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Formation of polyfluorofluorenes in the reactions of perfluoro-1,1diphenylalkanes with antimony pentafluoride

Tatyana V. Mezhenkova^a, Victor M. Karpov^{a,*}, Yaroslav V. Zonov^{a,b}

^a N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Novosibirsk 630090, Russia ^b Novosibirsk State University, Novosibirsk 630090, Russia

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Graphical abstract



Highlights

- Synthesis and reactions of perfluoro-1,1-diphenylalkanes with antimony pentafluoride.
- Cationic cyclization of perfluoro-1,1-diphenylalkanes into fluorenes.
- Perfluorinated 9-methyl-, 9-ethyl-, 9-isopropylfluorenes were obtained.

Abstract

Perfluoro-1,1-diphenylethane heated with SbF₅ at 130 °C with further treatment of the reaction mixture with HF-pyridine and then with water, gave perfluorinated 9-methylfluorene and 9-methyl-1,2,3,4-tetrahydrofluorene. Perfluoro-1,1-diphenylpropane under similar conditions formed perfluoro-9-ethylfluorene and perfluoro-9,9-dimethyl-1,2,3,4-tetrahydrofluorene. When perfluoroisobutylbenzene was heated with pentafluorobenzene in SbF₅ medium at 130 °C, with further treatment of the reaction mixture with HF-pyridine and then with water, perfluoro-9-isopropylfluorene was obtained. Perfluorodiphenylmethane heated with SbF₅, after treatment of the reaction mixture with water, gave perfluorobenzene; perfluorofluorene or its derivatives were not found in the mixture.

^{*} Corresponding author. Fax: +7-3832-34-4752. E-mail address: karpov@nioch.nsc.ru (V.M.Karpov)

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1. Introduction

Fluorinated aromatic compounds are essentially important to fundamental organic chemistry [1–3] and its applications, for example, to materials science, biomedicine and agriculture [1–11]. In particular, fluorine containing fluorenes also receive attention in both fundamental and applied aspects [11–20]. Of perfluorinated fluorenes, as far as we are aware, only perfluorofluorene [15], perfluoro-9-phenylfluorene [15], perfluoro-9-methylfluorene [21,22] and perfluoro-9-ethylfluorene [22] are known.

It has been shown by us earlier that perfluoro-9-methylfluorene along with other compounds was formed in the reaction of perfluoro-1-phenylindane with antimony pentafluoride [21]. We proposed that in the intermediate perfluoro-1-(2-tolyl)-1-phenylethan-1-yl cation there occurs cyclization with elimination of the trifluoromethyl cation to give 9-methylfluorene [21]. It was interesting to investigate the behavior of perfluoro-1,1-diphenylethane and similar compounds, which have no CF₃-group in the aromatic ring, under the action of SbF₅ with the aim to study the possibility of their cationic cyclization. It should be noted that in the hydrocarbon series diarylmethyl cations in a strong acid medium can undergo electrocyclization (conrotatory) of pentadienyl cations to cyclopentenyl cations is known in both hydrocarbon [26, 27] and fluorocarbon series [28]. This work describes transformations of some perfluoro-1,1-diphenylalkanes under the action of antimony pentafluoride.

2. Results and discussion

2.1. Reactions of perfluorinated 1,1-diphenylalkanes with SbF5

The heating of perfluoro-1,1-diphenylethane (1) with SbF₅ at 130 °C with further treatment of the reaction mixture with Olah's reagent (HF-pyridine) and then with water, gives a mixture of perfluorinated 9-methylfluorene (2) and 9-methyl-1,2,3,4-tetrahydrofluorene (3) along with small amounts of 9-methylfluoren-9-ol (4). When the reaction mixture was treated with water (without HF pretreatment), compounds 2 - 4, perfluoro-9-methyl-2,3,4,9-tetrahydrofluoren-1-one (5) and small amounts of perfluoro-9-methyl-2,3,4,4a-tetrahydrofluoren-9-ol (6) were obtained (Scheme 1). The yields of compounds are given for reaction mixtures (¹⁹F NMR, GLC).

Compound 1 was synthesized by the reaction of perfluoroethylbenzene (7) with C_6F_5H in the presence of SbF₅ at room temperature [29]. When we hold a mixture of ethylbenzene 7, C_6F_5H and excess of SbF₅ at room temperature, a solution of equimolar amounts of compound 1 and HF in antimony pentafluoride was prepared. Heating this solution at 130 °C, with further treatment of the reaction mixture with HF-pyridine and then with water, leads to the formation of compound 2, perfluoro-9-methyl-9-phenyl-1,2,3,4-tetrahydrofluorene (8) and small amounts of compound 3. When the reaction mixture was treated with water (without HF pretreatment), compounds 2 - 5, 8 were obtained (Scheme 1). Both reaction mixtures also contained compound 7 and some unidentified products.

The transformations of compound **1** under the action of SbF_5 can be rationalized by Scheme 2.

It may be suggested that in cation 10, generated from compound 1 [30], there occurs cyclization (resonance structure 10a) with further addition of fluoride ion to produce compound 11. The latter isomerizes into compound 12, for example, by elimination–addition of a fluoride ion. Compound 12 seems to disproportionate to fluorene 2 and tetrahydrofluorene 3. The mechanism of this process is not clear, but the disproportionation of polyfluorocyclohexadienes in an SbF₅ medium is known [31,32].

The reaction of ethylbenzene **7** with C_6F_5H resulting in compound **1** and HF seems to be reversible at 130 °C (Scheme 3). So the reaction mixture contains some amounts of pentafluorobenzene that can react with compounds **2** or/and **3** to give perfluoro-9-methyl-9-phenylfluorene (**9**) or/and compound **8**, respectively. Under the reaction conditions, fluorene **9** is apparently transformed into compound **8**.

As mentioned above, in the reaction of compound **1** with SbF₅ (in the absence of HF), fluorene **2** is evidently formed by disproportionation of compound **12**, but in the presence of HF, fluorene **2** is apparently formed by defluorination and/or disproportionation of compound **12**. It appears that compounds **8** and **9** can act as acceptors of fluorine atoms during the defluorination of compound **12** (cf. defluorination of perfluoro-1,2-dimethylindane [33] and perfluoro-1-methyl-2-phenylindane [34] in an SbF₅ medium with participation of intermediate compounds as acceptors of fluorine atoms).

In contrast to diphenylethane **1**, perfluorodiphenylmethane (**13**) under the action of antimony pentafluoride did not give fluorene derivatives. Compound **13** was synthesized by the reaction of perfluorotoluene with C_6F_5H in SbF₅ at room temperature [30,35]. Heating compound **13** with an excess of SbF₅ and further treatment of the reaction mixture with water gave perfluorobenzophenone (**14**). The same result was obtained when the mixture of perfluorotoluene,

 C_6F_5H and SbF_5 was held at room temperature (to give **13**+HF) and then heated at 200 °C (Scheme 4).

The difference in the behavior of compounds 1 and 13 in their reactions with antimony pentafluoride seems to be due to a larger positive charge in the benzene rings of cation 10 compared to the perfluorodiphenylmethyl cation (13c). Indeed, in going from the ion 13c to the ion 10, the participation of the pentafluorophenyl group in charge delocalization considerably increases [30]. Such consideration is in accordance with the data obtained for electrocyclization of diarylmethyl cations to fluorene derivatives in the hydrocarbon series [23–25].

The behavior of perfluoro-1,1-diphenylpropane (15) in an SbF₅ medium is similar to that of diphenylethane 1. Compound 15 was synthesized by interaction of perfluoropropylbenzene (16) with pentafluorobenzene in the presence of SbF₅ (Scheme 5). Heating diphenylpropane 15 with SbF₅ at 130 °C with further treatment of the reaction mixture with water, gives a mixture of perfluorinated 9-ethylfluoren-9-ol (17), 9-ethylfluorene (18), 9,9-dimethyl-2,3,4,9-tetrahydrofluoren-1-one (19) and 9,9-dimethyl-1,2,3,4-tetrahydrofluorene (20) (Scheme 5).

When the mixture of propylbenzene **16**, C_6F_5H and SbF_5 was held at room temperature (to give **15**+HF), then heated at 130 °C compounds **18** and **20** were formed after the treatment of the reaction mixture with HF-pyridine and then with water. When the reaction mixture was treated with water (without HF pretreatment), compounds **17** – **20** were obtained (Scheme 5).

A possible route for the formation of compounds **20** and **19** is presented in Scheme 4. Ethylfluorene **18** exists in SbF₅ medium as a salt of perfluoro-9-ethylfluorenyl cation (**21**) (cation **21** was generated by dissolving of compound **18** in SbF₅–SO₂ClF). In cation **21**, 1,2-shift of the trifluoromethyl group occurs to give cation **22**. Addition of the fluorine anion to cation **22** with subsequent fluorination form compound **20**. The hydrolysis of cation **23** generated from compound **20** leads to the formation of ketone **19**.

When perfluoroisobutylbenzene (24) was heated with pentafluorobenzene in SbF₅ medium at 130 °C, with further treatment of the reaction mixture with HF-pyridine and then with water, perfluoro-9-isopropylfluorene (25) was obtained (Scheme 5). The reaction mixture also contained some unidentified products. Compound 24 was prepared by the reaction of perfluorotoluene with perfluoropropene in the presence of SbF₅.

When the temperature was lowered to 50 °C, perfluorinated 2-methyl-1,1-diphenylpropane (26) and 2-methyl-1-phenylpropylidenecyclohexa-2,5-diene (27) along with compound 25 were formed. The mixture also contained unreacted compound 24 and C_6F_5H .

2.2. Generation of perfluoro-1,1-diphenylalk-1-yl cations

When compounds 1, 15 and 26+27 were dissolved in SbF₅–SO₂ClF, perfluorinated 1,1diphenyleth-1-yl (10), 1,1-diphenylprop-1-yl (28) and 2-methyl-1,1-diphenylprop-1-yl (29) cations were generated (Scheme 7).

The treatment of the solutions of the salts of cations **10**, **28** with water leads to the formation of perfluorinated 1,1-diphenylethanol (**30**) and 4-(1-phenylethylidene)cyclohexa-2,5-dienone (**31**), 1,1-diphenylpropan-1-ol (**32**) and 4-(1-phenylpropylidene)cyclohexa-2,5-dienone (**33**), respectively, together with some amounts of the precursors. Hydrolysis of the salt of cation **29** yielded perfluoro-4-(2-methyl-1-phenylpropylidene)cyclohexa-2,5-dienone (**34**) as a product of nucleophile attack at the more sterically available center of delocalized cation **29**. Precursors **26**+**27** and perfluoro-2-methyl-1,1-diphenylpropan-1-ol were not detected in the mixture (¹⁹F NMR).

2.3. Structure of compounds

The structures of the compounds were established by HRMS, elemental analysis and spectral characteristics. Assignment of signals in the ¹⁹F NMR spectra of compounds was made on the basis of chemical shifts of the signals, their fine structure and integral intensities.

Assignment of signals in the ¹⁹F NMR spectra of fluorenes 3, 5, 6, 8, 19, 25 was made by analogy with fluorenes 2, 4 [21], 17, 18, 20 [22], in the spectra of diphenylalkanes 15, 26, 32 – by analogy with diphenylalkanes 1 and 30 [29], compound 27 – by analogy with 1-(1-(o-tolyl)propylidene)cyclohexa-2,5-diene [34], compounds 31-34 – by analogy with 4-(1-(o-tolyl)propylidene)cyclohexa-2,5-dien-1-one [34].

The structures of the cations were identified by ¹⁹F NMR spectra. The peculiarities in the spectra of cations **21** and **28**, **29** agree with those for perfluoro-9-methylfluorenyl cation [21] and polyfluorinated diphenylmethyl cations [30], respectively.

Compounds 2, 4 [21], 14 [18], 17, 18, 20 [22], 1 and 30 [29] were identified by comparison of the ¹⁹F NMR data with data for authentic samples.

3. Conclusions

We have shown that perfluoro-1,1-diphenylalkanes, existing in an SbF₅ medium as the salts of perfluoro-1,1-diphenylalk-1-yl cations, can give polyfluorinated 9-alkylfluorenes when heated

with antimony pentafluoride. The investigations have revealed that the presence of a perfluoroalkyl group in the cationic centre proved to be a necessary requirement for the cyclization of the intermediate perfluoro-1,1-diphenylalk-1-yl cations to form fluorene skeleton.

4. Experimental

4.1. General methods

Analytical and spectral measurements were carried out in the Multi-Access Chemical Service Center of SB RAS. ¹⁹F NMR spectra were recorded on a Bruker AV 300 instrument (282.4 MHz). Chemical shifts are given in δ ppm from CCl₃F (¹⁹F), J values in Hz; C₆F₆ and SO₂ClF (– 162.9 and 99.9 ppm from CCl₃F) were used as internal standards. The molecular masses of the compounds were determined by high-resolution mass-spectrometry on a Thermo Electron Corporation DFS instrument (EI 70 eV). GC-MS: Hewlett Packard G1081A, combined with Hewlett Packard 5890 with mass selective detector HP 5971 (EI 70 eV). Contents (yields) of products in the reaction mixtures and the purity of analytical samples (≥97%) were established by GLC and ¹⁹F NMR spectroscopic data. Contents of products are given in mass percent. The reactions were carried out in a nickel bomb (V = 10 mL).

4.2. Reactions of perfluoro-1, 1-diphenylethane (1) with SbF_5

- A mixture of compound 1 (1.18 g, 2.72 mmol) and SbF₅ (4.80 g, 22.17 mmol) (molar ratio, 1:8.1 was heated at 130 °C for 15 h and HF-Py (7 mL) was added at -20 °C. The mixture was kept at 25 °C for 20 h, then poured onto ice, extracted with CHCl₃ and dried over MgSO₄. The solvent was distilled off to give 1.0 g of a mixture, containing 38% (yield 41.6%) of compound 2, 42% (38.6%) of 3 and 4% (4.4%) of 4. 0.61 g of a mixture, containing 54% of compound 2 and 42% of 3 was isolated by silica gel column chromatography (CCl₄ as eluent). By repeated chromatography of this mixture on a silica gel column (hexane as eluent) compound 3 (0.11 g) and compound 2 (0.31 g) were isolated.
- A mixture of compound 1 (2.10 g, 4.84 mmol) and SbF₅ (7.70 g, 35.48 mmol) (molar ratio, 1:7.3) was heated at 130 °C for 15 h. The mixture was treated with cold 5% hydrochloric acid, extracted with CHCl₃ and dried over MgSO₄. The solvent was distilled off to give 1.54 g of a mixture, containing 12% (yield 13.2%) of compound 2, 22% (20.2%) of 3, 25% (27.5%) of 4, 19% (18.3%) of 5 and 5% (4.6%) of 6. Compound 6 (0.04 g), compound 4 (0.19 g) and 0.53 g of a mixture, containing 17% of compound 2, 35% of 3 and 38% of 5, were isolated by silica gel column chromatography (CCl₄, then CHCl₃ as eluents). By repeated chromatography of this mixture on a silica gel column (hexane as eluent) product 5 (0.11 g) was isolated.

- 3. Pentafluorobenzene (0.63 g, 3.75 mmol) was added to a solution of ethylbenzene 7 (1.07 g, 10.08 mmol) in SbF₅ (6.47 g, 29.82 mmol) (molar ratio, 1:2.7:8). The mixture was kept at 25 °C for 20 h, then heated at 130 °C for 15 h and treated as in 4.2. (1) to give 1.1 g of a mixture, containing 54% (yield 40.1%) of compound 2, 4% (2.5%) of 3 and 22% (10.4%) of 8. Compound 2 (0.27 g) and compound 8 (0.08 g) were isolated by silica gel column chromatography (hexane as eluent).
- 4. Pentafluorobenzene (0.92 g, 5.47 mmol) was added to a solution of ethylbenzene 7 (1.42 g, 13.37 mmol) in SbF₅ (8.64 g, 39.82 mmol) (molar ratio, 1:2.4:7.3). The mixture was kept at 22 °C for 17 h, then heated at 130 °C for 15 h and treated as in 4.2. (2) to give 1.72 g of a mixture, containing 25% (yield 21.9%) of compound 2, 3% (2.2%) of 3, 24% (21.1%) of 4, 2% (1.5%) of 5 and 16% (8.9%) of 8.

4.2.1. Perfluoro-9-methyl-1,2,3,4-tetrahydrofluorene (3)

Liquid. ¹⁹F NMR: δ –76.0 (dm, 3F, CF₃), –102.9 (dm, 1F_A, CF₂-1) and –125.3 (dm, 1F_B, CF₂-1), –109.9 (dm, 1F_A, CF₂-4) and –118.1 (dm, 1F_B, CF₂-4), –126.2 (dm, 1F_A, CF₂-2) and –141.4 (dm, 1F_B, CF₂-2), –128.9 (dm, 1F_A, CF₂-3) and –143.0 (dm, 1F_B, CF₂-3), –131.1 (ddddd, 1F, F-5), –132.3 (qddd, 1F, F-8), –145.0 (ddd, 1F, F-6), –145.6 (ddd, 1F, F-7), –185.5 (m, 1F, F-9); $J_{A1,B1}$ = 301, $J_{A2,B2}$ = 277, $J_{A3,B3}$ = 274, $J_{A4,B4}$ = 309, $J_{A4,5}$ = 15, $J_{B4,5}$ = 40, $J_{5,6}$ = $J_{7,8}$ = 21, $J_{5,7}$ = 8, $J_{5,8}$ = 15, $J_{6,7}$ = 17, $J_{6,8}$ = 9, $J_{CF3-F(8)}$ = 22.5. HRMS, m/z: calcd. for C₁₄F₁₆ 471.9739; found 471.9743.

4.2.2. Perfluoro-9-methyl-2,3,4,9-tetrahydrofluoren-1-one (5)

Liquid. ¹⁹F NMR: δ -75.5 (dd, 3F, CF₃), -115.0 (dd, 1F_A, CF₂-4) and -116.1 (dd, 1F_B, CF₂-4), -126.8 (m, 1F_A, CF₂-2) and -128.3 (m, 1F_B, CF₂-2), -133.3 (m, 1F_A, CF₂-3) and -134.5 (m, 1F_B, CF₂-3), -127.5 (ddddd, 1F, F-5), -132.3 (qddd, 1F, F-8), -141.7 (ddd, 1F, F-7), -144.4 (ddd, 1F, F-6), -189.5 (q, 1F, F-9); $J_{A2,B2} = 290$, $J_{A3,B3} = 270$, $J_{A4,B4} = 310$, $J_{A4,5} = 28$, $J_{B4,5} = 30$, $J_{5,6} = 20$, $J_{5,7} = 10$, $J_{5,8} = 15$, $J_{6,7} = 17$, $J_{6,8} = 9$, $J_{7,8} = 21$, $J_{CF3-F(8)} = 19$, $J_{CF3-F(9)} = 12$. HRMS, m/z: calcd. for C₁₄F₁₄O 449.9720; found 449.9727.

4.2.3. Perfluoro-9-methyl-2,3,4,4a-tetrahydrofluoren-9-ol (6)

Liquid. ¹⁹F NMR: δ –77.7 (dm, 3F, CF₃), –112.3 (dm, 1F_A, CF₂-2) and –126.4 (dm, 1F_B, CF₂-2), –119.0 (dm, 1F_A, CF₂-3) and –138.3 (dm, 1F_B, CF₂-3), –121.4 (m, 1F, F-1), –123.5 (dm, 1F_A, CF₂-4) and –131.1 (ddm, 1F_B, CF₂-4), –134.7 (dddd, 1F, F-5), –135.8 (qddd, 1F, F-8), –144.3 (ddd, 1F, F-6), –146.5 (ddd, 1F, F-7), –165.3 (m, 1F, F-4a); $J_{A2,B2} = 292$, $J_{A3,B3} = 274$,

 $J_{A4,B4} = 267, J_{B4,5} = 65, J_{5,6} = J_{7,8} = 21, J_{5,7} = 7, J_{5,8} = 16.5, J_{6,7} = 19, J_{6,8} = 8, J_{CF3-F(8)} = 17.$ HRMS, *m/z*: calcd. for C₁₄HF₁₅O 469.9782; found 469.9784.

4.2.4. Perfluoro-9-methyl-9-phenyl-1,2,3,4-tetrahydrofluorene (8)

Liquid. ¹⁹F NMR: δ –65.9 (bm, 3F, CF₃), –101.1 (dm, 1F_A, CF₂-1) and –123.4 (dm, 1F_B, CF₂-1), –108.4 (dm, 1F_A, CF₂-4) and –117.0 (ddm, 1F_B, CF₂-4), –126.0 (dm, 1F_A, CF₂-2) and –141.1 (dm, 1F_B, CF₂-2), –129.8 (dm, 1F_A, CF₂-3) and –142.7 (dm, 1F_B, CF₂-3), –132.6 (ddddd, 1F, F-5), –134.8 (qddd, 1F, F-8), –138.2 (m, 1F, F-*ortho*), –139.9 (m, 1F, F-*ortho*), –146.8 (ddd, 1F, F-7), –147.9 (ddd, 1F, F-6), –149.7 (tt, 1F, F-*para*), –158.6 (m, 1F, F-*meta*), –160.2 (m, 1F, F-*meta*); $J_{A1,B1} = 298$, $J_{A2,B2} = 276$, $J_{A3,B3} = 273$, $J_{A4,B4} = 306$, $J_{A4,5} = 16$, $J_{B4,5} = 40$, $J_{5,6} = J_{7,8} = 20$, $J_{5,7} = J_{6,8} = 7$, $J_{5,8} = 16$, $J_{6,7} = 18$, $J_{CF3-F(8)} = 49$, $J_{meta,para} = 21$, $J_{ortho,para} = 5$. HRMS, m/z: calcd. for C₂₀F₂₀ 619.9675; found 619.9668.

4.3. Reactions of perfluorodiphenylmethane (13) with SbF_5

- A mixture of compound 13 (0.73 g, 1.9 mmol) and SbF₅ (5.02 g, 23.13 mmol) (molar ratio, 1:12.2) was heated at 200 °C for 10 h. The mixture was treated with cold 5% hydrochloric acid, extracted with CH₂Cl₂ and dried over MgSO₄. Distillation of the solvent gave 0.59 g of compound 14 (¹⁹F NMR spectrum).
- Pentafluorobenzene (0.98 g, 5.83 mmol) was added to a solution of perfluorotoluene (1.25 g, 5.30 mmol) in SbF₅ (8.01 g, 36.91 mmol) (molar ratio, 1.1:1:7). The mixture was kept at 22 °C for 5 h, then heated at 200 °C for 10 h and treated as in the previous experiment to give 1.76 g of compound 14 (¹⁹F NMR spectrum).

4.4. Preparation of perfluoro-1,1-diphenylpropane (15)

A mixture of compound **16** (2.17 g, 6.46 mmol), C₆F₅H (1.19 g, 7.08 mmol) and SbF₅ (7.00 g, 32.26 mmol) (molar ratio, 1:1.1:5) was stirred at 25 °C for 4 h. The mixture was treated with anhydrous HF (15 mL), then poured onto ice, extracted CH₂Cl₂ and dried over MgSO₄. The solvent was distilled off to give 2.81 g of a solid product, containing 86% (yield 77%) of compound **15**. Crystallization from CH₂Cl₂ – hexane gave 2.02 g of compound **15**. Colorless solid, mp 68–69 °C (CH₂Cl₂ – hexane). ¹⁹F NMR: δ –79.1 (d, 3F, CF₃), –121.4 (quind, 2F, CF₂), –136.6 (m, 4F, F-*ortho*), –148.9 (tt, 2F, F-*para*), –160.5 (m, 4F, F-*meta*), –163.2 (m, 1F, <u>CF</u>CF₂CF₃); *J*_{CF₂,*ortho* = 21, *J*_{CF₃,CF} = 15, *J*_{CF₂,CF} = 8, *J*_{meta,para} = 21, *J*_{ortho,para} = 5. HRMS, *m*/*z*: calcd. for C₁₅F₁₆ 483.9739; found 483.9733. Anal. Calcd for C₁₅F₁₆: C, 37.21; F, 62.79%. Found: C, 36.84; F, 63.12%.}

4.5. Reactions of perfluoro-1,1-diphenylpropane (15) with SbF5

- A mixture of compound 15 (1.11 g, 2.29 mmol) and SbF₅ (3.73 g, 17.19 mmol) (molar ratio, 1:7.5) was heated at 130 °C for 15 h, then it was treated as in 4.2.(2) to give 0.68 g of a mixture, containing 65% (yield 43.4%) of compound 17, 2% (1.3%) of 18, 15% (8.9%) of 19 and 4% (2.3%) of 20. Compound 17 (0.38 g) and compound 19 (0.075 g) were isolated by silica gel column chromatography (CCl₄, then CHCl₃ as eluents).
- Pentafluorobenzene (0.86 g, 5.12 mmol) was added to a solution of propylbenzene 16 (1.57 g, 13.06 mmol) in SbF₅ (8.11 g, 37.37 mmol) (molar ratio, 1:2.6:7.3). The mixture was kept at 23 °C for 10 h, then heated at 130 °C for 15 h and treated as in 4.2. (2) to give 1.9 g of a mixture, containing 51% (yield 46.7%) of compound 17, 25% (22.8%) of 18, 3% (2.4%) of 19 and 4% (3.1%) of 20.
- 3. Pentafluorobenzene (0.62 g, 3.69 mmol) was added to a solution of propylbenzene 16 (1.25 g, 10.40 mmol) in SbF₅ (6.43 g, 29.63 mmol) (molar ratio, 1:2.8:8). The mixture was kept at 23 °C for 10 h and heated at 130 °C for 15 h, then HF-Py (6 mL) was added. The mixture was kept at 25°C for 20 h and treated as in 4.2. (1) to give 1.48 g of a mixture, containing 68% (yield 60.6%) of compound 18 and 8% (6.1%) of 20. By silica gel column chromatography (hexane as eluent) 0.76 g of compound 18 was isolated.

4.5.1. Perfluoro-9,9-dimethyl-2,3,4,9-tetrahydrofluoren-1-one (19)

Liquid. ¹⁹F NMR: δ –64.8 (d, 6F, 2CF₃), –114.1 (dm, 2F, CF₂-4), –127.6 (m, 2F, CF₂-2), –128.1 (tddd, 1F, F-5), –129.1 (septddd, 1F, F-8), –133.9 (m, 2F, CF₂-3), –141.4 (ddd, 1F, F-7), – 145.6 (ddd, 1F, F-6); $J_{4,5}$ = 33, $J_{5,6}$ = 21, $J_{5,7}$ = $J_{6,8}$ = 9, $J_{5,8}$ = 15, $J_{6,7}$ = 18, $J_{7,8}$ = 20, $J_{CF3-F(8)}$ = 22. HRMS, m/z: calcd. for C₁₅F₁₆O 499.9688; found 499.9687.

4.5.2. Perfluoro-9-ethylfluorenyl cation (21)

Compound **18** (0.11 g, 0.25 mmol) was dissolved in SbF₅ (1.04 g, 4.8 mmol) (molar ratio, 1:19), then SO₂ClF (0.21 g) was added at 0 °C and ¹⁹F NMR spectrum of the solution was measured at 20 °C. The spectrum contained signals of cation **21** in the absence of the signals of precursor **18**. The solution was poured into water and extracted with CHCl₃. The extract was dried over MgSO₄ and the solvent was distilled off to give 0.09 g of a mixture, containing compounds **17** and **18** in the ratio 71:29 (¹⁹F NMR spectrum). Cation **21**. ¹⁹F NMR: δ -80.4 (m, 3F, CF₃), – 72.8 (td, 2F, F-1,8), –92.6 (dm, 2F, F-3,6), –109.0 (m, 2F, F-4,5), –112.0 (t, 2F, CF₂), –143.2 (m, 2F, F-2,7); *J*_{CF2-F(1)} = *J*_{CF2-F(8)} = 59, *J*_{1,3} = *J*_{6,8} = 45.

4.6. Synthesis of perfluoroisobutylbenzene (24)

A mixture of perfluorotoluene (10.74 g, 45.5 mmol), SbF₅ (6.47 g, 29.8 mmol) and perfluoropropene (9.43 g, 62.9 mmol) (molar ratio, 1:0.66:1.38) in a sealed glass ampoule was kept at 25 °C for 250 h. The mixture was treated with water; the organic layer was separated and dried over MgSO₄ to give 13.5g of a mixture containing compound **24** and perfluorotoluene in the ratio 4:1 (¹⁹F NMR). Distillation yielded 7.92 g of compound **24**, bp 153–154 °C. ¹⁹F NMR: δ –73.7 (td, 6F, 2CF₃), –100.1 (dtsept, 2F, CF₂), –137.2 (m, 2F, F-*ortho*), –146.5 (tt, F, F-*para*), –160.3 (m, 2F, F-*meta*), –184.3 (tsept, 1F, <u>CF</u>(CF₃)₂); $J_{CF_2,CF} = 22$, $J_{CF_2,ortho} = 20$, $J_{CF_2,CF_3} = 11$, $J_{CF_3,CF} = 6$, $J_{meta,para} = 21$, $J_{ortho,para} = 6$. HRMS, m/z: calcd. for C₁₀F₁₄ 385.9771; found 385.9772.

4.7. Reactions of perfluoroisobutylbenzene (24) with C_6F_5H in the presence of SbF_5

- Pentafluorobenzene (0.47 g, 2.8 mmol) was added to a solution of compound 24 (1.09 g, 2.8 mmol) in SbF₅ (4.89 g, 22.5 mmol) (molar ratio, 1:1:8). The mixture was kept at 23 °C for 21 h and heated at 130 °C for 15 h, then HF-Py (6 mL) was added. The mixture was kept at 23 °C for 24 h, then poured onto ice, extracted with CHCl₃ and dried over MgSO₄. Unreacted C₆F₅H and compound 24 (in part) were distilled off along with the solvent to give 1.1 g of a mixture, containing 58% (yield 45.6%) of compound 25 and 19% (19.2%) of 24. Compound 25 (0.34 g) was isolated by silica gel column chromatography (hexane as eluent).
- A mixture of compound 24 (1.38 g, 3.57 mmol), C₆F₅H (0.66 g, 3.93 mmol) and SbF₅ (3.87 g, 17.83 mmol) (molar ratio, 1:1.1:5) was heated at 55 °C for 28 h. The mixture was treated as in the previous experiment to give 1.21 g of a mixture, containing 17% (yield 11.6%) of compound 25, 15% (9.5%) of 26, 30% (19.0%) of 27 and 31% (27.2%) of 24. By silica gel column chromatography (hexane as eluent) 0.33 g of a mixture of isomers 27 (conformers A and B in the ratio 58:42) and 26 in the ratio 64:36 was isolated.

4.7.1. Perfluoro-9-isopropylfluorene (25)

Colorless solid, mp 80.5–82 °C (hexane). ¹⁹F NMR: δ –73.0 (m, 6F, 2CF₃), –132.8 (m, 2F, F-4,5), –133.3 (m, 2F, F-1,8), –146.1 (m, 2F, F-3,6), –151.3 (m, 2F, F-2,7), –170.9 (m, 1F, <u>CF(CF_3)_2</u>), –173.7 (m, 1F, F-9). HRMS, *m/z*: calcd. for C₁₆F₁₆ 495.9739; found 495.9733. Anal. Calcd for C₁₆F₁₆: C, 38.73; F, 61.27%. Found: C, 38.57; F, 61.39%.

Mixture with isomer **27** (**26**:**27** = 36:64). Compound **26**. ¹⁹F NMR: δ -71.5 (m, 6F, 2CF₃), – 136.3 (bm, 4F, F-*ortho*), –149.1 (m, 2F, F-*para*), –160.4 (m, 4F, F-*meta*), –164.3 (m, 1F, F-1), – 175.9 (quinm, 1F, <u>CF</u>(CF₃)₂); *J*_{CF,ortho} = 52. GC-MS, *m*/*z*: 534 [M]⁺ for **26**. HRMS, *m*/*z*: calcd. for C₁₆F₁₈ 533.9707; found 533.9709 (for the mixture of **26**+**27**).

4.7.3. Perfluoro-2-methyl-1-phenylpropylidenecyclohexa-2,5-diene (27)



Mixture with isomer **26** (**26**:**27** = 36:64). Compound **27** (conformers **A**:**B** = 58:42). ¹⁹F NMR, conformer **A**: δ -71.7 (m, 6F, 2CF₃), -110.0 (m, 2F, CF₂), -134.1 (dm, 1F, F-2), -137.5 (m, 2F, F-*ortho*), -141.4 (m, 1F, F-6), -148.8 (m, 1F, F-*para*), -149.7 (m, 1F, F-3), -150.9 (m, 1F, F-5), -156.1 (dm, 1F, <u>CF</u>(CF₃)₂), -160.9 (m, 2F, F-*meta*); *J*_{CF-F(2)} = 148; conformer **B**: δ -70.8 (dm, 6F, 2CF₃), -109.0 (m, 2F, CF₂), -138.7 (septm, 1F, F-2), -139.2 (m, 2F, F-*ortho*), -141.3 (m, 1F, F-6), -149.8 (m, 1F, F-*para*), -150.4 (m, 1F, F-3), -151.7 (m, 1F, F-5), -151.7 (m, 1F, <u>CF</u>(CF₃)₂), -161.6 (m, 2F, F-*meta*); *J*_{CF3-F(2)} = 48. GC-MS, *m/z*: 534 [M]⁺ for **27**. HRMS, *m/z*: calcd. for C₁₆F₁₈ 533.9707; found 533.9709 (for the mixture of **26+27**).

4.8. Generation of perfluoro-1,1-diphenylalk-1-yl cations

- Compound 1 (0.11 g, 0.25 mmol) was dissolved in SbF₅ (1.12 g, 5.16 mmol) (molar ratio, 1:20), then SO₂ClF (0.20 g) was added at 0 °C and ¹⁹F NMR spectrum of the solution was measured at 20 °C. The spectrum contained the signals of cation 10 in the absence of the signals of precursor 1. The solution was poured into water and extracted with CHCl₃. The extract was dried over MgSO₄ and the solvent was distilled off to give 0.09 g of a mixture, containing compounds 1, 30 and 31 in the ratio 21:72:7 (¹⁹F NMR spectrum). From 0.59 g of a similar mixture, obtained in another experiment, 0.025 g of compound 31 was isolated by silica gel column chromatography (CCl₄ as eluent).
- An analogous procedure was used to generate cation 28 (¹⁹F NMR spectrum) from compound 15 (0.12 g, 0.25 mmol) and SbF₅ (1.11 g, 5.12 mmol) (molar ratio, 1:20) in SO₂ClF (0.17 g). The solution was treated as in the previous experiment to give a mixture (0.10 g) containing compounds 15, 32 and 33 in the ratio 29:47:24 (¹⁹F NMR spectrum). From 0.65 g of a similar

mixture, obtained in another experiment, 0.08 g of compound **33** and 0.21 g of compound **32** were isolated by silica gel column chromatography (CCl₄, then CHCl₃ as eluents).

An analogous procedure was used to generate cation 29 (¹⁹F NMR spectrum) from isomers 26 and 27 (36:64, 0.13 g, 0.24 mmol) and SbF₅ (1.04 g, 4.79 mmol) (molar ratio, 1:20) in SO₂ClF (0.22 g). The solution was treated as in the previous experiment to give 0.12 g compound 34 (conformers A and B in the ratio 52:48).

4.8.1. Perfluoro-1,1-diphenyleth-1-yl cation (10)

¹⁹F NMR: δ -60.2 (quin, 3F, CF₃), -88.0 (tt, 2F, F-*para*), -104.6 (m, 4F, F-*ortho*), -146.9 (m, 4F, F-*meta*); $J_{CF_3,ortho} = 19$, $J_{meta,para} = 21$, $J_{ortho,para} = 34$, cf. [30].

4.8.2. Perfluoro-1,1-diphenylprop-1-yl cation (28)

¹⁹F NMR: δ-75.8 (m, 3F, CF₃), -101.9 (quin, 2F, CF₂), -87.2 (tt, 2F, F-*para*), -104.2 (m, 4F, F-*ortho*), -146.9 (m, 4F, F-*meta*); J_{CF₂,ortho} = 29, J_{meta,para} = 22, J_{ortho,para} = 34.

4.8.3. Perfluoro-2-methyl-1,1-diphenylprop-1-yl cation (29)

¹⁹F NMR: δ –66.5 (m, 6F, 2CF₃), –70.7 (tt, 1F, F-*para*), –96.4 (m, 2F, F-*ortho*), –105.5 (tt, 1F, F-*para*'), –114.0 (m, 2F, F-*ortho*'), –144.3 (m, 2F, F-*meta*), –149.7 (m, 2F, F-*meta*'), –155.5 (m, 1F, <u>CF</u>(CF₃)₂); J_{meta,para} = 23, J_{ortho,para} = 44, J_{meta',para}' = 22, J_{ortho',para}' = 22.

4.8.4. Perfluoro-4-(1-phenylethylidene)cyclohexa-2,5-dienone (31)



Yellow viscous liquid. ¹⁹F NMR: δ -58.4 (dm, 3F, CF₃), -130.0 (qdd, 1F, F-2), -134.5 (dd, 1F, F-6), -139.1 (m, 2F, F-*ortho*), -145.7 (d, 1F, F-5), -146.1 (d, 1F, F-3), -148.7 (tt, 1F, F-*para*), -160.5 (m, 2F, F-*meta*); $J_{CF3-F(2)} = 47$, $J_{2,6} = J_{5,6} = 7$, $J_{2,3} = 6$, $J_{meta,para} = 21$, $J_{ortho,para} = 3$. HRMS, m/z: calcd. for C₁₄F₁₂O 411.9752; found 411.9748. Anal. Calcd for C₁₄F₁₂O: C, 40.80; F, 55.32%. Found: C, 40.63; F, 54.79%.

4.8.5. Perfluoro-1,1-diphenylpropan-1-ol (32)

Colorless solid, mp 71–72 °C (CH₂Cl₂ – hexane). ¹⁹F NMR: δ –76.9 (m, 3F, CF₃), –117.7 (quin, 2F, CF₂), –138.2 (m, 4F, F-*ortho*), –150.8 (tt, 2F, F-*para*), –160.9 (m, 4F, F-*meta*); J_{CF₂,ortho}

= 22, *J_{meta,para}* = 21. HRMS, *m/z*: calcd. for C₁₅HF₁₅O 481.9782; found 481.9779. Anal. Calcd for C₁₅HF₁₅O: C, 37.37; H, 0.21; F, 59.11%. Found: C, 37.25; H, 0.32; F, 58.76%.

4.8.6. Perfluoro-4-(1-phenylpropylidene)cyclohexa-2,5-dienone (33)

Yellow solid, mp 78–79 °C (CH₂Cl₂ – hexane). ¹⁹F NMR: δ –80.0 (dm, 3F, CF₃), –104.2 (dm, 2F, CF₂), –127.7 (tqdd, 1F, F-2), –133.6 (dd, 1F, F-6), –138.4 (m, 2F, F-*ortho*), –145.2 (d, 1F, F-3), –145.7 (d, 1F, F-5), –148.6 (tm, 1F, F-*para*), –160.6 (m, 2F, F-*meta*); $J_{CF2-F(2)} = 68$, $J_{CF3-F(2)} = 29$, $J_{2,3} = 5$, $J_{2,6} = 7.5$, $J_{5,6} = 7$, $J_{meta,para} = 21$. HRMS, m/z: calcd. for C₁₅F₁₄O 461.9720; found 461.9716. Anal. Calcd for C₁₅F₁₄O: C, 38.98; F, 57.55%. Found: C, 38.61; F, 57.89%.

4.8.7. Perfluoro-4-(2-methyl-1-phenylpropylidene)cyclohexa-2,5-dienone (34)



Yellow solid, mp 94.5–96 °C (hexane). ¹⁹F NMR (conformers **A**:**B** = 52:48), conformer **A**: δ –71.4 (m, 6F, 2CF₃), –124.6 (dm, 1F, F-2), –133.0 (dd, 1F, F-6), –137.2 (m, 2F, F-*ortho*), –145.1 (d, 1F, F-3), –145.6 (d, 1F, F-5), –148.0 (m, 1F, F-*para*), –155.2 (dm, 1F, <u>CF</u>(CF₃)₂), –160.3 (m, 2F, F-*meta*); *J*_{CF-F(2)} = 152, *J*_{2,3} = 5, *J*_{2,6} = *J*_{5,6} = 7; conformer **B**: δ –70.5 (dm, 6F, 2CF₃), –129.8 (septdd, 1F, F-2), –132.7 (dd, 1F, F-6), –138.9 (m, 2F, F-*ortho*), –146.3 (d, 1F, F-3), – 146.7 (d, 1F, F-5), –148.7 (m, 1F, F-*para*), –151.4 (m, 1F, <u>CF</u>(CF₃)₂), –160.9 (m, 2F, F-*meta*); *J*_{CF3-F(2)} = 48, *J*_{2,3} = *J*_{5,6} = 6, *J*_{2,6} = 7. HRMS, *m*/*z*: calcd. for C₁₆F₁₆O 511.9688; found 511.9684. Anal. Calcd for C₁₆F₁₆O: C, 37.52; F, 59.48%. Found: C, 37.66; F, 59.35%.

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References

- [1] R.D. Chambers, Fluorine in Organic Chemistry, Blackwell Publishing, Oxford, 2004.
- [2] P. Kirsch, Modern Fluoroorganic Chemistry. Synthesis, Reactivity, Applications, Wiley-VCH, Weinheim, 2004.
- [3] R.E. Banks, B.E. Smart, J.C. Tatlow (Eds.), Organofluorine Chemistry: Principles and Commercial Applications, Plenum, New York, 1994.
- [4] C.D. Hewitt, M.J. Silvester, Fluoroaromatic compounds: synthesis, reactions and commercial applications, Aldrichimica Acta 21 (1988) 3–10.
- [5] F. Babudri, G.M. Farinola, F. Naso, R. Ragni, Fluorinated organic materials for electronic and optoelectronic applications: the role of the fluorine atom, Chem. Commun. (2007) 1003– 1022.
- [6] M.L. Tang, Z. Bao, Halogenated materials as organic semiconductors, Chem. Mater. 23 (2011) 446–455.
- [7] I.M. Tkachenko, N.A. Belov, Ya.L. Kobzar, A.V. Dorokhin, O.V. Shekera, V.P. Shantarovich, V.G. Bekeshev, V.V. Shevchenko, Synthesis of fluorinated poly(arylene ether)s with dibenzodioxin and spirobisindane units from new bis(pentafluorophenyl)- and bis(nonafluorobiphenyl)-containing monomers, J. Fluorine Chem. 195 (2017) 1–12.
- [8] I. Ojima (Ed.), Fluorine in Medicinal Chemistry and Chemical Biology, Wiley–Blackwell, Oxford, UK, 2009, pp. 291–311.
- [9] J.-P. Begue, D. Bonnet-Delpon, Bioorganic and Medicinal Chemistry of Fluorine, Wiley, Hoboken, 2008.
- [10] S. Purser, P.R. Moore, S. Swallow, V. Gouverneur, Fluorine in medicinal chemistry, Chem. Soc. Rev. 37 (2008) 320–330.
- [11] K. Ohkubo, Y. Sakamoto, T. Suzuki, T. Tsuzuki, D. Kumaki, S. Tokito, Synthesis, structure, and transport property of perfluorinated oligofluorenes, Chem. Eur. J. 14 (2008) 4472 – 4474.
- [12] M.J. Namkung, T.L. Fletcher, Fluorofluorenes. IV. J. Org. Chem. 26 (1961) 2243–2244.
- [13] M.J. Namkung, T.L. Fletcher, W.H. Wetzel, Fluorofluorenes. V. New difluoro-2acetamidofluorenes for the study of carcinogenic mechanisms, J. Med. Chem. 8 (1965) 551– 554.
- [14] M.J. Namkung, T.L. Fletcher, Fluorofluorenes. VI. Can. J. Chem. 45 (1967) 2569–2575.
- [15] Yu.V. Pozdnyakovich, V.D. Shteingarts, Generation and some transformations of polyfluorinated fluorenyl cations, Zh. Org. Khim. 14 (1978) 603–609; J. Org. Chem. USSR 14 (1978) 559–565 (English Translation).

- [16] V.M. Vlasov, G.G. Yakobson, E.S. Petrov, A.I. Shatenshtein, Perfluoro-9-phenylfluorenyl anion generation, spectra and thermodynamic stability, J. Fluorine Chem. 9 (1977) 321–325.
- [17] R. Filler, A.E. Fiebig M.Y. Pelister, Fluorocarbanion chemistry. Octafluorofluorene and companions, J. Org. Chem. 45 (1980) 1290–1295.
- [18] R.D. Chambers, D.J. Spring, Nucleophilic substitution in octafluorofluoren-9-one, Tetrahedron, 25 (1969) 565–572.
- [19] F. Marchetti, F. Marchetti, F. Masi, G. Pampaloni, V. Passarelli, A. Sommazzi, S. Spera, Synthesis, variable temperature NMR investigations and solid state characterization of novel octafluorofluorene compounds, J. Fluorine Chem. 130 (2009) 341–347.
- [20] F. Calderazzo, F. Masi, G. Pampaloni, V. Passarelli, R. Santi, A. Sommazzi, S. Spera, F. Tumminia, Perfluorofluorenyl anions and their use as co-catalysts in the zirconocene-promoted polymerization of olefins, J. Organomet. Chem. 690 (2005) 4886–4898.
- [21] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, V.R. Sinyakov, Skeletal transformations of perfluoro-1-phenylindan under the action of antimony pentafuoride, J. Fluorine Chem. 107 (2001) 53–57.
- [22] T.V. Mezhenkova, V.M. Karpov, V.E. Platonov, Formation of fluorene and anthracene derivatives in reactions of perfluorinated 1-alkyl-1-phenyl- and 1-alkyl-2-phenyl-1,2dihydrocyclobutabenzenes with antimony pentafluoride, Zh. Org. Khim. 47 (2011) 1004– 1011; Russ. J. Org. Chem. 47 (2011) 1018–1025 (English Translation).
- [23] T. Ohwada, K. Shudo, Reaction of diphenylmethyl cations in a strong acid. Participation of carbodications with positive charge substantially delocalized over the aromatic rings, J. Am. Chem. Soc. 110 (1988) 1862–1870.
- [24] Le H. Dao, M. Maleki, A.C. Hopkinson, E. Lee-Ruff, α-Carbonyl carbocations. 4. NMR detection and reactivities of diaryl α-carbonyl cations, J. Am. Chem. Soc. 108 (1986) 5237– 5242.
- [25] S. Cohen, The cyclization reaction of di-(p-halogenopheny1)-trifluoromethylcarbinols, J. Am. Chem. Soc. 79 (1957) 1499–1502.
- [26] P.H. Campbell, N.W.K. Chiu, K. Deugau, I.J. Miller, T.S. Sorensen, The stereochemistry of the pentadienyl–cyclopentenyl cation rearrangement, J. Am. Chem. Soc. 91 (1969) 6404– 6410.
- [27] R. Bladek, T.S. Sorensen, Kinetics of pentadienyl cation cyclizations, Can. J. Chem. 50 (1972) 2806–2816.
- [28] V.A. Petrov, G.G. Belen'kii, L.S., German, Isomeric transformations of perfluorinated dienes by the action of antimony pentafluoride, Izv. Akad. Nauk SSSR Ser. Khim. (1989) 385–391;
 Bull. Acad. Sci. USSR, Div. Chem. Sci. 38 (1989) 333–339 (English translation).

- [29] V.V. Brovko, V.A. Sokolenko, G.G. Yakobson, Alkylation of pentafluorobenzene with 1,1,2-trichlorotrifluoroethane and fluoroform in the presence of antimony pentafluoride, Zh. Org. Khim. 10 (1974) 300–303; J. Org. Chem. USSR (English Translation) 10 (1974) 300–302.
- [30] Yu.V. Pozdnyakovich, V.D. Shteingarts, Fluorine-containing carbocations. III. Alkylation of polyfluorobenzenes with polyfluorinated α,α-difluorobenzyl cations and generation of polyfluorinated α-fluorodiphenylmethyl cations, J. Fluorine Chem. 4 (1974) 297–316.
- [31] V.D. Shteingarts, Yu.V. Pozdnyakovich, G.G. Yakobson, Disproportionation of a heptafluorobenzenonium ion salt in an antimony pentafluoride solution as a possible method for forming the cation radical of hexafluorobenzene (Russ), Zh. Org. Khim. 7 (1971) 2002.
- [32] Yu.V. Pozdnyakovich, T.V. Chuikova, V.D. Shteingarts, Fluorine-containing carbocations. IX. Alkylation of pentafluorobenzene with perfluorinated arenonium ions and generation of perfluorinated 3-phenylbenzenonium 3- and 6-phenylnaphthalenonium ions (Russ), Zh. Org. Khim. 11 (1975) 1689–1698.
- [33] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, Rearrangement of the carbon skeleton of perfluorinated 1-isopropyl-, 1-methyl-1-isopropyl-, and 1-methyl-2-isopropylbenzocyclobutenes by the action of antimony pentafluoride, Izv. Akad. Nauk, Ser. Khim. (1992) 1419– 1424; Bull. Russ. Acad. Sci., Div. Chem. Sci. 41 (1992) 1110–1114 (English translation).
- [34] T.V. Mezhenkova, V.M. Karpov, V.E. Platonov, Yu.V. Gatilov, Skeletal transformations of perfluoro-1-ethyl-1-phenylbenzocyclobutene in the reaction with antimony pentafluoride, J. Fluorine Chem. 130 (2009) 951–958.
- [35] Yu.V. Pozdnyakovich, V.D. Shteingarts, Fluorine-containing carbocations. IV. The use of salt solutions of stable polyfluorinated α,α-difluorobenzyl and α-fluorodiphenylmethyl cations in antimony pentafluoride in the synthesis of polyfluorinated benzoic acids, benzophenones and diphenyldifluoromethanes, J. Fluorine Chem. 4 (1974) 317–326.



Scheme 1. Reaction of perfluoro-1,1-diphenylethane with SbF₅.







Scheme 3. The mechanistic pathway of the reaction of perfluoro-1,1-diphenylethane with SbF_5 in the presence of HF.



Scheme 4. The heating of perfluoro-1,1-diphenylmethane with SbF₅.



Scheme 5. Synthesis and reaction of perfluoro-1,1-diphenylpropane with SbF₅.



Scheme 6. Synthesis and reaction of perfluoroisobutylbenzene with C₆F₅H.



Scheme 7. Generation and hydrolysis of perfluoro-1,1-diphenylalk-1-yl cations.