

Reaction of Perfluoro-1-methylindan with $\text{SiO}_2\text{-SbF}_5$

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Abstract—The reaction of perfluoro-1-methylindan with $\text{SiO}_2\text{-SbF}_5$ depending on the amount of SiO_2 led to the formation after hydrolysis of the reaction mixture of perfluoro-3-methylindan-1-one, perfluoro-4-methylisochromen-1-one, 6-(1-carboxy-2,2,2-trifluoro-ethyl)-2,3,4,5-tetrafluoro-benzoic and 6-(carboxymethyl)-2,3,4,5-tetrafluoro-benzoic acids. Heating in the SbF_5 medium perfluoro-1-methylindan in a glass ampoule at 130°C , or perfluoro-3-methylindan-1-one at 70°C provided a solution of a perfluoro-4-methylisochromenium salt that on treating with anhydrous HF was converted into perfluoro-4-methyl-1*H*-isochromen, and on hydrolysis, into perfluoro-4-methylisochromen-1-one.

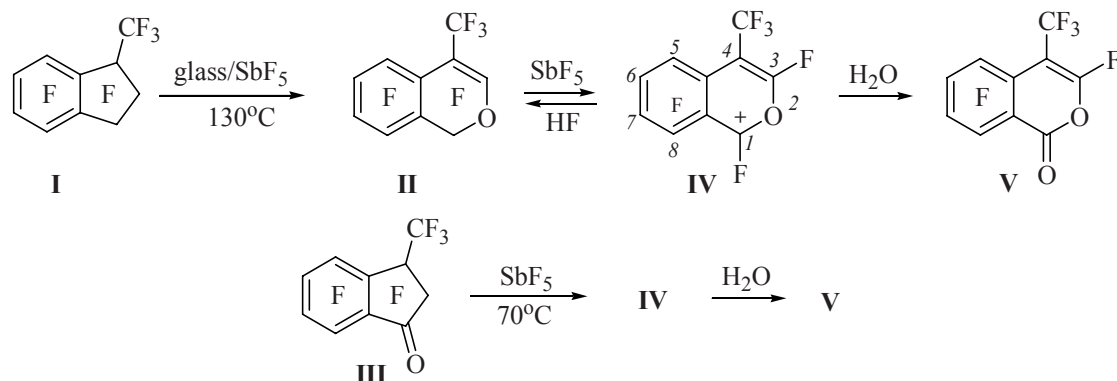
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We formerly found and investigated the cationoid rearrangements of benzocycloalkenes (benzocyclobutene, indan, tetralin) and of their perfluoroalkyl and perfluoroaryl derivatives under the action of Lewis acids [1, 2]. In particular, on heating perfluoro-1-methylindan (**I**) with SbF_5 in a small nickel bomb formed perfluoro-2-isopropyl-toluene [2], and in a glass ampoule, perfluoro-4-methyl-1*H*-isochromen (**II**), a product of reaction of compound **I** with antimony pentafluoride and glass serving as a source of inorganic oxides (see preliminary communication [3]). We recently showed that in the reaction of perfluorinated indan and 1-ethylindan with $\text{SiO}_2\text{-SbF}_5$ formed perfluoro-indan-1-one and perfluoro-3-ethylindan-1-one respectively that suffered skeletal transformations under the action of antimony pentafluoride [4, 5].

We report here on the study of the reaction of perfluoromethylindan (**I**) with SiO_2 in SbF_5 environment, and also of the behavior of perfluoro-3-methylindan-1-one (**III**) under the treatment with SbF_5 in order to establish the possibility of its cationoid skeletal rearrangements. Besides in more detail than in the preliminary communication [3] the reaction of compound **I** with glass in the presence of SbF_5 was described.

It was shown that at heating with SbF_5 in a sealed glass ampoule compound **I** reacted with the glass giving a salt of perfluoro-4-methylisochromenium (**IV**). The hydrolysis of the reaction mixture resulted in perfluoro-4-methylisochromen-1-one (**V**). The treatment of the reaction mixture with anhydrous HF and then with water gave compound **II**. The heating of ketone **III** with SbF_5

Scheme 1.



at 70°C also led to the formation of the solution of salt of cation **IV** whose hydrolysis provided compound **V**. Besides the reaction mixture contained unreacted ketone **III** (Scheme 1).

In the reaction of compound **I** with SiO₂ (0.6 mol per 1 mol of compound **I**) in SbF₅ at 70°C after treating the reaction mixture with water we obtained ketone **III** alongside compound **V** and a few 6-(1-carboxy-2,2,2-trifluoroethyl)-2,3,4,5-tetrafluorobenzoic acid (**VI**). The mixture also contained the unreacted compound **I** (Scheme 2).

The reaction of compound **I** with excess SiO₂ in SbF₅ at 70°C followed by treating the reaction mixture with water yielded 6-(carboxymethyl)-2,3,4,5-tetrafluorobenzoic acid (**VII**) alongside small quantities of compounds **III**, **V**, and **VI** (Scheme 2).

The reaction of compound **I** with glass and SiO₂ in the presence of SbF₅ apparently proceeds along Scheme 3. First from compound **I** under the action of SbF₅ cation **A** is generated that reacts, for example, with SiO₂ giving ketone **III**. Then cation **B** forms from ketone **III** and suffers the opening of the five-membered ring providing a benzoyl type cation **C**. After the addition to the latter of a fluoride ion the corresponding acid fluoride is obtained that under the action of SbF₅ presumably yields an allyl type cation **D**. The latter undergoes an intramolecular cyclization resulting in ion **E** whose isomerization into cation **IV** gives at subsequent hydrolysis compound **V**.

In the presence of excess SiO₂ cation **D** apparently reacts with SiO₂-SbF₅ generating ion **F**. It cannot be excluded that the latter by the addition-elimination of a fluoride ion isomerizes into cation **G** whose intramolecular cyclization followed by the addition of a fluoride ion also gives compound **V**. It is also presumable that the ring closure in cation **F** and the shift of the multiple bond into

the ring results in cation **H**. After the treatment of the reaction mixture with water the salt of cation **H** is hydrolyzed forming apparently compound **I** and then acid **J** that on decarboxylation gives acid **VII** (Scheme 3).

The alternative route to acid **VII** involving the reaction of the salt of cation **IV** with SiO₂ to give cation **H** seems hardly probable for it has been shown by a special experiment the in the reaction of the salt of cation **IV** with SiO₂ at 70°C acid **VII** forms in a low yield.

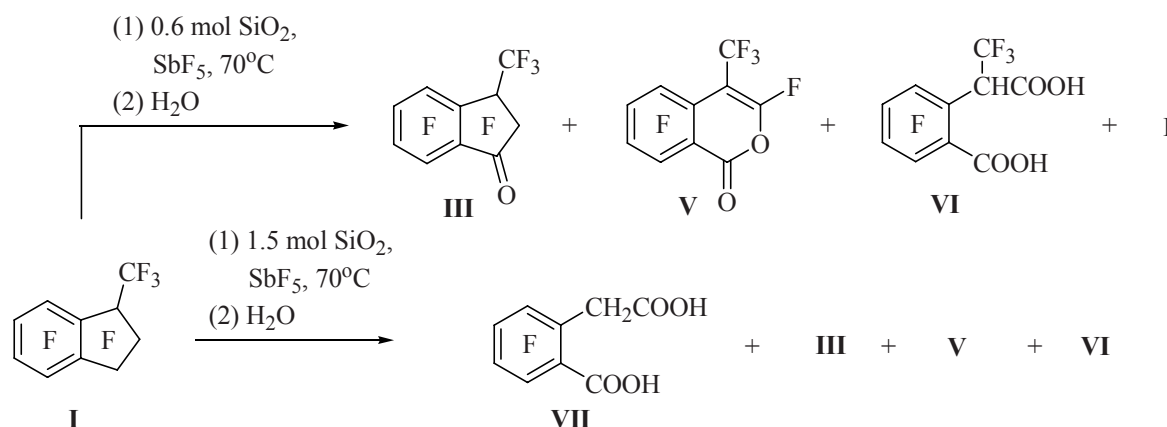
Scheme 3 describing the transformation of ketone **III** under the action of SbF₅ into cation **IV**, and also the formation of compound **I** in the reaction of cation **D** with SiO₂ is consistent with the scheme that was suggested for the explanation of transformations of perfluoro-3-ethylindan-1-one under the action of SbF₅ and SiO₂-SbF₅ respectively [5]. Therewith perfluoro-3-methyl-4-fluorocarbonylisochromen-1-one (analog of compound **I**) and perfluoro-2-(but-2-en-2-yl)benzoic acid (hydrolysis product of analog of cation **C**) were obtained in [5].

By reaction with water in acid medium compound **V** was converted in acid **VI**. The probable reaction path under these conditions is shown on Scheme 4 (a).

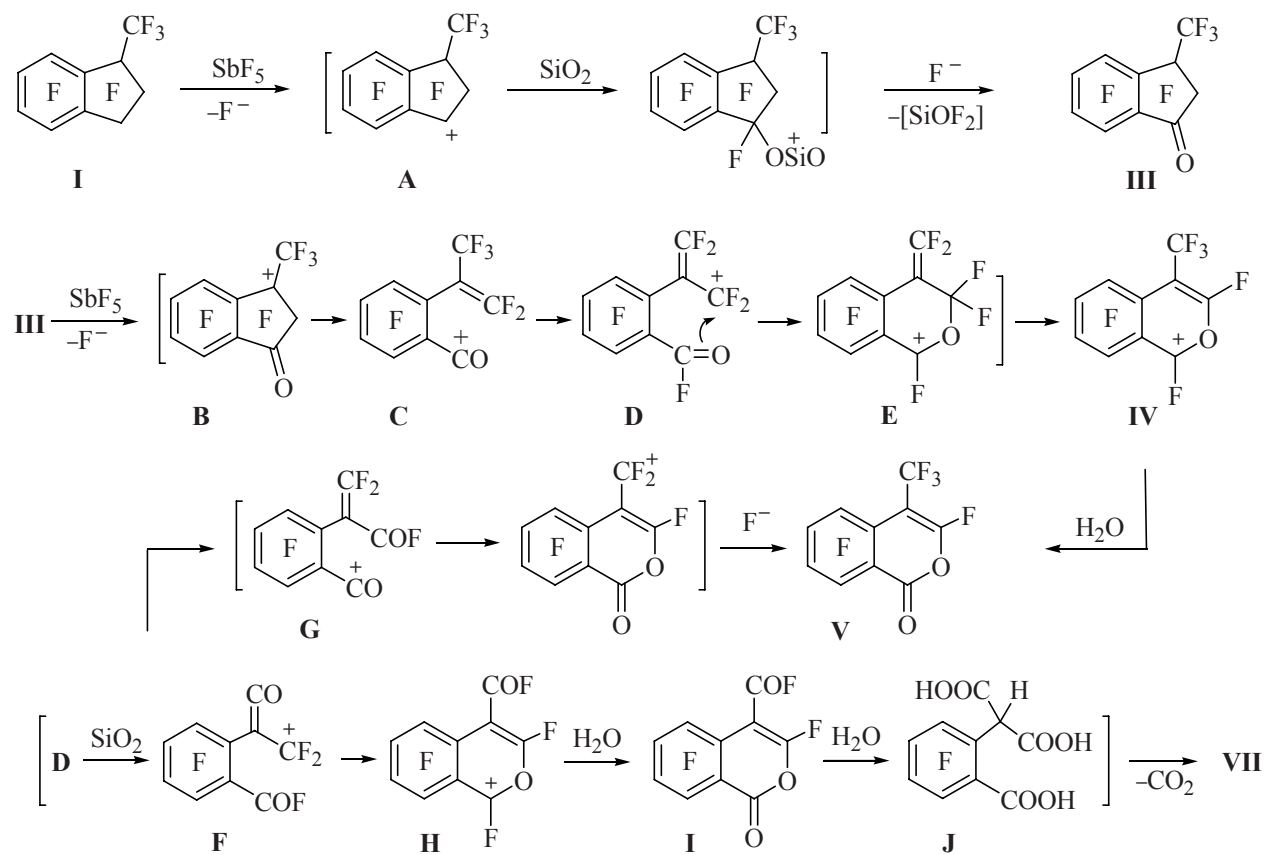
In contrast the reaction with water of compound **V** under alkaline conditions resulted in the formation of acid **VII** alongside a small quantity of acid **VI**. It was shown by an independent experiment that under these conditions acid **VII** formed from acid **VI** in a considerably lesser quantity than from compound **V**. It is therefore presumable that in alkaline medium acid **VII** formed from compound **V** mainly along pathway *b*.

The composition and structure of compounds were confirmed by elemental analysis and spectral characteristics. The structure of cation **IV** was established from the ¹⁹F NMR spectrum and was confirmed by the structure of its reaction products with anhydrous HF and

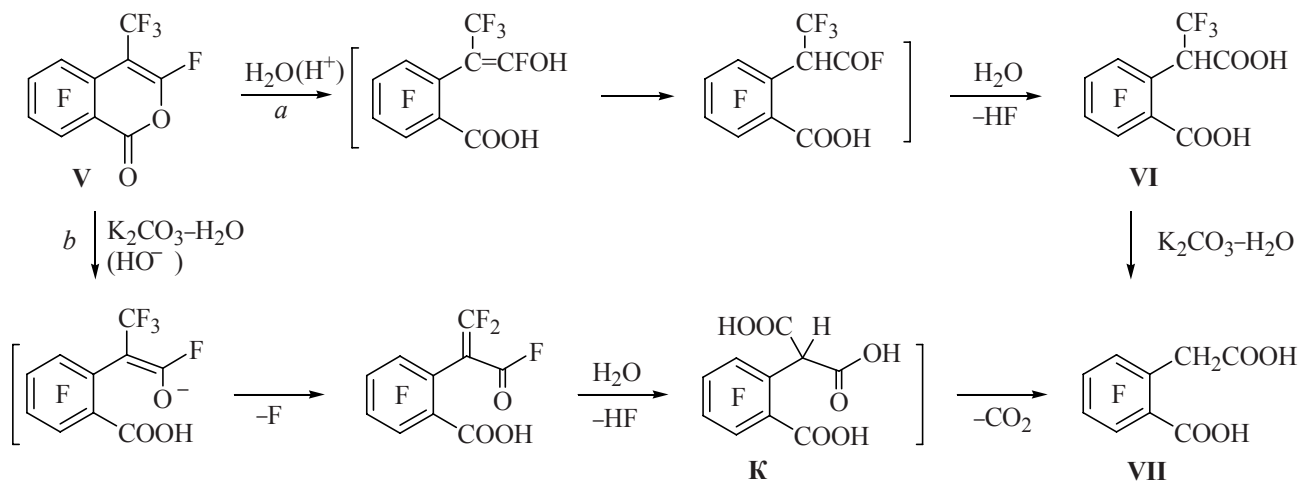
Scheme 2.



Scheme 3.



Scheme 4.



water. In the ^{19}F NMR spectrum of cation **IV** the signals of the fluorine atoms were shifted downfield compared to neutral compound **II**, and also the coupling constants of the fluorine atoms attached to the charged carbon were increased; the latter fact was characteristic of the fluorine-containing cations [5, 6].

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Bruker Vector 22. ^1H and ^{19}F NMR spectra were registered on a spectrometer Bruker AC-200 (at 200 and 188.3 MHz respectively). As internal references were

used HMDS (0.04 ppm from TMS), (CD₃)₂CO (residual proton 2.04 ppm from TMS), C₆F₆ and SO₂ClF (262.8 ppm from C₆F₆). Elemental composition was determined by high resolution mass spectrometry on a Finnigan MAT 8200 instrument. GLC analyses were performed on a chromatograph LKhM-72 (50–270°C, column 4000×4 mm, stationary phase SKTFT-50 on Chromosorb W, 15:100, He, 60 ml/min).

Reaction of perfluoro-1-methylindan (I) with glass in SbF₅. *a.* A mixture of 2.15 g (6.2 mmol) of compound **I** and 4.02 g (18.5 mmol) of SbF₅ was heated at 130°C in a sealed glass ampoule for 49 h. To the reaction mixture at –20°C was added ~4 ml of SO₂ClF, the mixture was stirred and charged into a fluoroplastic vessel containing ~12 ml of anhydrous HF cooled to –20°C. The mixture was kept for 40 min and afterwards it was poured into water with ice. The organic layer was separated, washed with NaHCO₃ solution, with water, and dried over MgSO₄. We obtained 0.95 g of product containing according to GLC 80% of **perfluoro-4-methyl-1H-isochromen (II)** (yield 38%), that was purified by preparative GLC (SKTFT-50 on celite, 125°C). Liquid. IR spectrum (CCl₄), ν , cm⁻¹: 1694 (C=C), 1525, 1497 (fluorinated aromatic ring). ¹⁹F NMR spectrum (CDCl₃), δ , ppm: 10.0 (1F, F⁷), 15.8 (1F, F⁶), 23.8 (1F, F⁸), 26.3 (1F, F⁵), 86.1 (1F, F³), 105.0 (3F, CF₃⁴), 110.8 (2F, CF₂¹); $J_{1,5}$ 2, $J_{1,6}$ 2, $J_{1,8}$ 23, $J_{3,4}$ 33, $J_{3,5}$ 4, $J_{3,6}$ 2, $J_{3,7}$ 5, $J_{3,8}$ 2, $J_{4,5}$ 39, $J_{5,6}$ 19, $J_{5,7}$ 5, $J_{5,8}$ 12, $J_{6,7}$ 20, $J_{6,8}$ 8, $J_{7,8}$ 21 Hz. Found $[M]^+$ 325.9778. C₁₀F₁₀O. Calculated M 325.9789.

b. A solution of 0.27 g (0.78 mmol) of compound **I** in 0.67 g (3.1 mmol) of SbF₅ was heated at 130°C in an NMR tube for 44 h. According to ¹⁹F NMR spectrum a mixture was obtained containing **perfluoro-4-methylisochromenium (IV) salt**. The content of the tube was treated with water, extracted with CH₂Cl₂, dried with MgSO₄, and the solvent was distilled off in a vacuum. We obtained 0.15 g (64%) of **perfluoro-4-methylisochromen-1-one (V)**, mp 75–76.5°C (from heptane). IR spectrum (CCl₄), ν , cm⁻¹: 1803 (C=O), 1680 (C=C), 1515, 1490 (fluorinated aromatic ring). ¹⁹F NMR spectrum (CH₂Cl₂), δ , ppm: 10.1 (1F, F⁷), 23.1 (1F, F⁶), 27.8 (1F, F⁵), 32.2 (1F, F⁸), 94.2 (1F, F³), 106.7 (3F, CF₃⁴); $J_{3,4}$ 39, $J_{3,5}$ 4, $J_{3,6}$ 2, $J_{3,7}$ 5, $J_{3,8}$ 3, $J_{4,5}$ 44, $J_{5,6}$ 19, $J_{5,7}$ 5, $J_{5,8}$ 13, $J_{6,7}$ 21, $J_{6,8}$ 13, $J_{7,8}$ 21 Hz. Found $[M]^+$ 303.9769. C₁₀F₈O₂. Calculated M 303.9770.

Formation of perfluoro-4-methylisochromenium (IV) salt from perfluoro-3-methylindan-1-one (III). A solution of 0.12 g (0.37 mmol) of compound **III**

(prepared in [7]) in 0.96 g (4.43 mmol) of SbF₅ was heated at 70–75°C in an NMR tube for 13 h, then 0.27 g of SO₂ClF was added, and the ¹⁹F NMR spectrum was registered. According to the spectrum the solution contained the salt of cation **IV** and a small quantity of ketone **III**. Then the content of the tube was worked up as described in the previous experiment. We obtained 0.07 g of a mixture containing according to the ¹⁹F NMR spectrum 85% (yield 54%) of compound **V** and 15% of ketone **III**.

¹⁹F NMR spectrum of perfluoro-4-methylisochromenium salt (SbF₅–SO₂ClF), δ , ppm: 26.8 (1F, F⁷), 39.3 (1F, F⁵), 52.2 (1F, F⁸), 64.2 (1F, F⁶), 99.6 (1F, F³), 108.0 (3F, CF₃⁴), 149.0 (1F, F¹); $J_{1,3}$ 10, $J_{1,5}$ 4, $J_{1,6}$ 10, $J_{1,8}$ 88, $J_{3,4}$ 37, $J_{3,5}$ 6, $J_{3,6}$ 4, $J_{3,7}$ 6, $J_{4,5}$ 44, $J_{5,6}$ 17, $J_{5,7}$ 11, $J_{5,8}$ 12, $J_{6,7}$ 20, $J_{6,8}$ 31, $J_{7,8}$ 18 Hz.

Reaction of perfluoro-1-methylindan (I) with SiO₂-SbF₅. *a.* A mixture of 0.37 g (1.06 mmol) of compound **I**, 0.04 g (0.67 mmol) of SiO₂ (silica gel calcined at 400–450°C) and 0.70 g (3.23 mmol) of SbF₅ was stirred at 70°C for 3 h, and treated with 5% aqueous HCl. The product was extracted into CH₂Cl₂, the extract was dried over MgSO₄, and the solvent was distilled off in a vacuum to obtain 0.33 g of a mixture containing according to the ¹⁹F NMR spectrum 61% (yield 59%) of ketone **III**, 19% (yield 18%) of compound **V**, 10% (yield 10%) of **6-(1-carboxy-2,2,2-trifluoroethyl)-2,3,4,5-tetrafluorobenzoic acid (VI)**, and 10% (yield 9%) of unreacted compound **I**.

b. A mixture of 0.43 g (1.24 mmol) of compound **I**, 0.11 g (1.83 mmol) of SiO₂, and 1.34 g (6.18 mmol) of SbF₅ was stirred at 70–75°C for 9.5 h, and treated with 5% aqueous HCl. The reaction mixture was first extracted with CHCl₃, then with ether, and the extracts were dried with MgSO₄. On removing the solvent in a vacuum we obtained from the chloroform extract 0.09 g of a mixture containing according to the ¹⁹F NMR spectrum 76% (yield 18%) of compound **V** and 24% (yield 6%) of ketone **III**. From the ether extract on removing the solvent and after sublimation (170–180°C, 2 mm Hg) 0.18 g of mixture was obtained containing according to the ¹⁹F NMR spectrum 5% (yield 3%) of acid **VI** and 95% (yield 54%) of **6-(carboxymethyl)-2,3,4,5-tetrafluorobenzoic acid (VII)**. By recrystallization of the mixture from benzene–ether 0.12 g of compound **VII** was isolated, mp 194–196°C. IR spectrum (KBr), ν , cm⁻¹: 1724, 1691 (C=O), 1524, 1483 (fluorinated aromatic ring). ¹H NMR spectrum [(CD₃)₂CO], δ , ppm: 3.96 d [2H, CH₂, J (CH₂, F⁵) 2 Hz], 9.61 br.s (2H, OH). ¹⁹F NMR

spectrum $[(\text{CD}_3)_2\text{CO}]$, δ , ppm: 6.0 (1F, F³), 9.8 (1F, F⁴), 22.5 (1F, F⁵), 24.8 (1F, F²); $J_{2,3}$ 21, $J_{2,4}$ 6, $J_{2,5}$ 12, $J_{3,4}$ 20, $J_{3,5}$ 3, $J_{4,5}$ 21 Hz, $J(\text{F}^5, \text{CH}_2)$ 2 Hz. Found $[M]^+$ 252.0047. $\text{C}_9\text{H}_4\text{F}_4\text{O}_4$. Calculated M 252.0046.

Behavior of cation IV salt in a system SiO_2 – SbF_5 .

A mixture of 0.38 g (1.17 mmol) of compound III and 1.43 g (6.60 mmol) of SbF_5 was heated at 80°C for 7 h, then 0.04 g (0.67 mmol) of SiO_2 was added, and the mixture was stirred at 70–75°C for 7 h. The mixture obtained was treated with 5% aqueous HCl, extracted first with CHCl_3 , then with ether, and the extracts were dried with MgSO_4 . On removing the solvent in a vacuum and sublimation (100°C, 10 mm Hg) we obtained from the chloroform extract 0.18 g (51%) of compound V. From the ether extract on removing the solvent and after sublimation (170–180°C, 2 mm Hg) 0.06 g of mixture was obtained containing according to the ^{19}F NMR spectrum 11% (yield 2%) of acid VI, 75% (yield 15%) of acid VII, and 14% (yield 3%) of tetrafluorophthalic acid.

Hydrolysis of perfluoro-4-methylisochromen-1-one (V). *a.* To a solution of 0.18 g (0.59 mmol) of compound V in 2 ml of ether was added 1.5 ml 10% aqueous HCl, and the mixture was stirred at 18°C for 4 days. The ether layer was separated, dried with MgSO_4 , and the solvent was distilled off in a vacuum to give 0.18 g (95%) of acid VI. Analytical sample of compound VI was obtained by recrystallization first from a mixture benzene–ether, then from water, mp 170–174°C (decomp.). IR spectrum (KBr), ν , cm^{-1} : 1741, 1718, 1695 (C=O), 1530, 1486 (fluorinated aromatic ring). ^1H NMR spectrum $[(\text{CD}_3)_2\text{CO}]$, δ , ppm: 5.61 q [1H, CH, $J(\text{CH}, \text{CF}_3)$ 9 Hz], 9.31 br.s (2H, OH). ^{19}F NMR spectrum $[(\text{CD}_3)_2\text{CO}]$, δ , ppm: 10.7 (1F, F³), 11.6 (1F, F⁴), 26.9 (1F, F²), 28.3 (1F, F⁵), 98.5 (3F, CF₃); $J_{2,3}$ 21, $J_{2,4}$ 6, $J_{2,5}$ 11, $J_{3,4}$ 20, $J_{3,5}$ 6, $J_{4,5}$ 20 Hz, $J(\text{F}^5, \text{CF}_3)$ 14, $J(\text{CF}_3, \text{CH})$ 9 Hz. Found $[M]^+$ 319.9925. $\text{C}_{10}\text{H}_3\text{F}_7\text{O}_4$. Calculated M 319.9920.

b. To a mixture of 0.06 g (0.20 mmol) of compound V, 0.15 g (1.06 mmol) of K_2CO_3 , and 2.5 ml of water 5 drops of ether were added, and the mixture was stirred at 20°C for 18 h. The solution obtained was acidified with HCl, extracted with ether, the extract was dried over MgSO_4 . On removing the solvent in a vacuum 0.05 g of mixture

was obtained containing according to the ^{19}F NMR spectrum 27% (yield 25%) of acid VI and 73% (yield 68%) of acid VII.

c. In the same way as in the previous run (*b*) from 0.06 g (0.19 mmol) of compound VI, 0.15 g (1.06 mmol) of K_2CO_3 , and 2 ml of water at 20°C in 19 h we obtained 0.05 g of mixture containing according to the ^{19}F NMR spectrum 81% of acid VI and 19% (yield 16%) of acid VII.

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