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Reaction of Perfluorobenzocycloalkenes with SiO_2–SbF_5 and Skeleton Transformations of Their Carbonyl Derivatives in SbF_5 Medium

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Abstract—The reaction of perfluorinated benzocyclobutene and tetraline with SiO_2–SbF_5 led to the formation in a high yield of their mono- and further dicarbonyl derivatives. The monocarbonyl derivatives on heating with SbF_5 underwent disproportionation into the corresponding perfluorobenzocycloalkenes and diketones. Both mono- and diketones in the SbF_5 medium are liable to suffer skeleton rearrangements yielding five- and six-membered oxygen-containing heterocycles and/or products of the opening of the alicyclic fragment of the substrate, and from the perfluorobenzocyclobutenone compounds were also obtained with a number of carbon atoms greater than that of the initial ketone.

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We recently found that the reaction of perfluoroindan (**I**) with SiO_2–SbF_5 cleanly led to perfluoroindan- 1-one (**II**). Therewith ketone **II** and perfluoroindan-1,3-dione **III** were shown to be able to suffer skeleton rearrangements effected by antimony pentafluoride [1]. Similar reactions were unknown for the other perfluorobenzocycloalkenes and their carbonyl derivatives**.**

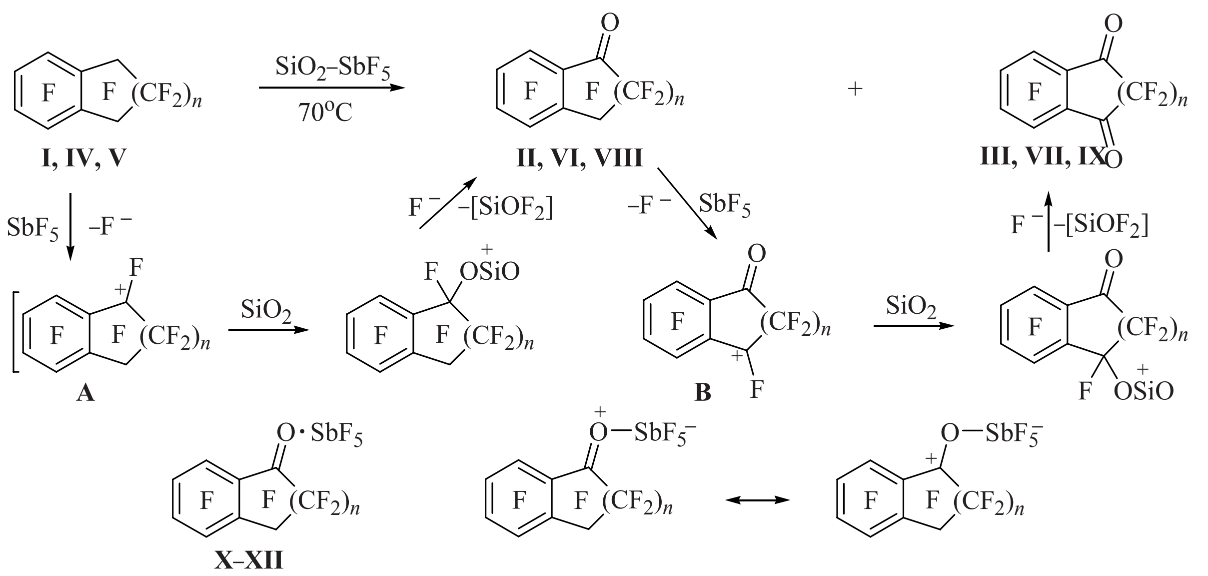
Aiming at establishing the general rules of such transformations of perfluorobenzocycloalkenes and their carbonyl derivatives and also at revealing the effect of the size of the alicyclic fragment in the substrate on the course of the process we investigated the reactions of perfluorobenzocyclobutene (**IV**) and perfluoro tetralin (**V**) with SiO_2–SbF_5 and ascertained the relative reactivity in this process of benzocycloalkenes **I**, **IV**, and **V**. Besides we studied the behavior of perfluorinated benzocyclobutenone (**VI**), benzocyclobutenedione (**VII**), tetralin-1-one (**VIII**), and tetralin-1,4-dione (**IX**) in SbF_5 medium.

It was shown that in reaction of compounds **I** [1], **IV**, and **V** with SiO_2 in SbF_5 medium (molar ratio benzocycloalkene:SiO_2:SbF_5 = 1:0.9:1.5) at 70°C formed predominantly ketones **II**, **VI**, and **VIII** alongside a small amount of diketones **III**, **VII**, and **IX** respectively (Scheme 1). The formation of compounds **II, III, VI**–**IX** can evidently be represented by a scheme involving the reaction of primarily generated perfluorobenzocycloalken-1-yl **A** and perfluorobenzocycloalkenon-1-yl **B** cations with SiO_2 (Scheme 1).

The considerable prevalence among the reaction products of benzocycloalkenes **I, IV**, and **V** with SiO_2–SbF_5 of their monocarbonyl derivatives **II**, **VI**, and **VIII** compared to diketones **III, VII**, and **IX** may be due to the fact that ketones **II**, **VI**, and **VIII** form with antimony pentafluoride complexes **X** [1], **XI**, and **XII** (Scheme 1). As a result the reaction of compounds **II**, **VI**, and **VIII** should occur with greater difficulty than the reaction of the corresponding benzocycloalkenes **I, IV**, and **V**. Besides the complexing reduces the amount of “free” SbF_5 that should also decelerate the reaction.

The application of the concurrent reactions method revealed that the reactivity of the perfluorinated benzocycloalkenes toward SiO_2–SbF_5 depended on the size of the alicyclic fragment of the substrate and decreased in going from benzocyclobutene **IV** to indan **I** and tetralin **V**. This sequence is consistent with the series of the decreasing relative stability of the corresponding perfluorobenzocycloalken-1-yl cations **A** [2].

Scheme 1.



n = 0 (**IV, VI, VII, XI**), 1 (**I–III, X**), 2 (**V, VIII, IX, XII**).

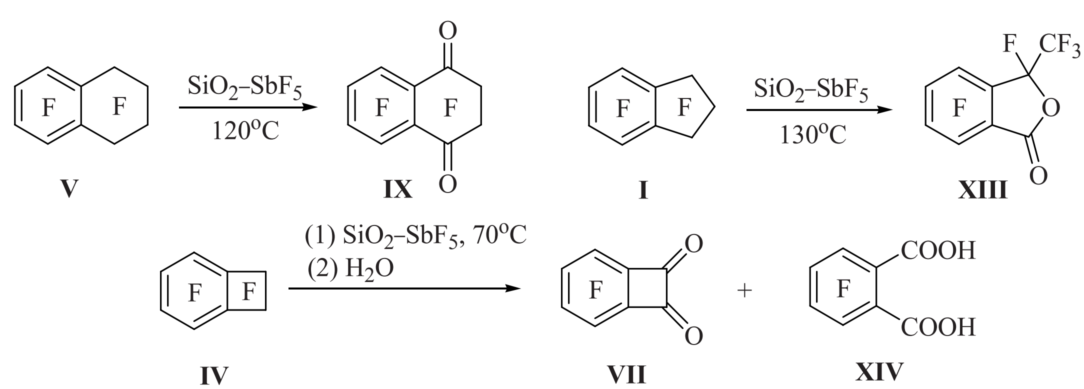
In the reaction of compound **V** with excess SiO_2–SbF_5 at 120°C the only reaction product was diketone **IX** (Scheme 2). Indan **I** under these conditions yielded perfluoro-3-methylphthalide (**XIII**) [1]. The reaction of benzocyclobutene **IV** with excess SiO_2–SbF_5 readily proceeded even at 70°C to give on hydrolysis of the reaction mixture compound **VII** alongside with a small amount of tetrafluorophthalic acid **XIV** (Scheme 2).

Acid **XIV** formed in the reaction of compound **IV** with SiO_2–SbF_5 evidently is the product of diketone **VII** conversion under the action of SbF_5. Actually, a special experiment showed that the treatment of compound **VII** with antimony pentafluoride at 130°C followed by hydrolysis gave acid **XIV** (Scheme 3).

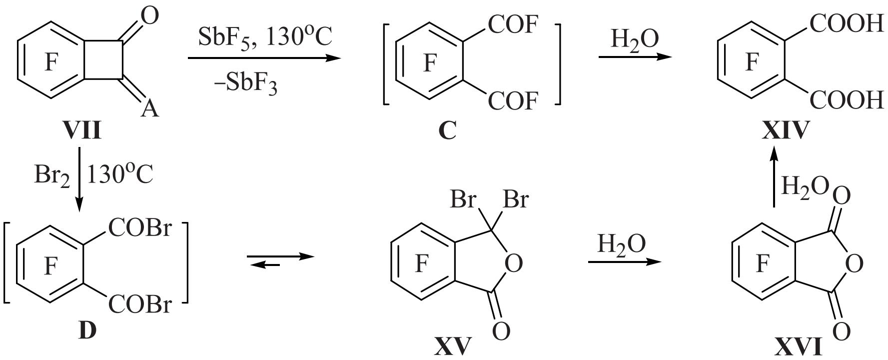
The transformation of compound **VII** into acid **XIV** evidently occurred through a stage of cleavage of the C(O)–C(O) bond in diketone **VII** effected by the antimony pentafluoride with the formation of acid difluoride **C**. The hydrolysis of the latter yielded acid **XIV** (Scheme 3). The cleavage of the four-membered ring of compound **VII** occurred also at its heating with bromine at 130°C. As a result diketone **VII** turned into 3,3-dibromo-4,5,6,7-tetrafluorophthalide (**XV**). This compound is a tautomer of acid dibromide **D** and on hydrolysis gives tetrafluorophthalic anhydride (**XVI**) and acid **XIV** (Scheme 3).

The five-membered ring of indanone **II** under treatment with SbF_5 at 130°C suffered the opening with the formation of 6-pentafluoroethyl-2,3,4,5-tetrafluoro-benzoic acid (**XVII**). Concurrent with the latter process compound **II** underwent disproportionation into perfluoroindan (**I**) and diketone **III** that under the

Scheme 2.



Scheme 3.



reaction conditions was converted into phthalide **XIII** [1].

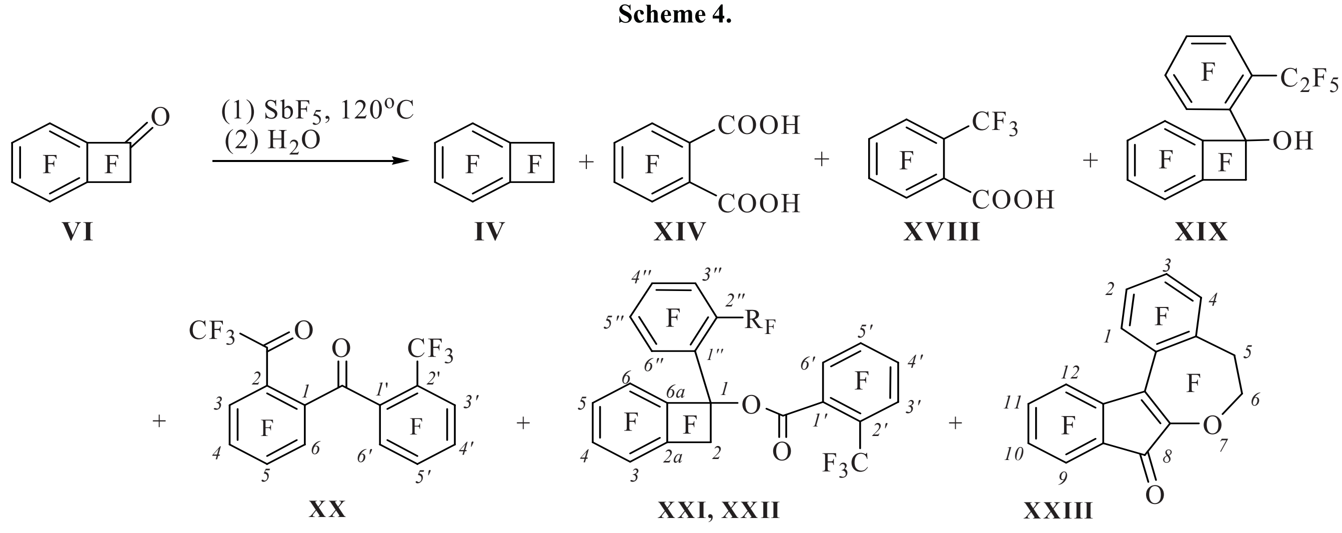
After heating ketone **VI** in the medium of SbF_5 at 120°C the hydrolysis of the reaction mixture led to the formation of compounds **IV** and **XIV** alongside with 6-trifluoromethyl-2,3,4,5-tetrafluorobenzoic acid (**XVIII**). The reaction mixture contained also perfluorinated hydroxy-1-(2-ethylphenyl)benzocyclobutene (**XIX**), 2-acetyl-2'-methylbenzophenone (**XX**), [1-(2-methyl-phenyl)benzocyclobuten-1-yl]-2-methylbenzo-ate (**XXI**), [1-(2-ethylphenyl)benzocyclobuten-1-yl]-2-methylbenzo-ate (**XXII**), and unreacted compound **VI** (Scheme 4). Besides in the reaction a small amount was obtained of 5,6-dihydro-7-oxadibenzo[*a*,*h*]azulen-8-one (**XXIII**) that contained by one carbon more than two molecules of initial compound **VI**.

The formation of reaction products **IV** and **XIV** may be ascribed to the dispropotionation of ketone **VI** into compound **IV** and diketone **VII** that as already mentioned yields acid **XIV**. The likely disproportionation route of ketones **II, VI**, and **VIII** into the corresponding perfluoro-benzocycloalkene and diketone is presented in Scheme 5.

It is presumable that acid **XVIII** forms in the reaction of ketone **VI** with SbF_5 through the rupture of the C(O)–CF_2 bond in ketone **VI** under the action of the antimony pentafluoride similarly to the conversion of compound **VII** into acid **XIV** (Scheme 3). It was however demonstrated that ketone **VI** in contrast to diketone **VII** did not react with bromine at 130°C. Therefore it cannot be excluded that the formation of acid **XVIII** in the reaction of ketone **VI** with SbF_5 results from the transformation of products generated by the opening of the four-membered ring of compound **VII** under the reaction conditions (Scheme 6).

Thus, first arising acid difluoride **C** can exist in a tauto-meric form **E** [3]. The replacement in the latter of a carbonyl by a difluoromethylene group under the action,

Scheme 4.



$R_F = CF_3$ (**XXI**), C_2F_5 (**XXII**).

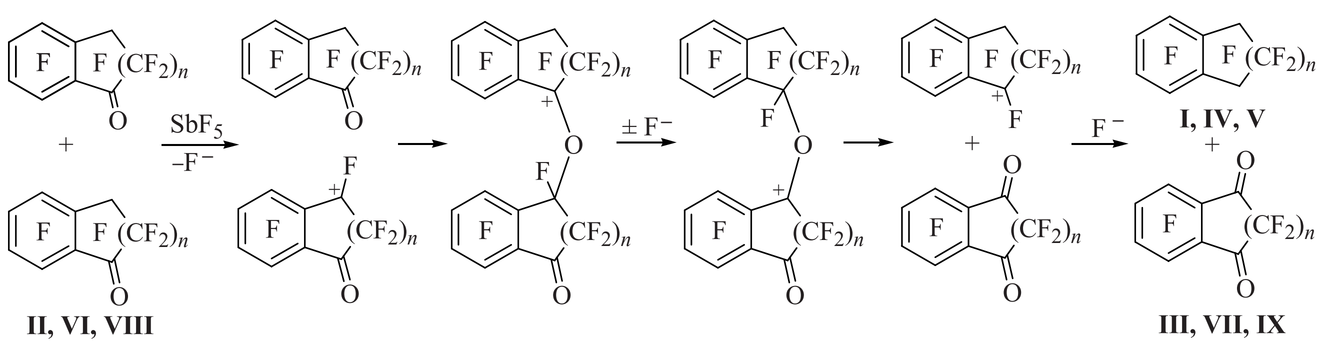
for instance, of initial ketone **VI** or/and the formed compound **IV** results in perfluorophthalane **XXIV**. The latter transformation involving oxygen transfer from one perfluorinated compound to another is essentially similar to the disproportionation process of ketones **II, VI**, and **VIII** (Scheme 5). Further compound **XXIV** under the action of SbF_5 is converted into acid fluoride **F**. Therewith the possibility of formation of the latter by replacement of an oxygen by a fluorine directly in acid difluoride **C** is not excluded. Hydrolysis of acid fluoride **E** provides acid **XVIII** (Scheme 6).

This interpretation does not contradict the fact that on addition to the reaction products of diketone **VII** with SbF_5 of perfluorotoluene as fluorine donor and oxygen acceptor followed by heating the mixture at 130°C the subsequent hydrolysis of the reaction mixture yields a mixture of acids **XIV** and **XVIII**. Besides a special experiment showed that phthalane **XXIV** on dissolution in antimony pentafluoride followed by hydrolysis was converted into acid **XVIII** (Scheme 6).

Compounds **XIX–XXIII** likely formed in the reaction of ketone **VI** with antimony pentafluoride by binding several molecules of compounds **IV** and **VI** followed by skeleton rearrangements in thus obtained products. Some among the probable routes of these transformations are presented in Scheme 7. For instance, the reaction of compound **IV** with cation **G** after the addition–elimination of the fluoride ion provides cation **H** whose hydrolysis leads to the formation of alcohol **XIX** [4, 5]. In the course of hydrolysis of the reaction mixture occurs presumably the reaction of alcohol **XIX** with cation **I** or/and with acid fluoride **F** resulting in ester **XXII**. The route of compound **XXII** formation by reaction of cation **H** with acid **XVIII** obtained by hydrolysis also cannot be ruled out.

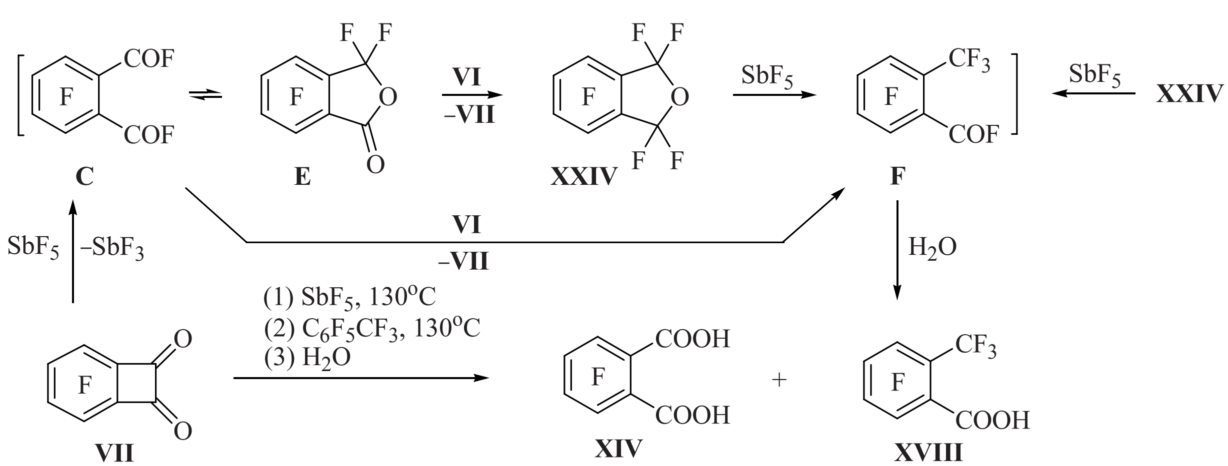
It is presumable that the reaction of ketone **VI** with ion **G** gives cation **J** that undergoes decarbonylation and after the addition–elimination of the fluoride ion provides cation **K**. The latter during the hydrolysis of the reaction mixture transforms into ester **XXI** analogously to the conversion of cation **H** into compound **XXII**.

Scheme 5.



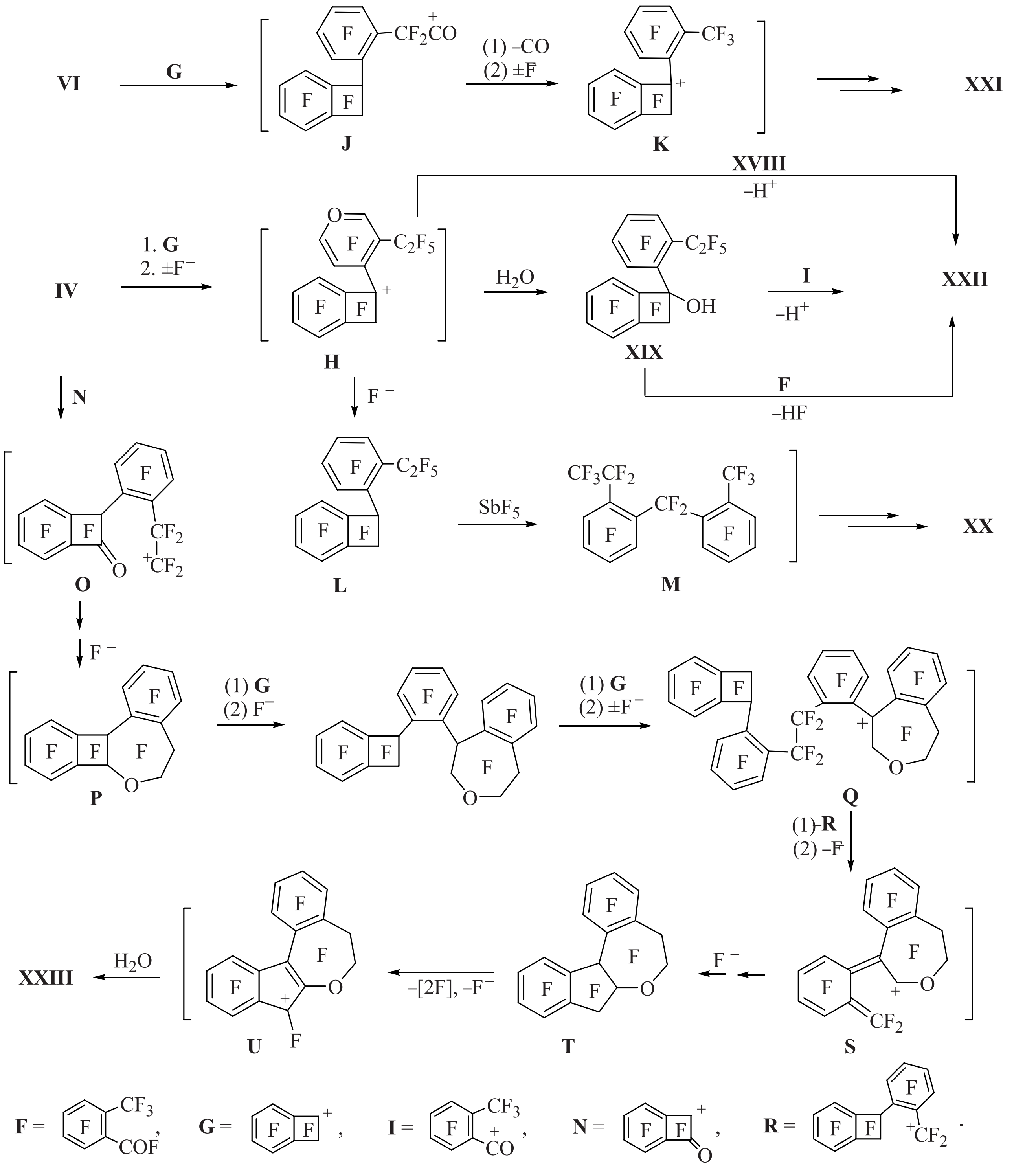
n = 0 (**IV, VI, VII**), 1 (**I–III**), 2 (**V, VIII, IX**).

Scheme 6.



The addition of a fluoride ion to cation **H** gives compound **L** that under the action of SbF_5 suffers the opening of the four-membered ring [4] resulting in diarylmethane **M**. The latter under the reaction conditions transforms into compound **XX**. Besides the transformation of one difluoromethylene group of compound **L** into a carbonyl followed by the conversion of the result-ing product into compound **XX** also cannot be ruled out.

Scheme 7.



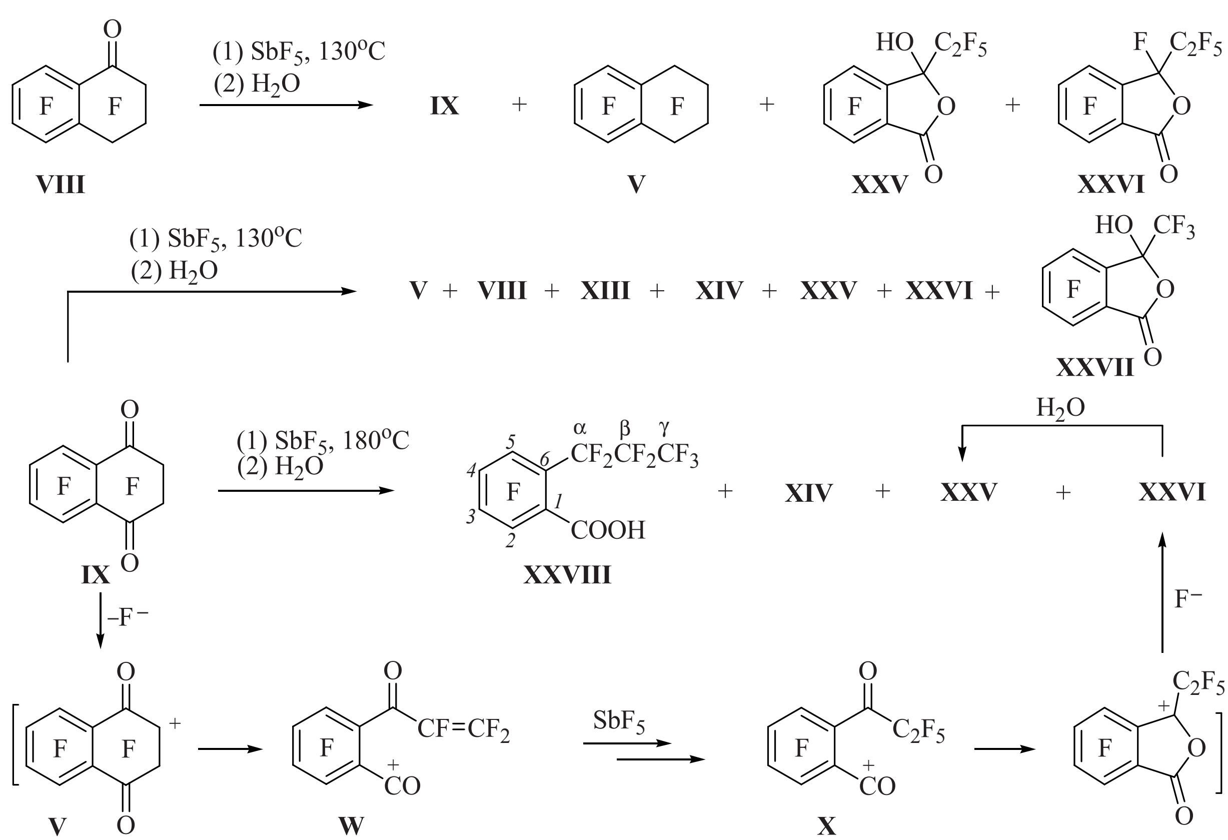
The reaction of benzocyclobutene **IV** with cation **N** gives intermediate **O** that undergoes cyclization into compound **P**. Two consecutive attacks of cation **G** convert compound **P** into ion **Q** that decomposes into cation **R** and a compound being a precursor of cation **S**. The cyclization of ion **S** leads to compound **T** that suffers defluorination by some polyfluorinated compound [6], eliminates a fluoride ion, and forms cation **U**. The hydrolysis of the latter provides compound **XXIII** (Scheme 7).

Tetralone **VIII** at heating with SbF_5 at 130°C disproportionated into a mixture of tetralin **V** and diketone **IX** containing also the initial compound. Besides the mixture contained small amounts of 3-hydroxyperfluoro-3-ethylphthalide (**XXV**) and perfluoro-3-ethylphthalide (**XXVI**) (Scheme 8). Diketone **IX** in its turn under similar conditions yielded not only ethylphthalides **XXV** and **XXVI** but also compounds **V** and **VIII** along with methylphthalide **XIII** and 3-hydroxyperfluoro-3-methylphthalide (**XXVII**). Yet the heating of compound **IX** solution in antimony pentafluoride at 180°C with subsequent hydrolysis of the reaction mixture resulted in a mixture of 6-heptafluoropropyl-2,3,4,5-tetrafluorobenzoic acid (**XXVIII**), phthalides **XXV** and **XXVI**, and acid **XIV** (Scheme 8).

One of the possible routes of diketone **IX** transformations effected by SbF_5 into compounds **XXV** and **XXVI** is presented in Scheme 8. First from compound **IX** cation **V** is generated that suffers ring opening to form ion **W**. The latter after adding a fluoride ion is fluorinated to give a compound from which cation **X** is generated. The intramolecular cyclization of **X** followed by a fluoride ion addition results in phthalide **XXVI** whose hydrolysis leads to the formation of hydroxyphthalide **XXV**. Besides another route to compound **XXVI** should not be ruled out where first cyclization of cation **W** occurs and then the fluorination of the double bond in the product obtained. The formation of acid **XXVIII** in the reaction of compound **IX** with SbF_5 evidently results from the transformations of phthalide **XXVI** by a scheme similar to that of transformation of compound **E** into acid **XVIII** (Scheme 6).

Raising the reaction temperature of tetralone **VIII** with antimony pentafluoride to 180°C results in the formation of a complex mixture containing alongside compounds **V, XVII, XVIII, XXV, XXVI**, and **XXVIII**

Scheme 8.

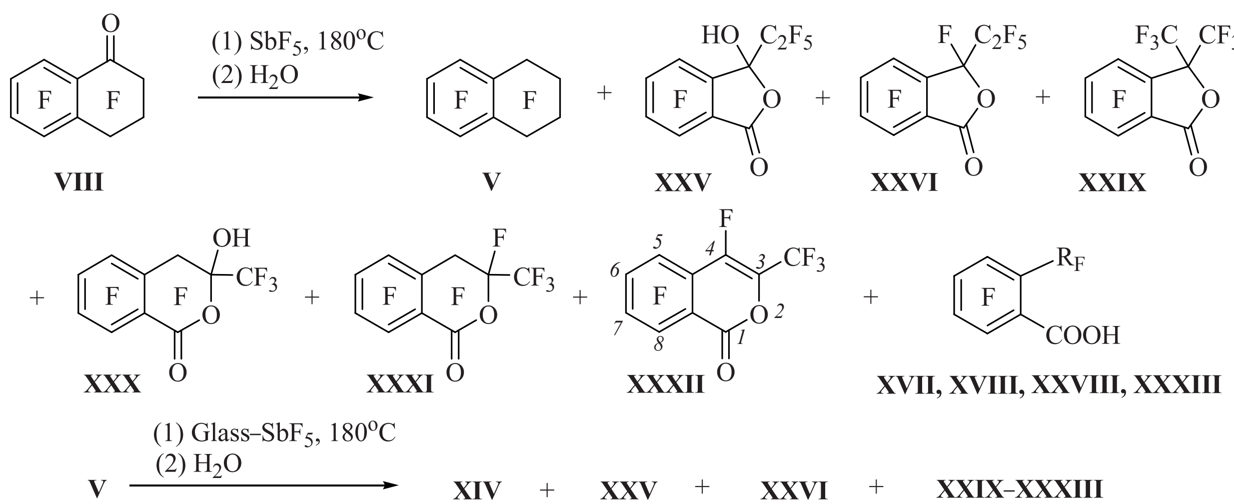


perfluorinated 3,3-dimethylphthalide **XXIX**, 3-hydroxy-3-methyl-3,4-dihydroisochromen-1-one (**XXX**), 3-methyl-3,4-dihydroisochromen-1-one (**XXXI**), 3-methylisochromen-1-one (**XXXII**), and 6-heptafluoroisopropyl-2,3,4,5-tetrafluorobenzoic acid (**XXXIII**) (Scheme 9).

Reaction products **XXIX** and **XXXIII** likely form in reaction of compound **VIII** with SbF_5 as a result of transformation of tetralin **V** under the reaction conditions. These transformations may be described by Scheme 10. First compound **V** under the action of SbF_5 forms perfluoro-2-isopropyltoluene (**XXXIV**) [5] that further reacts with oxygen-containing compounds present in the mixture to give acid fluoride **Y.** The hydrolysis of the latter leads to acid **XXXIII**, and by the action of the antimony pentafluoride cation **Z** is generated from the said acid fluoride. The cyclization and subsequent hydrolysis of cation **Z** results in the formation of phthalide **XXIX**. The possibility of this cyclization to occur is proved by the formation of compound **XXIX** at heating to 180°C of a mixture obtained by reacting isopropyltoluene **XXXIV** with SiO_2–SbF_5 at 70°C (Scheme 10).

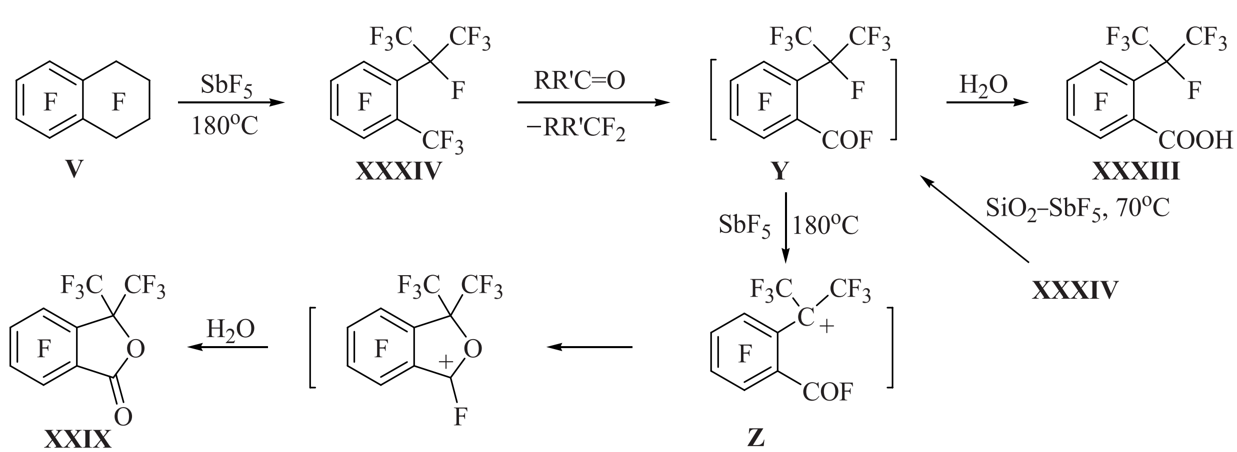
Compounds **XXVIII** and **XXX–XXXII** obtained in the reaction of tetralone **VIII** with antimony pentafluoride are evidently the products of skeleton rearrangements of ketone **VIII** itself and not of its disproportionation products. Some probable pathways of the occurring transformations are presented in Scheme 11. First by the action of SbF_5 cation **Z1** is generated from compound **VIII** where a ring opening takes place leading after addition–elimination of a fluoride ion to cation **Z2**.

Scheme 9.



$R_F = CF_3$ (**XVIII**), CF_2CF_3 (**XVII**), $CF_2CF_2CF_3$ (**XXVIII**), $CF(CF_3)_2$ (**XXXIII**).

Scheme 10.



The latter is an ion of allyl type whose cyclization might occur involving both charge centers. One of cyclization routes results in intermediate **A1** that through the fluorination of the double bond followed by the opening of the five-membered ring and by fluoride ion addition is converted into 6-heptafluoropropyl-2,3,4,5-tetrafluorobenzoyl fluoride (**XXXV**) whose hydrolysis gives acid **XXVIII**. It cannot be ruled out that compound **XXXV** forms also by fluorination of compound **B1**.

The other cyclization pathway of cation **Z2** after addition–elimination of a fluoride ion produces cation **C1** that through the contraction of the seven-membered ring followed by transition of the cation center transforms into tricyclic intermediate **D1**. The opening of the cyclopropane ring in the latter and addition of a fluoride ion to the arising cation results in compound **E1**. Besides it might be that compound **E1** formed by electrocyclic reaction from acid fluoride **B1**. Then compound **E1** in the presence of antimony pentafluoride serves as a source for generating cation **F1** whose hydrolysis yields compound **XXXII**. Moreover, compound **E1** can undergo fluorination giving reaction product **G1**. The latter eliminating a fluoride ion provides cation **H1** that converts on hydrolysis into compound **XXXI**. The formation of compound **G1** by alternative route, cyclization of acid fluoride **XXXV**, is hardly possible for the heating of the latter with antimony pentafluoride at 180°C with the subsequent hydrolysis of the reaction mixture does not lead to the formation of compounds **XXX** and **XXXI**.

A special experiment demonstrated that the hydrolysis of compound **XXXI** in acid medium provided compound **XXX**. Compound **XXXII** practically did not change under these conditions, whereas under the treatment with a water solution of $NaHCO_3$ it was converted into 3-hydroxy-3-trifluoromethyl-4,5,6,7,8-pentafluoro-3,4-dihydroisochromen-1-one **XXXVI** (Scheme 11).

We formerly showed that perfluoroindan (**I**) in the presence of SbF_5 reacted with glass as a source of inorganic oxides giving ketone **II** that under the reaction conditions suffered further transformations; therewith a ratio of reaction products differed considerably from that obtained by heating individual compound **II** with SbF_5 [1].

In this connection we studied the reaction of tetralin **V** with glass in the presence of antimony pentafluoride. For instance, the heating of tetralin **V** with SbF_5 in a glass ampule at 180°C followed by the hydrolysis of the reaction mixture provided a mixture containing prevailingly compounds **XIV, XXV**, and **XXVI** along with small amounts of compounds **XXIX–XXXIII** (Scheme 9).

The composition and structure of new compounds were established from elemental analysis and spectral characteristics. Besides compound **XXIII** was subjected to X-ray diffraction analysis on a single crystal, and the refining of the structure resulted in a high value of the factor R_1 (0.15). The data obtained made it possible to unambiguously establish the molecular structure (see the figure), but its detailed discussion is superfluous because of large inaccuracy. Note however that the molecule is essentially nonplanar, and the angle between the planes of the indenyl and benzene fragments equals 47.6(3)° for both molecules contained in the independent part of the cell.

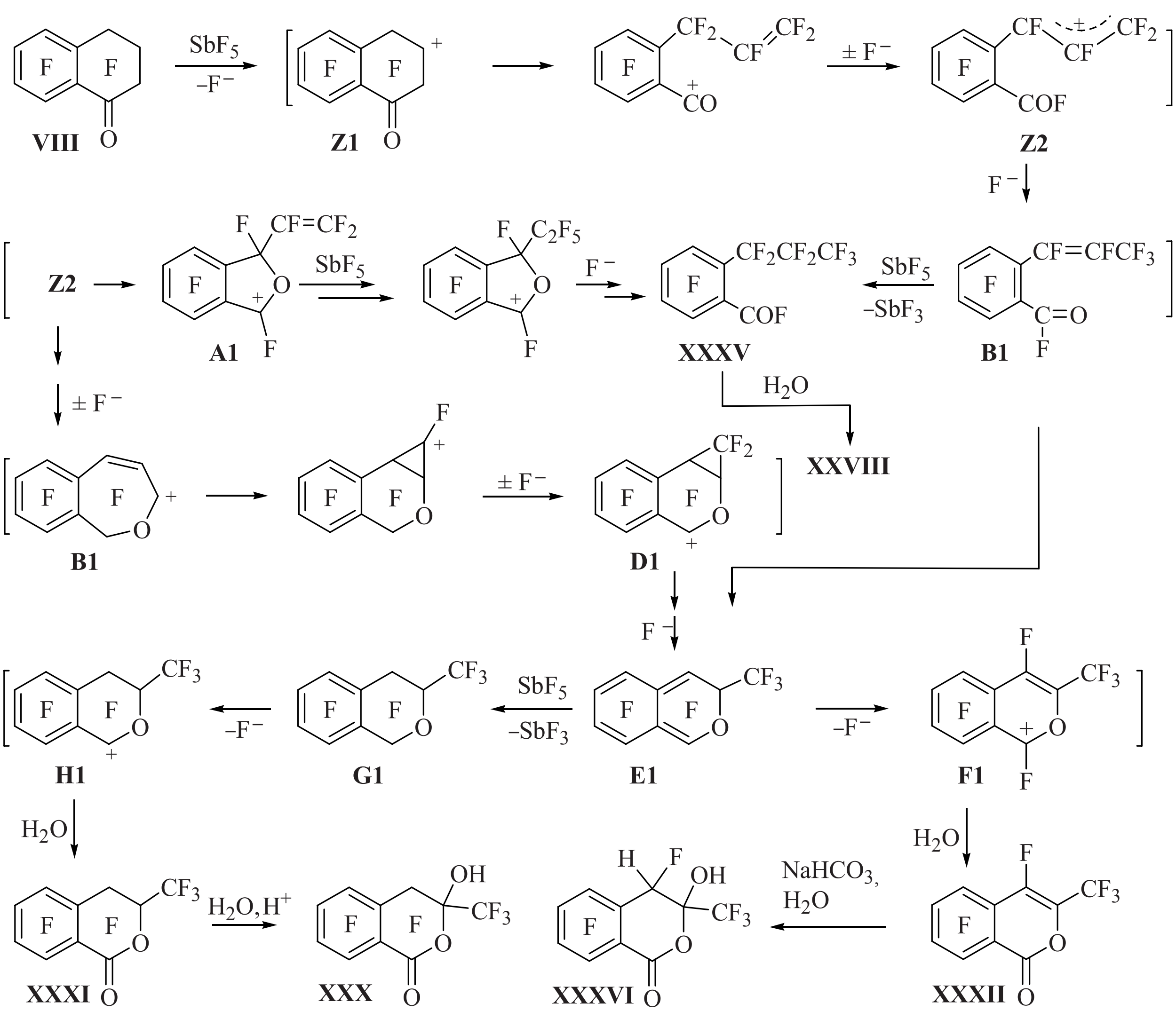
The assignment of signals in the ^{19}F NMR spectra of compounds was performed based on the values of the chemical shifts of the signals, their fine structure and integral intensity. The assignment of signals for complexes **XI** and **XII** (poorly resolved signals) was done by analogy with complex **X** [1] and 1-hydroxyperfluorobenzocycloalken-1-yl cations [3].

The coupling constants $J_{A,B}$ 199 and $J_{3,6}$ 23 Hz characteristic of polyfluorobenzocyclobutenes [4] belonging to the fluorine atoms of the CF_2^2 group and to fluorine atoms in the *para*-position with respect to each other observed in the ^{19}F NMR spectrum of compounds **XXI** and **XXII** indicate the presence in their structure of a polyfluorobenzocyclobutene moiety. The ^{19}F NMR spectrum of compound **XXIII** contained large coupling constants $J_{1,12}$ 46 and $J_{4,5B}$ 95 Hz ($J_{4,5A}$ < 5 Hz) due to the spatial proximity of the coupled nuclei [7]. According to the X-ray diffraction study the corresponding distances are: F^1–F^{12} 2.64(1), F^4–F^{5B} 2.46(1), F^4–F^{5A} 3.92(1) E.

Compounds **XXV, XXX**, and **XXXVI** can formally exist as 6-(pentafluoropropanoyl)-2,3,4,5-tetrafluorobenzoic (**XXXVII**), 6-(2-oxopentafluoropropyl)-2,3,4,5-benzoic (**XXXVIII**), and 6-(2-oxo-1,3,3,3-tetrafluoropropyl)-2,3,4,5-tetra-fluorobenzoic (**XXXIX**) acids respectively (Scheme 12).

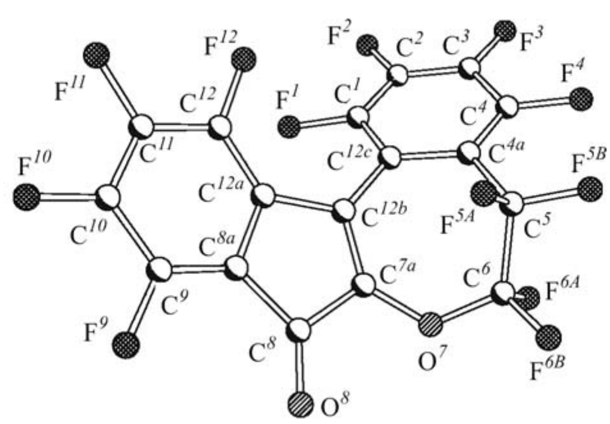
The existence of compounds **XXV** and **XXX** in $CDCl_3$ solution in the cyclic form is confirmed by the presence in their ^1H NMR spectra of signals at 4.82 and 5.19 ppm (OH) respectively, and also the nonequivalence of the fluorine atoms of the CF_2 groups in the ^{19}F NMR spectra. In contrast to phthalide **XXV** compound **XXX** in ether solution is present both in the cyclic form **XXX** and as acid **XXXVIII** in a ratio 45:55. In the ^1H and ^{19}F NMR

Scheme 11.



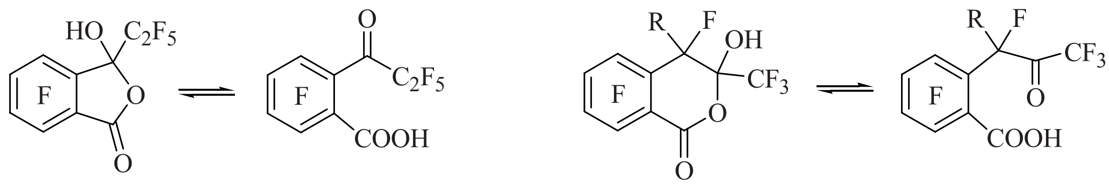
spectra of compound **XXXVI** solution in $CDCl_3$ two sets of signals are observed with close values of the chemical shifts belonging to two spatial isomers of the cyclic form **XXXVI** in a ratio 94:6. At the same time in the ^{19}F NMR spectrum of the ether solution of compound **XXXVI** also two groups of signals are present but with essentially different chemical shifts. Consequently, in the ether solution compound **XXXVI** exists as an equilibrium mixture of one cyclic isomer **XXXVI** and acid **XXXIX** in a ratio 80:20.

Compounds **IV–VIII**, **XIII**, **XIV**, **XVI–XIX**, **XXVII**, and **XXXIII** were identified by comparison of their ^{19}F NMR spectra with those of the corresponding authentic samples.



Structure of one of the two crystallographically independent molecules of perfluoro-5,6-dihydro-7-oxadibenzo[*a*,*h*]azulen-8-one (**XXIII**).

Scheme 12.



XXV XXXVII XXX, XXXVI XXXVIII, XXXIX

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Bruker Vector 22. UV spectra were measured on a spectrophotometer Hewlett Packard 8453. ^1H and ^{19}F NMR spectra were registered on spectrometers Bruker AC-200 and Bruker WP-200 SY (200 and 188.3 MHz respectively), ^{13}C NMR spectrum of the mixture of compounds **XXI** and **XXII** was taken on Bruker AV-300 instrument (75.5 MHz). As internal references served HMDS (0.04 ppm from TMS), $CHCl_3$ (7.24 ppm from TMS), C_6F_6, SO_2ClF (262.8 ppm from C_6F_6), $CDCl_3$ (76.9 ppm from TMS). Elemental composition of compounds was established by means of high resolution mass spectrometry on Finnigan MAT 8200 instrument. GLC analysis was performed on a chromatograph LKhM-72 (50–270°C, column 4000×4 mm, stationary phase BC-1, SKTF-50 or E-301 on Chromosorb W, 15:100, carrier gas helium, 60 ml/min). GC-MS analysis was carried out on a Hewlett-Packard G1081A instrument equipped with a gas chromatograph HP 5890 of II series and a mass-selective detector HP 5971 (electron impact, 70 eV), capillary column HP 5 (5% diphenyl, 95% dimethylsiloxane) 30 m×0.25 mm×0.25 µm, carrier gas helium, 1 ml/min.

X-ray diffraction analysis was performed with the use of diffractometer Bruker P4 [graphite monochromator, $\lambda(MoK_\alpha)$ 0.71073 E, θ/2θ-scanning, $2\theta < 50°$]. Single crystals of compound **XXIII** were grown by slow evaporation of the solvent from its solutions in a mixture hexane–CH_2Cl_2. Crystallographic data of compound **XXIII**: crystals triclinic, space group *P*-1, *a* 6.343(4), *b* 8.582(5), *c* 28.215(16) E, α 92.01(5), β 91.12(5), γ 94.62(5)°, *V* 1530(2) E^3, $C_{17}F_{12}O_2$, *Z* 4, d_{calc} 2.016 g/cm^3, µ 0.230 cm^{-1}. The extinction was accounted for using experimental curves of azimuthal scanning (T_{min}/T_{max} 0.45/0.79). The structure was solved by the direct method. The positions and temperature factors of the atoms were refined in an anisotropic approximation by full-matrix least-mean-square procedure. Refinement parameters: wR_2 0.4698, *S* 2.593 (for all 5360 reflections), R_1 0.1489 [for 4096 reflections with $I \geq 2\sigma(I)$]. All calculations were carried out with the use of SHELX software. It should be noted that the crystals were of poor quality (peaks width 2–4°), probably, because of tendency to twinning up to the formation of pseudomonoclinic crystal system. In the crystal under study the twinning contribution was 5.7%.

Reaction of perfluorobenzocyclobutene (IV) with SiO_2–SbF_5. *a*. A mixture of 1.91 g (7.7 mmol) of compound **IV**, 0.41 g (6.82 mmol) of SiO_2 (silica gel calcined at 400–450°C), and 2.51 g (11.58 mmol) of SbF_5 was stirred for 5 h at 70°C, then treated with 5% HCl, extracted with CH_2Cl_2, the extract was dried with $MgSO_4$, and the solvent was distilled off in a vacuum. We obtained 1.53 g of a mixture containing according to ^{19}F NMR spectrum and GLC 86% of ketone **VI** (yield 76%), 9% of diketone **VII** (yield 8%), and 5% of unreacted compound **IV**.

b. Analogously to the previous run from 2 g (8.06 mmol) of compound **IV**, 0.27 g (4.49 mmol) of SiO_2, and 3.5 g (16.14 mmol) of SbF_5 (70°C, 6.5 h) we obtained 1.6 g of a mixture containing according to ^{19}F NMR spectrum compounds **VI** and **VII** in a ratio 80:20, yields 72 and 18% respectively.

c. A mixture of 2.13 g (8.59 mmol) of compound **IV**, 0.77 g (12.81 mmol) of SiO_2, and 5.58 g (25.74 mmol) of SbF_5 was stirred for 5 h at 70°C, then treated with 5% HCl, extracted with CH_2Cl_2, then with ether, and the extracts were dried with $MgSO_4$. On distilling off in a vacuum the solvent from the dichloromethane extract we obtained 1.51 g (86%) of diketone **VII**, and on removing solvent from the ether extract we obtained after sublimation at 150°C (2 mm Hg) 0.14 g (7%) of acid **XIV**.

Reaction of perfluorotetralin (V) with SiO_2–SbF_5. *a*. Analogously to the experiment *a* with compound **IV** from 1.18 g (3.39 mmol) of compound **V**, 0.18 g (3 mmol) of SiO_2, and 1.1 g (5.07 mmol) of SbF_5 (70°C, 4 h) we obtained 0.96 g of a mixture containing according to ^{19}F NMR spectrum and GLC 87% of ketone **VIII** (yield

76%), 9% of diketone **IX** (yield 8%), and 4% of unreacted compound **V**.

b. Analogously to the experiment *a* with compound **IV** from 1.48 g (4.25 mmol) of compound **V**, 0.19 g (3.16 mmol) of SiO_2, and 1.85 g (8.53 mmol) of SbF_5 (70°C, 4.5 h) we obtained 1.11 g of a mixture containing according to ^{19}F NMR spectrum and GLC 89% of ketone **VII** (yield 71%), 5% of compound **IX** (yield 4%), and 6% of initial tetralin **V**.

c. A mixture of 1.28 g (3.68 mmol) of compound **V**, 0.24 g (4 mmol) of SiO_2, and 3.18 g (14.67 mmol) of SbF_5 was stirred for 3.5 h gradually raising the temperature from 75 to 120°C, then the reaction mixture was treated with 5% HCl, extracted with ether, and the solvent was removed in a vacuum. The residue was dissolved in CH_2Cl_2, dried on $MgSO_4$, and placed on a watch glass. We obtained 0.92 g (82%) of tetralinedione **IX**, the sample for analysis was prepared by sublimation at 60°C (20 mm Hg), mp 86–87°C. UV spectrum (hexane), λ_{max}, nm (log ε): 228 (4.32), 254 (3.94), 263 (3.94), 308 (3.50), 318 (3.51). IR spectrum (CCl_4), ν, cm^{-1}: 1748 (C=O), 1513, 1482 (fluorinated aromatic ring). ^{19}F NMR spectrum (CH_2Cl_2), δ, ppm: 36.5 s (4F, $2CF_2$), 31.2 m (2F, $F^{5,8}$), 24.6 m (2F, $F^{6,7}$). Found $[M]^+$ 303.9769. $C_{10}F_8O_2$. Calculated *M* 303.9771.

Concurrent reactions of perfluorinated benzocyclobutene IV, indan I, and tetralin V with SiO_2–SbF_5. *a*. A mixture of 0.65 g (2.18 mmol) of indan **I**, 0.54 g (2.18 mmol) of compound **IV**, 0.04 g (0.67 mmol) of SiO_2, and 1.5 g (6.91 mmol) of SbF_5 was stirred for 5 h at 70°C, then treated with 5% HCl, extracted with CH_2Cl_2, the extract was dried with $MgSO_4$, and the solvent was distilled off in a vacuum. We obtained 1.53 g (83%) of a mixture containing according to ^{19}F NMR spectrum compounds **I, II, IV**, and **VI** in a ratio 51:2:15:32.

b. Similarly to the previous run from 0.59 (1.98 mmol) of indan **I**, 0.69 g (1.98 mmol) of tetralin **V**, 0.04 (0.67 mmol) of SiO_2, and 1.73 g (7.98 mmol) of SbF_5 (70°C, 6 h) we obtained 1.06 g (85%) of a mixture containing according to ^{19}F NMR spectrum compounds **I, II, V**, and **VIII** in a ratio 12:37:47:4.

Reaction of perfluorobenzocyclobutenedione (VII) with SbF_5. *a*. A solution of 1.04 g (5.1 mmol) of compound **VII** in 3.32 g (15.31 mmol) of SbF_5 was heated for 4.5 h at 130°C, then the reaction mixture was treated with 5% HCl, extracted with ether, the extract was dried with $MgSO_4$, transferred to a watch glass, the solvent was evaporated, and the residue was sublimed at 150°C (2 mm Hg). We obtained 0.85 g (70%) of acid **XIV**.

b. A solution of 0.17 g (0.83 mmol) of compound **VII** in 4.22 g (19.37 mmol) of SbF_5 was heated for 4.5 h at 130°C, then 1 g (4.24 mmol) of perfluorotoluene was added, and the mixture was again heated for 9 h at 130°C. The mixture was treated with 5% HCl, extracted with ether, the extract was dried with $MgSO_4$. We obtained a solution containing according to ^{19}F NMR spectrum compounds **XIV** and **XVIII** in a ratio 85:15 along with perfluorinated toluene and benzoic acid. The solution was transferred to a watch glass, the solvent was evaporated, the crystalline residue was sublimed at 120°C (2 mm Hg). We obtained 0.44 g of a mixture containing according to ^{19}F NMR spectrum 28% of acid **XIV** (yield 66%), 5% of compound **XVIII** (yield 12%), and 67% of pentafluorobenzoic acid.

Reaction of perfluorobenzocyclobutenedione (VII) with Br_2. *a*. A mixture of 0.08 g (0.39 mmol) of compound **VII** and 0.6 g (3.75 mmol) of Br_2 was heated for 17.5 h at 130°C, washed with water solution of Na_2SO_3, acidified with HCl, extracted with ether, the extract was dried with $MgSO_4$. We obtained a solution containing compounds **XIV, XV**, and **XVI** in a ratio 35:53:12 (according to ^{19}F NMR spectrum). To the solution 2 ml of 10% HCl was added, and the mixture was left standing for 5 days, then the ether layer was separated, dried with $MgSO_4$, transferred to a watch glass, the solvent was evaporated, and we obtained 0.08 g (86%) of acid **XIV**.

b. A mixture of 0.2 g (0.98 mmol) of compound **VII** and 0.6 g (3.75 mmol) Br_2 was heated for 21 h at 130°C, the excess Br_2 was flushed away, and we obtained 0.34 g of a mixture of compounds **XV** and **XVI** (according to ^{19}F NMR spectrum) in a ratio 93:7 (yields 91 and 7% respectively). Analytical sample of compound **XV** (fluid) we obtained by "sublimation" at 100°C (2 mm Hg). IR spectrum (CCl_4), ν, cm^{-1}: 1831 (C=O), 1522, 1466 (fluorinated aromatic ring). ^{19}F NMR spectrum (CH_2Cl_2), δ, ppm: 27.0 (1F, F^7), 25.3 (1F, F^4), 24.0 (1F, F^5), 16.2 (1F, F^6); *J*(FF), Hz: $J_{4,5}$ 20, $J_{4,6}$ 7, $J_{4,7}$ 18, $J_{5,6}$ 18, $J_{5,7}$ 11, $J_{6,7}$ 21. Found $[M - Br]^+$ 282.9031. $C_8BrF_4O_2$. Calculated $[M - Br]$ 282.9010.

Reaction of perfluorobenzocyclobutenone (VI) with SbF_5. *a*. Into an NMR tube a mixture of 1.34 g (6.2 mmol) of SbF_5 and 0.19 g (0.82 mmol) of compound **VI** was placed, the mixture was dissolved, SO_2ClF was added, and ^{19}F NMR spectrum was registered containing signals from complex **XI**. ^{19}F NMR spectrum (SbF_5–SO_2ClF), δ (Δδ), ppm: 80.0 (13.9) (2F, CF_2), 62.6 (33.6) (1F, F^4), 57.3 (20.3) (1F, F^6), 36.5 (7.0) (1F, F^3), 33.7

(11.6) (1F, F^{5}). The solution was treated with 5% HCl, extracted with CH_2Cl_2, the extract was dried with $MgSO_4$, the solvent was distilled off in a vacuum to give 0.13 g of a mixture of compounds **VI** and **VII** in a ratio 82:18 (according to ^{19}F NMR spectrum) (yield 48 and 11% respectively).

b. A solution of 1.35 g (5.98 mmol) of compound **VI** in 4.89 g (22.41 mmol) of SbF_5 was heated for 6.5 h at 120°C, then treated with 5% HCl, extracted with CH_2Cl_2, then with ether, and the extracts were dried with $MgSO_4$. The ether extract was transferred to a watch glass, the solvent was evaporated, and the residue was sublimed at 170°C (2 mm Hg) to provide 0.35 g (25%) of acid **XIV**. Dichloromethane extract containing according to ^{19}F NMR spectrum compounds **IV, VI, XVIII, XIX, XX, XXI, XXII**, and **XXIII** in a ratio 5:15:44:2:24:3:6:1 was washed with water solution of $NaHCO_3$. The water layer was acidified with HCl, extracted with ether, the extract was dried with $MgSO_4$, transferred to a watch glass, the solvent was evaporated to give 0.28 g (18%) of acid **XVIII**. From the solution in CH_2Cl_2 the solvent was distilled off in a vacuum, the mixture obtained (0.67 g) was placed on a watch glass. On removal of the volatile components and sublimation of the residue at 130°C, (2 mm Hg) we obtained 0.54 g of a mixture of products. From 0.38 g we separated by column chromatography on silica gel (eluent CCl_4) 0.11 g (11%) of a mixture of compounds **XXI** and **XXII**, 0.01 g of compound **XXIII**, then (eluent $CHCl_3$) a fraction (0.19 g) containing according to ^{19}F NMR spectrum compounds **XIX** and **XX** in a ratio 12:88. Analytical sample of the mixture of compounds **XXI** and **XXII** in a ratio 40:60 (^{19}F NMR spectrum) was prepared by repeated column chromatography on silica gel (eluent a mixture CCl_4–hexane, 2:5 v/v) and by sublimation at 140°C (2 mm Hg). Analytical sample of compound **XXIII** was obtained by sublimation at 120°C (2 mm Hg) and by recrystallization. From the fraction containing compound **XX** we obtained by repeated column chromatography on silica gel (eluent $CHCl_3$) 0.16 g (16%) of compound **XX** (fluid). UV spectrum (hexane), λ_{max}, nm (log ε): 211 (4.19), 254 (4.01). IR spectrum (CCl_4), ν, cm^{-1}: 1764, 1690 (C=O), 1530, 1519, 1477 (fluorinated aromatic ring). ^{19}F NMR spectrum (CH_2Cl_2), δ, ppm: 107.1 (3F, $CF_3^{2'}$), 85.0 (3F, CF_3^{2}), 29.9 (1F, F^{6}), 27.5 (1F, $F^{3'}$), 26.3 (1F, F^{3}), 24.1 (1F, F^{4}), 22.4 (1F, $F^{6'}$), 17.3 (1F, $F^{5'}$), 16.0 (1F, F^{5}), 14.7 (1F, $F^{4'}$); *J*(FF), Hz: $J_{2,2'}$ 2, $J_{2,3}$ 5, $J_{2,6'}$ 3, $J_{2',3'}$ 17, $J_{3,4}$ 22, $J_{3,5}$ 7, $J_{3,6}$ 12, $J_{4,5}$ 19, $J_{4,6}$ 12, $J_{5,6}$ 22, $J_{3',4'}$ 21, $J_{3',5'}$ 9, $J_{3',6'}$ 11, $J_{4',5'}$ 20, $J_{4',6'}$ 6, $J_{5',6'}$ 22. Found, %: C 39.90; F 53.96. $[M-F]^+$ 470.9727. $C_{16}F_{14}O_2$. Calculated, %: C 39.21; F 54.26. $[M-F]$ 470.9691.

A mixture of compounds XXI and XXII. IR spectrum (CCl_4), ν, cm^{-1}: 1776 (C=O), 1527, 1522, 1488, 1471 (fluorinated aromatic ring). ^{19}F NMR spectrum (CH_2Cl_2), δ, ppm, compound **XXI**: 106.2 (3F, $CF_3^{2''}$, 105.5 (3F, $CF_3^{2'}$), 70.4 (1F, F_A) and 62.4 (1F, F_B, CF_2^{2}), 38.0 (1F, F^{6}), 29.7 (1F, $F^{3''}$), 29.1 (1F, $F^{6''}$), 27.2 (1F, $F^{3'}$), 25.4 (1F, F^{3}), 24.4 (1F, $F^{6,}$), 20.2 (1F, F^{5}), 18.9 (1F, F^{4}), 17.1 (1F, $F^{4''}$), 16.2 (1F, $F^{4'}$), 15.0 (1F, $F^{5''}$), 15.0 (1F, $F^{5'}$); *J*(FF), Hz: $J_{A,B}$ 199, $J_{A,3}$ 3, $J_{A,2''}$ 7, $J_{B,3}$ 3, $J_{B,2''}$ 25, $J_{3,4}$ 20, $J_{3,5}$ 7, $J_{3,6}$ 23, $J_{4,5}$ 18, $J_{4,6}$ 10, $J_{5'6}$ 18, $J_{6,6''}$ 43, $J_{2',3'}$ 19, $J_{3',4'}$ 21, $J_{3',5'}$ 9, $J_{3',6'}$ 11, $J_{4',5'}$ 21, $J_{4',6'}$ 9, $J_{5',6'}$ 21, $J_{6',2''}$ 8, $J_{2'',3''}$ 23, $J_{3'',4''}$ 21, $J_{3'',5''}$ 7, $J_{3'',6''}$ 9, $J_{4'',5''}$ 20, $J_{4'',6''}$ 9, $J_{5'',6''}$ 21; compound **XXII**: 105.9 (3F, $CF_3{}^{2'}$), 80.8 (3F, $CF_3{}^{2''}$), 72.2 (1F, F_A) and 61.9 (1F, F_B, $CF_2{}^{2}$), 59.5 (1F, F_A) and 51.9 (1F, F_B, $CF_2{}^{2''}$), 37.9 (1F, F^{6}), 34.1 (1F, $F^{3''}$), 30.6 (1F, $F^{6''}$), 27.4 (1F, $F^{3,}$), 25.8 (1F, $F^{6'}$), 25.0 (1F, F^{3}), 19.6 (1F, F^{5}), 18.7 (1F, F^{4}), 17.5 (1F, $F^{4'}$), 16.9 (1F, $F^{4''}$), 15.6 (1F, $F^{5''}$), 15.4 (1F, $F^{5'}$); *J*(FF), Hz: $J_{A,B}$ 199, $J_{A,3}$ 3, $J_{A,B''}$ 16, $J_{B,3}$ 3, $J_{B,A''}$ 14, $J_{B,B''}$ 74, $J_{3,4}$ 20, $J_{3,5}$ 7, $J_{3,6}$ 23, $J_{4,5}$ 18, $J_{4,6}$ 10, $J_{5,6}$ 18, $J_{6,6''}$ 46, $J_{2',3'}$ 21, $J_{3',4'}$ 21, $J_{3',5'}$ 10, $J_{3',6'}$ 11, $J_{4',5'}$ 21, $J_{4',6'}$ 10, $J_{5',6'}$ 22, *J*($F^{6'}$, $CF_3^{2'''}$) 9, *J*($CF_3^{2''}$, $F^{3'}$) 25, $J_{A'',B''}$ 288, $J_{A'',3''}$ 43, $J_{B'',3''}$ 7, $J_{3'',4''}$ 21, $J_{3'',5''}$ 7, $J_{3'',6''}$ 9, $J_{4'',5''}$ 20, $J_{4'',6''}$ 9, $J_{5'',6''}$ 21. ^{13}C NMR spectrum ($CDCl_3$), δ, ppm, compound **XXI**: 157.9 s (CO), 148.2–139.8 ($C^{3,3',3'',4,4',4'',5,5',5'',6,6',6''}$), 120.7 q ($^{1}J_{CF}$ 275 Hz) and 120.6 q ($CF_3^{2',2''}$, $^{1}J_{CF}$ 275 Hz), 123.0–112.4 ($C^{1',1'',2a,2',2'',6a}$), 114.2 t (CF_2^{2}, $^{1}J_{CF}$ 292 Hz), 87.6 d.d (C^{1}, $^{2}J_{CF}$ 30, 22 Hz); compound **XXII**: 157.6 s (CO), 148.2–139.8 ($C^{3,3',3'',4,4',4'',5,5',5'',6,6',6''}$), 120.6 q ($CF_3^{2'}$, $^{1}J_{CF}$ 275 Hz), 118.6 q.t ($CF_3^{2''}$, $^{1}J_{CF}$ 288, $^{2}J_{CF}$ 37 Hz), 123.0–112.4 ($C^{1',1'',2a,2',2'',6a}$), 114.4 t (CF_2^{2}, $^{1}J_{CF}$ 293 Hz), 112.0 t.q ($CF_2^{2''}$, $^{1}J_{CF}$ 262, $^{2}J_{CF}$ 41 Hz), 88.3 d.d (C^{1}, $^{2}J_{CF}$ 30, 22 Hz). Found, %: C 40.11. *M* 704 ($CHCl_3$, vapor phase osmometry). A mixture of $C_{23}F_{20}O_2$ (40 mol%) + $C_{24}F_{22}O_2$ (60 mol%). Calculated, %: C 39.49. *M* 718.

Perfluoro-5,6-dihydro-7-oxodibenzo[*a*,*h*]-azulen-8-one (XXIII). mp 144.5–146°C (from hexane–CH_2Cl_2). UV spectrum (hexane), λ_{max}, nm (log ε): 239 (4.29), 253 (4.06), 261 (4.05), 285 (3.68), 333 (3.49), 400 (2.94). IR spectrum (KBr), ν, cm^{-1}: 1745 (C=O), 1526, 1510, 1488 (fluorinated aromatic ring). ^{19}F NMR spectrum (CH_2Cl_2), δ, ppm: 90.2 (1F, F_A) and 85.5 (1F, F_B, CF_2^{6}), 59.0 (1F, F_A) and 44.3 (1F, F_B, CF_2^{5}), 34.1 d.m (1F, F^{1}), 28.2 (1F, F^{9}), 25.8 d.m (1F, F^{4}), 22.3 (1F, F^{12}), 20.0 (1F, F^{11}), 15.9 m (2F, $F^{2,3}$), 11.3 (1F, F^{10}); *J*(FF), Hz: $J_{1,12}$ 46, $J_{4,5B}$ 95, $J_{5A,5B}$ 282, $J_{5A,6A}$ 20, $J_{5A,6B}$ 14, $J_{5B,6A}$ 11, $J_{5B,6B}$ 15, $J_{6A,6B}$ 152, $J_{9,10}$ 21, $J_{9,11}$ 11, $J_{9,12}$ 13, $J_{10,11}$ 16, $J_{10,12}$ 5, $J_{11,12}$ 20. Found: $[M]^+$ 463.9700. $C_{17}F_{12}O_2$. Calculated: *M* 463.9707.

Reaction of perfluorophthalane (XXIV) with SbF_5. A mixture of 0.32 g (1.19 mmol) of compound **XXIV** and 1.5 g (6.93 mmol) of SbF_5 was stirred for 2 h at 20°C, then treated with 5% HCl, extracted with CH_2Cl_2, the extract was dried with $MgSO_4$, transferred to a watch glass; we obtained 0.22 g (70%) of **6-trifluoromethyl-2,3,4,5-tetrafluorobenzoic acid (XVIII)**.

Reaction of perfluorotetralin-1,4-dione (IX) with SbF_5. *a.* A solution of 0.76 g (2.5 mmol) of compound **IX** in 3.3 g (15.24 mmol) of SbF_5 was heated for 20 h at 130°C, then treated with 5% HCl, extracted with ether, the solvent was distilled off in a vacuum, the residue was dissolved in CH_2Cl_2 and dried with $MgSO_4$. On removing solvent in a vacuum we obtained 0.77 g (96%) of a mixture containing according to ^{19}F NMR spectrum compounds **V, VIII, XIII, XIV, XXV, XXVI**, and **XXVII** in a ratio 10:19:8:4:26:12:21.

b. A solution of 1 g (3.29 mmol) of compound **IX** in 4.04 g (18.63 mmol) of SbF_5 was heated for 18 h at 180°C, then treated with 5% HCl, extracted with CH_2Cl_2, then with ether, and the extracts were dried with $MgSO_4$. The ether extract was transferred to a watch glass, the solvent was evaporated, and the residue was sublimed at 130°C (3 mm Hg) to yield 0.07 g (9%) of **tetrafluorophthalic acid (XIV)**. Dichloromethane extract containing compounds **XXV, XXVI**, and **XXVIII** in a ratio 18:68:14 (according to ^{19}F NMR spectrum) was washed with water solution of $NaHCO_3$, and on distilling off the solvent in a vacuum we obtained 0.59 g (52%) of phthalide **XXVI**, whose analytical sample was prepared by sublimation at 90°C (30 mm Hg) and recrystallization. The water layer was acidified with HCl, extracted with CH_2Cl_2, the extract was dried with $MgSO_4$, transferred to a watch glass, the solvent was evaporated to give 0.26 g of a mixture containing compounds **XXV** and **XXVIII** in a ratio 53:47 (yields 11 and 12% respectively). By sublimation at 80°C (20 mm Hg) and recrystallization from hexane we isolated in an individual state 0.05 g of acid **XXVIII**, mp 81.5–82.5°C. UV spectrum (hexane), λ_{max}, nm (log ε): 213 (3.75), 270 (3.30). IR spectrum (CCl_4), ν, Cm^{-1}: 3503, 3036 (OH), 1774, 1733 (C=O), 1529, 1483 (fluorinated aromatic ring). ^1H (CCl_4), δ, ppm: 10.78 br.s (OH). ^{19}F NMR spectrum (CCl_4), δ, ppm: 81.1 (3F, CF_3), 56.2 (2F, CF_2^{α}), 36.8 (2F, CF_2^{β}), 29.6 (1F, F^5), 23.8 (1F, F^2), 17.0 (1F, F^3), 12.9 (1F, F^4); *J*(FF), Hz: $J(CF_3, CF_2^{\alpha})$ 10, $J(CF_2^{\alpha}, CF_2^{\beta})$ 11, $J(CF_2^{\alpha}, F^5)$ 22, $J(CF_2^{\beta}, F^5)$ 22, $J_{2,3}$ 22, $J_{2,4}$ 6, $J_{2,5}$ 11, $J_{3,4}$ 20, $J_{3,5}$ 10, $J_{4,5}$ 20. Found: $[M]^+$ 361.9801. $C_{10}HF_{11}O_2$. Calculated: *M* 361.9801.

Perfluoro-3-ethylphthalide (XXVI). mp 29–31°C (from hexane). UV spectrum (hexane), λ_{max}, nm (log ε): 231 (3.80), 283 (3.35). IR spectrum (CCl_4), ν, cm^{-1}: 1846 (C=O), 1522, 1507 (fluorinated aromatic ring). ^{19}F NMR spectrum (CH_2Cl_2), δ, ppm: 82.4 (3F, CF_3), 40.1 (1F, F^3), 39.2 (1F, F_A) and 37.5 (1F, F_B, CF_2), 30.4 (1F, F^4), 29.0 (1F, F^7), 25.2 (1F, F^5), 20.3 (1F, F^6); *J*(FF), Hz: $J_{A,B}$ 287, $J_{A,3}$ 3, $J_{B,3}$ 11, $J_{A,4}$ 13, $J_{B,4}$ 37, $J(CF_3, F^3)$ 9, $J_{3,4}$ 4, $J_{3,6}$ 4, $J_{4,5}$ 20, $J_{4,6}$ 9, $J_{4,7}$ 18, $J_{5,6}$ 18, $J_{5,7}$ 12, $J_{6,7}$ 20. Found: $[M]^+$ 341.9747. $C_{10}F_{10}O_2$. Calculated: *M* 341.9739.

3-Hydroxyperfluoro-3-ethylphthalide (XXV). To a solution of 0.5 g (1.46 mmol) of compound **XXVI** in 5 ml of ether was added 5 ml of 5% HCl, and the mixture was left standing for 13 days. The ether layer was dried with $MgSO_4$, transferred to a watch glass, and solvent was removed. Yield 0.41 g (82%), mp 130.5–131°C (from hexane–ether). UV spectrum (hexane), λ_{max}, nm (log ε): 228 (3.88), 280 (3.29). IR spectrum (KBr), ν, cm^{-1}: 3342 (OH), 1795, 1773 (C=O), 1522, 1510 (fluorinated aromatic ring). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.82 br.s (OH). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: 82.5 s (3F, CF_3), 39.1 (1F, F_A) and 37.7 (1F, F_B, CF_2), 27.0 (1F, F^4), 26.1 (1F, F^7), 21.8 (1F, F^5), 16.5 (1F, F^6); *J*(FF), Hz: $J_{A,B}$ 278, $J_{A,4}$ 14, $J_{B,4}$ 28, $J_{4,5}$ 20, $J_{4,6}$ 7, $J_{4,7}$ 19, $J_{5,6}$ 18, $J_{5,7}$ 10, $J_{6,7}$ 20. Found: $[M]^+$ 339.9772. $C_{10}HF_9O_3$. Calculated: *M* 339.9782.

Reaction of perfluorotetralin-1-one (VIII) with SbF_5. *a*. Into an NMR tube a mixture of 1.18 g (5.45 mmol) of SbF_5 and 0.22 g (0.67 mmol) of compound **VIII** was placed, SO_2ClF was added, and ^{19}F NMR spectrum was registered containing signals of complex **XII**. ^{19}F NMR spectrum (SbF_5–SO_2ClF), δ (Δδ), ppm: 61.4 (31.2) (1F, F^8), 58.2 (33.0) (1F, F^6), 57.3 (1.2) (2F, CF_2^4), 44.9 (9.6) (2F, CF_2^2), 39.5 (10.6) (1F, F^5), 31.6 (2.4) (2F, CF_2^3), 25.1 (6.2) (1F, F^7). The solution was treated with 5% HCl, extracted with CH_2Cl_2, the extract was dried with $MgSO_4$, 0.2 g (90%) of tetralone **VIII**.

b. A solution of 0.97 g (2.96 mmol) of ketone **VIII** in 2.52 g (11.64 mmol) of SbF_5 was heated for 3 h at 130°C, then it was treated with 5% HCl, extracted with CH_2Cl_2, the solvent was distilled off in a vacuum to provide 0.8 g (82%) of a mixture containing compounds **V, VIII, IX, XXV**, and **XXVI** in a ratio 16:69:8:4:3 (according to ^{19}F NMR spectrum).

c. A solution of 1.22 g (3.74 mmol) of ketone **VIII** in 4.25 g (19.6 mmol) of SbF_5 was heated for 19 h at 180°C, then it was treated with 5% HCl and extracted with CH_2Cl_2. The extract was washed with water solution of $NaHCO_3$, and we obtained a solution containing compounds **V, XXVI, XXIX, XXXI**, and **XXXII** in a ratio 39:19:2:29:11 (according to ^{19}F NMR spectrum). The water layer was acidified with HCl, extracted with CH_2Cl_2, the extract was dried with $MgSO_4$,and on removing the solvent in a vacuum we obtained 0.3 g (24%) of a mixture containing compounds **XVII, XVIII, XXV, XXVIII, XXX**, and **XXXIII** in a ratio 15:13:23:29:19:1 (according to ^{19}F NMR spectrum). From the solution containing non-acid products CH_2Cl_2 was distilled off, the residue was dissolved in 7 ml of ether and hydrolyzed for 10 days by adding 7 ml of 10% HCl. The ether layer was separated, the solvent was distilled off in a vacuum, the residue was dissolved in CH_2Cl_2, the solution was washed with water solution of $NaHCO_3$, dried with $MgSO_4$, the solvent was distilled off in a vacuum, and we obtained 0.26 g (21%) of a mixture containing compounds **V, XXIX**, and **XXXII** in a ratio 74:4:22 (according to ^{19}F NMR spectrum). The water layer was acidified with HCl, extracted with ether, the extract was dried with $MgSO_4$, transferred to a watch glass, and we obtained 0.24 g (19%) of a mixture containing compounds **XXV** and **XXX** in a ratio 40:60 (according to ^{19}F NMR spectrum). The mixture was additionally sublimed at 110°C (2 mm Hg) and recrystallized from CCl_4.

Perfluoro-3-hydroxy-3-methyl-3,4-dihydroisochromen-1-one (XXX). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm (for the mixture **XXV** + **XXX**): 5.19 br.s (OH). ^{19}F NMR spectrum (CH_2Cl_2), δ, ppm (for the mixture **XXV** + **XXX**): 82.6 (3F, CF_3), 62.3 (1F, F_A) and 43.4 (1F, F_B, CF_2), 31.4 (1F, F^8), 25.5 (1F, F^5), 22.5 (1F, F^6), 16.6 (1F, F^7); J(FF), Hz: $J_{A,B}$ 281, $J(F_A, CF_3)$ 13, $J(F_B, CF_3)$ 9, $J_{A,5}$ 7, $J_{B,5}$ 50, $J_{A,6}$ 1, $J_{B,6}$ 1, $J_{A,7}$ 4, $J_{B,8}$ 4, $J_{5,6}$ 21, $J_{5,7}$ 8, $J_{5,8}$ 13, $J_{6,7}$ 20, $J_{6,8}$ 13, $J_{7,8}$ 20. Found: $[M]^+$ 339.9776. (**XXV + XXX**). $C_{10}HF_9O_3$. Calculated: M 339.9782.

6-(2-Oxopentafluoropropyl)-2,3,4,5-tetrabenzoic acid (XXXVIII). ^{19}F NMR spectrum (for the mixture **XXV+XXX+XXXVIII** in ether), δ, ppm: 82.3 (3F, CF_3), 61.6 (2F, CF_2) 32.6 (1F, F^5), 22.8 (1F, F^2), 12.1 (1F, F^3), 10.1 (1F, F^4); J(FF), Hz: $J(CF_3, CF_2)$ 12, $J(CF_2, F^5)$ 28, $J_{2,3}$ 22, $J_{2,4}$ 5, $J_{2,5}$ 12, $J_{3,4}$ 20, $J_{3,5}$ 8, $J_{4,5}$ 20.

d. Similarly to the previous run from 0.96 g (2.94 mmol) of tetralone **VIII** and 5.13 g (23.66 mmol) of SbF_5 (180°C, 80 h) after distilling off the solvent from dichloromethane extract washed with water solution of $NaHCO_3$ we obtained 0.4 g (40%) of a mixture containing compounds **V, XXVI, XXIX, XXXI**, and **XXXII** in a ratio 7:10:9:59:15 (according to ^{19}F NMR spectrum), and 0.32 g (32%) of a mixture containing compounds **XVII, XVIII, XXV, XXVIII, XXX**, and **XXXIII** in a ratio 18:13:1:60:3:5 (according to ^{19}F NMR spectrum) after extraction of the water layer acidified with HCl.

Reaction of perfluorotetralin (V) with glass in the presence of SbF_5. A mixture of 1.11 g (3.19 mmol) of tetralin **V** and 4.83 g (22.28 mmol) of SbF_5 was heated for 31 h at 180°C in a sealed ampule, then it was treated with 5% HCl, extracted first with CH_2Cl_2, then with ether, and the extracts were dried with $MgSO_4$. The ether extract was transferred to a watch glass, the residue was sublimed at 130°C (2 mm Hg) to give 0.18 g (24%) of acid **XIV**. Dichloromethane extract containing compounds **XXV, XXVI, XXIX, XXX, XXXI**, **XXXII**, and **XXXIII** in a ratio 20:40:12:5:9:12:2 (according to ^{19}F NMR spectrum) was dried with $MgSO_4$, the solvent was distilled off in a vacuum, the residue was dissolved in 7 ml of ether and hydrolyzed for 10 days by adding 8 ml of 10% HCl. The ether layer was separated, the solvent was distilled off in a vacuum, the residue was dissolved in CH_2Cl_2, the solution was washed with water solution of $NaHCO_3$, dried with $MgSO_4$, the solvent was distilled off in a vacuum, and the residue was sublimed at 100°C (10 mm Hg) to yield 0.07 g (7%) of a mixture containing compounds **XXIX** and **XXXII** in a ratio 53:47 (according to ^{19}F NMR spectrum). Individual compounds **XXIX** and **XXXII** were isolated by column chromatography on silica gel (eluent first CCl_4, then $CHCl_3$) from the mixture obtained in several similar runs. The water layer was acidified with HCl, extracted with ether, the extract was dried with $MgSO_4$, transferred to a watch glass, evaporated, and we obtained 0.43 g (40%) of a mixture containing compounds **XXV, XXX**, and **XXXIII** in a ratio 80:18:2 (according to ^{19}F NMR spectrum).

Perfluoro-3,3-dimethylphthalide (XXIX). mp 57.5–59°C (from hexane, in a sealed capillary). UV spectrum (hexane), λ_{max}, nm (log ε): 205 (3.87), 227 (3.96), 233 (3.95), 279 (3.38). IR spectrum (CCl_4), ν, cm^{-1}: 1840 (C=O), 1522, 1506 (fluorinated aromatic ring). ^{19}F NMR spectrum (hexane), δ, ppm: 88.1 (6F, $2CF_3$), 29.4 (1F, F^4), 28.0 (1F, F^7), 23.0 (1F, F^5), 17.9 (1F, F^6); J(FF), Hz: $J(CF_3, F^4)$ 14, $J_{4,5}$ 20, $J_{4,6}$ 8, $J_{4,7}$ 19, $J_{5,6}$ 17, $J_{5,7}$ 11, $J_{6,7}$ 20. Found: $[M]^+$ 341.9744. $C_{10}F_{10}O_2$. Calculated: M 341.9739.

Perfluoro-3-methylisochromen-1-one (XXXII). mp 149–150°C (from hexane). UV spectrum (hexane), λ_{max}, nm (log ε): 227 (4.30), 241 (4.03), 248 (4.04), 260 (3.78), 269 (3.77) , 280 (3.59) , 317 (3.56). IR spectrum (CCl_4), ν, Cm^{-1}: 1786 (C=O), 1520, 1495 (fluorinated aromatic ring). ^{19}F NMR spectrum (CH_2Cl_2), δ, ppm: 96.1 d [3F, CF_3, $J(F^4, CF_3)$ 22 Hz], 31.8 m (1F, F^8), 22.7–22.1 m (2F, $F^{5,6}$), 16.0 m (1F, F^7), 9.4 m (1F, F^4). Found: $[M]^+$ 303.9774. $C_{10}F_8O_2$. Calculated: *M* 303.9771.

Reaction of perfluoro-2-isopropyltoluene (XXXIV) with SiO_2–SbF_5. A mixture of 0.85 g (2.2 mmol) of compound **XXXIV**, 0.07 g (1.16 mmol) of SiO_2, and 5.59 g (25.7 mmol) of SbF_5 was stirred for 5.5 h at 70°C. A part of the mixture (25%) was treated with 5% HCl, extracted with ether, the extract was dried with $MgSO_4$, transferred to a watch glass, the solvent was evaporated, and the residue was sublimed at 110°C (5 mm Hg) to obtain 0.12 g (60%) of acid **XXXIII**. The remaining mixture (75%) was heated for 21.5 h at 180°C, then treated with 5% HCl, extracted with ether, the extract was dried with $MgSO_4$. Thus we obtained a solution containing compounds **XXIX** and **XXXIII** in a ratio 4:96 (according to ^{19}F NMR spectrum). The solution was washed with water solution of $NaHCO_3$, transferred to a watch glass, the residue was sublimed at 110°C (5 mm Hg) to get 0.52 g (87%) of acid **XXXIII**.

6-Heptafluoropropyl-2,3,4,5-tetrafluorobenzoyl fluoride (XXXV). A mixture of 1.03 g (2.85 mmol) of acid **XXVIII**, 1 ml (13.9 mmol) of $SOCl_2$, and 2 drops of DMF was stirred for 17 h at 80°C (bath temperature). The vacuum distillation gave 0.91 g of acid chloride [bp 92–94°C (20 mm Hg)] that was heated with CsF (2.05 g, 13.49 mmol) for 10.5 h at 205°C. We isolated by distillation 0.78 g (75%) of acid fluoride **XXXV** (fluid). UV spectrum (hexane), λ_{max}, nm (log ε): 211 (3.73), 271 (3.30). IR spectrum (CCl_4), ν, cm^{-1}: 1861, 1847 (C=O), 1528, 1484 (fluorinated aromatic ring). ^{19}F NMR spectrum (CCl_4), δ, ppm: 220.0 (1F, COF), 81.4 (3F, CF_3), 56.3 (2F, CF_2^{α}), 36.6 (2F, CF_2^{β}), 30.9 (1F, F^5), 26.2 (1F, F^2), 18.2 (1F, F^3), 15.7 (1F, F^4); *J*(FF), Hz: $J(COF, CF_2^{\alpha})$ 4, $J(COF, CF_2^{\beta})$ 9, $J(COF, F^2)$ 9, $J(CF_3, CF_2^{\alpha})$ 10, $J(CF_2^{\alpha}, CF_2^{\beta})$ 11, $J(CF_2^{\alpha}, F^5)$ 22, $J(CF_2^{\beta}, F^5)$ 22, $J_{2,3}$ 21, $J_{2,4}$ 7, $J_{2,5}$ 11, $J_{3,4}$ 20, $J_{3,5}$ 10, $J_{4,5}$ 20. Found: $[M]^+$ 363.9763. $C_{10}F_{12}O$. Calculated: *M* 363.9757.

Reaction of 6-heptafluoropropyl-2,3,4,5-tetrafluorobenzoyl fluoride (XXXV) with SbF_5. A mixture of 0.68 g (1.87 mmol) of compound **XXXV** and 6.68 g (30.81 mmol) of SbF_5 was heated for 31 h at 180°C, then treated with 5% HCl, extracted with a mixture $CHCl_3$–ether, 3:1, the extract was dried with $MgSO_4$, transferred to a watch glass, the solvent was evaporated, and we obtained 0.62 g (61%) of a mixture containing compounds **XXV, XXVI**, and **XXVIII** in a ratio 4:6:90 (according to ^{19}F NMR spectrum).

3-Hydroxy-3-trifluoromethyl-4,5,6,7,8-pentafluoro-3,4-dihydroisochromen-1-one (XXXVI). A mixture of 0.04 g (0.13 mmol) of compound **XXXII**, 0.1 g (1.19 mmol) of $NaHCO_3$, 1.5 ml of water, and 5 drops of ether was stirred for 2 days, acidified with HCl, extracted with ether, the extract was dried with $MgSO_4$, transferred to a watch glass, the solvent was evaporated to yield 0.03 g (71%) of compound **XXXVI**, mp 150–150.5°C (from hexane). IR spectrum (KBr), ν, cm^{-1}: 3300 (OH), 1766, 1753 (C=O), 1523, 1505 (fluorinated aromatic ring). Found: $[M]^+$ 321.9888. $C_{10}H_2F_8O_3$. Calculated: *M* 321.9876. ^1H NMR spectrum ($CDCl_3$), δ, ppm, isomer **1** (94%): 5.93 d.d [1H, H^4, $J(H^4, F^4)$ 49, $J(H^4, F^8)$ 2 Hz], 5.38 br.s (1H, OH); isomer **2** (6%): 6.00 d 1H, H^4, $J(H^4, F^4)$ 48 Hz]. ^{19}F NMR spectrum (CH_2Cl_2), δ, ppm, isomer **1** (94%): 80.3 (3F, CF_3), 30.7 (1F, F^8), 21.0 (1F, F^5), 20.1 (1F, F^6), 14.2 (1F, F^7), –18.0 (1F, F^4); *J*(FF), Hz: $J(CF_3, F^4)$ 14, $J_{4,5}$ 2, $J_{4,6}$ 2, $J_{4,7}$ 8, $J_{4,8}$ 3, $J_{5,6}$ 21, $J_{5,7}$ 6, $J_{5,8}$ 14, $J_{6,7}$ 20, $J_{6,8}$ 12, $J_{7,8}$ 20, $J(F^4, H^4)$ 49, $J(F^8, H^4)$ 2; isomer **2** (6%): 81.3 d [3F, CF_3, $J(CF_3, F^4)$ 5 Hz], 30.5 (1F, F^8), 22.1 (1F, F^5), 20.4 (1F, F^6), 14.8 (1F, F^7), –25.2 d [1F, F^4, $J(F^4, H^4)$ 48 Hz]. ^{19}F NMR spectrum (ether), δ, ppm (in solution isomer **1** + acid **XXXIX**), acid **XXXIX**: 79.3 d [3F, CF_3, $J(CF_3, F^{\alpha})$ 11 Hz], 28.6 m (1F, F^5), 23.2 m (1F, F^2), 8.8 m (1F) and 8.5 m (1F, $F^{3,4}$), –33.7 d.m [1F, F^{α}, $J(F^{\alpha}, H^{\alpha})$ 45 Hz].

Perfluoro-3-methyl-3,4-dihydroisochromen-1-one (XXXI). To 0.5 g (1.47 mmol) of a mixture of compounds **XXV** and **XXX** in a ratio 47:53 was added 0.87 g (7.28 mmol) of $SOCl_2$ and 2 drops of DMF, the mixture was stirred for 20 h at 80°C (bath temperature). Excess $SOCl_2$ was distilled off in a vacuum, the residue (0.5 g) was dissolved in 4.54 g (20.94 mmol) of SbF_5 and was heated for 42 h at 70–75°C. Then to the mixture 1.2 ml of CF_3COOH was added, the reaction mixture was treated with 5% HCl, extracted with $CHCl_3$, the extract was washed with water solution of $NaHCO_3$ and dried with $MgSO_4$, the solvent was distilled off in a vacuum, and the residue was sublimed at 80°C (30 mm Hg) to obtain 0.39 g (77%) of a mixture of compounds **XXVI** and **XXXI** in a ratio 57:43 (according to the data of GC-MS and ^{19}F NMR spectrum). ^{19}F NMR spectrum (CH_2Cl_2), δ, ppm (a mixture of **XXVI + XXXI**): 83.1 (3F, CF_3), 64.9 (1F, F_A) and 41.3 (1F, F_B, CF_2), 37.2 (1F, F^3), 33.4 (1F, F^8), 26.9 (1F, F^5), 24.6 (1F, F^6), 18.5 (1F, F^7); *J*(FF), Hz: $J_{A,B}$ 289, $J_{A,3}$ 15, $J_{B,3}$ 14, $J(F_A, CF_3)$ 12, $J(F_B, CF_3)$ 10, $J_{A,5}$ 4, $J_{B,5}$ 50, $J_{A,6}$ 1, $J_{B,6}$ 1, $J_{A,7}$ 5, $J_{B,8}$ 4, $J(F^3, CF_3)$ 3, $J_{5,6}$ 21, $J_{5,7}$ 9, $J_{5,8}$ 13, $J_{6,7}$ 20, $J_{6,8}$ 14, $J_{7,8}$ 20.

Found: $[M]^+$ 341.9741 (**XXVI + XXXI**). $C_{10}F_{10}O_2$. Calculated: *M* 341.9739.

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