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Reaction of Perfluorinated 1-Ethyl-, 1,1-Diethyl-, and 1,2-Diethylcyclobutabenzenes with Pentafluorobenzene in SbF_5

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Abstract—Perfluoro(1-ethyl-1,2-dihydrocyclobutabenzene) reacts with pentafluorobenzene in SbF_5 to give perfluoro(1-ethyl-2-phenyl-1,2-dihydrocyclobutabenzene). Analogous reaction of a mixture of perfluoro-(1,1-diethyl-1,2-dihydrocyclobutabenzene) and perfluoro(1,2-diethyl-1,2-dihydrocyclobutabenzene) leads to the formation (after hydrolysis of the reaction mixture) of perfluorinated 7-phenyl-8,8-diethylbicyclo[4.2.0]octa-1,4,6-trien-3-one, 1,1-diethyl-2-(4-oxocyclohexa-2,5-dienylidene)-1,2-dihydrocyclobutabenzene, and 2-(pent-2-en-3-yl)benzophenone (from the 1,1-isomer) and perfluorinated (*E*)-1,2-diethyl-1-phenyl-1,2-dihydrocyclobutabenzene, 7,8-diethyl-8-phenylbicyclo[4.2.0]octa-1,4,6-trien-3-one, and 1-[2-(1-phenylprop-1-en-1-yl)-phenyl]propan-1-one (from the 1,2-isomer).

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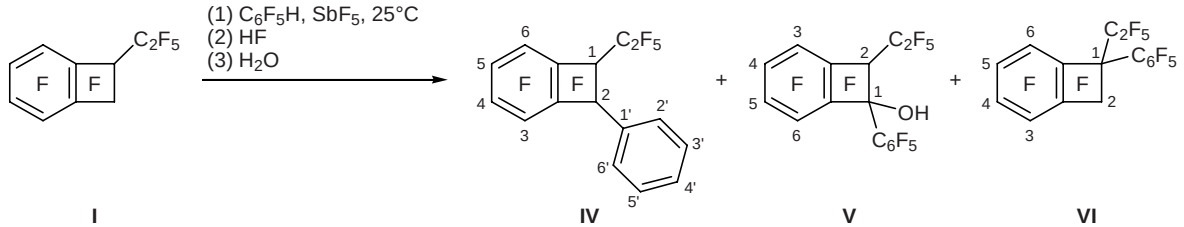
We previously studied reactions of perfluorinated cyclobutabenzene, indan, tetrahydronaphthalene [1], 1-methylcyclobutabenzene [2], 1-ethyl- and 1,1-diethylindans, and 1-ethyltetrahydronaphthalene [3] with pentafluorobenzene in the presence of SbF_5, which led to the formation of the corresponding pentafluorophenylcycloalkabenzenes. The reactions with perfluorinated 1-phenylindan, 1-phenyltetrahydronaphthalene, and 1-arylcyclobutabenzenes with antimony pentafluoride were found to involve skeletal rearrangements [4].

In continuation of our studies on pentafluorophenylation of polyfluorocycloalkabenzenes in the present work we examined reactions of perfluorinated 1-ethyl-1,2-dihydrocyclobutabenzene (**I**), 1,1-diethyl-1,2-dihydrocyclobutabenzene (**II**), and 1,2-diethyl-1,2-dihydrocyclobutabenzene (**III**) with pentafluorobenzene in SbF_5 with a view to obtain polyfluorinated cyclobutabenzenes containing both pentafluorophenyl and pentafluoroethyl groups. These compounds are necessary for studying the general relations holding in skeletal transformations of polyfluoroarylcycloalkabenzenes.

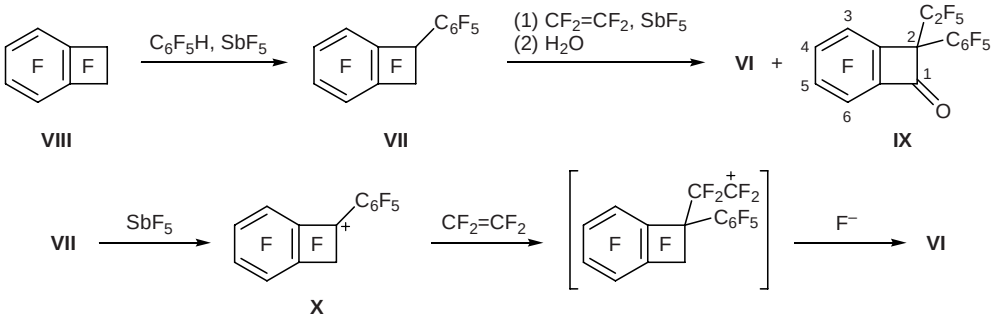
Compound **I** reacted with C_6F_5H in SbF_5 to produce (after treatment of the reaction mixture first with anhydrous hydrogen fluoride and then with water) perfluoro(1-ethyl-2-phenyl-1,2-dihydrocyclobutabenzene (**IV**, *E*/*Z* isomer ratio 70:30), perfluoro(2-ethyl-1-phenyl-1,2-dihydrocyclobutabenzen-1-ol) (**V**) (*E*/*Z* isomer ratio ~42:58), and a small amount of perfluoro(1-ethyl-1-phenyl-1,2-dihydrocyclobutabenzene) (**VI**) (Scheme 1). Compound **VI** was also obtained by reaction of perfluoro(1-phenyl-1,2-dihydrocyclobutabenzene) (**VII**) (prepared from perfluorocyclobutabenzene **VIII** and C_6F_5H in SbF_5 [1]) with tetrafluoroethylene

Scheme 1.

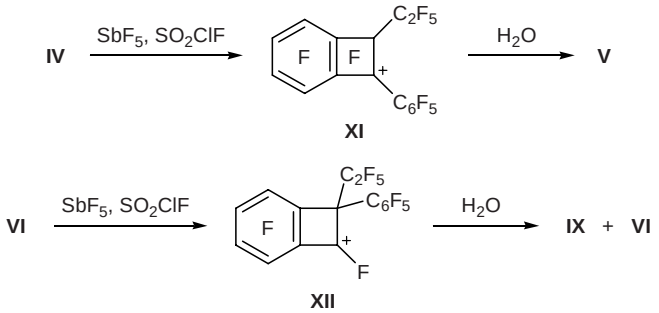


I **IV** **V** **VI**

Scheme 2.



Scheme 3.



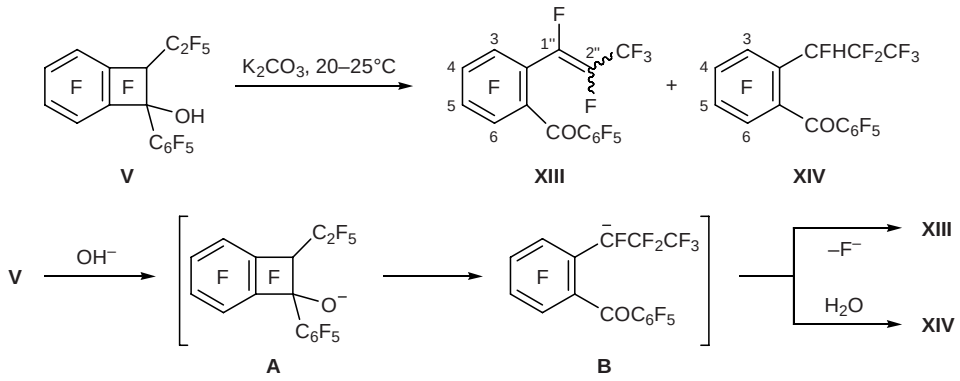
in the presence of SbF_5. In this case, no 1,2-isomer **IV** was formed, but the reaction mixture contained perfluoro(2-ethyl-2-phenyl-1,2-dihydrocyclobutabenzen-1-one) (**IX**) (Scheme 2).

Presumably, ethylcyclobutabenzene **I** reacts with C_6F_5H in SbF_5 according to the scheme proposed previously for the reactions of cyclobutabenzene **VIII** and perfluoro(1-methyl-1,2-dihydrocyclobutabenzene) with C_6F_5H [1,2]. Product **VI** is formed from compound **VII** via alkylation of tetrafluoroethylene with perfluoro(1-phenyl-1,2-dihydrocyclobutabenzen-1-yl) cation (**X**) generated from cyclobutabenzene **VII** by the action of SbF_5 [1] (Scheme 2) in a way similar to the reaction of polyfluorocyclobutabenzenes with fluorinated olefins in the presence of SbF_5 [5, 6].

The formation of hydroxy derivative **V** and ketone **IX** under the above conditions may be rationalized as follows. Compounds **IV** and **VI** in SbF_5 are likely to exist as cations **XI** and **XII**, respectively. In fact, cations **XI** and **XII** were detected by ^{19}F NMR spectroscopy upon dissolution of compounds **IV** and **VI** in the system SbF_5–SO_2ClF. Hydrolysis of a solution containing cation **XI** yields mainly compound **V**, whereas a mixture of precursor of **VI** and ketone **IX** is obtained from cation **XII** (Scheme 3).

Fluorinated alcohol **V** is stable in acid medium but is converted into a mixture of perfluoro[2-(prop-1-en-1-yl)benzophenone] (**XIII**) and 2-(1,2,2,3,3,3-hexafluoropropyl)nonafluorobenzophenone (**XIV**) on treatment with an aqueous solution of potassium carbonate

Scheme 4.

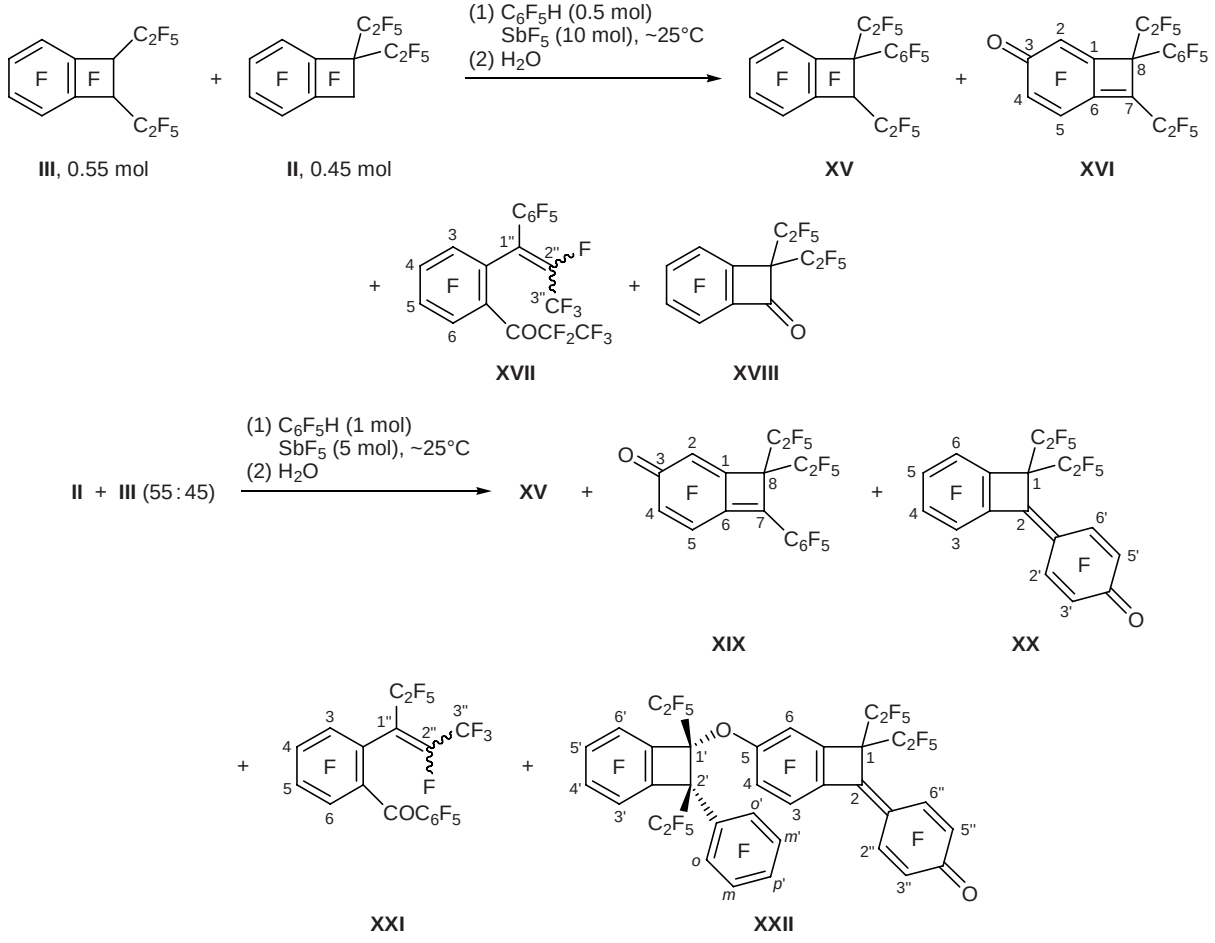


or during chromatography on a column charged with silica gel (pH ≥ 7). Presumably, deprotonation of hydroxy derivative **V** gives anion **A** which undergoes opening of the four-membered ring (like haloform reaction) with formation of anion **B**. Protonation of the latter yields compound **XIV**, while elimination of fluoride ion leads to product **XIII** (Scheme 4).

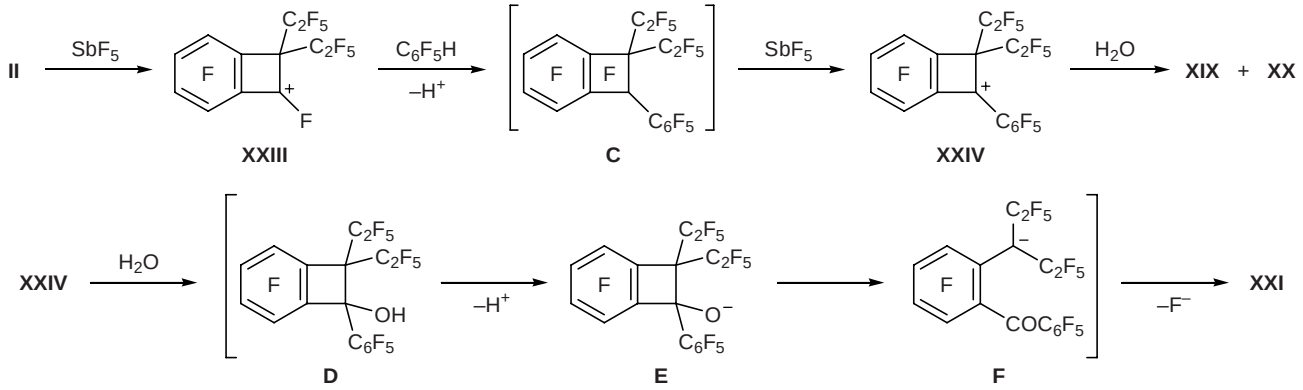
In the reaction of a mixture of isomeric diethylcyclobutabenzenes **II** and **III** with 0.5 equiv of C_6F_5H in 10 equiv of SbF_5, only 1,2-isomer **III** is involved. After treatment of the reaction mixture with water, a mixture of perfluorinated (*E*)-1,2-diethyl-1-phenyl-1,2-dihydrocyclobutabenzene (**XV**), 7,8-diethyl-8-phenylbicyclo[4.2.0]octa-1,4,6-trien-3-one (**XVI**), and 1-[2-(1-phenylprop-1-en-1-yl)phenyl]propan-1-one (**XVII**, *E*/*Z* ratio ~83:17) was obtained. 1,1-Isomer **II** gives rise to perfluoro(2,2-diethyl-1,2-dihydrocyclobutabenzen-1-one) (**XVIII**) (Scheme 5). In the presence of an equimolar amount of pentafluorobenzene (5 equiv of antimony pentafluoride), both isomers **II** and **III** are involved. In this case, 1,2-isomer **III** is converted mainly into compound **XV**, while the amount of ketones **XVI** and **XVII** is insignificant. 1,1-Isomer **II** yields perfluorinated 8,8-diethyl-7-phenylbicyclo[4.2.0]octa-1,4,6-trien-3-one (**XIX**), 4-(2,2-diethyl-1,2-dihydrocyclobutabenzen-1-ylidene)cyclohexa-2,5-dien-1-one (**XX**), and 2-(pent-2-en-3-yl)benzophenone (**XXI**, *E*/*Z* ratio 40:60). In addition, the reaction mixture contained a small amount of perfluoro-4-[5-(*cis*-1,2-diethyl-2-phenyl-1,2-dihydrocyclobutabenzen-1-yloxy)-2,2-diethyl-1,2-dihydrocyclobutabenzen-1-ylidene]cyclohexa-2,5-dien-1-one (**XXII**) (Scheme 5). During isolation of compounds **XVII** and **XXI** by column chromatography or on prolonged storage the *E* isomer was converted (either partially or completely) into the *Z* isomer.

A probable mechanism of the above transformations is shown in Scheme 6. 1,1-Diethylcyclobutabenzene **II** in SbF_5 loses fluoride ion to form perfluoro(2,2-diethyl-1,2-dihydrocyclobutabenzen-1-yl) cation (**XXIII**). Alkylation of pentafluorobenzene with cation **XXIII** gives compound **V** which is converted into per-

Scheme 5.



Scheme 6.

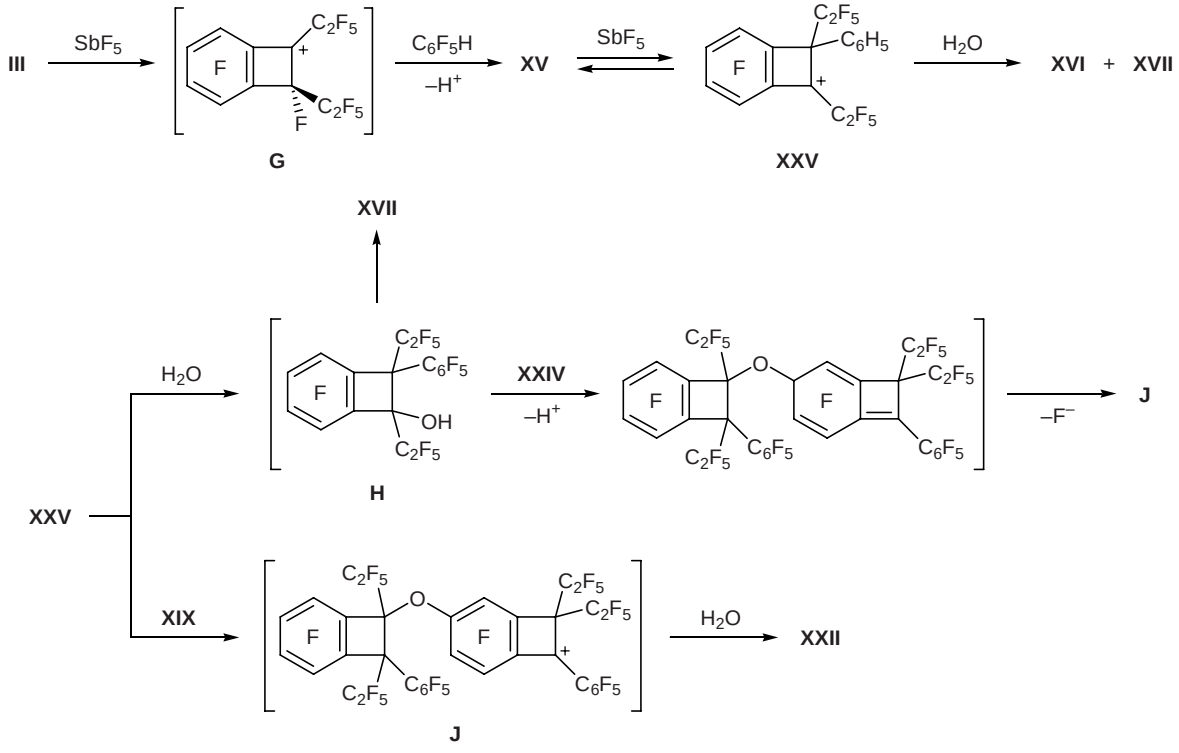


fluoro(2,2-diethyl-1-phenyl-1,2-dihydrocyclobutabenzen-1-yl) cation (**XXIV**). Hydrolysis of the latter leads to ketones **XIX** and **XX** and probably to alcohol **D**. Opening of the four-membered ring in structure **D** (like haloform reaction) yields benzophenone **XXI** through intermediate anions **E** and **F** (Scheme 6).

Perfluoro(1,2-diethyl-1,2-dihydrocyclobutabenzene) (**III**) in SbF_5 is likely to converted into cation **G** which alkylates pentafluorobenzene to give compound **XV**. Elimination of fluoride ion from **XV** by the action of SbF_5 yields cyclobutenyl cation **XXV**, and hydrolysis of the latter yields compounds **XVI** and **XVII** (Scheme 7). Presumably, compound **XVII** is formed through intermediate hydroxy derivative **H** in a way similar to the formation of benzophenone **XXI** shown in Scheme 6. Compound **XXII** may result from the reaction of alcohol **H** with cation **XXIV** or/and of cation **XXV** with ketone **XIX** through intermediate ion **J** (Scheme 7). This transformation is likely to occur in the course of treatment of the reaction mixture with water, i.e., when the mixture contains simultaneously hydrolysis products and cyclobutabenzene salts.

The formation of cations **XXIV** and **XXV** in the reaction of cyclobutabenzenes **II** and **III** with C_6F_5H in SbF_5 was detected by ^{19}F NMR spectroscopy. In addition, we found that cation **XXIII** is generated from

Scheme 7.



1,1-diethylcyclobutabenzene **II** in antimony pentafluoride and that the concentration of the corresponding cation **G** derived from 1,2-isomer **III** is insufficient to be detected by ^{19}F NMR spectroscopy. Nevertheless, as we already noted, 1,2-isomer **III** reacts with C_6F_5H at a higher rate than does 1,1-isomer **II**. Presumably, the reaction of pentafluorobenzene with cation **XXIII** is hindered for steric reasons (Scheme 6): the cationic center in **XXIII** is sterically shielded by two bulky pentafluoroethyl groups. By contrast, cation **G** allows pentafluorobenzene molecule to approach the cationic center at the side opposite to the C_2F_5 group on the neighboring carbon atom (Scheme 7).

The patterns observed in the NMR spectra of cations **XI**, **XII**, **XXIII**–**XXV** are consistent with published data for perfluoro(cyclobutabenzen-1-yl) cation [6] and cation **X** [1].

The structure of compounds **IV**–**VI**, **IX**, and **XIII**–**XXII** was determined on the basis of their ^{19}F NMR and high-resolution mass spectra. In addition, the molecular and crystalline structures of **XVI**, **XX**, and **XXII** were studied by X-ray diffraction [7]. The coordinates of atoms and geometric parameters of their molecules were deposited to the Cambridge Crystallographic Data Center (entry nos. 635817–635819). Signals in the ^{19}F NMR spectra were assigned taking into account their position, multiplicity, and intensity. The ^{19}F NMR data were also used to determine the configuration of molecules **IV**, **V**, **XIII**, **XV**, **XVII**, and **XXI**.

In the spectra of the *E* isomers of **IV** and **V**, signals from fluorine atoms at tertiary carbon atoms appear in a weaker field relative to the corresponding signals of the *Z* isomers, as in the spectra of polyfluorinated methylphenylcyclobutabenzenes [2]. Fluorine atoms in the CF_2 groups of the perfluoroethyl substituents in *E*-**XV** (*cis* arrangement of the C_2F_5 groups) appear as doublets with coupling constants $J_{AA'}$ = 52 and $J_{BB'}$ = 56 Hz, while the corresponding coupling constants for *trans*-oriented perfluoroethyl groups in isomer *Z*-**XV** do not exceed 5 Hz. Signals from fluorine nuclei in the vinyl group of *E*-**XIII** are split into doublets with a coupling constant $J_{1'',2''}$ of 141 Hz, indicating their *trans* orientation; signals from the *cis*-fluorine atoms in *Z*-**XIII** are characterized by a coupling constant of 7 Hz. The chemical shifts of the vinylic fluorine atoms and the corresponding coupling constants are consistent with the data reported for perfluoro(1-phenylprop-1-enes) [8].

In the ^{19}F NMR spectrum of *E*-**XVII**, the CF_3C= signal is a doublet of triplets with coupling constants $J_{2'',3''}$ and $J_{3'',2'(6')}$ of 9 and 4 Hz, respectively, which are typical of *cis* arrangement of the CF_3 and C_6F_5 groups. In the spectrum of *Z*-**XVII** the CF_3 signal appears as a doublet ($J_{2'',3'''}$ = 9 Hz). The *Z* isomer of **XXI** is characterized by a doublet signal from the CF_3 group at the double C=C bond ($J_{2'',3'''}$ = 8 Hz); the corresponding signal of the *E* isomer of **XXI** has a more complex structure indicating *cis* orientation of the CF_3 and C_2F_5 groups with respect to the double bond.

EXPERIMENTAL

The ^{19}F NMR spectra of the reaction mixtures, SbF_5–SO_2ClF solutions containing perfluorinated cationic species, and solutions of individual compounds in $CHCl_3$, as well as the ^1H NMR spectrum of ketone **XIV**, were recorded on a Bruker AC-200 instrument at 188.3 MHz for ^{19}F and 200 MHz for ^1H. The ^{19}F NMR spectra of *E*-**XV** and **XIX** were recorded on a Bruker AM-400 instrument (376.4 MHz), and of *Z*-**XV** and **XXII**, on a Bruker AV-300 spectrometer (282.4 MHz). The chemical shifts were measured using C_6F_6 and SO_2ClF (δ_F 262.8 ppm relative to C_6F_6) or residual solvent signal ($CHCl_3$, δ 7.24 ppm) as internal references. The elemental compositions were determined from the high-resolution mass spectra which were obtained on a Finnigan MAT-8200 mass spectrometer. GLC analysis was performed on an LKhM-72 chromatograph [4000×4-mm column; stationary phase VS-1 or E-301 on Chromosorb W, 15(25):100; carrier gas helium, flow rate 60 ml/min]. GC–MS analysis was performed on a Hewlett–Packard G1081A GC–MS system consisting of an HP 5890 Series II gas chromatograph (HP5 capillary column, 30 m×0.25 mm×0.25 μm, 5% of diphenyl- and 95% of dimethylsiloxane; carrier gas helium, 1 ml/min) and an HP 5971 mass-selective detector (electron impact, 70 eV).

Reaction of perfluoro(1-ethyl-1,2-dihydrocyclobutabenzene) (I) with pentafluorobenzene in SbF_5. A mixture of 4.02 g (11.6 mmol) of compound **I**, 7.52 g (34.7 mmol) of SbF_5, 2.14 g (12.7 mmol) of C_6F_5H, and 6 ml of C_6F_6 was stirred for 4 h at 25–27°C in a Teflon vessel. The mixture was then treated with 16 ml of anhydrous hydrogen fluoride, poured into an ice–water mixture, and extracted with chloroform. The organic phase was separated, washed with water, and dried over $MgSO_4$, and the solvent and C_6F_6 were distilled off to obtain 5.2 g of a mixture containing* 38% of (*E*)-perfluoro(1-ethyl-2-phenyl-1,2-dihydro-

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

cyclobutabenzene) (*E*-**IV**, yield 33%), 16% of (*Z*)-perfluoro(1-ethyl-2-phenyl-1,2-dihydrocyclobutabenzene (*Z*-**IV**, yield 14%), 18% of (*Z*)-perfluoro(2-ethyl-1-phenyl-1,2-dihydrocyclobutabenzen-1-ol) (*Z*-**V**, yield 16%), 13% of (*E*)-perfluoro(2-ethyl-1-phenyl-1,2-dihydrocyclobutabenzen-1-ol) (*E*-**V**, yield 11%), and 6% of perfluoro(1-ethyl-1-phenyl-1,2-dihydrocyclobutabenzene (**VI**, yield 5.5%). A 2.57-g portion of the product mixture was subjected to column chromatography on silica gel using as eluent chloroform which was preliminarily shaken with concentrated hydrochloric acid (10:1, by volume) and separated. We thus isolated 1.1 g of compound **IV** (*E*/*Z* ratio 71:29) and two fractions containing compound **V** (0.34 g with *E*/*Z* ratio ~14:86 and 0.14 g with *E*/*Z* ratio ~92:8).

By repeated chromatography of 1.1 g of compound **IV** (*E*/*Z* ratio 71:29) on silica gel (eluent hexane) we isolated a fraction (0.45 g) enriched in the *E* isomer (*E*/*Z* ratio ~83:17) and a fraction (0.07 g) enriched in the *Z*-isomer (*E*/*Z* ratio ~45:55). ^{19}F NMR spectrum, δ_F, ppm: isomer *E*-**IV**: 80.9 (3F, CF_3), 45.2 (1F, F_A) and 36.7 (1F, F_B) ($C\mathbf{F}_2CF_3$), 32.4 (1F, 2-F), 29.2 (1F, 6-F), 28.2 (1F, 3-F), 20.4 (1F, 4-F), 19.7 (1F, 5-F), 11.3 (1F, 1-F), 22.8 (2F, 2′-F, 6′-F), 14.8 (1F, 4′-F), 2.2 (2F, 3′-F, 5′-F); J_{FF}, Hz: J_{AB} = 293, $J_{3,4}$ = 18, $J_{3,5}$ = 8, $J_{3,6}$ = 23, $J_{4,5}$ = 18, $J_{4,6}$ = 9, $J_{5,6}$ = 18, $J_{3,2'(6')}$ = 12, J(6-F,CF_3) = 18; isomer *Z*-**IV**: 80.3 (3F, CF_3), 41.3 (1F, F_A) and 33.6 (1F, F_B) ($C\mathbf{F}_2CF_3$), 31.1 (1F, 2-F), 29.7 (1F, 6-F), 27.5 (1F, 3-F), 20.2 (1F, 4-F), 19.8 (1F, 5-F), 5.5 (1F, 1-F), ~18 i ~29 (2F, 2′-F, 6′-F), 14.4 (1F, 4′-F), ~2 (2F, 3′-F, 5′-F); J_{FF}, Hz: J_{AB} = 290, $J_{3,4} \approx 19$, $J_{3,5} \approx 9$, $J_{3,6} \approx 24$, $J_{3,2'(6')} \approx 9$. Found: $[M]^+$ 495.9743 (for *E*/*Z* mixture, ~45:55). $C_{16}F_{16}$. Calculated: *M* 495.9744. The mass spectra (GC–MS) of *Z*-**IV** and *E*-**IV** contained the molecular ion peaks with *m*/*z* 496.

Compound **V**. ^{19}F NMR spectrum, δ_F, ppm: isomer *E*-**V**: 80.7 (3F, CF_3), 46.7 (1F, F_A) and 35.6 (1F, F_B) ($C\mathbf{F}_2CF_3$), 28.4 (1F, 3-F), 26.0 (1F, 6-F), 19.0 (1F, 5-F), 16.7 (1F, 4-F), 20.9 (2F, 2′-F, 6′-F), 11.5 (1F, 1-F), 12.2 (1F, 4′-F), 1.7 (2F, 3′-F, 5′-F); J_{FF}, Hz: J_{AB} = 291, $J_{3,4}$ = 18, $J_{3,5}$ = 8, $J_{3,6}$ = 24, J(3-F,CF_3) = 19, $J_{4,5}$ = 19, $J_{4,6}$ = 7, $J_{5,6}$ = 19, $J_{6,2'(6')}$ = 12; isomer *Z*-**V**: 80.6 (3F, CF_3), 41.8 (1F, F_A) and 33.8 (1F, F_B) ($C\mathbf{F}_2CF_3$), 29.2 (1F, 3-F), 25.7 (1F, 6-F), 19.3 (1F, 5-F), 16.3 (1F, 4-F), 18.2 and 26.2 (2F, 2′-F, 6′-F), 4.5 (1F, 1-F), 12.0 (1F, 4′-F), 1.3 (2F, 3′-F, 5′-F); J_{FF}, Hz: J_{AB} = 290, $J_{3,4}$ = 18, $J_{3,5}$ = 9, $J_{3,6} \approx 24$, J(3-F,CF_3) = 21, $J_{4,5}$ = 19, $J_{4,6}$ = 7, $J_{5,6}$ = 19, $J_{6,2'(6')} \approx 9$. Found: $[M]^+$ 493.9779 (*E*/*Z* ratio ~14:86), 493.9799 (*E*/*Z* ratio ~92:8). $C_{16}HF_{15}O$. Calculated: *M* 493.9788.

Perfluoro(1-ethyl-1-phenyl-1,2-dihydrocyclobutabenzene) (VI). A mixture of 1.87 g (7.54 mmol) of perfluorinated cyclobutabenzene **VIII**, 4.9 g (22.6 mmol) of SbF_5, 1.39 g (8.27 mmol) of C_6F_5H, and 6 ml of C_6F_6 was stirred for 3.5 h at 25°C, 1.5 g (15 mmol) of tetrafluoroethylene was passed through the mixture over a period of 2.5 h at 27–29°C, and the mixture was treated with water at 10–20°C, acidified with 5% hydrochloric acid, and extracted with chloroform. The organic phase was separated and dried over $MgSO_4$, and the solvent and hexafluorobenzene were distilled off to leave 3.5 g of a mixture containing compound **VI** and perfluoro(2-ethyl-2-phenyl-1,2-dihydrocyclobutabenzen-1-one) (**IX**) at a ratio of 86:14 (^{19}F NMR data) and a small amount (<5%) of perfluoro(1,2-diethyl-1-phenyl-1,2-dihydrocyclobutabenzene) (**XV**, *E*/*Z* ratio ~2:1). The product mixture was subjected to column chromatography on silica gel using first hexane and then chloroform (preliminarily treated as described above) to isolate 2.9 g of a mixture containing 88% of compound **VI** (yield 68%), 5% of *E*-**XV**, 2% of *Z*-**XV**, and 0.4 g of **IX** (yield 11%). By several experiments we obtained 9.57 g of a mixture containing 74% of **VI**, 9% of *E*-**XV**, and 5% of *Z*-**XV**. It was subjected to column chromatography on silica gel using hexane as eluent to isolate 0.25 g of pure *Z*-**XV**, 5.2 g of **VI**, and 4 g of fractions containing compounds **VI** and **XV** at different ratios.

Compound **VI**. ^{19}F NMR spectrum, δ_F, ppm: 81.0 (3F, CF_3), 49.4 (1F, F_A) and 43.5 (1F, F_B) ($C\mathbf{F}_2CF_3$), 72.9 (1F, 2-F_A) and 63.8 (1F, 2-F_B), 34.9 (1F, 6-F), 25.5 (1F, 3-F), 20.3 (1F, 5-F), 17.6 (1F, 4-F), 20.6 (1F, 2′-F), 30.5 (1F, 6′-F), 13.7 (1F, 4′-F), 2.2 and 2.0 (1F each, 3′-F, 5′-F); J_{FF}, Hz: J_{AB} = 280, $J_{2A,2B}$ = 203, $J_{3,4}$ = 20, $J_{3,5}$ = 8, $J_{3,6}$ = 23, $J_{4,5}$ = 18, $J_{4,6}$ = 10, $J_{5,6}$ = 18, $J_{6,2'}$ = 95, J(6-F,CF_3) = 20, $J_{6',A}$ = 8, $J_{6',B}$ = 61, $J_{6',2A}$ = 33, $J_{A,2B} = J_{B,2B}$ = 21. Found: $[M]^+$ 495.9743. $C_{16}F_{16}$. Calculated: *M* 495.9744.

Compound **IX**. mp 67–71°C (from hexane). ^{19}F NMR spectrum, δ_F, ppm: 80.9 (3F, CF_3), 47.8 (2F, $C\mathbf{F}_2CF_3$), 35.2 (1F, 3-F), 34.6 (1F, 6-F), 28.2 (1F, 4-F), 17.8 (1F, 5-F), 26.2 (2F, 2′-F, 6′-F), 13.2 (1F, 4′-F), 2.4 (2F, 3′-F, 5′-F); J_{FF}, Hz: $J_{3,4}$ = 8, $J_{3,5}$ = 9, $J_{3,6}$ = 23, $J_{4,5}$ = 18, $J_{4,6}$ = 11, $J_{5,6}$ = 20, $J_{3,2'(6')} \approx 40$, J(3-F,CF_3) = 9. Found: $[M]^+$ 473.9729. $C_{16}F_{14}O$. Calculated: *M* 473.9725.

Compound *Z*-**XV**. ^{19}F NMR spectrum, δ_F, ppm: 81.5 (3F, 1-$CF_2C\mathbf{F}_3$), 80.7 (3F, 2-$CF_2C\mathbf{F}_3$), 56.9 (1F, 1-CF_A) and 45.8 (1F, 1-CF_B), 42.1 (1F, 2-CF_A) and 34.1 (1F, 2-CF_B), 33.0 (1F, 6-F), 27.6 (1F, 3-F), 19.8 (1F,

5-F), 17.4 (1F, 4-F), 18.7 (1F, 2′-F), 35.4 (1F, 6′-F), 7.5 (1F, 2-F), 14.6 (1F, 4′-F), 2.1 (2F, 3′-F, 5′-F); J_{FF}, Hz: $J_{1A,1B}$ = 271, $J_{2A,2B}$ = 280, $J_{3,4}$ = 19, $J_{3,5}$ = 9, $J_{3,6}$ = 22, J(3-F, 2-CF_3) = 21, $J_{4,5}$ = 19, $J_{4,6}$ = 10, $J_{5,6}$ = 19, $J_{6,2'}$ = 67, J(6-F,1-CF_3) = 28, $J_{6',1B}$ = 130, $J_{6',2B}$ = 62. Found: $[M]^+$ 595.9684. $C_{18}F_{20}$. Calculated: *M* 595.9680.

Perfluoro(2-ethyl-1-phenyl-1,2-dihydrocyclobutabenzen-1-yl) cation (XI). Compound **IV**, 0.23 g (0.46 mmol), was dissolved in 0.99 g (4.57 mmol) of SbF_5, and 0.3 g of SO_2ClF was added. The resulting solution contained cation **XI** and no precursor **IV** (^{19}F NMR data). It was poured into an ice–water mixture and extracted with chloroform, the extract was dried over $MgSO_4$, and the solvent was distilled off to leave 0.17 g of a mixture of compounds **V** (*E*/*Z* ratio 45:55) and **IV** (*E*/*Z* ratio 70:30) at a ratio of ~93:7 (^{19}F NMR data). ^{19}F NMR spectrum of cation **XI**, δ_F, ppm: 82.8 (3F, CF_3), 51.4 (1F, F_A) and 42.9 (1F, F_B) (C**F**$_2$CF$_3$), 77.3 (1F, 4-F), 69.1 (1F, 6-F), 35.5 (2F, 3-F, 5-F), 30.3 (1F, 2-F), 59.0 (1F, 2′-F), 61.1 (1F, 6′-F), 71.5 (1F, 4′-F), 12.9 (2F, 3′-F, 5′-F); J_{FF}, Hz: $J_{A,B}$ = 285, $J_{3,4}$ = $J_{4,5}$ = 18, $J_{4,6}$ = 40, $J_{2,6'} \approx$ 65, $J_{B,6'}$ = 69, $J_{6,2'}$ = 170.

Perfluoro(2-ethyl-2-phenyl-1,2-dihydrocyclobutabenzen-1-yl) cation (XII). Compound **VI**, 0.24 g (0.48 mmol), was dissolved in 1.09 g (5.03 mmol) of SbF_5, and 0.19 g of SO_2ClF was added. The resulting solution contained cation **XII** and no precursor **VI** (^{19}F NMR data). It was poured into an ice–water mixture and extracted with chloroform, the extract was dried over $MgSO_4$, and the solvent was distilled off to leave 0.22 g of a mixture of compounds **VI** and **IX** at a ratio of 1:1 (^{19}F NMR data). ^{19}F NMR spectrum of cation **XII**, δ_F, ppm: 83.1 (3F, CF_3), 52.3 (2F, C**F**$_2$CF$_3$), 214.6 (1F, 1-F), 107.2 (1F, 4-F), 78.8 (1F, 6-F), 47.8 (1F, 3-F), 36.8 (1F, 5-F), 26.2 (2F, 2′-F, 6′-F), 20.8 (1F, 4′-F), 2.3 (2F, 3′-F, 5′-F); J_{FF}, Hz: $J_{1,4}$ = 40, $J_{3,4}$ = $J_{4,5}$ = 20, $J_{4,6}$ = 55.

Reaction of perfluoro(2-ethyl-1-phenyl-1,2-dihydrocyclobutabenzen-1-ol) (V) with aqueous potassium carbonate. Compound **V**, 0.21 g (0.43 mmol, *E*/*Z* ratio 40:60), was dissolved in 2.5 ml of chloroform, 2.5 g of a 10% aqueous solution of potassium carbonate (0.25 g, 1.81 mmol) was added, and the mixture was stirred for 2 h at 25°C, treated with water, acidified with 5% hydrochloric acid, and extracted with chloroform. The extract was dried over $MgSO_4$, and the solvent was distilled off. The residue was 0.2 g of a mixture of perfluoro[2-(prop-1-en-1-yl)benzophenone] (**XIII**, *E*/*Z* ratio ~90:10) and 2-(1,2,2,3,3,3-hexafluoropropyl)nonafluorobenzophenone (**XIV**) at a ratio of 62:38 (^{19}F NMR data). The product mixture was dissolved in 2 ml of chloroform, 2 g of 10% aqueous K_2CO_3 was added, and the mixture was stirred for 4 h at 22°C and treated as described above to isolate 0.19 g of a mixture of **XIII** and **XIV** at the same ratio. A 1.13-g portion of that mixture was subjected to column chromatography on silica gel using hexane as eluent to isolate 0.15 g of a mixture of *E*-**XIII** and *Z*-**XIII** (82:18), 0.48 g of *E*-**XIII**, and 0.36 g of **XIV**.

Compound *E*-**XIII**. mp 71–72.5°C (from hexane). ^{19}F NMR spectrum, δ_F, ppm: 93.7 (3F, CF_3), 30.9 (1F, 3-F), 24.7 (1F, 6-F), 17.2 (1F, 4-F), 16.0 (1F, 5-F), 21.7 (2F, 2′-F, 6′-F), 17.5 (1F, 4′-F), 2.8 (2F, 3′-F, 5′-F), 29.6 (1F, 1″-F), 0.8 (1F, 2″-F). J_{FF}, Hz: $J_{3,4}$ = 21, $J_{3,5}$ = 8, $J_{3,6}$ = 12, $J_{3,2''}$ = 18, $J_{4,5}$ = 19, $J_{4,6}$ = 8, $J_{5,6}$ = 22, $J_{1'',2''}$ = 141, J(1″-F, CF_3) = 21, J(2″-F, CF_3) = 11. Found: $[M]^+$ 473.9734. $C_{16}F_{14}O$. Calculated: *M* 473.9725.

Compound *Z*-**XIII**. ^{19}F NMR spectrum (from *E*/*Z* isomer mixture, ~82:18), δ_F, ppm: 92.9 (3F, CF_3), 29.8 (1F, 3-F), 25.4 (1F, 6-F), 17.7 (1F, 4-F), 16.5 (1F, 5-F), 21.5 (2F, 2′-F, 6′-F), 17.2 (1F, 4′-F), 2.8 (2F, 3′-F, 5′-F), 50.8 (1F, 1″-F), 15.5 (1F, 2″-F); J_{FF}, Hz: $J_{3,4}$ = 22, $J_{3,5}$ = 8, $J_{3,6}$ = 11, $J_{4,5}$ = 19, $J_{4,6}$ = 8, $J_{5,6}$ = 22, $J_{1'',2''}$ = 7, J(1″-F, CF_3) = 6, J(2″-F, CF_3) = 13. GC–MS data for *E*/*Z* mixture: *m*/*z* 474 $[M]^+$.

Ketone **XIV**. mp 57.5–58.5°C (from hexane). ^1H NMR spectrum: δ 6.35 ppm, d.d. ^{19}F NMR spectrum, δ_F, ppm: 79.1 (3F, CF_3), –38.4 (1F, CFH), 40.6 (1F, F_A) and 32.5 (1F, F_B) (C**F**$_2$CF$_3$), 28.8 (1F, 3-F), 23.7 (1F, 6-F), 14.9 (1F, 4-F), 13.8 (1F, 5-F), 21.9 (2F, 2′-F, 6′-F), 17.7 (1F, 4′-F), 2.5 (2F, 3′-F, 5′-F); J_{FF}, Hz: $J_{A,B}$ = 285, $J_{3,4}$ = 20, $J_{3,5}$ = 7, $J_{3,6}$ = 11, $J_{4,5}$ = 21, $J_{4,6}$ = 7, $J_{5,6}$ = 23, $^2J_{HF}$ = 43, ^3J(H, F_B) = 20. Found: $[M]^+$ 493.9792. $C_{16}HF_{15}O$. Calculated: *M* 493.9788.

Reaction of perfluorinated 1,1-diethyl- and 1,2-diethyl-1,2-dihydrocyclobutabenzenes II and III with pentafluorobenzene in SbF_5. *a*. A mixture of compounds **II** and **III** (45:55), 1.02 g (2.28 mmol), was dissolved in 4.93 g (22.74 mmol) of SbF_5. According to the ^{19}F NMR data, the solution contained perfluoro(2,2-diethyl-1,2-dihydrocyclobutabenzen-1-yl) cation (**XXIII**) and compound **III**. Pentafluorobenzene, 0.2 g (1.19 mmol), was added to the solution, and the mixture was kept for 23 h at 23°C; it contained cation **XXIII** and perfluoro(1,2-diethyl-2-phenylcyclobutabenzen-1-yl) cation (**XXV**) at a ratio of ~1:1, while no other products were present (^{19}F NMR data). The mixture was treated with water at 0–5°C, acidified with 5% hydrochloric acid, and extracted with chloro-

form. The extract was dried over $MgSO_4$, and the solvent was distilled off. The residue was 1.06 g of a mixture containing 8% of initial compound **II**, 7% of **XV** (yield 10%, calculated on the initial compound **III**), 26% of perfluoro(7,8-diethyl-8-phenylbicyclo-[4.2.0]octa-1,4,6-trien-3-one) (**XVI**, yield 38%), 20% of (*E*)-perfluoro{1-[2-(1-phenylprop-1-en-1-yl)phenyl]-propan-1-one} (*E*-**XVII**, yield 29%), 4% of (*Z*)-perfluoro{1-[2-(1-phenylprop-1-en-1-yl)phenyl]propan-1-one} (*Z*-**XVII**, yield 6%), and 28% of perfluoro(2,2-diethyl-1,2-dihydrocyclobutabenzen-1-one) (**XVIII**). A 0.93-g portion of the product mixture was subjected to column chromatography on silica gel using as eluent first carbon tetrachloride and then chloroform preliminarily treated with concentrated hydrochloric acid as described above. We thus isolated 0.19 g of compound **XVII** (*E*/*Z* ratio ~80:20) and 0.16 g of **XVI**. By repeated chromatographic separation of 0.19 g of isomer mixture **XVII** on silica gel (eluent hexane) we isolated 0.02 g of *E*-**XVII** and 0.03 g of *Z*-**XVII**.

Compound **XVI**. mp 89.5–91°C (from hexane). ^{19}F NMR spectrum, δ_F, ppm: 81.7 (3F, CF_3), 79.4 (3F, CF_3), 61.0 (1F, F_A) and 45.6 (1F, F_B, 8-C**F**$_2$CF$_3$), 48.8 (2F, 7-C**F**$_2$CF$_3$), 43.4 (1F, 2-F), 32.0 (1F, 4-F), 28.2 (1F, 5-F), 27.2 (2F, 2′-F, 6′-F), 15.0 (1F, 4′-F), 2.9 (2F, 3′-F, 5′-F); J_{FF}, Hz: $J_{A,B}$ = 288, $J_{2,4}$ = 7, $J_{2,2'(6')}$ = 42, $J_{4,5}$ = 7. Found: $[M]^+$ 573.9665. $C_{18}F_{18}O$. Calculated: *M* 573.9662.

Isomer *E*-**XVII**. ^{19}F NMR spectrum, δ_F, ppm: 91.2 (3F, 3″-F), 80.9 (3F, CF_2C**F**$_3$), 56.3 (1F, 2″-F), 41.7 (2F, C**F**$_2$CF$_3$), 29.9 (1F, 3-F), 29.6 (1F, 6-F), 18.0 (1F, 4-F), 13.5 (1F, 5-F), 24.0 and 25.0 (1F each, 2′-F, 6′-F), 13.5 (1F, 4′-F), 1.8 (2F, 3′-F, 5′-F); J_{FF}, Hz: $J_{3,4}$ = 20, $J_{3,5}$ = 7, $J_{3,6}$ = 10, $J_{3,2'(6')} \approx$ 10, $J_{4,5}$ = 21, $J_{4,6}$ = 8, $J_{5,6}$ = 21, J(6-F, CF_3) = 7, $J_{2'',3''}$ = 9, $J_{3'',2'(6')}$ = 4. Found: $[M]^+$ 573.9662. $C_{18}F_{18}O$. Calculated: *M* 573.9662.

Isomer *Z*-**XVII**. ^{19}F NMR spectrum, δ_F, ppm: 92.7 (3F, 3″-F), 80.7 (3F, CF_2C**F**$_3$), 57.6 (1F, 2″-F), 42.2 (1F, F_A) and 40.8 (1F, F_B) (C**F**$_2$CF$_3$), 30.7 (1F, 3-F), 28.9 (1F, 6-F), 17.6 (1F, 4-F), 13.7 (1F, 5-F), 24.9 (2F, 2′-F, 6′-F), 13.2 (1F, 4′-F), 1.9 (2F, 3′-F, 5′-F); J_{FF}, Hz: $J_{A,B}$ = 302, $J_{3,4}$ = 21, $J_{3,5}$ = 7, $J_{3,6}$ = 10, $J_{3,2'(6')}$ = 10, $J_{4,5}$ = 20, $J_{4,6}$ = 8, $J_{5,6}$ = 21, $J_{6,A}$ = 22, $J_{6,B}$ = 28, J(6-F, CF_3) = 7, $J_{2'',3''}$ = 9, $J_{2'',2'(6')}$ = 17. Found: $[M]^+$ 573.9656. $C_{18}F_{18}O$. Calculated: *M* 573.9662.

Compound **XVIII**. ^{19}F NMR spectrum, δ_F, ppm: 80.8 (6F, CF_3), 50.6 (4F, CF_2), 37.0 (1F, 6-F), 29.6 (1F, 4-F), 29.3 (1F, 3-F), 19.8 (1F, 5-F); J_{FF}, Hz: $J_{3,4}$ = 19, $J_{3,5}$ = 8, $J_{3,6}$ = 23, $J_{4,5}$ = 17, $J_{4,6}$ = 13, $J_{5,6}$ = 20. Found: $[M]^+$ 425.9729. $C_{12}F_{14}O$. Calculated: *M* 425.9725.

Cation **XXIII**. ^{19}F NMR spectrum, δ_F, ppm: 83.7 (6F, CF_3), 57.0 (4F, C**F**$_2$CF$_3$), 210.5 (1F, 1-F), 114.3 (1F, 4-F), 84.7 (1F, 6-F), 44.3 (1F, 3-F), 40.5 (1F, 5-F); J_{FF}, Hz: $J_{1,4}$ = 44, $J_{3,4}$ = $J_{4,5}$ = 20, $J_{4,6}$ = 62.

b. A mixture of compounds **II** and **III** (45:55), 1.13 g (2.52 mmol), was dissolved in 2.74 g (12.64 mmol) of SbF_5, 0.47 g (2.8 mmol) of pentafluorobenzene was added, the mixture was stirred for 11 h at 27°C and was then kept for 14 h at that temperature, and its ^{19}F NMR spectrum was recorded. It contained cations **XXIII** and **XXV** and perfluoro(2,2-diethyl-1-phenylcyclobutabenzen-1-yl) cation (**XXIV**) at a ratio of ~10:55:35, while no other products were present. Hexafluorobenzene, 1 ml, was added, and the mixture was treated as described above in *a*. We obtained 1.36 g of a mixture containing 5% of compound **II**, 44% of *E*-**XV** (yield 70%),** 3% of ketone **XVI** (yield 5%), <3% of **XVII**, 2% of **XVIII**, 12% of perfluoro(8,8-diethyl-7-phenylbicyclo[4.2.0]octa-1,4,6-trien-3-one) (**XIX**, yield 24%), 7% of perfluoro[4-(2,2-diethyl-1,2-dihydrocyclobutabenzen-1-ylidene)cyclohexa-2,5-dien-1-one] (**XX**, yield 14%), 5% of (*E*)-perfluoro[2-(pent-2-en-3-yl)benzophenone] (*E*-**XXI**, yield 10%), 7% of (*Z*)-perfluoro[2-(pent-2-en-3-yl)benzophenone] (*Z*-**XXI**, yield 14%), and 6% of perfluoro-{4-[5-(*cis*-1,2-diethyl-2-phenyl-1,2-dihydrocyclobutabenzen-1-yloxy)-2,2-diethyl-1,2-dihydrocyclobutabenzen-1-ylidene]cyclohexa-2,5-dien-1-one} (**XXII**, yield 6%). A 1.23-g portion of that mixture was subjected to column chromatography on silica gel using carbon tetrachloride as eluent to isolate 0.42 g of *E*-**XV**, 0.11 g of **XXI** (*E*/*Z* ratio 40:60), 0.9 g of **XIX**, 0.03 g of **XXII**, and 0.05 g of **XX**. By repeated chromatographic separation of 0.11 g of isomer mixture *E*-**XXI**/*Z*-**XXI** on silica gel (eluent hexane) we isolated 0.025 g of pure *Z*-**XXI**.

Cation **XXIV**. ^{19}F NMR spectrum, δ_F, ppm (from a mixture with **XXIII** and **XXV**): 83.8 (6F, CF_3), 53.4 (4F, C**F**$_2$CF$_3$), 82.8 (1F, 4-F), 78.3 (1F, 6-F), 38.7 (1F, 3-F), 32.5 (1F, 5-F), 59–61 (2F, 2′-F, 6′-F), 71.9 (1F, 4′-F), 13.0–14.5 (2F, 3′-F, 5′-F).

Compound *E*-**XV**. ^{19}F NMR spectrum, δ_F, ppm: 81.1 (3F, 1-CF_2C**F**$_3$), 81.0 (3F, 2-CF_2C**F**$_3$), 53.5 (1F, F_{1A}) and 47.6 (1F, F_{1B}, 1-C**F**$_2$CF$_3$), 46.6 (1F, F_{2A}) and 41.1 (1F, F_{2B}, 2-C**F**$_2$CF$_3$), 33.3 (1F, 6-F), 27.9 (1F, 3-F), 20.0 (1F, 5-F), 17.3 (1F, 4-F), 19.9 (1F, 2′-F), 30.2 (1F, 6′-F), 22.7 (1F, 2-F), 14.4 (1F, 4′-F), 2.1 and 2.0 (1F each, 3′-F, 5′-F); J_{FF}, Hz: $J_{1A,1B}$ = 274, $J_{2A,2B}$ =

** The yields of **XV**–**XVII** were calculated on the initial isomer **III**, and the yields of **XIX**–**XXII**, on isomer **II**.

288, $J_{2,6'}$ = 22, J(2-F, CF_3) = 17, $J_{3,4}$ = 19, $J_{3,5}$ = 9, $J_{3,6}$ = 22, J(3-F, CF_3) = 24, $J_{4,5}$ = 19, $J_{4,6}$ = 9, $J_{5,6}$ = 18, $J_{6,2'}$ = 69, J(6-F, CF_3) = 27, $J_{6',1B}$ = 59, $J_{6',1B}$ = 57, $J_{1A,2A}$ = 52, $J_{1B,2B}$ = 56, $J_{1A,2B}$ = 13. Found: $[M]^+$ 595.9673. $C_{18}F_{20}$. Calculated: M 595.9680.

Compound **XIX**. ^{19}F NMR spectrum, δ_F, ppm: 81.6 (6F, CF_3), 51.0 (2F, F_A) and 48.9 (2F, F_B) (C**F**$_2$CF$_3$), 33.8 (1F, 2-F), 30.4 (1F, 4-F), 27.9 (1F, 5-F), 28.3 (2F, 2′-F, 6′-F), 19.8 (1F, 4′-F), 3.4 (2F, 3′-F, 5′-F); J_{FF}, Hz: $J_{A,B}$ = 290, $J_{2,4}$ = 8, $J_{2,5}$ = 8, $J_{4,5}$ = 8, $J_{5,2'(6')}$ = 31. Found: $[M]^+$ 573.9655. $C_{18}F_{18}O$. Calculated: M 573.9662.

Compound **XX**. mp 88–89°C (after sublimation at a residual pressure of 2 mm, 30°C). ^{19}F NMR spectrum, δ_F, ppm: 81.6 (6F, CF_3), 53.8 (2F, F_A) and 48.0 (2F, F_B, C**F**$_2$CF$_3$), 39.6 (1F, 3-F), 27.9 (1F, 6-F), 26.1 (1F, 5-F), 19.9 (1F, 4-F), 27.3 (1F, 6′-F), 25.4 (1F, 2′-F), 14.1 and 13.3 (1F each, 3′-F, 5′-F); J_{FF}, Hz: $J_{A,B}$ = 290, $J_{3,4}$ = 18, $J_{3,5}$ = 13, $J_{3,6}$ = 22, $J_{4,5}$ = 18, $J_{4,6}$ = 8, $J_{5,6}$ = 19, $J_{6,B}$ = 90, $J_{3,2'}$ = 178. Found: $[M]^+$ 573.9655. $C_{18}F_{18}O$. Calculated: M 573.9662.

Isomer *E*-**XXI**. ^{19}F NMR spectrum (*E*/*Z* isomer mixture, ~40:60), δ_F, ppm: 95.7 (3F, 3″-F), 78.7 (3F, CF_3), 67.9 (1F, 2″-F), 53.3 (1F, F_A) and 52.0 (1F, F_B) (C**F**$_2$CF$_3$), 28.9 (1F, 3-F), 25.8 (1F, 6-F), 17.6 (1F, 4-F), 13.8 (1F, 5-F), 21.4 (2F, 2′-F, 6′-F), 16.8 (1F, 4′-F), 2.6 (2F, 3′-F, 5′-F); J_{FF}, Hz: $J_{A,B}$ = 285, $J_{3,4}$ = 21, $J_{3,5}$ = 7, $J_{3,6}$ = 10, $J_{4,5}$ = 20, $J_{4,6}$ = 9, $J_{5,6}$ = 22, $J_{B,3''}$ = 24, $J_{A,3''}$ = 10, $J_{2'',3''} \approx 8$, J(3″-F, CF_3) ≈ 7. Found: $[M]^+$ 573.9666 (*E*/*Z*, ~40:60). $C_{18}F_{18}O$. Calculated: M 573.9662.

Isomer *Z*-**XXI**. ^{19}F NMR spectrum, δ_F, ppm: 92.5 (3F, 3″-F), 77.9 (3F, CF_3), 58.7 (1F, 2″-F), 50.3 (1F, F_A) and 49.5 (1F, F_B) (C**F**$_2$CF$_3$), 29.6 (1F, 3-F), 26.2 (1F, 6-F), 18.2 (1F, 4-F), 14.4 (1F, 5-F), 21.4 (2F, 2′-F, 6′-F), 16.7 (1F, 4′-F), 2.6 (2F, 3′-F, 5′-F); J_{FF}, Hz: $J_{A,B}$ = 278, $J_{3,4}$ = 22, $J_{3,5}$ = 7, $J_{3,6}$ = 11, $J_{4,5}$ = 20, $J_{4,6}$ = 9, $J_{5,6}$ = 23, $J_{A,2''}$ = 29, $J_{B,2''}$ = 10, $J_{2'',3''}$ = 8, J(2″-F, CF_3) = 15.

Compound **XXII**. mp 160–166°C (from hexane–CH_2Cl_2). ^{19}F NMR spectrum, δ_F, ppm: 86.0 (3F, 1′-CF_2C**F**$_3$), 81.3 (9F, 1-CF_2C**F**$_3$, 2′-CF_2C**F**$_3$), 57.8 (1F, F_A) and 47.5 (1F, F_B) (2′-C**F**$_2$CF$_3$), 56.1 (1F, F_A) and 50.4 (1F, F_B) (1′-C**F**$_2$CF$_3$), 55.1 (1F, F_A) and 47.3 (1F, F_B) (1-C**F**$_2$CF$_3$), 52.3 (1F, F_A) and 49.0 (1F, F_B) (1-C**F**$_2$CF$_3$), 39.8 (1F, 3-F), 37.7 (1F, *o*′-F), 33.0 (1F, 3′-F), 31.7 (1F, 4-F), 31.0 (1F, 6′-F), 28.0 (1F, 6-F), 26.5 (1F, 6″-F), 25.4 (1F, 2″-F), 19.9 (1F, *o*-F), 21.3 and 16.8 (1F each, 4′-F, 5′-F), 15.2 and 14.2 (1F each, 3″-F, 5″-F), 14.6 (1F, *p*-F), 2.2 and 1.6 (1F each, *m*-F, *m*′-F); J_{FF}, Hz: $J_{1A,1B}$ = 297, $J_{3A,3B}$ = 284, $J_{2A,2B}$ = 282, $J_{A,B}$ = 272, $J_{2'',3}$ = 180, $J_{6,2B} \approx J_{6,3B}$ = 89, $J_{1A,1B}$ = 65, $J_{B,1A} \approx 50$, $J_{3',o} \approx 55$. Found: $[M]^+$ 1147.9433. $C_{36}F_{36}O_2$. Calculated: M 1147.9323.

Perfluoro(1,2-diethyl-2-phenyl-1,2-dihydrocyclobutabenzen-1-yl) cation (XXV). Compound **XV**, 0.17 g (0.28 mmol), was dissolved in 0.88 g (4.06 mmol) of SbF_5, and 0.21 g of SO_2ClF was added. According to the ^{19}F NMR data, the resulting solution contained cation **XXV** and no precursor **XV**. The solution was poured into an ice–water mixture and extracted with chloroform, the extract was dried over $MgSO_4$, and the solvent was distilled off. The residue, 0.14 g, was a mixture of 57% of *E*-**XV**, 23% of **XVI**, and 8% of ketone **XVII**. ^{19}F NMR spectrum of cation **XXV**, δ_F, ppm: 85.1 and 83.9 (3F each, CF_3), 59.9 (1F, F_A) and 51.0 (1F, F_B) (C**F**$_2$CF$_3$, $J_{A,B}$ = 290 Hz), 57.7 (1F, F_A) and 52.3 (1F, F_B) (C**F**$_2$CF$_3$, $J_{A,B}$ = 285 Hz), 140.7 (1F, 4-F), 91.5 (1F, 6-F), 52.8 (1F, 3-F), 39.4 (1F, 5-F), 27.2 (2F, 2′-F, 6′-F), 21.5 (1F, 4′-F), 7.3 (2F, 3′-F, 5′-F); J_{FF}, Hz: $J_{3,4} = J_{4,5}$ = 22, $J_{4,6}$ = 80.

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