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Isomerization of Perfluoro-3,3-diethylindan-1-one into Perfluoro-1,3-dimethyl-4-ethyl-1*H*-isochromen under the Action of Antimony Pentafluoride

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Abstract—The heating of perfluoro-3,3-diethylindan-1-one with SbF_5 at 180°C after treatment of the reaction mixture with anhydrous HF afforded perfluoro-1,3-dimethyl-4-ethylisochromen, and after hydrolysis, perfluoro-1,3-dimethyl-4-ethyl-1*H*-isochromen-1-ol. The latter under the action of $NaHCO_3$ converted into 5,6,7,8-tetrafluoro-1,3-bis(trifluoromethyl)-1*H*-isochromen-1-ol. Both isochromenols reacted with $SOCl_2$ gave the corresponding polyfluoro-1-chloro-1*H*-isochromens. On dissolving isochromenols in CF_3SO_3H and isochromens in SbF_5 perfluoro-1,3-dimethyl-4-ethylisochromenyl and 5,6,7,8-tetrafluoro-1,3-bis(trifluoromethyl)isochromenyl cations were generated which by hydrolysis were converted into the corresponding isochromenols.

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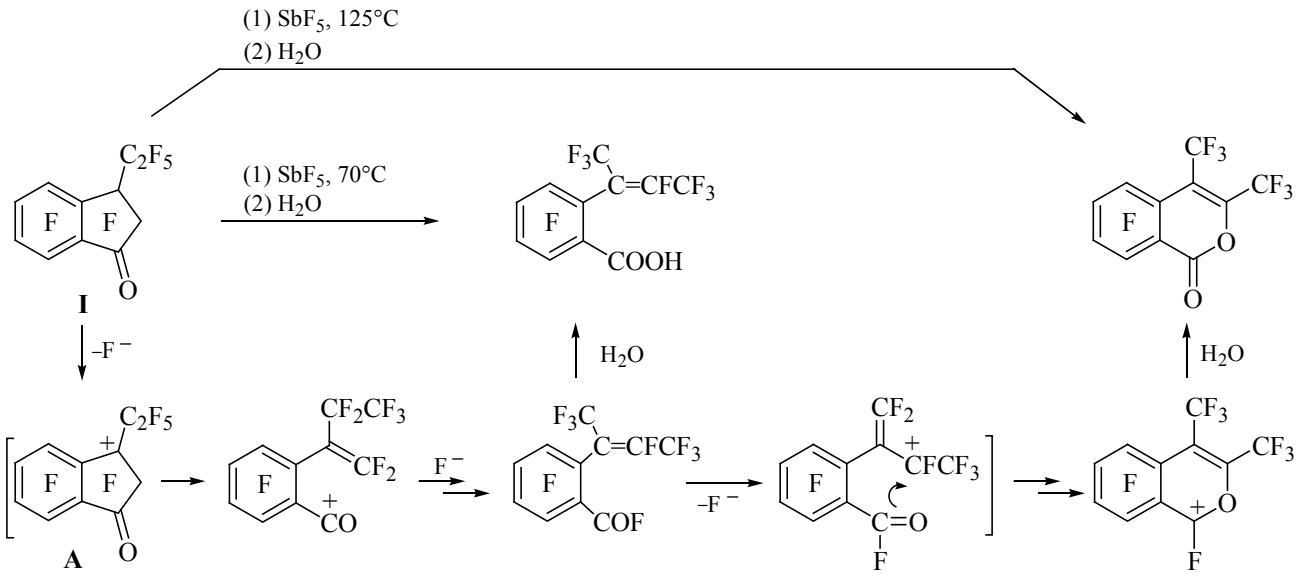
We formerly discovered and investigated previously unknown in perfluoroketones skeleton rearrangements of carbonyl derivatives of perfluorinated tetralin [1], indan [2], 1-methyl- [3] and 1-ethylindans [4], benzocyclobutene [1], 1-alkyl- [5], 1-phenyl-1-ethyl- [6], and 1,1-dialkylbenzocyclobutenes [5, 6] effected by the action of antimony pentafluoride. It was established that the direction of the reaction depended on the size of the carbonyl-

Scheme 1.



containing ring of the substrate and also on the presence and the position of its perfluoroalkyl substituents. In particular, the heating of perfluoro-3-ethylindan-1-one (**I**) with SbF_5 at 70°C resulted in perfluoro-2-(but-2-en-2-yl) benzoic acid, and at 125°C, in perfluoro-3,4-dimethylisochromen-1-one. The reaction apparently proceeds through cation **A** [4] (Scheme 1).

In contrast to compound **I** perfluoro-3,3-diethylindan-1-one (**II**) treated with SbF_5 at 130°C did not suffer the skeleton rearrangement [2]. This is apparently due to the presence in the position *3* of ketone **II** instead of a fluorine atom of the second perfluoroethyl group preventing the formation of cation similar to ion **A**. However formally a formation of the other cations is possible, e.g., by elimination of a fluoride ion from the carbon atom of the side chain of ketone **II**. It is therefore presumable that under more severe conditions the five-membered ring of the diethylindanone **II** would be able to undergo the skeleton rearrangements whose mechanism would be different from the mechanism of the opening of the five-membered ring in ethylindanone **I** [4], perfluoro-3-methylindan-1-one [3], and perfluoroindan-1-one [2].

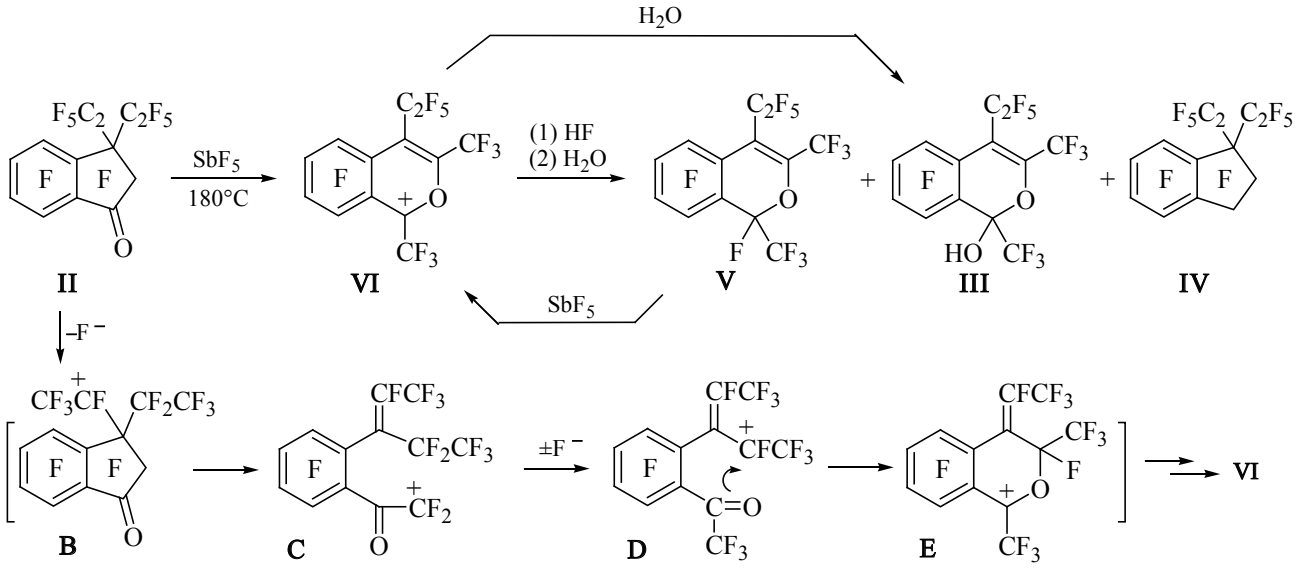
In this research we studied the behavior of ketone **II** in antimony pentafluoride under more severe conditions than in [2] in order to elucidate the possibility of its cationoid skeleton rearrangements.

It was demonstrated that the heating of diethylindanone **II** with antimony pentafluoride at 180°C over 15 h in a nickel pressure reactor with the subsequent hydrolysis of the reaction mixture resulted in perfluoro-1,3-dimethyl-4-ethyl-1*H*-isochromen-1-ol (**III**). The reaction mixture contained also a large amount of initial compound **II** (Scheme 2). The increased reaction time (74 h) led to the higher conversion of ketone **II**, but alongside compounds **II** and **III** the reaction mixture contained a number of intractable impurities and a small quantity of perfluoro-1,1-diethylindan (**IV**).

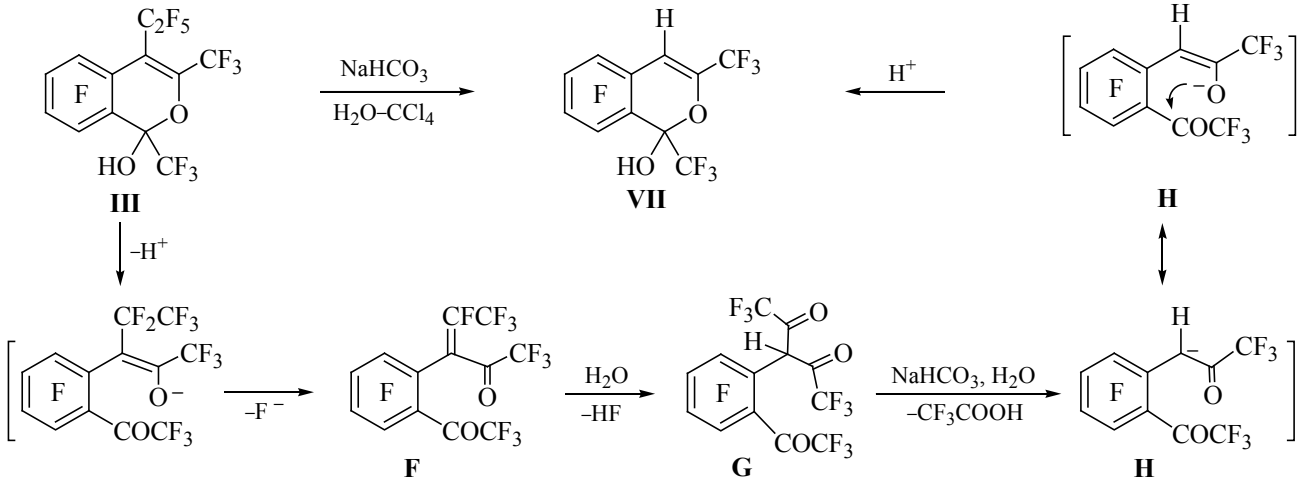
The heating of diethylindanone **II** with SbF_5 at 180°C over 27 h followed by treatment of the reaction mixture with anhydrous HF and then with water led to the formation of perfluoro-1,3-dimethyl-4-ethylisochromen (**V**) alongside initial ketone **II** and compounds **III** and **IV** as impurities. According to the ^{19}F NMR spectrum the reaction mixture before the treatment with HF contained a salt of perfluoro-1,3-dimethyl-4-ethylisochromenyl cation (**VI**). This cation was also generated from compound **V** in SbF_5 environment. The hydrolysis of the salt of cation **VI** gave alcohol **III** (Scheme 2).

One among the possible ways of cation **VI** formation from ketone **II** in the presence of SbF_5 is presented in Scheme 2. Initially under the action of SbF_5 from compound **II** cation **B** is generated. Then in ion **B** the five-membered ring undergoes opening resulting in cation **C** that isomerizes into cation **D**. The intramolecular attack of the positively charged carbon atom of the allyl system of ion **D** on the oxygen atom affords cation **E** where the transition of the exocyclic multiple bond C=C into the ring furnishes cation **VI**.

Scheme 2.



Scheme 3.



The assumed mechanism of the opening of the five-membered ring in diethylindanone **II** is unlike the opening mechanism of the five-membered ring in ethylindanone **I** [4]. For instance in diethylketone **II** the rupture of the C–C bond occurs in ion **B** with a cation center in the side chain (Scheme 2), whereas in ethylketone **I** the cleavage of bond occurs in ion **A** with a cation center in the benzyl position (Scheme 1). This mechanism has not been previously observed in the polyfluorinated indan derivatives, but it is analogous to the opening mechanism of the four-memebered ring in the perfluorinated 2,2-diethylbenzocyclobutenone [6] and 2-alkylbenzocyclobutenes [5], and also in 1,1-dialkylbenzocyclobutenes [7] at the treatment with antimony pentafluoride. Besides the formolysis of nonfluorinated (indan-1-yl)methyl tosylate that also proceeds with the involvement of an intermediate cationoid species containing an indan frame and a cationic center in the side chain, resulted not in the opening of the five-membered ring, but in its extension by the migration of an aryl group to the cation center with the formation of tetralin derivatives [8].

The attempt to isolate individual alcohol **III** by column chromatography on silica gel was unsuccessful for we failed to elute compound **III** from the column. This fact may be due to the lability of compound **III** even in the presence of relatively weak bases. Actually, alcohol **III** under the action of $NaHCO_3$ in a two-phase system H_2O–CCl_4 at room temperature converted into 5,6,7,8-tetrafluoro-1,3-bis(trifluoromethyl)-1*H*-isochromen-1-ol (**VII**) (Scheme 3).

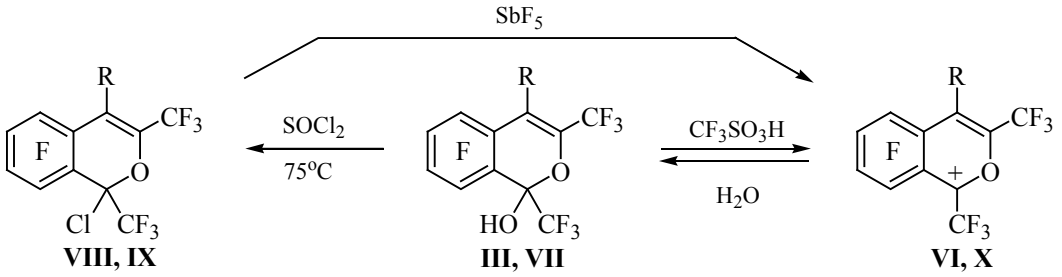
The possible way of compound **III** conversion into alcohol **VII** is presented in Scheme 3. Apparently initially compound **III** is deprotonated with the opening of the pyran ring and the elimination of the fluoride ion giving diketone **F**. The latter under the reaction conditions transforms into triketone **G**. Further in compounds **G** a bond C–C is ruptured by the type of the haloform cleavage to give the trifluoroacetic acid and anion **H** which suffers an intramolecular cyclization resulting in alcohol **VII**. The formation in the reaction of the trifluoroacetic acid was confirmed by the ^{19}F NMR spectroscopy. The reactions analogous to the cleavage of triketone **G** were formerly observed in the reactions of compounds $CHX(COCF_3)_2$ (X = H [9], CF_3, $COCF_3$ [10]) with water.

Alcohols **III** and **VII** treated with $SOCl_2$ gave 5,6,7,8-tetrafluoro-4-pentafluoroethyl-1,3-bis(trifluoromethyl)-1-chloro-1*H*-isochromen (**VIII**) and 5,6,7,8-tetrafluoro-1,3-bis(trifluoromethyl)-1-chloro-1*H*-isochromen (**IX**) respectively (Scheme 4).

In the antimony pentafluoride medium from compounds **VIII** and **IX** ion **VI** and 5,6,7,8-tetrafluoro-1,3-bis(trifluoromethyl)isochromenyl cation (**X**) are generated. These cations are also generated at dissolution of alcohols **III** and **VII** in the trifluoromethanesulfonic acid. Therewith isochromenol **VII** in CF_3SO_3H is completely converted into cation **X**, and isochromenol **III** into cation **VI,** only partially. On hydrolysis of the salts of cations **VI** and **X** alcohols **III** and **VII** form respectively (Scheme 4).

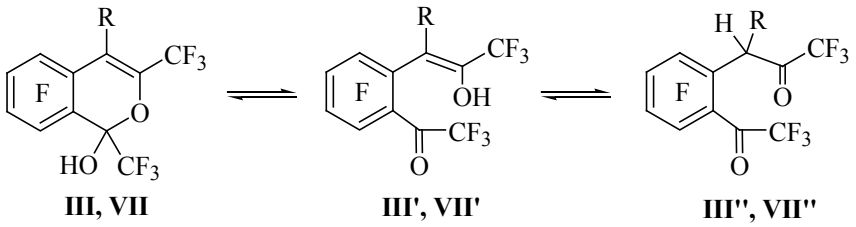
Compounds **III** and **VII** can formally exist in the cyclic and/or acyclic **III', III', VII', VII'** forms (Scheme 5).

Scheme 4.



R = C_2F_5 (**III, VI, VIII**), H (**VII, IX, X**).

Scheme 5.



IR spectra of compounds **III** and **VII** in CCl_4 and ^{13}C NMR spectra in $CDCl_3$ do not contain absorption band or signals characteristic of C=O groups. This means that compounds **III** and **VII** in CCl_4 and $CDCl_3$ solutions are present in the cyclic form.

The composition and structure of compounds were established from the data of elemental analysis, high resolution mass spectrometry, and spectral characteristics. The assignment of the signals in the ^{19}F NMR spectra of compounds and cations **VI** and **X** was performed from the chemical shifts of the signals, their fine structure, and integral intensity. The regularity observed in the spectra of cations **VI** and **X** are in agreement with similar regularities for the other polyfluoroisochromenyl cations [4, 6].

EXPERIMENTAL

IR spectra were registered on a spectrophotometer Bruker Vector 22. UV spectra were taken on a spectrophotometer Hewlett Packard 8453 ^{19}F, ^{13}C, and ^{1}H spectra were recorded on a spectrometer Bruker AV-300 (operating frequencies 282.4, 75.5, 300 MHz respectively). The chemical shifts are reported downfield with respect to C_6F_6 (^{19}F) and TMS (^{1}H, ^{13}C), internal references C_6F_6 and SO_2ClF (δ_F 262.8 ppm), $CDCl_3$ (δ_C 76.9 ppm), $CHCl_3$ (δ_H 7.24 ppm). The elemental composition was determined by high resolution mass spectrometry on instruments Finnigan MAT 8200 and Thermo Electron Corporation DFS. The GLC analysis was performed on a chromatograph LKhM-72 (50–270°C, column 4000 × 4 mm, stationary phase SKFFT-50 on Chromosorb W, the ratio stationary phase–inert carrier 15 : 100, carrier gas helium, flow rate 60 ml/min). GC-MS analyses were carried out on an instrument Hewlett Packard G1081A coupled with a gas chromatograph HP 5890 of series II and a mass-selective detector HP 5971 (EI, 70 eV). Capillary column HP 5 (5% phenyl-, 95% dimethylsiloxane): 30 m × 0.25 mm × 0.25 μm. Carrier gas helium, flow rate 1 ml/min. The content of compounds in mixtures (yield) was established from the data of GLC, GC-MS, and ^{19}F NMR spectra.

Reaction of perfluoro-3,3-diethylindan-1-one (II) with SbF_5. *a*. A mixture of 1.78 g (3.74 mmol) of compound **II** [2] and 6.76 g (31.18 mmol) of SbF_5 was heated in a nickel pressure reactor of 10 ml capacity over 15 h at 180°C. Then the mixture was transferred into 5% water solution of HCl, extracted with CH_2Cl_2, the extract was dried with $MgSO_4$. On distilling off the solvent in a vacuum we obtained 1.64 g of mixture containing compound **II** and perfluoro-1,3-dimethyl-4-ethyl-1*H*-isochromen-1-ol **(III)** in a ratio 78 : 22 (^{19}F NMR data).

b. Similarly to experiment *a* from 1.8 g (3.78 mmol) of

compound **II** and 6.56 g (30.26 mmol) of SbF_5 (180°C, 74 h) we obtained 1.69 g of a mixture containing 35% of ketone **II**, 50% of compound **III**, and 7% of perfluoro-1,1-diethylindana (**IV**).

c. A mixture of 5.0 g (10.5 mmol) of compound **II** and 13.59 g (62.68 mmol)of SbF_5 was heated in a nickel pressure reactor over 27 h at 180°C. To a part of the mixture obtained (1.56 g) was added 0.31 g of SO_2ClF, and the ^{19}F NMR spectrum was registered containing unresolved signals of cation **VI**. Then the mixture was treated with 30 ml of anhydrous HF and was poured on ice, the reaction products were extracted into CH_2Cl_2. The organic layer was separated, washed with water, dried with $MgSO_4$, and the solvent was distilled off. We obtained 4.35 g of a mixture containing according to the ^{19}F NMR spectrum compounds **II**, **III, IV**, and **perfluoro-1,3-dimethyl-4-ethyl-1*H*-isochromen (V)** in the ratio 50 : 2 : 6 : 42. The mixture was subjected to column chromatography on silica gel (eluent hexane) to obtain 1.53 g (31%) of compound **V** and by elution with $CHCl_3$ 1.99 g of ketone **II**.

Compound V. Liquid. UV spectrum (hexane), λ_{max}, nm (lgε): 221 (3.81), 259 (3.79), 288 (3.59). IR spectrum (CCl_4), ν, cm^{-1}: 1523, 1492 (fluorinated aromatic ring). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 104.6 d.q (C*1*, $^1J_{CF}$ 242, $^2J_{CF}$ 41 Hz), 107.5 d.d (C*8a*, $^2J_{CF}$ 22, 12 Hz), 110.3 t (C*4*, $^2J_{CF}$ 30 Hz), 111.4 d (C*4a*, $^2J_{CF}$ 13 Hz), 113.5 t.q (CF_2, $^1J_{CF}$ 261, $^2J_{CF}$ 43 Hz), 117.8 q (3-CF_3, $^1J_{CF}$ 275 Hz), 118.8 q.t (4-CF_3, $^1J_{CF}$ 289, $^2J_{CF}$ 37 Hz), 119.4 q.d (1-CF_3, $^1J_{CF}$ 289, $^2J_{CF}$ 39 Hz), 142.2 d.d.d (C*6,7*, $^1J_{CF}$ 263, $^2J_{CF}$ 17, 12 Hz) and 143.9 d.d.d ($^1J_{CF}$ 262, $^2J_{CF}$ 18, 12 Hz), 143.7 q (C*3*, $^2J_{CF}$ 42 Hz), 143.5 d.d (C*5,8*, $^1J_{CF}$ 259, $^2J_{CF}$ 13 Hz) and 145.4 d.d ($^1J_{CF}$ 262, $^2J_{CF}$ 13 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: 15.3 (1F, F*7*), 16.9 (1F, F*6*), 28.2 (1F, F*8*), 32.8 (1F, F*5*), 46.3 br.s (1F, F*1*), 64.9 br.d.d (1F, F_B) and 68.4 br.d (1F, F_A, CF_2), 78.1 br.s (3F, 1-CF_3), 88.3 (3F, 4-CF_3), 95.1 m (3F, 3-CF_3); *J*(FF), Hz: *J*(*8*, 1-CF_3) 18, *J*(3-CF_3–4-CF_3) 8, *J*(*5*, 4-CF_3) 30, $J_{A,B}$ 280, $J_{B,5}$ ~45, $J_{1,6}$ 3, $J_{1,8}$ 30, $J_{5,6}$ 20, $J_{5,7}$ 8, $J_{5,8}$ 12, $J_{6,7}$ 20, $J_{6,8}$ 9, $J_{7,8}$ 21. Found M^+ 475.9690. $C_{13}F_{16}O$. Calculated *M* 475.9688.

Perfluoro-1,3-dimethyl-4-ethyl-1*H*-isochromen-1-ol (III). In 1.02 g (4.7 mmol) of SbF_5 was dissolved 0.3 g (0.63 mmol) of compound **V**, and ^{19}F NMR spectrum was registered containing the signals of cation **VI**. The reaction mixture was poured into 45% water solution of H_2SO_4 and extracted with CH_2Cl_2. The solvent was evaporated from the extract in a vacuum. The residue was dissolved in 5 ml of hexane, filtered, and the solvent was distilled off in a vacuum. We obtained 0.25 g (84%) of compound **III** that was additionally purified by "sublimation" in a vacuum (40°C, 2 mm Hg). Liquid. IR spectrum (CCl_4), ν, cm^{-1}: 3556 (OH), 1519, 1490 (fluorinated aromatic ring). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 4.44 br.s (1H, OH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 96.3 q (C*1*, $^2J_{CF}$ 37 Hz), 109.5 t (C*4*, $^2J_{CF}$ 30 Hz), 110.7 m (C*4a,8a*) and 112.0 d ($^2J_{CF}$ 13 Hz), 113.8 t.q (CF_2, $^1J_{CF}$ 260, $^2J_{CF}$ 42 Hz), 119.0 q.t (4-CF_3, $^1J_{CF}$ 289, $^2J_{CF}$ 37 Hz), 118.1 q (1,3-CF_3, $^1J_{CF}$ 275 Hz) and 121.2 q ($^1J_{CF}$ 290 Hz), 142.1–145.6 (C*5,6,7,8*), 145.2 q (C*3*, $^2J_{CF}$ 40 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: 13.8 (1F, F*7*), 14.4 (1F, F*6*), 28.4 (1F, F*8*), 31.8 (1F, F*5*), 64.0 (1F, F_B) and 70.1 br.d (1F, F_A, CF_2), 77.4 br.s (3F, 1-CF_3), 88.7 (3F, 4-CF_3), 94.8 (3F, 3-CF_3); *J*(FF), Hz: *J*(*8*, 1-CF_3) 12, *J*(3-CF_3–4-CF_3) 8, *J*(*A*, 3-CF_3) 22, *J*(*B*, 3-CF_3) 6, *J*(*5*, 4-CF_3) 31, $J_{A,B}$ 279, $J_{A,5}$ 15, $J_{B,5}$ 54, $J_{5,6}$ 20, $J_{5,7}$ 7, $J_{5,8}$ 12, $J_{6,7}$ 20, $J_{6,8}$ 8, $J_{7,8}$ 21. Found, %: C 33.20; H 0.07; F 60.23. $C_{13}HF_{15}O_2$. Calculated, %: C 32.93; H 0.21; F 60.11.

Reaction of compound III with $NaHCO_3$. *a*. A mixture of 1.19 g of compounds **II** and **III** (in molar ratio 70:30) was dissolved in 15 ml of CCl_4, washed with a saturated water solution of $NaHCO_3$, dried with $MgSO_4$, and the solvent was distilled off. We obtained 1.05 g of a mixture containing according to the ^{19}F NMR data compound **II** and 5,6,7,8-tetrafluoro-1,3-bis(trifluoromethyl)-1*H*-isochromen-1-ol **(VII)** in the ratio 70:30. The mixture was subjected to column chromatography on silica gel. Elution with $CHCl_3$ yielded 0.7 g of compound **II** and 0.23 g (86%) of alcohol **VII**. The analytical sample of alcohol **VII** was obtained by "sublimation" at 90°C in a vacuum (30 mm Hg).

b. A solution of 0.26 g (0.55 mmol) of compound **III** in 2 ml of CCl_4 was washed with a saturated solution of $NaHCO_3$. The water layer was separated, acidified with aqueous HCl and extracted with diethyl ether. The solution in CCl_4 and diethyl ether extract were combined and dried with $MgSO_4$. The obtained mixture according to ^{19}F NMR spectrum contained equal amounts of compound **VII** and CF_3COOH. The mixture was washed with the water solution of $NaHCO_3$, dried with $MgSO_4$, and the solvent was distilled off to obtain 0.18 g (92%) of compound **VII**.

Compound VII. Liquid. UV spectrum (hexane), λ_{max}, nm (log ε): 263 (3.86), 272 (3.81), 292 (3.64), 302 (3.62). IR spectrum (CCl_4), ν, cm^{-1}: 3558 (OH), 3124 (CH), 1520, 1495 (fluorinated aromatic ring). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.61 d (1H, H*4*, J_{H^4,F^8} 2 Hz), 4.59 br.s

(1H, OH). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 95.1 d (C^4, $^1J_{CH}$ 78 Hz), 96.6 q (C^1, $^2J_{CF}$ 37 Hz), 106.8 d ($C^{4a,8a}$, $^2J_{CF}$ 10 Hz) and 114.2 d ($^2J_{CF}$ 15 Hz), 118.5 q (1,3-CF_3, $^1J_{CF}$ 272 Hz) and 121.4 q ($^1J_{CF}$ 290 Hz), 141.4 q (C^3, $^2J_{CF}$ 39 Hz), 141.5 d.d.d ($C^{6,7}$, $^1J_{CF}$ 258, $^2J_{CF}$ 17, 12 Hz) and 142.5 d.d.d ($^1J_{CF}$ 259, $^2J_{CF}$ 16, 13 Hz), 142.4 d.d ($C^{5,8}$, $^1J_{CF}$ 255, $^2J_{CF}$ 12 Hz) and 146.3 d.d ($^1J_{CF}$ 260, $^2J_{CF}$ 12 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: 11.0 (1F, F^7), 12.5 (1F, F^6), 17.4 (1F, F^5), 28.4 (1F, F^8), 75.1 (3F, 1-CF_3), 89.1 s (3F, 3-CF_3); *J*(FF), Hz: $J(8, 1\text{-}CF_3)$ 15, $J_{5,6}$ 20, $J_{5,7}$ 2, $J_{5,8}$ 13, $J_{6,7}$ 20, $J_{6,8}$ 8, $J_{7,8}$ 20, J_{8,H^4} 2. Found M^+ 355.9891. $C_{11}H_2F_{10}O_2$. Calculated *M* 355.9895.

1,3-Bis(trifluoromethyl)-5,6,7,8-tetrafluoro-1-chloro-1*H*-isochromen (IX). To a mixture of 0.1 g (0.28 mmol) of compound **VII** and 0.83 g (6.97 mmol) of $SOCl_2$ was added 2 drops of DMF, and the mixture was stirred for 9.5 h at 75°C. $SOCl_2$ was distilled off, the product was obtained by distillation at 70°C in a vacuum (20 mm Hg). The product was dissolved in CH_2Cl_2, the solution was washed with a solution of $NaHCO_3$, dried with $MgSO_4$, and the solvent was distilled off. Yield 0.054 g (51%). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 6.93 d (1H, H^4 J_{H^4,F^8} 2 Hz). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: 12.7 (1F, F^7), 13.3 (1F, F^6), 18.6 (1F, F^5), 31.5 (1F, F^8), 84.1 (3F, 1-CF_3), 89.4 c (3F, 3-CF_3); *J*(FF), Hz: $J(8, 1\text{-}CF_3)$ 35, $J_{5,6}$ 21, $J_{5,7}$ 4, $J_{5,8}$ 13, $J_{6,7}$ 20, $J_{6,8}$ 9, $J_{7,8}$ 20, $J_{8,H}$ 2. Found M^+ 373.9568. $C_{11}HClF_{10}O$. Calculated *M* 373.9556.

4-Pentafluoroethyl-1,3-bis(trifluoromethyl)-5,6,7,8-tetrafluoro-1-chloro-1*H*-isochromen (VIII). To 2.57 g of a mixture of compounds **II** and **III** (at the molar ratio 82:18) and 0.66 g of $SOCl_2$ was added 2 drops of DMF, and the mixture was stirred for 6.5 h at 80°C. Excess $SOCl_2$ was distilled off in a vacuum to obtain 2.42 g of a mixture containing according to ^{19}F NMR data compounds **II** and **VIII** in a ratio 83:17. With the use of column chromatography on silica gel (eluent hexane) we isolated 1.79 g of ketone **II** and 0.28 g (58%) of compound **VIII**. The analytical sample of compound **VIII** was obtained by "sublimation" at 90°C in a vacuum (30 mm Hg). Liquid. UV spectrum (hexane), λ_{max}, nm (log ε): 213 (4.20), 261 (3.87), 289 (3.56). IR spectrum (CCl_4), ν, cm^{-1}: 1517, 1492 (fluorinated aromatic ring). ^{19}F NMR spectrum ($CDCl_3$), δ, ppm: 14.2 (1F, F^6), 14.7 (1F, F^7), 30.1 (1F, F^8), 33.4 (1F, F^5), 63.9 ($1F_B$) and 71.0 br.d ($1F_A$, CF_2), 87.0 (3F, 1-CF_3), 88.9 (3F, 4-CF_3), 94.8 (3F, 3-CF_3); *J*(FF), Hz: $J(8, 1\text{-}CF_3)$ 40, J(3-CF_3–4-CF_3) 8, $J(A, 3\text{-}CF_3)$ 21, $J(B, 3\text{-}CF_3)$ 6, $J(5, 4\text{-}CF_3)$ 30, $J_{A,B}$ 280, $J_{A,5}$ 18, $J_{B,5}$ 49, $J_{5,6}$ 20, $J_{5,7}$ 7, $J_{5,8}$ 12, $J_{6,7}$ 20, $J_{6,8}$ 8, $J_{7,8}$ 20. Found M^+ 491.9410. $C_{13}ClF_{15}O$. Calculated *M* 491.9398.

Perfluoro-1,3-dimethyl-4-ethylisochromenyl cation (VI). *a*. In 1.03 g (4.75 mmol) of SbF_5 was dissolved 0.19 g (0.39 mmol) of compound **VIII**, and 0.29 g of SO_2ClF was added. The ^{19}F NMR spectrum of the solution obtained contained the signals of cation **VI**. The solution was poured into 5% water solution of HCl, extracted with CCl_4, the extract was dried with $MgSO_4$, and the solvent was distilled off. We obtained 0.16 g of a mixture that according to the data of GC-MS contained 80% of alcohol **III** (yield 70%).

b. To 0.99 g (6.6 mmol) of CF_3SO_3H was added 0.11 g (0.23 mmol) of alcohol **III**. The ^{19}F NMR spectrum of solution obtained contained the signals of cation **VI** and alcohol **III** in a ratio 65 : 35.

Cation VI. ^{19}F NMR spectrum (SbF_5–SO_2ClF), δ, ppm: 35.5 (1F, F^7), 48.5 (1F, F^5), 59.0 (1F, F^8), 69.1 (2F, CF_2), 71.4 (1F, F^6), 89.4 (3F, 4-C_2F_5), 99.4 (3F, 1-CF_3), 103.4 (3F, 3-CF_3). ^{19}F NMR spectrum (CF_3SO_3H), δ, ppm: 35.4 (1F, F^7), 47.7 (1F, F^5), 57.7 (1F, F^8), 69.2 (2F, CF_2), 70.6 (1F, F^6), 89.7 (3F, 4-CF_3), 99.4 (3F, 1-CF_3), 103.6 (3F, 3-CF_3); *J*(FF), Hz: $J(8, 1\text{-}CF_3)$ 40, J(3-CF_3–4-CF_3) 8, J(3-CF_3–CF_2) 19, $J(5, 4\text{-}CF_3)$ 31, $J(5, CF_2)$ ~60, $J_{5,6}$ 18, $J_{5,7}$ 15, $J_{5,8}$ 10, $J_{6,7}$ 20, $J_{6,8}$ 34, $J_{7,8}$ 18.

1,3-Bis(trifluoromethyl)-5,6,7,8-tetrafluoro-isochromenyl cation (X). *a*. In 2.13 g (9.82 mmol) of SbF_5 was dissolved 0.045 g (0.12 mmol) of compound **IX**, and 0.1 g of SO_2ClF. was added. The ^{19}F NMR spectrum of the solution obtained contained the signals of cation **X**. The solution was poured in water, extracted with CH_2Cl_2, the extract was dried with $MgSO_4$, and the solvent was distilled off. We obtained 0.031 g (72%) of alcohol **VII**.

b. To 0.90 g (6 mmol) of CF_3SO_3H was added 0.11 g (0.31 mmol) of alcohol **VII**. The ^{19}F NMR spectrum of the solution obtained contained the signals of cation **X** and no signals of alcohol **VII**. The solution was poured in water, extracted with CH_2Cl_2, the extract was dried with $MgSO_4$, and the solvent was distilled off. We obtained 0.1 g (91%) of alcohol **VII**.

Cation X. ^1H (CF_3SO_3H, internal reference CH_2Cl_2, δ_H 5.28 ppm from TMS), δ, ppm: 9.45 s (H^4). ^{19}F NMR spectrum (SbF_5–SO_2ClF), δ, ppm: 31.2 (1F, F^5 or F^7), 33.2 (1F, F^5 or F^7), 51.3 (1F, F^8), 60.9 (1F, F^6), 96.0 s (3F, 3-CF_3), 98.8 (3F, 1-CF_3). ^{19}F NMR spectrum (CF_3SO_3H), δ, ppm: 31.6 (1F, F^5 or F^7), 33.2 (1F, F^5 or F^7), 49.7 (1F,

F^{8}), 59.9 (1F, F^{6}), 96.6 s (3F, 3-CF_3), 99.0 (3F, 1-CF_3); J(FF), Hz: J(*8*, 1-CF_3) 35, $J_{5,6}$ 9, $J_{6,7}$ 9, $J_{5,7}$ 10, $J_{5,8}$ 15, $J_{7,8}$ 15, $J_{6,8}$ 26.

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