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Skeletal transformations of perfluoro-1-phenylindan under the action of antimony pentafluoride

V.M. Karpov*, T.V. Mezhenkova, V.E. Platonov, V.R. Sinyakov

N.N. Vorozhtsov Institute of Organic Chemistry, Novosibirsk 630090, Russia

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Abstract

Perfluoro-1-phenylindan (**1**) was obtained from perfluoroindan and pentafluorobenzene in the presence of SbF_5. Compound **1** heated with antimony pentafluoride at 170°C and then treated with water gave a mixture of perfluorinated 9-methylfluorene (**5**), 9-hydroxy-9-methylfluorene (**6**), 9-methyl-1,2,3,4,5,6,7,8-octahydroanthracene (**7**), 1,9-dimethyl-5,6,7,8-tetrahydro-β-naphthindan (**8**). When heated with SbF_5 in the presence of HF and then treated with water, compound **1** is transformed to a mixture of products **5**, **6**, perfluoro-1,2,3,4,5,6,7,8-octahydroanthracene (**9**), perfluoro-10-methyl-9(10H)anthracenone (**10**) and 10-H-perfluoro-10-methyl-9(10H)anthracenone (**11**). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Skeletal transformations; Perfluorophenylindan; Antimony pentafluoride; NMR spectroscopy; Mass spectrometry

1. Introduction

We have previously reported the reactions of alicyclic ring cleavage, contraction and expansion of polyfluorinated benzocycloalkenes (benzocyclobutene, indan, tetralin) by antimony pentafluoride [1–7]. It has been shown that availability of a perfluoroalkyl group in a substrate has an appreciable effect on the behaviour of the benzocycloalkene.

The reactions of polyfluorobenzocycloalkenes containing polyfluoroaryl groups as substituents with antimony pentafluoride have not previously been investigated.

In order to establish the systematic tendencies of cationoid skeletal transformations of polyfluorobenzocycloalkenes we have synthesised perfluoro-1-phenylindan (**1**) and studied its behaviour under the action of SbF_5.

2. Results and discussion

Compound (**1**) was obtained by electrophilic alkylation of pentafluorobenzene (PFB) by perfluoroindan (**2**) in the presence of SbF_5 by the method used for the alkylation of polyfluorobenzenes by polyfluorobenzyl cations [8]. Treatment of the reaction mixture with anhydrous HF, then with water leads to the formation of product **1** along with a small amount of 1-hydroxy-perfluoro-1-phenylindan (**3**). The latter was obtained as the only product by treatment of the reaction mixture with water (Scheme 1).

The reason for these reactions is that in an SbF_5 medium, compound **1** exists as a salt of the perfluoro-1-phenyl-1-indanyl cation (**4**). Thus, when PFB is added to the solution of compound **2** in excess of SbF_5 cation **4** is generated. The latter was also generated from phenylindan **1** in an SbF_5 medium or in the system SbF_5–SO_2FCl.

It has been shown that when heated with SbF_5, compound **1** undergoes skeletal transformations. In this case not only the alicyclic, but also the aromatic fragment was involved in the reaction. Thus, compound **1** heated with antimony pentafluoride at 170°C and then treated with water gives a mixture of perfluorinated 9-methylfluorene (**5**), 9-hydroxy-9-methylfluorene (**6**), 9-methyl-1,2,3,4,5,6,7,8-octahydroanthracene (**7**), 1,9-dimethyl-5,6,7,8-tetrahydro-β-naphthindan (**8**) together with small amounts of perfluoro-1,2,3,4,5,6,7,8-octahydroanthracene (**9**) and perfluoro-10-methyl-9(10H)anthracenone (**10**) (Scheme 2). When the reaction mixture was treated with anhydrous HF then with water, compounds **5–9** were obtained. In this case the amount of compound **5** increased, whereas the amount of hydroxy-derivative **6** decreased.

Heating at 170°C a solution of compound **1** and HF in antimony pentafluoride, obtained in the reaction of indan **2** with PFB in SbF_5, and subsequent treatment of the reaction mixture with H_2O, leads to the formation of compounds **5**, **6**,

* Corresponding author. Fax: +7-383-235-4752.

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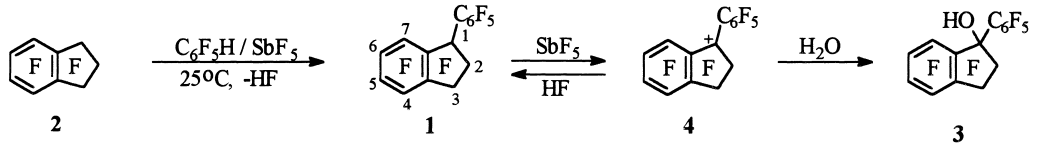


Scheme 1.

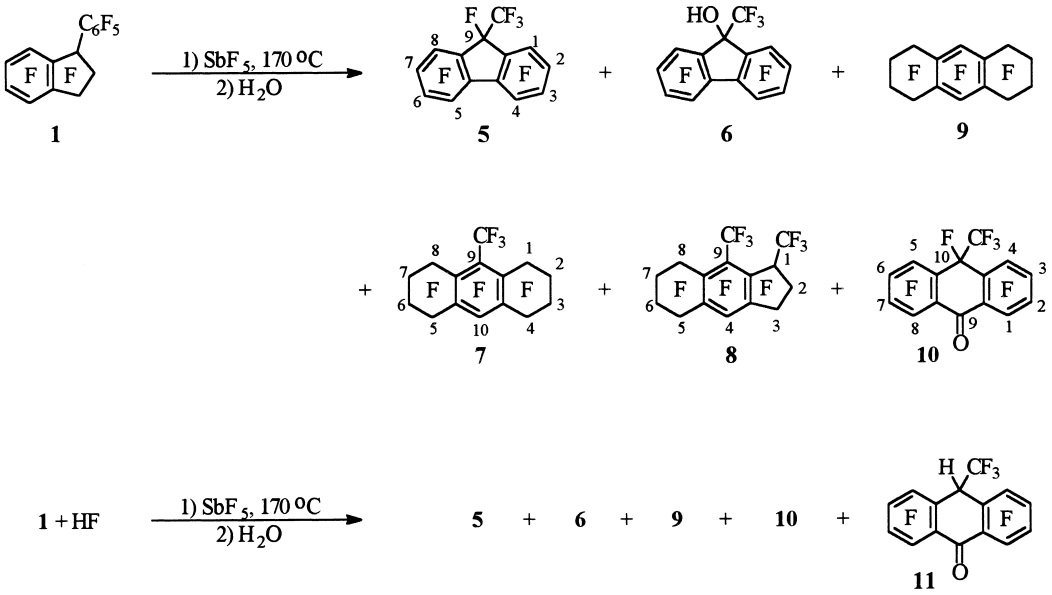
9, **10** and 10-H-perfluoro-10-methyl-9(10H)anthracenone (**11**) (Scheme 2).

Some possible routes of formation of products **5–11** from compound **1** are represented in the Scheme 3 (for mechanisms of skeletal transformations of other polyfluoroindans see [2,3,5]). Compound **1** exists in an SbF_5 medium as a salt of cation **4**, which possibly undergoes cleavage of the five-membered ring to give the benzyl type cation **12**. Intramolecular attack of the ortho-position of the pentafluorophenyl ring by the benzyl carbon atom in cation **12** seems to give compound **13** after fluoride ion addition (route 1). Electrophilic addition of HF at positions 2 (or 4), 9 of compound **13** (route 1a) and subsequent elimination of HF leads to perfluoro-9-methyl-9,10-dihydroanthracene (**14**) (cf. 1,4-addition in electrophilic reactions of 2-chloroperfluoro-1,3-butadiene [9]; addition of HF to polyfluorobenzocyclobutenes in the system HF–SbF_5 [10]; dehydrofluorination of polyfluoroalkanes under the action of SbF_5 [11,12]). At the same time addition of HF at the positions 9, 2 of compound **13** (route 1b) seems to lead to product **15**, which then undergoes defluorination or (and) disproportionation to give dihydroanthracene **16** (cf. formation of perfluoro-2,3-dimethylindene from perfluoro-1,2-dimethylindan [3,5] and disproportionation of polyfluorocyclohexadienes in an SbF_5 medium [13,14]).

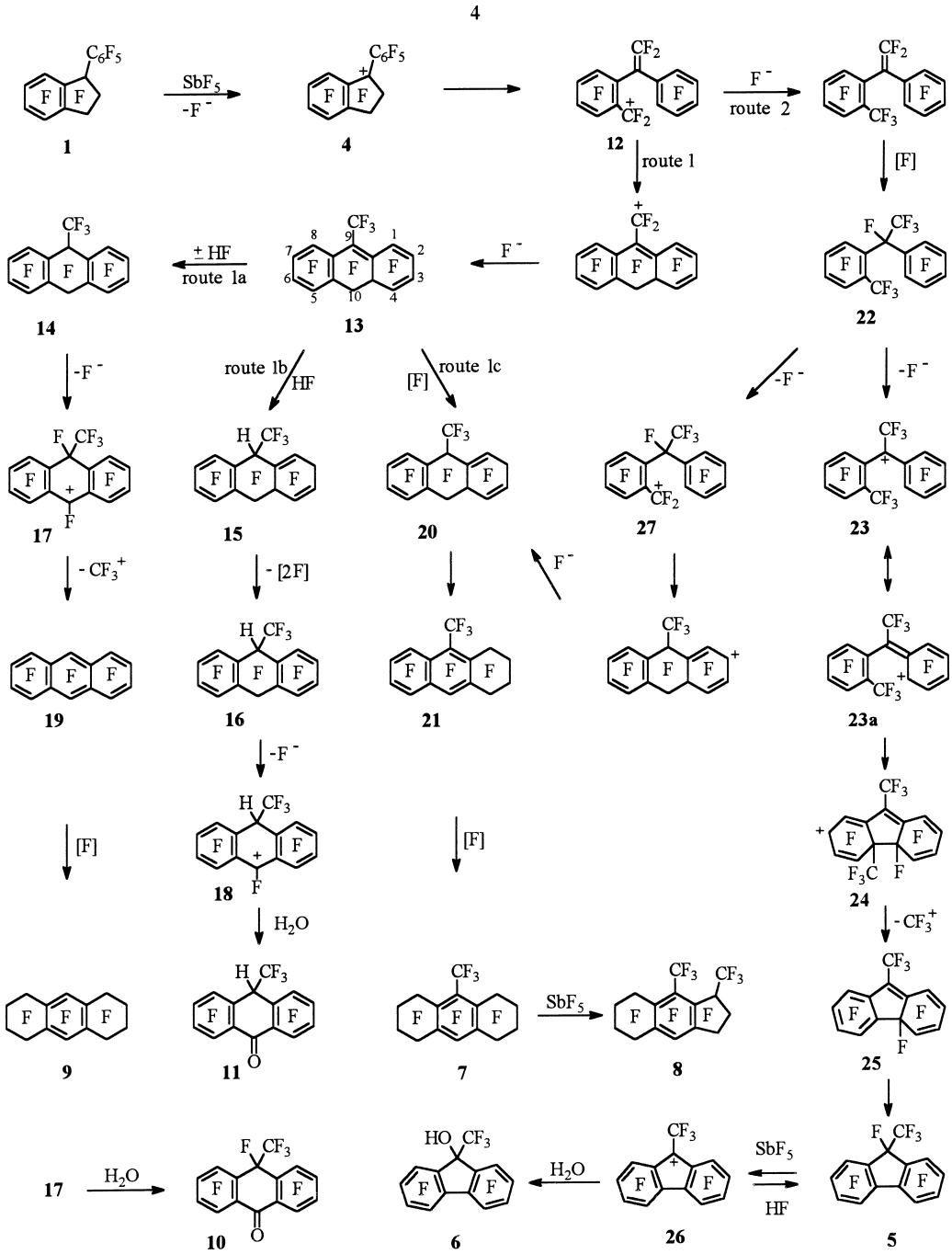
It may be suggested, that hydrolysis of cations **17** and **18** which are generated from dihydroanthracenes **14** and **16** under the action of SbF_5 leads to the formation of ketones **10** and **11**. Perfluoroanthracene (**19**) seems to be formed as a result of CF_3^+ elimination from cation **17**. Further fluorination of compound **19** under the action of SbF_5 gives product **9**.

In the absence of HF, isomerisation of compound **13** to **14** apparently proceeds more slower than its fluorination. It may be assumed that fluorination of compound **13** occurs by addition of SbF_4–F to the positions 2, 9 (or 9, 2) with subsequent elimination of SbF_3 (route 1c) to give product **20** (cf. fluorination of fluoroolefins and addition of SbF_5 to fluoroolefins [15]). Further fluorination of compound **20** or (and) its isomer **21** by SbF_5 leads to product **7**. Fluorination of octafluoronaphthalene and its derivatives by SbF_5 leading to the formation of polyfluorotetralins is known [16]. Compound **7** undergoes contraction of an alicyclic ring to form product **8**. Similar isomerisation of perfluoro-5-ethyltetralin to perfluoro-1-methyl-7-ethylindan under the action of SbF_5 was found by us earlier [6,7].

According to route 2 cation **12** possibly adds the fluoride ion and then undergoes fluorination to form compound **22**. It may be suggested that in ion **23**, generated from compound **22**, there occurs intramolecular substitution of the "aromatic" CF_3-group as a result of aromatic ring attack by a positively charged ortho-carbon of the pentafluorophenyl group (resonance structure **23a**) with subsequent elimination of CF_3^+ from cation **24** leading to the product **25**. The latter then isomerises to compound **5**. An analogous mechanism of cationoid cyclisation of diaryl-2,2,2-trifluoroethanols to



Scheme 2.



Scheme 3.

9-trifluoromethyl-derivatives of fluorene is discussed in [17]. Compound **5** exists in an SbF_5 medium as a salt of the perfluoro-9-methylfluorenyl cation (**26**), that was confirmed by a separate experiment. Hydrolysis of a salt of cation **26** leads to hydroxyderivative **6**, and treatment by HF gives methylfluorene **5**.

It cannot be excluded that not only cation **23**, but also cation **27** was generated from compound **22** under the action of SbF_5. Intramolecular cyclisation of cation **27**, as well as cyclisation of ion **12** (route 1–1c), should finally lead to products **7** and **8**.

The structures of the compounds were established by elemental analysis and spectral characteristics.

Patterns observed in the ^{19}F NMR spectra of compounds **5** and **6** are in agreement with those for perfluorinated fluorene and 9-phenylfluorene [18]. In the spectrum of compound **8** chemical shifts and fine structure of the signals, which belong to the fluorine atoms of indan fragment of molecule are in agreement with those for perfluoro-1,7-dimethylindan [3]. The spectrum of compound **9** is in agreement with that reported in literature [19]. Assignment of signals in the spectra of cations **4** and **26** has been made in a similar

way as for polyfluorobenzyl cations [20] and polyfluorofluorenyl cations [18].

3. Experimental details

^{19}F NMR spectra were recorded on a Bruker WP-200 SY instrument (188.3 MHz) for $CHCl_3$ solutions of reaction mixtures and of individual compounds (810 mol%). Chemical shifts are given in δ ppm downfield from C_6F_6 as an internal standard.

The elemental composition of compounds was determined by means of high-resolution mass spectrometry on a Finnigan Mat 8200 instrument.

Contents (yields) of products in reaction mixtures were established by GLC methods and ^{19}F NMR spectroscopic data.

3.1. Perfluoro-1-phenylindan (1)

Pentafluorobenzene (1.9 g) was added over 5 min to a stirred mixture containing 3.38 g of perfluoroindan **2**, 7.37 g SbF_5 (1:1:3) and 3.5 ml of C_6F_6 at 20°C. The mixture was stirred for 3.5 h at 22°C, then treated with 12 ml of anhydrous HF and poured onto ice. The organic layer was separated and dried over $MgSO_4$ to give after distillation of C_6F_6, 4.03 g of the product, containing 78% (yield 61%) of compound **1** and 15% (12%) of compound **3**. Compound **1** of 3.3 g was isolated on a silica-gel column (CCl_4 as eluent).

Compound **1**: Analysis: Found: C, 40.47; F, 59.41%. $C_{15}F_{14}$ requires: C, 40.36; F, 59.64%. ^{19}F NMR δ: 62.8 ($1F_A$, F^3); 51.0 ($1F_B$, F^3, $J_{AB} = 260$ Hz); 43.8 ($1F_A$, F^2); 33.6 ($1F_B$, F^2, $J_{AB} = 240$ Hz); 24.0 (4F, F^4, F^7, $F^{2'}$, $F^{6'}$); 19.3 (1F, F^1); 18.7 (1F, F^6); 18.2 (1F, F^5); 14.3 (1F, $F^{4'}$); 2.5 (2F, $F^{3'}$, $F^{5'}$) ppm.

3.2. 1-Hydroxyperfluoro-1-phenylindan (3)

Pentafluorobenzene (2.72 g) was added at 20°C to a stirred solution, containing 4.36 g of indan **2**, 9.58 g of SbF_5 (1.1:1:3) and 8 ml of C_6F_6. The mixture was stirred for 3 h at 25°C and then treated with water. The organic layer was separated and dried over $MgSO_4$ to give after distillation of C_6F_6, 5.95 g of indan **3** (yield 91%).

Compound **3**: mp 43–44°C (from hexane). Analysis: Found: C, 40.55; H, 0.15; F, 55.52%. $C_{15}HF_{13}O$ requires: C, 40.56; H, 0.23; F, 55.61; O, 3.6%. ^{19}F NMR δ: 64.8 ($1F_A$, F^3); 50.4 ($1F_B$, F^3, $J_{AB} = 260$ Hz); 45.0 ($1F_A$, F^2); 32.5 ($1F_B$, F^2, $J_{AB} = 235$ Hz); 23.0 (1F, F^7); 22.7 (2F, $F^{2'}$, $F^{6'}$); 22.0 (1F, F^4); 17.3 (1F, F^6); 14.6 (1F, F^5); 12.5 (1F, $F^{4'}$); 2.2 (2F, $F^{3'}$, $F^{5'}$) ppm.

3.3. Perfluoro-1-phenyl-1-indanyl cation (4)

1. Pentafluorobenzene (0.15 g) was added at room temperature to the solution of 0.24 g of indan **2** in 1.05 g of SbF_5 (1.1:1:6) placed in an ampoule for recording NMR spectra and the mixture was stirred by shaking. According to the ^{19}F NMR spectrum recorded after 3 h a solution of a salt of cation **4** was obtained.
2. Indan **1** (0.24 g) was dissolved in 1.16 g of SbF_5 (1:10), and the spectrum was recorded. The solution was diluted with 0.4 g of SO_2ClF, and the spectrum was recorded again. The ^{19}F NMR spectra of the solutions of indan **1** in SbF_5 and in the system SbF_5–SO_2ClF also contained the signals of cation **4** and did not contain the signals of the precursor **1**.

Cation **4**: ^{19}F NMR δ (in SO_2ClF): 81.1 (1F, F^5); 69.7 (2F, $F^{4'}$, F^7); 59.0 (2F) and 56.0 (4F, $F^{2'}$, $F^{6'}$, F^2, F^3); 37.4 (1F, F^4); 29.8 (1F, F^6); 14.0 (2F, $F^{3'}$, $F^{5'}$) ppm ($J_{57} = 47$; $J_{45} = J_{56} = 20$ Hz).

3.4. Interaction of perfluoro-1-phenylindan (1) with SbF_5

1. Indan **1** (1.55 g) and 5.28 g of SbF_5 (1:7) was heated at 170°C in a 10 ml nickel bomb for 15 h. The mixture was treated with 6 ml of anhydrous HF, then poured on to ice, extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was distilled off to give 1.28 g of the product, containing 42% (yield 39.1%) of **5**, 10% (9.3%) of **6**, 6% (3.9%) of **7**, 22% (14.5%) of **8**, 4% (2.9%) of **9**.

   Pure compound **5** and a mixture containing (GC-MS) 18% of **7** and 80% of **8** were isolated on a silica-gel column (hexane as eluent). The individual compound **7** was isolated from the mixture obtained by us in another reaction that will be published in the future.

   *Perfluoro-9-methylfluorene (**5**)*: mp 47–49°C (from ethanol). Analysis: Found: C, 42.16; F, 57.69%. $C_{14}F_{12}$ requires: C, 42.45; F, 57.55%. ^{19}F NMR δ: 86.3 (3F, CF_3); 30.3 (2F, F^4, F^5); 27.0 (2F, F^1, F^8); 16.1 (2F, F^3, F^6); 11.9 (2F, F^2, F^7); −17.0 (1F, F^9) ppm ($J_{CF_3-F^1} = 21$; $J_{CF_3-F^9} = 11$ Hz).

   *Perfluoro-9-methyl-1,2,3,4,5,6,7,8-octahydroanthracene (**7**)*: mp 67–68°C. MS: Found: M^+ 559.96409. $C_{15}F_{20}$ requires: M 559.96804. ^{19}F NMR δ: 109.4 (3F, CF_3); 67.1 (1F, F^{10}); 56.9 (8F, F^1, F^4, F^5, F^8); 28.4 (4F, F^2 and F^7 or F^3 and F^6); 25.9 (4F, F^3 and F^6 or F^2 and F^7) ppm ($J_{CF_3-F^1} = 30$; $J_{4,10} = 25$ Hz).

   *Perfluoro-1,9-dimethyl-5,6,7,8-tetrahydro-β-naphthindan (**8**)*: MS: Found: M^+ 559.96796. $C_{15}F_{20}$ requires: M 559.96804. ^{19}F NMR δ: 108.3 (3F, CF_3^9); 89.2 (3F, CF_3^1); 61.5 (1F, F^4); 60.0 ($1F_A$, F^8); ∼56.2 ($1F_B$, F^8, $J_{AB} \sim 300$ Hz); ∼58.6 ($1F_A$, F^5); ∼56.2 ($1F_B$, F^5, $J_{AB} \sim 300$ Hz); 56.4 ($1F_A$, F^3); 50.0 ($1F_B$, F^3, $J_{AB} \sim 275$ Hz); 41.6 ($1F_A$, F^2); 30.5 ($1F_B$, F^2, $J_{AB} \sim 250$ Hz); 29.1 ($1F_A$, F^6 or F^7); 26.8 ($1F_B$, F^6 or F^7, $J_{AB} \sim 280$ Hz); 27.8 ($1F_A$, F^7or F^6); 25.6 ($1F_B$, F^7or F^6, $J_{AB} \sim 275$ Hz); −10.9 (1F, F^1) ppm ($J_{CF_3^9-F^1} = 52$; $J_{CF_3^9-F^8} = 31$; $J_{CF_3-CF_3} = 13$ Hz).
2. Indan **1** (1.53 g) and 5.2 g of SbF_5 (1:7) was heated at 170°C in a 10 ml nickel bomb for 15 h. The reaction

mixture was poured on to ice, extracted with $CHCl_3$ and dried over $MgSO_4$. The solvent was distilled off to give 1.32 g of the product, containing 20% (yield 19.4%) of **5**, 39% (38.1%) of **6**, 5% (3.4%) of **7**, 18% (12.4%) of **8**, 3% (2.3%) of **9** and compound **10** (<1%).

3. Pentafluorobenzene (0.65 g) was added at room temperature to the solution of 1.15 g of indan **2** in 6.7 g of SbF_5 (1:1:8) in a nickel bomb. The mixture was held at room temperature for 50 h, then heated at 170°C for 15 h and treated as in (2) to give 1.41 g of the product, containing 13% (yield 12%) of **5**, 32% (29.7%) of **6**, 2% (1.4%) of **9**, 14% (12%) of **10** and 15% (13.5%) of **11**.
4. In a similar manner, from 1.05 g of indan **2**, 0.59 g of pentafluorobenzene and 5.36 g of SbF_5 (1:1:7) was obtained 1.3 g of the product, containing 6% (yield 5.6%) of **5**, 44% (41.2%) of **6**, 5% (3.6%) of **9**, 15% (13.1%) of **10** and 11% (10%) of **11**. Individual compounds **5**, **6**, **9**, **10** and compound **11** contaminated with about 15% of **10** were isolated by preparative GLC from the pooled products obtained in several analogous experiments.

*9-Hydroxyperfluoro-9-methylfluorene (**6**)*: mp 105.5–107°C (from hexane). MS: Found: M^+ 393.98538. $C_{14}HF_{11}O$ requires: M 393.98516. ^{19}F NMR δ: 84.9 (3F, CF_3); 29.3 (2F, F^4, F^5); 23.1 (2F, F^1, F^8); 13.6 (2F, F^3, F^6); 10.9 (2F, F^2, F^7) ppm ($J_{CF_3-F^1} = 19$ Hz).

*Perfluoro-1,2,3,4,5,6,7,8-octahydroanthracene (**9**)* (cf. [17]): mp (in a sealed capillary) 128.5–129.5°C (from hexane). MS: Found: M^+ 509.96884. $C_{14}F_{18}$ requires: M 509.97124. ^{19}F NMR δ: 54.4 (8F, F^1, F^4, F^5, F^8); 51.9 (2F, F^9, F^{10}); 27.2 (8F, F^2, F^3, F^6, F^7) ppm.

*Perfluoro-10-methyl-9(10H)anthracenone (**10**)*: mp (in a sealed capillary) 166.5–168°C (from hexane). MS: Found: M^+ 423.97648. $C_{15}F_{12}O$ requires: M 423.97574. ^{19}F NMR δ: 82.3 (3F, CF_3); 28.4 (2F, F^4, F^5); 25.2 (2F, F^1, F^8); 19.5 (2F, F^3, F^6); 15.2 (2F, F^2, F^7); −11.4 (1F, F^{10}) ppm ($J_{4,10} = 57.5$; $J_{12} = J_{23} = J_{34} = J_{56} = J_{67} = J_{78} = 20$; $J_{CF_3-F^4} = 12.5$; $J_{13} = J_{68} = 11.5$; $J_{CF_3-F^{10}} = 10$; $J_{24} = J_{57} = 8.5$ Hz).

*10-H-perfluoro-10-methyl-9(10H)anthracenone (**11**)*: MS: Found: M^+ 405.98494. $C_{15}HF_{11}O$ requires: M 405.98516. ^1H NMR δ: 5.4 ppm (quartet, $J_{H-CF_3} = 7$ Hz). ^{19}F NMR δ: 90.9 (3F, CF_3); 25.1 (2F, F^1, F^8); 22.2 (2F, F^4, F^5); 16.5 (2F, F^3, F^6); 11.9 (2F, F^2, F^7) ppm ($J_{12} = J_{23} = J_{34} = J_{56} = J_{67} = J_{78} = 20$; $J_{14} = J_{58} = 14$; $J_{13} = J_{68} = 10$; $J_{CF_3-F^4} = 9$; $J_{CF_3-H} = 7$; $J_{24} = J_{57} = 5$ Hz).

3.5. Perfluoro-9-methylfluorenyl cation (**26**)

Fluorene **5** (0.2 g) was dissolved in 0.97 g SbF_5 (1:8.9) and the spectrum was recorded. The solution was diluted with 0.24 g of SO_2ClF, and the spectrum was recorded again. The ^{19}F NMR spectra of the solutions of fluorene **5** in SbF_5 and in the system SbF_5–SO_2ClF contained the signals of cation **26** and did not contain the signals of the precursor **5**.

Cation **26**: ^{19}F NMR δ (in SO_2ClF): 99.0 (3F, CF_3); 89.1 (2F, F^1, F^8); 70.2(2F, F^3, F^6); 54.1 (2F, F^4, F^5); 19.5 (2F, F^2, F^7) ppm ($J_{CF_3-F^1} = 43$ Hz).

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