

FLUORINE MODIFIED ALIPHATIC DICARBOXYLIC ESTERS AS SEMI-PRODUCTS OF FLUORINE MAT PRODUCTION

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Here we have considered the opportunity of obtaining the fluorine containing esters of aliphatic alcohols using commercially available partly fluorinated alcohols for the purpose to create products containing materials. We have discussed Here as well the perspectives of their application as oils, liquid heat-transfers, bases for hydrosystems and lubricating oils.

The rushing development of fluoroorganic compounds chemistry is tightly bonded with the materials. The production of such perfluorinated organic compounds, which meet the modern physic and dielectric characteristics, work in a wide temperature range and thermal loads and practical application has been developed [1,2].

The total replacement of hydrogen atoms for fluorine atoms in an organic molecule results in a number of characteristics, what is used for creating a new generation of materials with splendid properties. The availability of a stable production base is an important point for wide use of new fluorinated materials. The produced perfluoroolefines had been the main raw materials' base till recent time. In this regard the fluorinated alcohols obtained commercially by aliphatic alcohols influencing tetrafluoroethylene and hexafluoropropene in the presence of radical initiators' presence attract our attention [3-5].

They became one of the initial ones to obtain different compounds during fluororganic synthesis. The modification of existing polymer materials by polyfluorinated telomeric alcohols allows changing to a great extent their physical and chemical properties expanding by that the application opportunities of such compounds in different directions [6]. It is enough to mention the opportunities of polyacrylates and methacrylates modified by fluorine ester part for creation of the shielding coats on textile materials [7]. Such fluorine alcohols as nucleophiles and based on that a number of fluorine materials had been created. For example, the fluorine in ester part of such unsaturated acids as acrylic [8], maleinic [9, 10], and fumaric [11].

Modified by their ester fragment mono- and di-carboxylic acids form the base for production of structural materials, liquid heat-transfers, hydrosystems and lubricating oils for high-speed steels, copper and other metals corrosion [12-14]. High thermal endurance and oxidization properties for a wide range of temperatures, high self-ignition temperature (reaching over 400°C) and pyrolysis are just some of their advantages compare to the hydrocarbon analogues. that is

for that class of the organic substances is not surprising. A special attention was paid to the monomers when obtaining elastomers [15], as hydraulic liquid and additives for lubricating oils

Sodium and potassium salts of perfluoroalkylmaleates of $H(CF_2)_nCH_2OC(O)CH=CHCOOH$ (n as surfactants [10, 17], wetting agents [10], hydraulic liquids [18] and antisoiling agents [19].

To improve the lubricating properties of oils based on fluorosiliconorganic liquid a 0,5-1% of acid ester of formula $R(CF_2)_nCH_2OC(O)CH=CHC(O)OCH_2(CF_2)_nR$, where $R = H, F$; $n = 2-6$ mN/m of such esters is equal: at $n = 2 - 31.21$; $n = 4 - 27.57$; $n = 6 - 25$ [15]) is introduced a of 1-octen with modified alcohols of $F(CF_2CF_2)_nCH_2CH_2OH$ ($n = 3,4,5$) type and maleinic acid carpet coloring agents [21]. alcohols of RCH_2OH ($R = C_7F_{15}$, perfluorocyclohexyl) type were itaconic and fumaric acids applied for fabrics impregnation to make them water-, soil-, and fat-

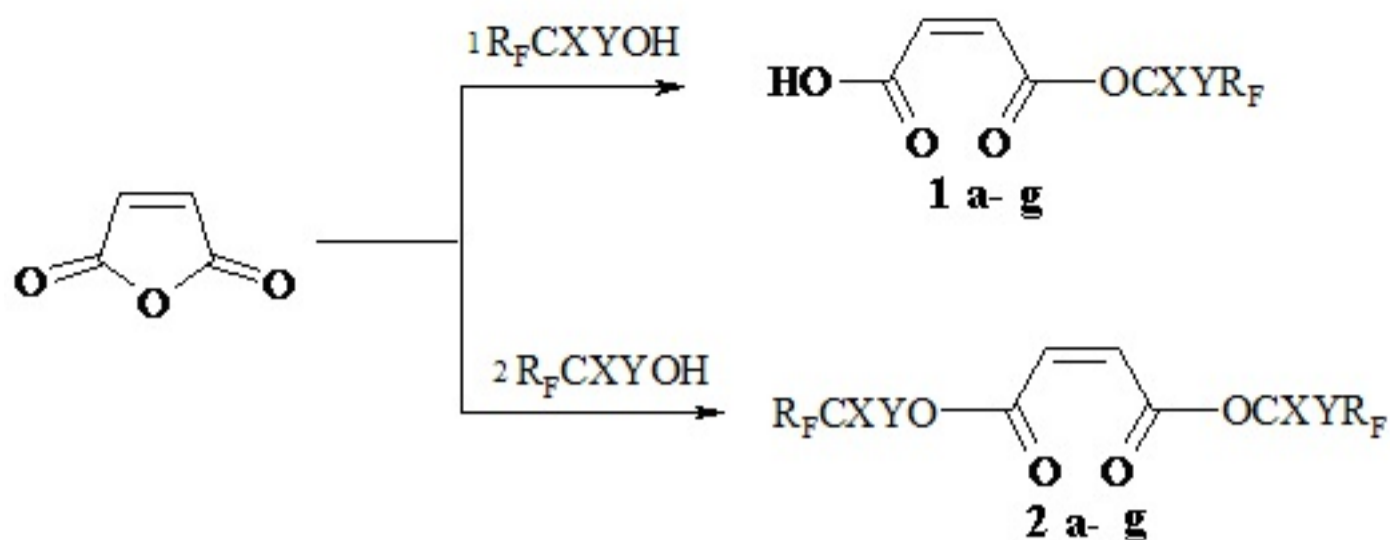
Here for this work we Have determined our goal as obtaining the maleinic acid ethers (look and esters of dicarboxylic acids (adipinic, succinic and malonic) with the use of new partly fluorin

It is known, that interaction of fluorine containing alcohols and maleinic acid anhydride fluoroalkoxymaleinates [14, 17] or in esters of maleinic acids [8-10,24]. Thus, at equimolar alcohols $R(CF_2CF_2)_nCH_2OH$ ($R = H, F$; $n = 1-3$) at 90-120 °C and period of 10-20 h in the presence of sulphuric acid with the yield of 36-45 % [9], and at 50-75 °C (10-40 h) without catalyst with acid esters of fluoroalkoxymaleinates are formed. $RFCH_2CH_2OH$ fluorocontaining alcohols react acid in the same way that is at 50-55 °C and period of 6 H in the presence of Et_3N in toluene (in the form of *cis*-isomers) are formed with the yield of 97.3 %. At the same time regardless alcohol at the reagents' ratio of 1:2 the esterification of maleinic acid using fluorine alcohols sulphide or catalytic quantities of sulphuric acid at 110 °C (7 h) in toluene [9,12,16,22,24] or °C (24 H) in the presence of triethylamine results in bis(fluoroalkoxy)-maleinates. The esterification of maleinic acid maleinate by 1,3-bis(-hydroxypropyl)-1,1,3,3-siliconorganic maleinates produces corresponding acid [8].

Here we have drawn the optimization of the modes of carrying out the interaction process and maleinic acid anhydride. It has been determined, that when using the equimolar quantities presence of catalytic quantities of triethylamine regardless of the used fluorine alcohol structure acid **Ia-g** in the form of *cis*-isomers are obtained with the high yields, while at the ratio of reagents ethers of maleinic acid **Ila-g** in the form of *cis*-isomers as well (scheme 1, table 1). Their composition confirmed by the data of the elemental analysis, molecular weight and NMR 1H and ^{19}F spectra and **Ile** compounds are obtained in the form of the diastereoisomer mixture.

In the IR spectra you can find the presence of the intensive absorption fields, caused by the following groups: $C=C$ (1750 cm^{-1}), CF_2 ($1250-1050\text{ cm}^{-1}$) and double bond $C=C$ (1640 cm^{-1}).

Scheme1



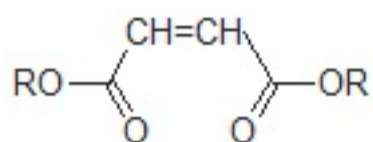
| Compound | a | b | c | d | e |
|----------|---------------|-----------------|----------------|-----------------|---------------|
| R_F | CF_3CHFCF_2 | $HCF_2(CF_2)_5$ | $CF_3(CF_2)_5$ | $HCF_2(CF_2)_7$ | CF_3CHFCF_2 |
| X | H | H | H | H | H |
| Y | H | H | H | H | Me |

Table 1. Analytical Data of Polyfluoroalkoxymaleinates

| Compound | Yield, % | Boiling Point/ mm Hg (Melting Point) | Found, % | | | Formula | C |
|----------|----------|--|----------------|--------------|----------------|----------------------|----|
| | | | C | H | F | | |
| la | 76 | 90-91 / 6 | 34.15 34.24 | 2.01 2.17 | 40.54 40.68 | $C_8H_6F_6O_4$ | 34 |
| lb | 40 | (72-73) | 32.45 32.46 | 1.62 1.35 | 45.92 45.79 | $C_9H_6F_8O_4$ | 33 |
| lc | 73.5 | 146- 147 / 6 (93-95) | 29.26 29.56 | 1.02 1.09 | 55.84 55.96 | $C_{11}H_5F_{13}O_4$ | 29 |

| | | | | | | | |
|-----|----|-------------|----------------|--------------|----------------|--|----|
| ld | 79 | 178-179 | 29.54 29.63 | 1.08 1.14 | 57.46 57.56 | C ₁₃ H ₆ F ₁₆ O ₄ | 29 |
| le | 92 | 91-92 / 6 | 36.44 36.57 | 2.54 2.70 | 38.54 38.85 | C ₉ H ₈ F ₆ O ₄ | 30 |
| lf | 84 | 70-75 / 6 | 38.24 38.38 | 3.15 3.32 | 37.5 37.6 | C ₁₀ H ₁₀ F ₆ O ₄ | 30 |
| lg | 81 | 75-76 | 35.71 35.99 | 2.07 2.33 | 33.37 33.42 | C ₇ H ₆ F ₄ O ₄ | 30 |
| lla | 67 | 105-106 / 6 | 32.49 32.65 | 1.99 1.95 | 50.41 50.47 | C ₁₂ H ₈ F ₁₂ O ₄ | 30 |
| llc | 46 | 148-150 / 3 | 27.94 27.82 | 1.34 1.19 | 63.51 63.32 | C ₁₈ H ₆ F ₂₆ O ₄ | 29 |
| lld | 55 | 162-163 / 3 | 28.01 27.84 | 0.95 0.82 | 64.56 64.37 | C ₂₂ H ₈ F ₃₂ O ₄ | 29 |
| lle | 58 | 120-122 / 8 | 35.67 35.89 | 2.58 2.36 | 48.44 48.56 | C ₁₄ H ₁₂ F ₁₂ O ₄ | 30 |
| llf | 84 | 105-106 / 6 | 32.49 32.65 | 1.61 1.87 | 51.54 51.47 | C ₁₂ H ₈ F ₁₂ O ₄ | 30 |
| llg | 85 | 133-134/18 | 35.42 35.52 | 2.22 2.28 | 43.77 43.79 | C ₁₀ H ₈ F ₈ O ₄ | 30 |
| llh | 88 | 113-114/6 | 38.68 38.98 | 3.78 3.89 | 40.10 40.56 | C ₁₂ H ₁₂ F ₈ O ₄ | 30 |

Table 2. NMR ^1H and ^{19}F spectra of maleinic acid esters



| Compound | R | CH=CH | \square , ppm (structure, J H | |
|----------|---|------------------------------------|---|---|
| | | | ^1H | ^{19}F |
| (IIa) | $\overset{1}{\text{CF}_3}\overset{2}{\text{CH}}\overset{3}{\text{F}}\overset{4}{\text{CF}_2}\text{CH}_2$ | $\overset{5}{\text{CH}}=\text{CH}$ | 4.28 (H ⁴ ,m); 4.74 (H ² , dm 47.4; 5.4) | 86.2 (F ³); 40.3 (F ¹); J _{FF} 44.9; dd 17.7; |
| (IIb) | $\overset{1}{\text{H}}\overset{2}{\text{CF}_2}\overset{3}{\text{CF}_2}\overset{4}{\text{CF}_2}\overset{5}{\text{CF}_2}\overset{6}{\text{CF}_2}\overset{7}{\text{CF}_2}\text{CH}_2$ | $\overset{8}{\text{CH}}=\text{CH}$ | 4.07 (H ⁷ t 13.4); 5.45 (H ¹ tt 52.0; 4.8); 5.71 (H ⁸ s) | 25.6 (F ²); 33.6 (F ³ s); 41.4 (F ⁷ t 11 |
| (IIc) | $\overset{1}{\text{CF}_3}\overset{2}{\text{CF}_2}\overset{3}{\text{CF}_2}\overset{4}{\text{CF}_2}\overset{5}{\text{CF}_2}\overset{6}{\text{CF}_2}\overset{7}{\text{CF}_2}\text{CH}_2$ | $\overset{8}{\text{CH}}=\text{CH}$ | 4.73 (H ⁷ t 14.0); 6.48 (H ⁸ , s) | 82.8 (F ⁶ m); 41.0 (F ⁴ m); 37.7 |
| (IIe) | $\overset{1}{\text{CF}_3}\overset{2}{\text{CH}}\overset{3}{\text{F}}\overset{4}{\text{CF}_2}\overset{5}{\text{C}}\overset{6}{\text{H}}\overset{7}{\text{CH}_3}$ | $\overset{8}{\text{CH}}=\text{CH}$ | 6.31 (H ⁵ s); 5.38 (H ⁴ m); 5.15 (H ² dm 37.2; 0.8); 1.42 (H ⁶ s) | 89.5 (F ³); 40.5 (F ¹); J _{FF} 276); 41.6) |
| (IIf) | $\overset{1}{\text{H}}\overset{2}{\text{CF}_2}\overset{3}{\text{CF}_2}\overset{4}{\text{CF}_2}\overset{5}{\text{CF}_2}\text{CH}_2$ | $\overset{6}{\text{CH}}=\text{CH}$ | 6.53 (H ⁶ s); 6.48 (H ¹ tt 46.0; 2.6); 4.85 (H ⁵ t 13.8); | 25.7 (F ²); 2.6); 33 (F ³ s); 4 |
| (IIg) | | | | |

| | | | | |
|--------|--|--------------------------|---|--|
| | $\begin{array}{c} 1 \quad 2 \quad 3 \\ \text{HCF}_2\text{CF}_2\text{CH}_2 \end{array}$ | $^4 \text{CH}=\text{CH}$ | 6.27 (H ⁴ s); 5.57 (H ¹ tt 52.6; 4.0); 4.30 (H ³ t 18.0) | 39.3 (F ¹ m) |
| (IIIH) | $\begin{array}{c} 1 \quad 2 \quad \text{H} \\ \text{CHF}_2\text{CF}_2 - \text{C} - \text{C} \\ \quad \quad \quad \quad \quad \\ \quad \quad \quad \quad \quad \text{CH}_3 \end{array}$ | $^4 \text{CH}=\text{CH}$ | 6.95 (H ⁴ s); 6.00 (H ¹ tt 52.6; 4.8); 5.42 (H ² m); 1.47 (H ⁵ d 6.2) | 37.0 AB-system 27.6 and system 51.8) |

The yield of ethers of maleinic acid depends on the structure of the used alcohol or catalyst. For polyfluorinated alcohols the yield as a rule, depends on the length of carbon chain, while for the other alcohols a special demands play an important role and while they grow the yield of target product. The forming of mixtures of the corresponding ethers of maleinic acid and their potassium salt depends on the structure of alcohol used.

Thus, the interaction of maleinic acid anhydride and 2,2,3,4,4,4-Hexafluorobutanol-1, dimethyl-propanol-1 over KOH results in formation of mixture of potassium salt (Z)-4(2,2,3,4,4,4-hexafluoro-5-methyl-oxo-but-2-enic acid **IIIa** and its ester **IIa** and potassium salt (Z)-6,6,7,7-tetrafluoro-5-methyl-oxo-but-2-enic acid **IIIb** and its ester **IIb** respectively.

The synthesis of the **IIa-g** esters can be carried out in a most convenient manner if we use maleinic acid of corresponding fluoroalcohol in the medium of boiling toluene over the small quantity of concentrated sulphuric acid with azeotropic distillation of water (reaction period no longer than 1 hour is required). In some cases we can observe the formation of two maleate isomers. Thus, when we use trihydrooctafluoropentoxymaleate we can get the mixture of two isomers with the ratio about 1:1 caused by maleinic acid isomerization into fumaric acid. At the same time, the tertiary alcohol and HCF₂CF₂C(CH₃)₂OH couldn't have been introduced into the reaction with maleinic acid under the above conditions. We should note, that the excess of the fluoroalcohol used after the distillation does not require purification and can be used again.

Before [17] it was proved, that at interaction of acid ester of maleinic acid, for example formamide with glycidyltrimethylammonium chloride the salts were obtained.

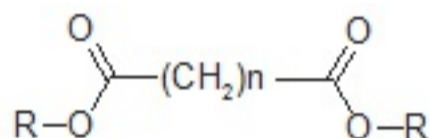
At 54 °C the salt [C₆F₁₃CH₂CH₂OC(O)CH=CHCH(OH)CH₂NMe₃]⁺·Cl⁻ (yield 59.8 %) was isolated. The forming of salts by carboxylic group by the influence of either trialkylamines or of quaternary ammonium salts proved indeed, that at triethanolamine influence on **Ia-g** acid esters of maleinic acid the corresponding potassium salts were formed (scheme 2). Influencing of some quaternary ammonium salts on **IIIa, IIIg** potassium salts respectively. Such salts are foaming and surface active (according to our information the surface tension of the salts was about 27.59 mN/m and 24.55 mN/m). That data points out the higher foaming ability of these salts compare to potassium salts of **IIIa, IIIg**.

Scheme 2

| | | | | | | | |
|---------------|------|-------------------|----------------|--------------|----------------|--|----|
| (IXa) | 55.5 | 91- 92/2-3 | 31.32 31.06 | 2.29 2.26 | 52.76 52.67 | C ₁₁ H ₈ F ₁₂ O ₄ | 30 |
| (IXb) | 76.7 | 150- 151/2-3 | 27.22 28.07 | 1.45 1.89 | 62.60 62.51 | C ₁₇ H ₈ F ₂₄ O ₄ | 29 |
| (IXf) | 47.5 | 133- 135 / 2-3 | 29.48 29.10 | 1.51 1.13 | 57.22 57.38 | C ₁₃ H ₈ F ₁₆ O ₄ | 29 |
| (IXg) | 66.3 | 88-89 /2-3 | 33.07 33.33 | 2.74 2.56 | 46.10 45.85 | C ₉ H ₈ F ₈ O ₄ | 30 |
| (Xa) | 59 | 152- 154 / 2-3 | 32.56 32.78 | 2.56 2.78 | 50.94 51.14 | C ₁₂ H ₁₀ F ₁₂ O ₄ | 30 |
| (Xb) | 65.4 | 160- 162 / 3-4 | 28.81 28.90 | 1.49 1.57 | 61.22 61.33 | C ₁₈ H ₁₀ F ₂₄ O ₄ | 29 |
| (Xf) | 48.6 | 120- 121 / 2-3 | 30.98 31.01 | 2.02 1.75 | 55.95 55.97 | C ₁₄ H ₁₀ F ₁₆ O ₄ | 30 |
| (XIa) | 46.4 | 131- 132 / 2-3 | 35.15 35.44 | 3.12 2.90 | 48.29 48.11 | C ₁₄ H ₁₄ F ₁₂ O ₄ | 30 |
| (XIb) | 94.3 | 168- 170/3 | 31.37 31.57 | 2.08 2.32 | 58.46 58.50 | C ₂₀ H ₁₄ F ₂₄ O ₄ | 30 |
| (XIc) | 72.7 | 142- 143 / 3 | 30.19 30.09 | 1.33 1.62 | 60.44 60.59 | C ₂₀ H ₁₂ F ₂₆ O ₄ | 29 |
| (XI f) | 58.5 | 168- 170 / 3 | 33.99 33.71 | 2.30 2.67 | 52.92 52.63 | C ₁₆ H ₁₄ F ₁₆ O ₄ | 30 |

| | | | | | | | |
|---------|------|-------------------|----------------|--------------|----------------|--|----|
| (XIg) | 69.5 | 153- 154 / 2-3 | 38.75 38.54 | 3.56 3.60 | 40.91 41.16 | C ₁₂ H ₁₄ F ₈ O ₄ | 38 |
| (XIIa) | 95 | 145- 146 / 2-3 | 35.26 35.43 | 3.09 3.03 | 48.21 48.08 | C ₁₄ H ₁₄ F ₁₂ O ₄ | 38 |
| (XIIIa) | 63.8 | 148- 150 / 3 | 38.13 38.32 | 3.72 3.84 | 45.04 45.19 | C ₁₆ H ₁₈ F ₁₂ O ₄ | 38 |
| (XIIIg) | 58.4 | 132- 133 / 2-3 | 41.26 41.04 | 4.52 4.43 | 37.86 38.11 | C ₁₄ H ₁₈ F ₈ O ₄ | 48 |

Table 4. NMR ¹H and ¹⁹F spectra of Dicarboxylic Acids Esters



| Compound | R | (CH ₂) _n | □, ppm (structure, J | |
|----------|--|---------------------------------|---|--|
| | | | ¹ H | ¹⁹ F |
| (IXa) | ¹ ² ³ ⁴ CF ₃ CHFCF ₂ CH ₂ | ⁵ CH ₂ | 5.07 (H ² dm 42.2), 4.57 (H ⁴ t 9.6), 3.56 (H ⁵ s) | 85.8 and 41 system -52.9 43.3;36 |
| (IXb) | ¹ ² ³ ⁴ ⁵ ⁶ ⁷ HCF ₂ CF ₂ CF ₂ CF ₂ CF ₂ CF ₂ CH ₂ | ⁸ CH ₂ | 6.10 (H ¹ tt 51.8; 4.8), 4.68 (H ⁷ t 17.6), 3.56 (H ⁸ s) | 26.4 34.2 ((F ^{4,5}), 13) |
| (IXf) | ¹ ² ³ ⁴ ⁵ HCF ₂ CF ₂ CF ₂ CF ₂ CH ₂ | ⁶ CH ₂ | 6.10 (H ¹ ,tt 51.6; 5.2), | 26.3 2.4), 36 |

| | | | | |
|---------------|--|--|---|---|
| | | | 4.67 (H ⁵ t 13.6), (H ⁶ s) | (F ³), 3.57 11.9) |
| (IXj) | ¹ ² ³ HCF ₂ CF ₂ CH ₂ | ⁴ CH ₂ | 5.55 (H ¹ tt 52.6; 4.15 (F ³ t 13.0), (H ⁴ s) | 22.1 35.9 (F |
| (Xb) | ¹ ² ³ ⁴ ⁵ ⁶ ⁷ HCF ₂ CF ₂ CF ₂ CF ₂ CF ₂ CH ₂ | ⁸ ⁹ CH ₂ CH ₂ | 6.09 (H ¹ tt 52.0; 4.62 (H ⁷ t 14), (H ^{8,9} s) | 26.5 34.3 (F ^{3,4}), 44.3 (F |
| (Xf) | ¹ ² ³ ⁴ ⁵ HCF ₂ CF ₂ CF ₂ CF ₂ CH ₂ | ⁶ ⁷ CH ₂ CH ₂ | 6.11 (H ¹² tt 51.6; 4.62 (H ⁵ t 14), (H ^{6,7} s) | 26.6 34.1 (F 44.4 (F |
| (XIa) | ¹ ² ³ ⁴ CF ₃ CHFCF ₂ CH ₂ | ⁵ ⁶ ⁷ ⁸ CH ₂ CH ₂ CH ₂ CH ₂ | 5.15 (H ² t), 4.47 (H ⁴ t 48), (H ^{5,8} s), (H ^{6,7} s) | 89.3 and 4. system -49.8 42.9;7. |
| (XIb) | ¹ ² ³ ⁴ ⁵ ⁶ ⁷ HCF ₂ CF ₂ CF ₂ CF ₂ CF ₂ CH ₂ | ⁸ ⁹ ¹¹ CH ₂ CH ₂ CH ₂ CH ₂ | 6.00 (H ¹ tt 54.0; 4.48 (H ⁷ t 13.4), (H ^{8,11} s), (H ^{9,10} s) | 26.5 34.4 (F ^{3,4}), 44.4 (F |
| (XIc) | ¹ ² ³ ⁴ ⁵ ⁶ ⁷ CF ₃ CF ₂ CF ₂ CF ₂ CF ₂ CH ₂ | ⁸ ⁹ ¹⁰ ¹¹ CH ₂ CH ₂ CH ₂ CH ₂ | 3.71 (H ⁷ t 13.6), (H ^{8,11} s), (H ^{9,10} s) | 78.4 40.1 (F 37.2 (F 33.6 (F |
| (XI f) | | | 6.20 (H ¹ tt 51.8; 5.4), | 26.2 |

The structure of ethers is confirmed by the data of NMR ^1H and ^{19}F (Table 4), IR spectra that, the position of signals in NMR spectra are typical for initial fluorine alcohols and they spectra the oscillations of OH group are not presented and intensive oscillations are appearing C-F bonds ($1308\text{-}1124\text{ cm}^{-1}$). As for the oscillations of C-H bonds well they are in the area depending on the used acid are of complicated structure.

Experimental Part

NMR ^1H and ^{19}F spectra were obtained at Bruker WP 400 SY spectrometer (400, 188 MHz) with inner standards hexamethyldisiloxane (HMDS), C_6F_6 . IR-spectra were recorded Specord M chromatograph. Mass-spectra (energy of ionizing electrons is 70 eV) were registered using chromatograph detector (Hewlett Packard G 1800 A GCD) (we used the column of 30 m length, 0.25 mm diameter, inner side with the 0.25 μm layer of copolymer 5% diphenyl -95% dimethylsiloxane (HP-5), gas flow rate equals 280 $^\circ\text{C}$. The temperature of column was increasing starting from 50 $^\circ\text{C}$ at a rate of 10 degree per min reaching 280 $^\circ\text{C}$ (it was held at that point for 5 min). All reactions were analyzed by NMR ^{19}F method.

The analysis of reaction mixtures was carried out at chromatograph LHM 72 (15% Chromosorb W, column 4000 mm, diameter 4 mm). Characteristics of new compounds and their yields are listed in Tables 1 and 3.

Common Synthesis Methods for Polyfluoroalkoxymaleates

The mixture of 49 g (0.5 mole) of maleinic anhydride and 58 g (0.5 mole) of 1,1,3-trihydroxy-2,2,2-trifluoropropane heated while being mixed at the T of 85 $^\circ\text{C}$ during 40 h, the reaction mixture was cooled, the mixture was separated and re-crystallized out of toluene. We obtained 83 g (74 %) of tetrafluoropropylmaleate. Other polyfluoroalkoxymaleates were obtained the same way (Table 1).

Common Synthesis Methods for Dicarboxylic Acid Esters

The mixture of 24.5 g of maleinic acid (or dicarboxylic acid), 249 g of 1,1,7-trihydrodecane, 250 ml of concentrated sulphuric acid and 250 ml of toluene was boiled along with stirring at 110-120 $^\circ\text{C}$ with water was distilled. The reaction mixture was cooled, neutralized by 3%-solution of sodium bicarbonate through with water till the neutral reaction (according to litmus), dried with CaCl_2 . Upon the removal of vacuum of water-jet pump, the residuum was distilled twice in vacuum. We obtained 152 g (70.7 %) of 2-(2,2,2-trifluoroheptoxy)maleate (**IIb**) with the yield of 70.7 %, b. p. 152-153 $^\circ\text{C}$ / 2 mm Hg. [according to data [24] b. p. 149-153 $^\circ\text{C}$ / 5 mm Hg., n_D^{30} 1.3470, and according to [12] standing the compound is crystallized, melting point is 62-63 $^\circ\text{C}$.

Analogously we have obtained bis(polyfluoroalkoxy) maleates: **II f** (85 %), **II g** (82 %). Their characteristics are similar to the ones represented in [9,12], and the characteristics of **IIc** (yield 92 %) agree with data [12].

Synthesis Methods for Esters of Aliphatic Dicarboxylic Acids

Mixture of 0.01 g-mole of dicarboxylic acid, 0.02 g-mole of corresponding fluorocontaining alcohol, 250 ml of concentrated sulphuric acid is being boiled along with distillation of toluene azeotrope with water. After distillation of 0.02 g-mole of water, the reaction mixture is cooled and 70 $^\circ\text{C}$ with vacuum of water-jet pump. Then it is washed through with 3% solution of sodium bicarbonate (according to litmus), dried with CaCl_2 . It is distilled in the vacuum, the characteristics of the products are listed in Table 1.

CONCLUSIONS

1. Polyfluoroalkoxymaleates and bis(polyfluoroalkoxy)maleates are obtained depending on

taken by the interaction of partly fluorinated alcohols and maleinic acid anhydride over sulphuric acid

2. During the laboratory checking of optimal conditions for synthesis of maleinic acid est technological scheme for commercial production has been offered
3. The esterification of malonic, succinic and adipinic acids has been carried out using influ alcohols over the catalytic quantities of concentrated sulphuric acid.

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