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## **Reaction of Perfluorobenzocyclobutene with Excess Pentafluorobenzene in SbF**<sub>5</sub>

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**Abstract**—The reaction of perfluorobenzocyclobutene with excess pentafluorobenzene in SbF<sub>5</sub>, followed by hydrolysis, gave a mixture of perfluoro-1,3,3-triphenyl-1,3-dihydro-2-benzofuran-1-ol, perfluoro-1,1,2-triphenylbenzocyclobuten-5-one, and perfluoro-4-(2,2-diphenylbenzocyclobuten-1-ylidene)cyclohexa-2,5-dien-1-one. When the reaction mixture was treated for a long time with Olah's reagent (HF–pyridine), isomeric perfluoro-9,10-diphenyl-1,4-, -1,10-, -2,9-, and -9,10-dihydroanthracenes were formed and were converted to perfluoro-9,10-diphenylanthracene by the action of SbF<sub>5</sub>.

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Perfluoro-1,2-dialkyl-1-phenylbenzocyclobutenes in which the perfluoroalkyl groups in positions *1* and *2* are different react with antimony pentafluoride through opening of the four-membered ring and/or its expansion to five-membered ring, whereas the pentafluorobenzene ring remains unchanged [1]. The reaction of perfluoro-1,2-diethyl-1-phenylbenzocyclobutene with antimony pentafluoride involves both opening of the four-membered ring and unusual expansion of the pentafluorobenzene ring to seven-membered ring [2, 3]. This is the only example of cationoid expansion of polyfluorobenzene ring. In order to find out the possibility of analogous transformations in the series of perfluoro-1,2-diaryl-1-phenylbenzocyclobutenes it was necessary to study the behavior of perfluoro-1,1,2triphenylbenzocyclobutene under the action of antimony pentafluoride.

For this purpose, perfluorobenzocyclobutene 1 was treated with excess pentafluorobenzene (3 equiv) in  $SbF_5$  at 50–55°C. The subsequent hydrolysis of the







reaction mixture led to the formation of a mixture of perfluoro-1,3,3-triphenyl-1,3-dihydro-2-benzofuran-1ol **2**, perfluoro-1,1,2-triphenylbenzocyclobuten-5-one **3**, and perfluoro-4-(2,2-diphenylbenzocyclobuten-1ylidene)cyclohexa-2,5-dien-1-one **4**. In addition, the reaction mixture contained perfluoro-1-phenylbenzocyclobuten-1-ol **5** and perfluoro[1,2-phenylenebis-(phenylmethanone)] **6** (Scheme 1).

When the reaction mixture obtained under analogous conditions from compound 1 and 3 equiv of  $C_6F_5H$  in SbF<sub>5</sub> was treated first with a mixture of pyridine and hydrogen fluoride (Olah's reagent) over a period of 0.5 h and then with water, the product was a mixture of perfluoro-1,1,3-triphenyl-1,3-dihydro-2-benzofuran 7 and small amounts of perfluoro-9,10-diphenyl-9,10-dihydroanthracene 8, perfluoro-4-[(2-benzylphenyl)(phenyl)methylidene]cyclohexa-2,5-dien-1-one 9, and compounds 2, 5, and 6. In addition, perfluoro-1-phenylbenzocyclobutene 10 and perfluoro-1,2-diphenylbenzocyclobutene 11 were detected together with unidentified compounds (Scheme 2).

Prolonged treatment (65 h) with Olah's reagent of the mixture obtained from 1 and 3 equiv of  $C_6F_5H$  in SbF<sub>5</sub> at 50–55°C and subsequent hydrolysis afforded perfluoro-9,10-diphenyl-9,10-dihydroanthracene 8, perfluoro-9,10-diphenyl-1,10-dihydroanthracene 12, perfluoro-9,10-diphenyl-2,9-dihydroanthracene 13, perfluoro-9,10-diphenyl-1,4-dihydroanthracene 14, and compounds 2, 6, 10, and 11. By special experiments we showed that hydrolysis of a mixture of 11 and SbF<sub>5</sub> yields diketone 6 and that compound 8 or a mixture of 8, 12, 13, and 14 is thus converted to perfluoro-9,10-diphenylanthracene 15 (Scheme 2).

Compound **15** is likely to be formed as a result of disproportionation of **8**, **12**, **13**, or **14** and/or their defluorination under the given conditions. Disproportionation of polyfluorinated cyclohexadienes to the corresponding aromatic compounds and cyclohexenes by the action of SbF<sub>5</sub> was reported in [4, 5]; disproportionation [6, 7] and defluorination of perfluoro-1,2-dialkylindans with other fluorinated hydrocarbons in SbF<sub>5</sub> [8, 9] are also known.



Presumably, the reaction of 1 with excess pentafluorobenzene involves initial formation of perfluoro-1-phenylbenzocyclobutene 10 which generates cation A by the action of SbF<sub>5</sub> [10]; cation A takes up pentafluorobenzene molecule to give perfluoro-1,1-diphenylbenzocyclobutene 16, and the latter isomerizes to structure 11 via 1,2-migration of the pentafluorophenyl group in intermediate cation B and subsequent addition of fluoride ion to cation C (Scheme 3).

Cations **B** and **C** react further with pentafluorobenzene to produce perfluoro-1,1,2-triphenylbenzocyclobutene **17** which is likely to be converted in SbF<sub>5</sub> to cation **D** due to elimination of fluoride ion. The hydrolysis of **D** leads to compounds **3** and **4** as a result of nucleophile addition to sterically more accessible electrophilic centers (marked with an asterisk in structure **D** shown in Scheme 3). The possibility of pentafluorophenyl group migration to the neighboring cationic center was considered by us previously [1, 11], in particular in the isomerization of perfluoro(2-ethyl-1methyl-2-phenyl-benzocyclobuten-1-yl) cation to perfluoro(1-ethyl-2-methyl-2-phenylbenzocyclobuten-1yl) cation [1].

The formation of **11** by reaction of cation **E** with  $C_6F_5H$  seems less probable since its concentration in  $SbF_5$  is extremely low as compared to cation **A**. Furthermore, neither perfluoro-1-phenylindan **18** nor perfluoro-1-phenyltetralin **19** takes up pentafluoro-benzene at any benzylic position. This behavior of **18** and **19** may be rationalized by the fact that these compounds, as well as **10**, in  $SbF_5$  exist as the corre-

sponding perfluoro-1-phenylbenzocycloalken-1-yl cations [10], which should hamper reaction at the CF<sub>2</sub> group. Furthermore, increased dihedral angle between the pentafluorophenyl substituent and the plane including the tetrafluorobenzene ring, cationic center, and atoms linked thereto reduces steric accessibility of the cationic center in going from cation **A** to those derived from **18** and **19**. According to MNDO calculations, this dihedral angle in cations generated from **10**, **18**, and **19** is ~23, ~64, and ~85°, respectively [10].

Before proceeding to consider paths of formation of other compounds given in Schemes 1 and 2, it should be emphasized that the reaction mixture obtained from compound 1 and excess  $C_6F_5H$  in SbF<sub>5</sub> was a viscous semi-solid material. Therefore, its hydrolysis occurred at the phase boundary with water, so that additional transformations involving both components of the reaction mixture (SbF<sub>5</sub>, HF) and water could be possible in the interface layer. Here, local overheating cannot be ruled out.

Perfluorodihydroanthracenes 8 and 12–14 are likely to be formed as a result of transformations of perfluorotriphenylbenzocyclobutene 17 (Scheme 4). In keeping with the proposed mechanism, protonation of 17 with HF–SbF<sub>5</sub> yields cations  $F_1$  and  $F_2$  which undergo isomerization to cations  $G_1$  and  $G_2$  through opening of the four-membered ring in a way similar to that considered previously for polyfluoroalkylbenzocyclobutenes and perfluoro-1-(2-ethylphenyl)- and perfluoro-1-(4-ethylphenyl)benzocyclobutenes [7, 8, 12]. The cyclization of  $G_1$  and  $G_2$  with elimination of





proton gives compound **20**, and the latter isomerizes to dihydroanthracenes **8** and **12–14**.

Presumably, compound **20** is converted to isomeric structure **8** through transition state  $TS_1$  with participation of HF, whereas isomer **13** is formed through transition state  $TS_2$  (Scheme 4). The isomerization of **8** to dihydroanthracene **12** and then to **13** and **14** can be represented in a similar way. Analogous six-membered cyclic transition state was presumed previously, e.g., for the isomerization of 1,2,3,4,5,6,7-heptafluoroindene to 1,1,2,4,5,6,7-heptafluoroindene by the action of HF [13], as well as for the isomerization of terminal fluoroolefins into internal ones in the presence of antimony pentafluoride [14].

The reaction of  $G_1$  with water (Scheme 5) gives compound 21 whose fluorination and subsequent dehydrofluorination yields ketone 22. Abstraction of fluoride ion from the latter by the action of SbF<sub>5</sub> generates cation **H**, and cyclization of **H** followed by addition of fluoride ion leads to perfluoro-1,1,3-triphenyl-1,3-dihydro-2-benzofuran 7. Compound 7 is converted to perfluoro-1,3,3-triphenyl-1,3-dihydro-2-benzofuran-1-ol **2** via successive reactions with SbF<sub>5</sub> and H<sub>2</sub>O.

Alternatively, proton elimination from cation  $G_1$  produces compound 23 which is fluorinated to 24, and abstraction of fluoride ion from 24 yields cation I. Hydrolysis of I gives compound 9 and hydroxy derivative 25. The latter undergoes cyclization to 7 by the action of SbF<sub>5</sub>. Compound 24 can also be converted to cation J whose hydrolysis leads to ketone 22, and the subsequent steps leading to structure 7 are the same as those considered above (Scheme 5).

Scheme 6 outlines the transformation sequence of diphenylbenzocyclobutene 11 to diketone 6 on treatment with water of a mixture of 11 and  $SbF_5$ . Com-



pound 11 in SbF<sub>5</sub> is likely to lose fluoride ion, generating cation C which reacts with water to form hydroxy derivative 26. Compound 26 is converted to cation K by the action of SbF<sub>5</sub>, and intramolecular attack of the cationic center on the oxygen atom in K, followed by elimination of proton, yields epoxy derivative 27. The latter isomerizes to perfluoro-1,3-diphenyl-2-benzofuran 28 whose fluorination leads to perfluoro-1,3-diphenyl-1,3-dihydro-2-benzofuran 29 and then (after elimination of fluoride ion) to cation L. Opening of the five-membered ring in L gives cation M which is hydrolyzed with water to afford diketone 6. The proposed sequence of formation of diketone 6 from compound 11 is analogous to that given in [15]

for the transformation of perfluoro-1,2-diethylbenzocyclobutene to perfluoro-1,3-diethyl-1,3-dihydro-2benzofuran-1,3-diol in the reaction with  $SiO_2$ -SbF<sub>5</sub>. Presumably, compound **29** can also be formed from diphenylbenzocyclobutene **11** according to a scheme analogous to Scheme 5 (transformation of **17** to **7**).

The structure of compounds 2–4, 6–9, and 11–15 was determined by elemental analysis, high-resolution mass spectrometry, and <sup>19</sup>F NMR spectroscopy. The structure of 2 was also confirmed by <sup>13</sup>C NMR. In particular, the <sup>13</sup>C NMR spectrum of 2 in CDCl<sub>3</sub> contained no signal assignable to carbonyl carbon atom, and no carbonyl stretching band was observed in its IR spectrum. These findings ruled out alternative



**Fig. 1.** Structure of the molecule of perfluoro-4-[(2-benzyl-phenyl)(phenyl)methylidene]cyclohexa-2,5-dien-1-one (9) according to the X-ray diffraction data.

perfluoro[(2-benzoylphenyl)diphenylmethanol] structure. Compounds **5** and **10** were identified by comparing their <sup>19</sup>F NMR spectra with those of authentic samples [10]. The structure of **3** and **4** was determined by comparing their <sup>19</sup>F NMR spectra with those of perfluoro-1-phenyl-1,2-diethylbenzocyclobuten-5-one and perfluoro-4-(2,2-diethylbenzocyclobuten-1ylidene)cyclohexa-2,5-dien-1-one [16]. In addition, X-ray analysis of single crystals of **8**, **9**, and **13–15** was performed. Figure 1 shows the molecular structure of compound **9**.

The bond lengths in molecule 9 are close to the corresponding bond lengths in the molecule of 4-(diphenylmethylidene)cyclohexa-2,5-dien-1-one [17]. The diphenylmethylidene fragment in structure 9 slightly deviates from coplanarity with the cyclohexadienone fragment (torsion angle  $C^5C^4C^7C^8$  16.7°). Approximately similar torsion angle (14.5°) was observed in 4-(diphenylmethylidene)cyclohexa-2,5dien-1-one. However, the corresponding angle in perchloro-4-(diphenylmethyliden)cyclohexa-2,5-dien-1-one [18] is increased to 34.9°, presumably for steric reasons. Mutual orientation of the tetrafluorobenzene and pentafluorobenzene rings in molecule 9 is characterized by the torsion angle  $C^4 C^7 C^8 C^{13}$  61.7 and  $C^4C^7C^{14}C^{19}$  56.1°. Molecules 9 in crystal form centrosymmetric dimers with short contacts between the carbonyl groups ( $O \cdots C$  3.11 Å); also, a number of  $C-F\cdots\pi$  interactions are observed with the fluorinecentroid distances ranging from 3.46 to 3.73 Å. The molecular and crystal structures of cis-8, trans-8, and 13–15 were discussed in [19].

## EXPERIMENTAL

The analytical and spectral data were obtained at the Joint Chemical Service Center, Siberian Branch, Russian Academy of Sciences. The IR spectra were recorded on a Bruker Vector 22 spectrometer. The  $^{19}$ F NMR spectra of *cis*-8 in (CD<sub>3</sub>)<sub>2</sub>CO and of the other compounds in CDCl<sub>3</sub> and the <sup>13</sup>C NMR spectrum of 2 in CDCl<sub>3</sub> were measured on a Bruker AV-300 spectrometer at 282.4 ( $^{19}$ F) and 75.5 MHz ( $^{13}$ C); the chemical shifts are given downfield from  $C_6F_6$  (<sup>19</sup>F) or Me<sub>4</sub>Si; C<sub>6</sub>F<sub>6</sub> and CDCl<sub>3</sub> ( $\delta_C$  76.9 ppm) were used as internal standards. The elemental compositions were determined from the high-resolution mass spectra which were obtained on a Thermo Electron Corporation DFS instrument. GLC analysis was performed with an LKhM-72 chromatograph [4000×4-mm column packed with SKTFT-50 on Chromosorb W (15:100), oven temperature 50–270°C; carrier gas helium, flow rate 60 mL/min]. Compositions of the reaction mixtures and products were determined by GLC and <sup>19</sup>F NMR. Silica gel Merck (0.063-0.200 mm) was used for column chromatography.

The X-ray diffraction data for compound 9 were obtained on a Bruker Kappa Apex diffractometer (Mo  $K_{\alpha}$  radiation, 296 K). Monoclinic crystal system, space group  $P2_1/n$ ; unit cell parameters: a =10.5237(5), b = 13.8880(5), c = 16.2409(7) Å;  $\beta =$ 96.527(2)°; Z = 4;  $d_{calc} = 1.995 \text{ g/cm}^3$ ;  $\mu = 0.231 \text{ mm}^{-1}$ ;  $\theta \le 27.9^{\circ}$ . Total of 43786 reflection intensities were measured, including 5601 independent reflections. Final divergence factors: R = 0.0534 [for 4545 reflections with  $I > 2\sigma(I)$ ],  $wR_2 = 0.1367$  (for all independent reflections). The positions of non-hydrogen atoms were refined in anisotropic approximation. All calculations were performed using SHELXTL software package. The coordinates of atoms and geometric parameters were deposited to the Cambridge Crystallographic Data Centre [CCDC entry nos. 1554816 (9) and 1547527-1547531 (cis-8, trans-8, 13, 14, and 15, respectively).

Reaction of perfluorobenzocyclobutene 1 with pentafluorobenzene in antimony pentafluoride. *a*. A mixture of 1.77 g (7.14 mmol) of compound 1, 3.6 g (21.43 mmol) of pentafluorobenzene, and 9.29 g (42.85 mmol) of SbF<sub>5</sub> was heated for 50 h at 50–55°C in a sealed glass ampule. The ampule was cooled to 0°C and opened, the reaction mixture was transferred into an ice–water mixture (200 mL) with stirring, 30 mL of concentrated aqueous HCl was added, and the mixture was extracted with methylene chloride (3×20 mL). The extract was dried over MgSO<sub>4</sub>, and the solvent was distilled off. The residue was 4.8 g of a mixture containing (according to the GLC and <sup>19</sup>F NMR data), compounds **2** (50%), **3** (10.5%), **4** (3%), **5** (6%), and **6** (11%). By silica gel column chromatography (eluent chloroform) we isolated 0.1 g (14%) of **6**, 0.5 g (48%) of **2**, and 0.2 g of isomer mixture **3**/**4** (91:9). In addition, fractions containing compounds **6** and **2**, **2** and **3**, and others were isolated.

Perfluoro-1,3,3-triphenyl-1,3-dihydro-2-benzofuran-1-ol (2). mp 128-129.5°C (from hexane). IR spectrum (KBr), v, cm<sup>-1</sup>: 3604 (O-H), 1529, 1499 (C=C<sub>aron</sub>). <sup>13</sup>C NMR spectrum,  $\delta_{C}$ , ppm: 83.2 s (C<sup>3</sup>), 105.1 s (C<sup>1</sup>), 112.7 t (C<sup>i</sup>, <sup>2</sup>J<sub>CF</sub> ≈12 Hz), 113.0 t (C<sup>i</sup>, <sup>2</sup>J<sub>CF</sub> ≈ 12 Hz), 115.5 t (C<sup>i</sup>, <sup>2</sup>J<sub>CF</sub> ≈ 10 Hz), 122.9 d (C<sup>3a</sup>) or  $C^{7a}$ ,  ${}^{2}J_{CF} \approx 14$  Hz), 123.6 d ( $C^{7a}$  or  $C^{3a}$ ,  ${}^{2}J_{CF} \approx$ 16 Hz), 138–145 d.m (19C, C–F,  ${}^{1}J_{CF} \approx 250-260$  Hz). <sup>19</sup>F NMR spectrum,  $\delta_{\rm F}$ , ppm: 1.5 m (2F, *m*-F), 1.8 m (2F, m-F), 2.1 m (2F, m-F), 10.8 t.t (1F, p-F, J = 21), 4 Hz), 11.2 t.t (1F, p-F, J = 21, 4 Hz), 11.3 t.t (1F, p-F, J = 21, 4 Hz), 11.8 d.d.d (1F, 5-F or 6-F, J = 20, 19,5 Hz), 12.5 d.d.d (1F, 6-F or 5-F, J = 20, 19, 5 Hz), 20.3 m (1F, 4-F or 7-F), 20.3 m (2F, o-F), 21.0 m (1F, 7-F or 4-F), 21.4 m (2F, o-F), 22.1 m (2F, o-F). Found, %: C 44.49; H 0.22; F 51.13. [*M*]<sup>+</sup> 705.9726. C<sub>26</sub>HF<sub>19</sub>O<sub>2</sub>. Calculated, %: C 44.22; H 0.14; F 51.11. M 705.9673.

Perfluoro-1,1,2-triphenylbenzocyclobuten-5-one (3) and perfluoro-4-(2,2-diphenylbenzocyclobuten-1-ylidene)cyclohexa-2,5-dien-1-one (4) (mixture of isomers at a ratio of 91:9). mp 186-192°C (from hexane-CH<sub>2</sub>Cl<sub>2</sub>). IR spectrum (KBr), v, cm<sup>-1</sup>: 1659 (C=O), 1526, 1493 (C=C<sub>arom</sub>). <sup>19</sup>F NMR spectrum,  $\delta_F$ , ppm: isomer **3**: 2.4 m (4F, m-F, 1-C<sub>6</sub>F<sub>5</sub>), 3.4 m (2F, *m*-F, 2<sup>-</sup>C<sub>6</sub>F<sub>5</sub>), 11.6 t.t (2F, *p*-F, 1<sup>-</sup>C<sub>6</sub>F<sub>5</sub>, J = 21, 4 Hz), 18.2 t.t (1F, *p*-F, 2-C<sub>6</sub>F<sub>5</sub>, J = 21, 5 Hz), 22.7 m (4F, o-F, 1-C<sub>6</sub>F<sub>5</sub>), 26.9 d.d (1F, 4-F,  $J_{3,4} = J_{4,6} = 8$  Hz), 27.3 m (2F, *o*-F, 2<sup>-</sup>C<sub>6</sub>F<sub>5</sub>), 28.0 t.d.d (1F, 3-F,  $J_{3,o-F} = 38$ ,  $J_{3,6} = J_{3,4} = 8$  Hz), 28.7 quint.d.d (1F, 6-F,  $J = 14, J_{3,6} =$  $J_{4,6} = 8$  Hz); isomer 4: 2.7 m (4F, *m*-F, C<sub>6</sub>F<sub>5</sub>), 11.0 d (1F, 3'-F,  $J_{2',3'}$  = 11 Hz), 11.9 t.t (2F, *p*-F, C<sub>6</sub>F<sub>5</sub>, *J* = 21, 4 Hz), 12.0 d (1F, 5'-F,  $J_{5',6'}$  = 11 Hz), 15.6 d.d.d (1F, 4-F,  $J_{3,4} = 19$ ,  $J_{4,5} = 18$ ,  $J_{4,6} = 5$  Hz), 23.9 m (1F, 6-F), 24.1 m (4F, o-F, C<sub>6</sub>F<sub>5</sub>), 25.6 d.d.d (1F, 6'-F,  $J_{3,6'}$  = 163,  $J_{5',6'} = 11, J_{2',6'} = 6$  Hz), 25.8 m (1F, 5-F), 25.8 m (1F, 2'-F), 39.0 d.d.d.d (1F, 3-F,  $J_{3,6'} = 163$ ,  $J_{3,4} = J_{3,6} = 19$ ,  $J_{3,5} = 12$  Hz). Found, %: C 46.44; F 51.05.  $[M]^+$  669.9647. C<sub>26</sub>F<sub>18</sub>O. Calculated, %: C 46.59; F 51.02. M 669.9662.

**Perfluoro[1,2-phenylenebis(phenylmethanone)]** (6). mp 124–126°C (from hexane). IR spectrum (KBr), v, cm<sup>-1</sup>: 1699, 1685 (C=O), 1524, 1505 (C=C<sub>arom</sub>). <sup>19</sup>F NMR spectrum,  $\delta_F$ , ppm: 2.6 m (4F, *m*-F), 16.2 m (2F, 4-F, 5-F), 17.1 t.t (2F, *p*-F, *J* = 21, 6 Hz), 21.7 m (4F, *o*-F), 24.4 m (2F, 3-F, 6-F). Found: [*M*]<sup>+</sup> 537.9666. C<sub>20</sub>F<sub>14</sub>O<sub>2</sub>. Calculated: *M* 537.9675.

b. A mixture of 0.43 g (1.74 mmol) of compound 1, 0.87 g (5.21 mmol) of pentafluorobenzene, and 3.01 g (13.88 mmol) of SbF<sub>5</sub> was heated for 30 h at 50–55°C in a sealed ampule. The ampule was cooled to 0°C and opened, and the mixture was added to 10 mL of HFpyridine at 0-20°C. The mixture was stirred for 0.5 h at 25°C, cooled to 0°C, and transferred into an icewater mixture (100 mL) with stirring. The mixture was then treated with 10 mL of concentrated aqueous HCl and extracted with methylene chloride  $(3 \times 10 \text{ mL})$ , the extract was dried over MgSO<sub>4</sub>, and the solvent was distilled off. The residue was 1.06 g of a mixture containing (GLC, <sup>19</sup>F NMR) compounds 2 (4%), 5 (7%), 6 (5%), 7 (22%), cis-8 (4%), 9 (4%), and 10 (10%) and isomers **11a** (16%) and **11b** (10%). By column chromatography on silica gel using first carbon tetrachloride and then chloroform as eluents we isolated 0.46 g of a mixture of 7, cis-8, 10, 11a, and **11b** at a ratio of 28:5:23:27:17 (<sup>19</sup>F NMR) and 0.02 g (3.5%) of 9. Repeated chromatography with hexane as eluent afforded 0.09 g of a mixture of 10 and 11a (60:40; <sup>19</sup>F NMR), 0.06 g of 7, and 0.12 g of a mixture of 7 and 11b (45:55) (<sup>19</sup>F NMR).

**Perfluoro-1,1,3-triphenyl-1,3-dihydro-2-benzofuran (7).** mp 168–171°C (from hexane). <sup>19</sup>F NMR spectrum,  $\delta_F$ , ppm: 1.8 m (4F, *m*-F, C<sub>6</sub>F<sub>5</sub>), 2.4 m (2F, *m*-F), 12.0 t.t (1F, *p*-F, *J* = 21, 4 Hz), 12.1 t.t (1F, *p*-F, *J* = 22, 4 Hz), 12.9 t.t (1F, *p*-F, *J* = 21, 5 Hz), 13.9 t.d (1F, 5-F, *J* = 19, 4 Hz), 14.3 t.t (1F, 6-F, *J* = 19, 5 Hz), 21.5 m (2F, *o*-F), 21.8 m (1F, 4-F or 7-F), 22.2 m (3F, 7-F or 4-F, *o*-F), 22.9 m (2F, *o*-F), 88.9 t (1F, 3-F, *J* = 27 Hz). Found:  $[M]^+$  707.9623. C<sub>26</sub>F<sub>20</sub>O. Calculated: *M* 707.9624.

**Perfluoro-4-[(2-benzylphenyl)(phenyl)methylidene]cyclohexa-2,5-dien-1-one (9).** mp 189–192°C (from hexane–CHCl<sub>3</sub>). <sup>19</sup>F NMR spectrum,  $\delta$ , ppm: 1.9 m (1F, *m*-F, C<sub>6</sub>F<sub>5</sub>), 2.0 m (1F, *m*-F, C<sub>6</sub>F<sub>5</sub>), 2.7 m (2F, *m*-F, CF<sub>2</sub>C<sub>6</sub>F<sub>5</sub>), 13.5 d (1F, 2-F, *J* = 9 Hz), 13.6 d (1F, 2-F, *J* = 10 Hz), 14.2 d.d.d and 14.6 d.d.d (1F each, 4'-F, 5'-F, *J* = 21, 21, 6 Hz), 14.9 t (1F, *p*-F, CF<sub>2</sub>C<sub>6</sub>F<sub>5</sub>, *J* = 21 Hz), 15.8 t.t (1F, *p*-F, C<sub>6</sub>F<sub>5</sub>, *J* = 21, 5 Hz), 21.8 m (2F, *o*-F, CF<sub>2</sub>C<sub>6</sub>F<sub>5</sub>), 23.2 m (1F, *o*-F, C<sub>6</sub>F<sub>5</sub>), 24.7 m (1F, 6'-F), 25.5 d.d (1F, 5-F, *J* = 9, 6 Hz), 26.6 m (1F, *o*-F, C<sub>6</sub>F<sub>5</sub>), 27.8 m (2F, 3-F, 3'-F), 86.1 m and 80.2 m (1F each, CF<sub>2</sub>, <sup>2</sup>*J* = 287 Hz). Found:  $[M]^+$  707.9621. C<sub>26</sub>F<sub>20</sub>O. Calculated: *M* 707.9624.

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**Perfluoro**-*cis*(or *trans*)-1,2-diphenylbenzocyclobutene (11a). <sup>19</sup>F NMR spectrum (from a mixture with 10),  $\delta_F$ , ppm: 1.8 m (4F, *m*-F), 13.4 t (2F, *p*-F, *J* = 21 Hz), 18.2 m (2F, 4-F, 5-F), 22.9 m (4F, *o*-F), 26.3 m (2F, 3-F, 6-F), 30.6 m (2F, 1-F, 2-F). Found:  $[M]^+$  543.9742. C<sub>20</sub>F<sub>16</sub>. Calculated: *M* 543.9739.

**Perfluoro**-*trans*(or *cis*)-1,2-diphenylbenzocyclobutene (11b). <sup>19</sup>F NMR spectrum (from a mixture with 7),  $\delta_F$ , ppm: 3.0 m (4F, *m*-F), 14.8 t (2F, *p*-F, *J* = 21 Hz), 18.2 m (2F, 4-F, 5-F), 23.3 m (4F, *o*-F), 25.6 m (2F, 1-F, 2-F), 26.3 m (2F, 3-F, 6-F). Found:  $[M]^+$  543.9740. C<sub>20</sub>F<sub>16</sub>. Calculated: *M* 543.9739.

c. A mixture of 0.75 g (3.02 mmol) of compound 1, 1.52 g (9.05 mmol) of pentafluorobenzene, and 5.22 g (24.08 mmol) of SbF<sub>5</sub> was heated for 30 h at 50–55°C in a sealed glass ampule. The ampule was cooled to 0°C and opened, and the mixture was transferred into 15 mL of HF-pyridine at 0-20°C. The mixture was stirred for 65 h at 25°C, cooled to 0°C, and transferred into an ice-water mixture (250 mL) with stirring, 30 mL of concentrated aqueous HCl was added, and the mixture was extracted with methylene chloride  $(3 \times 20 \text{ mL})$ . The extract was dried over MgSO<sub>4</sub>, the solvent was distilled off, the residue was treated with 5 mL of chloroform, and the precipitate, 0.2 g (9.6%) of trans-8 was filtered off. The filtrate was evaporated. and the residue, 1.79 g, was a mixture containing (according to the GLC and <sup>19</sup>F NMR data) compounds 2 (27%), 6 (4%), cis-8 (11%), 10 (2%), 11a (9%), 11b (2%), 12 (10%), 13 (12%), and 14 (2%). By column chromatography on silica gel using carbon tetrachloride as eluent we isolated from that mixture 0.51 g of a solid consisting of cis-8, 12, 13, and 14 at a ratio of 30:30:35:5 (<sup>19</sup>F NMR). Recrystallization from chloroform gave 0.09 g (9.4%) of cis-8. The mother liquor was evaporated to leave 0.42 g of product mixture which was subjected to repeated chromatography with hexane as eluent. We thus isolated 0.011 g (1.7%)of 14, 0.09 g of a mixture of cis-8, 12, 13, and 14 at a ratio of 6:6:68:20 (<sup>19</sup>F NMR) and 0.08 g of a mixture of cis-8, 12, and 13 at a ratio of 29:42:29 (<sup>19</sup>F NMR). Found, %: C 45.12; F 54.73. Found:  $[M]^+$  691.9680. C<sub>26</sub>F<sub>20</sub>. Calculated, %: C 45.11; F 54.89. M 691.9675.

**Perfluoro**-*cis*-9,10-diphenyl-9,10-dihydroanthracene (*cis*-8). mp 267–268°C (from CHCl<sub>3</sub>; sealed capillary). <sup>19</sup>F NMR spectrum,  $\delta_F$ , ppm: 0.8 m (4F, *m*-F), 10.6 t (2F, *p*-F, *J* = 21 Hz), 14.5 m (4F, 2-F, 3-F, 6-F, 7-F), 23.4 m (4F, *o*-F), 26.8 m (4F, 1-F, 4-F, 5-F, 8-F), 38.6 m (2F, 9-F, 10-F). Found, %: C 44.95.  $[M]^+$  691.9673. C<sub>26</sub>F<sub>20</sub>. Calculated, %: C 45.11. *M* 691.9675.

**Perfluoro**-*trans*-9,10-diphenyl-9,10-dihydroanthracene (*trans*-8). mp 355–360°C (decomp., from acetone; sealed capillary). <sup>19</sup>F NMR spectrum,  $\delta_F$ , ppm: 0.9 m (4F, *m*-F), 9.8 t (2F, *p*-F, *J* = 21 Hz), 13.3 m (4F, 2-F, 3-F, 6-F, 7-F), 21.3 m (4F, *o*-F), 24.7 m (2F, 9-F, 10-F), 26.0 m (4F, 1-F, 4-F, 5-F, 8-F). Found, %: C 45.21. [*M*]<sup>+</sup> 691.9670. C<sub>26</sub>F<sub>20</sub>. Calculated, %: C 45.11. *M* 691.9675.

**Perfluoro-9,10-diphenyl-1,10-dihydroanthracene** (12). NMR spectrum<sup>19</sup>F (from a mixture with *cis*-8 and 13),  $\delta_F$ , ppm: -0.3 m (2F, *m*-F, 9-C<sub>6</sub>F<sub>5</sub>), 1.6 m (2F, *m*-F, 10-C<sub>6</sub>F<sub>5</sub>), 7.9 m (1F, 3-F), 10.6 t (1F, *p*-F, 9- or 10-C<sub>6</sub>F<sub>5</sub>, J = 21 Hz), 10.6 m (1F, 2-F), 10.8 t (1F, *p*-F, 10- or 9-C<sub>6</sub>F<sub>5</sub>, J = 21 Hz), 13.5 d.d.d.d (1F, 7-F, J = 20, 20, 7, 5 Hz), 15.5 d.d.d (1F, 6-F, J = 20, 20, 7 Hz), 21.7 m (2F, *o*-F, 10-C<sub>6</sub>F<sub>5</sub>), 23.1 m (1F, *o*-F, 9-C<sub>6</sub>F<sub>5</sub>), 24.0 m (1F, *o*-F, 9-C<sub>6</sub>F<sub>5</sub>), 25.0 m (1F, 5-F), 27.3 m (1F, 10-F), 34.6 m (1F, 8-F), 47.2 m (1F, 4-F), 80.6 m and 76.4 m (1F each, 1-F, <sup>2</sup>J = 302 Hz).

**Perfluoro-9,10-diphenyl-2,9-dihydroanthracene** (13). <sup>19</sup>F NMR spectrum (from a mixture with *cis-8*, 12, and 14),  $\delta_F$ , ppm: 1.1 m (2F, *m*-F), 1.8 m (2F, *m*-F), 8.6 m (1F, 3-F), 11.0 t (1F, *p*-F, J = 21 Hz), 11.2 t (1F, *p*-F, J = 21 Hz), 14.0 d.d.d. (1F, 6-F, J = 20, 20, 7,6 Hz), 15.6 d.d.d (1F, 7-F, J = 20, 20, 7 Hz), 20.6 m (1F, *o*-F, 10-C<sub>6</sub>F<sub>5</sub>), 21.0 m (1F, 4-F), 21.2 m (1F, *o*-F, 10-C<sub>6</sub>F<sub>5</sub>), 21.6 m (2F, *o*-F, 9-C<sub>6</sub>F<sub>5</sub>), 25.6 m (2F, 5-F, 8-F), 27.6 m (1F, 9-F), 45.1 m (1F, 1-F), 57.4 m and 56.4 m (1F each, 2-F, <sup>2</sup>J = 302 Hz).

**Perfluoro-9,10-diphenyl-1,4-dihydroanthracene** (14). mp 232–237°C (decomp., from hexane–CHCl<sub>3</sub>; sealed capillary). <sup>19</sup>F NMR spectrum,  $\delta_F$ , ppm: –0.1 m (4F, *m*-F), 8.2 m (2F, 2-F, 3-F), 11.2 t (2F, *p*-F, *J* = 21 Hz), 15.4 m (2F, 6-F, 7-F), 22.7 m (2F, 5-F, 8-F), 24.1 m (4F, *o*-F), 68.4 m (4F, 1-F, 4-F). Found:  $[M]^+$  691.9684. C<sub>26</sub>F<sub>20</sub>. Calculated: *M* 691.9675.

**Reaction of perfluoro-1,2-diphenylbenzocyclobutene (11) with SbF<sub>5</sub>.** A mixture of compounds **10** (0.11 mmol) and **11a** (0.09 mmol), 0.094 g, was dissolved in 0.57 g (2.63 mmol) of SbF<sub>5</sub>, and the mixture was kept for 5 h at 25°C. It was then treated with water at 0–20°C and extracted with methylene chloride ( $3 \times 2$  mL), the extract was dried over MgSO<sub>4</sub>, and the solvent was distilled off. The residue was 0.078 g of a mixture of compounds **5**, **6**, **10**, and **11a** at a ratio of 50:40:5:5 (<sup>19</sup>F NMR).

**Perfluoro-9,10-diphenylanthracene (15).** *a*. A solution of 0.08 g (0.12 mmol) of *trans*-**8** in 1.02 g

(4.70 mmol) of SbF<sub>5</sub> was stirred for 50 h at 25°C. The mixture was treated with water at 0–20°C and extracted with methylene chloride (3×2 mL), the extract was dried over MgSO<sub>4</sub>, and the solvent was distilled off. The residue was 0.07 g of a dark material which was subjected to column chromatography on silica gel using chloroform as eluent to isolate 0.05 g (66%) of **15**. mp 220–221°C (from hexane–CH<sub>2</sub>Cl<sub>2</sub>). <sup>19</sup>F NMR spectrum,  $\delta_F$ , ppm: –0.2 m (4F, *m*-F), 9.8 t (2F, *p*-F, *J* = 21 Hz), 11.6 m (4F, 2-F, 3-F, 6-F, 7-F), 20.9 m (4F, 1-F, 4-F, 5-F, 8-F), 21.1 m (4F, *o*-F). Found:  $[M]^+$  653.9704. C<sub>26</sub>F<sub>18</sub>. Calculated: *M* 653.9707.

b. As described above in a, 0.057 g of **15** was obtained from 0.12 g (0.17 mmol) of a mixture of *cis*-**8**, **12**, **13**, and **14** at a ratio of 30:30:35:5 and 1.88 g (8.67 mmol) of SbF<sub>5</sub>.

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