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Transformations of Perfluorinated 2-Alkyl- and 2,2-Dialkylbenzocyclobutenones in SbF₅ and SiO₂–SbF₅

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Abstract—Perfluorinated 2-methyl- and 2-ethylbenzocyclobutenones on heating in SbF₅ underwent isomerization into perfluorindan-1-one and perfluoro(2-methylindan-1-one), while their reaction with SiO₂–SbF₅ gave perfluorinated 3-methyl- and 3-ethylphthalides, respectively. Perfluorinated 2-ethyl-2-methyl- and 2,2-diethylbenzocyclobutenones reacted with SbF₅ to produce perfluorinated 2-(but-2-en-2-yl)- and 2-(pent-2-en-3-yl)-benzoic acids, and their transformations in SbF₅ over SiO₂ afforded 5,6,7,8-tetrafluoro-1-oxo-3-trifluoromethyl-1*H*-isochromene-4-carboxylic acid and perfluoro(4-ethyl-3-methyl-1*H*-isochromen-1-one), respectively.

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We previously reported on carbocationoid skeletal transformations of carbonyl derivatives of perfluorinated tetralin [1], indan [2], 1-methyl- [3] and 1-ethylindanes [4], benzocyclobutene [1], and 1-ethyl-1phenyl- and 1,1-diethylbenzocyclobutenes [5], which were previously unknown for perfluoro ketones. We found that the behavior of polyfluorinated substrate depends on the size of the carbonyl-containing ring and on the nature of perfluoroalkyl groups therein. The effect of SiO₂ on the transformations of perfluoro-(3-ethylindan-1-one) and perfluoro(3-methylindan-1one) in SbF₅ was revealed [3, 4]. Cationoid skeletal rearrangements of other carbonyl derivatives of polyfluorobenzocycloalkenes were not reported previously.

In the present work we examined the behavior of perfluorinated 2-methyl-, 2-ethyl-, 2-ethyl-2-methyl-, and 2,2-diethylbenzocyclobutenones I-IV in SbF₅ and in the system SiO₂-SbF₅ with a view to reveal general

relations holding in such transformations of polyfluorobenzocycloalkenone derivatives.

Perfluoro(2-methylbenzocyclobuten-1-one) (I) on heating in SbF₅ at 75°C underwent isomerization into perfluoroindan-1-one (V). Apart from compound V, the mixture obtained after treatment of the reaction mixture with water contained small amounts of 2-pentafluoroethyl-3,4,5,6-tetrafluorobenzoic acid (VI), perfluoro(3-methylphthalide) (VII), 4,5,6,7-tetrafluoro-3-hydroxy-3-trifluoromethyl-2-benzofuran-1one (VIII), and unreacted compound I (Scheme 1). Presumably, expansion of the four-membered ring in ketone I occurs according to Scheme 2. Opening of the four-membered ring in cation A generated from compound I by abstraction of fluoride ion yields benzoyl cation **B** which undergoes intramolecular cyclization to cation C, and addition of fluoride ion to the latter gives indanone V.











The formation of acyclic intermediate B from ketone I is confirmed by the presence among the products of an appreciable amount of acid VI (5-7%) which is likely to result from addition of fluoride ion to benzovl cation **B**, fluorination of perfluoro(2-vinylbenzoyl) fluoride thus obtained, and hydrolysis of the fluorination product (Scheme 2). By special experiment we showed that acid VI is not formed via transformation of indanone V under analogous conditions (only traces of VI were detected, $\sim 0.5\%$). On the other hand, the presence of phthalides VII and VIII among the products may be rationalized by transformations of perfluoro(indan-1,3-dione) generated from indanone V via disproportionation or reaction with inorganic oxides [2] formed by reaction of antimony pentafluoride with atmospheric moisture.

Ethylbenzocyclobutenone II underwent isomerization into perfluoro(2-methylindan-1-one) (IX) on heating in SbF₅ under more severe conditions as compared to analogous transformation of methylbenzocyclobutenone I. Hydrolysis of the reaction mixture obtained by heating ketone II with SbF₅ at 120°C (4.5 h) gave a mixture of indanone IX, initial compound II, and small amounts of 3,4,5,6-tetrafluoro-2-heptafluoropropylbenzoic acid (X), perfluoro(3-ethylphthalide) (XI), and 4,5,6,7-tetrafluoro-3-hydroxy-3-pentafluoroethyl-2-benzofuran-1-one (XII) (Scheme 3).

Prolonged heating of compound II in SbF₅ at 130°C (39 h) resulted in the formation of compounds IX–XI together with perfluoro(3-methylisochroman-1one) (XIII) and perfluoro(2-methylindan) (XIV), the



XI, X = F; XII, X = OH.



conversion of initial ketone II being complete. Raising the temperature to 180°C led to predominant formation of acid X; in addition, heterocyclic compounds XI and XIII and perfluoro(3-methylisochromen-1-one) (XV) were formed (Scheme 3).

Presumably, the mechanism of isomerization of pentafluoroethyl-substituted ketone II into methylindanone IX (Scheme 4) is analogous to the transformation of ketone I into indanone V (Scheme 2). More severe conditions for the reaction with ketone II are likely to be necessary because of the lower stability of cation D as compared to A (due to the presence of a trifluoromethyl group rather than fluorine atom at the cationic center in ion D [6]). Analogous reactivity series was observed previously while studying expansion of the four-membered ring in perfluorinated 1-methyl- and 1-ethylbenzocyclobutenes [7].

Phthalides XI and XII and methylindan XIV are likely to be formed in the reaction of ketone II with antimony pentafluoride via disproportionation of indanone IX into indan XIV and perfluoro(2-methylindan-1,3-dione) E (Scheme 4). The latter is converted into phthalides XI and XII by analogy with the transformation of perfluoroindan-1,3-dione into phthalides VII and VIII, which was described previously [2]. This assumption is supported by the fact that compounds XI and XIV are formed in approximately equal amounts in the reaction of II with SbF₅ at 130°C. The formation of acid X and six-membered heterocyclic compounds XIII and XV from benzocyclobutenone II is also illustrated by Scheme 4. Opening of the four-membered ring in ketone II gives cation F which can also be generated by reversible opening of the five-membered ring in indanone IX resulting from the reaction of ketone II with SbF₅. Cation F in SbF₅ can undergo isomerization into cation G through intermediate H. Possible schemes of further transformations of intermediates G and H, leading to compounds X, XIII, and XV, were considered previously [1].

Skeletal transformations of perfluorinated 2,2-dialkylbenzocyclobutenones III and IV by the action of SbF₅ require milder conditions than in the reactions with 2-alkyl-substituted analogs I and II. Perfluoro-(2-ethyl-2-methylbenzocyclobuten-1-one) (III) was heated with antimony pentafluoride at 50°C, and hydrolysis of the reaction mixture gave perfluoro[2-(but-2-en-2-yl)benzoic acid] (XVI). When the reaction temperature was raised to 125°C, a solution containing perfluorinated 4-ethyl- and 3,4-dimethylisochromenyl cations XVII and XVIII was obtained, and subsequent hydrolysis gave a mixture of perfluoro(4-ethylisochromen-1-one) (XIX), perfluoro(3,4-dimethylisochromen-1-one) (XX), and 5,6,7,8-tetrafluoro-3-hydroxy-3,4-bis-(trifluoromethyl)isochroman-1-one (XXI) (Scheme 5).

Scheme 5 shows a probable path for the formation of acid XVI in the reaction of ketone III with SbF₅. Initially, abstraction of fluoride ion from molecule III gives cation J, opening of the four-membered ring in J generates cation K, and the latter undergoes isomerization into unsaturated cation L by the action of SbF₅. Hydrolysis of L yields acid XVI. Isochromenyl cations XVII and XVIII are formed via heterocyclization of





XVII, **XIX**, $X = C_2F_5$, Y = F; **XVIII**, **XX**, $X = Y = CF_3$.

allyl-type cation (which is isomeric to L) generated from acid **XVI** fluoride according to the scheme described previously [4].

On the whole, the behavior of diethylbenzocyclobutenone IV in antimony pentafluoride is similar to that of ketone III, but a longer reaction time and/or higher temperature are necessary. In the reaction of IV with SbF₅ at 70°C (after treatment of the reaction mixture with water) we obtained perfluoro[2-(pent-2-en-3yl)benzoic acid] (XXII), whereas prolonged heating of ketone IV with SbF₅ at 125°C produced a solution containing perfluoro(4-ethyl-3-methylisochromenyl) cation (XXIII), and hydrolysis of the latter gave perfluoro(4-ethyl-3-methylisochromen-1-one) (XXIV) [5] (Scheme 6).

Let us consider now the behavior of perfluorinated 2-alkyl- and 2,2-dialkylbenzocyclobutenones in the system SiO_2 -SbF₅. Heating of ketones I and II in antimony pentafluoride in the presence of SiO_2 at 75°C

and subsequent hydrolysis of the reaction mixture led to the formation of methylphthalides **VII** and **VIII** and ethylphthalides **XI** and **XII**, respectively (Scheme 7). These results may be interpreted assuming that the reaction of methylbenzocyclobutenone **I** with SiO_2 -SbF₅ gives indanone **V** (Scheme 1) which undergoes further transformations by the action of SiO_2 -SbF₅. This assumption is confirmed by the fact that ketone **V** under analogous conditions gives rise to a mixture of phthalides **VII** and **VIII** (Scheme 7).

On the other hand, the results of the reaction of ethylbenzocyclobutenone II with SiO_2-SbF_5 cannot be rationalized in a similar way. As noted above, the isomerization of ketone II into indanone IX by the action of SbF_5 occurs at 120°C, whereas the reaction of II with SiO_2-SbF_5 yields phthalides XI and XII at 75°C. By special experiment we showed that compound II remains almost unchanged on heating in SbF_5 at 75°C over a comparable period of time. In addition, we



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I, VII, VIII, $R_F = CF_3$; II, XI, XII, $R_F = C_2F_5$.

examined the behavior of indanone IX in the system SiO₂–SbF₅ at 75°C. In this case, phthalides XI and XII were formed only as minor products, while the major product was acid XXV. The transformation of methylindanone IX into acid XXV is likely to follow Scheme 7. Ketone IX reacts with SiO₂–SbF₅ to give indandione **H** which (like perfluoroindan-1,3-dione [2, 8]) undergoes isomerization into ethylidenephthalide M by the action of SbF₅. Compound M is converted into acid fluoride N via reaction with SiO₂-SbF₅, and hydrolysis of N leads to acid XXV. In addition, fluorination of M with SbF₅ gives perfluorophthalide XI which is then hydrolyzed to hydroxyphthalide XII [1]. In keeping with the proposed scheme, the formation of acid **XXV**, on the one hand, and phthalides XI and XII, on the other, are concurrent pathways of the transformation of intermediate M in SiO₂-SbF₅. Taking into account that acid **XXV** was absent among products of the reaction of ethylbenzocyclobutenone II with SiO₂-SbF₅ at 75°C and that

compound **II** did not undergo isomerization into indanone **IX** at the same temperature, we presumed that phthalides **XI** and **XII** are formed in the reaction of **II** with SiO₂–SbF₅ according to a different mechanism, i.e., the presence of SiO₂ radically changes the direction of skeletal transformations of ketone **II** in antimony pentafluoride.

The reaction of perfluorinated benzocyclobutenone III with SbF_5 -SiO₂ at 75°C, followed by hydrolysis of the reaction mixture, gave perfluoro(3-methyl-1-oxoisochromene-4-carboxylic acid) (XXVI). Under analogous conditions, diethylbenzocyclobutenone IV was converted into isochromenone XXIV containing an impurity of perfluoro(4-acetyl-3-methylisochromen-1one) (XXVII) (Scheme 8). Presumably, acid XXVI is formed in the reaction of III with SiO₂-SbF₅ as a result of initial opening of the four-membered ring in the initial ketone by the action of SbF₅ (Scheme 5) and subsequent transformations of the ring opening product





in SiO₂–SbF₅ according to the scheme proposed in [4]. The transformation of ketone IV into compound XXIV in the reaction with SiO₂–SbF₅ at 75°C may be illustrated by Scheme 8. Opening of the four-membered ring in IV by the action of SbF₅ generates cation **O** which undergoes isomerization into cation **P** via addition–elimination of fluoride ion. Cation **P** reacts with SiO₂ to give compound **Q** whose intramolecular cyclization through intermediate benzoyl cation **R** yields compound XXIV. An alternative mechanism of the transformation IV \rightarrow XXIV in SiO₂–SbF₅ at 75°C, involving cyclization of intermediate **P** to isochromenyl cation XXIII and subsequent conversion of the latter into compound XXIV, seems to be improbable, for the cyclization $\mathbf{P} \rightarrow \mathbf{XXIII}$ requires a higher temperature (125°C; Scheme 6) [5].

Acetylisochromenone **XXVII** formed in the reaction of **IV** with SiO_2-SbF_5 is likely to result from further transformations of compound **XXIV**. The latter can also be converted into **XXVII** via a series of hydrolytic reactions. The reaction of **XXIV** with dilute hydrochloric acid gave a mixture containing 5,6,7,8tetrafluoro-3-hydroxy-4-pentafluoroethyl-3-trifluoromethylisochroman-1-one (**XXVIII**) as the major product (Scheme 9). By treatment of that mixture with NaHCO₃ in the two-phase system H₂O–CH₂Cl₂ we obtained acetylisochromenone **XXVII** together with a small amount of 5,6,7,8-tetrafluoro-3-trifluoromethyl-



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isochroman-1-one (XXIX). The observed hydrolytic transformations of compound XXIV are analogous to the reactions described in [4] for dimethylisochromenone XX.

Thus we have shown that perfluorinated 2-alkylbenzocyclobutenones I and II in antimony pentafluoride undergo isomerization to perfluoroindanones V and IX. The process is likely to follow a path involving cleavage of the four-membered ring in the initial ketone, which is consistent with the formation of perfluorinated 2-alkenylbenzoic acids XVI and XXII from 2,2-dialkylbenzocyclobutenones III and IV under analogous conditions. The transformations of perfluorinated 2,2-dialkylbenzocyclobutenones III and IV in the system SiO₂-SbF₅, leading to isochromenones XXVI and XXVII, also begin with opening of the carbonyl-containing ring by the action of SbF₅. Presumably, the transformations of four-membered ring in ethylbenzocyclobutenone II and probably in methylbenzocyclobutenone I occurring in SbF₅ in the presence of SiO₂ and leading to phthalides XI and VII follow a different path where SiO₂ plays the key role, but the mechanism of participation of SiO₂ still remains unclear.

The structure of compounds III, XXV, and XXVII was confirmed by high-resolution mass spectrometry and other spectral methods. Compound XXV displayed in the ¹⁹F NMR spectrum a large spin-spin coupling constant ($J_{FF} = 93$ Hz) between the fluorine atom at the exocyclic double bond (3'-F) and 4-F, indicating E configuration of the double bond (the 3'-F and 4-F atoms appear spatially close) [9]. The $J_{3',4}$ value is similar to analogous coupling constants for perfluorinated 1-ethylideneindane [10] and 3-ethylideneindan-1-one [11]. Compound XXVIII was formed as a mixture of stereoisomers, and its structure was assigned by comparing its ¹H and ¹⁹F NMR spectra with those of perfluoroisochroman-1-one XXI reported previously [4]. The configuration of particular isomers of **XXVIII** was determined on the basis of the ¹⁹F-¹⁹F coupling constants for the 3-CF₃ and 4-CF₂ groups. The $J_{\rm FF}$ values for isomer **XXVIIIa** with *cis* orientation of the fluoroalkyl groups were equal to 5.5 and 29.5 Hz, and the corresponding values for trans isomer **XXVIIIb** were less than 2 Hz.

Compounds VI–VIII [2], X–XIII, XV [1], XIV [7], XVI–XXI, XXVI, XXIX [4], and XXII–XXIV [5] were described previously; they were identified by comparing their ¹⁹F NMR spectra with the spectra of authentic samples. The IR spectra were recorded on a Bruker Vector 22 spectrometer. The UV spectra were measured on a Hewlett–Packard 8453 spectrophotometer. The ¹H and ¹⁹F NMR spectra were obtained on a Bruker AV-300 instrument at 300 and 282.4 MHz, respectively, using the residual solvent signal (¹H, acetone- d_5 , δ 2.04 ppm) or C₆F₆ (¹⁹F) as reference. The elemental compositions were determined from the high-resolution mass spectra which were recorded on a Thermo Electron Corporation DFS instrument. The reactions were carried out in glass vessels or a nickel bomb (V = 10 ml). The reaction mixtures were analyzed by ¹⁹F NMR spectroscopy.

Initial compounds I, II, IV, V, and IX were synthesized according to the procedure reported in [12]. Previously unknown ketone III was prepared in a similar way.

Perfluoro(2-ethyl-2-methylbenzocyclobuten-1one) (III). A mixture of perfluorinated 1-ethyl-1-methylbenzocyclobutene and 2-ethyl-1-methylbenzocyclobutene (XXX) at a ratio of 55:45, 6.14 g (15.43 mmol), was added to a solution of 1.25 g (10.95 mmol) of trifluoroacetic acid in 5.02 g (23.13 mmol) of antimony pentafluoride, and the mixture was vigorously stirred for 5 h at 20°C. The upper layer (1.01 g, compound XXX) was separated, 5% hydrochloric acid was added to the residue, and the organic phase (4.78 g) containing 63% of ketone III (yield 93%) and 37% of compound XXX was separated. A 1.00-g portion of that mixture was separated by column chromatography on silica gel using first hexane and then chloroform as eluent to isolate 0.23 g of compound XXX and 0.50 g of ketone III, bp 67–68°C (17 mm). UV spectrum (hexane), λ_{max} , nm (log ϵ): 203 (4.31), 242 (3.98), 249 (3.94), 276 (3.11). IR spectrum (CCl₄), v, cm⁻¹: 1831 (C=O), 1523, 1484 (fluorinated aromatic ring). ¹⁹F NMR spectrum (CDCl₃), δ_F , ppm: 97.3 (3F, α -CF₃), 80.5 (3F, β -CF₃), 49.5 and 48.7 (1F each, CF₄F_B), 37.5 (1F, 6-F), 29.9 (1F, 4-F), 28.4 (1F, 3-F), 19.6 (1F, 5-F); J_{FF} , Hz: $J_{AB} = 290$, $J_{\alpha,\beta} = 5$, $J_{\alpha,A} = 9$, $J_{\alpha,B} = 9.5$, $J_{\alpha,3} =$ 2.5, $J_{\beta,A} = 1$, $J_{\beta,B} = 1$, $J_{\beta,3} = 7$, $J_{A,3} = 3$, $J_{B,3} = 2.5$, $J_{3,4} = 3$ 19, $J_{3,5} = 8$, $J_{3,6} = 23.5$, $J_{4,5} = 17.5$, $J_{4,6} = 12.5$, $J_{5,6} =$ 20. Found: m/z 375.9752 $[M]^+$. C₁₁F₁₂O. Calculated: *M* 375.9758.

Reaction of perfluoro(2-methylbenzocyclobuten-1-one) (I) with SbF₅. *a*. A solution of 0.24 g (0.87 mmol) of compound I in 1.84 g (8.48 mmol) of SbF₅ was heated for 8 h at 75°C. The mixture was treated with 5% hydrochloric acid and extracted with

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methylene chloride, the extract was dried over MgSO₄, and the solvent was distilled off under reduced pressure to obtain 0.20 g of a mixture containing 12% of compound I, 72% (yield 61%) of ketone V, 8% (7%) of acid VI, 3% (3%) of phthalide VII, and 5% (4%) of phthalide VIII.

b. Following an analogous procedure, from 0.42 g (1.52 mmol) of compound I and 3.04 g (14.02 mmol) of SbF₅ (75°C, 17 h) we obtained 0.37 g of a mixture containing 6% of compound I, 79% (yield 70%) of ketone V, 5% (5%) of acid VI, 7% (6%) of phthalide VII, and 3% (3%) of phthalide VIII.

Reaction of perfluoroindan-1-one (V) with SbF₅. Likewise, the reaction of 0.48 g (1.74 mmol) of ketone V with 3.42 g (15.77 mmol) of SbF₅ (75°C, 17 h, nickel bomb) gave 0.43 g of a mixture containing 93% of ketone V, 0.5% of acid VI, 4% of phthalide VII, and 2% of phthalide VIII.

Reaction of perfluoro(2-ethylbenzocyclobuten-1-one) (II) with SbF₅. *a*. A mixture of 0.17 g (0.52 mmol) of compound II and 1.10 g (5.07 mmol) of SbF₅ was heated for 4.5 h at 120°C. The mixture was treated with 5% hydrochloric acid and extracted with methylene chloride, the extract was dried over MgSO₄, and the solvent was distilled off under reduced pressure to obtain 0.15 g of a mixture containing 58% of compound II, 37% (yield 33%) of ketone IX, 1% of phthalide XII, and 3% of acid X.

b. Following an analogous procedure, from 0.57 g (1.74 mmol) of ketone II and 3.07 g (14.16 mmol) of SbF₅ (130°C, 39 h, nickel bomb) we obtained 0.54 g of a mixture containing compounds IX–XI, XIII, and XIV at a ratio of 17:27:11:33:12 (overall yield 94%).

c. As described above in *a*, the reaction of 1.09 g (3.34 mmol) of ketone **II** with 5.81 g (26.80 mmol) of SbF₅ (180°C, 63 h, nickel bomb) gave 0.94 g of a mixture containing compounds **X**, **XI**, **XIII**, and **XV** at a ratio of 70:6:10:14 (overall yield 81%).

Reaction of perfluoro(2-ethyl-2-methylbenzocyclobuten-1-one) (III) with SbF₅. *a*. A mixture of 0.37 g (0.98 mmol) of compound III and 2.15 g (9.90 mmol) of SbF₅ was heated for 11 h at 50°C. The mixture was diluted with 1.63 g of hexafluorobenzene, treated with 5% hydrochloric acid, and extracted with methylene chloride, and the extract was dried over MgSO₄. The extract contained hexafluorobenzene and acid **XVI** as a mixture of *E* and *Z* isomers at a ratio of ~25:75. The solvent and C_6F_6 were distilled off under reduced pressure, and vacuum sublimation of the residue (100°C, 3 mm) gave 0.27 g (74%) of acid **XVI**. *b*. A mixture of 0.44 g (1.16 mmol) of compound III and 2.51 g (11.58 mmol) of SbF₅ was heated for 7 h at 125°C (nickel bomb). The ¹⁹F NMR spectrum of the resulting solution contained signals assignable to cations **XVII** and **XVIII** and perfluoro(4-fluorocarbonyl-3-methylisochromenyl) cation [4] at a ratio of 13:75:12. The mixture was treated with 5% hydrochloric acid and extracted with methylene chloride, the extract was dried over MgSO₄, and the solvent was distilled off under reduced pressure to obtain 0.38 g of a mixture containing compounds **XIX–XXI** and **XXVI** at a ratio of 11:64:9:16 (overall yield 93%).

Reaction of perfluoro(2-methylbenzocyclobuten-1-one) (I) with SiO₂–SbF₅. A mixture of 0.27 g (0.98 mmol) of compound **I**, 0.06 g (1.00 mmol) of SiO₂ (silica gel calcined at 400–450°C), and 2.07 g (9.55 mmol) of SbF₅ was stirred for 8 h at 75°C. The mixture was treated with 5% hydrochloric acid and extracted with methylene chloride, the extract was dried over MgSO₄, and the solvent was distilled off under reduced pressure to obtain 0.18 g of a mixture containing 38% of phthalide **VII** and 62% of phthalide **VIII** (overall yield 64%).

Reaction of perfluoroindan-1-one (V) with SiO₂– **SbF**₅. Following an analogous procedure, from 0.53 g (1.92 mmol) of ketone V, 0.11 g (1.85 mmol) of SiO₂, and 4.02 g (18.55 mmol) of SbF₅ (75°C, 8 h) we obtained 0.48 g of a mixture containing 25% of phthalide **VII** and 75% of phthalide **VIII** (overall yield 86%).

Reaction of perfluoro(2-ethylbenzocyclobuten-1-one) (II) with SiO₂–SbF₅. A mixture of 0.34 g (1.03 mmol) of compound **II**, 0.06 g (1.00 mmol) of SiO₂, and 2.21 g (10.18 mmol) of SbF₅ was stirred for 10 h at 75°C. The mixture was then treated with 5% hydrochloric acid and extracted with diethyl ether, the extract was dried over MgSO₄, the solvent was distilled off, and vacuum sublimation of the residue (130°C, 30 to 2 mm) gave 0.32 g of a mixture containing 10% of phthalide **XI** and 90% of phthalide **XII** (overall yield 90%).

Reaction of perfluoro(2-methylindan-1-one) (IX) with SiO₂–SbF₅. A mixture of 0.30 g (0.91 mmol) of compound IX, 0.06 g (1.00 mmol) of SiO₂, and 2.09 g (9.65 mmol) of SbF₅ was stirred for 9 h at 75°C. The mixture was treated with 5% hydrochloric acid and extracted with methylene chloride–diethyl ether (2:1, by volume), and the extract was dried over MgSO₄. It contained compounds XI and XII, fluoro[(3*E*)-4,5,6,7tetrafluoro-1-oxo-2-benzofuran-3-ylidene]acetic acid (XXV) and tetrafluorophthalic acid at a ratio of

9:8:65:18. The solvent was distilled off, and vacuum sublimation (100-150°C, 2 mm) of the residue gave 0.14 g of a mixture of compounds XI, XII, and XXV and tetrafluorophthalic acid at a ratio of 19:25:12:44; further sublimation at 200°C (2 mm) afforded 0.11 g (43%) of acid XXV. By repeated vacuum sublimation (180°C, 2 mm) and washing of the sublimed crystalline material with diethyl ether (4 ml) we obtained an analytically pure sample (0.06 g) of compound XXV with mp 245.5–246°C. IR spectrum (KBr), v, cm⁻¹: ~2800 br (O–H), 1828, 1803, 1695 (C=O), 1524, 1498 (fluorinated aromatic ring). ¹H NMR spectrum (acetone- d_6): δ 6.5 ppm, br.s (OH). ¹⁹F NMR spectrum (acetone- d_6), δ_F , ppm: 33.9 (1F, 4-F), 24.2 (1F, 7-F), 20.9 (1F, 5-F), 20.2 (1F, 3'-F), 15.6 (1F, 6-F); J_{FF}, Hz: $J_{3',4} = 93$, $J_{3',5} = 3$, $J_{3',6} = 6$, $J_{3',7} = 2$, $J_{4,5} = 19$, $J_{4,6} = 7, J_{4,7} = 18, J_{5,6} = 18, J_{5,7} = 10, J_{6,7} = 20.$ Found: m/z 279.9780 $[M]^+$. C₁₀HF₅O₄. Calculated: M 279.9795.

Reaction of perfluoro(2-ethyl-2-methylbenzocyclobuten-1-one) (III) with SiO₂–SbF₅. A mixture of 0.42 g (1.11 mmol) of compound III, 0.07 g (1.20 mmol) of SiO₂, and 2.39 g (11.01 mmol) of SbF₅ was stirred for 10 h at 75°C. The mixture was treated with 5% hydrochloric acid and extracted with diethyl ether, the extract was dried over MgSO₄, the solvent was distilled off, and the residue was subjected to vacuum sublimation (170°C, 2 mm) to isolate 0.33 g (90%) of acid XXVI.

Reaction of perfluoro(2,2-diethylbenzocyclobuten-1-one) (IV) with SiO₂–SbF₅. A mixture of 0.70 g (1.64 mmol) of compound IV, 0.11 g (1.76 mmol) of SiO₂, and 3.59 g (16.54 mmol) of SbF₅ was stirred for 30 h at 75°C. The mixture was treated with 5% hydrochloric acid and extracted with methylene chloride, the extract was dried over MgSO₄, the solvent was distilled off, and vacuum sublimation of the residue (100°C, 2 mm) gave 0.50 g of a mixture of compounds XXIV and **XXVII** at a ratio of 80:20 (overall yield 77%).

Hydrolytic transformations of perfluoro(4-ethyl-3-methylisochromen-1-one) (XXIV). Compound XXIV, 0.18 g (0.44 mmol), was dissolved in 2 ml of diethyl ether, 5 ml of 5% hydrochloric acid was added, and the mixture was stirred for 25 h. The organic phase was separated, dried over MgSO₄, and evaporated on a watch glass to obtain 0.16 g of a mixture containing 35% of 5,6,7,8-tetrafluoro-*r*-3-hydroxy-*t*-4-pentafluoroethyl-3-trifluoromethylisochroman-1-one (XXVIIIa), 44% of 5,6,7,8-tetrafluoro-*r*-3-hydroxy-*c*-4-pentafluoroethyl-3-trifluoromethylisochroman-1-one (XXVIIIb), 8% of perfluoro(4-acetyl-3-methylisochromen-1-one) (XXVII), 4% of compound XXIX, and two unidentified compounds (4 and 6%). The product mixture was dissolved in 4 ml of methylene chloride with addition of 0.2 ml of diethyl ether, the solution was stirred with a saturated aqueous solution of NaHCO₃ over a period of 1 min, the organic layer was separated and dried over MgSO₄, and the solvent was distilled off under reduced pressure to isolate 0.11 g (67%) of compound XXVII. The aqueous phase was acidified with hydrochloric acid and extracted with diethyl ether, the extract was dried over MgSO₄, and removal of the solvent gave 0.03 g of XXIX.

Compound **XXVII**. mp 66.5–67°C (from hexane). UV spectrum (hexane), λ_{max} , nm (log ε): 226 (4.38), 267 (3.75), 310 (3.63). IR spectrum (CCl₄), v, cm⁻¹: 1798, 1766 (C=O), 1518, 1491 (fluorinated aromatic ring). ¹⁹F NMR spectrum (CH₂Cl₂), δ , ppm: 95.6 (3F, 3-CF₃), 85.9 (3F, 4-CF₃), 34.0 (1F, 8-F), 28.9 (1F, 5-F), 23.3 (1F, 6-F), 16.8 (1F, 7-F); *J*_{FF}, Hz: *J*_{3,4} = 4.5, *J*_{4,5} = 12, *J*_{5,6} = 20, *J*_{5,7} = 5.5, *J*_{5,8} = 13, *J*_{6,7} = 20.5, *J*_{6,8} = 13.5, *J*_{7,8} = 20. Found: *m*/*z* 381.9693 [*M*]⁺. C₁₂F₁₀O₃. Calculated: *M* 381.9688.

Compound **XXVIII**. ¹H NMR spectrum (CDCl₃), δ , ppm: isomer XXVIIIa: 4.82 br.s (1H, OH), 4.41 d.d (1H, 4-H); $J(4-H, F_R) = 22$, $J(4-H, F_A) = 4$ Hz; isomer XXVIIIb: 5.28 br.s (1H, OH), 4.53 d.d (1H, 4-H); $J(4-H, F_B) = 17.5, J(4-H, F_A) = 7$ Hz. ¹⁹F NMR spectrum (CDCl₃), $\delta_{\rm F}$, ppm: XXVIIIa: 80.8 (3F, 3-CF₃), 79.4 (3F, 4-CF₃), 51.9 (1F, F_A) and 38.6 (1F, F_B) (CF₂), 30.2 (1F, 8-F), 23.8 (1F, 5-F), 19.9 (1F, 6-F), 12.9 (1F, 7-F); J_{FF} , Hz: $J(3-\text{CF}_3, \text{F}_A) = 29.5$, $J(3-\text{CF}_3, \text{F}_B) = 5.5$, $J(4-CF_3, 5-F) = 12.5, J_{AB} = 277, J_{A,5} = 4, J_{5,6} = 21,$ $J_{5,7} = 5.5, J_{5,8} = 13.5, J_{6,7} = 20, J_{6,8} = 12, J_{7,8} = 20.5,$ $J(F_A, 4-H) = 4$, $J(F_B, 4-H) = 22$; **XXVIIIb**: 82.1 (3F, 4-CF₃), 79.6 s (3F, 3-CF₃), 55.1 (1F, F_A) and 46.8 $(1F, F_B)$ (CF₂), 30.3 (1F, 8-F), 24.4 (1F, 5-F), 20.6 (1F, 6-F), 14.1 (1F, 7-F); J_{FF} , Hz: $J(4-CF_3, 5-F) = 3$, $J_{AB} =$ 283, $J_{A,5} = 10$, $J_{B,5} = 6$, $J_{5,6} = 21$, $J_{5,7} = 6$, $J_{5,8} = 13.5$, $J_{6,7} = 20, J_{6,8} = 12, J_{7,8} = 20.5, J(F_A, 4-H) = 7,$ $J(F_B, 4-H) = 17.5.$

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