplets, $2F^3$); 60,1 dd ($1F^4$, $J_{F4F\cdot trans-F5} = 112$ Hz; $J_{F4F\cdot F6} = 68$ Hz); 39,7 dd ($1F^6$, $J_{F6F\cdot F5} = 90$ Hz); 47,0 dd ($1F^5$); 64,2 + 68,5 (2 o-F); 83,4 + 84,2 (2 m-F).

References

1. W.A.Sheppard, C.M.Sharts, Organic Fluorine Chemistry (Russ.Trans.), "Mir", M., 1972, p. 17
2. Z.N.Nudelman, Fluororubbers: basics, processing, application, "PIF RIAS", M., Productive Ed., 2007, p.383.
3. B A.P.King, C.G.Krespan, US Pat. 4384128 (1983).
4. I.L.Knunyants, L.S.German, G.G.Belenkii, G.I.Savicheva, RF Pat. 519919 (1992);
5. I.P.Kolenko, T.I.Filyakova, A.Ya.Zapevalov, E.P.Mochalina, L.S.German, V.R.Polischuk, Izv. Acad. Sci. USSR, Ser. Chim., 1979, 667 [Bull.Acad.Sci., Div.Chem.Sci. (Eng.Trans.), 1979, 28, 622].
6. a) S.Selman, US Pat. 3308107 (1967); b) US Pat. 3321517 (1967); c) US Pat. 3404162 (1968).
7. D.C.England, US Pat. 3962279 (1975).
8. V.S.Yuminov, S.V.Kartsev, V.L.Maximov, A.V.Fokin, Izv. Acad.Sci. USSR, Ser.Chim., 1988, 392, [Bull.Acad.Sci., Div.Chem.Sci. (Eng.Trans.), 1988, 37, 311].B
9. S.R.Sterlin, E.A.Avetisyan, Izv. Russ. Acad. Sci., Div.Chem.Sci., 2009, Iss. 6, p. 1292 [Bull.Acad.Sci.(Eng.Trans.), 2009, N 6, 1318].

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