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Transformation of perfluorinated benzocycloalkenes and alkylbenzenes to their carbonyl derivatives under the action of CF_3COOH/SbF_5

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Dedicated to Professor L.M. Yagupolskii, on the occasion of his 85th birthday.

Abstract

Perfluorinated benzocycloalkenes (benzocyclobutene, indan, tetralin), alkylbenzocycloalkenes and alkylbenzenes react with CF_3COOH/SbF_5 at 20–50 °C giving the corresponding carbonyl derivatives.

Keywords: Fluorinated; Benzocyclobutene; Indan; Tetralin; Alkylbenzene; Carbonyl derivatives; Trifluoroacetic acid; Antimony pentafluoride

1. Introduction

Perfluoroindan-1-one (**1**) and perfluoro-3-ethylindan-1-one (**2**) undergo skeletal transformations under the action of antimony pentafluoride [1,2]. Ketone **1** for this investigation was synthesized in a good yield in the reaction of perfluoroindan (**3**) with SiO_2/SbF_5 at 70 °C [1]. At the same time perfluoro-1-ethylindan (**4**) heated with SiO_2/SbF_5 at 75 °C and then treated with water, gives 4-carboxyperfluoro-3-methylisochromen-1-one. The process proceeds through the intermediate formation of ketone **2**, which was detected in the reaction mixture only in a small amount because ketone **2** undergoes skeletal transformations under the reaction conditions [2].

For the synthesis of compound **2** and other ketones, required for the investigation of their cationoid skeletal rearrangements, under milder conditions as compared with the reaction with SiO_2/SbF_5 it was worthwhile to try to replace SiO_2 by other sources of nucleophilic oxygen. For this purpose we have studied reactions of indan **3** with 2,2,3,3-tetrafluoropropanol, acetic and trifluoroacetic acids in the presence of SbF_5. This work also describes reactions of ethylindan **4** and other aromatic fluorocarbons with CF_3COOH/SbF_5.

2. Results and discussion

Reaction of indan **3** with 2,2,3,3-tetrafluoropropan-1-ol in an SbF_5 medium at 20–50 °C forms a solution of a salt of 1-(2,2,3,3-tetrafluoropropoxy)-perfluoroindan-1-yl cation (**5**). Hydrolysis of the latter gives indanon **1**. The reaction of compound **3** with CH_3COOH in the presence of SbF_5 at 50 °C forms ketone **1**. The reaction mixture also contains unchanged indan **3** (Scheme 1).

Compound **3** readily reacts with CF_3COOH in the presence of SbF_5 at room temperature to give indanone **1** in a high yield (Scheme 2). Reaction of compound **3** with CF_3COOH/SbF_5 at 50 °C gives ketone **1** together with perfluoroindan-1,3-dione (**6**). When the reaction temperature is raised to 95 °C perfluoro-3-methylenephthalide (**7**) is formed as a main product. The reaction mixture also contains ketone **1**, perfluoro-3-methylphthalide (**8**) and 4,5,6,7-tetrafluoro-3-trifluoromethylphthalide (**9**) (Scheme 2).

It is known that CF_3COOH in the presence of SbF_5 gives $H[SbF_5(OCOCF_3)]$ [3]. The formation of indanone **1** in the reaction of compound **3** with CF_3COOH/SbF_5 can be rationalized as shown in Scheme 2. Compound **3** with SbF_5 seems to generate perfluoroindan-1-yl cation (**3c**), which reacts with CF_3COOH to form perfluoro-1-acetoxyindan (**10**). Then perfluoro-1-acetoxyindan-1-yl cation (**10c**) produced from compound **10** is split into indanone **1** and the trifluoroacetyl cation. The latter adds fluoride anion to give trifluoroacetyl

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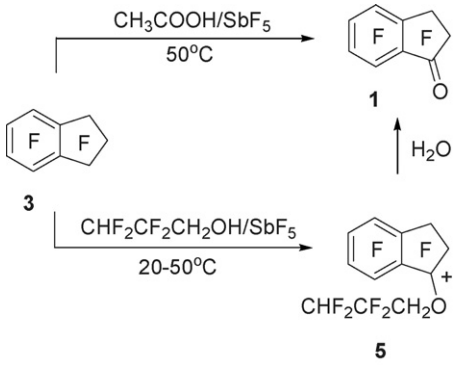


Scheme 1.

fluoride, which was trapped with sodium methylate as methyltrifluoroacetate.

The formation of indandione **6** can be represented in a similar way through the intermediate generation of perfluoroindan-3-one-1-yl cation (**1c**) according to Scheme 2. Compounds **7**, **8** and **9** are the products of transformations of indandione **6** under the reaction conditions similar to indandione **6** transformations under the action of SbF_5 [1] or HF/SbF_5 [4].

Taking into account the fact of higher reactivity of CF_3COOH/SbF_5 as compared with CH_3COOH/SbF_5 and $CHF_2CF_2CH_2OH/SbF_5$ in their reactions with indan **3** giving indanone **1**, for the synthesis of carbonyl derivatives of other perfluoroaromatic compounds, we have studied reactions of some aromatic fluorocarbons with CF_3COOH/SbF_5.

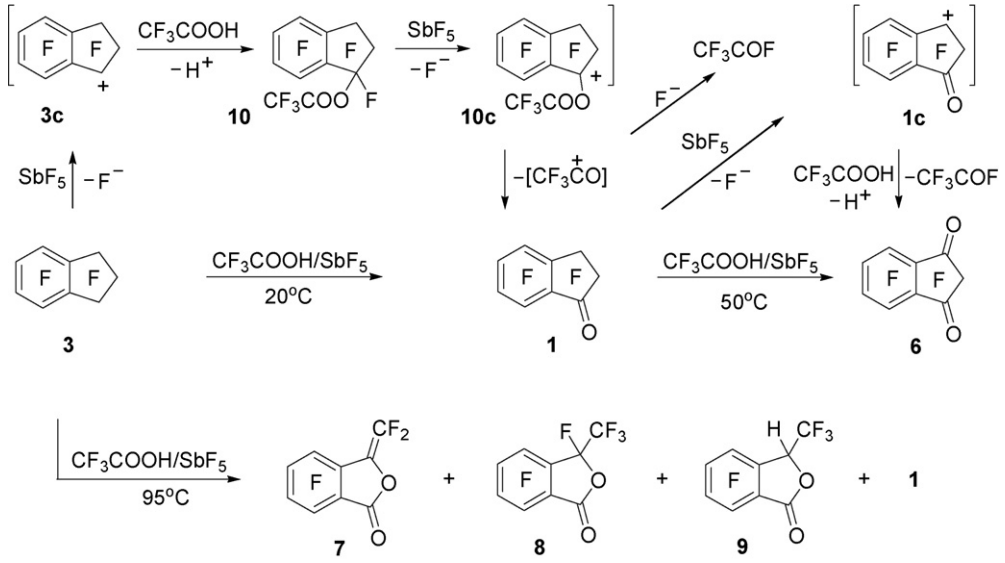
Perfluorotetralin (**11**) heated with CF_3COOH/SbF_5 at 50 °C gives perfluorotetralin-1-one (**12**). The reaction mixture also contains small amount of unchanged tetralin **11**. When the reaction temperature is raised to 95 °C, a mixture of ketone **12** and perfluorotetralin-1,4-dione (**13**) is obtained (Scheme 3).

The reaction of perfluorobenzocyclobutene (**14**) with CF_3COOH/SbF_5 proceeds readily at room temperature and gives perfluorobenzocyclobutenone (**15**) together with perfluorobenzocyclobutendione (**16**). Selective formation of ketone **15** can be achieved by the use of stoichiometric amounts of trifluoroacetic acid, whereas excess of CF_3COOH and heating up to 40 °C facilitate production of diketone **16**. When the reaction temperature is raised to 95 °C, after treatment of the reaction mixture with water, tetrafluorophthalic acid (**17**) is obtained as the only product (Scheme 3).

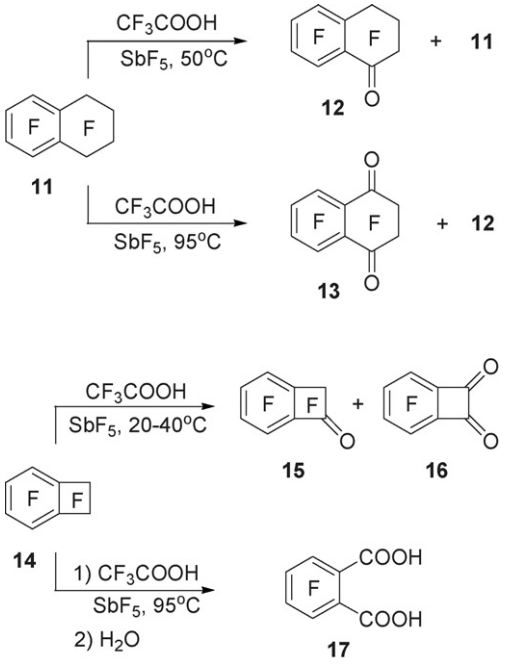
Perfluorinated 1-alkyl- and 1,1-dialkyl-benzocyclobutenes and indans also react with CF_3COOH/SbF_5 to give the corresponding benzocyclobutenones and indanones in a good yield. Thus, perfluorinated 1-methylbenzocyclobutene (**18**), 1-ethylbenzocyclobutene (**19**), 1,1-diethylbenzocyclobutene (**20**), 1-methylindan (**21**), 1-ethylindan (**4**), 1,1-dimethylindan (**22**), 1,1-diethylindan (**23**) are transformed to perfluorinated 2-methylbenzocyclobutenone (**24**), 2-ethylbenzocyclobutenone (**25**), 2,2-diethylbenzocyclobutenone (**26**), 3-methylindan-1-one (**27**), 3-ethylindan-1-one (**2**), 3,3-dimethylindan-1-one (**28**), 3,3-diethylindan-1-one (**29**), respectively (Scheme 4). These transformations smoothly proceed at room temperature and are not complicated by further skeletal rearrangements, in contrast to the reaction of indan **4** with SiO_2/SbF_5 [2].

Perfluoro-2-methylindan (**30**) reacts with CF_3COOH/SbF_5 at room temperature to give perfluoro-2-methylindan-1-one (**31**). Perfluoromethylindans containing a CF_3 group in the aromatic ring, heated with CF_3COOH/SbF_5 at 50 °C, form perfluoromethylindanones with a carbonyl group in the position meta to the CF_3 group. Thus perfluoro-4-methylindan (**32**) and perfluoro-5-methylindan (**33**) are transformed to perfluoro-4-methylindan-1-one (**34**) and perfluoro-6-methylindan-1-one (**35**), respectively. This is in accordance with the larger relative stability of the corresponding perfluoromethylindan-1-yl cations [5–7]. Perfluoro-3-methylindene (**36**) also reacts with CF_3COOH/SbF_5 to give perfluoro-3-methylinden-1-one (**37**) (Scheme 5).

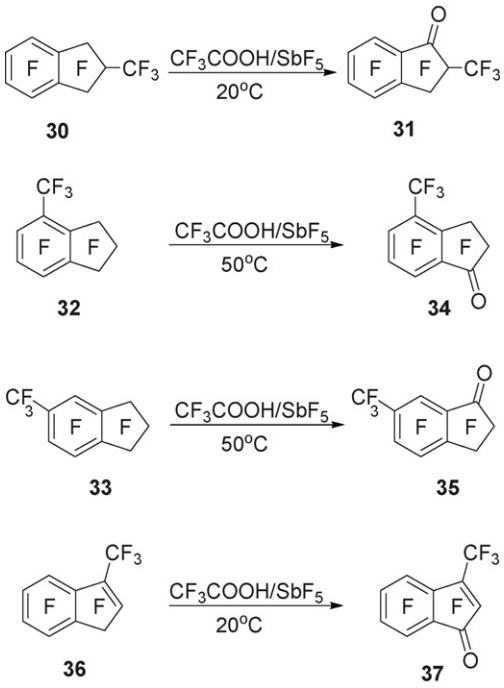
The interaction of perfluorotoluene (**38**) and perfluoro-4-methyltoluene (**39**) with CF_3COOH/SbF_5, after treatment of the reaction mixture with water, leads to the formation of



Scheme 2.



Scheme 3.

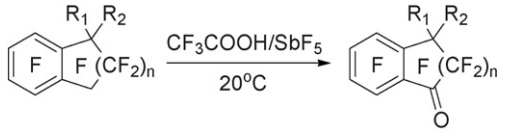


Scheme 5.

perfluorobenzoic (**40**) and perfluoro-4-methylbenzoic (**41**) acids, respectively, together with the starting compounds. Perfluoro-2-isopropyltoluene (**42**) heated with excess of CF_3COOH/SbF_5 at 50 °C with further treatment of the reaction mixture with water gives perfluoro-2-isopropyl-benzoic acid (**43**). Perfluoropropylbenzene (**44**) also reacts with trifluoroacetic acid in the presence of SbF_5 at 50 °C to give perfluoropropiophenone (**45**). The reaction mixture also contains unchanged compound **44** (Scheme 6).

The relative reactivity of perfluorobenzocycloalkenes in the reaction with CF_3COOH/SbF_5, established by the method of competitive reactions, decreases in the following order: benzocyclobutene **14** > indan **3** > tetralin **11**. This sequence is in accord with the order of decreasing of relative stabilities of corresponding perfluorobenzocycloalken-1-yl cations [5] generated at first stage of the reaction.

Indan **3** is more reactive than indene **36**, although perfluoroindan-1-yl cation (**3c**) is less stable as compared with perfluoro-1-methylindenyl cation (**36c**) [5,8]. Analogously, the reactivity of indan **3** is more than that of toluene **38** and the relative stabilities of ion **3c** and perfluorobenzyl cation (**38c**) are inversed. The results indicate that in these cases the generation of cations **36c** and **38c** cannot be limiting stage of the reaction.

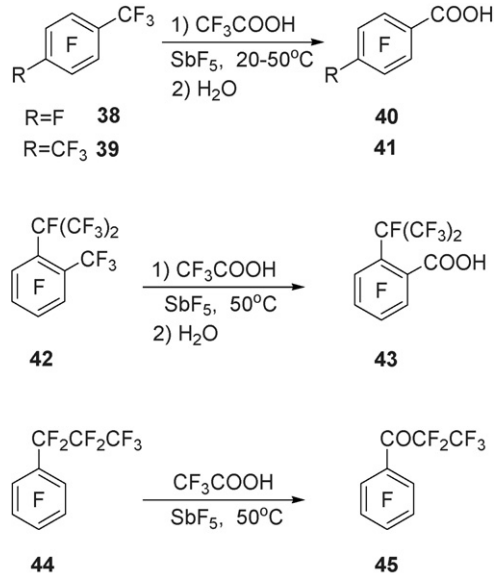


R_1	R_2	n=0	n=1	n=0	n=1
CF_3	F	**18**	**21**	**24**	**27**
C_2F_5	F	**19**	**4**	**25**	**2**
CF_3	CF_3	-	**22**	-	**28**
C_2F_5	C_2F_5	**20**	**23**	**26**	**29**

Scheme 4.

3. Experimental

Starting materials were obtained according to Refs.: **3**, **11**, **21**, **32**, **33** [9]; **4**, **19**, **20**, **23**, **46** [5]; **14**, **18** [10]; **22** [11]; **36** [12]; **42** [13]; **44** [14]; CF_3COOH and SbF_5 were obtained commercially. All reactions were carried out in glassware.



Scheme 6.

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 Bruker WP-200 SY and Bruker AC-200 instrument (188.3 and 200 MHz, respectively). Chemical shifts are given in δ ppm from CCl_3F and TMS, J values in Hz; C_6F_6 (−162.9 ppm from CCl_3F) and $(Me_3Si)_2O$ (0.04 ppm 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 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 **1**, **8**, **29** [1], **6** [15], **7**, **9** [4], **12** [16], **15** [5], **16** [10], **24** [17], **37** [18], **45** [19] were identified by comparison of the ^{19}F NMR data with data for authentic samples.

Assignment of signals in the ^{19}F NMR spectrum of cation **5** (signals of bicyclic moiety were not well resolved) was made by analogy with that for 1-hydroxyperfluoroindan-1-yl cation [4].

3.1. Reaction of perfluoroindan (3) with 2,2,3,3-tetrafluoropropan-1-ol in the presence of SbF_5

In an ampoule for recording NMR spectra, compound **3** (0.18 g), 2,2,3,3-tetrafluoropropan-1-ol (0.07 g) and SbF_5 (0.86 g) (molar ratio, 1:0.9:6.5) was placed. The mixture was stirred and then kept at 20 °C. The solution contained (^{19}F NMR) cation **5** together with the initial compounds. The conversion of indan **3** amounted to 58% (26 h) and 67% (120 h). Then the mixture was heated at 50 °C for 12 h and ^{19}F NMR spectrum of the solution was measured. The spectrum contained signals of cation **5** and the conversion of indan **3** raised to 90%. 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 0.16 g of mixture, which contained (^{19}F NMR) 77% (yield 79%) of **1**, 8% (yield 8%) of **3** and 15% of 2,2,3,3-tetrafluoropropan-1-ol.

3.1.1. 1-(2,2,3,3-Tetrafluoropropoxy)-perfluoroindan-1-yl cation (5)

^{1}H NMR (SbF_5): δ 5.73 (t, 1H, $^{2}J_{H-CF_2} = 53$, CF_2H), 5.52 (t, 2H, $^{3}J_{CH_2-CF_2} = 10$, CH_2). ^{19}F NMR (SbF_5): δ −90.1 (1F, F-5), −99.1 (1F, F-7), −103.5 (2F, CF_2-3), −110.3 (2F, CF_2-2), −121.1 (t, 2F, $^{3}J_{CF_2-CH_2} = 10$, CH_2CF_2), −126.2 (1F, F-4), −133.2 (1F, F-6), −134.4 (d, 2F, $^{2}J_{CF_2-H} = 53$, CF_2H).

3.2. Reaction of perfluoroindan (3) with CH_3COOH/SbF_5

A mixture of compound **3** (0.89 g), CH_3COOH (0.25 g) and SbF_5 (1.94 g) (molar ratio, 1:1.4:3) was stirred at 50 °C for 3.5 h. The mixture was poured into 5% hydrochloric acid 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 0.70 g of mixture, which contained (^{19}F NMR) compounds **1** and **3** in the ratio 47:53 (yield 38% and 42%).

3.3. Reaction of perfluoroindan (3) with CF_3COOH/SbF_5

1. A mixture of compound **3** (0.85 g), CF_3COOH (0.45 g) and SbF_5 (1.85 g) (molar ratio, 1:1.4:3) was kept at 20 °C for 2.5 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 ketone **1** (yield 88%).
2. A mixture of compound **3** (0.53 g, 1.78 mmol), CF_3COOH (0.48 g, 4.21 mmol) and SbF_5 (1.15 g, 5.3 mmol) was heated at 40 °C for 15 h. Then 0.56 g (2.58 mmol) of SbF_5 was added and the resulting mixture was heated for 8.5 h at 40 °C and for 11.5 h at 50 °C. The mixture was poured into 5% hydrochloric acid and extracted with ether. The solvent was distilled off and the residue was dissolved in CH_2Cl_2. The solution was dried over $MgSO_4$. The solvent was distilled off to give 0.36 g of mixture, which contained (^{19}F NMR) compounds **1** and **6** in the ratio 50:50 (yield 38% and 38%).
3. A mixture of compound **3** (1.32 g), CF_3COOH (1.11 g) and SbF_5 (2.88 g) (molar ratio, 1:2.2:3) in a sealed ampoule was heated at 95 °C for 11 h. The mixture was treated with 5% hydrochloric acid and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. The solvent was distilled off to give 1.09 g of mixture, which contained (^{19}F NMR) 10% (yield 9%) of **1**, 77% (73%) of **7**, 11% (10%) of **8** and 2% (2%) of **9**.
4. To a solution of CF_3COOH (1.1 g, 9.65 mmol) in SbF_5 (4.47 g, 20.6 mmol) compound **3** (2 g, 6.71 mmol) was dropped at 20 °C and gaseous product was absorbed by the solution of CH_3ONa prepared from Na (0.5 g, 21.74 mmol) and 15 ml of CH_3OH. After subsequent distillation the resulting CH_3OH solution contained 0.47 g (yield 54%, measured by ^{19}F NMR, $C_6H_5CF_3$ was used as internal standard) of CF_3COOCH_3 (^{19}F NMR, identified by adding of authentic sample). The reaction mixture of products with SbF_5 treated analogously to procedure (1) gave 1.74 g of ketone **1** (yield 94%).

3.4. Reaction of perfluorotetralin (11) and perfluorobenzocyclobutene (14) with CF_3COOH/SbF_5

1. A mixture of compound **11** (0.9 g), CF_3COOH (0.41 g) and SbF_5 (1.69 g) (molar ratio, 1:1.4:3) was stirred at 50 °C for 12 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 0.82 g of mixture, which contained (GLC) 2% of **11**, 97% (yield 94%) of **12** and 1% of **13**.
2. A mixture of compound **11** (0.92 g), CF_3COOH (0.72 g) and SbF_5 (2.87 g) (molar ratio, 1:2.4:5) in a sealed ampoule was heated at 95 °C for 28 h. The mixture was treated with 5% hydrochloric acid and extracted with

ether. The extract was dried over $MgSO_4$. The solvent was distilled off and the residue was sublimed (90 °C, 5 Torr) to give 0.81 g of mixture, which contained (^{19}F NMR) compounds **12** and **13** in the ratio 36:64 (yield 35% and 62%, respectively).

3. Analogously to procedure (1), the reaction of compound **14** (0.67 g), CF_3COOH (0.31 g) and SbF_5 (1.75 g) (molar ratio, 1:1:3) gave (20 °C, 1.5 h) 0.53 g of mixture, which contained (^{19}F NMR) compounds **15** and **16** in the ratio 96:4 (yield 84% and 3%, respectively).
4. Analogously to procedure (1), the reaction of compound **14** (0.87 g), CF_3COOH (0.56 g) and SbF_5 (2.29 g) (molar ratio, 1:1.4:3) gave (20 °C, 2 h) 0.67 g of mixture, which contained (^{19}F NMR) compounds **15** and **16** in the ratio 84:16 (yield 72% and 14%, respectively).
5. A mixture of compound **14** (0.38 g, 1.53 mmol), CF_3COOH (0.18 g, 1.58 mmol) and SbF_5 (1 g, 4.61 mmol) was kept at 20 °C for 24 h. Then more CF_3COOH (0.24 g, 2.11 mmol) was added and the resulting mixture was heated for 24 h at 20 °C and for 6 h at 40 °C. The mixture was poured into 5% hydrochloric acid and extracted with $CHCl_3$. The solvent was distilled off to give 0.29 g of mixture, which contained (^{19}F NMR) 18% (yield 16%) of **15**, 69% (63%) of **16** and 13% of unidentified impurities.
6. Analogously to procedure (2), the reaction of compound **14** (0.9 g), CF_3COOH (0.99 g) and SbF_5 (2.35 g) (molar ratio, 1:2.4:3) gave (95 °C, 28 h) after sublimation (150 °C, 2 Torr) 0.73 g of acid **17** (yield 85%).

3.5. Reaction of perfluorinated alkylbenzocycloalkenes with CF_3COOH/SbF_5

3.5.1. Perfluoro-1-methylbenzocyclobutene (18)

A mixture of compound **18** (2.67 g), CF_3COOH (1.43 g) and SbF_5 (5.82 g) (molar ratio, 1:1.4:3) was kept at 20 °C for 2 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 2.32 g of ketone **24** (yield 94%).

3.5.2. Perfluoro-1-ethylbenzocyclobutene (19)

A mixture of compound **19** (5.33 g), CF_3COOH (2.44 g) and SbF_5 (9.96 g) (molar ratio, 1:1.4:3) was kept at 20 °C for 2 h. The mixture was poured into 5% hydrochloric acid. Organic phase was separated and dried over $MgSO_4$ to give 4.86 g of ketone **25** (yield 97%).

3.5.2.1. Perfluoro-2-ethylbenzocyclobuten-1-one (25). Liquid. UV (hexane) λ_{max}, nm (lg ε): 213 (4.25), 247 (3.98), 273 (3.08). IR (CCl_4) ν, cm^{-1}: 1830, 1813 (C=O); 1522, 1483 [fluorinated aromatic ring (FAR)]. ^{19}F NMR (CH_2Cl_2): δ −82.0 (3F, CF_3), −122.3 (2F, CF_2), −125.8 (1F, F-6), −132.2 (1F, F-3), −133.0 (1F, F-4), −140.4 (1F, F-5), −155.9 (1F, F-2); $J_{CF_3-CF_2} = 1$, $J_{CF_3-F(2)} = 11$, $J_{CF_3-F(3)} = 6$, $J_{CF_2-F(2)} = 12$, $J_{CF_2-F(3)} = 3$, $J_{2,3} = 4$, $J_{2,4} = 2$, $J_{2,5} = 5$, $J_{2,6} = 2$, $J_{3,4} = 19$, $J_{3,5} = 9$, $J_{3,6} = 25$, $J_{4,5} = 18$, $J_{4,6} = 12$, $J_{5,6} = 20$. HRMS *m/z*, 325.9795 (M^+). Calcd for $C_{10}F_{10}O$ = 325.9789.

3.5.3. Perfluoro-1,1-diethylbenzocyclobutene (20)

To a solution of CF_3COOH (1 g, 8.77 mmol) in SbF_5 (4.1 g, 18.91 mmol) mixture (5.65 g, 12.61 mmol) containing compound **20** and perfluoro-1,2-diethylbenzocyclobutene (**46**) in the ratio 47:53 (^{19}F NMR) was added. Resulting mixture was stirred at 20 °C for 21 h. Then upper phase (1.46 g) consisting of compound **46** was separated. The residue treated analogously to the previous procedure gave 3.99 g of mixture, which contained (GLC, ^{19}F NMR) 62% (yield 98%) of **26** and 38% of **46**. The individual ketone **26** (0.31 g) was isolated from the mixture (0.9 g) by silica gel column chromatography (hexane as eluent).

3.5.3.1. Perfluoro-2,2-diethylbenzocyclobuten-1-one (26). Liquid. UV (hexane) λ_{max}, nm (lg ε): 210 (4.15), 242 (3.96), 249 (4.00), 279 (2.85), 286 (2.85). IR (CCl_4) ν, cm^{-1}: 1834 (C=O); 1523, 1484 (FAR). ^{19}F NMR (CH_2Cl_2): δ −81.5 (6F, m, $2CF_3$), −111.6 (4F, m, $2CF_2$), −125.6 (1F, F-6), −133.0 (1F, F-4), −133.4 (1F, m, F-3), −142.9 (1F, F-5); $J_{3,4} = 19$, $J_{3,5} = 8$, $J_{3,6} = 23$, $J_{4,5} = 17$, $J_{4,6} = 13$, $J_{5,6} = 20$. HRMS *m/z*, 425.9729 (M^+). Calcd for $C_{12}F_{14}O$ = 425.9725.

3.5.4. Perfluoro-1-methylindan (21)

Analogously to procedure (Section 3.5.1), the reaction of compound **21** (0.3 g), CF_3COOH (0.24 g) and SbF_5 (1 g) (molar ratio, 0.6:1.4:3) gave (20 °C, 3 h) 0.27 g of ketone **27** (yield 96%).

3.5.4.1. Perfluoro-3-methylindan-1-one (27). Liquid. UV (hexane) λ_{max}, nm (lg ε): 214 (4.13), 245 (3.98), 252 (4.02), 286 (3.18), 293 (3.20). IR (CCl_4) ν, cm^{-1}: 1776 (C=O); 1515 (FAR). ^{19}F NMR (CH_2Cl_2): δ −76.1 (3F, CF_3), −118.0 ($1F_A$) and −126.9 ($1F_B$, CF_2-2), −132.1 (1F, F-7), −132.9 (1F, F-4), −134.9 (1F, F-5), −142.7 (1F, F-6), −177.3 (1F, F-3); $J_{CF_3-F(A)} = 2$, $J_{CF_3-F(B)} = 16$, $J_{CF_3-F(3)} = 10$, $J_{CF_3-F(4)} = 17$, $J_{A,B} = 285$, $J_{A,3} = 4$, $J_{B,3} = 4$, $J_{3,4} = 6$, $J_{3,6} = 4$, $J_{3,7} = 1$, $J_{4,5} = 20$, $J_{4,6} = 9$, $J_{4,7} = 18$, $J_{5,6} = 18$, $J_{5,7} = 13$, $J_{6,7} = 21$. HRMS *m/z*, 325.9782 (M^+). Calcd for $C_{10}F_{10}O$ = 325.9789.

3.5.5. Perfluoro-1-ethylindan (4)

Analogously to procedure (Section 3.5.1), the reaction of compound **4** (1.25 g), CF_3COOH (0.5 g) and SbF_5 (2.05 g) (molar ratio, 1:1.4:3) gave (20 °C, 5 h) 1.16 g of ketone **2** (yield 98%).

3.5.5.1. Perfluoro-3-ethylindan-1-one (2). Liquid. UV (hexane) λ_{max}, nm (lg ε): 213 (4.20), 251 (4.00), 293 (3.24). IR (CCl_4) ν, cm^{-1}: 1783 (C=O); 1513 (FAR). ^{19}F NMR ($CHCl_3$): δ −80.4 (3F, CF_3), −115.6 ($1F_A$) and −127.4 ($1F_B$, CF_2-2, $J_{A,B} = 278$), −118.5 ($1F_A$) and −120.9 ($1F_B$, $\mathbf{CF_2}CF_3$, $J_{A,B} = 297$), ∼−132. 4 (2F, F-4, F-7), −135.6 (1F, F-5); −142.8 (1F, F-6), −180.4 (1F, F-3). HRMS *m/z*, 375.9759 (M^+). Calcd for $C_{11}F_{12}O$ = 375.9757.

3.5.6. Perfluoro-1,1-dimethylindan (22)

Analogously to procedure (Section 3.5.1), the reaction of compound **22** (0.71 g), CF_3COOH (0.28 g) and SbF_5 (1.16 g)

(molar ratio, 1:1.4:3) gave (20 °C, 5.5 h) 0.66 g of ketone **28** (yield 98%).

3.5.6.1. Perfluoro-3,3-dimethylindan-1-one (28). Liquid. UV (hexane) λ_{max}, nm (lg ε): 213 (3.99), 244 (4.01), 251 (4.01), 293 (3.25). IR (CCl_4) ν, cm^{-1}: 1783 (C=O); 1515, 1507 (FAR). ^{19}F NMR (CH_2Cl_2): δ −65.7 (6F, $2CF_3$), −118.7 (2F, CF_2), ∼−132.1 (2F, F-4, F-7), −135.5 (1F, F-5); −144.5 (1F, F-6). HRMS *m/z*, 375.9774 (M^+). Calcd for $C_{11}F_{12}O$ = 375.9757.

3.5.7. Perfluoro-1,1-diethylindan (23)

Analogously to procedure (Section 3.5.2), the reaction of compound **23** (1.42 g), CF_3COOH (0.45 g) and SbF_5 (1.86 g) (molar ratio, 1:1.4:3) gave (20 °C, 7.5 h) 1.34 g of ketone **29** (yield 99%).

3.5.8. Perfluoro-2-methylindan (30)

A solution of compound **30** in SbF_5 was prepared by heating of compound **19** (1.8 g, 5.17 mmol) with SbF_5 (6.06 g, 27.95 mmol) in a nickel bomb at 130 °C for 12 h [20]. Then CF_3COOH (1.43 g, 12.54 mmol) was added to the solution. The resulting mixture, analogously to procedure (Section 3.5.1), gave (20 °C, 20 h) 1.6 g of mixture, which contained (GLC, ^{19}F NMR) 88% (yield 84%) of compound **31**. An analytical sample of product **31** was prepared by short-path distillation (80 °C, 40 Torr).

3.5.8.1. Perfluoro-2-methylindan-1-one (31). Liquid. UV (hexane) λ_{max}, nm (lg ε): 214 (4.13), 244 (3.96), 251 (4.02), 285 (3.17), 293 (3.17). IR (CCl_4) ν, cm^{-1}: 1771 (C=O); 1516 (FAR). ^{19}F NMR (CH_2Cl_2): δ −74.8 (3F, CF_3), −99.6 ($1F_A$) and −107.0 ($1F_B$, CF_2-3), −132.6 (1F, F-7), −134.8 (1F, F-5), −136.6 (1F, F-4), −142.4 (1F, F-6), −181.3 (1F, F-2); $J_{CF_3-F(2)} = 11$, $J_{CF_3-F(A)} = 2$, $J_{CF_3-F(B)} = 15$, $J_{2,A} = 1$, $J_{2,B} = 4$, $J_{2,5} = 1$, $J_{2,6} = 1$, $J_{A,B} = 277$, $J_{A,4} = 5$, $J_{A,5} = 1$, $J_{A,6} = 3$, $J_{B,4} = 9$, $J_{B,5} = 1$, $J_{B,6} = 2$, $J_{B,7} = 2$, $J_{4,5} = 20$, $J_{4,6} = 9$, $J_{4,7} = 18$, $J_{5,6} = 18$, $J_{5,7} = 13$, $J_{6,7} = 20$. HRMS *m/z*, 325.9791 (M^+). Calcd for $C_{10}F_{10}O$ = 325.9789.

3.5.9. Perfluoro-4-methylindan (32)

Analogously to procedure (Section 3.5.1), the reaction of compound **32** (2.07 g), CF_3COOH (0.95 g) and SbF_5 (3.87 g) (molar ratio, 1:1.4:3) gave (50 °C, 3 h) 1.79 g of ketone **34** (yield 92%). An analytical sample of compound **34** was prepared by short-path distillation (90 °C, 40 Torr) and then additionally purified by silica gel column chromatography ($CHCl_3$ as eluent).

3.5.9.1. Perfluoro-4-methylindan-1-one (34). Liquid. UV (hexane) λ_{max}, nm (lg ε): 208 (4.51), 241 (4.00), 276 (2.64). IR (CCl_4) ν, cm^{-1}: 1785, 1768 (C=O); 1517, 1472 (FAR). ^{19}F NMR (CH_2Cl_2): δ −57.7 (3F, CF_3), −106.7 (2F, CF_2-3), −110.9 (1F, F-5), −122.4 (1F, F-7),−125.2 (2F, CF_2-2), −144.6 (1F, F-6); $J_{CF_3-F(3)} = 16$, $J_{CF_3-F(5)} = 20$, $J_{2,3} = 2$, $J_{3,6} = 2$, $J_{5,6} = 19$, $J_{5,7} = 23$, $J_{6,7} = 21$. HRMS *m/z*, 325.9790 (M^+). Calcd for $C_{10}F_{10}O$ = 325.9789.

3.5.10. Perfluoro-5-methylindan (33)

Analogously to procedure (Section 3.5.1), the reaction of compound **33** (2.24 g), CF_3COOH (1.03 g) and SbF_5 (4.18 g) (molar ratio, 1:1.4:3) gave (50 °C, 3 h) 1.95 g of ketone **35** (yield 93%). An analytical sample of compound **35** was prepared by short-path distillation (90 °C, 20 Torr) and then additionally purified by crystallization.

3.5.10.1. Perfluoro-6-methylindan-1-one (35). mp 42–43 °C (hexane). UV (hexane) λ_{max}, nm (lg ε): 216 (4.15), 244 (3.93), 250 (3.92), 285 (3.53), 294 (3.62), 354 (2.56). IR (CCl_4) ν, cm^{-1}: 1782, 1765 (C=O); 1506 (FAR). ^{19}F NMR (CH_2Cl_2): δ −57.5 (3F, CF_3), −107.8 (1F, F-7), −110.7 (2F, CF_2-3), −113.7 (1F, F-5), −125.3 (2F, CF_2-2), −137.7 (1F, F-4); $J_{CF_3-F(5)} = 22$, $J_{CF_3-F(7)} = 23$, $J_{2,3} = 3$, $J_{3,4} = 7$, $J_{4,5} = 20$, $J_{4,7} = 22$, $J_{5,7} = 6$. HRMS *m/z*, 325.9787 (M^+). Calcd for $C_{10}F_{10}O$ = 325.9789.

3.6. Reaction of perfluoro-3-methylindene (36) with CF_3COOH/SbF_5

A mixture of compound **36** (0.79 g), CF_3COOH (0.41 g) and SbF_5 (1.66 g) (molar ratio, 1:1.4:3) was kept at 20 °C for 5.5 h. The solution contained compound **37** (^{19}F NMR, identified by adding of authentic sample). The solution treated analogously to procedure (Section 3.5.1) gave 0.71 g of ketone **37** (yield 98%).

3.7. Reaction of perfluorinated alkylbenzenes with CF_3COOH/SbF_5

3.7.1. Perfluorotoluene (38)

1. A mixture of compound **38** (1.01 g), CF_3COOH (0.68 g) and SbF_5 (2.79 g) (molar ratio, 1:1.4:3) was stirred at 20 °C for 5.5 h. The mixture was poured into 5% hydrochloric acid and extracted with ether. The extract was dried over $MgSO_4$. The solution contained compounds **38** and **40** in the ratio 30:70 (^{19}F NMR). The mixture was spontaneously evaporated in the air to dryness and the residue was sublimed (120 °C, 10 Torr) to give 0.54 g of acid **40** (yield 60%).
2. Analogously to the previous procedure, the reaction of compound **38** (1.35 g), CF_3COOH (0.91 g) and SbF_5 (3.73 g) (molar ratio, 1:1.4:3) gave (50 °C, 11 h) solution, which contained (^{19}F NMR) compounds **38** and **40** in the ratio 14:86 and then 0.93 g of acid **40** (yield 76%).

3.7.2. Perfluoro-4-methyltoluene (39)

1. Analogously to procedure (1 of Section 3.7.1), the reaction of compound **39** (1.08 g), CF_3COOH (0.6 g) and SbF_5 (2.45 g) (molar ratio, 1:1.4:3) gave (20 °C, 8.5 h) solution, which contained (^{19}F NMR) compounds **39** and **41** in the ratio 34:66 and then 0.56 g of acid **41** (yield 57%).
2. Analogously to procedure (1 of Section 3.7.1), the reaction of compound **39** (0.98 g), CF_3COOH (0.55 g) and SbF_5 (2.24 g) (molar ratio, 1:1.4:3) gave (50 °C, 11 h) solution, which contained (^{19}F NMR) compounds **39** and **41** in the ratio 16:84 and then 0.65 g of acid **41** (yield 72%).

*3.7.3. Perfluoro-2-isopropyltoluene (**42**)*

Analogously to procedure (1 of Section 3.7.1), the reaction of compound **42** (0.24 g), CF_3COOH (0.21 g) and SbF_5 (0.84 g) (molar ratio, 0.5:1.4:3) gave (50 °C, 4 h) after sublimation (110 °C, 5 Torr) 0.19 g of acid **43** (yield 84%).

*3.7.3.1. Perfluoro-2-isopropylbenzoic acid (**43**).* mp 136–136.5 °C (hexane–CH_2Cl_2, in a sealed capillary). UV (hexane) λ_{max}, nm (lg ε): 215 (3.79), 255 (3.57). IR (KBr) ν, cm^{-1}: 1740 (C=O); 1530, 1481, 1430 (FAR). ^1H NMR (CCl_4): δ 10.62 (s, OH). ^{19}F NMR (ether): δ −74.4 (6F, $2CF_3$), −132.0 (1F, F-3), −139.4 (1F, F-6), −147.5 (1F, F-5), −153.0 (1F, F-4), −172.3 (1F, F-2); $J_{CF_3-F(2)} = 5$, $J_{CF_3-F(3)} = 26$, $J_{2,3} = 2$, $J_{2,4} = 4$, $J_{3,4} = 20$, $J_{3,5} = 9$, $J_{3,6} = 10$, $J_{4,5} = 20$, $J_{4,6} = 5$, $J_{5,6} = 22$. HRMS *m/z*, 361.9805 (M^+). Calcd for $C_{10}HF_{11}O_2$ = 361.9801.

*3.7.4. Perfluoropropylbenzene (**44**)*

A mixture of compound **44** (0.99 g), CF_3COOH (0.47 g) and SbF_5 (1.91 g) (molar ratio, 1:1.4:3) was stirred at 50 °C for 7.5 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 0.94 g of mixture, which contained (^{19}F NMR) compounds **44** and **45** in the ratio 48:52 (yield 47% and 51%, respectively).

*3.8. Competitive reactions of compounds **3**, **11**, **14**, **36** and **38** with CF_3COOH/SbF_5*

*3.8.1. Perfluoroindan (**3**) and perfluorobenzocyclobutene (**14**)*

A mixture of indan **3** (0.46 g), compound **14** (0.38 g), CF_3COOH (0.17 g) and SbF_5 (1.99 g) (molar ratio, 0.5:0.5:0.5:3) was stirred at 20 °C for 3.5 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 0.65 g (yield 82%) of mixture, which contained (^{19}F NMR) 8% of **1**, 42% of **3**, 45% of **15** and 5% of **16**.

*3.8.2. Perfluoroindan (**3**) and perfluorotetralin (**11**)*

Analogously to the previous procedure, the reaction of indan **3** (0.45 g), compound **11** (0.52 g), CF_3COOH (0.17 g) and SbF_5 (1.95 g) (molar ratio, 0.5:0.5:0.5:3) gave (20 °C, 4 h) 0.85 g (yield 90%) of mixture, which contained (^{19}F NMR) 45% of **1**, 3% of **3**, 50% of **11** and 2% of **12**.

*3.8.3. Perfluoroindan (**3**) and perfluoro-3-methylindene (**36**)*

Analogously to procedure (Section 3.8.1), the reaction of compound **3** (0.53 g), indene **36** (0.55 g), CF_3COOH (0.21 g) and SbF_5 (2.3 g) (molar ratio, 0.5:0.5:0.5:3) gave (20 °C, 3 h) 0.95 g (yield 93%) of mixture, which contained (^{19}F NMR) 49% of **1**, 4% of **3**, 11% of **36** and 36% of **37**.

*3.8.4. Perfluoroindan (**3**) and perfluorotoluene (**38**)*

Analogously to procedure (Section 3.8.1), the reaction of indan **3** (0.58 g), compound **38** (0.46 g), CF_3COOH (0.22 g) and SbF_5 (2.55 g) (molar ratio, 0.5:0.5:0.5:3) gave (20 °C, 3.5 h) 0.89 g (yield 91%) of mixture, which contained (^{19}F NMR) 50% of **1**, 30% of **38** and 20% of **40**.

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