ELSEVIER

Journal of Fluorine Chemistry 77 (1996) 133–137

JOURNAL OF FLUORINE CHEMISTRY

The alicyclic ring cleavage and other transformations of perfluorinated 1-alkyl-, 1,1- and 1,2-dialkyl-benzocyclobutenes in the system Br_2–SbF_5

V.M. Karpov *, T.V. Mezhenkova, V.E. Platonov

Institute of Organic Chemistry, Novosibirsk 630090, Russian Federation

Abstract

In the reactions of perfluorinated 1-methyl- (**2**) and 1-ethyl-benzocyclobutene (**3**) with bromine in an SbF_5 medium, cleavage of the four-membered ring of the starting compounds giving 2-bromoperfluoroisopropylbenzene (**8**) and 2-bromoperfluoro-sec-butylbenzene (**9**), respectively, was observed. In the system Br_2-SbF_5, perfluorinated 1,1- (**4**) and 1,2-diethylbenzocyclobutene (**5**) undergo bromofluorination of the aromatic ring and breaking of the C^1–C^2 bond of the four-membered ring. Thus, in the Br_2–SbF_5 system, compound **5** gives 4-bromoperfluoro-1,2-dipropylcyclohexene (**10**) and perfluoro-1,2-dipropylcyclohexene (**11**), and isomer **4** gives perfluoro-1,1-diethyl-3,4,5,6-tetrahydrobenzocyclobutene (**15**) and perfluoro-1-methyl-2-(pent-2-ene-3-yl)cyclohexene (**16**). The latter is obtained by heating compound **15** with SbF_5 or CsF.

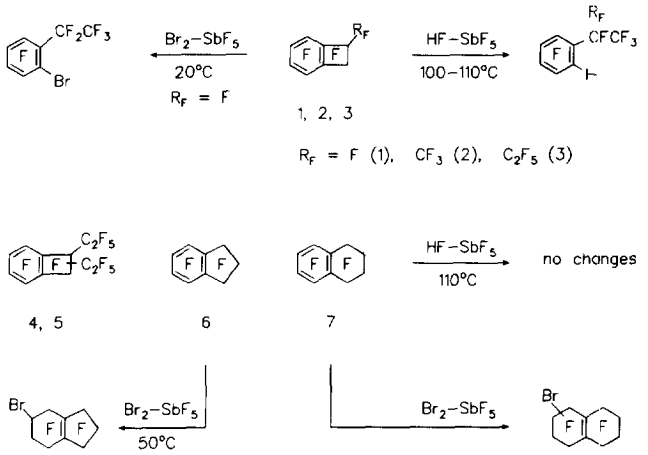
Keywords: Alicyclic ring cleavage; Perfluoroalkyl benzocyclobutenes; Perfluorodialkylbenzocyclobutenes; Br_2–SbF_5 system; NMR spectroscopy; Mass spectrometry

1. Introduction

Recently, we have described the electrophilic addition of HF in a medium of SbF_5 to perfluorobenzocyclobutene (**1**), perfluoro-1-methylbenzocyclobutene (**2**) and perfluoro-1-ethylbenzocyclobutene (**3**), leading to the formation of *o-H*-perfluoroalkylbenzenes — the cleavage products of the four-membered ring in the starting compounds. Perfluorinated 1,1- (**4**) and 1,2-diethylbenzocyclobutenes (**5**), perfluoroindan (**6**) and perfluorotetralin (**7**) were essentially unchanged under similar conditions (Scheme 1). The difference in the behaviour of benzocycloalkenes may be associated with the relative stability of intermediate cations and with the different strain in the alicyclic fragment of the benzocycloalkenes [1].

The interaction of compound **1** with bromine in an SbF_5 medium proceeds at a lower temperature than with HF-SbF_5 and leads to the formation of 2-bromoperfluoroethylbenzene [2]. In the Br_2-SbF_5 system, indan **6** [2] and tetralin **7** [3] give products arising from bromofluorination of the aromatic ring (Scheme 1).

In order to establish the common transformation tendencies of polyfluorobenzocycloalkenes under the action of electrophilic reagents, we have studied the behaviour of benzocyclobutenes **2–5** in the Br_2–SbF_5 system.



Scheme 1.

2. Results and discussion

We have found that alkylbenzocyclobutenes **2** and **3** in the Br_2–SbF_5 system are transformed to 2-bromoperfluoroisopropylbenzene (**8**) and 2-bromoperfluoro-sec-butylbenzene (**9**), respectively, which are the cleavage products of the C^2–C^3 bond of the four-membered ring of the starting compounds. Scheme 2 shows one such possible reaction route.

It should be noted that benzocyclobutene **1** is not transformed by bromine at 200°C in the absence of SbF_5 [2]. In

* Corresponding author.

PII S0022-1139(96)03390-8

the reaction of compounds **2** and **3** with SbF_5 in the absence of bromine, an expansion of the four-membered ring to the five-membered one was observed [4] (Scheme 3).

In contrast to the alkyl derivatives **2** and **3**, in the system Br_2–SbF_5 dialkylbenzocyclobutenes **4** and **5** undergo bromofluorination of the aromatic ring and breakage of the C^1–C^2 bond of the four-membered cycle. Thus isomer **5** reacts with Br_2 and SbF_5 to form a mixture of 4-bromoperfluoro-1,2-dipropylcyclohexene (**10**) and perfluoro-1,2-dipropylcyclohexene (**11**). When heated with SbF_5, compound **10** is transformed to product **11** (Scheme 4).

It may be suggested that benzocyclobutene **5** is first transformed to the bicycloalkene **12**, which undergoes cleavage of the four-membered ring to give the diene **13**. Bromofluorination of diene **13** and subsequent substitution of bromine by fluorine in olefins **14** lead to the formation of compounds **10** and **11**. This does not exclude the possibility of substitution of bromine by fluorine in the intermediate cycloolefins **12** and **13**, and subsequent fluorination of the reaction products leading to compound **11**.

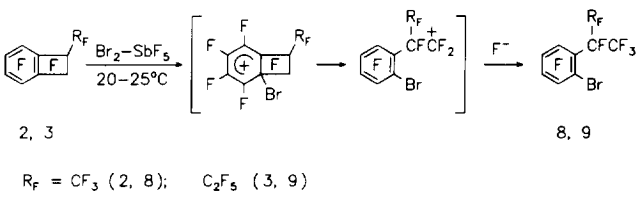
In contrast to benzocyclobutene **5**, in the system Br_2–SbF_5 isomer **4** gives only a small amount of perfluoro-1-methyl-2-(pent-2-ene-3-yl)cyclohexene (**16**), which is the cleavage product of the four-membered ring. In this case the main reaction product was perfluoro-1,1-diethyl-3,4,5,6-tetrahydrobenzocyclobutene (**15**). It has been shown by separate experiments, that the reactions of compound **15** with SbF_5 or CsF at 130 °C over a lengthy period of time lead to the formation of diene **16**. This transformation does not proceed in the absence of SbF_5 or CsF (Scheme 5).

Diene **16** may be alternatively synthesized from perfluoro-2-(pent-2-ene-3-yl)toluene (**17**) in the Br_2–SbF_5 system. In addition to product **16**, the reaction mixture also contained the bromoperfluoro-1-methyl-2-(pent-2-ene-3-yl)cyclohexenes **18**. It has been shown that when treated with SbF_5 isomers **18** give diene **16**.

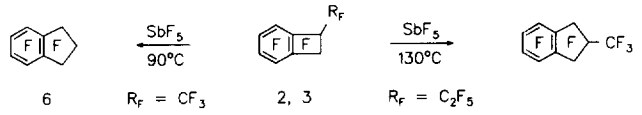
Transformation of compound **15** to **16** apparently proceeds by cleavage of the four-membered ring of cyclobutene **15** (route 1) with subsequent isomerization of diene **19** under the action of SbF_5 (route 1a) or CsF (route 1b) according to Scheme 6.

It seems less probable that this process proceeds by a route of type 2, which is possible in the reaction of compounds **4** and **5** with SbF_5 [5] (Scheme 7).

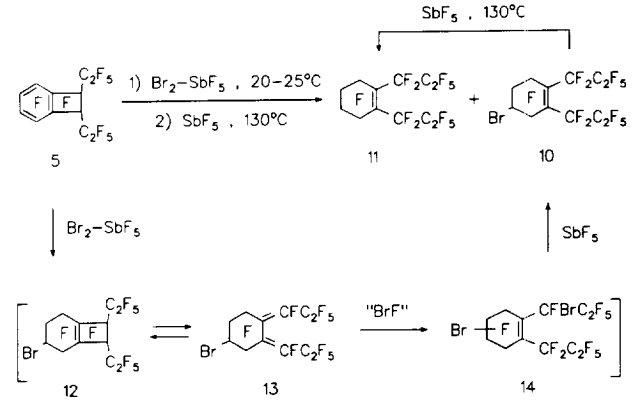
Following route 2, transformation of compound **15** to diene **16** should proceed under more rigid conditions as compared with benzocyclobutene **4** (the relative stability of cation **20** should be lower than that of the benzyl-type cation **23**, whereas the relative stabilities of cations **21** and **22** should be comparable). On the other hand, cleavage of the four-membered ring of cycloalkene **12** should proceed to a lesser extent relative to compound **15** as is observed in the case of benzocyclobutenes **4** (130 °C) and **5** (170 °C) [5]. What actually happens is that the four-membered ring in compound **15** is opened to a lesser extent than in compound **12**. This fact may be explained in terms of route 1 Scheme 6, if it is assumed



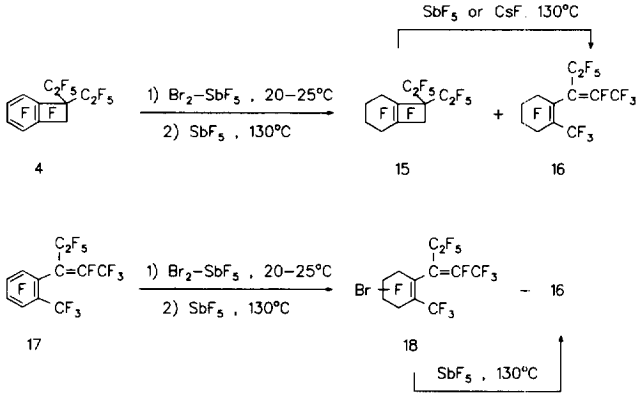
Scheme 2.



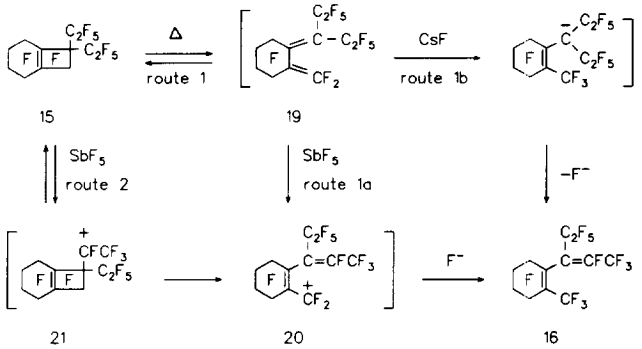
Scheme 3.



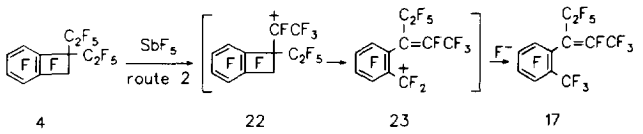
Scheme 4.



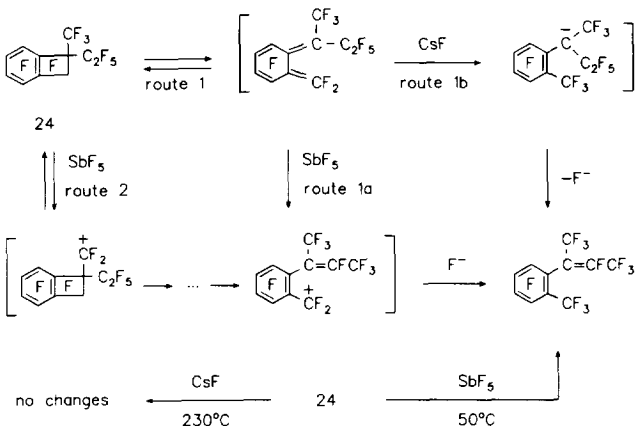
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

that compound **12** has a *trans* configuration. Hence, it is known that the activation energy for ring-opening of perfluorinated *trans*-3,4-dialkylcyclobutenes to give corresponding *Z,Z*-butadienes is lower than that for ring-opening of perfluorinated *cis*-3,4-dialkylcyclobutenes, perfluoro-3-methylcyclobutene and perfluorocyclobutene [6].

It should be noted that for benzocyclobutenes **4** and **5**, as well as for perfluoro-1-ethyl-1-methylbenzocyclobutene (**24**) and perfluoro-1-ethyl-2-methylbenzocyclobutene (**25**), their sole interaction with SbF_5 is unlikely to proceed via route 1 [5] (Scheme 8). Thus, in terms of route 1, isomerization of these benzocyclobutenes should proceed not only under the action of SbF_5, but under the action of CsF as well.

In the present study we have shown that compounds **24** and **25** remained unchanged under the action of CsF even at higher temperature (230 °C) in contrast to their reaction with SbF_5 at 50 °C [5] (Scheme 8).

The structures of the compounds were established by elemental analysis and spectral characteristics.

The chemical shifts of the signals and the coupling constants in the ^{19}F NMR spectra of compounds **8** and **9** are in agreement with similar shifts and constants for other polyfluoroalkylbenzenes [1,2,7]. However, the ^{19}F NMR spectra of compounds **11**, **15** and **16** exhibit chemical shifts for the signals of the CF_2 groups associated with the six-membered cycle which are in agreement with those for perfluoro-4,5,6,7-tetrahydroindan (**26**) [8] and perfluorooctalin [9], whereas the chemical shifts for the other CF_2 groups, as well as for the CF_3 groups, are in agreement with the shifts of similar groups in perfluoro-1,2-dipropylbenzene [5], benzocyclobutene **4** [10] and compound **17** [5].

A comparative analysis of the spectra of tetrahydroindan **26** [8] and 5-bromoperfluoro-4,5,6,7-tetrahydroindan [2], as well as of cyclohexenes **10** and **11**, allows the assignment of structure **10** and the exclusion of the alternative structure (3-bromoperfluoro-1,2-dipropylcyclohexene).

Compound **12** was not isolated, but its assumed formation is based on the fact that high-field signals of tertiary fluorine atoms appear in the ^{19}F NMR spectrum of the mixture obtained from compound **5** and Br_2–SbF_5 under mild conditions (cf. Ref. [10]).

3. Experimental details

^{19}F NMR spectra were recorded on a Varian A-56/60A instrument (56.4 MHz) for reaction mixtures in the absence of solvent and on a Bruker WP-200 SY instrument (188.3 MHz) for $CHCl_3+CDCl_3$ solutions of individual compounds (≤ 10 mol%). Chemical shifts are given in δ ppm downfield from C_6F_6 as internal standard. IR spectra were recorded for CCl_4 solutions on a UR-20 spectrometer. UV spectra were recorded for heptane solutions on a Specord UV–vis instrument. The elemental composition of the various compounds was determined by means of high-resolution mass spectrometry on a Finnigan Mat 8200 instrument.

3.1. 2-Bromoperfluoroisopropylbenzene (8)

Dibromine (Br_2) (0.33g) was added to a stirred solution of 1.02 g of benzocyclobutene **2** in 5.17 g of SbF_5 (0.6:1:7) [1]. The mixture was stirred for 5.5 h at 24 °C and then poured on to ice. The organic layer was separated and dried over $MgSO_4$ to give 1.15 g of a product containing 84% [2] of compound **8**. A sample for analysis was isolated by preparative GLC.

Compound **8**: MS: Found: M^+ 395.898 9. C_9BrF_{11} requires M 395.900 8. IR (υ, cm^{-1}): 1465; 1520; 1630 (fluorinated aromatic ring). UV (λ_{max}, nm (log ϵ)): 278 (3.38). ^{19}F NMR δ: 87.9 (6F, $2CF_3$); 43.1 (1F, F^3); 33.8 (1F, F^6); 15.8 (1F, F^4); 9.1 (1F, F^5); −10.3 (1F, $F^{1'}$) ppm ($J_{CF_3-F^6}=27$, $J_{45}=J_{56}=19$, $J_{34}=22$, $J_{46}=8$, $J_{1'3}\sim J_{35}\sim J_{36}\sim 6$, $J_{CF_3-F^{1'}}=5$, $J_{1'5}=3$ Hz).

3.2. 2-Bromoperfluoro-sec-butylbenzene (9)

Dibromine (Br_2) (0.32 g) was added to a stirred solution of 1.17 g of benzocyclobutene **3** in 5.09 g of SbF_5 (0.6:1:7). The mixture was stirred for 5 h at 20 °C and then treated as in the previous experiment to give 1.25 g of the product containing 86% of compound **9**. A sample for analysis was isolated by preparative GLC.

Compound **9**: Analysis: Found: Br, 17.86; F, 55.65%; M^+, 445.898 2. $C_{10}BrF_{13}$ requires: Br, 17.88; F, 55.25%; M, 445.897 6. IR (υ, cm^{-1}): 1465; 1520; 1630 (fluorinated aromatic ring). UV (λ_{max}, nm (log ϵ)): 279 (3.44). ^{19}F NMR

[1] The molar ratio of the reagents employed is quoted in brackets hereafter.

[2] Contents of main products in reaction mixtures were established by GLC methods and ^{19}F NMR spectroscopic data.

δ: 89.5 (3F, CFCF_3); 82.4 (3F, CF_2CF_3); 43-45 (3F, F^3 and CF_2CF_3); 35.4 (1F, F^6); 16.1 (1F, F^4); 9.4 (1F, F^5); −12.8 (1F, $F^{1'}$ ppm ($J_{CF_3-F^6}=29.5$, $J_{CF_2CF_3-F^6}=16$, $J_{45}=J_{56}=20$, $J_{34}=23$, $J_{46}=8$, $J_{35}=J_{CF_3-CF_3}=5$, $J_{F^5-F^{1'}}=3$ Hz).

3.3. Interaction of benzocyclobutene 5 with bromine in an SbF_5 medium

Method a Dibromine (Br_2) (0.15g) was added to a stirred solution of 0.71 g of benzocyclobutene **5** in 2.54 g of SbF_5 (0.6:1:0.7). The mixture was stirred for 4.5 h at 25°C, treated with 1 ml of anhydrous HF and poured on to ice cooled with liquid N_2. The organic layer was separated and dried over $MgSO_4$ to give 0.82 g of a mixture containing the starting compound (22%) along with the reaction products.

In a similar manner, from a mixture of 2.57 g of SbF_5 and 0.15 g of Br_2 was obtained 0.72 g of a product containing compound **10** (60%-70%) and possibly compound **12** [3] along with some impurities which could not be identified.

A portion of this product (0.57 g) and 1.49 g of SbF_5 were heated in a sealed tube for 10 h at 130 °C. The mixture was cooled to room temperature and poured on to ice and the aqueous layer then acidified with hydrochloric acid. The organic layer was separated and dried over $MgSO_4$ to give 0.47 g of a mixture containing 20% of compound **10** and 52% of product **11**.

Method b A mixture consisting of 3.65 g of benzocyclobutene **5**, 17.65 g of SbF_5 and 0.65 g of Br_2 was held in a sealed tube for 17 h at 20-25 °C and then heated for 15 h at 130 °C. It was then treated as in the previous experiment to give 4.48 g of a mixture containing 18% of compound **10** and 52% of compound **11**. The individual compounds **10** and **11** were isolated by preparative GLC.

Compound **10**: MS: Found: M^+ 621.889 1. $C_{12}BrF_{21}$ requires M 621.884 8. ^{19}F NMR δ: 81.1 (6F, $2CF_3$); 79.8, 67.7 (2F, A components of two AB systems, $F^{3,6}$); 51.9, 44.8 (2F, B components of two AB systems, $F^{3,6}$, $J_{AB}=320$ Hz); 62.8 (2F_A); 58.3 (2F_B, $2CF_2CF_2CF_3$, $J_{AB}=290$ Hz); 44.0 (4F, $2CF_2CF_2CF_3$); 44.4 (1F_A, F^5); 32.3 (1F_B, F^5, $J_{AB}=280$ Hz); 24.4 (1F, F^4) ppm.

Compound **11**: Analysis: Found: C, 25.59; F 74.48%. $C_{12}F_{22}$ requires: C, 25.64; F 74.36%. ^{19}F NMR δ: 81.1 (6F, $2CF_3$); 60.5 (4F, $2CF_2CF_2CF_3$); 53.7 (4F, $F^{3,6}$); 43.8 (4F, $2CF_2CF_2CF_3$); 26.7 (4F, $F^{4,5}$) ppm.

3.4. Reaction of compound 17 with bromine in an SbF_5 medium

Method a In a similar manner, starting from 1.52 g of compound **17**, 6.6 g of SbF_5 and 0.33 g of Br_2 (1:9:0.6) (20–25 °C, 17 h; then 130 °C, 25 h), was obtained 1.67 g of a mixture containing 74% of compound **16** and 21% of product **18**. The individual compound **16** and the mixture of isomers **18** were isolated by preparative GLC.

Compound **16**: MS: Found: M^+ 523.966 3. $C_{12}F_{20}$ requires M 523.968 0. IR (υ, cm^{-1}): 1700 (C=C). ^{19}F NMR δ: 103.6 (3F, CF_3^1); 92.4 (3F, $CFCF_3$); 81.2 (3F, CF_2CF_3); 66.3 (1F); 57.8 (1F_A); 54.1 (1F_B, CF_2CF_3, $J_{AB}=290$ Hz); 56.4, 55.5 (2F, A components of two AB systems, $F^{3,6}$); 46.9, 46.1 (2F, B components of two AB systems, $F^{3,6}$, $J_{AB}=310$ Hz); 32.2, 31.1 (2F, A components of two AB systems, $F^{4,5}$); 23.2, 22.7 (2F, B components of two AB systems, $F^{4,5}$, $J_{AB}=280$ Hz) ppm.

Mixture of isomers **18**: MS: Found: M^+ 583.890 7. $C_{12}BrF_{19}$ requires M 583.888 0. IR (υ, cm^{-1}): 1700 (C=C). ^{19}F NMR δ: for one isomer: ~104 (3F, CF_3^1); ~92 (3F, $CFCF_3$); 82.9 (3F, CF_2CF_3) ppm; for the other isomer: ~104 (3F, CF_3^1); ~92 (3F, $CFCF_3$); 80.8 (3F, CF_2CF_3) ppm (ratio of isomers ~1:2). The signals of the other fluorine atoms occured at δ 76.7–23.5 ppm.

Method b A mixture consisting of 0.43 g of compound **17**, 1.73 g of SbF_5 and 0.1 g of Br_2 (1:8.3:0.6) was heated in a sealed tube for 5.5 h at 130 °C. It was then treated as in the previous experiments to give 0.47 g of a mixture containing compounds **16** (58%) and **18** (36%).

In a similar manner, from 0.3 g of this product and 1.69 g of SbF_5 (130 °C, 10 h) was obtained 0.16 g of the product containing 88% of compound **16**.

3.5. The behaviour of benzocyclobutenes 4 and 5 in the Br_2–SbF_5 system

Dibromine (Br_2) (0.4g) was added to a stirred solution consisting of 1.87 g of compounds **4** and **5** in 6.35 g of SbF_5 (0.6:0.48:0.52:7). The mixture was stirred further for 5.5 h at 22 °C and then held without stirring for 15 d at 20–25 °C. The mixture was then treated with 1.5 ml of anhydrous HF and poured on to ice cooled with liquid N_2. The organic layer was separated and dried over $MgSO_4$ to give 1.7 g of a mixture containing 88% of bromofluorination products.

A portion (1.44 g) of this mixture and 6.35 g of SbF_5 were heated in a sealed tube for 10 h at 130 °C. The mixture was cooled to room temperature and poured on to ice and the aqueous layer acidified with hydrochloric acid. The organic layer was separated and dried over $MgSO_4$ to give 1.05 g of a product containing 86% of compounds **11**, **15** and **16** in the ratio 6.3:4:1. The individual compound **15** was isolated by preparative GLC.

Compound **15**: Analysis: Found: C, 27.22; F, 72.47%. $C_{12}F_{20}$ requires: C, 27.50; F, 72.50%. ^{19}F NMR δ: 82.7 (6F, $2CF_3$); 62.0 (2F); 55.6 (2F_A); 52.7 (2F_B, $2CF_2CF_3$, $J_{AB}=300$ Hz); 46.1 (2F); 45.6 (2F); 29.3 (2F); 28.7 (2F) ppm.

3.6. Isomerization of compound 15 to product 16 under the action of SbF_5 and CsF

Method a A portion (0.92 g) of the mixture of compounds **11**, **15** and **16** obtained in a previous experiment, and 5.61 g

[3] Signals corresponding to tertiary fluorine atoms occurred at δ 4–2 ppm in the ^{19}F NMR spectrum of the mixture (cf. Ref. [10]).

of SbF_5 were heated in a sealed tube for 50 h at 130 °C. The mixture was cooled to room temperature and poured on to ice. The organic layer was separated and dried over $MgSO_4$ to give 0.75 g of the product containing 95% of compounds **11**, **15** and **16** in the ratio 7:1:4.

Method b Compound **15** (0.1 g) and 0.23 g of CsF (1:8) were heated in a sealed tube for 51 h at 130 °C. Distillation yielded 0.07 g of the product containing compounds **15** and **16** in the ratio 1:2.3.

Method c Compound **15** (0.04 g) was heated in a sealed tube for 47.5 h at 130 °C to give 0.04 g of the starting compound.

3.7. The behaviour of perfluorinated 1-ethyl-1-methyl- (24) and 1-ethyl-2-methylbenzocyclobutenes (25) under the action of CsF

Compounds **24** and **25** (0.39 g) and 0.93 g of CsF (0.52:0.48:6.2) were heated in a sealed tube for 7 h at 230 °C. Distillation yielded 0.35 g of the starting compounds **24** and **25** in the same ratio.

Acknowledgements

We gratefully thank the International Science Foundation and Russian Government (Grant N J7I100) and the Russian Foundation for Fundamental Researches (Project N 95-03-08374a) for financial support.

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