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Formation and skeletal transformations of perfluoroindan-1-one and perfluoroindan-1,3-dione in the reaction of perfluoroindan with SiO_2/SbF_5

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Dedicated to Professor Richard D. Chambers, on the occasion of 70th birthday

Abstract

Perfluoroindan-1-one (**2**) is obtained in the reaction of perfluoroindan (**1**) with SiO_2/SbF_5 at 70 °C. Compound **1** heated with SiO_2/SbF_5 at 130 °C and then treated with water, gives 3-hydroxy-perfluoro-3-methylphthalide (**4**). Ketone **2** is converted, under the action of SbF_5 at 130 °C, to perfluoro-2-ethylbenzoic acid (**9**) and disproportionates to compound **1** and perfluoroindan-1,3-dione (**3**); the latter is transformed to phthalide **4** under the reaction conditions.

Keywords: Skeletal transformations; Perfluoroindan; Perfluoroindan-1-one; Perfluoroindan-1,3-dione; Silicon dioxide; Antimony pentafluoride; NMR spectroscopy

1. Introduction

Perfluorinated benzocycloalkenes (benzocyclobutene, indan, tetralin) and their perfluoroalkyl and perfluoroaryl derivatives, when heated with antimony pentafluoride, undergo skeletal transformations leading to cleavage, expansion or contraction of the alicyclic ring of benzocycloalkenes [1–4] (see also [1–7] in Ref. [2]). For example, when heated with SbF_5 in a nickel bomb, perfluoro-1-methylindan 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 [5] (Scheme 1).

Apparently, the reaction with glass proceeds via intermediate formation of perfluoro-3-methylindan-1-one. On the other hand, selective ''hydrolysis'' of CF_3 groups in perfluorinated methyl- and propenyl-benzene derivatives proceeds under the action of SiO_2/SbF_5 to give the corresponding acids in a good yield [6].

In this connection it seemed reasonable to study the reaction of perfluorobenzocycloalkenes with silica in the presence of SbF_5 and transformations of the carbonyl derivatives of perfluorobenzocycloalkenes under the action of antimony pentafluoride. This work describes the reactions of perfluoroindan (**1**) with SiO_2 and with a glass in an SbF_5 medium and transformations of perfluoroindan-1-one (**2**) and perfluoroindan-1,3-dione (**3**) under the action of antimony pentafluoride.

It should be noted that the carbonyl group of perfluorinated 3-methylindenone, 1-methylindan-2-one, indan-2-one [7] and indanone **2** [8] is involved in the reactions with H_2O_2 in the $HF–SbF_5$ system to form six-membered oxygen containing heterocyclic compounds. When heated with antimony pentafluoride, perfluorinated ketones [9] and vinylketones [10] having a CF_3 group in the position β to the carbonyl group undergo intramolecular cyclization to give derivatives of oxolane and 2,5-dihydrofuran, respectively.

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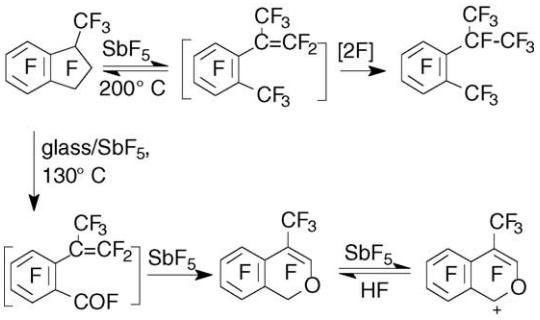


Scheme 1.

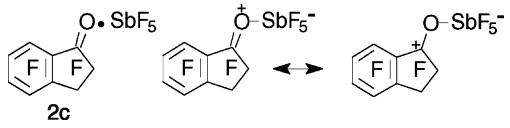
2. Results and discussion

We have found that reaction of indan **1** with SiO_2 (SiO_2 was prepared by heating of silica gel at 400–450 °C) in the presence of 1.5 mol of SbF_5 per 1 mol of compound **1** at 70 °C (5 h) gives indanone **2** and small amount of indandione **3**. Increase in the reaction time (13 h) leads to a small increase of diketone **3** yield. Decrease of SbF_5 from 1.5 to 0.5 mol per 1 mol of indan **1** lowers the conversion of the latter (Scheme 2).

The formation of indanone **2** and diketone **3** can be rationalized by a mechanism involving the interaction of the perfluoroindan-1-yl cation initially generated [11] and perfluoroindan-3-one-1-yl cation with SiO_2 according to the Scheme 2.

Formation of indanone **2** as the dominant component in comparison with diketone **3** from indan **1** could be explained by the fact that indanone **2** gives complex **2c** (its formation will be discussed below) with antimony pentafluoride (Scheme 3). As a result, the reaction of indanone **2** with SiO_2/SbF_5 should be difficult as compared with indan **1**. On the other hand, the complexing decreases the amounts of "free" SbF_5, and the reaction of indan **1** with SiO_2 is impeded.

The reaction of indan **1** with SiO_2 (70–75 °C) in the presence of 3 mol of SbF_5 per 1 mol of compound **1** gives, after treatment reaction mixture with water, indanone **2**, indandione **3** together with 3-hydroxy-perfluoro-3-methylphthalide (**4**). The reaction at 130 °C forms compound **4** with perfluoro-3-methylphthalide (**5**) and a small amount of tetrafluorophthalic acid (**6**). The latter is the main product of the reaction at 180 °C. Phthalides **4**, **5** are, probably, formed via intermediate diketone **3**. Indeed, a separate experiment has shown that the reaction of diketone **3** with antimony pentafluoride gives phthalides **4** and **5** with small amounts of acid **6** (Scheme 4).



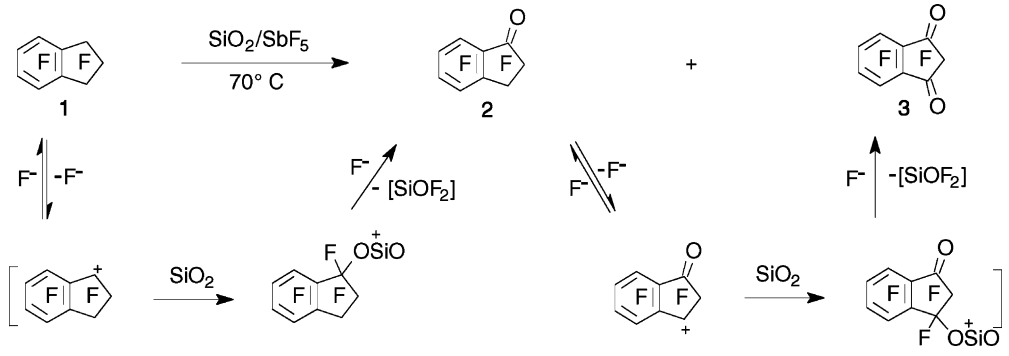
Scheme 3.

Transformation of diketone **3** to products **4**, **5** in the presence of antimony pentafluoride, possibly, proceeds in the following way (Scheme 5). At first complex **3c** is formed from diketone **3** and SbF_5. The five-membered cycle of the complex **3c** may undergo ring opening to give the intermediate **7**. The latter is further fluorinated yielding perfluoro-2-acetylbenzoyl fluoride (**5a**) and then product **5**, or/and intermediate **7** is transformed into perfluoro-3-methylenephthalide (**8**) which is fluorinated to product **5**. Hydrolysis of compounds **5** and **5a** leads to phthalide **4**.

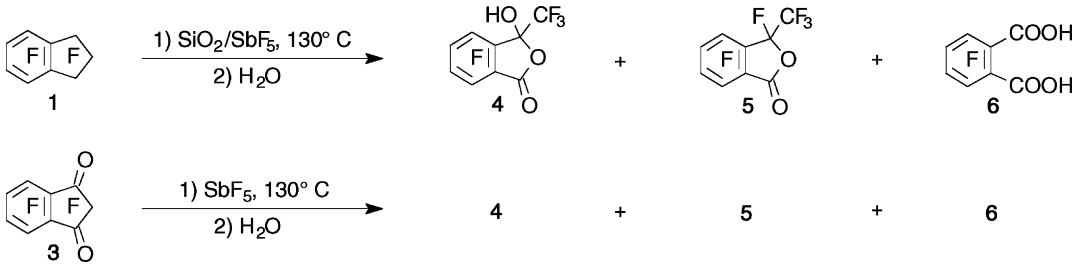
It has been shown that indanone **2** also undergoes skeletal transformations under the action of SbF_5 at high temperature. Thus, indanone **2**, heated with antimony pentafluoride at 130 °C (2 h) and then treated with water, gives a mixture of perfluoro-2-ethylbenzoic acid (**9**), phthalides **4**, **5** and indan **1**. The reaction mixture also contains unchanged ketone **2** (Scheme 6).

Transformation of indanone **2** in the presence of SbF_5 to the acid **9** may be represented by Scheme 6. At first compound **2** with SbF_5 seems to generate the cation **10**. The five-membered cycle of the latter may undergo ring opening analogous to that in perfluoro-1-methylindan (Scheme 1) and indan **1** under the action of SbF_5 [1]. This yields the benzoyl type ion **11**, which adds fluoride anion and then undergoes fluorination to form product **12**. Hydrolysis of the latter gives the acid **9**.

Fluorination of indanone **2** to product **12** under the action of antimony pentafluoride with cleavage of the bond C(O)–CF_2 in indanone **2** (not in the cation **10**) seems unlikely,



Scheme 2.



Scheme 4.

because perfluoro-3,3-diethylindan-1-one (**13**) is the only product of the reaction of perfluoro-1,1-diethylindan (**14**) with SiO_2/SbF_5 at 130 °C (Scheme 6).

Formation of the products **1**, **4**, **5** in the reaction of indanone **2** with antimony pentafluoride could be explained by disproportionation of ketone **2** to indan **1** and indandione **3** (Scheme 7), which gives products **4** and **5** under the reaction conditions, that was shown above.

When a solution of ketone **2** in indan **1** was heated with SbF_5, ketone **2** disproportionated to a lesser extent as compared with ketone **2** in the absence of indan **1**. As a result, the acid **9** is formed in higher yield. When heated with antimony pentafluoride at 130 °C in a glass ampoule during a lengthy period of time (35 h), indan **1** reacts with glass to give, after hydrolysis, acid **9** and, unexpectedly, perfluoro-2-ethylbenzoic anhydride **9a** only with a small admixture of compounds **4** and **5** (Scheme 6). This may be explained by the smaller relative rate of the reaction of indan **1** with glass as compared with SiO_2 and, as a consequence, formation of ketone **2** in small concentration can occur. As a result, ketone **2** is transformed rather to acid **9** (first reaction order for **2**, Scheme 6), than disproportionating to indan **1** and diketone **3** (second reaction order for **2**, Scheme 7).

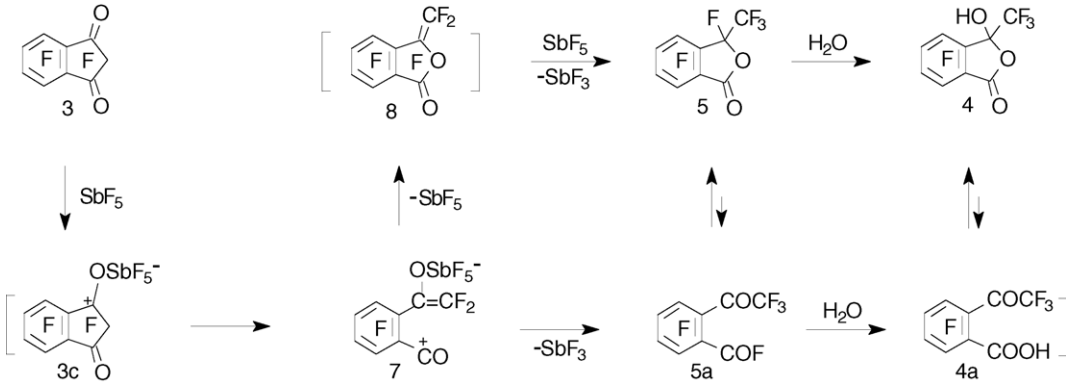
3. Experimental

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 instrument (188.3 and 200 MHz, respectively) whereas ^{13}C NMR spectrum of the compound **4** was recorded on a Bruker AM 400 instrument (100.6 MHz). Chemical shifts are given in δ ppm downfield from C_6F_6 (^{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 $CDCl_3$ (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 GLC and ^{19}F NMR spectroscopic data.

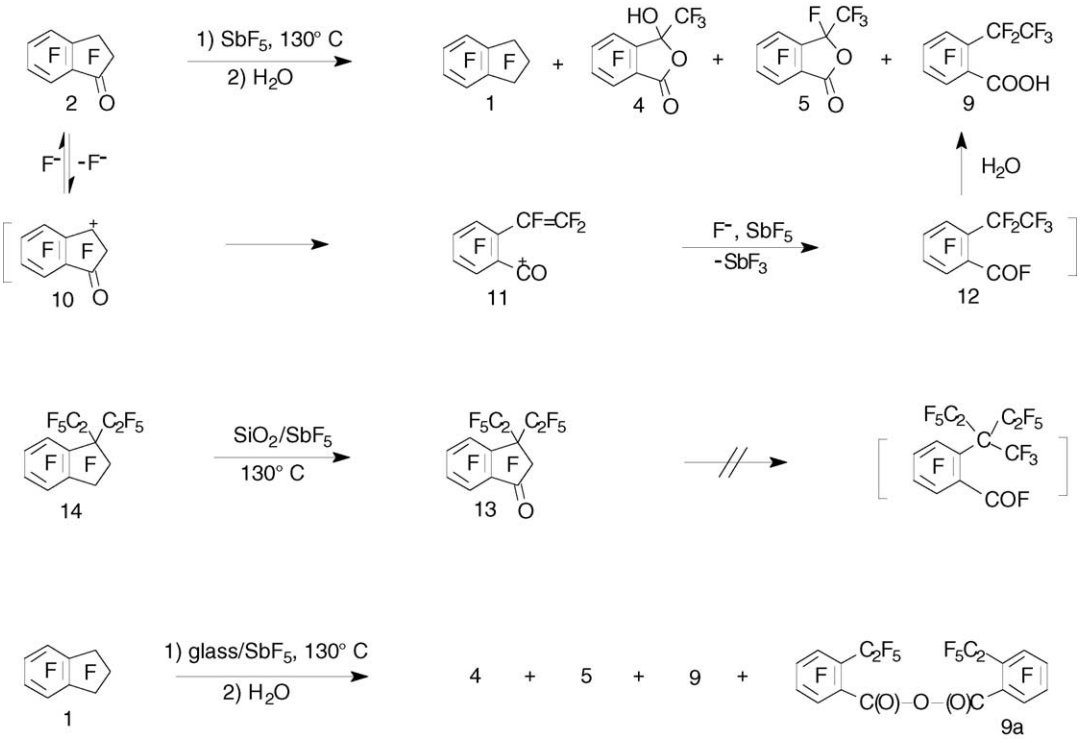
The structures of the compounds were established by elemental analysis, HRMS and spectral characteristics. Assignment of signals in the ^{19}F NMR spectra was made on the basis of chemical shifts of the signals, their fine structure and integral intensities. Compounds **2**, **3**, **6** were identified by comparison of the ^{19}F NMR data with data for authentic samples [12,13].

Formally, compounds **4** and **5** could exist as phthalides **4**, **5** and/or their open-chain forms **4a** and **5a**, respectively (Scheme 5). According to the ^{19}F NMR spectrum, compound **5** exists in the phthalide form. Signals at 4.71 ppm (OH, ^{1}H NMR) and at 99.3 ppm (C-3, ^{13}C NMR) testify to phthalide form of compound **4**. This is in accord with the fact that in a solution and in the solid state 2-acetylbenzoic acid exists in the phthalide form [14,15].

Assignment of signals in the ^{19}F NMR spectrum of complex **2c** (signals were not well resolved) was made by



Scheme 5.

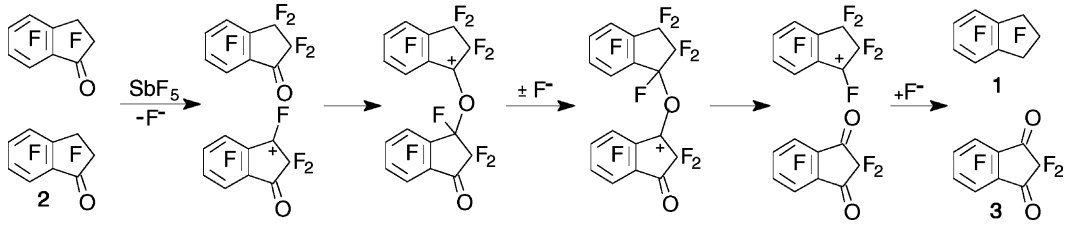


Scheme 6.

analogy with that for 1-chlorooctafluoroindan-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 complex **2c** down-field $\Delta\delta_F$ resemble those of 1-chlorooctafluoroindan-1-yl cation [16], a smaller scale of $\Delta\delta_F$ can be due to a less positive charge transfer onto ring.

*3.1. Reaction of perfluoroindan (**1**) with SiO_2/SbF_5 at 70 °C*

1. A mixture of 3.37 g of compound **1**, 0.6 g of SiO_2 and 3.68 g of SbF_5 (molar ratio, 1:0.88:1.5) was stirred at 70 °C for 5 h. The mixture was poured into 5% hydrochloric acid (0–5 °C) and extracted with CH_2Cl_2 and then with ether. The extracts were dried over $MgSO_4$. The solvents were distilled off to give 2.51 g (yield 80%) of indanone **2** (from CH_2Cl_2 extract) and 0.41 g of organic and inorganic products (from ether extract). By sublimation of the latter at 70–75 °C (15 Torr, then 2 Torr) a mixture (0.2 g), containing 73% of indanone **2** and 27% of indandione **3** (GLC), was isolated.
2. Analogously to the previous procedure, the reaction of indan **1** (3.64 g), SiO_2 (0.64 g) and SbF_5 (3.97 g) (molar ratio, 1:0.88:1.5) gave (70 °C, 13 h) 2.64 g (yield 78%) of indanone **2** (from CH_2Cl_2 extract) and 0.32 g of indandione **3** (from ether extract).
3. Analogously to procedure (1), the reaction of indan **1** (3.58 g), SiO_2 (0.63 g) and SbF_5 (1.2 g) (molar ratio, 1:0.88:0.5) gave (70 °C, 4 h) 2.8 g of a mixture containing 39% (yield 33%) of **2** and 59% (46%) of indan **1**.
4. Analogously to procedure (1), the reaction of indan **1** (16.62 g), SiO_2 (1.17 g) and SbF_5 (24.18 g) (molar ratio, 1:0.51:2) gave (70 °C, 9 h) 13.12 g (yield 85%) of indanone **2**.
5. A mixture of compound **1** (1.42 g), SiO_2 (0.46 g) and SbF_5 (3.25 g) (molar ratio, 1:1.54:3) was stirred at



Scheme 7.

70–75 °C for 4.5 h. The mixture was poured into 5% hydrochloric acid (0–5 °C) and extracted with ether. The solvent was distilled off to give 1.08 g of product, containing compounds **2**, **3** and **4** in the ratio 38:43:19 (^{19}F NMR), yield 31, 34 and 15%, respectively.

3.2. Reaction of perfluoroindan (*1*) with SiO_2/SbF_5 at 130 and 180 °C

1. A mixture of compound **1** (2.48 g), SiO_2 (0.55 g) and SbF_5 (5.42 g) (molar ratio, 1:1.1:3) was stirred at 90 °C for 0.5 h. Then for 0.5 h the temperature of the bath was raised to 130 °C, and the mixture was kept at this temperature for 2 h. The mixture was poured into 5% hydrochloric acid (0–5 °C) and extracted with CH_2Cl_2 and then with ether. The extracts were dried over $MgSO_4$. The ether was distilled off and the residue was sublimed to give 0.11 g of a mixture of compounds **3**, **4** and **6** in the ratio 9:24:67 (^{19}F NMR). The CH_2Cl_2 extract, contained phthalides **4** and **5** in the ratio 27:73 (^{19}F NMR), was washed with aqueous solution of $NaHCO_3$ and dried over $MgSO_4$. The solvent was distilled off to give 1.39 g (yield 57%) of compound **5**, which was additionally purified by short-path distillation (80 °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 0.48 g (yield 20%) of compound **4**, which was sublimed (130 °C, 20 Torr).

   *3-Hydroxy-perfluoro-3-methylphthalide (**4**)*: mp 99–100 °C (benzene–hexane). UV (C_2H_5OH) λ_{max}, nm (lg ε): 228 (3.91), 278 (3.30). IR (CCl_4) ν, cm^{-1}: 3549, 3382 (OH); 1826, 1796 (C=O); 1521, 1506 [fluorinated aromatic ring (FAR)]. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.71 (s, OH). ^{13}C NMR (100.6 MHz, $CDCl_3$): δ 160.8 (s, C-1), 146.1 (dt, $^1J_{CF}$ = 267 Hz, $^2J_{CF}$ = 14 Hz) and 143.5 (dt, $^1J_{CF}$ = 263 Hz, $^2J_{CF}$ = 14 Hz, C-5 and C-6), 144.5 (dd, $^1J_{CF}$ = 267 Hz, $^2J_{CF}$ = 13 Hz) and 142.9 (dd, $^1J_{CF}$ = 264 Hz, $^2J_{CF}$ = 13 Hz, C-4 and C-7), 123.4 (d, $^2J_{CF}$ = 14 Hz) and 110.8 (d $^2J_{CF}$ = 12 Hz, C-3a and C-7a), 120.6 (q, $^1J_{CF}$ = 286 Hz, CF_3), 99.3 (q, $^2J_{CF}$ = 37 Hz, C-3). ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 79.7 (3F, CF_3), 26.8 (1F, F-7), 26.3 (1F, F-4), 23.1 (1F, F-5), 17.0 (1F, F-6); $J_{CF_3\text{-}F(4)}$ = 13 Hz, $J_{4,5}$ = 20 Hz, $J_{4,6}$ = 7 Hz, $J_{4,7}$ = 20 Hz, $J_{5,6}$ = 18 Hz, $J_{5,7}$ = 11 Hz, $J_{6,7}$ = 20 Hz. Anal. Calcd. for $C_9HF_7O_3$: C, 37.3; H, 0.3; F, 45.8%. Found: C, 37.3; H, 0.3; F, 45.9%.

   *Perfluoro-3-methylphthalide (**5**)*: liquid. UV (hexane) λ_{max}, nm (lg ε): 230 (3.96), 282 (3.45). IR (CCl_4) ν, cm^{-1}: 1844 (C=O); 1522, 1508 (FAR). ^{19}F NMR (188.3 MHz, CCl_4): δ 79.7 (3F, CF_3), 36.6 (1F, F-3), 28.9 (1F, F-7), 28.3 (1F, F-4), 23.7 (1F, F-5), 19.3 (1F, F-6); $J_{CF_3-F(3)}$ = 5 Hz, $J_{CF_3\text{-}F(4)}$ = 15 Hz, $J_{3,4}$ = 3 Hz, $J_{3,6}$ = 3 Hz, $J_{4,5}$ = 20 Hz, $J_{4,6}$ = 8 Hz, $J_{4,7}$ = 19 Hz, $J_{5,6}$ = 17 Hz, $J_{5,7}$ = 11 Hz, $J_{6,7}$ = 20 Hz. HRMS *m/z*, 291.9771 (M^+). Calcd. for $C_9F_8O_2$ = 291.9771.

2. Analogously to the previous procedure, a mixture of indan **1** (1.46 g), SiO_2 (0.33 g) and SbF_5 (3.19 g) (molar ratio, 1:1.1:3) was heated at 85 °C (2 h) and then at 130 °C (3 h). The mixture was treated with 5% hydrochloric acid (0–5 °C), extracted with ether and dried over $MgSO_4$. The ether solution contained compounds **4**, **5** and **6** in the ratio 42:52:6 (^{19}F NMR). An amount of 5 ml of 5% hydrochloric acid was added into the solution and the mixture was stirred at room temperature for 10 h. The ether solution was dried over $MgSO_4$. The solvent was distilled off to give 1.3 g of product containing compounds **4** and **6** in the ratio 94:6 (^{19}F NMR).
3. A mixture of indan **1** (1.19 g), SiO_2 (0.53 g) and SbF_5 (2.6 g) (molar ratio, 1:2.2:3) was heated at 85 °C (2 h). Then for 4 h a temperature was raised to 180 °C, and the mixture was kept at this temperature for 3 h. The mixture was treated with 5% hydrochloric acid (0–5 °C), extracted with ether and dried over $MgSO_4$. The solvent was distilled off to give after sublimation (130 °C, 1 Torr) 0.8 g of product containing compounds **4** and **6** in the ratio 8:92 (^{19}F NMR).

3.3. Reaction of perfluoroindan (*1*) with glass in the presence of SbF_5 at 130 °C

A mixture of compound **1** (1.03 g) and SbF_5 (3.0 g) (molar ratio, 1:4) in a sealed ampoule was heated at 130–135 °C for 35 h. The mixture was treated with 5% hydrochloric acid (0–5 °C), stirred at 30 °C for 3 h and extracted with CH_2Cl_2. The extract was washed with aqueous solution of $NaHCO_3$ and dried over $MgSO_4$. The solvent was distilled off to give 0.36 g of a mixture of compounds **1**, **5** and **9a** in the molar ratio 34:34:32 (^{19}F NMR). The mixture was spontaneously evaporated in the air to dryness to give 0.18 g (yield 17%) of compound **9a**. The aqueous solution was acidified with HCl, extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was distilled off to give 0.48 g of a mixture of compounds **4** and **9** in the ratio 10:90 (^{19}F NMR). The yield of acid **9** is 41%. Analytical samples of compounds **9** and **9a** were prepared by sublimation (80 °C, 1 Torr) and (110 °C, 3 Torr), respectively, and then crystallization.

*Perfluoro-2-ethylbenzoic acid (**9**)*: mp 83.5–84.5 °C (hexane). UV (C_2H_5OH) λ_{max}, nm (lg ε): 271 (3.34). IR (CCl_4) ν, cm^{-1}: 3502, 3080 (OH); 1774, 1733 (C=O); 1528, 1482 (FAR). ^{1}H NMR (200 MHz, CCl_4): δ 11.14 (s, OH). ^{19}F NMR (188.3 MHz, CCl_4): δ 77.6 (3F, CF_3), 53.0 (2F, CF_2), 29.3 (1F, F-3), 23.8 (1F, F-6), 16.8 (1F, F-5), 12.9 (1F, F-4); $J_{CF_3-CF_2}$ = 2 Hz, $J_{CF_3-F(3)}$ = 15 Hz, $J_{CF_2\text{-}F(3)}$ = 22 Hz, $J_{3,4}$ = 21 Hz, $J_{3,5}$ = 10 Hz, $J_{3,6}$ = 11 Hz, $J_{4,5}$ = 20 Hz, $J_{4,6}$ = 6 Hz, $J_{5,6}$ = 22 Hz. HRMS *m/z*, 311.9833 (M^+). Calcd. for $C_9HF_9O_2$ = 311.9829.

*Perfluoro-2-ethylbenzoic anhydride (**9a**)*: mp 86.5–87.5 °C (hexane). UV (hexane) λ_{max}, nm (lg ε): 271 (3.40). IR (CCl_4) ν, cm^{-1}: 1845, 1796 (C=O); 1528, 1481

(FAR). ^{19}F NMR (188.3 MHz, CCl_4): δ 77.5 (3F, CF_3), 53.2 (2F, CF_2), 30.1 (1F, F-3), 24.3 (1F, F-6), 17.5 (1F, F-5), 14.7 (1F, F-4); $J_{CF_3-CF_2}$ = 2 Hz, $J_{CF_3\text{-}F(3)}$ = 15 Hz, $J_{CF_2\text{-}F(3)}$ = 21 Hz, $J_{3,4}$ = 21 Hz, $J_{3,5}$ = 10 Hz, $J_{3,6}$ = 11 Hz, $J_{4,5}$ = 20 Hz, $J_{4,6}$ = 6 Hz, $J_{5,6}$ = 21 Hz. HRMS *m/z*, 605.9560 (M^+). Calcd. for $C_{18}F_{18}O_3$ = 605.9564.

3.4. Reaction of perfluoroindan-1,3-dione (3) with SbF_5

A mixture of compound **3** (0.6 g) and SbF_5 (1.53 g) (molar ratio, 1:3) in a sealed ampoule was heated at 130 °C for 2 h. The mixture was treated with 5% hydrochloric acid (0–5 °C), extracted with CH_2Cl_2 and then with ether. The extracts were dried over $MgSO_4$. The solvents were distilled off to give 0.62 g (yield 90%) of a mixture of phthalides **4** and **5** in the ratio 20:80 (^{19}F NMR) from CH_2Cl_2 extract, and 0.02 g of the acid **6** from ether extract.

3.5. Reaction of perfluoroindan-1-one (2) with SbF_5

1. A mixture of compound **2** (0.94 g) and SbF_5 (2.22 g) (molar ratio, 1:3) in a sealed ampoule was heated at 130 °C for 3 h. The mixture was poured into 5% hydrochloric acid (0–5 °C), extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. The solvent was distilled off to give 0.88 g of a mixture, containing (^{19}F NMR) 31% (yield 27%) of **1**, 19% (17%) of **2**, 12% (10%) of **4**, 19% (17%) of **5**, 19% (16%) of **9**.
2. To a mixture of indan **1** (1.22 g, 4.09 mmol) and SbF_5 (2.12 g, 9.78 mmol) stirred at 130 °C, ketone **2** (0.67 g, 2.44 mmol) was added for 1 h. Then indan **1** (0.3 g, 1.01 mmol) was added to the mixture and the latter was stirred at 130 °C for 2.5 h. The mixture was poured into 5% hydrochloric acid (0–5 °C) and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. The solvent was distilled off to give 2.13 g of a mixture, containing (^{19}F NMR) 66% of **1**, 1% of **2**, 3% (yield 10%) of **4**, 4% (11%) of **5**, 26% (74%) of **9**.

3.6. Complex (2c) of perfluoroindan-1-one (2) with SbF_5

To 1.15 g of SbF_5 placed in an ampoule for recording of NMR spectra 0.18 g of ketone **2** (molar ratio, **2**:SbF_5 = 1:8) was added. The mixture was stirred and ^{19}F NMR spectrum of the solution was recorded at +20 °C. The spectrum contained ill-resolved signals of complex **2c**. SO_2ClF (0.2 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 bad-resolved signals of complex **2c** as well. ^{19}F NMR (188.3 MHz, SbF_5–SO_2ClF), SO_2ClF (262.8 ppm from C_6F_6) was used as internal standard: δ ($\Delta\delta$) 62.0 (33.8) (1F, F-5), 58.1 (4.1) (2F, F-3), 56.0 (25.5) (1F, F-7), 47.5 (9.7) (2F, F-2), 34.5 (8.0) (1F, F-4), 27.5 (7.2) (1F, F-6).

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 0.13 g (yield 72%) of indanone **2**.

3.7. Reaction of perfluoro-1,1-diethylindan (14) with SiO_2/SbF_5

A mixture of 2.73 g of compound **14**, 0.2 g of SiO_2 and 3.56 g of SbF_5 (molar ratio, 1:0.61:3) was stirred at 130–135 °C for 3 h. The mixture was poured into 5% hydrochloric acid (0–5 °C) and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. The solvent was distilled off to give 2.54 g (yield 97%) of ketone **13**.

*Perfluoro-3,3-diethylindan-1-one (***13***)*: bp 58 °C (3 torr). UV (hexane) λ_{max}, nm (lg ε): 253 (4.10), 289 (3.46), 294 (3.46). IR (CCl_4) ν, cm^{-1}: 1781 (C=O); 1513 (FAR). ^{19}F NMR (188.3 MHz, CH_2Cl_2): δ 85.7 (6F, m, $2CF_3$), 58.3 (4F, m, $2CF_2$), 50.7 (2F, m, F-2), 35.8 (1F, m, F-4), 30.2 (1F, F-7), 27.6 (1F, F-5); 19.0 (1F, F-6); $J_{4,5}$ = 19 Hz, $J_{4,6}$ = 10 Hz, $J_{4,7}$ = 16 Hz, $J_{5,6}$ = 19 Hz, $J_{5,7}$ = 13 Hz, $J_{6,7}$ = 21 Hz. HRMS *m/z*, 475.9742 (M^+). Calcd. for $C_{13}F_{16}O$ = 475.9694.

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