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Opening of the Four-Membered Ring in Perfluorinated 1-Alkyl-2-phenyl- and 1-Aryl-1,2-dihydrocyclobutabenzenes in the System I_2–SbF_5

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Abstract—Reactions of perfluorinated 1-phenyl-, 1-(2-ethylphenyl)-, 1-(4-ethylphenyl)-, 1-methyl-2-phenyl-, and 1-ethyl-2-phenyl-1,2-dihydrocyclobutabenzenes with iodine in antimony pentafluoride at 130°C, followed by hydroysis of the reaction mixture, resulted in the formation of perfluorinated 2-methyl-, 2-ethyl-2′-methyl-, 4-ethyl-2′-methyl-, 2-ethyl-, and 2-propylbenzophenones via opening of the four-membered ring in the initial cyclobutabenzene at the C^1–C^2 bond. The presence of hydrogen fluoride facilitates the process and promotes profound transformations leading to anthracene derivatives.

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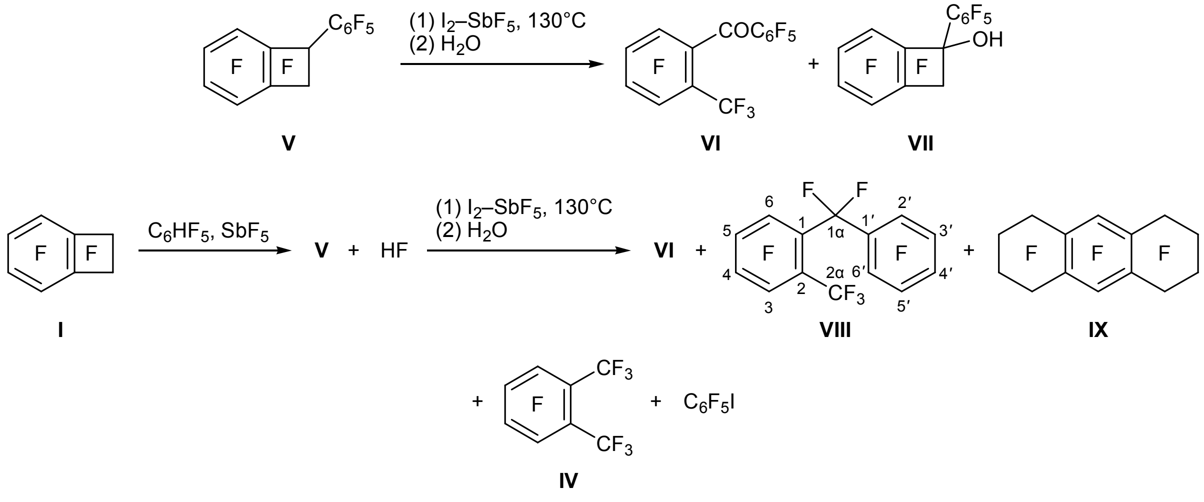
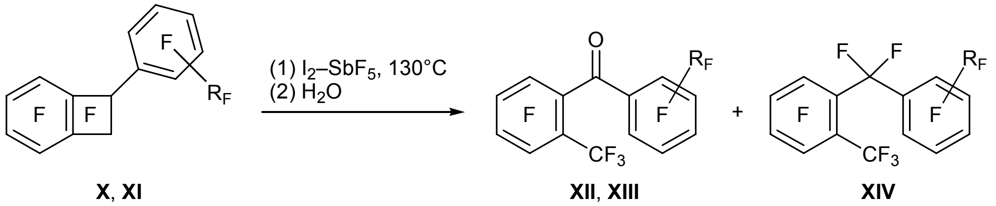
We previously showed that dimerization of perfluoro(1,2-dihydrocyclobutabenzene) (**I**) in SbF_5 and reactions of compound **I**, perfluoro(1-methyl-1,2-dihydrocyclobutabenzene) (**II**), and perfluoro(1-ethyl-1,2-dihydrocyclobutabenzene) (**III**) with Br_2 or HF in the presence of SbF_5 involve opening of the four-membered ring at the C_{arom}–C^2 bond with formation of the corresponding 2-X-perfluoro(alkylbenzenes) [X = perfluoro(1,2-dihydrocyclobutabenzen-1-yl, Br, H] [1–3]. In contrast, opening of the four-membered ring in compound **I** in the system I_2–SbF_5 occurs at both C_{arom}–C^2 and C^1–C^2 bonds, leading to 1,2,3,4-tetrafluoro-5-iodo-6-(perfluoroethyl)benzene together with perfluoro(*o*-xylene) (**IV**) [4]. However, no iodo derivatives were formed in analogous reactions of cyclobutabenzenes **II** and **III**, and the major products were the corresponding perfluoro(1,2-dialkylbenzenes) [5].

With a view to elucidate how the nature of perfluorinated substituents in the four-membered ring of perfluorinated 1,2-dihydrocyclobutabenzenes affects

Scheme 1.



Scheme 2.



X, **XII**, $R_F = 2\text{-}C_2F_5$; **XI**, **XIII**, **XIV**, $R_F = 4\text{-}C_2F_5$.

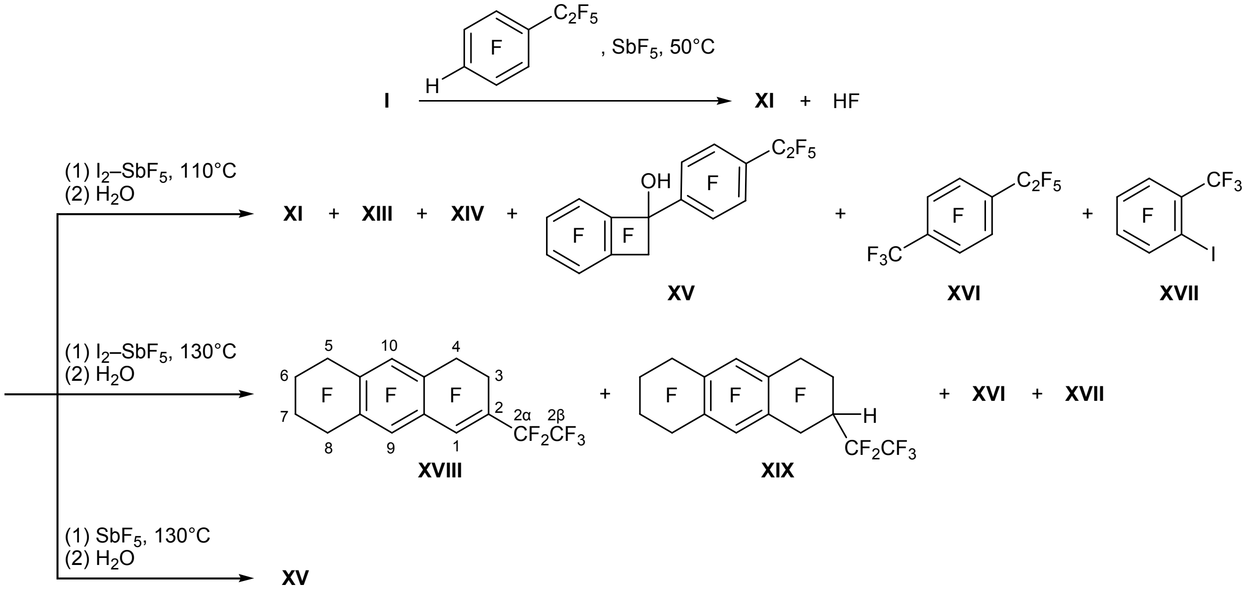
the direction of their cationoid skeletal transformations, in the present work we examined the behavior of a series of perfluorinated 1-alkyl-2-phenyl- and 1-aryl-1,2-dihydrocyclobutabenzenes in the system I_2–SbF_5.

Heating of perfluoro(1-phenyl-1,2-dihydrocyclobutabenzene) (**V**) with iodine in SbF_5 at 130°C resulted in opening of the four-membered ring with formation (after treatment of the reaction mixture with water) of perfluoro(2-methylbenzophenone) (**VI**); however, the degree of opening of the cyclobutene ring was not high, and the major product was perfluorinated 1-phenyl-1,2-dihydrocyclobutabenzen-1-ol (**VII**; Scheme 1). Analogous reaction with compound **V** generated *in situ* together with 1 equiv of HF by reaction of perfluoro(1,2-dihydrocyclobutabenzene) (**I**) with pentafluorobenzene in SbF_5 [6] was characterized by complete conversion of **V**; apart from products of opening of the four-membered ring, perfluorinated benzophenone **VI** and perfluoro(1-benzyl-2-methylbenzene) (**VIII**), perfluoro(1,2,3,4,5,6,7,8-octahydroanthracene) (**IX**), perfluoroxylene (**IV**), and pentafluoroiodobenzene were formed (Scheme 1).

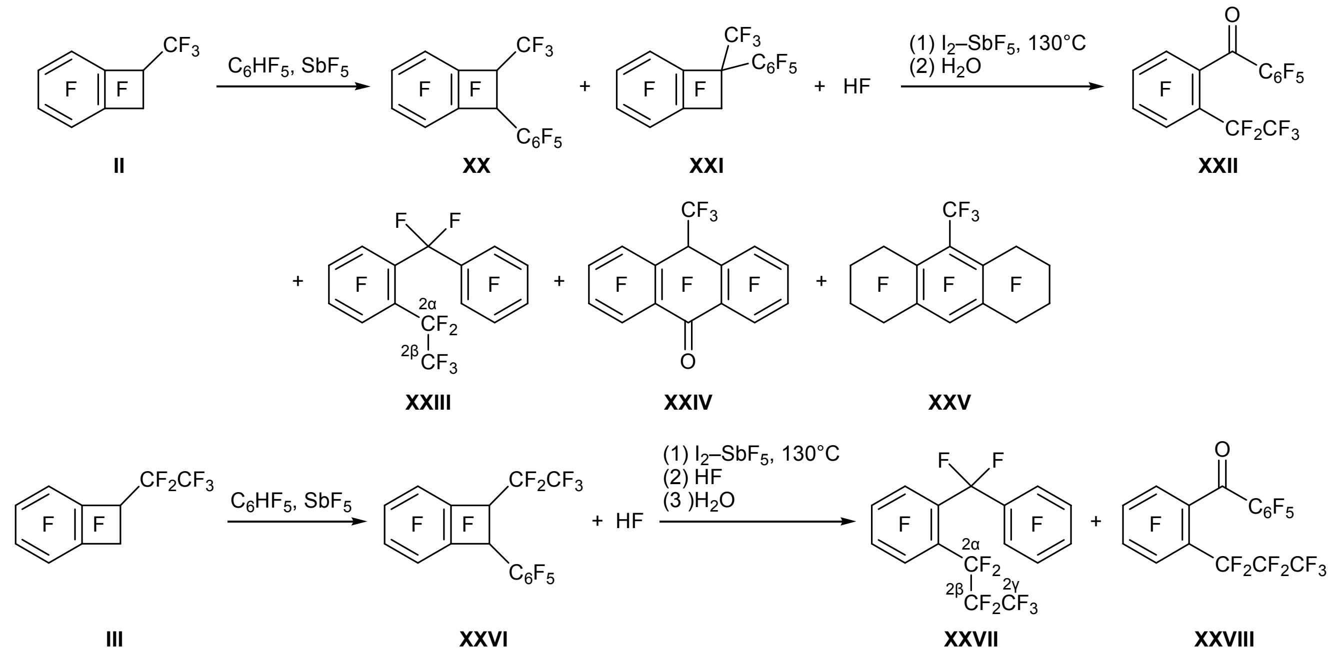
Perfluoro[1-(2-ethylphenyl)-1,2-dihydrocyclobutabenzene] (**X**) reacted with I_2–SbF_5 at 130°C to give (after hydrolysis) perfluoro(2-ethyl-2′-methylbenzophenone) (**XII**), whereas analogous reaction of perfluoro[1-(4-ethylphenyl)-1,2-dihydrocyclobutabenzene] (**XI**) afforded perfluoro(4-ethyl-2′-methylbenzophenone) (**XIII**) and a small amount of perfluoro[1-(4-ethylbenzyl)-2-methylbenzene] (**XIV**) (Scheme 2). No products of four-membered ring opening were obtained from compounds **V** and **XI** in SbF_5 at 130°C in the absence of iodine, while compound **X** was partially converted into perfluorinated benzophenone **XII** only under considerably prolonged heating [7].

Cleavage of cyclobutabenzene **XI** by the action of I_2 in SbF_5 in the presence of HF requires milder conditions. Treatment of a mixture of **XI** and HF {generated by reaction of compound **I** with 1,2,4,5-tetrafluoro-3-(pentafluoroethyl)benzene in SbF_5 [7]} with I_2 at 100°C and subsequent hydrolysis gave a mixture containing compounds **XIII** and **XIV** together with unreacted compound **XI** and perfluoro[1-(4-ethylphenyl)-1,2-dihydrocyclobutabenzen-1-ol] (**XV**); in addition,

Scheme 3.



Scheme 4.

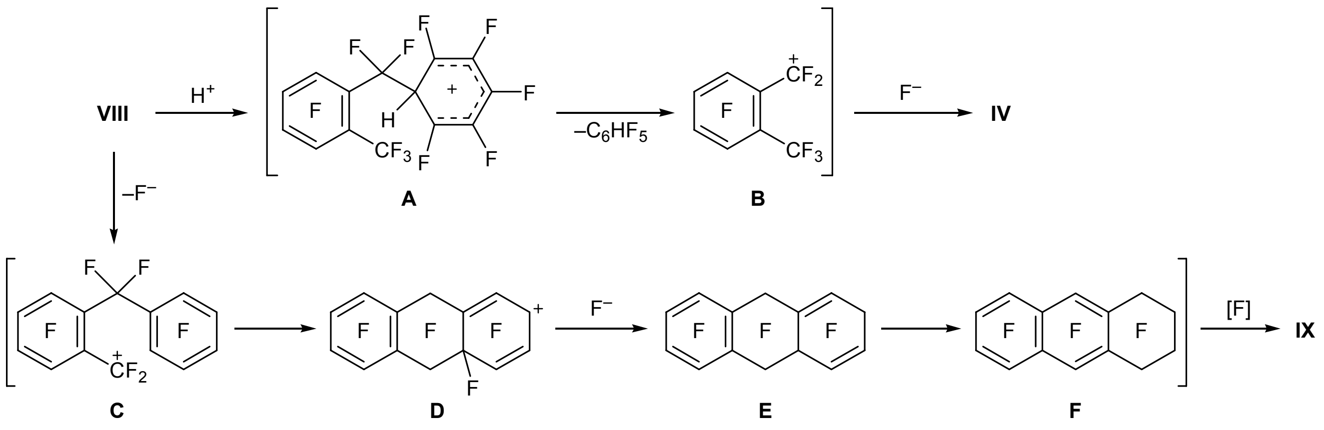


small amounts of perfluoro(4-ethyltoluene) (**XVI**) and 1,2,3,4-tetrafluoro-5-iodo-6-trifluoromethylbenzene (**XVII**) were formed (Scheme 3). Raising the temperature to 130°C led to the formation of perfluoro(2-ethyl-3,4,5,6,7,8-hexahydroanthracene) (**XVIII**) and 2*H*-perfluoro(2-ethyl-1,2,3,4,5,6,7,8-octahydroanthracene) (**XIX**), the former prevailing; also, compounds **XVI** and **XVII** were obtained. By special experiment we showed that no reaction occurred in the absence of I$_2$, other conditions being equal; treatment of the reaction mixture with water gave hydroxy derivative **XV**.

The reaction of a mixture of isomeric perfluorinated 1-methyl-2-phenyl- and 1-methyl-1-phenyl-1,2-dihydrocyclobutabenzenes **XX**/**XXI** and HF {generated from perfluorinated methylcyclobutabenzene **II** and C$_6$F$_5$H in SbF$_5$ [8]} with I$_2$ in SbF$_5$ at 130°C, followed by hydrolysis, gave perfluoro(2-ethylbenzophenone) (**XXII**) and perfluoro(1-benzyl-2-ethylbenzene) (**XXIII**) from 1,2-isomer **XX** and perfluoro(10-methyl-9,10-dihydroanthracen-9-one) (**XXIV**) and perfluoro-(9-methyl-1,2,3,4,5,6,7,8-octahydroanthracene) (**XXV**) from 1,1-isomer **XXI** (Scheme 4). When the reaction was carried out in the absence of iodine, 1,2-isomer **XX** did not undergo skeletal transformations, whereas only compound **XXIV** was obtained from 1,1-isomer **XXI** [9].

Perfluoro(1-phenyl-2-ethyl-1,2-dihydrocyclobutabenzene) (**XXVI**) obtained in a mixture with HF from perfluoro(1-ethyl-1,2-dihydrocyclobutabenzene) (**III**) and pentafluorobenzene in SbF$_5$ [10] reacted with I$_2$–

Scheme 5.



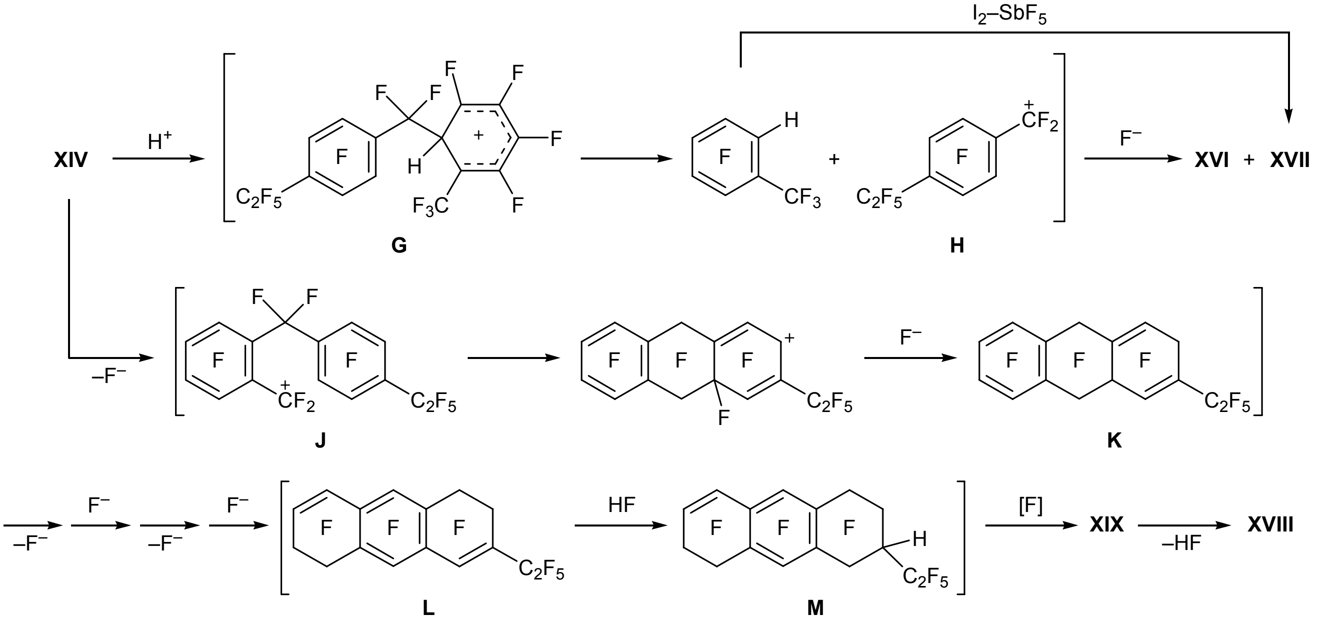
SbF_5 at 130°C, yielding (after treatment of the reaction mixture first with anhydrous HF and then with water) perfluoro(1-benzyl-2-propylbenzene) (**XXVII**) and perfluoro(2-propylbenzophenone) (**XXVIII**) (Scheme 4). Skeletal transformations of **XXVI** in the absence of iodine occur under more severe conditions [9].

A probable mechanism of opening of the four-membered ring in polyfluorinated benzocyclobutenes by the action of I_2–SbF_5 was discussed by us previously [4, 5]. It was presumed that cleavage of the C^1–C^2 bond occurs with participation of I_2 molecule although iodine in SbF_5 exists mainly as I_2^+ species [11]. The fact that compounds **V** and **XI** react with I_2–SbF_5 in the presence of HF more readily (Schemes 1–3) may be rationalized assuming increase in the concentration of I_2 and reduction in the concentration of I_2^+ in the system upon addition of HF [12].

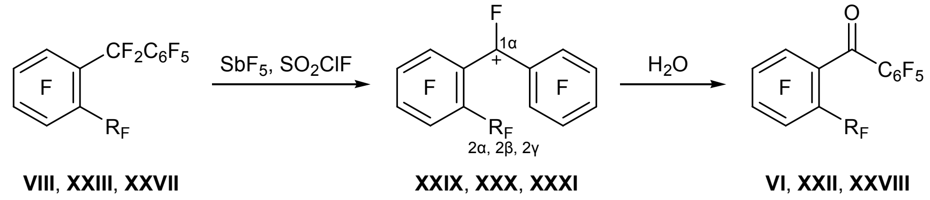
Perfluoroxylene **IV** and pentafluoroiodobenzene are likely to be formed in the reaction of compound **V** with I_2–SbF_5 in the presence of HF as a result of attack by proton on the pentafluorophenyl group in compound **VIII**. σ-Complex **A** thus generated decomposes into C_6F_5H and benzyl cation **B** (Scheme 5). The latter takes up fluoride ion to give xylene **IV**, while C_6F_5H reacts with I_2 in SbF_5 to produce C_6F_5I. Presumably, anthracene derivative **IX** also results from transformation of compound **VIII**. Cation **C** generated from **VIII** by the action of SbF_5 undergoes cyclization to cation **D** which takes up fluoride ion, yielding tetrahydroanthracene **E**. Migration of double C=C bonds in the latter to the central ring gives isomer **F**, and its subsequent fluorination leads to product **IX** (Scheme 5). The formation of anthrone **XXIV** from compound **XXI** (Scheme 4) was considered by us previously [9]. Octahydroanthracene **XXV** is likely to be the product of fluorination of perfluoro(9-methyl-9,10-dihydroanthracene) in SbF_5; obviously, this process is favored by the presence of iodine, for no compound **XXV** is formed at 130°C in the absence of iodine [9].

In the reaction of **XI** with I_2–SbF_5 in the presence of HF, compounds **XVI**–**XIX** are likely to originate from diarylmethane **XIV**, following a scheme analogous to the transformations of **VIII**. Proton addition to the methylphenyl group in **XIV** gives σ-complex **G** which decomposes with formation of benzyl cation **H** and 1,2,3,4-tetrafluoro-5-trifluoromethylbenzene. The latter reacts with iodine in SbF_5 to give compound **XVII**, and cation **H** takes up fluoride ion to produce perfluoro(1-ethyl-4-methylbenzene) (**XVI**) (Scheme 6). Cyclization of diarylmethane **XIV** with participation of benzyl cation **J** gives tetrahydroanthracene **K** which undergoes isomerization into intermediate **L**, e.g., via successive elimination–addition of fluoride ion. Addition of HF at the double bond of tetrahydroanthracene **L** leads to structure **M**. Fluorination of the latter yields compound **XIX** which loses HF molecule with formation of hexahydroanthracene **XVIII**. The transformation sequence **XIX** → **XVIII** shown in Scheme 6 is based on experimental data according to which the reaction mixture obtained at 130°C (Scheme 3) con-

Scheme 6.



Scheme 7.



VI, **VIII**, **XXIX**, $R_F = CF_3$; **XXII**, **XXIII**, **XXX**, $R_F = C_2F_5$; **XXVII**, **XXVIII**, **XXXI**, $R_F = C_3F_7$.

tained after 4 h compounds **XIX** and **XVIII** at a ratio of 60 : 40; after 10 h, the ratio changed to 31 : 69 and no longer changed.

The formation of hydroxy derivatives **VII** and **XV** and ketones **XII** and **XIII** in the above reactions (Schemes 1, 3) may be rationalized assuming that perfluorinated cyclobutabenzenes **V** and **XI**, perfluoro-[1-(2-ethylbenzyl)-2-methylbenzene], and diarylmethane **XIV** in SbF_5 exist as salts of the corresponding perfluorinated 1-aryl-1,2-dihydrocyclobutabenezen-1-yl and diarylmethyl cations which were detected by ^{19}F NMR spectroscopy [6, 7]; their hydrolysis yields compounds **VII**, **XV**, **XII**, and **XIII**. Presumably, ketones **VI**, **XXII**, and **XXVIII** (Schemes 1, 4) are formed in a similar way. In fact, dissolution of compounds **VIII**, **XXIII**, and **XXVII** in $SbF_5–SO_2ClF$ generates perfluorinated (2-methylphenyl)-, (2-ethylphenyl)-, and (2-propylphenyl)phenylmethyl cations **XXIX–XXXI**, respectively, and their hydrolysis yields ketones **VI**, **XXII**, and **XXVIII** (Scheme 7).

The structure of cations **XXIX–XXXI** was determined on the basis of their ^{19}F and ^{13}C NMR spectra and was confirmed by the structure of the hydrolysis products. In the ^{19}F NMR spectrum of **XXIX** at 25°C, the 2′-F and 6′-F atoms in the pentafluorophenyl group give rise to one broadened signal at δ 60.2 ppm; lowering the temperature to –30°C makes these atoms magnetically nonequivalent due to restricted rotation of the pentafluorophenyl group, and the spectrum displays two signals at δ_F 64.0 and 56.5 ppm. The corresponding fluorine signals were not observed in the ^{19}F NMR spectra of **XXX** and **XXXI** at 20°C, whereas signals from the CF_2 fragments in the perfluoroethyl and perfluoropropyl groups were appreciably broadened. In the spectra recorded at reduced temperature (–10°C for cation **XXX** or –30°C for **XXXI**), two separate signals appeared due to 2′-F and 6′-F, and fluorine nuclei in the CF_2 group became nonequivalent (*AB* spin system, $J_{AB} \approx 290–300$ Hz). The observed downfield shifts of signals from fluorine atoms in the aromatic rings of cations **XXIX–XXXI** as compared to their precursors **VIII**, **XXIII**, and **XXVII**, as well as increased coupling constants for fluorine atoms in the positions conjugated with the cationic center, are consistent with the data reported previously for polyfluorinated benzyl [13] and diarylalkyl cations [7, 14, 15].

The structure of compounds **VI**, **VIII**, **XVI–XIX**, **XXII**, **XXIII**, **XXVII**, and **XXVIII** was determined on the basis of their high-resolution mass spectra and ^{19}F NMR spectra. The other compounds were identified by comparing their ^{19}F NMR spectra with those of authentic samples (**VII** [6], **IX**, **XXIV**, **XXV** [16], **XII–XV** [7]).

EXPERIMENTAL

The ^{19}F NMR spectra of reaction mixtures and solutions of individual compounds **VI**, **VIII**, **XVI–XIX**, **XXII**, **XXIII**, **XXVII**, and **XXVIII** in $CDCl_3$ and ^1H NMR spectrum of **XIX** were recorded on a Bruker AV-300 spectrometer at 282.4 and 300 MHz, respectively. The ^{19}F and ^{13}C NMR spectra of solutions containing cations **XXIX–XXXI** (in $SbF_5–SO_2ClF$) were measured on a Bruker AV-400 instrument at 376.5 and 100 MHz, respectively. The chemical shifts are given relative to C_6F_6 (^{19}F) and TMS (^1H, ^{13}C); C_6F_6 or SO_2ClF (δ_F 262.8 ppm relative to C_6F_6) and $CHCl_3$ (δ 7.24 ppm) were used as internal references, and acetone-d_6 (δ_C 29.9 ppm) was used as external reference. The elemental compositions of compounds **VI**, **VIII**, **XVIII**, **XIX**, **XXII**, **XXIII**, **XXVII**, and **XXVIII** were determined from their high-resolution mass spectra which were obtained on a Thermo Electron Corporation DFS instrument. The IR spectra were recorded on a Bruker Vector 22 spectrometer. Gas chromatographic–mass spectrometric analysis of a mixture of compounds **XVI** and **XVII** was performed on a Hewlett–Packard G1081A GC–MS system consisting of an HP 5890 Series II gas chromatograph and an HP 5971 mass-selective detector (electron impact, 70 eV); HP-5 capillary column (5%-phenyl-95%-methylpolysiloxane), 30 m × 0.25 mm × 0.25 μm; carrier gas helium, flow rate 1 ml/min. GLC analysis was performed on an LKhM-72 chromatograph equipped with a 4000×4-mm column packed with SKTFT-50 on Chromosorb W (15:100); oven temperature programming from 50 to 270°C; carrier gas helium, flow rate 60 ml/min.

Reaction of perfluoro(1-phenyl-1,2-dihydrocyclobutabenzene) (V) with I_2–SbF_5. *a*. A mixture of 4.14 g (19.10 mmol) of SbF_5 and 0.35 g (1.38 mmol) of I_2 was heated for 0.5 h at 130°C in a 10-cm^3 nickel high-pressure reactor with intermittent shaking, 0.56 g (1.41 mmol) of compound **V** was added to the resulting solution, and the mixture was heated for 10 h at 130°C, cooled to 0°C, transferred into ice water, and extracted with methylene chloride. The extracts were dried over $MgSO_4$, and the solvent was distilled off to obtain 0.46 g of a mixture of compounds **VI** and **VII** at a ratio of 17:83 (^{19}F NMR).

In all subsequent experiments the procedures for dissolution of I_2 in SbF_5 and treatment of the reaction mixtures were similar.

b. Compound **I**, 0.89 g (3.59 mmol), and pentafluorobenzene, 0.60 g (3.57 mmol), were added to a solution of 0.46 g (1.81 mmol) of iodine in 5.46 g (25.18 mmol) of SbF_5, and the mixture was kept for 20 h at 20°C. The resulting mixture contained perfluoro(1-phenyl-1,2-dihydrocyclobutabenzene) (**V**) [6]; it was heated for 7 h at 130°C. After appropriate treatment, we obtained 1.28 g of a mixture containing* 9% of compound **IV**, 52% of **VI**, 10% of **VIII**, 10% of **IX**, and 5% of pentafluoroiodobenzene. The product mixture was subjected to column chromatography on silica gel using first hexane and then carbon tetrachloride as eluents to isolate 0.09 g of perfluoro(1-benzyl-2-methylbenzene) (**VIII**) and 0.55 g of perfluoro(2-methylbenzophenone) (**VI**).

Compound **VI**. mp 49–50.5°C (from hexane). IR spectrum (CCl_4), ν, cm^{-1}: 1708 (C=O), 1648, 1525, 1497, 1480 (fluorinated aromatic ring). ^{19}F NMR spectrum, δ_F, ppm: 2.9 (2F, 3′-F, 5′-F), 13.8 (1F, 4-F), 16.3 (1F, 5-F), 19.0 (1F, 4′-F), 21.6 (1F, 6-F), 22.4 (2F, 2′-F, 6′-F), 26.9 (1F, 3-F), 106.8 (3F, 2α-F); $J_{2\alpha,3} = 18$, $J_{3,4} = J_{4,5} = 20$, $J_{3,5} = 9$, $J_{3,6} = 11$, $J_{4,6} = 6$, $J_{5,6} = 22$, $J_{4',2'(6')} = 7$, $J_{4',3'(5')} = 21$ Hz. Found: *m/z* 411.9750 $[M]^+$. $C_{14}F_{12}O$. Calculated: *M* 411.9752.

Compound **VIII**, mp 47–48.5°C (from hexane). ^{19}F NMR spectrum, δ_F, ppm: 2.4 (2F, 3′-F, 5′-F), 14.6 (1F, 4′-F), 15.1 (1F, 4-F), 15.9 (1F, 5-F), 22.2 (2F, 2′-F, 6′-F), 28.7 (1F, 3-F), 29.4 (1F, 6-F), 86.7 (2F, 1α-F), 108.3 (3F, 2α-F); $J_{1\alpha,2} = 17$, $J_{1\alpha,6} = 35$, $J_{1\alpha,2'(6')} = 15$, $J_{2\alpha,3} = 32$, $J_{3,4} = J_{4,5} = J_{5,6} = J_{4',3'(5')} = 21$, $J_{3,5} = J_{4,6} = 9$, $J_{3,6} = 10$, $J_{4',2'(6')} = 5$ Hz. Found: *m/z* 433.9774 $[M]^+$. $C_{14}F_{14}$. Calculated: *M* 433.9771.

Reaction of perfluoro[1-(2-ethylphenyl)-1,2-dihydrocyclobutabenzene] (X) with I_2–SbF_5. A mixture of 0.79 g (3.18 mmol) of compound **I** and 4.72 g (21.77 mmol) of SbF_5 was heated for 9 h at 90°C to obtain compound **X** [1], 0.40 g (1.59 mmol) of iodine was added, and the mixture was heated for 10 h at 130°C. After appropriate treatment, we obtained 0.74 g of a mixture containing 85% of compound **XII**.

Reaction of perfluoro[1-(4-ethylphenyl)-1,2-dihydrocyclobutabenzene] (XI) with I_2–SbF_5. *a*. The reaction of 0.8 g (1.61 mmol) of compound **XI** with 0.41 g (1.61 mmol) of I_2 and 4.90 g (22.60 mmol) of SbF_5 (10 h, 130°C) gave 0.73 g of a mixture containing 69% of **XIII** and 8% of **XIV**.

b. A mixture of 0.80 g (3.23 mmol) of compound **I**, 0.87 g (3.25 mmol) of 1,2,4,5-tetrafluoro-3-perfluoroethylbenzene, and 4.91 g (22.65 mmol) of SbF_5 was heated for 6 h at 50°C to generate compound **XI** [7], 0.41 g (1.62 mmol) of I_2 was added, and the mixture was heated for 10 h at 110°C. After appropriate treatment, we obtained 1.32 g of a mixture of compounds **XI**, **XII**, and **XIV**–**XVII** at a ratio of 6:29:13:42:8:2 (^{19}F NMR).

c. As described above in *b*, from 0.70 g (2.84 mmol) of compound **I**, 0.76 g (2.84 mmol) of 1,2,4,5-tetrafluoro-3-perfluoroethylbenzene, 4.31 g (19.88 mmol) of SbF_5, and 0.36 g (1.42 mmol) of I_2 (10 h, 130°C) we obtained 1.34 g of a mixture containing 16% of **XVI**, 3% of **XVII**, 43% of **XVIII**, and 19% of **XIX**. By column chromatography on silica gel using hexane as eluent we isolated 0.1 g of a mixture containing 30% of perfluoro(4-ethyltoluene) (**XVI**) and 56% of 2-iodoheptafluorotoluene (**XVII**) (according to the GC–MS and ^{19}F NMR data), 0.13 g of 1,1,2,2,3,3,4,4,5,5,6,6,-8,8,9,10-hexadecafluoro-7-(perfluoroethyl)-1,2,3,4,-5,6,7,8-octahydroanthracene (**XIX**), and 0.39 g of perfluoro(2-ethyl-3,4,5,6,7,8-hexahydroanthracene) (**XVIII**).

Compound **XVI**. ^{19}F NMR spectrum, δ_F, ppm: 24.8 (2F), 26.1 (2F), 50.4 (2F, CF_2CF_3), 76.5 (3F, CF_2CF_3), 104.9 (3F, CF_3). GC–MS: *m/z* 336 $[M]^+$.

Compound **XVII**. ^{19}F NMR spectrum, δ_F, ppm: 10.9 (1F, 5-F), 15.4 (1F, 4-F), 28.5 (1F, 6-F), 56.3 (1F, 3-F), 106.1 (3F, CF_3); $J_{1,6} = 34$, $J_{3,4} = 23$, $J_{3,5} = 6$,

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* Hereinafter the compositions of product mixtures (wt %) are given according to the GLC and ^{19}F NMR data.

$J_{3,6}$ = 10, $J_{4,5}$ = $J_{5,6}$ = 19, $J_{4,6}$ = 9 Hz [17]. GC–MS: m/z 344 $[M]^+$.

Compound **XVIII**. Liquid (purity 98%). ^{19}F NMR spectrum, δ_F, ppm: 27.3 (4F, 6-F, 7-F), 41.4 (2F, 4-F), 45.2 (2F, 3-F), 49.8 (1F, 10-F), 50.5 (2F, 2α-F), 52.2 (1F, 9-F), 68.7 (1F, 1-F), 54.2 (2F, 8-F), 54.4 (2F, 5-F), 77.2 (3F, 2β-F); $J_{1,9}$ = 86, $J_{1,2\alpha}$ = 26, $J_{1,2\beta}$ = 10, $J_{1,3}$ = 18, $J_{1,10}$ = 8, $J_{2\alpha,2\beta}$ = 3, $J_{2\alpha,3}$ = 13, $J_{2\beta,3}$ = $J_{3,4}$ = 7, $J_{4,10}$ = 34, $J_{5,10}$ = 23, $J_{8,9}$ = 24, $J_{9,10}$ = 21 Hz. Found: m/z 571.9670 $[M]^+$. $C_{16}F_{20}$. Calculated: M 571.9675.

Compound **XIX**. Liquid (purity 98%). ^{1}H NMR spectrum ($CDCl_3$): δ 3.78 ppm. ^{19}F NMR spectrum, δ_F, ppm: 27.3 (4F, 6-F, 7-F), 43.3 and 36.0 (1F each, 3-F), 50.0 and 48.3 (1F each, 2α-F, J_{AB} = 291 Hz), 50.6 (1F, 10-F), 52.2 (1F, 9-F), 54.5 (4F, 5-F, 8-F), 61.9 and 34.0 (1F each, 4-F), 76.8 and 68.5 (1F each, 1-F), 78.0 (3F, 2β-F); $J_{1A,1B}$ = 299, $J_{3A,3B}$ = 271, $J_{4A,4B}$ = 291, $J_{4B,10}$ = 49 Hz. Found: m/z 591.9735 $[M]^+$. $C_{16}HF_{21}$. Calculated: M 591.9737.

d. As described above in *b*, from 0.82 g (3.31 mmol) of compound **I**, 0.89 g (3.31 mmol) of 1,2,4,5-tetrafluoro-3-perfluoroethylbenzene, 4.77 g (22.0 mmol) of SbF_5, and 0.42 g (1.65 mmol) of I_2 (4 h, 130°C) we obtained 1.74 g of a mixture containing 14% of **XVI**, 6% of **XVII**, 21% of **XVIII**, and 31% of **XIX**.

e. As described above in *b*, from 0.66 g (2.65 mmol) of compound **I**, 0.71 g (2.65 mmol) of 1,2,4,5-tetrafluoro-3-perfluoroethylbenzene, 4.02 g (18.54 mmol) of SbF_5, and 0.34 g (1.32 mmol) of I_2 (15 h, 130°C) we obtained 1.23 g of a mixture containing 10% of **XVI**, 3% of **XVII**, 41% of **XVIII**, and 19% of **XIX**.

Reaction of perfluoro[1-(4-ethylphenyl)-1,2-dihydrocyclobutabenzene] (XI) with SbF_5. A mixture of 0.68 g (2.74 mmol) of compound **I**, 0.73 g (2.72 mmol) of 1,2,4,5-tetrafluoro-3-perfluoroethylbenzene, and 4.74 g (21.86 mmol) of SbF_5 was heated for 6 h at 50°C in a nickel high-pressure reactor to obtain compound **XI** [7], and the mixture was then heated for 30 h at 130°C. After appropriate treatment we isolated 0.86 g of compound **XV** (according to the ^{19}F NMR data).

Reaction of perfluoro(1-methyl-2-phenyl-1,2-dihydrocyclobutabenzene) (XX) and perfluoro-(1-methyl-1-phenyl-1,2-dihydrocyclobutabenzene) (XXI) with I_2–SbF_5. A mixture of 1.01 g (3.37 mmol) of compound **II**, 0.57 g (3.37 mmol) of pentafluorobenzene, and 5.11 g (23.57 mmol) of SbF_5 was kept for 20 h at 20°C to obtain a mixture of compounds **XX** and **XXI** at a ratio of 89:11 [8], 0.43 g (1.69 mmol) of I_2 was added, and the mixture was heated for 14 h at 130°C. After appropriate treatment we isolated 1.45 g of a mixture containing 58% of **XXII**, 18% of **XXIII**, 3% of **XXIV**, and 6% of **XXV**. The product mixture was subjected to column chromatography on silica gel using first hexane and then carbon tetrachloride as eluents to isolate 0.20 g of perfluoro(1-benzyl-2-ethylbenzene) (**XXIII**) and 0.69 g of perfluoro(2-ethylbenzophenone) (**XXII**).

Compound **XXII**. mp 38–40°C (from hexane). IR spectrum (CCl_4), ν, cm^{-1}: 1709 (C=O), 1648, 1634, 1525, 1499, 1475 (fluorinated aromatic ring). ^{19}F NMR spectrum, δ_F, ppm: 2.7 (2F, 3′-F, 5′-F), 13.7 (1F, 4-F), 17.3 (1F, 5-F), 19.0 (1F, 4′-F), 22.2 (1F, 6-F), 22.7 (2F, 2′-F, 6′-F), 30.3 (1F, 3-F), 56.2 (2F, 2α-F), 78.1 (3F, 2β-F); $J_{2\alpha,3}$ = 21, $J_{2\beta,3}$ = 16, $J_{3,4}$ = $J_{4,5}$ = 20, $J_{3,5}$ = 10, $J_{3,6}$ = 11, $J_{4,6}$ = 6, $J_{5,6}$ = 22, $J_{4',2'(6')}$ = 7, $J_{4',3'(5')}$ = 21 Hz. Found: m/z 461.9729 $[M]^+$. $C_{15}F_{14}O$. Calculated: M 461.9725.

Compound **XXIII**. Liquid (purity 98%). ^{19}F NMR spectrum, δ_F, ppm: 2.4 (2F, 3′-F, 5′-F), 14.5 (1F, 4′-F), 15.3 (1F, 4-F), 16.9 (1F, 5-F), 22.3 (2F, 2′-F, 6′-F), 30.6 (1F, 6-F), 32.8 (1F, 3-F), 60.9 (2F, 2α-F), 80.7 (3F, 2β-F), 87.9 (2F, 1α-F); $J_{1\alpha,2\beta}$ = 16, $J_{1\alpha,6}$ = 41, $J_{1\alpha,2'(6')}$ = 15, $J_{2\alpha,3}$ = 32, $J_{2\beta,3}$ = 18, $J_{3,4}$ = $J_{4,5}$ = $J_{5,6}$ = $J_{4',3'(5')}$ = 21, $J_{3,5}$ = 10, $J_{3,6}$ = $J_{4,6}$ = 9, $J_{4',2'(6')}$ = 5 Hz. Found: m/z 483.9752 $[M]^+$. $C_{15}F_{16}$. Calculated: M 483.9744.

Reaction of perfluoro(1-ethyl-2-phenyl-1,2-dihydrocyclobutabenzene) (XXVI) with I_2–SbF_5. A mixture of 1.09 g (3.13 mmol) of compound **III**, 0.53 g (3.16 mmol) of pentafluorobenzene, and 4.97 g (22.92 mmol) of SbF_5 was kept for 20 h at 20°C to generate compound **XXVI** [10], 0.40 g (1.58 mmol) of iodine was added, and the mixture was heated for 14 h at 130°C. The mixture was then cooled to 0°C, 6 ml of anhydrous hydrogen fluoride was added, and the mixture was poured into ice water and extracted with methylene chloride. The extract was dried over $MgSO_4$, and the solvent was distilled off to obtain 1.43 g of a mixture containing 59% of **XXVII** and 19% of **XXVIII**. The product mixture was subjected to column chromatography on silica gel using first hexane and then carbon tetrachloride as eluents to isolate 0.75 g of perfluoro(1-benzyl-2-propylbenzene) (**XXVII**) and 0.21 g of perfluoro(2-propylbenzophenone) (**XXVIII**).

Compound **XXVII**. Liquid (purity 98%). ^{19}F NMR spectrum, δ_F, ppm: 2.4 (2F, 3′-F, 5′-F), 14.6 (1F, 4′-F), 15.4 (1F, 4-F), 17.0 (1F, 5-F), 22.2 (2F, 2′-F, 6′-F), 30.7 (1F, 6-F), 32.8 (1F, 3-F), 40.5 (2F, 2β-F), 63.9 (2F, 2α-F), 81.2 (3F, 2γ-F), 87.5 (2F, 1α-F); $J_{1\alpha,2\alpha} = J_{1\alpha,2\beta} = 23$, $J_{1\alpha,6} = 39$, $J_{1\alpha,2'(6')} = 15$, $J_{2\alpha,2\gamma} = 10$, $J_{2\alpha,3} = 33$, $J_{2\beta,3} = 24$, $J_{3,4} = J_{4,5} = J_{5,6} = J_{4,3'(5')} = 21$, $J_{3,5} = 10$, $J_{3,6} = J_{4,6} = 9$, $J_{4',2'(6')} = 5$ Hz. Found: *m*/*z* 533.9706 $[M]^+$. $C_{16}F_{18}$. Calculated: *M* 533.9712.

Compound **XXVIII**. mp 40–41°C (from hexane). IR spectrum (CCl_4), ν, cm^{-1}: 1709 (C=O), 1648, 1634, 1524, 1497, 1475 (fluorinated aromatic ring). ^{19}F NMR spectrum, δ_F, ppm: 2.7 (2F, 3′-F, 5′-F), 13.7 (1F, 4-F), 17.5 (1F, 5-F), 19.0 (1F, 4′-F), 22.2 (1F, 6-F), 22.5 (2F, 2′-F, 6′-F), 30.5 (1F, 3-F), 37.1 (2F, 2β-F), 59.0 (2F, 2α-F), 81.7 (3F, 2γ-F); $J_{2\alpha,2\gamma} = 10$, $J_{2\alpha,3} = J_{2\beta,3} = J_{5,6} = 22$, $J_{3,4} = J_{4,5} = 20$, $J_{3,5} = 10$, $J_{3,6} = 11$, $J_{4,6} = 6$, $J_{4',2'(6')} = 7$, $J_{4,3'(5')} = 21$ Hz. Found: *m*/*z* 511.9689 $[M]^+$. $C_{16}F_{16}O$. Calculated: *M* 511.9694.

Perfluoro[(2-methylphenyl)(phenyl)methyl] cation (XXIX). Compound **VIII**, 0.14 g (0.32 mmol), was dissolved in 0.99 g (4.57 mmol) of SbF_5, and 0.22 g of SO_2ClF was added. The resulting solution contained cation **XXIX**, while compound **VIII** was absent (according to the ^{19}F and ^{13}C NMR data). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 108.9 and 109.4 (C^1, $C^{1'}$), 114.8 q.d (C^2, $^2J_{CF} = 38, 11$), 117.4 q ($C^{2\alpha}$, $^1J_{CF} = 276$), 138.0 d.t ($C^{3'}$, $C^{5'}$, $^1J_{CF} = 270$, $^2J_{CF} = 12$), 141.2 d.t (C^5, $^1J_{CF} = 274$, $^2J_{CF} = 13$), 147.2 d.d (C^3, $^1J_{CF} = 275$, $^2J_{CF} = 12$), 149.4 d (C^4, $^1J_{CF} = 283$), 149.4 d (C^6, $^1J_{CF} \approx 280$), 152.1d ($C^{2'}$, $C^{6'}$, $^1J_{CF} = 294$), 162.1 d ($C^{4'}$, $^1J_{CF} = 307$), 193.2 d ($C^{1\alpha}$, $^1J_{CF} = 359$). ^{19}F NMR spectrum at 25°C, δ_F ($\Delta\delta_F$),** ppm: 16.0 (13.6) (2F, 3′-F, 5′-F), 23.7 (7.8) (1F, 5-F), 40.3 (11.6) (1F, 3-F), 46.0 (30.9) (1F, 4-F), 47.2 (17.8) (1F, 6-F), ~60.2 (38.0) (2F, 2′-F, 6′-F), 82.3 (67.7) (1F, 4′-F), 109.4 (1.1) (3F, 2α-F), 217.8 (131.1) (1F, 1α-F); $J_{1\alpha,2'(6')} \approx 80$, $J_{1\alpha,4'} \approx J_{3,4} \approx J_{4,5} \approx J_{4,6} \approx J_{5,6} \approx J_{4',3'(5')} \approx 20$, $J_{1\alpha,2\alpha} \approx J_{2\alpha,3} \approx 21$, $J_{3,5} \approx 14$, $J_{4',2'(6')} \approx 40$ Hz; ^{19}F NMR spectrum at –30°C, δ_F, ppm: 16.4 and 16.1 (2F, 3′-F, 5′-F), 24.2 (1F, 5-F), 40.8 (1F, 3-F), 47.1 (1F, 4-F), 48.3 (1F, 6-F), 56.5 (1F, 6′-F), 64.0 (1F, 2′-F), 82.0 (1F, 4′-F), 109.9 (3F, 2α-F), 217.3 (1F, 1α-F).

The solution was poured into ice water, the mixture was extracted with chloroform, and the extract was dried over $MgSO_4$ and evaporated to isolate 0.12 g of ketone **VI**.

Perfluoro[(2-ethylphenyl)(phenyl)methyl] cation (XXX). Compound **XXIII**, 0.10 g (0.21 mmol), was dissolved in 0.60 g (2.77 mmol) of SbF_5, and 0.27 g of SO_2ClF was added. The resulting solution contained cation **XXX**, while compound **XXIII** was absent (according to the ^{19}F and ^{13}C NMR data). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 109. 8 t.q ($C^{2\alpha}$, $^1J_{CF} = 262$, $^2J_{CF} = 43$), 110.1 (C^1, $C^{1'}$), 114.2 (C^2), 116.1 q.t ($C^{2\beta}$, $^1J_{CF} = 286$, $^2J_{CF} = 35$), 138.7 d ($C^{3'}$, $C^{5'}$, $^1J_{CF} = 271$), 142.1 d (C^5, $^1J_{CF} = 273$), 148.3 d (C^3 or C^6, $^1J_{CF} = 272$), 148.7 d (C^4, $^1J_{CF} = 284$), 149.0 d (C^6 or C^3, $^1J_{CF} = 271$), 153.0 d ($C^{2',}$ $C^{6'}$, $^1J_{CF} = 301$), 163.4 d ($C^{4'}$, $^1J_{CF} = 311$), 195.1 d ($C^{1\alpha}$, $^1J_{CF} = 359$). ^{19}F NMR spectrum at 25°C, δ_F ($\Delta\delta_F$), ppm: 16.5 (14.1) (2F, 3′-F, 5′-F), 24.6 (7.7) (1F, 5-F), 41.7 (26.4) (1F, 4-F), 43.4 (10.6) (1F, 3-F), 44.1 (13.5) (1F, 6-F), 61.5 (0.6) (2F, 2α-F), 81.3 (0.6) (3F, 2β-F), 85.6 (71.1) (1F, 4′-F), 221.1 (133.2) (1F, 1α-F); $J_{1\alpha,2'(6')} \approx 85$, $J_{1\alpha,4'} = 23$, $J_{1\alpha,2\beta} = 24$, $J_{2\alpha,3} = 18$, $J_{3,4} \approx J_{4,5} \approx J_{4,6} \approx J_{5,6} \approx 20$, $J_{3,5} \approx 15$, $J_{4',2'(6')} \approx 40$ Hz. ^{19}F NMR spectrum at –10°C, δ_F ($\Delta\delta_F$), ppm: 16.1 and 17.0 (2F, 3′-F, 5′-F), 25.0 (1F, 5-F), 42.6 (1F, 4-F), 43.9 (1F, 3-F), 44.8 (1F, 6-F), 58.2 (35.9) (1F, 6′-F), 63.1 and 60.7 (1F, each, 2α-F), 66.3 (44.0) (1F, 2′-F), 81.6 (3F, 2β-F), 85.3 (1F, 4′-F), 220.7 (1F, 1α-F); $J_{AB} \approx 300$ Hz.

The solution was poured into ice water, the mixture was extracted with chloroform, and the extract was dried over $MgSO_4$ and evaporated to isolate 0.09 g of ketone **XXII**.

Perfluoro[(phenyl)(2-propylphenyl)methyl] cation (XXXI). Compound **XXVII**, 0.12 g (0.22 mmol), was dissolved in 1.04 g (4.80 mmol) of SbF_5, and 0.22 g of SO_2ClF was added to obtain a solution containing cation **XXXI**, while compound **XXVII** was absent (according to the ^{19}F and ^{13}C NMR data). ^{13}C NMR spectrum, δ_C, ppm (*J*, Hz): 106.5 t.t.q ($C^{2\beta}$, $^1J_{CF} = 267$, $^2J_{CF} = 38, 38$), 110.0 (C^1, $C^{1'}$), 112.2 t.t ($C^{2\alpha}$, $^1J_{CF} = 264$, $^2J_{CF} = 36$), 114.2 (C^2), 115.4 q.t ($C^{2\gamma}$, $^1J_{CF} = 287$, $^2J_{CF} = 33$), 138.5 d.t ($C^{3'}$, $C^{5'}$, $^1J_{CF} = 271$, $^2J_{CF} = 12$), 142.0 d.t (C^5, $^1J_{CF} = 274$, $^2J_{CF} = 13$), 148.2 d (C^3 or C^6, $^1J_{CF} = 271$), 148.5 d (C^4, $^1J_{CF} = 284$), 148.9 d (C^6 or C^6, $^1J_{CF} = 272$), 152.8 d ($C^{2',}$ $C^{6'}$, $^1J_{CF} = 299$), 163.6 d ($C^{4'}$, $^1J_{CF} = 311$), 194.9 d ($C^{1\alpha}$, $^1J_{CF} = 364$). ^{19}F NMR spectrum at 25°C, δ_F ($\Delta\delta_F$), ppm: 16.5 (14.1) (2F, 3′-F, 5′-F), 24.8 (7.8) (1F, 5-F), 41.0 (0.5) (2F, 2β-F), 41.8 (26.4) (1F, 4-F), 43.9 (11.1) (1F, 3-F), 44.1 (13.4) (1F, 6-F), 64.9 (1.0) (2F, 2α-F), 83.6 (2.4) (3F, 2γ-F), 85.6 (71.9) (1F, 4′-F), 220.8 (133.3) (1F, 1α-F). ^{19}F NMR spectrum at –30°C, δ_F ($\Delta\delta_F$), ppm: 16.4 and 17.1 (2F, 3′-F, 5′-F), 25.3 (1F, 5-F), 42.4 and 39.9 (1F each, 2β-F, $J_{AB} = 291$ Hz), 43.1 (1F, 4-F), 44.6 (1F, 3-F), 45.3 (1F, 6-F), 58.1 (35.9) (1F, 6′-F), 66.2 (44.0) (1F, 2′-F), 66.3 and 64.2 (1F each, 2α-F_2, $J_{AB} = 300$ Hz), 84.1 (3F, 2γ-F), 85.1 (1F, 4′-F), 220.1 (1F, 1α-F).

** Change of the chemical shift relative to the corresponding value for the precursor.

The solution was poured into ice water, the mixture was extracted with chloroform, and the extract was dried over $MgSO_4$ and evaporated to isolate 0.11 g of ketone **XXVIII**.

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