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Reaction of perfluoro-1-ethylindan with SiO_2/SbF_5 and skeletal transformations of perfluoro-3-ethylindan-1-one under the action of SbF_5 and SiO_2/SbF_5

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Dedicated to the Centenary of Academician, Professor N.N. Vorozhtsov, Jr.

Abstract

Perfluoro-1-ethylindan heated with excess of SiO_2 in an SbF_5 medium at 75 °C and then treated with water, gives 4-carboxy-perfluoro-3-methylisochromen-1-one. Perfluoro-3-ethylindan-1-one is converted, under the action of SbF_5 at 70 °C, to perfluoro-2-(but-2-en-2-yl)benzoic acid as a mixture of *E*- and *Z*-isomers. When the reaction temperature is raised to 125 °C, a solution of salts of perfluoro-3,4-dimethyl-1H-isochromen-1-yl and perfluoro-4-ethyl-1H-isochromen-1-yl cations is obtained. Increase in the reaction time lowers the content of a salt of the latter cation in the solution. Hydrolysis of the solution of the salts gives perfluoro-3,4-dimethylisochromen-1-one and perfluoro-4-ethylisochromen-1-one.

Keywords: Skeletal transformations; Perfluoro-1-ethylindan; Perfluoro-3-ethylindan-1-one; Silicon dioxide; Antimony pentafluoride; NMR spectroscopy

1. Introduction

Perfluorinated benzocyclobutene, indan, tetralin and their perfluoroalkyl and perfluoroaryl derivatives when heated with antimony pentafluoride undergo skeletal transformations to give products of cleavage, expansion or contraction of the alicyclic ring of benzocycloalkenes [1–4] (see also references [1–7] cited in article [2]). Thus, perfluoro-1-ethylindan (**1**) isomerizes into perfluoro-1,1-dimethylindan and perfluoro-2-(but-2-en-2-yl)toluene; the latter cyclizes to perfluoro-1,2-dimethylindan [5]. Perfluoro-1-methylindan, when heated with SbF_5 in a nickel bomb, is transformed to perfluoro-2-isopropyltoluene [1], and when heated with SbF_5 in a glass ampoule, it reacts with glass as a source of inorganic oxides to give perfluoro-4-methyl-1H-isochromene [6] (Scheme 1).

Apparently, the reaction with glass proceeds via intermediate formation of perfluoro-3-methylindan-1-one. On the other hand, we have found that perfluoroindan reacts with SiO_2/SbF_5 to give perfluoroindan-1-one in a good yield. The latter under the action of SbF_5 undergoes five-membered ring cleavage to form perfluoro-2-ethylbenzoic acid [7].

In this connection it was worthwhile to study the reaction of a number of perfluoroalkylindanes with silica in the presence of SbF_5 and the behaviour of their carbonyl derivatives under the action of antimony pentafluoride with the aim to study the possibility of their cationoid skeletal transformations. This work describes the reactions of ethylindan **1** with SiO_2/SbF_5 and with glass in an SbF_5 medium and transformations of perfluoro-3-ethylindan-1-one (**2**) under the action of antimony pentafluoride.

2. Results and discussion

It has been shown that reaction of ethylindan **1** with SiO_2 (0.6 mol per 1 mol of compound **1**) in the presence of SbF_5 at 70 °C gives, after treatment of the reaction mixture with water, indanone **2** together with 4-fluorocarbonyl-perfluoro-3-methylisochromen-1-one (**3**), 4-carboxy-perfluoro-3-methylisochromen-1-one (**4**) and 5,6,7,8-tetrafluoro-3-hydroxy-3-trifluoromethyl-3,4-dihydroisochromen-1-one (**5**). The reaction mixture also contains unchanged compound **1** (Scheme 2). Reaction of indan **1** with excess of SiO_2 in an SbF_5 medium at

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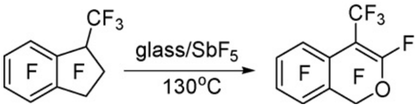


Scheme 1.

75 °C forms a solution of a salt of 4-fluorocarbonyl-perfluoro-3-methyl-1H-isochromen-1-yl cation (**6**). Hydrolysis of the latter gives acid **4**. The reaction of indan **1** with excess of SiO_2/SbF_5 at 130 °C forms compound **4** together with tetrafluorophthalic acid (**7**) (Scheme 2).

These data indicate that ketone **2** undergoes further transformations under the reaction conditions of ethylindan **1** with SiO_2/SbF_5. Apparently, it may be connected with skeletal transformations of compound **2** in the presence of antimony pentafluoride. Ketone **2** was synthesized under milder conditions by reaction of ethylindan **1** with CF_3COOH in the presence of SbF_5 at room temperature [9] and behaviour of ketone **2** in an SbF_5 medium was investigated.

Heating ketone **2** with SbF_5 at 70 °C (7 h) gives, after treatment of the reaction mixture with water, perfluoro-2-(but-2-en-2-yl)benzoic acid (**8**) as a mixture of *E*- and *Z*-isomers together with small amounts of perfluoro-3,4-dimethylisochromen-1-one (**9**). The reaction mixture also contains unchanged compound **2** (Scheme 3).

Transformation of indanone **2** in the presence of SbF_5 to the acid **8** may be represented by Scheme 3. At first, compound **2** with SbF_5 seems to generate the cation **2c**. The five-membered ring of the latter may undergo ring opening to yield the benzoyl type ion **10**, which undergoes isomerization with removal of the double bond inside the chain to form fluoroanhydride **11**. Hydrolysis of the latter gives acid **8**. This scheme is analogous to that for five-membered ring opening of ethylindan **1** under the action of antimony pentafluoride [5].

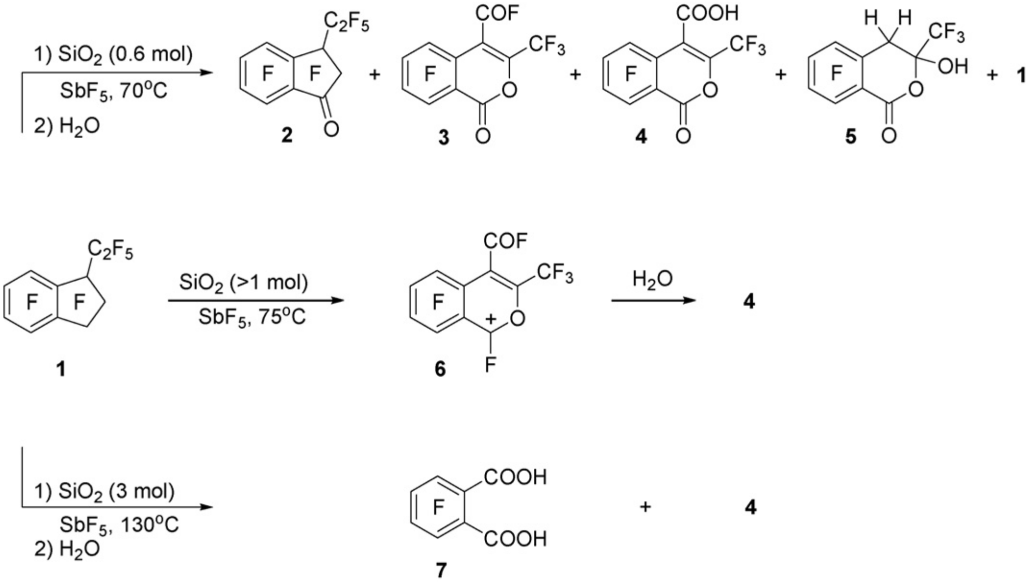
When the reaction temperature is raised to 125 °C (7 h), a solution of salts of perfluoro-3,4-dimethyl-1H-isochromen-1-yl (**12**) and perfluoro-4-ethyl-1H-isochromen-1-yl cations (**13**) is obtained. Hydrolysis of the solution of the salts gives compound **9** and perfluoro-4-ethyl-isochromen-1-one (**14**). The reaction mixture also contains acid **8** and 5,6,7,8-tetrafluoro-3-hydroxy-3,4-bis(trifluoromethyl)-3,4-dihydroisochromen-1-one (**15**) (Scheme 4). Formation of the latter from compound **9** will be discussed below (Scheme 6).

The probable mechanism for the transformation of indanone **2** in the presence of SbF_5 to salts of cations **12** and **13** can be formulated as shown in Scheme 4. At first ketone **2** isomerizes into fluoroanhydride **11** (Scheme 3). Then an allyl type cation **16** is generated from compound **11** under the action of antimony pentafluoride. An intramolecular attack of one or another positively charged carbon atom of the allyl system of cation **16** at the fluorocarbonyl oxygen atom gives cations **17** and **18**. These ions undergo isomerization with removal of the double bond inside the cycle to form cations **12** and **13**.

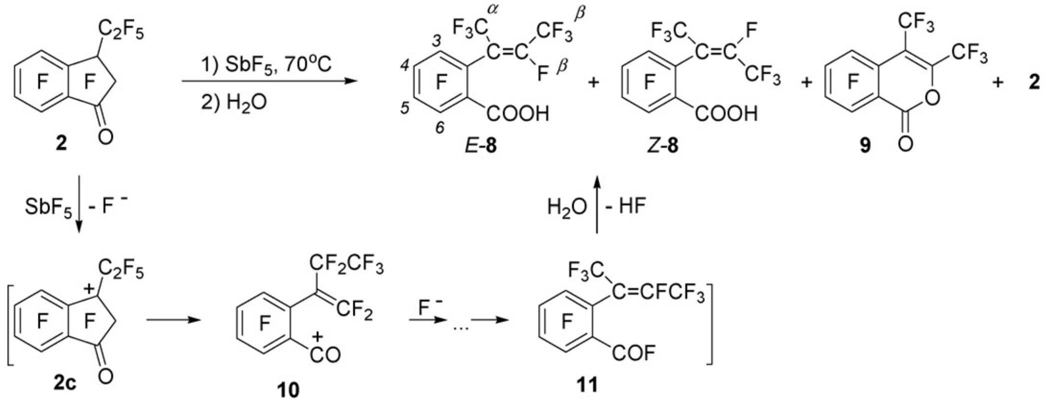
The mixture of compounds **9** and **14**, obtained in the reaction of ketone **2** with SbF_5 at 125 °C (7 h), apparently, is a result of kinetic control of the reaction. Indeed, increase in the reaction time (130 °C, 57 h) led, after treatment of the reaction mixture with water, to the formation of the mixture, which did not contain compound **14** (Scheme 4). It may be explained in the following way. The isomerization of cations **12** and **13** one to another seems to be reversible, with the equilibrium shifted towards the thermodynamically more stable cation **12**, that makes it possible to convert cation **13** to cation **12**.

Consider possible routes of reaction between ethylindan **1** and SiO_2/SbF_5 (Scheme 5). At first cation **1c** is generated from indan **1** and SbF_5. Then cation **1c** reacts with SiO_2 to form indanon **2** analogously to the formation of perfluoroindan-1-one in the reaction of perfluoroindan with SiO_2/SbF_5 [7].

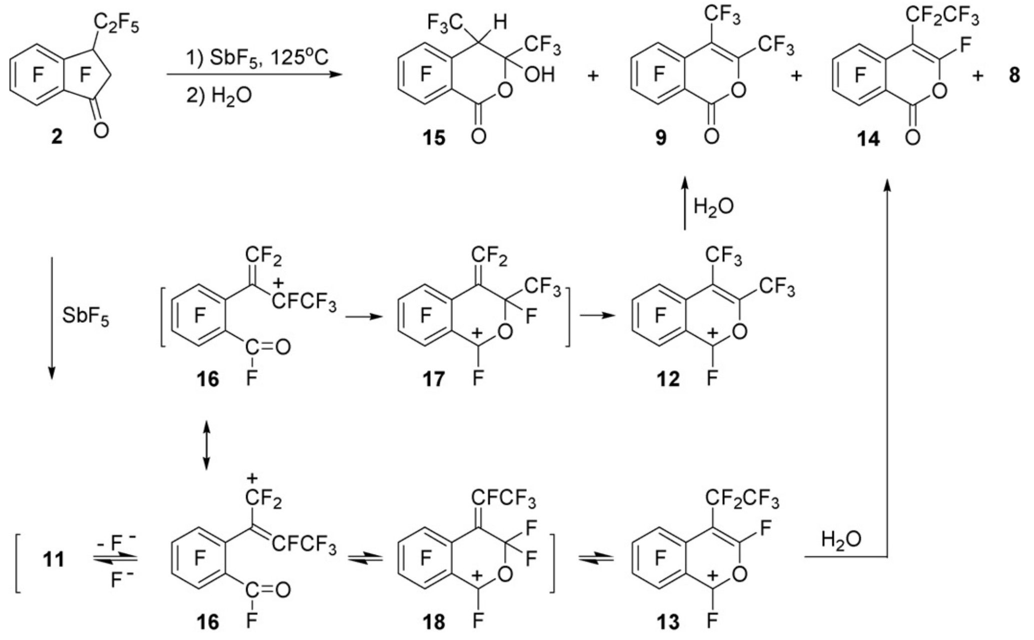
The interaction of ketone **2** with SbF_5 generates cation **16** (its formation was discussed above, Scheme 4), which reacts with SiO_2 to give cation **19**. Intramolecular cyclization of the latter forms cation **20**, which isomerizes to produce cation **6**.



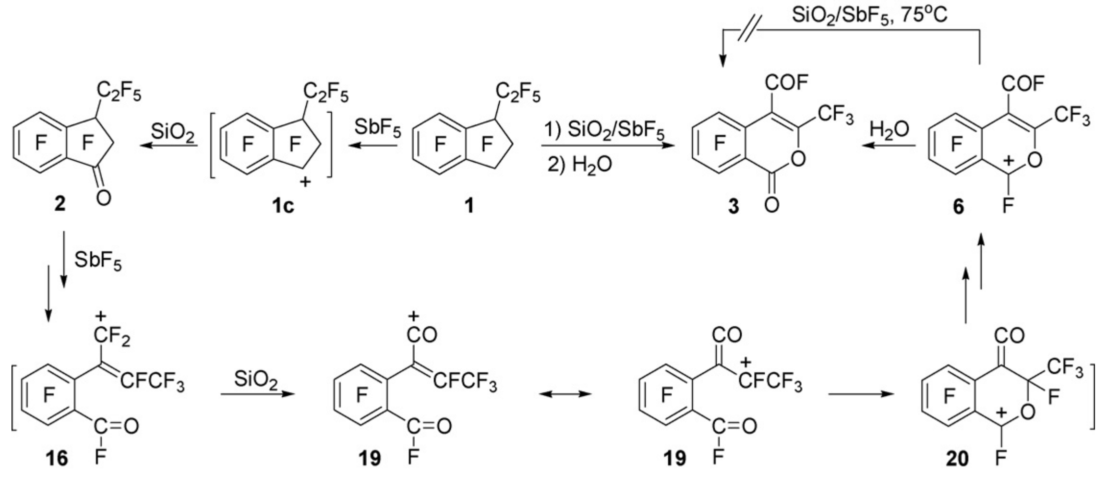
Scheme 2.



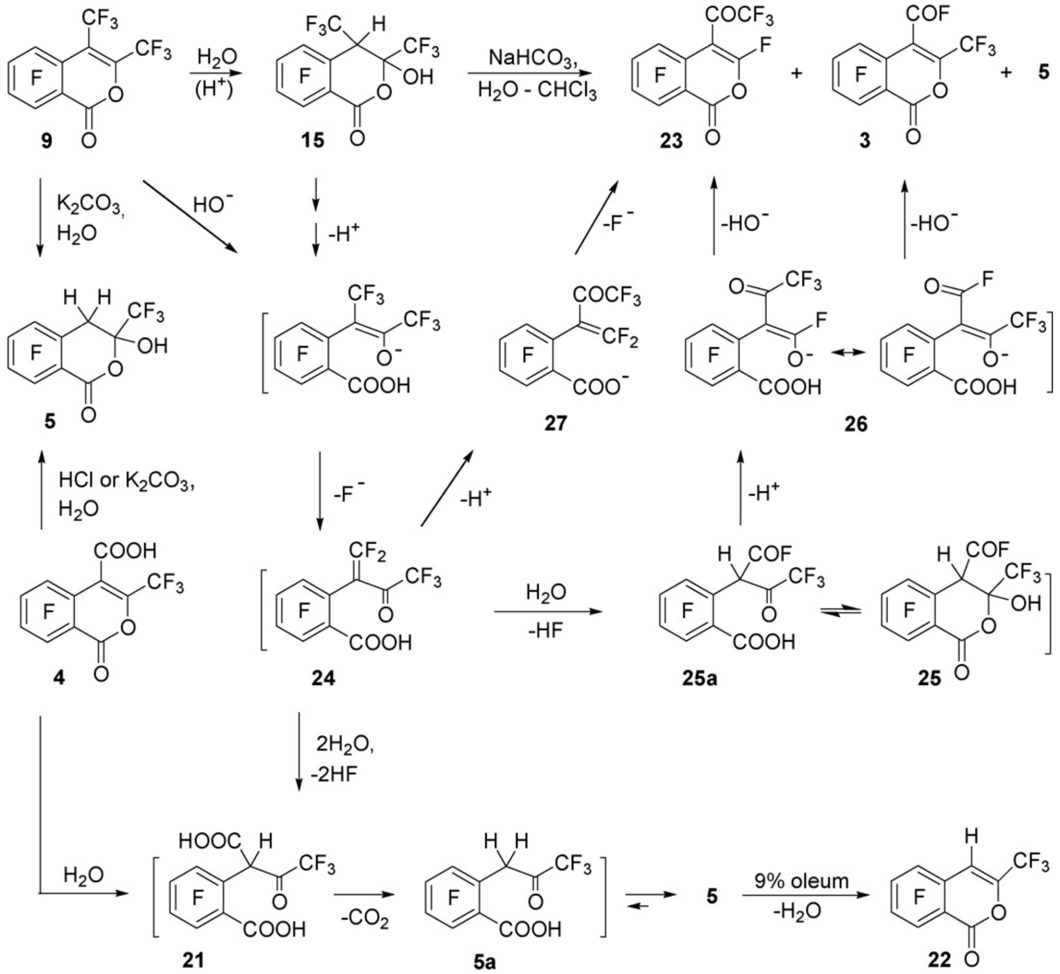
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

Hydrolysis of the latter gives compound **3**. It has been shown in a separate experiment that compound **3** is not the product of the reaction of a salt of cation **6** with SiO_2/SbF_5.

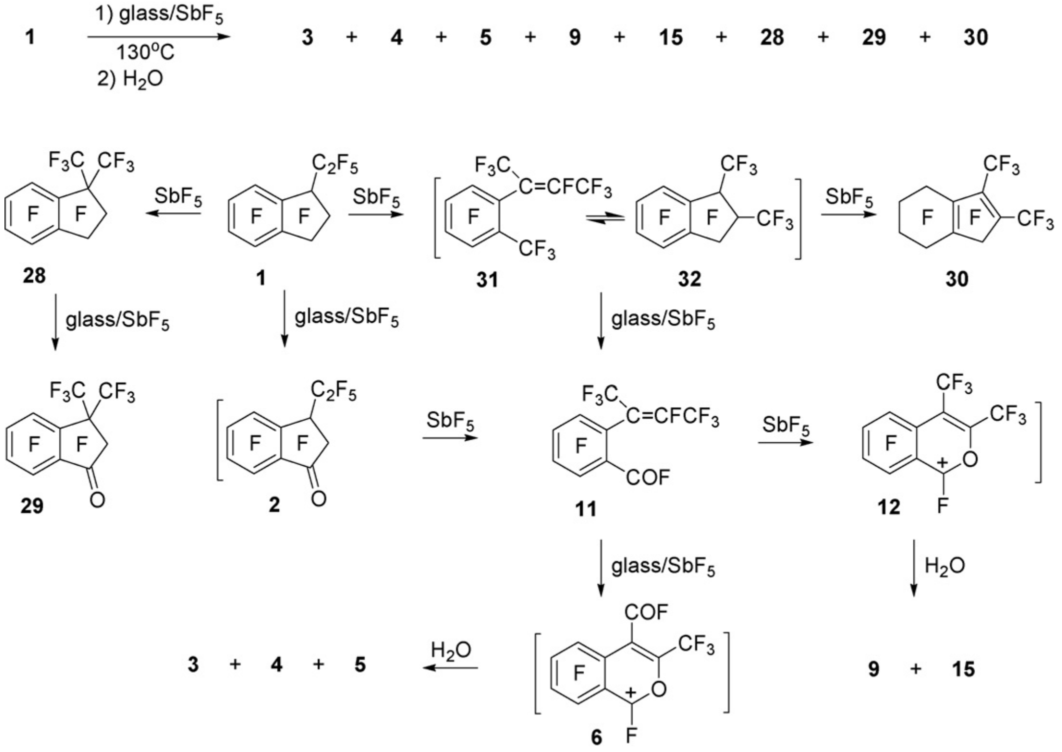
The alternative mechanism for the transformation of indanone **2** to a salt of **6** under the action of SiO_2/SbF_5, which includes interaction of products of cyclization of cation **16** (Scheme 4) with SiO_2, seems unlikely, because the reaction of compound **1** with SiO_2/SbF_5 proceeds at 70 °C, while the reaction of ketone **2** with SbF_5 leading to the formation of a salt of cation **12** (Scheme 4) at this temperature proceeds very slowly. In addition, it was shown that a salt of cation **12** practically does not react with SiO_2 even at 125 °C.

Some amounts of compound **15** were obtained in the reaction of ethylindanone **2** with SbF_5 (Scheme 4). It has been shown by a separate experiment that compound **15** is formed in the reaction of compound **9** with water in an acidic medium. Compound **9**, when treated with aqueous solution of potassium carbonate, is transformed to compound **5**. The latter is also formed in the reaction of acid **4** with water in an alkaline medium as well as in an acidic (Scheme 6).

Apparently, the reaction of acid **4** with water proceeds via intermediate formation of *β*-keto acid **21** that is decarboxylated to give compound **5** (at the bottom of Scheme 6). Dehydration of the latter with oleum forms 5,6,7,8-tetrafluoro-3-trifluoromethylisochromen-1-one (**22**).

Compound **15** under the action of $NaHCO_3$ in two-phase system H_2O–$CHCl_3$ gives a mixture of compounds **3**, **5** and perfluoro-4-acetylisochromen-1-one (**23**). The probable routes for these transformations and for the reaction of compound **9** with K_2CO_3 can be formulated as shown in Scheme 6. At first both compounds **9** and **15** form acid **24**. The latter is transformed to acid **21**, which gives compound **5**. On the other hand, one fluorine atom of CF_2 group of acid **24** is substituted by OH to give finally compound **25a**, which produces delocalised anion **26**. An intramolecular attack of one or another negatively charged oxygen atom of conjugated system of anion **26** at the carbon atom of the carboxyl group gives compounds **3** and **23**. It is also possible that anion **27** generated in the reaction with $NaHCO_3$ from acid **24** undergoes intramolecular cyclization to form compound **23**. Also that dehydration of compound **25** under the reaction conditions gives product **3**, cannot be excluded.

Consider the reaction of ethylindan **1** with a glass in an SbF_5 medium. Heating compound **1** with antimony pentafluoride at 130 °C in a sealed ampoule with further treatment of the reaction mixture with water leads to compounds **3**, **4**, **5**, **9**, **15**.

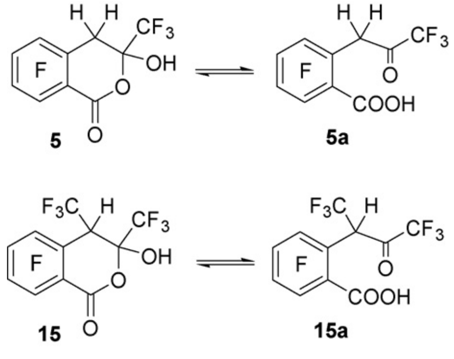


Scheme 7.

The mixture also contains perfluoro-1,1-dimethylindan (**28**), perfluoro-3,3-dimethylindan-1-one (**29**) and perfluoro-2,3-dimethyl-4,5,6,7-tetrahydro-1H-indene (**30**) (Scheme 7).

The probable routes for the transformations of ethylindan **1** under the action of glass/SbF_5 can be formulated as shown in Scheme 7. On heating with SbF_5 at 130 °C in a nickel bomb, ethylindan **1** gives compounds **28**, **30**, **31** and **32** [5]. One can assume that compounds **1**, **28**, **31** and **32** react with glass/SbF_5, similar to the reaction of ethylindan **1** with SiO_2/SbF_5, to produce carbonyl derivatives **2**, **29**, **11**. Ethylindanone **2**, as well as compound **11** under the action of antimony pentafluoride forms a salt of cation **12**. Moreover, compound **11** under the action of glass/SbF_5 produces a salt of cation **6**. As it was mentioned above, hydrolysis of salts of cations **6** and **12** gives compounds **3**, **4**, **5**, **9** and **15**.

Formally, compounds **5** and **15** could exist as cyclic **5** and **15** or/and open-chain **5a** and **15a** forms, respectively (Scheme 8).



Scheme 8.

Signals at 5.20 ppm (OH, ^{1}H NMR) and at 97.6 ppm (C-3, ^{13}C NMR) testify that compound **5** in $CDCl_3$ solution has cyclic structure. ^{1}H NMR spectrum of compound **15** ($CDCl_3$) contains two signals of groups OH at 4.72 and at 5.15 ppm relating to two isomers of cyclic form of compound **15** (E:$Z \sim$ 65:35). According to the ^{19}F NMR spectra, ether solution of compound **5** contains cyclic **5** and open-chain **5a** forms in the ratio 80:20, respectively. In the case of ether solution of compound **15** (E:$Z \sim$ 70:30) the content of open-chain form **15a** is not more than 2%.

The structures of *E*- and *Z*-isomers of acid **8** were defined on the base of the $J_{CF_3(\alpha)-CF_3(\beta)}$ values, which is equal to 11 Hz for *E*-isomer and less than 2 Hz for *Z*-isomer [8]. The structures of *E*- and *Z*-isomers of compound **15** were defined on the base of the $J_{CF_3(3)-CF_3(4)}$ values, which is equal to 10 Hz for *E*-isomer and less than 2 Hz for *Z*-isomer.

3. Experimental

IR spectra were taken on a Bruker Vector 22 IR spectrophotometer. UV spectra were measured on a Hewlett Packard 8453 UV spectrophotometer. ^{19}F NMR and ^{1}H spectra were recorded on a Bruker WP-200 SY and AC-200 instrument (188.3 and 200 MHz, respectively) whereas ^{13}C NMR spectrum of the compound **5** was recorded on a Bruker AM-400 instrument (100.6 MHz). Chemical shifts are given in δ ppm from CCl_3F (^{19}F) and TMS (^{1}H and ^{13}C), J values in Hz; C_6F_6 and SO_2ClF (−162.9 and 99.9 ppm from CCl_3F), $(Me_3Si)_2O$, $CHCl_3$ (0.04 and 7.24 ppm from TMS) and $CDCl_3$ (76.9 from TMS) were used as internal standards. The molecular masses of the compounds were determined by high-resolution spectrometry on a Finnigan Mat 8200 instrument (EI 70 eV). Contents (yields) of products in the reaction mixtures were established by ^{19}F NMR spectroscopic data.

The structures of the compounds were established by elemental analysis, HRMS and spectral characteristics. Assignment of signals in the ^{19}F NMR spectra of the compounds and cations **6**, **12** and **13** was made on the basis of chemical shifts of the signals, their fine structure and integral intensities. Compounds **2**, **29** [9], **28**, **30** [5] were identified by comparison of the ^{19}F NMR data with data for authentic samples.

Antimony pentafluoride was obtained commercially, SiO_2 was prepared by heating of commercial silica gel at 400–450 °C, ethylindan **1** was obtained according to reference [10]. The reactions were carried out in glassware, unless otherwise specified.

*3.1. Reaction of perfluoro-1-ethylindan (**1**) with SiO_2/SbF_5*

1. A mixture of compound **1** (1.50 g), SiO_2 (0.14 g) and SbF_5 (1.24 g) (molar ratio, 1:0.6:1.5) was stirred at 70 °C for 5 h. The mixture was poured into 5% hydrochloric acid and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. The solvent was distilled off to give 1.20 g of mixture, which contained 40% of **1**, 24% (yield 21%) of **2**, 29% (25%) of **3**, 3% (2%) of **4** and 4% (3%) of **5**. The mixture was spontaneously evaporated in the air to dryness to give 0.39 g of a mixture of compounds **3**, **4** and **5**, which was dissolved in CH_2Cl_2 and washed with aqueous solution of $NaHCO_3$ and dried over $MgSO_4$. The solvent was distilled off to give 0.22 g of compound **3**. An analytical sample of compound **3** was prepared by crystallization.

   4-Fluorocarbonyl-perfluoro-3-methylisochromen-1-one (**3**): mp 86.5–87.5 °C (hexane–CH_2Cl_2). UV (hexane) λ_{max}, nm (lg ε): 226 (4.36), 267 (3.76), 310 (3.60). IR (CCl_4) ν, cm^{-1}: 1854, 1797 (C=O); 1519, 1492 [fluorinated aromatic ring (FAR)]. ^{19}F NMR (CH_2Cl_2): δ 56.5 (1F, COF), −68.3 (3F, s, CF_3), −129.1 (1F, F-8), −137.3 (1F, F-5), −139.5 (1F, F-6), −146.2 (1F, F-7); $J_{COF-F(5)} = 12$, $J_{5,6} = 20$, $J_{5,7} = 6$, $J_{5,8} = 14$, $J_{6,7} = 20$, $J_{6,8} = 14$, $J_{7,8} = 20$. HRMS *m/z*, 331.9719 (M^+). Calcd for $C_{11}F_8O_3$ = 331.9720.
2. Analogously to the previous procedure, a mixture of ethylindan **1** (1.29 g), SiO_2 (0.39 g) and SbF_5 (2.46 g) (molar ratio, 1:2:3.5) was heated at 75 °C (6.5 h). The mixture was treated with 5% hydrochloric acid and extracted with ether. The extract was dried over $MgSO_4$. The ether solution contained compounds **3**, **4** and **5** in the ratio 6:90:4. The solvent was distilled off and the residue was sublimed (140 °C, 1 Torr) to give 0.87 g of mixture, which contained compounds **4**, **5** and **22** in the ratio 87:5:8 (yield 71, 4 and 6%, respectively). An analytical sample of acid **4** was prepared by crystallization.

   4-Carboxy-perfluoro-3-methylisochromen-1-one (**4**): mp 192.5–194.5 °C (CCl_4). UV (hexane) λ_{max}, nm (lg ε): 220 (4.33), 317 (3.64). IR (KBr) ν, cm^{-1}: 3501, 3208 (OH); 1762, 1743 (C=O); 1520, 1492 (FAR). ^{1}H NMR [$(CD_3)CO$–CCl_4]: δ 11.05 (s, OH). ^{19}F NMR [$(CD_3)CO$–CCl_4]: δ −68.5 (3F, s, CF_3), −131.8 (1F, F-8), −138.4 (1F, F-5), −143.5 (1F, F-6), −150.1 (1F, F-7); $J_{5,6} = 20$, $J_{5,7} = 5$, $J_{5,8} = 14$, $J_{6,7} = 20$, $J_{6,8} = 12$, $J_{7,8} = 20$. Anal. Calcd for $C_{11}HF_7O_4$: C, 40.0; H, 0.3; F, 40.3. Found: C, 39.8; H, 0.2; F, 40.7%.
3. A mixture of compound **1** (0.61 g), SiO_2 (0.08 g) and SbF_5 (3.35 g) (molar ratio, 1:0.9:10) was stirred at 100 °C (1.5 h) and then at 115 °C (3 h). SO_2ClF was added to the resulting mixture at −15 °C and ^{19}F NMR spectrum of the solution was measured at +20 °C. The spectrum contained signals of cation **6**. The solution was poured into 5% hydrochloric acid and extracted with ether. The extract was dried over $MgSO_4$. The solvent was distilled off and the residue was sublimed (160 °C, 1 Torr) to give 0.43 g (yield 85%) of acid **4**.

   4-Fluorocarbonyl-perfluoro-3-methyl-1H-isochromen-1-yl cation (**6**): ^{19}F NMR (SbF_5–SO_2FCl): δ 60.2 (1F, COF), −7.3 (1F, F-1), −63.6 (3F, s, CF_3), −100.1 (1F, F-6), −107.8 (1F, F-8), −125.5 (1F, F-5), −129.4 (1F, F-7); $J_{1,5} = 4$, $J_{1,6} = 9$, $J_{1,8} = 81$, $J_{COF-F(5)} = 12$, $J_{5,6} = 19$, $J_{5,7} = 13$, $J_{5,8} = 12$, $J_{6,7} = 20$, $J_{6,8} = 31$, $J_{7,8} = 18$.
4. A mixture of compound **1** (0.65 g), SiO_2 (0.15 g) and SbF_5 (3.56 g) (molar ratio, 1:1.5:10) was stirred at 75–80 °C for 7 h. SO_2ClF was added to the mixture at −15 °C and ^{19}F NMR spectrum of the solution was measured at +20 °C. The spectrum contained poorly-resolved signals of cation **6**. Then compound **3** (0.07 g) was added to the solution. ^{19}F NMR spectrum of the resulting solution contained some extra signals as compared with the previous spectrum. The solution was poured into 5% hydrochloric acid and extracted with ether. The extract was dried over $MgSO_4$. The solvent was distilled off and the residue was sublimed (160 °C, 1 Torr) to give 0.52 g (yield 85%) of acid **4**.
5. A mixture of compound **1** (0.71 g), SiO_2 (0.32 g) and SbF_5 (3.87 g) (molar ratio, 1:3:10) was stirred at 90 °C (2 h) and then at 130 °C (11 h). The mixture was treated with 5% hydrochloric acid and extracted with ether. The extract was dried over $MgSO_4$. The ether was distilled off and the residue was sublimed (160 °C, 2 Torr) to give 0.38 g of a mixture, which contained compounds **4** and **7** in the ratio 52:48 (yield 39 and 36%, respectively).

*3.2. Reaction of perfluoro-1-ethylindan (**1**) with glass in the presence of SbF_5 at 130 °C*

A mixture of compound **1** (1.35 g) and SbF_5 (3.67 g) (molar ratio, 1:5) in a sealed ampoule was heated at 130 °C for 49 h. The mixture was treated with 5% hydrochloric acid and extracted with $CHCl_3$ and then with ether. The extracts were dried over $MgSO_4$. The ether solution contained compounds **4** and **5** in the ratio 66:34 and the chloroform solution contained compounds **3**, **4**, **5**, **9**, **15**, **28**, **29** and **30** in the ratio 12:11:4:22:14:9:11:17, respectively. The $CHCl_3$ extract was washed with aqueous solution of $NaHCO_3$ and dried over $MgSO_4$. The solvent was distilled off to give 0.84 g of mixture, which contained 18% (yield 12%) of **3**, 29% (19%) of **9**, 6% (4%) of **23**, 11% (7%) of **28**, 15% (10%) of **29** and 21% (14%) of **30**. The aqueous solution was acidified with HCl, extracted with ether and dried over $MgSO_4$. The solution contained compounds **4** and **5** in the ratio 27:73. Then it was combined with the previous ether extract, the solvent was distilled off and the residue was sublimed (190 °C, 2 Torr) to give 0.24 g of mixture, which contained compounds **4**, **5** and **22** in the ratio 38:42:20 (yield 9, 10 and 5%, respectively).

3.3. Reaction of perfluoro-3-ethylindan-1-one (2) with SbF_5

1. A mixture of compound **2** (0.33 g) and SbF_5 (1.14 g) (molar ratio, 1:6) was heated at 70 °C for 7 h. Then C_6F_6 (0.6 ml) was added and the mixture was poured into 5% hydrochloric acid and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. The solvent and C_6F_6 were distilled off to give 0.21 g of mixture, which contained 2% of **2**, 75% (yield 48%) of *Z*-**8**, 21% (13%) of *E*-**8**, and 2% (1%) of **9**. Sublimation (120 °C, 20 Torr) of the mixture gave 0.05 g of liquid products and 0.16 g of solid products. From the latter fraction 0.08 g of acid **8** (*E*:*Z* ~ 9:91) was obtained by the single crystallization from hexane.

   Perfluoro-2-(but-2-ene-2-yl)benzoic acid (**8**): mixture of two isomers, ratio *E*:*Z* ~ 9:91: mp 70–82 °C (hexane). UV (hexane) λ_{max}, nm (lg ε): 211 (3.95), 224 (3.88), 277 (3.38). IR (CCl_4) ν, cm^{-1}: 3505, 3054 (OH), 1752, 1717 (C=O); 1523, 1481 (FAR). ^1H NMR (CCl_4): δ 11.42 (s, OH). *E*-isomer: ^{19}F NMR (CCl_4): δ −58.9 (3F, CF_3-α), −69.7 (3F, CF_3-β), −107.2 (1F, F-β), −131.3 (1F, F-6), −135.5 (1F, F-3), −145.9 (1F, F-4), −149.1 (1F, F-5); $J_{F(\beta)-CF_3(\beta)} = 7$, $J_{F(\beta)-CF_3(\alpha)} = 11$, $J_{F(\beta)-F(3)} = 3$, $J_{CF_3(\beta)-CF_3(\alpha)} = 11$, $J_{CF_3(\alpha)-F(3)} = 3$, $J_{3,4} = 22$, $J_{3,5} = 6$, $J_{3,6} = 12$, $J_{4,5} = 20$, $J_{4,6} = 10$, $J_{5,6} = 21$.

   Z-isomer: ^{19}F NMR (CCl_4): δ −62.4 (3F, CF_3-α), −70.5 (3F, CF_3-β), −110.1 (1F, F-β), −131.4 (1F, F-6), −134.9 (1F, F-3), −146.0 (1F, F-4), −148.3 (1F, F-5); $J_{F(\beta)-CF_3(\beta)} = 8$, $J_{F(\beta)-CF_3(\alpha)} = 18$, $J_{F(\beta)-F(3)} = 3$, $J_{CF_3(\alpha)-F(3)} = 2$, $J_{3,4} = 22$, $J_{3,5} = 6$, $J_{3,6} = 12$, $J_{4,5} = 20$, $J_{4,6} = 10$, $J_{5,6} = 21$. HRMS (mixture of *E* and *Z*-isomers) *m*/*z*, 373.9799 (M^+). Calcd for $C_{11}HF_{11}O_2 = 373.9801$.
2. A mixture of compound **2** (0.21 g) and SbF_5 (0.94 g) (molar ratio, 1:7.8) in an ampoule with Teflon™ FEP inliner for recording of NMR spectra was heated at 125 °C for 7 h. Then SO_2ClF (0.20 g) was added to the mixture at −15 °C and ^{19}F NMR spectrum of the solution was measured at +20 °C. The spectrum contained signals of cations **12** and **13** in the ratio 82:18. The solution was poured into 5% hydrochloric acid and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. The solution contained compounds **8**, **9**, **14** and **15** in the ratio 10:62:13:15. The extract was washed with aqueous solution of $NaHCO_3$ and dried over $MgSO_4$. The solvent was distilled off and the residue was sublimed (100 °C, 2 Torr) to give 0.12 g (yield 61%) of mixture, which contained compounds **9** and **14** in the ratio 84:16.

   Perfluoro-3,4-dimethyl-1H-isochromen-1-yl cation (**12**): ^{19}F NMR (SbF_5–SO_2ClF): δ −9.3 (1F, F-1), −55.3 (3F, CF_3-4), −60.2 (3F, CF_3-3), −99.3 (1F, F-6), −108.2 (1F, F-8), −116.7 (1F, F-5), −130.9 (1F, F-7); $J_{1,5} = 4$, $J_{1,6} = 9$, $J_{1,8} = 92$, $J_{CF_3(3)-CF_3(4)} = 14$, $J_{CF_3(4)-F(5)} = 46$, $J_{5,6} = 20$, $J_{5,7} = 16$, $J_{5,8} = 11$, $J_{6,7} = 20$, $J_{6,8} = 31$, $J_{7,8} = 20$.

   Perfluoro-4-ethyl-1H-isochromen-1-yl cation (**13**): ^{19}F NMR (SbF_5–SO_2ClF): δ −14.5 (1F, F-1), −60.9 (1F, F-3), −82.0 (3F, CF_3), −97.6 (1F, F-6), −104.5 (2F, CF_2), −109.8 (1F, F-8), −119.6 (1F, F-5), −136.3 (1F, F-7); $J_{1,3} = 10$, $J_{1,5} = 4$, $J_{1,6} = 10$, $J_{1,8} = 94$, $J_{CF_3-F(3)} = 6$, $J_{CF_3-F(5)} = 23$, $J_{CF_2-F(3)} = 41$, $J_{CF_2-F(5)} = 75$, $J_{3,7} = 6$, $J_{5,6} = 20$, $J_{5,7} = 12$, $J_{5,8} = 12$, $J_{6,7} = 20$, $J_{6,8} = 30$, $J_{7,8} = 19$.

   Perfluoro-4-ethylisochromen-1-one (**14**): mixture with isomer **9**, ratio 9:14 ~ 84:16: IR (CCl_4) ν, cm^{-1}: 1799 (C=O); 1518, 1485 (FAR). Compound **14**: ^{19}F NMR (CH_2Cl_2): δ −66.1 (1F, F-3), −83.8 (3F, CF_3), −105.6 (2F, CF_2), −130.9 (1F, F-8), −131.9 (1F, F-5), −139.3 (1F, F-6), −152.6 (1F, F-7); $J_{CF_3-CF_2} = 2$, $J_{CF_3-F(3)} = 10$, $J_{CF_3-F(5)} = 24$, $J_{CF_2-F(3)} = 38$, $J_{CF_2-F(5)} = 72$, $J_{3,5} = 5$, $J_{3,6} = 2$, $J_{3,7} = 5$, $J_{3,8} = 3$, $J_{5,6} = 19$, $J_{5,7} = 5$, $J_{5,8} = 13$, $J_{6,7} = 21$, $J_{6,8} = 14$, $J_{7,8} = 21$. HRMS (mixture of **9** and **14**) *m*/*z*, 353.9745 (M^+). Calcd for $C_{11}F_{10}O_2 = 353.9739$.
3. Analogously to the previous experiments, a solution of compound **2** (0.13 g) in SbF_5 (0.74 g) (molar ratio, 1:10) was prepared and heated at 125 °C. In 35 h the solution contained (^{19}F NMR) cations **6**, **12** and **13** in the ratio 8:80:12 and in 70 h the ratio of the cations became 8:90:2, respectively. Then 0.03 g of SiO_2 was added to the solution and the mixture was heated at 125 °C for 16 h. ^{19}F NMR spectrum of the mixture was measured at +20 °C. The spectrum mainly contained ill-resolved signals of cation **12**. The mixture was treated with 5% hydrochloric acid and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. The solvent was distilled off to give 0.08 g of mixture, which contained compounds **4** and **9** in the ratio 13:87 (yield 9 and 58%, respectively).
4. A mixture of compound **2** (1.03 g) and SbF_5 (5.93 g) (molar ratio, 1:10) was heated in a nickel bomb at 130 °C for 57 h. The mixture was poured into 5% hydrochloric acid and extracted with $CHCl_3$. The extract was dried over $MgSO_4$. The solution contained compounds **3**, **4**, **5**, **9** and **15** in the ratio 3:4:2:61:30. The extract was washed with aqueous solution of $NaHCO_3$ and dried over $MgSO_4$. The solvent was distilled off and the residue was sublimed (100 °C, 5 Torr) to give 0.56 g of mixture, which contained compounds **3**, **9** and **23** in the ratio 8:75:17 (yield 5, 44 and 10%, respectively). An analytical sample of compound **9** was prepared by crystallization. The aqueous solution was acidified with HCl, extracted with ether and dried over $MgSO_4$. The solvent was distilled off to give 0.13 g of mixture, which contained compounds **4** and **5** in the ratio 18:82 (yield 3 and 13%, respectively).

   Perfluoro-3,4-dimethylisochromen-1-one (**9**): mp 97–98 °C (hexane–CH_2Cl_2). UV (hexane) λ_{max}, nm (lg ε): 225 (4.34), 266 (3.78), 309 (3.59). IR (CCl_4) ν, cm^{-1}: 1799 (C=O); 1518, 1485 (FAR). ^{19}F NMR (CH_2Cl_2): δ −57.1 (3F, CF_3-4), −65.2 (3F, CF_3-3), −130.5 (1F, F-5), −131.2 (1F, F-8), −139.7 (1F, F-6), −147.5 (1F, F-7); $J_{CF_3(3)-CF_3(4)} = 14$, $J_{CF_3(4)-F(5)} = 42$, $J_{5,6} = 19$, $J_{5,7} = 8$, $J_{5,8} = 13$, $J_{6,7} = 21$, $J_{6,8} = 13$, $J_{7,8} = 21$. HRMS *m*/*z*, 353.9735 (M^+). Calcd for $C_{11}F_{10}O_2 = 353.9739$.

*3.4. Hydrolysis of 4-carboxy-perfluoro-3-methylisochromen-1-one (**4**) and perfluoro-3,4-dimethylisochromen-1-one (**9**)*

1. To a solution of acid **4** (0.19 g) in 5 ml of ether 5 ml of 5% hydrochloric acid was added and the mixture was stirred at 20 °C for 26 days. Ether solution was separated and dried over $MgSO_4$. The solvent was distilled off to give 0.16 g of mixture, which contained 66% of **4** and 34% (yield 29%) of **5**.
2. Analogously to procedure (1), from 0.12 g of compound **9** (20 °C, 4 d) 0.11 g of compound **15** (E:Z ~ 65:35) was obtained (yield 87%).

   5,6,7,8-Tetrafluoro-3-hydroxy-3,4-bis(trifluoromethyl)-3,4-dihydroisochromen-1-one (**15**): mixture of two isomers, ratio E:Z ~ 65:35: mp 133–139 °C (CH_2Cl_2). UV (hexane) λ_{max}, nm (lg ε): 212 (4.00), 230 (3.82), 284 (3.52), 316 (2.93). IR (CCl_4) ν, cm^{-1}: 3388 (OH); 1770 (C=O); 1523, 1502 (FAR). *E*-isomer: ^1H NMR ($CDCl_3$): δ 4.72 (1H, s, OH), 4.38 (1H, q, $J_{H(4)-CF3(4)} = 7$, H-4). ^{19}F NMR ($CDCl_3$): δ −67.6 (3F, CF_3-4), −83.3 (3F, CF_3-3), −132.6 (1F, F-8), −139.5 (1F, F-5), −142.6 (1F, F-6), −150.4 (1F, F-7); $J_{CF_3(3)-CF_3(4)} = 10$, $J_{CF_3(4)-H(4)} = 7$, $J_{CF_3(4)-F(5)} = 8$, $J_{F(5)-H(4)} = 1$, $J_{5,6} = 20$, $J_{5,7} = 5$, $J_{5,8} = 14$, $J_{6,7} = 20$, $J_{6,8} = 12$, $J_{7,8} = 20$.

   Z-isomer: ^1H NMR ($CDCl_3$): δ 5.15 (1H, s, OH), 4.44 (1H, q, $J_{H(4)-CF3(4)} = 7$, H-4). ^{19}F NMR ($CDCl_3$): δ −65.4 (3F, CF_3-4), −83.8 (3F, c, CF_3-3), −132.3 (1F, F-8),−139.0 (1F, F-5), −142.1 (1F, F-6), −149.1 (1F, F-7); $J_{CF_3(4)-H(4)} = 7$, $J_{CF_3(4)-F(5)} = 7$, $J_{F(5)-H(4)} = 1$, $J_{5,6} = 20$, $J_{5,7} = 6$, $J_{5,8} = 14$, $J_{6,7} = 20$, $J_{6,8} = 12$, $J_{7,8} = 20$. HRMS (mixture of *E* and *Z*-isomers) *m/z*, 371.9815 (M^+). Calcd for $C_{11}H_2F_{10}O_3 = 371.9844$.
3. A mixture of acid **4** (0.63 g) and K_2CO_3 (0.54 g) (molar ratio, 1:2.05) was dissolved in 5 ml of H_2O and heated at 45 °C for 4 h. The aqueous solution was acidified with HCl and extracted with ether. The extract was dried over $MgSO_4$. The solvent was distilled off to give 0.57 g (yield 98%) of compound **5**. An analytical sample of product **5** was prepared by sublimation (100 °C, 2 Torr) and then crystallization.

   5,6,7,8-Tetrafluoro-3-hydroxy-3-trifluoromethyl-3,4-dihydroisochromen-1-one (**5**): mp 108–109 °C (hexane–CH_2Cl_2). UV (heptane) λ_{max}, nm (lg ε): 230 (4.09), 255 (3.29), 261 (3.25), 282 (3.33). IR (CCl_4) ν, cm^{-1}: 3563, 3314 (OH); 1778, 1750 (C=O); 1518, 1499 (FAR). ^1H NMR ($CDCl_3$): δ 5.20 (1H, s, OH), 3.48 (1H, d, $J_{A,B} = 17$, H_A-4) и 3.23 (1H, dd, $J_{A,B} = 17$, $J_{H(B)-F(7)} = 2$, H_B-4). ^{13}C NMR ($CDCl_3$, ^1H decoupled): δ 156.2 (s, C-1), 149.3 (dd, $^1J_{CF} = 271$, $^2J_{CF} = 12$) and 144.5 (dd, $^1J_{CF} = 251$, $^2J_{CF} = 11$, C-5 and C-8), 144.9 (ddd, $^1J_{CF} = 266$, $^2J_{CF} = 16, 13$) and 140.6 (ddd, $^1J_{CF} = 257$, $^2J_{CF} = 16$, 12, C-6 and C-7), 120.9 (q, $^1J_{CF} = 285$, CF_3), 119.0 (d, $^2J_{CF} = 16$) and 107.7 (m, C-4a and C-8a), 97.6 (q, $^2J_{CF} = 35$, C-3), 24.4 (s, C-4). ^{19}F NMR ($CDCl_3$): δ −86.7 (3F, s, CF_3), −133.3 (1F, F-8), −142.7 (1F, F-5), −143.7 (1F, F-6), −154.9 (1F, F-7); $J_{F(5)}-CH_2 = 1$, $J_{F(7)-H(B)} = 2$, $J_{5,6} = 21$, $J_{5,7} = 3$, $J_{5,8} = 14$, $J_{6,7} = 20$, $J_{6,8} = 12$, $J_{7,8} = 20$. HRMS *m/z*, 303.9975 (M^+). Calcd for $C_{10}H_3F_7O_3 = 303.9970$.

   2,3,4,5-Tetrafluoro-6-(3,3,3-trifluoro-2-oxopropyl)benzoic acid (**5a**): ^{19}F NMR (ether), mixture with cyclic form **5**, ratio **5**:**5a** ~ 80:20: δ −85.8 (3F, CF_3), −135.6 (1F, F-5), −138.4 (1F, F-2), −153.8 (1F, F-4), −157.6 (1F, F-3); $J_{CH_2-F(5)} = 2$, $J_{CF_3-F(5)} = 1$, $J_{2,3} = 22$, $J_{2,4} = 5$, $J_{2,5} = 12$, $J_{3,4} = 20$, $J_{3,5} = 4$, $J_{4,5} = 21$.
4. Analogously to the previous procedure, from compound **9** (0.06 g) and K_2CO_3 (0.09 g) (molar ratio, 1:3.8) stirred with 2 ml of H_2O and 15 drops of ether (16 °C, 21 h) 0.05 g of compound **5** was obtained (yield 97%).

*3.5. Perfluoro-4-acetylisochromen-1-one (**23**)*

A solution of compound **15** (0.34 g) in 10 ml of $CHCl_3$ was washed with aqueous solution of $NaHCO_3$ and dried over $MgSO_4$. The solution contained compound **3** and **23** in the ratio 12:88. The solvent was distilled off and the residue was sublimed (110 °C, 10 Torr) to give 0.16 g (yield 50%) of mixture, which contained 26% of **3** and 74% of **23**. The aqueous solution was acidified with HCl and extracted with ether. The extract was dried over $MgSO_4$. The solvent was distilled off to give 0.11 g (yield 37%) of compound **5**.

Perfluoro-4-acetylisochromen-1-one (**23**): mixture with isomer **3**, ratio **3**:**23** ~ 26:74: IR (CCl_4) ν, cm^{-1}: 1854, 1815, 1800, 1760 (C=O); 1515, 1494 (FAR). Compound **23**: ^{19}F NMR (CH_2Cl_2): δ −71.7 (1F, F-3), −77.8 (3F, CF_3), −130.7 (1F, F-8), −137.7 (1F, F-5), −139.9 (1F, F-6), −152.4 (1F, F-7); $J_{CF_3-F(3)} = 8$, $J_{CF_3-F(5)} = 8$, $J_{3,5} = 3$, $J_{3,6} = 2$, $J_{3,7} = 5$, $J_{3,8} = 3$, $J_{5,6} = 20$, $J_{5,7} = 5$, $J_{5,8} = 13$, $J_{6,7} = 20$, $J_{6,8} = 14$, $J_{7,8} = 20$. HRMS (mixture of **3** and **23**) *m/z*, 331.9719 (M^+). Calcd for $C_{11}F_8O_3 = 331.9719$.

*3.6. 5,6,7,8-Tetrafluoro-3-trifluoromethylisochromen-1-one (**22**)*

A solution of compound **5** (0.31 g) in 1 ml of 9% oleum was kept at room temperature for 4 days. Then the solution was poured into water, extracted with CH_2Cl_2, washed with aqueous solution of $NaHCO_3$ and dried over $MgSO_4$. The solvent was distilled off to give 0.27 g (yield 93%) of compound **22**. An analytical sample of product **22** was prepared by crystallization.

5,6,7,8-Tetrafluoro-3-trifluoromethylisochromen-1-one (**22**): mp 102.5–103 °C (CH_2Cl_2). UV (hexane) λ_{max}, nm (lg ε): 224 (4.38), 236 (4.07), 243 (4.04), 255 (3.83), 264 (3.82), 313 (3.62). IR (CCl_4) ν, cm^{-1}: 3119 (C–H), 1782 (C=O); 1516, 1495 (FAR). ^1H NMR (CCl_4): δ 7.07 (d, $J_{H(4)-F(8)} = 2$, H-4). ^{19}F NMR (CH_2Cl_2): δ −73.0 (3F, s, CF_3), −131.2 (1F, F-8), −143.6 (1F, F-6), −145.1 (1F, F-5), −147.5 (1F, F-7); $J_{F(8)-H(4)} = 2$, $J_{5,6} = 20$, $J_{5,7} = 3$, $J_{5,8} = 15$, $J_{6,7} = 20$, $J_{6,8} = 12$, $J_{7,8} = 20$. HRMS *m/z*, 285.9850 (M^+). Calcd for $C_{10}HF_7O_2 = 285.9865$.

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