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Pentafluorophenylation of Perfluorinated Benzocyclobutene, Indan, and Tetralin by Reaction with Pentafluorobenzene in SbF_5 *

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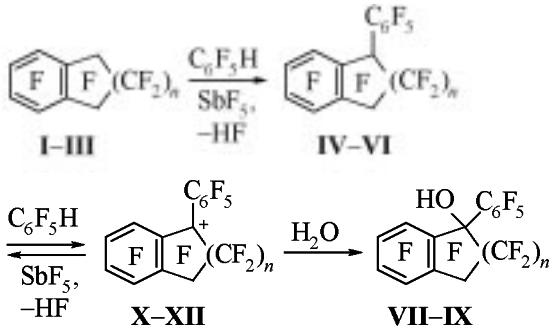
Abstract—The reactivity of perfluorinated benzocyclobutene, indan, and tetralin in reaction with pentafluorobenzene in SbF_5 medium, and also the relative stability of generated therewith perfluoro-1-phenylbenzocycloalkenyl cations decrease with increasing alicyclic fragment in the benzocycloalkene. Treating the solutions of salts of the above cations with anhydrous HF results in the corresponding perfluoro-1-phenylbenzocycloalkenes, and the hydrolysis of salts furnishes their 1-hydroxy derivatives. In a reaction of 1-hydroxyperfluoro-1-phenylbenzocyclobutene, -indan, and -tetralin with $SOCl_2$ the hydroxy group is replaced by chlorine. Besides with indan and tetralin derivatives form respectively 7-pentafluorophenyloctafluoro-3-chlorobicyclo[4.3.0]hepta-1,4,6-triene and 7-pentafluorophenyldecafluoro-3-chlorobicyclo[4.4.0]octa-1,4,6-triene.

We formerly investigated cationoid rearrangements of perfluorinated benzocyclobutene (**I**), indan (**II**), and tetralin (**III**) and their perfluoroalkyl derivatives effected by Lewis acids [1–4]. Recently by an example of reaction between perfluoro-1-phenylindan (**IV**) we discovered skeletal rearrangements of perfluoro-1-arylbenzocycloalkenes [5]. To reveal the general rules governing cationoid transformations in this kind of compounds it would be desirable to study also the reaction between antimony pentafluoride and pentafluoro-1-phenylbenzocyclobutene (**V**) and perfluoro-1-phenyltetralin (**VI**). However the latter compounds were not described. At the same time reactions of fluoroindan (**II**) [5] and perfluoroalkylbenzenes [6] with pentafluorobenzene in the presence of SbF_5 resulting in the corresponding pentafluorophenyl derivatives are known.

Scheme 1.



n = 0 (**I, V, VII, XI**), 1 (**II, IV, VIII, X**), 2 (**III, VI, IX, XII**).

In this connection in the present study the possibility of formation of phenylbenzocycloalkenes **V, VI** in reaction of compounds **I** and **III** with pentafluorobenzene in the presence of SbF_5 was investigated and relative reactivity of benzocycloalkenes **I–III** in this process was established.

We demonstrated that compounds **II** [5], **I**, and **III** reacted with equimolar amount of pentafluorobenzene in the presence of SbF_5 to furnish after successive treatment with anhydrous HF and water the corresponding pentafluorophenyl derivatives **IV–V**. Besides from compounds **I** and **II** formed respectively 1-hydroxyperfluoro-1-phenylbenzocyclobutene (**VII**) (at **VII : V** ratio ~1 : 1) and 1-hydroxyperfluoro-1-phenylindan (**VIII**) (at **VIII : IV** ratio 1 : 5 [5]). Compound **VI** after the above treatment was isolated without admixture of 1-hydroxyperfluoro-1-phenyltetralin (**IX**). The hydrolysis of reaction mixtures without preliminary treatment with HF afforded hydroxy derivatives **VII–IX** (Scheme 1).

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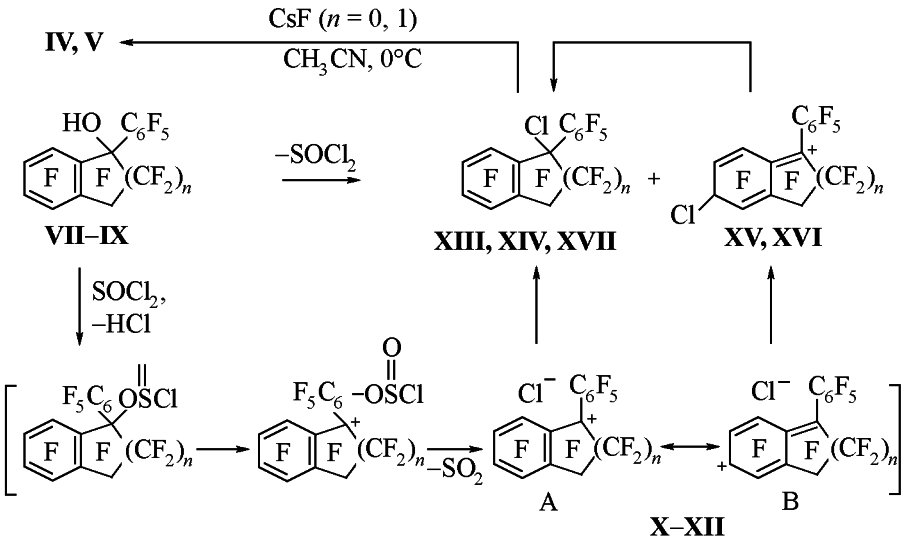
Scheme 2.



n = 0 (**VII, XI, XIII**), 1 (**VIII, X, XIV, XV**), 2 (**IX, XII, XVI, XVII**).

The reaction of compounds **II** [5] and **I** with pentafluorobenzene goes to completion at 20–25°C in the presence of 3 mol of SbF_5 per 1 mol of substrate, but compound **III** under these conditions reacts only partially. A complete conversion of the latter is attained at 50–55°C in the presence of 5 mol of SbF_5. At the use of 1.2 mol of SbF_5 per 1 mol of compound **I** the reaction does not go to completion even when the temperature is raised to 50°C.

By concurrent reactions method we revealed that the rate of reaction with pentafluorobenzene in the SbF_5 medium is higher for fluorobenzocyclobutene (**I**) than for fluoroindan (**II**). Thus the relative reactivity of benzocycloalkenes toward pentafluorobenzene depends on the size of the alicyclic fragment in the substrate and decreases in going from fluorocyclobutene (**I**) to indan (**II**) and tetralin (**III**), **I** > **II** > **III**, in agreement with the reactivity of these compounds in reactions with fluoroolefins [7, 8].

Perfluoro-1-phenylbenzocycloalkenes **IV**–**VI** in the antimony pentafluoride medium exist as salts of perfluoro-1-phenylindanyl (**X**) [5], perfluoro-1-phenylbenzobutenyl (**XI**), and perfluoro-1-phenyltetralinyl (**XII**) cations respectively. Actually, on pentafluorobenzene addition to the solution of compound **I** or **III** in excess SbF_5 cations **XI** and **XII** are generated (Scheme 1). These ions also arise on dissolving compounds **V, VI** in a system SbF_5–SO_2ClF.

It was shown that the relative stability of phenylbenzocycloalkenyl cations decreased in the series **XI** > **X** > **XII**. For instance, on adding compound **V** to a solution of cation **X** salt in SbF_5–SO_2ClF ion **X** transforms into its precursor **IV**, and ion **XI** is generated from compound **V**. Similarly was demonstrated the greater relative stability of cation **X** than that of ion **XII**.

The experimental data obtained in solution are in agreement with the calculated by MNDO method relative stability of cations **X**–**XII** in the gas phase. It turned out that the calculated relative stability of phenylindanyl (**X**) and phenyltetralinyl (**XII**) cations was lower than that of phenylbenzocyclobutenyl cation (**XI**) by 1.4 and 11.6 kcal mol^{-1} respectively.

The different relative stability of cations **X**–**XII** apparently governs the amount of hydroxy derivatives **VII**–**IX** arising on treating the products of reaction between compounds **I**–**III** and fluorobenzene first with anhydrous HF and then with water (Scheme 1). Actually, the lower the cation stability, the more the equilibrium is shifted by HF toward the cation precursor **IV**–**VI**, and the less hydroxy derivative forms at the subsequent treatment with water.

In reaction of hydroxy derivatives **VII**–**IX** with thionyl chloride the process direction depends on the size of the alicycle in the substrate. Thus hydroxybenzocyclobutene **VII** reacted partially with $SOCl_2$ yielding 1-chloroperfluoroalkene **XIII** already at room temperature. Compound **XIII** was obtained in high yield at boiling compound **VII** with excess $SOCl_2$ in CCl_4 (Scheme 2).

Hydroxyindan **VIII** under similar conditions forms a mixture of 1-pentafluorophenyloctafluoro-1-chloro-

Table 1. Calculated (MNDO) total (q_c^{tot}) and π-charges (q_c^{π}) on carbon atoms of cations **X**–**XII** (notation of atoms as in Table 2)

Cation no.	q_c^{tot} (q_c^{π})									
	C^1	C^2	C^3	C^4	C^5	$C^{2'}$	$C^{6'}$	$C^{3'}$	$C^{5'}$	$C^{4'}$
X[a]	0.284	0.382	0.070	0.327	0.215	0.231	0.254	0.120	0.115	0.249
	(0.390)	(0.198)	(–0.116)	(0.170)	(0.009)	(0.018)	(0.042)	(–0.079)	(–0.080)	(0.061)
XI[b]	0.242	0.358	0.095	0.264	0.236	0.281	0.297	0.083	0.080	0.308
	(0.360)	(0.148)	(–0.094)	(0.095)	(0.013)	(0.085)	(0.106)	(–0.109)	(–0.110)	(0.129)
XII[c]	0.280	0.378	0.059	0.354	0.190	0.222	0.238	0.130	0.129	0.229
	(0.398)	(0.215)	(–0.120)	(0.201)	(0.003)	(0.005)	(0.020)	(–0.069)	(–0.071)	(0.037)

[a] $C^{1'}$, –0.237 (–0.262); C^{1a}, –0.163 (–0.156); C^{5a}, –0.096 (–0.021); C^6, 0.450 (0.297); C^7, 0.381 (0.294).

[b] $C^{1'}$, –0.195 (–0.227); C^{1a}, –0.189 (–0.162); C^{5a}, –0.129 (–0.049); C^6, 0.508 (0.303).

[c] $C^{1'}$, –0.270 (–0.287); C^{1a}, –0.126 (–0.149); C^{5a}, –0.062 (–0.000); C^6, 0.428 (0.297); C^7, 0.371 (0.291) ; C^8, 0.384 (0.295).

indan (**XIV**) and 7-pentafluorophenyloctafluoro-3-chlorobicyclo[4.3.0]hepta-1,4,6-triene (**XV**), the latter prevailing. The reaction carried out at more stringent conditions (90°C) with no solvent gives rise predominantly chloroindan **XIV** with some triene **XV** that at longer process isomerizes into chloroindan **XIV**. Chloro derivatives **XIII** and **XIV** heated with cesium fluoride in acetonitrile transform into the corresponding perfluoro derivatives **V** and **IV** (Scheme 2).

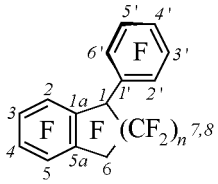
The treatment of hydroxytetralin **IX** under conditions of hydroxyindan **VIII** reaction with $SOCl_2$ in CCl_4 gave rise only to small amount of 7-pentafluorophenyldecafluoro-3-chlorobicyclo[4.4.0]octa-1,4,6-triene (**XVI**), and only a prolonged process furnished a mixture of triene **XVI** and 1-pentafluorophenyldecafluoro-1-chlorotetralin (**XVII**) with residual initial compound **IX**. The heating of hydroxytetralin (**IX**) with $SOCl_2$ to 100°C without solvent in a sealed ampule also provided a mixture of compounds **XVI** and **XVII**. Therewith with growing conversion the relative amount of chlorotetralin **XVII** increased, and that of triene **XVI** decreased. At long heating (100°C, ~3 weeks) the mixture formed contained no triene **XVI**, but only chlorotetralin **XVII** with unidentified impurities.

Dissimilar directions in reactions of hydroxy derivatives **VII**–**IX** with $SOCl_2$ may be apparently rationalized within a framework of the currently assumed mechanism of hydroxy group substitution by chlorine [9] taking into account the specific geometrical and electronic structures of cations **X**–**XII**. Thus, it is presumable that in the intermediately formed ion pairs of cations **X**–**XII** with the chloride anion (Scheme 2) the probability of chloride ion addition to the benzyl position of the cation (resonance structure A) decreases in the series **XI** < **X** < **XII** because of growing sterical hindrances. Actually, the angle of pentafluorophenyl group torsion relative to the plane of the other aromatic ring (where are also situated the cationic center and the atoms attached thereto) attains ~23, ~64 and ~85 deg in compounds **XI**, **X**, and **XII** respectively according to MNDO calculations. In this ion series also grows the possibility of Cl^- addition to the carbon atom in the *para*-position with respect to benzyl atom (resonance structure B). Indeed, the sterical accessibility of this cationic center in cations **X**–**XII** should be relatively similar, and the positive charge thereon grows in the series **XI** < **X** < **XII** (Table 1).

The results of quantum-chemical calculations of the geometrical and electronic stricture of ions **X**–**XII** are consistent with the data obtained by analysis of their ^{19}F NMR spectra.

Thus in the spectra of cations **X**–**XII** (Table 2) the signals from aromatic fluorine atoms are shifted downfield with respect to the analogous signals in the spectra of their precursors **IV**–**VI**. Therewith the strongest shift with respect to precursor ($\Delta\delta_F$) suffer the signals from fluorine atoms in both aromatic rings located in the *para*- and *ortho*-positions to carbocation center. The values $J_{2,4}$ and $J_{2'(6'),4'}$ of fluorine atoms in the resonance (charged) positions of the cations increased as compared with the analogous constants in the precursors **IV**–**VI**. These features of spectra for cations **X**–**XII**, cations of benzyl type, are in agreement with those of perfluoro-1-benzocyclobutenyl [10], octafluoro-1-chloro-1-indanyl [11], and polyfluorinated benzyl cations [12] where the values

Table 2. Chemical shifts of signals and their deviation from those in precursors in ^{19}F NMR spectra of cations **X**–**XII** (notation of atoms does not correspond to nomenclature rules)



n = O (**X**), 1 (**XI**), 2 (**XII**)

Cation no.	δ_F, ppm from C_6F_6 ($\Delta\delta_F$, ppm from precursor)						
	F^2	F^3	F^4	F^5	$F^{2',6'}$	$F^{3',5'}$	$F^{4'}$
X[a]	69.7 (45.7)	29.8 (11.1)	81.1 (62.9)	37.4 (13.4)	~56.0 (32.0)	14.0 (11.5)	69.7 (55.4)
XI[b]	67.1 (36.3)	35.6 (15.3)	75.3 (55.5)	35.3 (8.0)	59.9 (38.0) 58.9 (37.0)[c]	12.8 (10.6) 12.4 (10.2)	71.3 (57.0)
XII[d]	71.6 (42.9)	28.5 (10.8)	86.3 (69.3)	46.9 (19.3)	52.0 (26.7) or 51.1 (25.8)	13.8 (12.0) 13.8 (10.2)	65.7 (51.3)

[a] 59.0 and 56.0 ppm ($2F^6$, $2F^7$), $J_{2,4}$ 47, $J_{3,4}$~ $J_{4,5}$ ~20 [5]; $J_{2(6')4'}$ ~29, $J_{3(5')4'}$ ~21 Hz.

[b] 84.9 ppm ($2F^6$); $J_{2,4}$ 38, $J_{3,4}$~$J_{4,5}$ ~19, $J_{2'(6')4'}$ ~31, $J_{3'(5')4'}$ ~21 Hz.

[c] $F^{6'}$, $J_{2,6'}$ ~165, $J_{2,2'}$ < 5 Hz.

[d] 58.5, 51.1 or 52.0 ($2F^6$, $2F^8$), 32.7 ppm ($2F^7$); $J_{2,4}$ 55, $J_{3,4}$~$J_{4,5}$ ~20, $J_{2(6')4'}$ ~27, $J_{3(5')4'}$ ~21 Hz.

$\Delta\delta_F$ and J are believed to be connected with direct participation of fluorine atoms in charge distribution and conjugation [12].

In going from phenylbenzocyclobutenyl cation **XI** to phenylindanyl **X** and phenyltetralinyl **XII** ones the values $\Delta\delta(F^4)$ and $J_{2,4}$ grow, and $\Delta\delta(F^{4'})$ and $J_{2'(6'),4'}$ decrease evidencing apparently the increase in the torsion angle of pentafluorophenyl group with respect to the ion plane in the series **XI** < **X** < **XII** and the reduced participation of the pentafluorophenyl group in the charge delocalization along the series **XI** > **X** > **XII**. Besides unlike the spectra of cations **X** and **XII** in the ^{19}F NMR spectrum of ion **XI** the $F^{2'}$ and $F^{6'}$ atoms appear as two signal, i.e. they are nonequivalent. Therewith a large coupling constant $J_{2,6'}$ 165 Hz ($J_{2,2'}$ < 5 Hz) indicates the spacial proximity of the interacting nuclei, in the other words, the small torsional angle of the pentafluorophenyl group in cation **XI**.

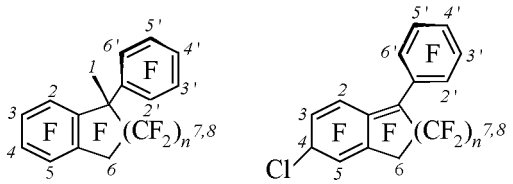
It should be noted that due to the change in the closest neighborhood of atoms $F^{2,2',6'}$ the values $\Delta\delta(F^2)$ and $\Delta\delta(F^{2',6'})$ in going from neutral compounds **IV**–**VI** to ions **X**–**XII** cannot characterize the charge distribution in the ions as it do $\Delta\delta(F^4)$ and $\Delta\delta(F^{4'})$ in the neutral compounds.

The composition and structure of compounds were established from elemental analyses and spectral characteristics.

The assignment of signals in the ^{19}F NMR spectra was carried out basing on the chemical shifts of the signals, their fine structure, and integral intensity (Table 3). The rules governing the spectra of polyfluorophenylbenzocycloalkenes are consistent with those previously established for polyfluorinated benzocyclobutenes [7–10], indans [2, 3, 7, 8], and tetralins [4, 7] with no pentafluorophenyl group.

In the ^{19}F NMR spectra of phenyltetralins **VI, IX, XVII** at room temperature two signals correspond to ortho and meta fluorine atoms in the pentafluorophenyl group, apparently due to very slow (in the NMR time scale) rotation of this group around an ordinary C–C bond. In the indan (**IV, VIII, XIV**) and benzocyclobutene (**V, VII, XIII**) derivatives the rotation of pentafluorophenyl group occurs apparently easier than in analogous tetralin compounds. As a result in their ^{19}F NMR spectra the ortho and meta fluorine atoms of the pentafluorophenyl group appear each as one broadened signal, and in the spectra of chloro derivatives **XIII, XIV** the signals of *ortho* fluorine atoms are not seen.

Table 3. [19]F NMR spectra of compounds **IV**–**IX, XIII, XIV, XVII**[a,b] and trienes **XV, XVI** (notation of atoms does not correspond to nomenclature rules)



Compd. no.	δ, ppm from C_6F_6[c]													J_{AB}, Hz	
	F^2	F^3	F^4	F^5	F^6		F^7		F^8		$F^{2,6'}$	$F^{3',5'}$	$F^{4'}$	*AB*	*A'B'* (*A''B''*)
					A	*B*	*A'*	*B'*	*A''*	*B''*					
IV	24	18.7	18.2	24	62.8	51.0	43.8	33.6			24	2.5	14.3	260	240
V	30.8	20.3	19.8	27.3	67.6	58.3					21.9	2.2	14.3	200	
VI[d]	28.7	17.7	17.0	27.6	61.4	50.2	32.8	22.4	41.2	29.5	25.2[e]	1.8	14.4	292	275
											25.4	3.6			(282)
VII	28.9	19.2	16.6	26.5	65.7	55.8					20.3	1.4	11.5	198	
VIII	23.0	17.3	14.6	22.0	64.8	50.4	45.0	32.5			22.7	2.2	12.5	260	235
IX[f]	27.9	16.6	13.8	26.2	67.4	46.6	37.4	20.4	45.1	27.3	27.1	2.4	12.8	290	275
											17.8	2.8			(280)
XIII	29.6	20.4	17.9	26.8	69.1	62.6						1.9	12.6	188	
XIV	25.4	18.0	15.4	22.7	61.5	52.5	49.1	43.3				2.1	13.8	262	232
XVII	26.8	17.1	14.4	26.6	63.1	48.9	39.3	23.7	48.4	37.9	32.7,	1.4,	14.0	290	260
	or			or							32.4	3.5			(270)
	26.6			26.8											
XV	11.1	~26	57.3	41.8	49.0	48.0	53.6	52.1			~26	2.4	14.6	259	263
XVI	17.9	21.8	52.8	54.9	47–50	24.2	47–50	24.2 25.0	2.0	13.7					

[a] $J_{2,4}$ 6–9, $J_{3,5}$ 7–9, $J_{2,3}$ 19–21, $J_{3,4}$ 17–21, $J_{4,5}$ 19–21, $J_{2(6),4}$ 4–6, $J_{3(5),4}$ 21 Hz.
[b] $J_{2,5}$ 23–24 (**V, VII, XIII**), 16–17 (**IV, VIII, XIV**), 10–12 Hz (**VI, IX, XVII**).
[c] δ_F^1: 19.3 (**IV**), 32.8 (**V**), 12.5 ppm (**VI**).
[d] $J_{5,6A}$ ~10, $J_{5,6B}$ 35 Hz.
[e] $F^{6'}$, $J_{1,6}$ 72 Hz.
[f] $J_{5,6A}$ 6, $J_{5,6B}$ 42 Hz.

In the [19]F NMR spectra of trienes **XV, XVI** the signal of CFCl group appears as a triplet with a characteristic coupling constant $J_{3,4} \sim J_{4,5}$ ~27 Hz. The analogous coupling constant in the spectrum of 7-methylperfluorobicyclo[4.3.0]hepta-1,4,6-triene is 22 Hz [13].

EXPERIMENTAL

[19]F NMR spectra of reaction mixtures and individual compounds in $CHCl_3$ solution of concentration below 10 mol% were registered on spectrometer Bruker WP-200SY at operating frequency 199.3 MHz, internal reference C_6F_6. Elemental composition of compounds was determined from high resolution mass spectra measured on Finnigan MAT 8200 instrument. GLC analysis was carried out on chromatograph LKhM-72 [oven programmed from 50 to 270°C, column 4000 × 4 mm, stationary phase SKTFT-50 on Chromosorb W, 12(25) : 100. carrier gas helium, flow rate 60 ml min^{-1}]. Elemental analyses of compounds **V–VII, IX, XIII–XVII** are given in Table 4.

Reaction of perfluorobenzocyclobytene (I) with C_6F_5H in SbF_5 medium. (a) To a stirred mixture of

compound **I** (5.31 g, 21.4 mmol), SbF_5 (13.92 g, 64.2 mmol), and C_6F_6 (15 ml) was added C_6F_5H (3.96 g, 23.6 mmol) within 10 min at 23°C. The mixture was stirred at the same temperature for 4 h, then it was treated with water at 0–10°C, the organic layer was separated, dried with $MgSO_4$, C_6F_6 and excess C_6F_5H were distilled off. We obtained 8.15 g (97%) of compound **VII** (^{19}F NMR spectrum). Analytical sample (viscous fluid) was obtained by "sublimation" in a vacuum (130°C, 5 mm Hg).

(b) Similarly to the preceding experiment from compound **I** (1.58 g, 6.4 mmol), C_6F_5H (1.18 g, 7.0 mmol), SbF_5 (1.66 g, 7.7 mmol) in C_6F_6 (6 ml) was obtained after 10 h at 50°C and 15 h at 20°C a mixture containing compounds **VII, I**, and C_6F_5H in a ratio 1 : 1.5 : 1.6 (by ^{19}F NMR spectrum). On distilling off C_6F_6 and unreacted initial compounds 0.98 g of product **VII** (by ^{19}F NMR spectrum) was obtained.

(c) To a stirred mixture of compound **I** (2.82 g, 11.4 mmol), SbF_5 (7.4 g, 34.1 mmol) and C_6F_6 (3.5 ml) was added 2.1 g (12.5 mmol) of C_6F_5H within 5 min at 20°C. The mixture was stirred for 4 h at 20°C, then it was treated with anhydrous HF and poured on ice. The organic layer was separated, washed with water, dried with $MgSO_4$, C_6F_6 and excess C_6F_5H were distilled off. We obtained 3.6 g (yield 80%) of a mixture of compounds **V** and **VII** in a ratio ~1 : 1 (by ^{19}F NMR spectrum). By column chromatography on silica gel (eluent $CHCl_3$) was isolated 1.6 g of phenylbenzocyclobutene **V**, mp 54.5–55°C (from hexane), and 1.3 g of compound **VII**.

(d) Similarly to the run (a) from compounds **I** (0.48 g, 1.9 mmol) and **II** (0.58 g, 1.9 mmol), C_6F_5H (0.32 g, 1.9 mmol), SbF_5 (2.53 g, 11.7 mmol) in C_6F_6 (2 ml) was obtained (28°C, 3 h) a mixture that after removing of C_6F_6 and compound **II** furnished 0.57 g of product containing compounds **VII** and **VIII** in 13 : 1 ratio (according to ^{19}F NMR spectrum).

Reaction of perfluorotetralin (III) with C_6F_5H in SbF_5 medium. (a) A mixture of compound **III** (2.67 g, 7.7 mmol), C_6F_5H (1.42 g, 8.5 mmol), SbF_5 (8.3 g, 38.3 mmol), and C_6F_6 (4 ml) was stirred for 6 h at 50–55°C, treated with anhydrous HF (18 ml), and then poured on ice. The organic layer was separated, washed with water, dried with $MgSO_4$, C_6F_6 and excess C_6F_5H were distilled off. We obtained 3.21 g of crude phenyltetralin **VI** (97% according to GLC and ^{19}F NMR spectrum). By purification by column chromatography on silica gel (eluent CCl_4) was separated 3.11 g (yield 82%) of compound **VI**, mp 68–69°C (from hexane).

Table 4. Elemental analyses of compounds **V**–**VII, IX, XIII**–**XVII**

Compd. no.	Found, %		Formula	Calcd., %	
	C (H)	F (Cl)		C (H)	F (Cl)
VI	38.77	61.27	$C_{16}F_{16}$	38.71	61.29
IX	39.19	57.76	$C_{16}HF_{15}O$	38.87	57.69
	(0.17)			(0.20)	
XVI+XVII	37.47	(6.95)	$C_{16}ClF_{15}$	37.48	(6.92)
V[a]	(395.9811)		$C_{14}F_{12}$	(395.9808)	
VII[a]	(393.9848)		$C_{14}HF_{11}O$	(393.9851)	
XIII[a]	(411.9506)		C14ClF11	(411.9513)	
XIV[a]	(461.9473)		C15ClF13	(461.9481)	
XV	(461.9469)		C15ClF13	(461.9481)	

[a] Molecular weight is given.

(b) A mixture of compound **III** (1.68 g, 4.8 mmol), C_6F_5H (0.9 g, 5.4 mmol), and SbF_5 (5.27 g, 24.3 mmol) was stirred for 6 h at 50–55°C, then was added C_6F_6 (2.5 ml), the reaction products were treated with water at 0–10°C, then extracted with $CHCl_3$, the extract was dried on $MgSO_4$, C_6F_6 and $CHCl_3$ were distilled off. We obtained 1.91 g of crude hydroxyphenyltetralin **IX** (96% according to GLC and ^{19}F NMR spectrum). By purification by column chromatography on silica gel (eluent $CHCl_3$) was separated 1.73 g (yield 73%) of compound **IX**, mp 58–99°C (from hexane).

(c) To a stirred mixture of compound **III** (1.51 g, 4.3 mmol), SbF_5 (2.38 g, 11.0 mmol) in C_6F_6 (1.5 ml) was added C_6F_5H (0.8 g, 4.8 mmol) at 20°C. The mixture was stirred for 4.5 h at 25°C, treated with water at 0–10°C, the organic layer was separated, and dried with $MgSO_4$. According to ^{19}F NMR data the mixture contained compounds **IX**, **III**, and C_6F_5H a at ratio ~1.5 : 1 : 1.2. On distilling off the solvent and initial compounds we obtained 1.16 g of compound **IX**.

1-Pentafuorophenylhexafluoro-1-chlorobenzocyclobutene (XIII). (a) To a mixture of compound **VII** (1.84 g, 4.7 mmol) and $SOCl_2$ (1.09 g, 9.2 mmol) in CCl_4 (10 ml) was added 3 drops of DMF, and the mixture was stirred for 5.5 h at 23°C. According to ^{19}F NMR spectrum the mixture contained compounds **VII** and **XIII** in a ratio ~2.6 : 1. Then the mixture was stirred at heating to 75°C for 7 h, CCl_4 and excess $SOCl_2$ were distilled off, the residue was washed with water, then extracted with $CHCl_3$. The extract was dried with $MgSO_4$, the solvent was removed to

furnish 1.8 g (yield 94%) of compound **XIII** (by ^{19}F NMR spectrum).

(b) To a mixture of compound **VII** (0.36 g, 0.9 mmol) and $SOCl_2$ (1.08 g, 9.0 mmol) in CCl_4 (2 ml) was added 2 drops of DMF, the mixture was stirred for 11 h at 75°C, worked up as in the preceding run. We obtained 0.33 g (yield 96%) of compound **XIII**.

7-Pentafluorophenyloctafluoro-3-chlorobicyclo-[4.3.0]hepta-1,4,6-triene (XV). (a) Similarly to the preceding experiment from compound **VIII** (0.4 g, 0.9 mmol), $SOCl_2$ (1.08 g, 9.0 mmol), DMF (2 drops) in CCl_4 (2 ml) was obtained (75°C, 11 h) 0.4 g of a mixture of compounds **XIV** and **XV** in ~1 : 2.4 ratio (according to ^{19}F NMR spectrum). Triene **XV** was isolated as individual compound by column chromatography on silica gel (eluent hexane) from a mixture that contained the products of several similar experiments.

1-Pentafluorophenyloctafluoro-1-chloroindan (XIV). Compound **VIII** (0.5 g 1.1 mmol), $SOCl_2$ (0.66 g, 5.5 mmol) and DMF (2 drops) was heated to 90°C in a sealed ampule for 20 h. According to ^{19}F NMR spectrum the resulting products mixture contained compounds **XIV** and **XV** in a ratio ~2.5 : 1. More $SOCl_2$ was added (0.17 g, 1.4 mmol), and heating to 90°C was continued for 20 h. Then the products were treated with water, extracted into $CHCl_3$, and the extract was dried on $MgSO_4$. On removing the solvent 0.53 g of crude phenylindan **XIV** (91% according to GLC and ^{19}F NMR spectrum) was obtained, yield 93%. Compound **XIV** was isolated in individual state by column chromatography on silica gel (eluent hexane).

7-Pentafluorophenyldecafluoro-3-chlorobicyclo-[4.4.0]octa-1,4,6-triene (XVI) and 1-pentafluorophenyldecafluoro-1-chlorotetralin (XVII). (a) Compound **IX** (0.45 g, 0.9 mmol), $SOCl_2$ (1.08 g, 9 mmol), and DMF (2 drops) in CCl_4 (2 ml) were stirred at 75°C for 11 h. According to ^{19}F NMR spectrum the mixture contained compounds **IX**, **XVI** in a ratio ~8 : 1, and no phenyltetralin **XVII**. The stirring at 75°C was continued for 67 h more, and then the reaction mixture was subjected to the same workup as in the previous run. We obtained 0.38 g of a mixture containing compounds **IX**, **XVI**, and **XVII** in a ratio ~'1.1 : 1.8 : 1 (^{19}F NMR data). By column chromatography on silica gel (eluent hexane) a mixture of triene **XVI** and phenyltetralin **XVII** was separated with the ratio of compounds **XVI : XVII** ~1.5 : 1 (^{19}F NMR spectrum).

(b) Compound **IX** (0.62 g, 1.3 mmol), $SOCl_2$ (1.01 g, 8.5 mmol), and DMF (4 drops) were heated in a sealed ampule to 100°C. According to ^{19}F NMR spectrum the mixture after 147 h contained compounds **IX, XVI**, and **XVII** in a ratio ~1 : 4,5 : 8, in 300 h compounds **XVI** and **XVII** in a ratio ~1:$, and in 470 h phenyltetralin **XVII** did not contain triene **XVI**. Excess $SOCl_2$ was distilled off, the residue was dissolved in $CHCl_3$, the solution was washed with water and dried with $MgSO_4$. Then the solvent was distilled off to furnish 0.61 g of a mixture containing according to GLC and ^{19}F NMR spectrum 64% of phenyltetralin **XVII** alongside unidentified impurities (apparently tetralin derivatives containing 2–3 chlorine atoms). By column chromatography on silica gel (eluent hexane) a substance was separated containing 90% of phenyltetralin **XVII**.

Reaction of 1-pentafuorophenylhexafluoro-1-chlorobenzocyclobutene (XIII) with CsF. Compound **XIII** (0.5 g, 1.2 mmol), CsF (0.96 g, 6.3 mmol), and CH_3CN (0.5 ml) were heated in a sealed ampule to 100°C for 15 h. Then the reaction mixture was treated with water, extracted with CCl_4, the extract was dried on $MgSO_4$, and on removing the solvent we obtained 0.46 g (yield 96%) of phenylbenzocyclobutene **V** (^{19}F NMR data).

Reaction of 1-pentafluorophenyloctafluoro-1-chloroindan (XIV) with CsF. In the same way as in the preceding experiment from compound **XIV** (0.53 g, 1.1 mmol) and CsF (0.9 g, 5.9 mmol) in CH_3CN (0.5 ml) was obtained (100°C, 14 h) 0.5 g of substance containing a lot of tar. It was subjected to steam distillation to afford 0.41 g of compound that according to GLC and ^{19}F NMR data contained 90% of phenylindan **IV**, yield 72%.

Perfluoro-1-phenyl-1-benzocyclobutenyl cation (XI). (a) Compound **I** (0.2 g, 0.8 mmol) was dissolved in SbF_5 (1.07 g, 4.9 mmol), then C_6F_5H (0.15 g, 0.9 mmol) was added at 20°C, the mixture was stirred, and the solution was maintained at this temperature for 3 h. The formation of cation **XI** was proved by ^{19}F NMR spectrum. Then the mixture was poured on ice, extracted with CH_2Cl_2, the extract was dried on $MgSO_4$, the solvent was distilled off, and the remaining 0.23 g of substance contained compounds **V** and **VII** in a ratio ~1 : 10 (^{19}F NMR spectrum).

(b) Phenylbenzocyclobutene **V** (0.2 g, 0.5 mmol) was dissolved in SbF_5 (0.77 g, 3.5 mmol) and SO_2ClF (0.2 ml). According to ^{19}F NMR spectrum the solution contained only cation **XI** salt and no precursor **V**.

(c) Phenylindan **IV** (0.12 g, 0.3 mmol) was added to solution of SbF_5 (0.09 g, 0.4 mmol) in SO_2ClF (0.5 ml) at –10°C, and the mixture was stirred. According to ^{19}F NMR spectrum the solution contained cation **X** salt and phenylindan **IV** in a ratio ~1 : 0.7. Then phenylbenzocyclobutene **V** (0.11 g, 0.3 mmol), SbF_5 (0.04 g, 0.2 mmol), and SO_2ClF (0.2 ml) were added, the mixture was stirred to form a heterogeneous system. In the ^{19}F NMR spectrum of the mixture at –10°C were observed signals of cation **XI** and phenylindan **IV** in a ratio ~1 : 3.5. The mixture was treated with water, extracted with dichloromethane, the extract was dried with $MgSO_4$, the solvent was removed. The mixture of compounds obtained (0.2 g) contained substances **IV, V**, and **VII** in a ratio ~11 : 1 : 9 as shown by ^{19}F NMR spectrum.

Perfluoro-1-phenyl-1-tetralinyl cation (XII). (a) Compound **III** (0.24 g, 0.7 mmol) was dissolved in SbF_5 (0.9 g, 4.2 mmol), then C_6F_5H (0.13 g, 0.76 mmol) was added, the mixture was stirred, heated to 50°C for 2.5 h to obtain a solution of cation **XII** as seen from ^{19}F NMR spectrum. Then the mixture was poured on ice, extracted with CH_2Cl_2, the extract was dried on $MgSO_4$, the solvent was distilled off. We obtained 0.28 g of mixture containing according to GLC and ^{19}F NMR data compounds **VI** (44%) and **IX** (45%).

(b) Phenyltetralin **VI** (0.24 g, 0.5 mmol) was added to a solution of SbF_5 (0.72 g, 3.3 mmol) in SO_2ClF (0.2 ml), and the mixture was stirred. As shown by ^{19}F NMR spectrum, the solution contained cation **XII** salt and no precursor **V**.

(c) Phenyltetralin **VI** (0.09 g, 0.18 mmol) was added to a solution of SbF_5 (0.11 g, 0.5 mmol) in SO_2ClF (0.5 ml) at –10C, and the mixture was stirred. As shown by ^{19}F NMR spectrum, the solution contained cation **XII** salt and no precursor **V**. Then was added phenylindan **IV** (0.09 g, 0.2 mmol), and the mixture was stirred at –10°C. According to ^{19}F NMR spectrum the solution contained salts of cations **XII, X**, and phenyltetralin **VI** in a ratio ~1 : 3 : 2. The mixture was treated with water, extracted with dichloromethane, the extract was dried with $MgSO_4$, the solvent was removed. The residue weighing 0.15 g contained according to GLC and ^{19}F NMR spectrum compounds **IV** (4%), **VI** (44%), **IX** (11%), and **VIII** (39%).

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