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Oxygen replacement by fluorine in carbonyl derivatives of perfluoroaromatic compounds and isomerization of perfluoroindan-1, 3-dione to perfluoro-3-methylenephthalide under the action of HF/SbF_5 ☆

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Dedicated to the Centenary of Academician, Professor I.L. Knunyants.

Abstract

When acted upon by HF/SbF_5 at 95 °C, carbonyl groups of perfluorinated acetophenone (**10**), 3,4-dihydronaphthalen-1(2H)-one (**8**), 2,3-dihydronaphthalene-1,4-dione (**9**), benzocyclobutenone (**6**), benzocyclobutenedione (**7**) and indan-1-one (**1**) are converted into difluoromethylene groups to give the corresponding perfluoroaromatic products. Perfluoroindan-2-one (**5**), under the same conditions, is transformed to bis(perfluoroindan-2-yl) ether (**21**). On heating with HF/SbF_5, perfluoroindan-1,3-dione (**2**) isomerizes into perfluoro-3-methylenephthalide (**4**) at 95 °C, and gives 4,5,6,7-tetrafluoro-3-trifluoromethyl-phthalide (**14**) at 130 °C. Compound **4** in the absence of a solvent dimerizes giving perfluorodispiro[phthalide-3,1′-cyclobutane-2′,3″-phthalide] (**18**), and when heated with SbF_5 at 130 °C, it is converted into perfluoro-3-methylphthalide (**3**). When acted upon by HF/SbF_5 at 95 °C, perfluorinated benzoic acid (**12**) and phthalic anhydride (**13**) give the corresponding products with trifluoromethyl groups.

Keywords: Perfluorinated; Acetophenone; Benzoic acid; Phthalic anhydride; Indan-1-one; Indan-2-one; Indan-1,3-dione; 3,4-Dihydronaphthalen-1(2H)-one; 2,3-Dihydronaphthalene-1,4-dione; Benzocyclobutenone; Benzocyclobutenedione; Antimony pentafluoride; Replacement of carbonyl oxygen by fluorine

1. Introduction

Previously, cationoid skeletal transformations of perfluorinated benzocyclobutene, indan, tetralin and their perfluoroalkyl and perfluoroaryl derivatives under the action of antimony pentafluoride have been found and investigated, see for example articles [2–5] and references [1–7] cited in article [3]. Recently, we have found that carbon framework of perfluoroketones can also change under the action of SbF_5 [6]. Thus, perfluoroindan-1-one (**1**) heated with SbF_5 and then treated with water, gives perfluoro-2-ethylbenzoic acid together with the products of ketone **1** disproportionation–perfluoroindan and perfluoroindan-1,3-dione (**2**). The latter is transformed to perfluoro-3-methylphthalide (**3**), for example, via the intermediate complex **2a** and perfluoro-3-methylenephthalide (**4**) according to Scheme 1 [6].

We have now investigated the behaviour of the protonated diketone **2**, which is a cationic analog of complex **2a**, ketone **1** and other perfluoroaromatic carbonyl derivatives in superacid medium with the aim of studying the possibility of their cationoid skeletal transformations. This work describes the behaviour of compounds **1**, **2**, perfluorinated indan-2-one (**5**), benzocyclobutenone (**6**), benzocyclobutenedione (**7**), 3,4-dihydronaphthalen-1(2H)-one (**8**), 2,3-dihydronaphthalene-1,4-dione (**9**), acetophenone (**10**), benzaldehyde (**11**), benzoic acid (**12**) and phthalic anhydride (**13**), in the system of HF/SbF_5.

2. Results and discussion

When heated with HF/SbF_5 at 95 °C for 3 h, indandione **2** isomerizes to phthalide **4**. The reaction mixture also contains

☆ Preliminary communication see [1].

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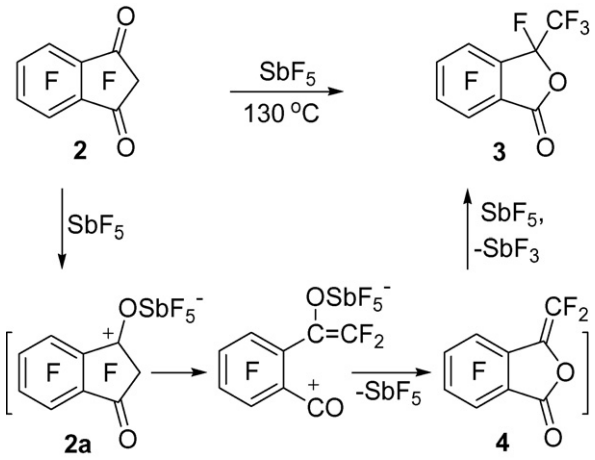


Scheme 1.

small amounts of 4,5,6,7-tetrafluoro-3-trifluoromethylphthalide (**14**), indanone **1** and unchanged compound **2** (Scheme 2). Increase in the reaction time (43 h) leads to the formation of a mixture contained phthalides **3**, **4**, **14** and small amounts of perfluoroindan (**15**). Phthalide **14** is the main product of the reaction of indandione **2** with HF/SbF_5 at 130 °C. As far as we know, transformation of indandione **2** to phthalide **4** is the first example of isomerization of fluorinated indandiones into 3-methylenephthalides. However, earlier it was reported that 2,2-diphenylindan-1,3-dione under the action of trifluoromethanesulfonic acid isomerizes to 3-(diphenylmethylene)phthalide [7].

The probable mechanism for the isomerization of indandione **2** to phthalide **4** can be formulated as shown in Scheme 2. Initially, protonation of compound **2** gives 1-hydroxy-perfluoroindan-3-one-1-yl cation (**2c**). Opening of the five-membered ring in ion **2c** leads to cation **16**. Intramolecular cyclization of the latter and subsequent deprotonation gives phthalide **4**. Compound **4** adds HF to form phthalide **14**, apparently, with intermediate generation of 1-hydroxy-perfluoro-3-methylenephthalan-1-yl cation (**4c**) (its formation will be discussed below) according to Scheme 2.

When heated with SbF_5 at 125 °C, compound **4** is fluorinated to give phthalide **3**. Compound **4**, treated with dibromine, forms 3-bromo-3-(bromodifluoromethyl)-4,5,6,7-tetrafluorophthalide (**17**) (Scheme 2). In the absence of a solvent, compound **4** cyclodimerizes to give perfluorodispiro[phthalide-3,1′-cyclobutane-2′,3″-phthalide] (**18**) rather than its isomer with a 1,3-disubstituted cyclobutane fragment. The formation of dimer **18** could be explained by the higher stability of the intermediate benzyl–benzyl diradical **18a** rather than **18b**, cf. [8].

Based on NMR data, dimer **18** is formed as a mixture of two isomers with the ratio of *E:Z* ~ 50:50. The ^{13}C NMR spectrum exhibits two signals at 116.9 (ddt, $^1J_{CF}$ = 302, 297, $^2J_{CF}$ = 27 Hz) and 116.8 (tt, $^1J_{CF}$ = 301, $^2J_{CF}$ = 27 Hz) ppm, assigned to the CF_2 groups of 1,2-disubstituted cyclobutane fragment. At the same time these data exclude the structures with a 1,3-disubstituted cyclobutane fragment, for which signals of CF_2 groups should not have $^2J_{CF}$.

The ^{19}F NMR spectrum exhibits signals of two *pseudo*-AB-systems at −116.3 (2F, ddm, *J* = 224, 19 Hz) and −120.4 (2F, ddm, *J* = 224, 31 Hz); −117.2 (2F, dtm, *J* = 224, 34 Hz) and −122.7 (2F, dm, *J* = 224 Hz) ppm assigned to the CF_2 groups of *E*-**18** and *Z*-**18**, respectively. The fine structures of the *pseudo*-AB-system signals indicate that each fluorine atom of the CF_2 groups of *E*-**18** has spatial proximity to one benzene fluorine atom. For *Z*-**18**, one fluorine atom of every CF_2 groups has two closely located benzene fluorine atoms and the other fluorine atom of the CF_2 groups has no closely located benzene fluorine atoms.

According to a single crystal X-ray structure determination for *E*-**18**, distances (F-4)-(F-A), (F-4)-(F-B′) are equal to 2.894(3), 2.786(3) Å, and (F-4″)-(F-A′), (F-4″)-(F-B) are equal to 2.936(3), 2.755(3) Å, respectively (Scheme 2, Fig. 1).

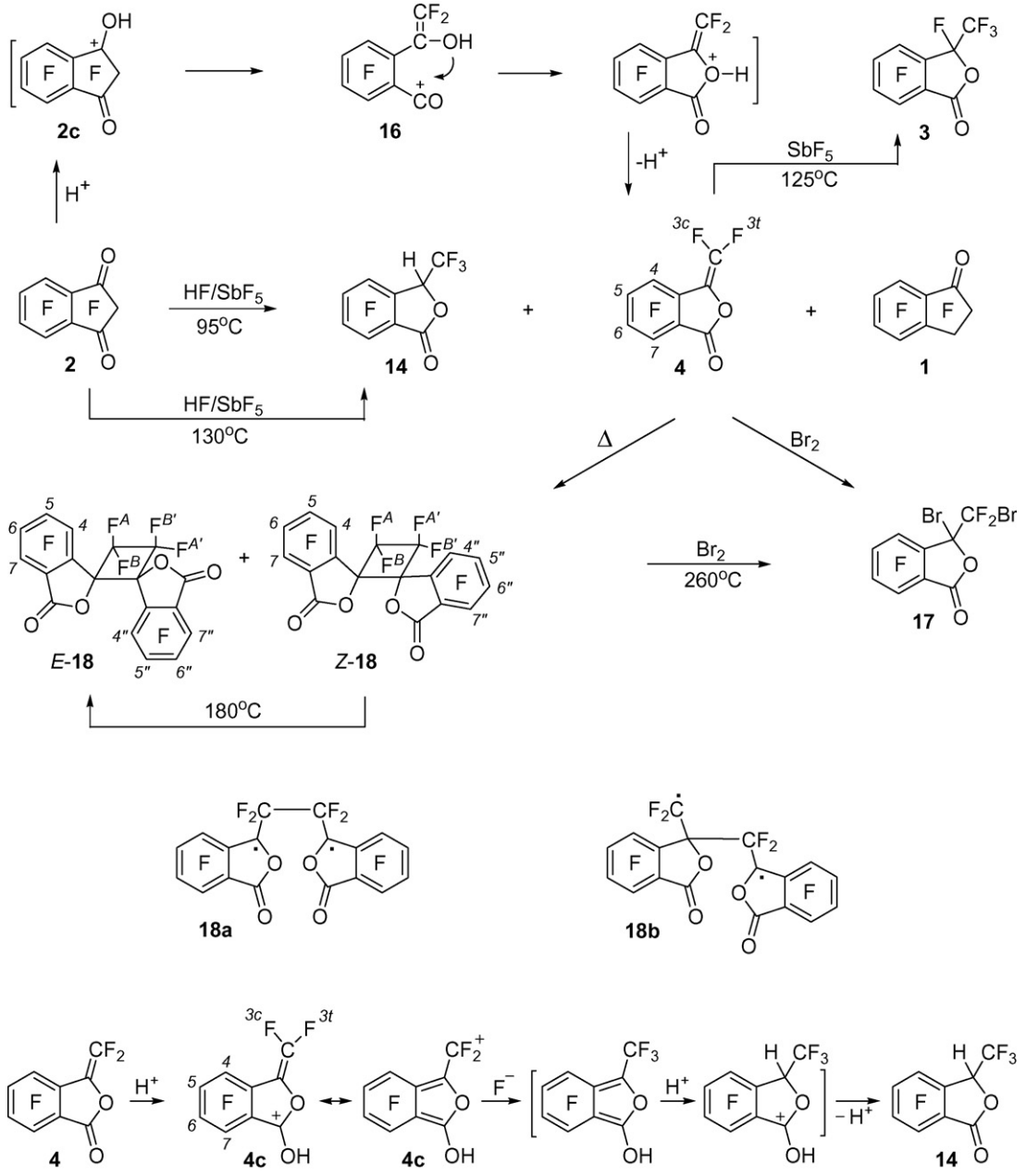
On heating at 180 °C *Z*-**18** isomer is transformed into isomer *E*-**18** apparently through the intermediate diradical **18a**. Gas phase DFT (PBE/TZ2P, PRIRODA program [9]) calculations show that isomer *E*-**18** is more stable by 6.1 kcal mol^{-1} than *Z*-**18**. Attempts to trap diradical **18a** with bromine were unsuccessful. Thus, when heated with dibromine at 180 °C the mixture of *E*-**18** and *Z*-**18** isomers was transformed into isomer *E*-**18**, which contained small amounts of phthalide **17**. When the temperature was raised to 260 °C, dimer **18** was divided into parts to give phthalide **17** (Scheme 2).

Indanone **1** obtained in the reaction of diketone **2** with HF/SbF_5, apparently, is a product of oxygen replacement by fluorine in indandione **2** under the reaction conditions (Scheme 2). It has been found that when acted upon by HF/SbF_5 at 95 °C, the carbonyl group of indanone **1** is also converted into difluoromethylene group to give perfluoroindan (**15**). The reaction mixture also contains unchanged ketone **1** (Scheme 3). As far as we are aware, there are no previous reports of HF/SbF_5 being used as a fluorinating agent for replacement of carbonyl oxygen by fluorine [10,11].

One possible route for the transformation of ketone **1** to indan **15** is presented in Scheme 3. Compound **1** is protonated to give the 1-hydroxy-perfluoroindan-1-yl cation (**1c**) (its formation will be discussed below), which adds fluoride anion to form perfluoroindan-1-ol (**19**). The protonation of the latter with subsequent elimination of water leads to the perfluoroindan-1-yl cation (**15c**), which adds fluoride anion to produce compound **15**.

Another possible route for the transformation of ketone **1** to indan **15** is presented in Scheme 4. The initially generated cation **1c** reacts with indanone **1** to give compound **20** after fluoride anion addition. The protonation of compound **20** with subsequent elimination of water leads to the perfluoro-1-(indan-1-yloxy)indan-1-yl cation (**20c**), which is split into indanone **1** and cation **15c**. The latter adds fluoride anion to form indan **15**.

When heated with HF/SbF_5 at 95 °C, perfluoroindan-2-one (**5**) gives bis(perfluoroindan-2-yl) ether (**21**) and perfluoro-2-(indan-2-yloxy)indan-1-one (**22**) (Scheme 5). One can assume that ether **21** reacts with oxides, formed under the reaction conditions, to give product **22**. The reaction mixture does not contain compounds **5** and **15**. When the temperature is raised to



Scheme 2.

130 °C, a more complex mixture is obtained that contains products **14**, **15**, **21** and **22** together with unidentified impurities. It has been shown in a separate experiment that in an HF/SbF_5 solution at room temperature compound **5** exists as perfluoroindan-2-ol (**23**).

Formation of ether **21** may be represented by Scheme 5. The lower relative stability of cation **24c** than that of cation **15c** should hinder the cleavage of cation **21c** to indanone **5** and cation **24c** as compared with transformation of cation **20c** to indanone **1** and cation **15c**. As a result, cation **21c** adds fluoride anion to give ether **21**. On heating at 130 °C, compound **21** apparently undergoes acidic cleavage to form indan **15**.

The reaction of perfluorobenzocyclobutenone (**6**) with HF/SbF_5 at 95 °C leads to the formation of perfluorobenzocyclobutene (**25**) together with o-H-perfluoroethylbenzene (**26**). The reaction mixture also contains unchanged compound **6** (Scheme 6). Fluorobenzene **26**, apparently, is a product of opening of the four-membered ring of compound **25** with HF under the reaction conditions [12]. Perfluorobenzocyclobutenedione (**7**) also reacts with HF/SbF_5 at 95 °C to give ketone **6** together with product **25** and unchanged compound **7** (Scheme 6).

When 3,4-dihydronaphthalen-1(2H)-one (**8**) is heated with HF/SbF_5 at 95 °C, the carbonyl group is converted into difluoromethylene to form perfluorotetralin (**27**). The reaction mixture also contains small amounts of unchanged ketone **8** (Scheme 7). Under the same conditions 2,3-dihydronaphthalene-1,4-dione (**9**) gives compounds **8** and **27** together with starting diketone **9**.

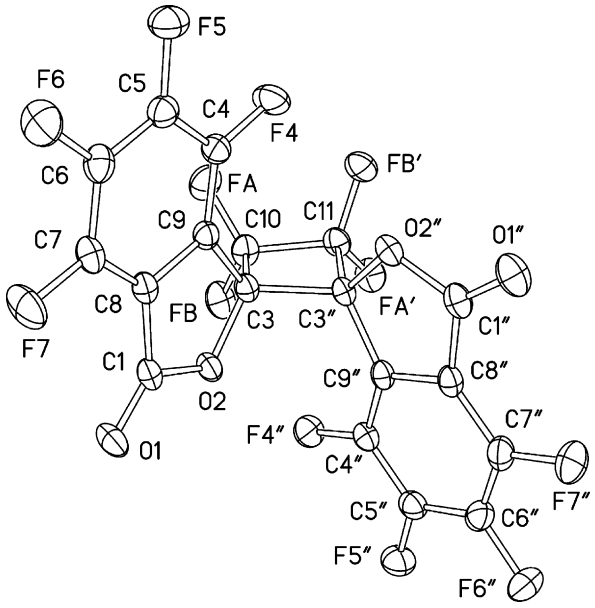
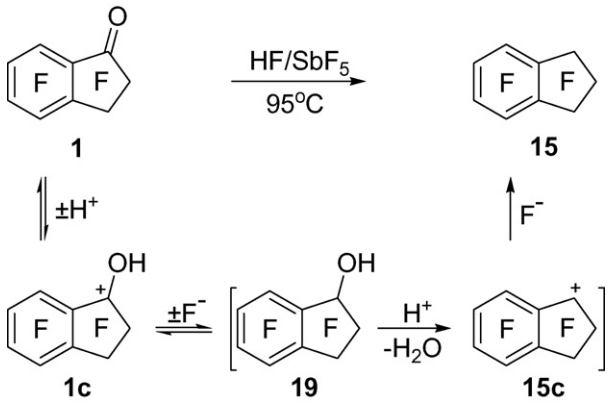


Fig. 1. Molecular structure of perfluorodispiro[phthalide-3,1′-cyclobutane-2′,3″-phthalide] (*E*-**18**) in crystal. Thermal ellipsoids are drawn at the 25% probability level. Selected bond lengths (Å) and torsion angle (°): C3–C3″ 1.581(3), C3–C10 1.569(3), C3″–C11 1.567(3), C10–C11 1.555(3), C10–C3–C3″–C11 8.4(2).

The reaction of perfluoroacetophenone (**10**) with HF/SbF_5 at 95 °C leads to the formation of perfluoroethylbenzene (**28**) in good yield. In contrast, perfluorobenzaldehyde (**11**) under the reaction conditions gives difluoromethylpentafluorobenzene (**29**) in very low yield (Scheme 8).

Perfluorobenzoic acid (**12**) also reacts with HF/SbF_5. Thus, prolonged heating of acid **12** with HF/SbF_5 at 95 °C with further treatment of the reaction mixture with water gives perfluorotoluene (**30**) together with perfluorobenzoyl fluoride (**31**). The mixture also contains acid **12** (Scheme 8). The interaction of tetrafluorophthalic anhydride (**13**) with HF/SbF_5 leads to the formation of perfluoro-2-methylbenzoic acid (**32**), perfluoro-*o*-xylene (**33**) and perfluorophthalide (**34**) together with tetrafluorophthalic acid (Scheme 8).

The reactions of polyfluorinated carbonyl derivatives with HF/SbF_5 seem to be reversible. For example, in the case of compounds **11** and **29** equilibrium apparently is shifted towards aldehyde **11** (Scheme 8). Indeed, when fluorotoluene **29** was added to a mixture of compound **28** and inorganic oxides [O<] formed in the reaction of ketone **10** with HF/SbF_5 and the resulting mixture was heated at 95 °C, fluorotoluene **29** was transformed mainly into aldehyde **11** (Scheme 9).

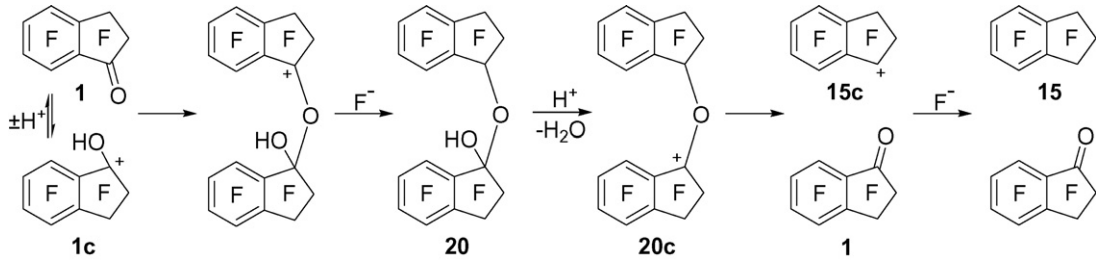


Scheme 3.

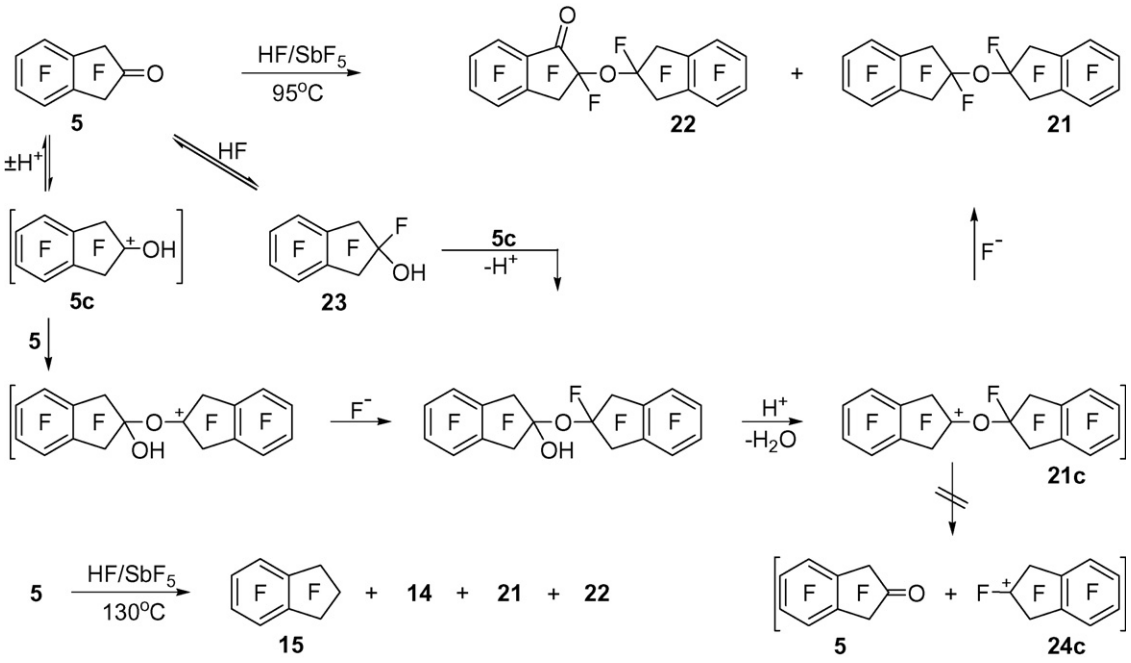
It was mentioned above that compound **5** in an HF/SbF_5 solution adds HF to form hydroxyindan **23** (Scheme 5). When dissolved in an HF/SbF_5 system, compound **1** is protonated to give equilibrium of indanone **1** and cation **1c,** shifted towards cation **1c**. Analogously to that, cation **4c**, 1-hydroxy-perfluorobenzocyclobuten-1-yl (**6c**) and 1-hydroxy-perfluoro-tetralin-1-yl (**8c**) cations were generated from compounds **4**, **6** and **8**, respectively (Schemes 2 and 10).

Assignment of signals in the ^{19}F NMR spectra of cations **1c**, **4c**, **6c** and **8c** was made by analogy with that for perfluorobenzocyclobuten-1-yl [13], 1-chlorooctafluoroindan-1-yl [14], perfluoro-3-methyleneindan-1-yl [15], perfluoro-1-phenylbenzocycloalken-1-yl [16], polyfluorinated benzyl [17] and diphenylmethyl cations [18], for which changes in chemical shift in going from precursor to ion ($\Delta\delta_F$) are attributed to direct participation of fluorine atoms in charge distribution and in an conjugation. It should be noted that for the benzene moiety of cations **1c**, **6c** and **8c** down-field $\Delta\delta_F$ resemble those of perfluoro-1-phenylbenzocycloalken-1-yl cations [16], a smaller scale of $\Delta\delta_F$ can be due to a less positive charge transfer onto ring.

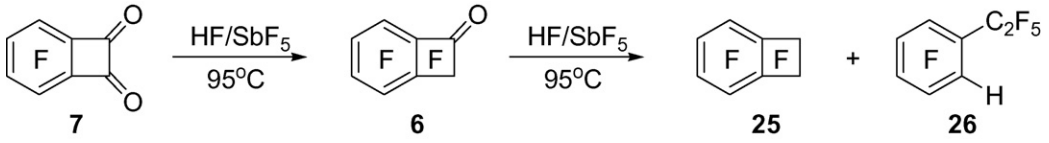
The ^{19}F NMR spectrum of indandione **2** solution in an HF/SbF_5 medium exhibits three unresolved signals with equal intensities and δ_F −107.1, −110.8 and −112.5 ppm. This testifies that for cation **2c** there is an exchange of H^+ between two oxygen atoms of ion **2c** or/and there is the fast equilibrium between cation **2c** and dication **2dc** (Scheme 11).



Scheme 4.



Scheme 5.

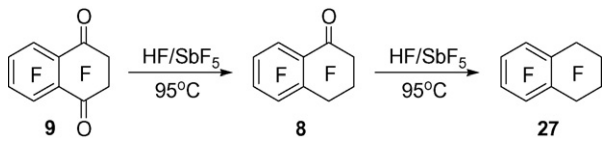


Scheme 6.

Using $\Delta\delta_F$ values of cation **1c** as increments, calculation of $\Delta\delta_F$ for cation **2c** gives δ_F −98.0(F-5), −102.4 (F-7), −123.3 (F-4), −128.1 (F-6), −113.4 (F-2) ppm. In the case of exchange of H^+ between the carbonyl groups of cation **2c** the signals should be situated at −113.0 (F-5, F-6), −112.8 (F-4, F-7), −113.4 (F-2) ppm. The spectrum of dication **2dc** should have signals, which are significantly shifted downfield from −113 ppm. These calculated and experimental data apparently testify that in an HF/SbF_5 solution there is the equilibrium between cation **2c** and dication **2dc**, shifted towards the former. Behaviour of diketones **7** and **9** in an HF/SbF_5 solution is similar to that of compound **2** under the same conditions.

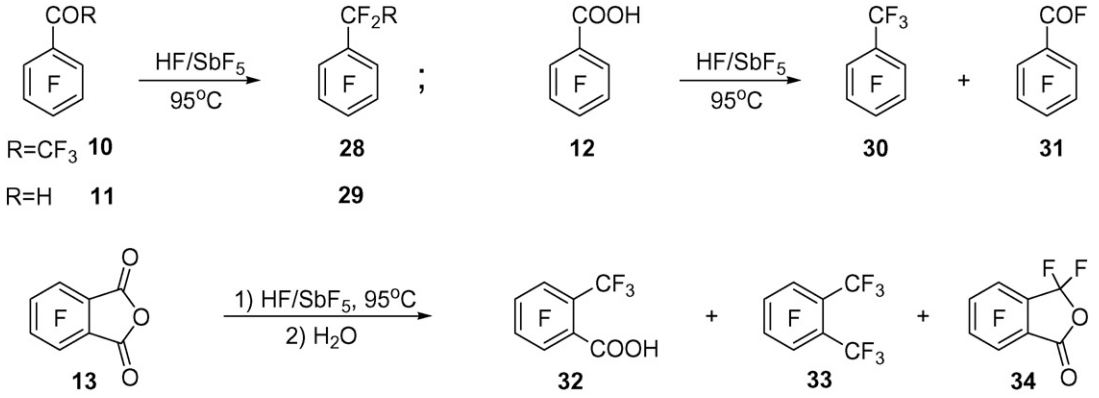
3. Experimental

IR spectra were taken on a Bruker Vector 22 IR spectrophotometer. UV spectra were measured on a Hewlett Packard 8453 UV spectrophotometer. ^{19}F and ^{1}H NMR spectra were recorded on a Bruker WP-200 SY instrument (188.3 and 200 MHz, respectively) whereas ^{13}C NMR spectra of compounds **14** and **18** were recorded on a Bruker AV 300 (75.5 MHz) and Bruker AM 400 (100.6 MHz) instruments, respectively. Chemical shifts are given in δ ppm from CCl_3F (^{19}F) and TMS (^{1}H and ^{13}C); C_6F_6 (−162.9 ppm from CCl_3F), $(Me_3Si)_2O$, $CHCl_3$ (0.04 and 7.24 ppm from TMS) and $(CD_3)_2CO$ (29.8 ppm from TMS) were used as internal standards. GC–MS: Hewlett Packard G1081A, combined with Hewlett Packard 5890 with mass selective detector HP 5971 (EI 70 eV). The molecular masses of the compounds were determined by high-resolution mass spectrometry on a Finnigan Mat 8200 instrument (EI 70 eV). Contents (yields) of products in the reaction mixtures were established by GC–MS method and ^{19}F NMR spectroscopic data.

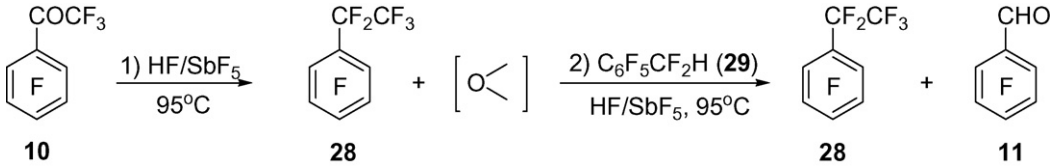


Scheme 7.

The X-ray diffraction experiment was carried out on a Bruker P4 diffractometer (graphite-monochromated Mo Kα radiation) at room temperature. Intensity data were collected using $\theta/2\theta$-scan, $2\theta < 60^\circ$. Reflection intensities were corrected for absorption by integration method. The structure was solved by direct methods, using SHELXS-97 program and refined by anisotropic full-matrix least-squares against F^2 of all reflections using SHELXL-97 program. Crystallographic data for the structure of *E*-**18** in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary



Scheme 8.



Scheme 9.

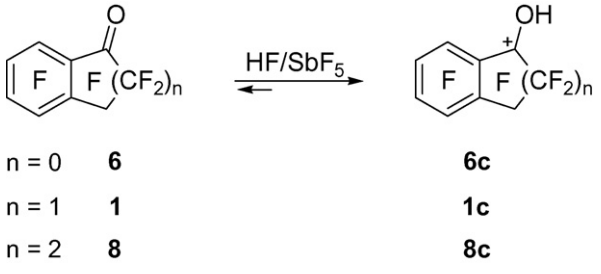
publication no. CCDC 611160. Copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 122 3336033 or e-mail: deposit@ccdc.cam.ac.uk).

The structures of the compounds were established by elemental analysis, HRMS and spectral characteristics. The structure of compound *E*-**18** was confirmed by single crystal X-ray diffraction as well. Assignment of signals in the ^{19}F NMR spectra was made on the basis of chemical shifts of the signals, their fine structure and integral intensities. Compounds **1**–**3**, **6**–**13**, **15**, **25**–**31**, **33** were identified by comparison of the ^{19}F NMR data with those for authentic samples.

Mixture of HF/SbF_5 (molar ratio HF:SbF_5 = 1.8-2.15: 1) was used in all experiments.

*3.1. Reaction of perfluoroindan-1,3-dione (**2**) with HF/SbF_5*

1. A mixture of 0.8 g of compound **2**, 1.2 g of HF/SbF_5 (molar ratio of **2**:HF:SbF_5 = 1:2.7:1.5) was heated in a Teflon™ closed container (20 ml) at 95 °C for 3 h. The mixture was poured into 5% hydrochloric acid and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. The solution contained compounds **1**, **2**, **4** and **14** in the ratio 2:5:92:1 (^{19}F NMR). The solution was washed with 5% hydrochloric acid (removal of **2**) and dried over $MgSO_4$. The solvent was distilled off to give 0.58 g of mixture, which contained compounds **1**, **4**, **14** and **18** (<5%). The mixture in a sealed ampoule was heated at 130 °C for 7 h to give 0.56 g (yield 70%) of compound **18** (*E*:*Z* ~ 50:50). Analytical sample of compound **18** (*E*:*Z* ~ 40:60) was prepared by crystallization (CH_2Cl_2-hexane) and then sublimation (170 °C, 2 Torr).

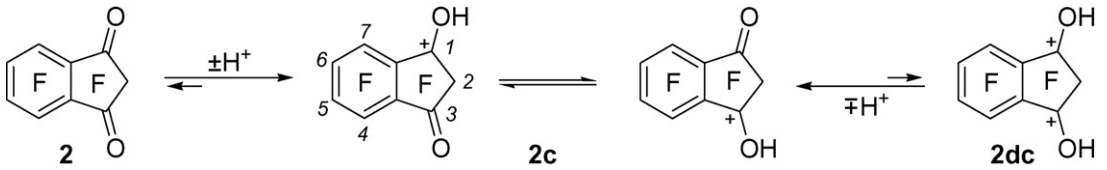


Scheme 10.

Perfluorodispiro[*phthalide-3,1′-cyclobutane-2′,3″-phthalide*] (**18**), mixture of two isomers, ratio *E*:*Z* ~ 40:60: mp 153–197 °C. UV (C_2H_5OH) λ_{max}, nm (lg ε): 202 (4.56), 262 (3.84), 272 (3.86), 311 (3.53). IR (KBr) ν, cm^{-1}: 1821 (C=O); 1523, 1507 [fluorinated aromatic ring (FAR)].

E-isomer: NMR ^{13}C ($(CD_3)_2CO$): δ 160.8 (C-1, C-1″), 147-144 (C-4, C-4″, C-5, C-5″, C-6, C-6″, C-7, C-7″), 120.7 and 112.8 (C-3a, C-3a″ and C-7a, C-7a″), 116.9 (C-3′, C-4′(CF_2)), 89.7–89.5 (C-3, C-3″). NMR ^{19}F ($(CH_3)_2CO$): δ −116.3 (2F, F-A, F-A′), −120.4 (2F, F-B, F-B′), −132.0 (2F, F-4, F-4″), −139.6 (2F, F-7, F-7″), −142.3 (2F, F-5, F-5″), −147.5 (2F, F-6, F-6″); $J_{A,B}$ = 224 Hz, $J_{4,A}$ = 19 Hz, $J_{4,B'}$ = 31 Hz $J_{4,5}$ = 20 Hz, $J_{4,6}$ = 7 Hz, $J_{4,7}$ = 17 Hz, $J_{5,6}$ = 18 Hz, $J_{5,7}$ = 9 Hz, $J_{6,7}$ = 20 Hz.

Z-isomer: NMR ^{13}C ($(CD_3)_2CO$): δ 161.4 (C-1, C-1″), 147-144 (C-4, C-4″, C-5, C-5″, C-6, C-6″, C-7, C-7″), 121.4 and 112.2 (C-3a, C-3a″, and C-7a, C-7a″), 116.8 (C-3′, C-4′(CF_2)), 89.7–89.5 (C-3, C-3″). NMR ^{19}F ($(CH_3)_2CO$): δ −117.2 (2F, F-A, F-A′), −122.7 (2F, F-B, F-B′), –130.2 (2F, F-4, F-4″), −138.8 (2F, F-7, F-7″), −141.9 (2F, F-5, F-5″), −147.3 (2F, F-6, F-6″); $J_{A,B}$ = 224 Hz, $J_{4,A} = J_{4,A'}$ = 34 Hz, $J_{4,5} \sim 20$ Hz, $J_{4,6} \sim 5$ Hz, $J_{4,7} \sim 17$ Hz, $J_{5,6} \sim 18$ Hz, $J_{5,7} \sim 10$ Hz, $J_{6,7} \sim 21$ Hz (spectrum is not of the first order). Anal. Calcd for $C_{18}F_{12}O_4$: M 508; C, 42.5%; Found (mixture of *E* and *Z*-isomers): M 506 (acetone); C, 42.8%.



Scheme 11.

Perfluoro-3-methylenephthalide (***4***): IR (CCl_4) ν, cm^{-1}: 1823, 1809 (C=O); 1734 (C=CF_2); 1526, 1497 (FAR). ^{19}F NMR (CH_2Cl_2): δ −84.8 (1F, F-3t), −99.1 (1F, F-3c), −137.3 (1F, F-4), −138.1 (1F, F-7), −141.8 (1F, F-5), −150.2 (1F, F-6); $J_{3c,3t}$ = 33 Hz, $J_{3c,4}$ = 54 Hz, $J_{3c,5}$ = 2 Hz, $J_{3c,6}$ = 6 Hz, $J_{3c,7}$ = 2 Hz, $J_{3t,4}$ = 7 Hz, $J_{3t,5}$ = 3 Hz, $J_{3t,6}$ = 8 Hz, $J_{4,5}$ = 19 Hz, $J_{4,6}$ = 4 Hz, $J_{4,7}$ = 19 Hz, $J_{5,6}$ = 18 Hz, $J_{5,7}$ = 10 Hz, $J_{6,7}$ = 20 Hz.

2. In a nickel bomb (10 ml) analogously to the previous procedure, the reaction of indandione **2** (0.58 g), 1.46 g of HF/SbF_5 (molar ratio, 1:4.9:2.5) gave (95 °C, 43 h) a solution ($CHCl_3$), contained compounds **3**, **4**, **14** and **15** in the ratio 12:35:50:3 (^{19}F NMR). The solvent was removed in vacuo at 20 °C to give 0.53 g of mixture of compounds **3**, **4**, **14** and **15** (yield 10, 30, 43, 3%, respectively).
3. Analogously to procedure (1), the reaction of indandione **2** (0.77 g), 1.93 g of HF/SbF_5 (molar ratio, 1:4.9:2.5) gave (130 °C, 11 h) a solution ($CHCl_3$), contained compounds **3**, **14** and **15** in the ratio 2:97:1 (^{19}F NMR). The mixture was spontaneously evaporated in the air to dryness to give 0.72 g (yield 87%) of compound **14**.

4,5,6,7-Tetrafluoro-3-trifluoromethyl-phthalide (**14**): mp 93.5–94.5 °C (hexane). UV (hexane) λ_{max}, nm (lg ε): 225 (3.90), 231 (3.88), 277 (3.22). IR (CCl_4) ν, cm^{-1}: 2965 (CH); 1823, 1796 (C=O); 1520, 1504 (FAR). ^1H NMR (CCl_4): δ 5.77 (q, J_{H-CF_3} = 5 Hz, H-3). ^{13}C NMR ($CDCl_3$): δ 161.6 (s, C-1), 145.7 (ddd, $^1J_{CF}$ = 266 Hz, $^2J_{CF}$ = 16, 13 Hz) and 142.7 (dt, $^1J_{CF}$ = 262 Hz, $^2J_{CF}$ = 14 Hz, C-5 and C-6), 144.9 (dd, $^1J_{CF}$ = 268 Hz, $^2J_{CF}$ = 12 Hz) and 142.5 (dd, $^1J_{CF}$ = 260 Hz, $^2J_{CF}$ = 13 Hz, C-4 and C-7), 122.2 (d, $^2J_{CF}$ = 15 Hz) and 110.2 (d $^2J_{CF}$ = 13 Hz, C-3a and C-7a), 121.3 (q, $^1J_{CF}$ = 281 Hz, CF_3), 74.0 (dq, $^1J_{CH}$ = 162 Hz, $^2J_{CF}$ = 38 Hz, C-3). ^{19}F NMR (CCl_4): δ −77.7 (3F, CF_3), −136.7 (1F, F-7), −138.9 (1F, F-4), −142.0 (1F, F-5), −148.0 (1F, F-6); J_{H-CF_3} = 5 Hz, $J_{CF_3F(4)}$ = 14 Hz, $J_{4,5}$ = 20 Hz, $J_{4,6}$ = 6 Hz, $J_{4,7}$ = 19 Hz, $J_{5,6}$ = 18 Hz, $J_{5,7}$ = 10 Hz, $J_{6,7}$ = 20 Hz. HRMS *m/z*, 273.9855 (M^+). Calcd for $C_9HF_7O_2$ = 273.9865.

3.2. Reactions of perfluoro-3-methylenephthalide (*4*) with SbF_5 and Br_2

1. In a nickel bomb (10 ml) analogously to procedure (1) of the previous experiment, the reaction of indandione **2** (0.84 g), 1.3 g of HF/SbF_5 (molar ratio, 1:3.2:1.5) gave (95 °C, 3 h) 0.74 g of mixture of compounds **1**, **2**, **4** and **14** in the ratio 11:8:79:2 (^{19}F NMR). The mixture was heated at 125 °C for 3 h with 2.71 g of SbF_5 (molar ratio, **4**:SbF_5 = 1:3.8). 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 0.71 g of mixture, which contained (^{19}F NMR) 30% (yield 22%) of 3-hydroxy-perfluoro-3-methylphthalide [6], 64% (47%) of **3**, 3% (2%) of **14**, 4% (2%) of perfluoro-2-ethylbenzoic acid [6].
2. A mixture of 1.44 g of compound **2**, 2.17 g of HF/SbF_5 (molar ratio of **2**:HF:SbF_5 = 1:2.7:1.5) was heated in a nickel bomb (10 ml) at 95 °C for 3 h. The mixture was poured into 5% hydrochloric acid and extracted with CCl_4. The extract was dried over $MgSO_4$. Dibromine (1.5 g) was added into the extract at room temperature and the mixture was kept at this temperature for 20 h. The mixture was washed with aqueous solutions of Na_2SO_3, then with $NaHCO_3$ and dried over $MgSO_4$. The solvent was distilled off to give 1.96 g (yield 83%) of compound **17**, which was additionally purified by short-path distillation (90 °C, 3–4 Torr).

3-Bromo-3-(bromodifluoromethyl)-4,5,6,7-tetrafluorophthalide (**17**): liquid. IR (CCl_4) ν, cm^{-1}: 1836 (C=O); 1522, 1505 (FAR). ^{19}F NMR (CH_2Cl_2): δ −55.1 ($1F_A$) and −56.2 ($1F_B$, CF_2Br), −133.0 (1F, F-4), −135.4 (1F, F-7), −138.6 (1F, F-5), −145.1 (1F, F-6); $J_{A,B}$ = 170 Hz, $J_{A,4}$ = 32 Hz, $J_{B,4}$ = 13 Hz, $J_{4,5}$ = 20 Hz, $J_{4,6}$ = 8 Hz, $J_{4,7}$ = 19 Hz, $J_{5,6}$ = 18 Hz, $J_{5,7}$ = 11 Hz, $J_{6,7}$ = 20 Hz. HRMS *m/z*, 332.8945 (M^+-Br). Calcd for $C_9BrF_6O_2$ = 332.8986. Anal. Calcd for $C_9Br_2F_6O_2$: Br, 38.6; F, 27.5%. Found: Br; 38.8; F, 27.8%.

3.3. Heating of dimer*18* with Br_2 and in its absence

1. 0.16 g of dimer **18** (*E:Z* ~ 50:50) in ampoule, sealed under argon, was heated at 180 °C for 21 h to give 0.16 g of compound *E*-**18** without *Z*-**18** (^{19}F NMR).*E-Perfluorodispiro*[*phthalide-3,1′-cyclobutane-2′,3″-phthalide*] (E-**18**): mp 172–173 °C (CH_2Cl_2 – hexane). UV (C_2H_5OH) λ_{max}, nm (lg ε): 205 (4.54), 274 (3.73), 282 (3.71), 313 (3.27), 321 (3.27). IR (KBr) ν, cm^{-1}: 1820 (C=O); 1522, 1507 [fluorinated aromatic ring (FAR)]. Single crystals of compound *E*-**18** were grown by slow evaporation of a solvent from CH_2Cl_2 – hexane solution.

   Crystallographic data and refinement parameters:

   Formula $C_{18}F_{12}O_4$, *M* = 508.18, monoclinic, space group *Cc*, *a* = 11.5028(10), *b* = 19.2746(11), *c* = 7.8848(5) Å, β = 94.855(6)°, *V* = 1741.9(2) $Å^3$, *Z* = 4, D_{calc} = 1.938 g/cm^3, μ = 0.219 mm^{-1}, 2842 total reflexions, 2655 unique reflexions (R_{int} = 0.0474), *R* = 0.0300 for 2478 $I > 2\sigma(I)$, 308 parameters, wR_2 = 0.0868 and GOF = 1.049 for all data, max/min $\Delta\rho$ 0.217/−0.153.
2. A mixture of 0.17 g of dimer **18** (*E:Z* ~ 50:50) with 0.6 g of Br_2 (molar ratio, 1:11) in a sealed ampoule was heated at

180 °C for 19 h. A mixture was dissolved in CH_2Cl_2, washed with aqueous solution of Na_2SO_3 and dried over $MgSO_4$. The solvent was distilled off to give 0.16 g of a mixture of compounds ***E*-18** and **17** in the molar ratio 95:5 (^{19}F NMR), yield 90 and 2%, respectively.

3. Analogously to the previous procedure, the reaction of dimer **18** (0.06 g) with Br_2 (0.32 g) (molar ratio, 1:17) gave (260 °C, 9 h) 0.09 g of a mixture contained ~95% (yield 87%) of compound **17** (NMR ^{19}F).

3.4. Reaction of perfluoroindan-1-one (*1*) with HF/ SbF_5

1. A mixture of 0.61 g of compound **1**, 1.4 g of HF/SbF_5 (molar ratio of **1**:HF:SbF5 = 1:4.9:2.5) was heated in a nickel bomb (10 ml) at 95 °C for 15.5 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 0.52 g of mixture, which contained compounds **1** and **15** in the ratio 48:52 (yield 38 and 42%).
2. Analogously to the previous procedure, the reaction of indanone **1** (0.6 g) and HF/SbF_5 (1.39 g) (molar ratio, 1:4.9:2.5) gave (95 °C, 43 h) 0.54 g of mixture, which contained compounds **1** and **15** in the ratio 14:86 (yield 12 and 72%).

3.5. Reaction of perfluoroindan-2-one (*5*) with HF/SbF_5

1. To 0.89 g of HF/SbF_5 placed in an ampoule with Teflon FEP inliner for recording of NMR spectra 0.38 g of ketone **5** (molar ratio, **5**:HF:SbF_5 = 1:5.4:2.5) was added. The mixture was stirred and ^{19}F NMR spectrum of the solution was recorded. The spectrum contained ill-resolved signals of compound **23**. ^{19}F NMR (188.3 MHz, C_6F_6 was used as external standard): δ −113.4 ($2F_A$) and −124.8 ($2F_B$, $J_{A,B}$ = 250 Hz, CF_2-1,3); −132.9 (1F, F-2); −134.5 (2F, F-4, F-7); −143.9 (2F, F-5, F-6) ppm. The solution was poured into 5% hydrochloric acid and extracted with ether. The extract was dried over $MgSO_4$. The solvent was distilled off to give 0.33 g (yield 93%) of 2,2-dihydroxyperfluoroindan (^{19}F NMR), which is hydrate form of ketone **5** [19].
2. A mixture of 0.6 g of compound **5**, 1.39 g of HF/SbF_5 (molar ratio of **5**:HF:SbF_5 = 1:4.9:2.5) was heated in a nickel bomb (10 ml) at 95 °C for 16 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 0.52 g of mixture, which contained compounds **21** and **22** in the ratio 79:21 (yield 66 and 18%). The individual compounds **21** (0.34 g) and **22** (0.09 g) were isolated by silica gel column chromatography (CCl_4 as eluent) and then purified by sublimation (130 °C, 2 Torr).

   Bis(*perfluoroindan-2-yl*) *ether* (***21***): mp 152–152.5 °C. UV (C_2H_5OH) λ_{max}, nm (lg ε): 267 (3.32). IR (KBr) ν, cm^{-1}: 1522 (FAR). ^{19}F NMR (376.4 MHz, ether): δ −95.1 ($4F_A$) and −112.7 ($4F_B$, $J_{A,B}$ = 264 Hz, CF_2-1, CF_2-3), −133.8 (2F, F-2), −138.5 (4F, F-4, F-7), −142.7 (4F, F-5, F-6). HRMS *m/z*, 573.9662 (M^+). Calcd for $C_{18}F_{18}O$ = 573.9662.

   Perfluoro-2-(*indan-2-yloxy*)*indan-1-one* (***22***): mp 148.5–150 °C. UV (hexane) λ_{max}, nm (lg ε): 215 (4.11), 243 (4.03), 251 (4.08), 269 (3.22), 293 (3.26). IR (KBr) ν, cm^{-1}: 1775 (C=O); 1519 (FAR). ^{19}F NMR (ether): δ −95.5 and −96.5 (A-components of two AB-systems), −111.4 and −111.8 (B-components of two AB-systems, $2CF_2$, $J_{A,B}$ = 263 Hz), −99.8 ($1F_A$) and −110.8 ($1F_B$, $J_{A,B}$ = 267 Hz, CF_2), −127.6 (1F, F-2), −132.9 (1F, F-7), −134.3 (1F, F-2′), −136.3 (1F, F-5), −137.7 (1F, F-4), −138.6 (2F, F-4′, F-7′), −142.9 (2F, F-5′, F-6′), −143.7 (1F, F-6); $J_{4,3A}$ and $J_{4,3B}$ = 6 and 8 Hz, $J_{4,5}$ = 20 Hz, $J_{4,6}$ = 8 Hz, $J_{4,7}$ = 18 Hz, $J_{5,6}$ = 18 Hz, $J_{5,7}$ = 13 Hz, $J_{6,7}$ = 20 Hz. HRMS *m/z*, 551.9641 (M^+). Calcd for $C_{18}F_{16}O_2$ = 551.9643.
3. Analogously to the previous procedure, the reaction of indanone **5** (0.56 g) and HF/SbF_5 (1.29 g) (molar ratio, 1:4.9:2.5) gave (130 °C, 11 h) 0.42 g of mixture, which contained 15% of **14**, 11% of **15**, 17% of **21**, 21% of **22** together with unidentified impurities (^{19}F NMR, GC–MS).

3.6. Reaction of perfluorinated benzocyclobutenone (*6*), benzocyclobutenedione (*7*), 3,4-dihydronaphthalen-1(2H)-one (*8*) and 2,3-dihydronaphthalene-1,4-dione (*9*) with HF/ SbF_5

1. A mixture of 0.5 g of compound **6**, 1.41 g of HF/SbF_5 (molar ratio of **6**:HF:SbF_5 = 1:4.9:2.5) was heated in a nickel bomb (10 ml) at 95 °C for 15.5 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 0.47 g of mixture, which contained (^{19}F NMR) compounds **6**, **25** and **26** in the ratio 50:39:11 (yield 44, 34 and 10%, respectively).
2. Analogously to the previous procedure, the reaction of compound **7** (0.37 g) and HF/SbF_5 (1.14 g) (molar ratio, 1:4.9:2.5) gave (95 °C, 15.5 h) 0.35 g of mixture, which contained compounds **6**, **7** and **25** in the ratio 43:41:16 (yield 38, 36 and 14%, respectively).
3. Analogously to procedure (1), the reaction of compound **8** (0.59 g) and HF/SbF_5 (1.15 g) (molar ratio, 1:4.9:2.5) gave (95 °C, 15.5 h) 0.53 g of mixture, which contained compounds **8**, and **27** in the ratio 10:90 (yield 8 and 76%, respectively).
4. A mixture of 0.59 g of compound **9**, 1.21 g of HF/SbF_5 (molar ratio of **9**:HF:SbF_5 = 1:4.9:2.5) was heated in a nickel bomb (10 ml) at 95 °C for 15.5 h. The mixture was poured into 5% hydrochloric acid and extracted with ether. The extract was dried over $MgSO_4$. The solvent was distilled off, the mixture obtained was dissolved in CH_2Cl_2 and dried over $MgSO_4$. The solvent was distilled off to give 0.51 g of mixture, which contained (^{19}F NMR) compounds **8**, **9** and **27** in the ratio 41:44:15 (yield 35, 36 and 12%, respectively).

3.7. Reaction of perfluorinated acetophenone (*10*) and benzaldehyde (*11*) with HF/SbF_5

1. In a nickel bomb (10 ml) analogously to procedure (1) of the previous experiment, the reaction of compound **10** (0.62 g)

and HF/SbF_5 (1.5 g) (molar ratio, 1:4.9:2.5) gave (95 °C, 15.5 h) 0.54 g (yield 80%) of compound **28**.

2. Analogously to the previous procedure, the reaction of compound **11** (0.45 g) and HF/SbF_5 (1.45 g) (molar ratio, 1:4.9:2.5) gave (95 °C, 18 h) 0.35 g of mixture, which contained (^{19}F NMR) compound **11** and small amount (<3%) of compound **29**.
3. A mixture of 0.74 g of compound **10**, 1.84 g of HF/SbF_5 (molar ratio of **10**:HF:SbF_5 = 1:5.4:2.5) was heated in a nickel bomb (10 ml) at 95 °C for 15.5 h. Then compound **29** (0.61 g, molar ratio of **10**:**29** = 1:1) was added to the reaction mixture. The resulting mixture was heated at 95 °C for 22 h and treated analogously to procedure (1). It was obtained 1.24 g of mixture, which contained (^{19}F NMR) compounds **11**, **28** and **29** in the ratio 47:48:5 (yield 87, 88 and 10%, respectively).
4. A mixture of 0.38 g of compound **29**, 1.14 g of HF/SbF_5 (molar ratio of **29**:HF:SbF_5 = 1:5.4:2.5) was kept in a Teflon container at room temperature for 24 h. The mixture was poured into 5% hydrochloric acid and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. The solution contained compounds **11** and **29** in the ratio 33:67 (^{19}F NMR).

3.8. Reaction of perfluorinated benzoic acid (*12*) and phthalic anhydride (*13*) with HF/SbF_5

1. A mixture of 0.56 g of acid **12**, 1.73 g of HF/SbF_5 (molar ratio of **12**:HF:SbF_5 = 1:5.4:2.5) was heated in a nickel bomb (10 ml) at 95 °C for 15 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 0.43 g of mixture, which contained (^{19}F NMR) compounds **12**, **30** and **31** in the ratio 31:57:12 (yield 22, 41 and 9%, respectively).
2. A mixture of 0.5 g of anhydride **13**, 2.91 g of HF/SbF_5 (molar ratio of **13**:HF:SbF_5 = 1:9.8:5) was heated in a nickel bomb (10 ml) at 95 °C for 62 h. The mixture was poured into 5% hydrochloric acid and extracted with CH_2Cl_2 and then with ether. The extracts were dried over $MgSO_4$. The solvent from ether extract was distilled off to give 0.1 g of tetrafluorophthalic acid. The CH_2Cl_2 extract contained compounds **13**, **32**, **33** and **34** in the ratio 20:17:4:59 (^{19}F NMR). This extract was washed with aqueous solution of $NaHCO_3$ and dried over $MgSO_4$. The solvent was distilled off to give 0.26 g of product containing compounds **13**, **33** and **34** in the ratio 5:3:92 (^{19}F NMR). Phthalide **34** was additionally purified by short-path distillation (110 °C, 40 Torr). The aqueous solution was acidified with HCl, extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was distilled off to give 0.08 g (yield 13%) of acid **32**, which was purified by sublimation (100 °C, 2 Torr).

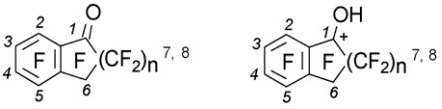
Perfluorophthalide (**34**): liquid. IR (CCl_4) ν, cm^{-1}: 1861, 1841 (C=O); 1523, 1508 (FAR). ^{19}F NMR (CH_2Cl_2): δ −76.7 (2F, F-3), −133.6 (1F, F-7), −137.5 (1F, F-4), −138.2 (1F, F-5), −143.3 (1F, F-6); $J_{3,4}$ = 4 Hz, $J_{3,6}$ = 2 Hz, $J_{3,7}$ = 2 Hz, $J_{4,5}$ = 20 Hz, $J_{4,6}$ = 8 Hz, $J_{4,7}$ = 19 Hz, $J_{5,6}$ = 17 Hz, $J_{5,7}$ = 12 Hz, $J_{6,7}$ = 20 Hz. HRMS *m/z*, 241.9813 (M^+). Calcd for $C_9F_8O_2$ = 241.9802. Tetrafluorophthaloyl difluoride as acyclic isomer of compound **34** was characterized in Ref. [20].

Perfluoro-2-methylbenzoic acid (**32**): mp 90.5–92 °C. UV (hexane) λ_{max}, nm (lg ε): 212 (3.73), 268 (3.14). IR (CCl_4) ν, cm^{-1}: 3504, 3038 (OH); 1773, 1733 (C=O); 1530, 1487 (FAR). ^{1}H NMR (CCl_4): δ 11.19 (s, OH). ^{19}F NMR (CCl_4): δ −58.4 (3F, CF_3), −136.7 (1F, F-3), −139.3 (1F, F-6), −147.2 (1F, F-5), −150.1 (1F, F-4); $J_{CF_3-F(3)}$ = 19 Hz, $J_{3,4}$ = 20 Hz, $J_{3,5}$ = 9 Hz, $J_{3,6}$ = 12 Hz, $J_{4,5}$ = 20 Hz, $J_{4,6}$ = 6 Hz, $J_{5,6}$ = 21 Hz. HRMS *m/z*, 261.9879 (M^+). Calcd for $C_8HF_7O_2$ = 261.9865.

3.9. Protonation of perfluorinated indan-1-one (*1*), benzocyclobutenone (*6*) and 3,4-dihydronaphthalen-1(2H)-one (*8*) with HF/SbF_5

1. To 0.6 g of HF/SbF_5 placed in an ampoule with Teflon FEP inliner for recording of NMR spectra 0.26 g of ketone **1** (molar ratio, **1**:HF:SbF_5 = 1:4.9:2.5) was added. The mixture was stirred and ^{19}F NMR spectrum of the solution was recorded (Table 1), perfluoroindan (the most upfield signal 19.5 ppm from C_6F_6) was used as internal standard. The solution 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 0.23 g (yield 88%) of ketone **1** (^{19}F NMR).
2. Analogously to the previous procedure, solution of compound **6** (0.26 g) in HF/SbF_5 was prepared and ^{19}F NMR spectrum was measured, then compound **6** (0.22 g, yield 85%) was recovered.

Table 1
^{19}F NMR spectra of ketones **1**, **6**, **8** (CH_2Cl_2) and cations **1c**, **6c**, **8c** (HF/SbF_5)



	1	1c	6	6c	8	8c
δ (ppm)						
F-2	−132.4	−103.5	−125.9	−106.9	−132.7	−94.4
F-3	−142.6	−135.4	−140.8	−129.4	−144.0	−138.0
F-4	−134.7	−97.4	−133.9	−98.8	−137.7	−100.2
F-5	−136.5	−128.5	−133.4	−126.6	−134.0	−122.9
F-6	−109.0	−105.1	−96.8	−84.4	−106.8	−105.6
F-7	−125.2	−115.0	–	–	−133.7	−131.8
F-8	–	–	–	–	−127.6	−117.8
$J_{F,F}$ (Hz)						
$J_{2,3}$	20	18	20	16	20	19
$J_{2,4}$	13	36	12	30	15	41
$J_{2,5}$	18	13	25	22	13	6
$J_{2,6}$	–	–	2	–	2	
$J_{3,4}$	18	17	17	17	20	19
$J_{3,5}$	9	12	8	13	9	13
$J_{3,6}$	2	–	–	–	2	–
$J_{4,5}$	20	19	20	18	20	19
$J_{5,6}$	7	6	3	–	22	25

3. Analogously to procedure (1), solution of ketone **8** (0.34 g) in HF/SbF_5 was prepared and ^{19}F NMR spectrum was measured, then ketone **8** (0.3 g, yield 88%) was recovered.

*3.10. Protonation of perfluorinated indan-1,3-dione (**2**), 3-methylenephthalide (**4**), benzocyclobutenedione (**7**) and 2,3-dihydronaphthalene-1,4-dione (**9**) in HF/SbF_5*

1. Analogously to the previous experiments, solution of compound **2** (0.29 g) in an HF/SbF_5 (molar ratio, **2**:HF:SbF_5 = 1:4.9:2.5) was prepared and ^{19}F NMR spectrum was recorded (spectrum of **2c** is given in Section 2 of the paper). Then the solution was heated at 95 °C for 3 h and ^{19}F NMR spectrum of solution of compound **4** in HF/SbF_5 was measured at r.t. The solution was poured into 5% hydrochloric acid and extracted with $CHCl_3$. The extract was dried over $MgSO_4$. The solvent was distilled off to give 0.19 g of mixture, which contained (^{19}F NMR) compounds **1**, **4**, **14** and **15** in the ratio 6:73:19:2 (yield 4, 46, 12 and 1%, respectively). ^{19}F NMR of **4c** (HF/SbF_5): δ –63.3 (1F, F-3t), −75.1 (1F, F-3c), −124.4 (1F, F-7), −125.2 (1F, F-5), −132.5 (1F, F-4), −144.4 (1F, F-6); $J_{3c,3t}$ = 24 Hz, $J_{3c,4}$ = 41 Hz, $J_{3c,6}$ = 4 Hz, $J_{3t,4}$ = 7 Hz, $J_{3t,5}$ = 4 Hz, $J_{3t,6}$ = 7 Hz, $J_{4,5}$ = 17 Hz, $J_{4,6}$ = 8 Hz, $J_{4,7}$ = 17 Hz, $J_{5,6}$ = 17 Hz, $J_{5,7}$ = 19 Hz, $J_{6,7}$ = 18 Hz.
2. Analogously to procedure (1) of the previous experiment, solution of compound **7** (0.26 g) in HF/SbF_5 was prepared and ^{19}F NMR spectrum was measured, then compound **7** (0.19 g, yield 73%) was recovered. ^{19}F NMR of **7c** (HF/SbF_5): δ −109.3 (2F) and −111.8 (2F) (F-3, F-4, F-5, F-6).
3. Analogously to the previous experiments, solution of compound **9** (0.31 g) in HF/SbF_5 was prepared and ^{19}F NMR spectrum was recorded, then compound **9** (0.2 g, yield 65%) was recovered. ^{19}F NMR of **9c** (HF/SbF_5): δ −103.4 (2F) and −115.6 (2F) (F-5, F-6, F-7, F-8), −119.9 (4F, 2F-2, 2F-3).

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