ELSEVIER

Journal of Fluorine Chemistry 117 (2002) 73–81

JOURNAL OF FLUORINE CHEMISTRY

www.elsevier.com/locate/jfluchem

Cationoid rearrangements in reactions of perfluoro-1-arylbenzocyclobutenes with antimony pentafluoride

Victor M. Karpov*, Tatyana V. Mezhenkova, Vyacheslav E. Platonov[1], Vladimir R. Sinyakov

N.N. Vorozhtsov Institute of Organic Chemistry, Novosibirsk 630090, Russia

Received 23 May 2002; received in revised form 23 July 2002; accepted 2 August 2002

Dedicated to Prof. em. Dr. mult. Dr. h.c. Alois Haas, on the occasion of 70th birthday

Abstract

In the presence of antimony pentafluoride at 130 °C, the four-membered ring of perfluoro-1-(2-ethylphenyl)benzocyclobutene (**2**) undergoes cleavage, forming perfluoro-2-ethyl-2′-methyldiphenylmethane (**5**). Compound **5** is converted, under the action of SbF_5 at 170 °C, to perfluoro-8,9-dimethyl-1,2,3,4-tetrahydrofluorene (**8**). Perfluoro-1-(4-ethylphenyl)benzocyclobutene (**3**) remains unchanged at 130 °C, whereas at 170 °C it gives a mixture of perfluorinated 4′-ethyl-2-methyldiphenylmethane (**9**), 6-ethyl-1,2,3,4-tetrahydroanthracene (**11**) and 2-ethyl-9,10-dihydroanthracene (**12**). When heated with SbF_5 at 170 °C, perfluoro-1-phenylbenzocyclobutene (**1**) remains unchanged. Solution of compounds **2**, **3**, **5** and **9** in SbF_5–SO_2ClF generated the perfluorinated 1-(2-ethylphenyl)-1-benzocyclobutenyl (**29**), 1-(4-ethylphenyl)-1-benzocyclobutenyl (**30**), 2-ethyl-2′-methyldiphenylmethyl (**31**) and 4′-ethyl-2-methyldiphenylmethyl (**32**) cations, respectively.

Keywords: Skeletal transformations; Perfluoroarylbenzocyclobutenes; Antimony pentafluoride; NMR spectroscopy

1. Introduction

Previously, we have found and investigated the skeletal transformations of perfluorobenzocycloalkenes (benzocyclobutene, indan and tetralin) and their perfluoroalkyl derivatives under the action of Lewis acids, changing the alicyclic fragment of the molecule [1–7]. It was shown that in these reactions perfluoroalkylbenzocyclobutenes undergo expansion of the four-membered ring to the five-membered one; alternatively, the alicycle opens to form polyfluorostyrenes, which subsequently undergo cyclization into polyfluoroindans or fluorination [1,4,5]. The skeletal transformations of perfluoroarylbenzocycloalkenes were not known. Recently, we have found that the carbon framework of the molecule in perfluoro-1-phenylindan changes under the action of SbF_5, with both alicyclic and aromatic fragments of the substrate involved in the reaction [8].

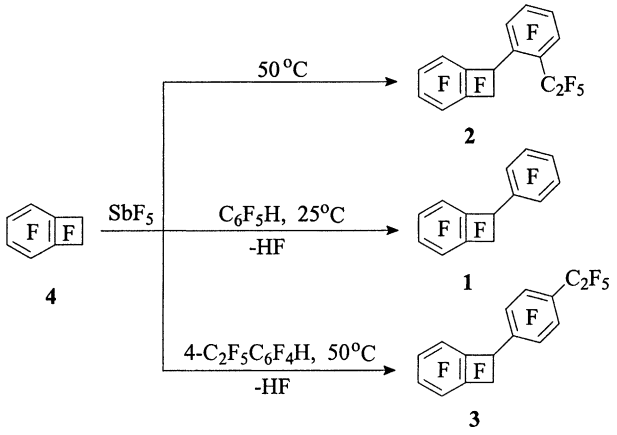
The aim of this study is to investigate the behavior of perfluoro-1-phenylbenzocyclobutene (**1**), perfluoro-1-(2-ethylphenyl)benzocyclobutene (**2**) and perfluoro-1-(4-ethylphenyl)benzocyclobutene (**3**) under the action of SbF_5 to study the effect of the perfluoroaryl group and the size of alicycle on the route of the skeletal transformations of polyfluorobenzocycloalkenes. Product **2** was obtained previously by dimerization of perfluorobenzocyclobutene (**4**) in SbF_5 at 50 °C [2]; product **1** was synthesized by interaction of compound **4** with pentafluorobenzene in the presence of SbF_5 [9]; product **3** was prepared by an analogous reaction from compound **4** and 4-*H*-perfluoroethylbenzene in the present work (Scheme 1).

2. Results and discussion

In the presence of antimony pentafluoride, perfluoro-1-(ethylphenyl)-benzocyclobutenes **2** and **3** undergo skeletal transformations, whereas perfluoro-1-phenylbenzocyclobutene (**1**) fails to do so under analogous conditions. At 130 °C, the four-membered ring of **2** opens under the action of SbF_5. Thus, prolonged heating of benzocyclobutene **4** with antimony pentafluoride at 130 °C with further treatment of the reaction mixture with anhydrous HF and then with water leads to perfluoro-2-ethyl-2′-methyldiphenylmethane (**5**)

* Corresponding author. Fax: +7-3832-34-4752.
E-mail addresses: karpov@nioch.nsc.ru (V.M. Karpov), platonov@nioch.nsc.ru (V.E. Platonov).
[1] Tel.: +7-3832-34-4437; fax: +7-3832-34-4752.

0022-1139/02/$ – see front matter
PII: S0022-1139(02)00196-3



Scheme 1.

together with perfluoro-2-ethyl-2′-methylbenzophenone (**6**). The mixture also contains compound **2** and 1-hydroxyperfluoro-1-(2-ethylphenyl)benzocyclobutene (**7**) (Scheme 2).

The reaction at 170 °C (7 h) forms perfluoro-8,9-dimethyl-1,2,3,4-tetrahydrofluorene (**8**) along with products **5** and **6**; at increased reaction time, more tetrahydrofluorene **8** is formed, whereas the proportions of **5** and **6** decrease (Scheme 2).

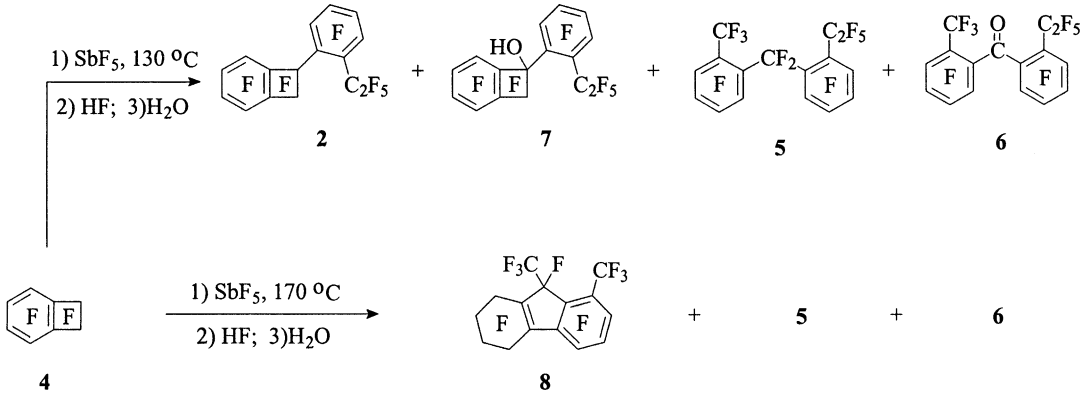
In contrast to arylbenzocyclobutene **2**, its isomer **3** does not change in the presence of antimony pentafluoride at 130 °C; at 170 °C (7 h) it gives, after treatment with anhydrous HF and then with water, minor products of alicycle opening: perfluoro-4′-ethyl-2-methyldiphenylmethane (**9**) and perfluoro-4′-ethyl-2-methylbenzophenone (**10**) together with perfluoro-6-ethyl-1,2,3,4-tetrahydroanthracene (**11**), perfluoro-2-ethyl-9,10-dihydroanthracene (**12**) and perfluoro-2-ethyl-9(10*H*)anthracenone (**13**). The reaction mixture also contains unchanged compound **3**. Prolonged reaction time (14 h) and treatment with H_2O leads to products **11** and **13** together with perfluoro-2-ethyl-9,10-anthraquinone (**14**), whereas compounds **3** and **9** are absent (Scheme 3). At still longer reaction times, the relative content of tetrahydroanthracene **11** increases, and those of compounds **12–14** decrease.

Let us consider possible routes of reactions between arylbenzocyclobutenes **2** and **3** and antimony pentafluoride. Opening of the four-membered cycle in compound **2** seems to occur as follows (Scheme 4). Reversible elimination of the fluoride anion from the difluoromethylene fragment of the ethyl group of benzocyclobutene **2** under the action of SbF_5 leads to cation **15**. Since the positive charge of the latter is shared also by the carbon atom bonded to the benzocyclobutenyl fragment, the four-membered cycle of the latter may undergo ring opening analogous to that in perfluoro-1-alkylbenzocyclobutenes under the action of SbF_5 [4] (Scheme 4). This yields the benzyl cation **16**, which adds the fluoride anion, giving compound **17**. The latter is fluorinated to product **5**.

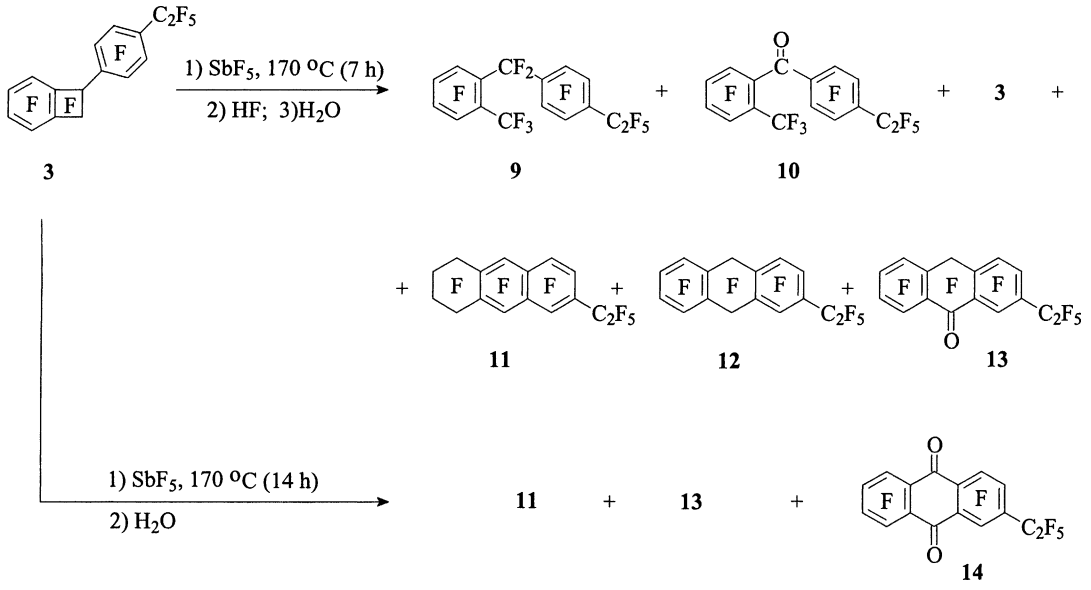
A possible route for formation of compound **8** from diphenylmethane **5** is presented in Scheme 5. The benzyl cation **18** formed at the first stage undergoes an intramolecular rearrangement, as a result of which it isomerizes into ion **19**. The latter is transformed into the diphenylmethyl cation **20** by addition–elimination of the fluoride anion. An attack of the positively charged carbon atom of one aromatic ring (resonance structure **20a**) at the other ring of cation **20** with further elimination of CF_3^+ and isomerization of the resulting compound leads to fluorene **21** (cf. formation of perfluoro-9-methylfluorene from perfluoro-1-phenylindan in the presence of SbF_5 [8]), which is further fluorinated, giving tetrahydrofluorene **8** (cf. fluorination of polyfluoroarenes in the presence of SbF_5 [10–12]).

The skeletal transformations of arylbenzocyclobutene **3** under the action of SbF_5 start analogously to the transformations of its isomer, benzocyclobutene **2**. Thus, the benzyl cation **22** formed from compound **3** is evidently converted to cation **23**. Cyclization of the latter (Scheme 6, route 1) with further addition of the fluoride anion and isomerization of the intermediate compound **24** gives dihydroanthracene **12**, which is fluorinated to give tetrahydroanthracene **11** under the reaction conditions. Addition of the fluoride anion to cation **23** (route 2) and subsequent fluorination of product **25** form compound **9**.

It should be noted that, in addition to the formation of products **11** and **12** according to route 1, an alternative



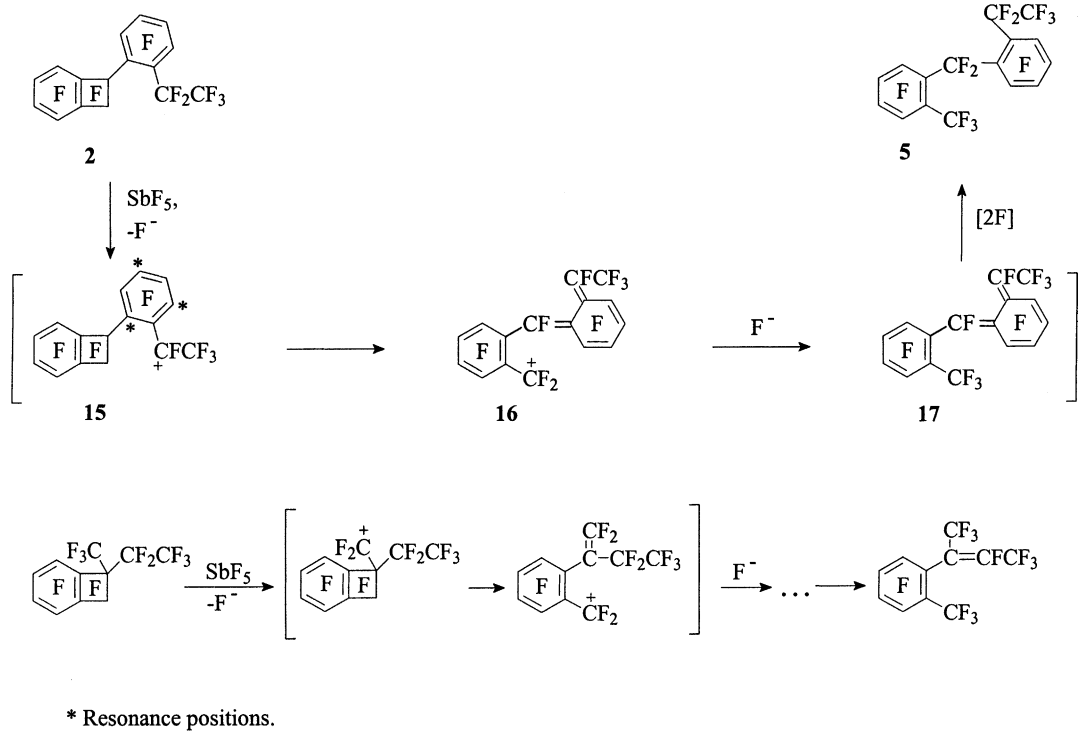
Scheme 2.



Scheme 3.

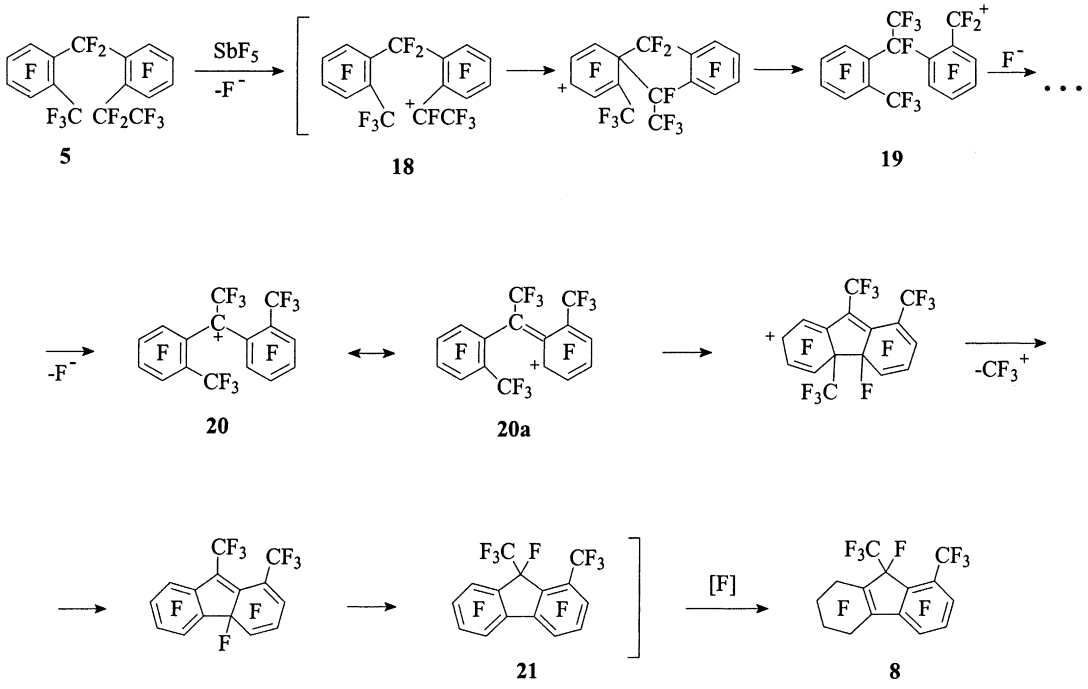
route is possible, which involves generation of cation **26** from diphenylmethane **9** and cyclization of **26** into compound **27** as a result of an attack of the aromatic ring by the benzyl carbon atom with further addition of the fluoride anion. Isomerization of compound **27** by addition–elimination of the fluoride anion may lead to tetrahydroanthracene **11**, and defluorination and/or disproportionation form dihydroanthracene **12** (cf. formation of perfluoro-2,3-dimethylindene from perfluoro-1,2-dimethylindan [3,5] and disproportionation of polyfluorocyclohexadienes in SbF_5 [13,14]).

Thus, in the framework of the above routes for transformations of compounds **2** and **3** under the action of antimony pentafluoride, it is postulated that cations **15** and **22**, respectively, undergo skeletal rearrangements. The latter are not the most stable cations generated from compounds **2** and **3**, but their concentration is apparently sufficient for the reaction to occur with an observable rate. The cations formed by



* Resonance positions.

Scheme 4.

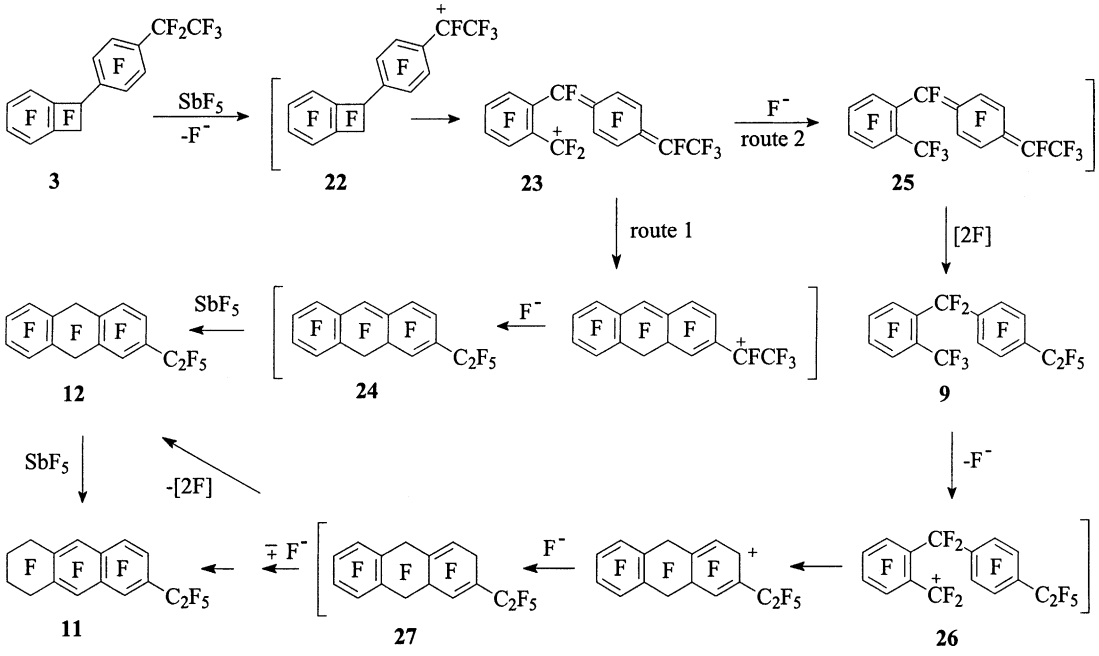


Scheme 5.

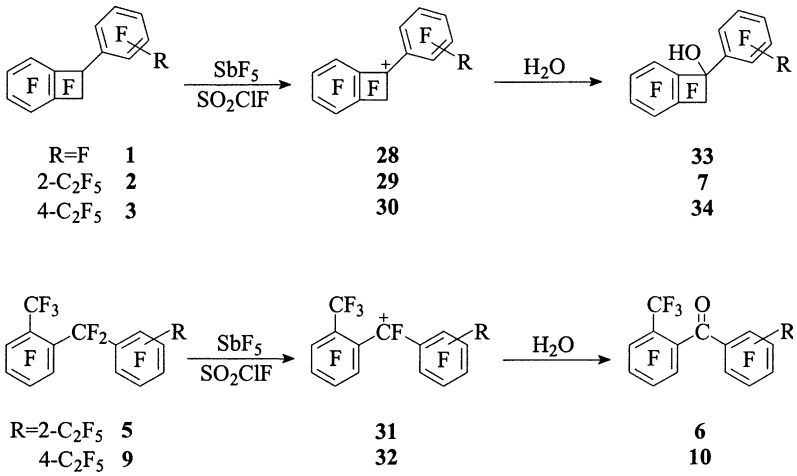
elimination of the fluoride anion from position 1 of compounds **2** and **3** are more stable.

Indeed, the reactions of arylbenzocyclobutenes **1**, **2** and **3** in SbF_5–SO_2ClF generate perfluorinated 1-phenyl-1-benzocyclobutenyl (**28**) [9], 1-(2-ethylphenyl)-1-benzocyclobutenyl (**29**) and 1-(4-ethylphenyl)-1-benzocyclobutenyl (**30**) cations. Analogously, perfluoro-2-ethyl-2′-methyldiphenylmethyl (**31**) and perfluoro-4′-ethyl-2-methyldiphenylmethyl (**32**) cations were generated from diphenylmethanes **5** and **9**, respectively (Scheme 7).

The treatment of the solutions of the salts of cations **28**–**30** with water leads to 1-hydroxyperfluoro-1-phenylbenzocyclobutene (**33**) [9], compound **7** and 1-hydroxyperfluoro-1-(4-ethylphenyl)benzocyclobutene (**34**). Hydrolysis of the salts of cations **31** and **32** yields ketones **6** and **10**, respectively. The structures of the cations were identified by ^{19}F



Scheme 6.



Scheme 7.

NMR spectra. The peculiarities in the spectra of cations **29**–**32** (Table 1), which are benzyl type cations, agree with those for the perfluoro-1-phenyl-1-benzocycloalkenyl [8,9], polyfluorinated benzyl [15] and diphenylmethyl cations [16], for which $\Delta\delta_F$ and J are attributed to direct participation of fluorine atoms in charge distribution and in conjugation [15,16].

In the ^{19}F NMR spectra of cations **28** and **30**, the F-2′ and F-6′ atoms are non-equivalent. The larger value of $J_{6,6'}$ 156, 165 Hz ($J_{6,2'} < 5$ Hz) indicates that the interacting nuclei are closely spaced, or, in other words, that the perfluoroaryl group in cations **28** and **30** is rotated through a small angle. In cation **29**, $J_{6,6'}$ is 58 Hz, indicating that the perfluoro-2-ethylphenyl group is rotated through a larger angle in this cation compared with the rotation angle of the perfluoroaryl group in ions **28** and **30**, in which case the perfluoro-2-ethylphenyl group is oriented by its F-6′ atom toward the aromatic ring. On passing from cation **28** to **30** and **29**, $\Delta\delta$(F-4) and $J_{4,6}$ increase, indicating that the positive charge in the tetrafluorophenylene part of the ion increases and that participation of the perfluoroaryl group in charge delocalization decreases in the series **28** > **30** > **29**. In the ^{19}F NMR spectrum of the diarylmethyl cation **32**, the F-2′ and F-6′ atoms give one signal, probably indicating that the 4-ethylphenyl group rotates freely in the ion. In cation **31**, $\Delta\delta$(F-4, 6) and $J_{4,6}$ are larger than the analogous values for the isomeric cation **32**, indicating that the methylphenyl fragment of ion **31** has a larger portion of positive charge compared to ion **32**. Moreover, the larger values of $\Delta\delta$(F-4, 6) and $J_{4,6}$ compared to $\Delta\delta$(F-4′, 6′) and $J_{4',6'}$ for cation **31** suggest that the methylphenyl fragment takes a greater part in charge delocalization compared to the ethylphenyl fragment of this ion. The low value of $J_{6,6'}$ in cations **32** (10 Hz) and **31** (<5 Hz) indicates that the alkylphenyl fragments deviate from the plane of the cation center and the atoms bonded to it. The high values of spin–spin coupling constants for F-α interaction (across space) with the fluorine atoms of the perfluoroalkyl groups in ions **31** and **32** suggest that the alkylphenyl fragments are orientated by the perfluoroalkyl groups toward the F-α atom.

The structures of compounds were established by spectral characteristics. Assignment of signals in the ^{19}F NMR spectra of compounds was made on the basis of chemical shifts of the signals, their fine structure and integral intensities. The ^{19}F NMR spectral data for compounds are given in Tables 2 and 3.

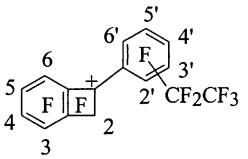
3. Experimental

The ^{19}F NMR spectra of $CHCl_3$ solutions of the reaction mixtures, $CHCl_3$ solutions of the individual compounds (<10 mol%), and SbF_5–SO_2ClF solutions of the cation salts were recorded on a WP-200SY (188.3 MHz) instrument. C_6F_6 was used as internal standard (SO_2ClF in the case of cations, 262.8 ppm from C_6F_6). The chemical shifts are given in δ ppm downfield from C_6F_6 (−162.9 ppm from CCl_3F). The element compositions of the compounds were determined by high-resolution mass spectrometry on a Finnigan Mat 8200 instrument. Yields of products in the reaction mixtures were determined by GLC and ^{19}F NMR.

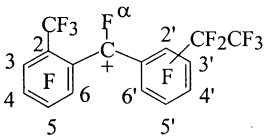
*3.1. Reaction of perfluorobenzocyclobutene (**4**) with 4-H-perfluoroethylbenzene in the presence of SbF_5*

A 1:1.1:5 mixture of benzocyclobutene **4** (1.89 g), 4-*H*-perfluoroethylbenzene (2.25 g) and SbF_5 (8.26 g) was stirred for 6 h at 50 °C. Then C_6F_6 (2 ml) was added, and the mixture was treated with anhydrous HF (14 ml), poured onto ice, and extracted with $CHCl_3$. The extract was dried over $MgSO_4$. $CHCl_3$ and C_6F_6 were distilled off to give 3.7 g of the product containing compounds **3** and **34** in the ratio ~4:1. Benzocyclobutene **3** (2.88 g, yield 76%) and compound **34** (0.67 g, 18%) were isolated by silica gel column chromatography (CCl_4 and then CH_2Cl_2 as eluent).

Table 1
^{19}F NMR spectral data of benzocyclobutenyl and diphenylmethyl cations



28-30

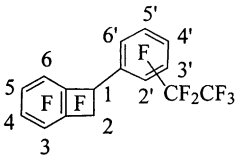


31, 32

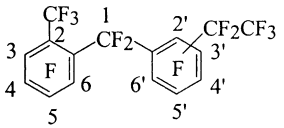
Cation	δ_F ($\Delta\delta_F$[a], ppm)											$J_{F,F}$ (Hz)								
	F-α	F-2	F-3	F-4	F-5	F-6	F-2′	F-3′	F-4′	F-5′	F-6′	$J_{3,4}$	$J_{3,5}$	$J_{3,6}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$	$J_{6',4'}$ ($J_{2',4'}$)	$J_{3',4'}$ ($J_{5',4'}$)	$J_{6,6'}$ ($J_{6,2'}$)
28 [9]		84.9 (22.0)	35.3 (8.0)	75.3 (55.5)	35.6 (15.3)	67.1 (36.0)	59.9 (38.0)	12.4[b] (10.2)	71.3 (57.0)	12.8[b] (10.6)	58.9 (37.0)	19	11	12	19	38	20	31 (31)	21	165 (<5)
29[c]		93.3 (28.7)	38.0 (11.1)	94.0 (75)	39.0 (19.3)	74.6 (46.2)	60.9[d] (6.3), 81.7[e] (1.9)	45.5 (11.4)	52.4 (36.6)	24.3 (7.1)	58.2 (32.5)	18	11	13	20	49	18	31	19	58
30[f]		82.2 (18.6)	38.7 (11.0)	90.8 (70.3)	38.4 (17.6)	75.1 (44.1)	56.4 (32.5)	34.2 (8.7)	52.3[d] (1.5), 79.6[e] (3.0)	34.2 (8.7)	55.5 (32.5)	18	11	12	19	48	19			156 (<5)
31[g]	242.0 (149.7)	109.5[e] (0.8)	47.0 (16.9)	69.7 (52.7–54.4)	26.0 (9.0–10.7)	66.7 (36.1–37.4)	62.3[d] (1.3), 82.0[e] (1.3)	49.0 (14.0)	58.0 (41–42.7)	26.1 (9.1–10.8)	56.9 (26.3–27.6)	20	14	<5	19	41	21	32	18–20	<5
32[h]	231.6 (146.9)	109.8[e] (1.5)	46.2 (17.1)	65.4 (49.6)	25.7 (9.4)	63.2 (33.5)	51.8 (27.6)	36.5 (10.7)	52.4[d] (1.9), 79.8[e] (3.3)	36.5 (10.7)	51.8 (27.6)	20	14	<5	19	39	21			10 (10)

[a] Changes in chemical shift in going from precursor to ion.
[b] Interchangeable values.
[c] $J_{F^{3'}\text{-}CF_2} = J_{F^{2}\text{-}CF_2} = 25$ Hz, $J_{F^{3'}\text{-}CF_3} = 18$ Hz, $J_{3',5'} = 13$ Hz, $J_{5',6'} = 19$ Hz.
[d] CF_2 group.
[e] CF_3 group.
[f] $J_{F^{3'(5')}\text{-}CF_2} = 33$ Hz, $J_{F^{3'(5')}\text{-}CF_3} = 7$ Hz.
[g] $J_{F^{3}\text{-}CF_3{}^2} = 28$ Hz, $J_{F^{\alpha}\text{-}CF_3{}^2} = J_{F^{\alpha}\text{-}CF_3{}^{2'}} = 30$ Hz, $J_{F^{\alpha}\text{-}F^{6}} = J_{F^{\alpha}\text{-}CF_2{}^{2'}} = 21$ Hz, $J_{F^{3'}\text{-}CF_2{}^{2'}} = 35$ Hz, $J_{3',5'} = 20$ Hz.
[h] $J_{F^{3}\text{-}CF_3} = 26$ Hz, $J_{F^{\alpha}\text{-}CF_3{}^2} = 28$ Hz, $J_{F^{\alpha}\text{-}F^{2'(6')}} = 61$ Hz.

Table 2
^{19}F NMR spectral data of benzocyclobutenes and diphenylmethanes



2, 3, 34

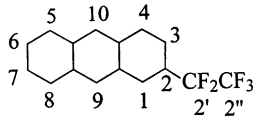


5, 9, 10

Compound	δ_F (ppm)													$J_{F,F}$ (Hz)							
	F-1	F-2		F-3	F-4	F-5	F-6	F-2′		F-3′	F-4′	F-5′	F-6′	$J_{3,4}$	$J_{3,5}$	$J_{3,6}$	$J_{4,5}$	$J_{4,6}$	$J_{5,6}$	$J_{6,6'}$ ($J_{6,2'}$)	$J_{A,B}$ ($J_{A',B'}$)
		A	B					A′	B′												
2[a,b]	35.0	69.2	60.0	26.9	19.0	19.7	28.4	60.2[c], 79.8[d]	49.1[c], 79.8[d]	34.1	15.8	17.2	25.7	19	8	24	18	8	19	16	205 (285)
3[e]	30.8	68.0	59.2	27.7	20.5	20.8	31.0	23.9		25.5	50.8[c], 76.6[d]	25.5	23.9	19	8	24	18	9	18	20 (20)	200
5[a]	92.3	108.7[d]	108.7[d]	30.1	15.3[f]	15.8[f]	30.6 or 29.0	62.5[c], 80.7[d]	59.4[c], 80.7[d]	35.0	15.8[f]	17.0[f]	30.6 or 29.0								(280)
9[g]	84.7	108.3[d]	108.3[d]	29.1	15.8	16.3	29.7	24.2		25.8	50.4[c], 76.5[d]	25.8	24.2	21	9	9	21	9	21		
10[h]		106.9[d]	106.9[d]	27.5	14.9	16.8	22.2	23.6		26.2	50.4[c], 76.6[d]	26.2	23.6	21	9	11	20	6	22		
34		66.1	56.6	26.9	17.3	19.8	29.2	22.4		24.6	50.7[c], 76.4[d]	24.6	22.4	20	8	24	18	8	19	20 (20)	199

[a] Chemical shifts (without assignment) of compound **2** (in $(CH_3)_2CO$) are reported in [2], compound **5** (in $CHCl_3$) in [17].
[b] $J_{3',4'} = J_{4',5'} = J_{5',6'} = 21$ Hz, $J_{4',6'} = 9$ Hz, $J_{F^1\text{-}F_A} = 18$ Hz, $J_{F^1\text{-}F_B} = 11$ Hz, $J_{F^1\text{-}F_{B'}} = 60$ Hz, $J_{F^1\text{-}CF_3} = 25$ Hz, $J_{3',5'} = J_{3',6'} = J_{F_A\text{-}F_{B'}} = 10$ Hz, $J_{F_B\text{-}F_{B'}} = 76$ Hz, $J_{F_{A'}\text{-}F^{3'}} = 57$ Hz, $J_{F^{3'}\text{-}CF_3} = 20$ Hz.
[c] CF_2 group.
[d] CF_3 group.
[e] $J_{F^{3'}\text{-}CF_2} = J_{F^{5'}\text{-}CF_2} = 31$ Hz, $J_{F^{3'}\text{-}CF_3} = J_{F^{5'}\text{-}CF_3} = 14$ Hz.
[f] Interchangeable values.
[g] $J_{F^6\text{-}CF_2{}^1} = 34$ Hz, $J_{F^3\text{-}CF_3{}^2} = 32$ Hz, $J_{CF_3{}^2\text{-}CF_2{}^1} = J_{F^{6'}\text{-}CF_2{}^1} = J_{F^{2'}\text{-}CF_2{}^1} = 17$ Hz.
[h] $J_{F^3\text{-}CF_3{}^2} = 18$ Hz.

Table 3
^{19}F NMR spectral data of compounds **11–14**[a]



Compound	δ_F (ppm)											$J_{F,F}$ (Hz)						
	F-1	F-3	F-4	F-5	F-6	F-7	F-8	F-9	F-10	F-2′	F-2″	$J_{1,4}$	$J_{1,2'}$	$J_{1,2''}$	$J_{2',3}$	$J_{2'',3}$	$J_{3,4}$	$J_{4,10}$
11[b]	53.5	32.7	20.4	55.6 or 56.0	27.0	27.0	55.6 or 56.0	52.2	48.6	51.1	76.7	16	34	7	34	7	20	72
12	51.8	39.0	25.0	26.0 or 25.7	16.2 or 16.5	16.2 or 16.5	26.0 or 25.7	78.0 or 78.4	78.0 or 78.4	50.5	76.6	18	33	7	33	7	18	18
13[c,d]	50.8	41.7	24.8	24.9	18.8	14.7	24.3		79.5	52.6	78.4	18	34	8	34	7	19	20
14[c]	49.5	41.0	22.6	23.9	18.0 or 17.3	18.0 or 17.3	23.9			52.6	78.4	18	34	9	34	6	18	

[a] The ^{19}F NMR spectra of perfluorinated 9,10-dihydroanthracene, 9(10*H*)anthracenone and 9,10-anthraquinone are reported in [18].
[b] $J_{1,9} = 92$ Hz, $J_{5,10} = J_{8,9} = 23$ Hz.
[c] Spectrum was recorded for $(CH_3)_2CO$ solution of compound.
[d] $J_{5,6} = J_{6,7} = J_{5,10} = 20$ Hz, $J_{7,8} = 19$ Hz, $J_{5,7} = 8$ Hz, $J_{5,8} = J_{6,8} = 13$ Hz.

*Perfluoro-1-(4-ethylphenyl)benzocyclobutene (**3**)*: HRMS *m/z*, 495.97478 (M^+). Calcd. for $C_{16}F_{16} = 495.97444$.

*1-Hydroxyperfluoro-1-(4-ethylphenyl)benzocyclobutene (**34**)*: mp 92.5–93.5 °C (from CCl_4). HRMS *m/z*, 493.97855 (M^+). Calcd. for $C_{16}HF_{15}O = 493.97877$.

3.2. Reaction of perfluoro-1-phenylbenzocyclobutene (*1*) with antimony pentafluoride

Benzocyclobutene **1** (1.24 g) and SbF_5 (4.74 g) (1:7) were heated in a nickel bomb (10 ml) for 7 h at 170 °C. The mixture was poured onto ice and extracted with $CHCl_3$. The extract was dried over $MgSO_4$. The solvent was distilled off to give product **33** (1.1 g, yield 89%). The ^{19}F NMR spectrum of compound **33** coincides with the spectrum of the authentic sample [9].

3.3. Reaction of perfluorobenzocyclobutene (*4*) with antimony pentafluoride

1. Benzocyclobutene **4** (0.88 g) and SbF_5 (5.37 g) (1:7) were heated in a nickel bomb (10 ml) for 57.5 h at 130 °C. The mixture was treated with anhydrous HF (15 ml), poured onto ice and extracted with $CHCl_3$. The extract was dried over $MgSO_4$. The solvent was distilled off to give a product (0.48 g) containing 22% (yield 12%) of **2**, 44% (22%) of **5**, 7% (3.7%) of **6** and 13% (7%) of **7**. The ^{19}F NMR spectra of compounds **2** and **5–7** coincide with the spectra of the authentic samples [2,17].
2. Analogously to the previous procedure, the reaction of benzocyclobutene **4** (1.66 g) and SbF_5 (5.09 g) (1:3.5) gave (170 °C, 7 h, treatment with 5 ml of HF) a mixture (1.37 g) containing 42% (yield 32%) of **5**, 17% (13.6%) of **6** and 26% (20%) of **8**. The individual compound **8** was isolated using preparative GLC.

   *Perfluoro-8,9-dimethyl-1,2,3,4-tetrahydrofluorene (**8**)*: HRMS *m/z*, 521.9703 (M^+). Calcd. for $C_{15}F_{18} =$ 521.9712. ^{19}F NMR spectrum: δ 104.6 (ddq, 3F, $J_{F,F} = 34$, 19 and 10 Hz, CF_3-8), 89.1 (m, 3F, CF_3-9), 55.9 (m, 1F) and 41.7 (m, 1F, $J_{A,B} = 301$ Hz, CF_2-1), 50.8 (m, 1F) and 47.3 (m, 1F, $J_{A,B} = 300$ Hz, CF_2-4), 41.2 (m, 1F, F-5), 39.2 (m, 1F, F-7), 33.9 (m, 1F) and 24.8 (m, 1F, $J_{A,B} = 277$ Hz, CF_2-2), 31.2 (m, 1F) and 22.7 (m, 1F, $J_{A,B} = 275$ Hz, CF_2-3), 15.8 (m, 1F, F-6), −20.9 (m, 1F, F-9).
3. Analogously to the previous procedure, the reaction of benzocyclobutene **4** (1.87 g) and SbF_5 (5.73 g) (1:3.5) gave (170 °C, 15 h, treatment with 5 ml of HF) 1.51 g of a mixture containing 18% (yield 13.5%) of **5**, 5% (4%) of **6** and 51% (39%) of **8**.

3.4. Reaction of perfluoro-1-(4-ethylphenyl)benzocyclobutene (*3*) with antimony pentafluoride

1. Benzocyclobutene **3** (1.87 g) and SbF_5 (5.76 g) (1:7) were heated in a nickel bomb (10 ml) for 30 h at 130 °C. The mixture was treated with anhydrous HF (5 ml), poured onto ice and extracted with $CHCl_3$. The extract was dried over $MgSO_4$. The solvent was distilled off to give 1.64 g of a product containing compound **3** and **34** in the ratio ~1:1 (^{19}F NMR spectrum).
2. Analogously to the previous experiment, the reaction of benzocyclobutene **3** (2.03 g) and SbF_5 (6.22 g) (1:7) gave (170 °C, 7 h) 1.59 g of a mixture containing 14% (yield 11%) of **3**, 6% (4.4%) of **9**, 2% (1.5%) of **10**, 26% (19%) of **11**, 19% (15%) of **12**, 10% (8%) of **13** and 4% (3%) of **34**. The individual compounds **9** and **11–13** were isolated by silica gel column chromatography (CCl_4 and then $CHCl_3$ as eluent).
3. Benzocyclobutene **3** (1.67 g) and SbF_5 (5.12 g) (1:7) were heated in a nickel bomb (10 ml) for 14 h at 170 °C. The mixture was poured into an ice–water mixture (100 ml) and $CHCl_3$ (20 ml) was added. The residue (0.5 g) containing compounds **13** and **14** in the ratio

1:2.7 (^{19}F NMR spectrum) was filtered off. The organic layer was then separated and dried over $MgSO_4$. $CHCl_3$ was distilled off to give 1.0 g of a mixture containing 47% of **11** and 14% of **13**. Yields of compounds **11**, **13** and **14** are 26, 17.5 and 24%, respectively.

*Perfluoro-4-ethyl-2-methyldiphenylmethane (**9**)*: HRMS *m/z*, 533.97171 (M^+). Calcd. for $C_{16}F_{18}$ = 533.97124.

*Perfluoro-6-ethyl-1,2,3,4-tetrahydroanthracene (**11**)*: mp 64.5–66 °C (from pentane). HRMS *m/z*, 533.97171 (M^+). Calcd. for $C_{16}F_{18}$ = 533.97124.

*Perfluoro-2-ethyl-9,10-dihydroanthracene (**12**)*: mp (in a capillary) 119–120 °C (from hexane). HRMS *m/z*, 495.97330 (M^+). Calcd. for $C_{16}F_{16}$ = 495.97444.

*Perfluoro-2-ethyl-9(10H)anthracenone (**13**)*: mp (in a capillary) 200–202 °C (after sublimation at 120°C, 5 torr). HRMS *m/z*, 473.97322 (M^+). Calcd. for $C_{16}F_{14}O$ = 473.97254.

*Perfluoro-2-ethyl-9,10-anthraquinone (**14**)*: mp (in a capillary) 292–293.5 °C (from acetone). HRMS *m/z*, 451.97043 (M^+). Calcd. for $C_{16}F_{12}O_2$ = 451.97065.

4. Analogously to the experiment 1, the reaction of benzocyclobutene **3** (1.05 g) and SbF_5 (3.21 g) (1:7) gave (170 °C, 30 h) 0.97 g of mixture containing 40% (yield 34%) of **11**, 20% (18%) of **12** and 11% (11%) of **13**.

3.5. Perfluoro-1-(2-ethylphenyl)-1-benzocyclobutenyl cation (29)

Benzocyclobutene **2** (0.15 g) was added to a solution of SbF_5 (1.14 g) in SO_2ClF (0.24 g) (**2**:SbF_5 = 1:17.4) at −10 °C. The mixture was stirred. The ^{19}F NMR spectrum was measured at +20 °C. The solution contained the salt of cation **29**, and precursor **2** was not found. The solution was poured into water and extracted with $CHCl_3$. The extract was dried over $MgSO_4$, and $CHCl_3$ was distilled off to give compound **7** (0.11 g, yield 73%).

3.6. Perfluoro-1-(4-ethylphenyl)-1-benzocyclobutenyl cation (30)

An analogous procedure was used to generate cation **30** from benzocyclobutene **3** (0.23 g) and SbF_5 (1.17 g) (**3**:SbF_5 = 1:11.6) in SO_2ClF (0.19 g). Hydrolysis of the salt of cation **30** yielded compound **34** (0.17 g, yield 74%).

3.7. Perfluoro-2-ethyl-2′-methyldiphenylmethyl cation (31)

Cation **31** was generated by the analogous procedure from diphenylmethane **5** (0.2 g) and SbF_5 (1.01 g) (**5**:SbF_5 = 1:12.4) in SO_2ClF (0.2 g). Hydrolysis of the salt of cation **31** gave compound **6** (0.16 g, yield 84%).

3.8. Perfluoro-4′-ethyl-2-methyldiphenylmethyl cation (32)

Cation **32** was generated by the analogous procedure from diphenylmethane **9** (0.03 g) and SbF_5 (1.01 g) (**9**:SbF_5 = 1:83) in SO_2ClF (0.28 g). Hydrolysis of the salt of this cation gave compound **10** (0.02 g, yield 74%), which was additionally purified on Silufol and then sublimated (90–95 °C, 3 torr).

*Perfluoro-4′-ethyl-2-methylbenzophenone (**10**)*: mp 66–68 °C. HRMS *m/z*, 511.97020 (M^+). Calcd. for $C_{16}F_{16}O$ = 511.96935.

Acknowledgements

We gratefully acknowledge the Russian Foundation for Basic Researches (project no. 99-03-32876a) and Siberian Branch of RAS (IG SB RAS-00-N47) for financial support.

References

[1] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, G.G. Yakobson, J. Fluorine Chem. 28 (1985) 115.
[2] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, G.G. Yakobson, Bull. Soc. Chim. Fr. (1986) 980.
[3] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, Izv. Akad. Nauk SSSR Ser. Khim. (1990) 645.
[4] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, G.G. Yakobson, Izv. Akad. Nauk SSSR Ser. Khim. (1990) 1114.
[5] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, Izv. Akad. Nauk Ser. Khim. (1992) 1419.
[6] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, J. Fluorine Chem. 77 (1996) 101.
[7] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, Zh. Org. Khim. 33 (1997) 755.
[8] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, V.R. Sinyakov, J. Fluorine Chem. 107 (2001) 53.
[9] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, V.R. Sinyakov, L.N. Shchegoleva, Zh. Org. Khim., in press.
[10] Yu.V. Pozdnyakovich, V.D. Shteingarts, Zh. Org. Khim. 14 (1978) 2237.
[11] V.V. Bardin, G.G. Furin, G.G. Yakobson, Izv. Sib. Otd. Akad. Nauk SSSR Ser. Khim. Nauk 6 (1978) 142.
[12] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, Zh. Org. Khim. 35 (1999) 1204.
[13] V.D. Shteingarts, Yu.V. Pozdnyakovich, G.G. Yakobson, Zh. Org. Khim. 7 (1971) 2002.
[14] Yu.V. Pozdnyakovich, T.V. Chuikova, V.D. Shteingarts, Zh. Org. Khim. 11 (1975) 1689.
[15] Yu.V. Pozdnyakovich, V.D. Shteingarts, J. Fluorine Chem. 4 (1974) 283.
[16] Yu.V. Pozdnyakovich, V.D. Shteingarts, J. Fluorine Chem. 4 (1974) 297.
[17] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, Mendeleev Commun. (1997) 71.
[18] B.G. Oksenenko, V.D. Shteingarts, G.G. Yakobson, Zh. Org. Khim. 7 (1971) 745.