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Short communication

Expansion of the pentafluorobenzene ring of perfluoro-1, 2-diethyl-1-phenylbenzocyclobutene under the action of SbF_5

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Abstract

Perfluoro-1,2-diethyl-1-phenylbenzocyclobutene under the action of SbF_5 gives, after treatment of the reaction mixture with water, perfluoro-4-[1-(6-propyl-phenyl)-propylidene]cyclohexa-2,5-dienone along with the products of unusual pentafluorobenzene ring expansion – perfluorinated 4*b*,10-diethylbenzo[*a*]azulen-7(4*bH*)-one and 10-ethylbenzo[*a*]azulen-6(10*H*)-one.

Keywords: Fluorinated; Benzocyclobutene; Ring expansion; Antimony pentafluoride

1. Introduction

Previously, we have found and investigated the skeletal transformations of perfluoro-benzocycloalkenes (benzocyclobutene, indan and tetralin) and their perfluoroalkyl and perfluoroaryl derivatives in the reactions with antimony pentafluoride [1–9]. In these reactions perfluoroalkylbenzocyclobutenes undergo expansion of the four-membered ring to a five-membered ring; alternatively, the alicyclic ring cleavage of benzocyclobutenes leads to polyfluorostyrenes, which subsequently undergo cyclization into polyfluoroindans or fluorination [1,4,5]. In perfluoro-1-(2- or 4-ethylphenyl)benzocyclobutenes under the action of SbF_5 both alicyclic and aromatic fragments of the substrate are involved in the reaction to give polyfluorinated fluorene or anthracene derivatives. In contrast to this, perfluoro-1-phenylbenzocyclobutene does not undergo skeletal transformations under the same conditions [10].

It was interesting to investigate the behaviour of perfluorophenylbenzocyclobutenes, containing perfluoroethyl groups together with pentafluorophenyl one in the alicyclic fragment of the molecule, under the action of SbF_5 with the aim to study the possibility of their cationoid skeletal rearrangements. This work describes unusual transformations of perfluoro-1, 2-diethyl-1-phenylbenzocyclobutene (**1**) under the action of antimony pentafluoride.

2. Results and discussion

Heating a solution of compound **1** and HF in antimony pentafluoride, obtained in the reaction of perfluoro-1,2-diethylbenzocyclobutene (**2**) with C_6F_5H in SbF_5 [11], and subsequent treatment of the reaction mixture with H_2O leads to the formation of perfluorinated 4-[1-(6-propylphenyl)propylidene]cyclohexa-2,5-dienone (**3**), 4*b*,10-diethylbenzo[*a*]azulen-7(4*bH*)-one (**4**) and 10-ethylbenzo[*a*]azulen-6(10*H*)-one (**5**) (Scheme 1). The reaction mixture also contains some unidentified compounds.

The structures of compounds **4** and **5** were determined by X-ray crystallography (Figs. 1 and 2). The structure of dienone **3** was established by HRMS and ^{19}F NMR spectroscopy.

Opening of the four-membered ring in compound **1** under the action of SbF_5 seems to occur analogous to that in perfluoro-1-alkylbenzocyclobutenes [4,5]. Thus, reversible elimination of the fluoride ion from benzocyclobutene **1** under the action of SbF_5 possibly leads to cation **6**, which undergoes alicyclic ring opening to give cation **7**. Addition of the fluoride ion to the latter and subsequent fluorination leads to product **8**. Hydrolysis of cation **9**, generated from compound **8** under the action of SbF_5, gives ketone **3** (Scheme 2).

One can assume that perfluorinated benzo[*a*]azulenes, formed in the reaction, exist in an SbF_5 medium as salts of

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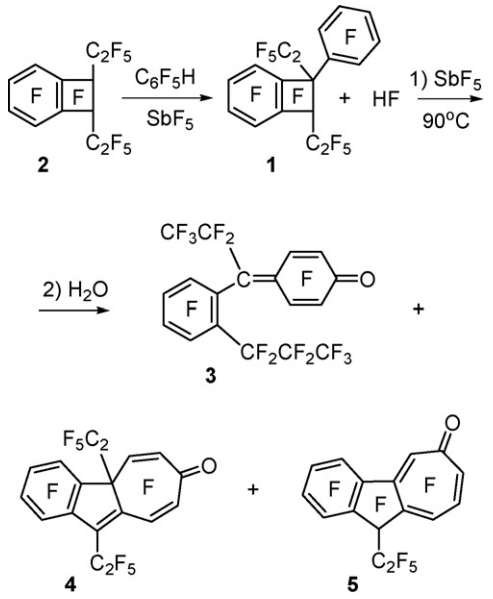


Scheme 1.

cations **10** and **11**. Hydrolysis of the salts gives compounds **4** and **5**, respectively (Scheme 3).

It may be proposed that cation **10** eliminates $C_2F_5^+$ to yield compound **12**. Fluorination of the latter forms compound, which under the action of antimony pentafluoride loses the fluoride anion to generate cation **11**. A possibility of elimination of CF_3^+ from perfluorinated carbocations has been discussed [8,9]. The mechanism of the expansion of the pentafluorobenzene ring to the seven-membered one is still not clearly understood. The reaction will be studied more detail and the results will be discussed in a subsequent article.

According to a single crystal X-ray structure determination the seven-membered ring of **5** is close to planar with root-mean-square deviation of 0.099 Å and small boat-like distortion.

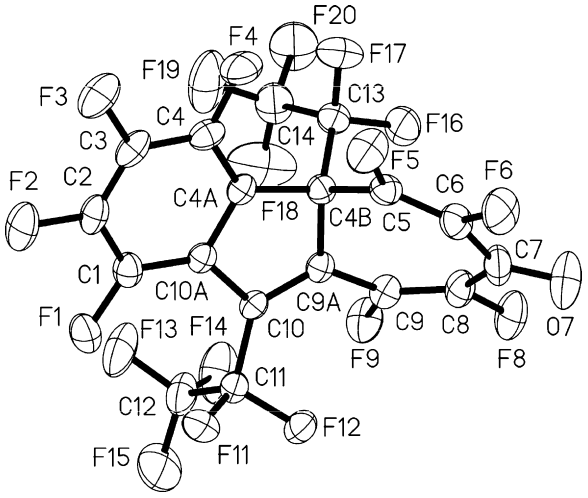


Fig. 1. Molecular structure of **4** (only one of two independent molecules is shown). Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and torsion angles (°): C5–C6 1.324(5), 1.320(5), C6–C7 1.479(6), 1.477(5), C7–O7 1.209(4), 1.212(4), C7–C8 1.466(6), 1.466(6), C8–C9 1.314(5), 1.320(5), C4A–C4B–C13–C14 54.0(4), 57.1(4), C9A–C10–C11–C12 101.4(4), 100.3(5).

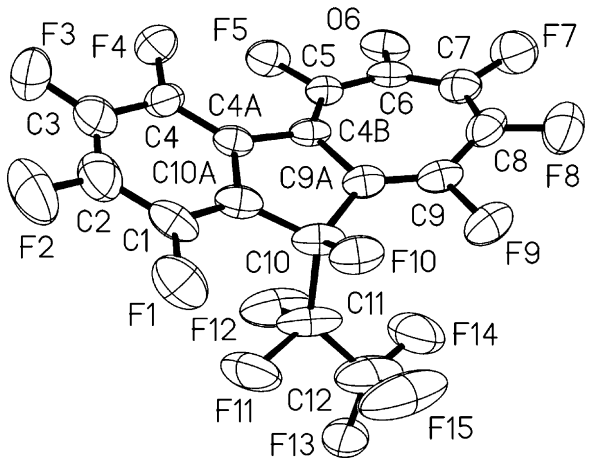
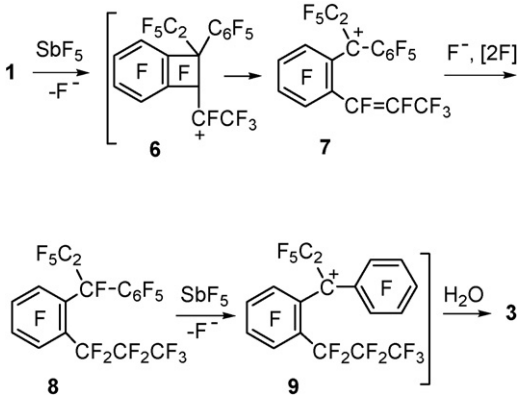
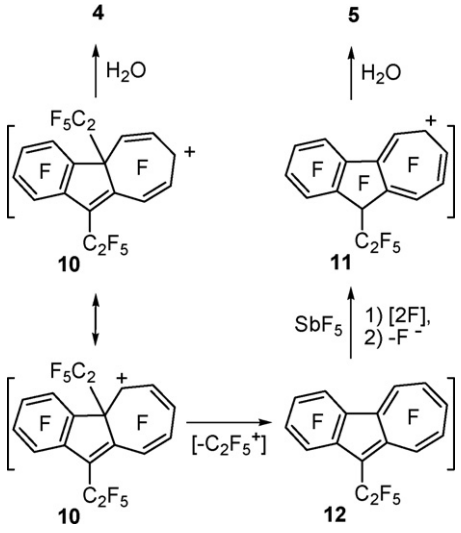


Fig. 2. Molecular structure of **5**. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å) and torsion angle (°): C4B–C5 1.33(1), C5–C6 1.45(1), C6–O6 1.24(1), C6–C7 1.42(2), C7–C8 1.36(2), C9A–C10–C11–C12 70(2).



Scheme 2.

Bond length alternation of this ring is identical within errors to the alternation of 3-methoxypentafluorotropone [12]. The conformation of the seven-membered ring (distorted twist-chair) in two independent molecules of **4** is slightly different;



Scheme 3.

the C9, C9A atom deviations from the C4B, C5, C6, C7, C8 plane of the first molecule are equal to 0.414(5), 0.805(5) Å, while C5, C4B atom deviations from the C6, C7, C8, C9, C9A plane of the second molecule are 0.412(5), 0.886(5) Å accordingly. It can be noted that bond length alternation of the C=C–C(=O)–C=C fragment is more in **4** than in **5**.

3. Experimental

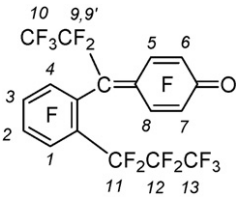
^{19}F NMR spectrum of compound **3** was recorded on a Bruker AC-200 instrument (188.3 MHz). Chemical shifts are given in δ ppm from CCl_3F, J values in Hz; C_6F_6 (−162.9 ppm from CCl_3F) was used as internal standard. The molecular masses of compounds **3–5** were determined by high-resolution mass spectrometry on a Finnigan Mat 8200 instrument (EI 70 eV).

Perfluorodiethylbenzocyclobutene **2** was obtained according to Ref. [13]; C_6F_5H and SbF_5 are commercial products.

3.1. Reaction of perfluoro-1,2-diethyl-1-phenylbenzocyclobutene (*1*) with SbF_5

To a solution of benzocyclobutene **2** (0.54 g) in SbF_5 (1.79 g) pentafluorobenzene (0.2 g) (molar ratio of **2**:SbF_5:C_6F_5H = 1:7:1) was added and the mixture was stirred at 25 °C for 7 h. Then resulting solution of compound **1** and HF in SbF_5 (molar ratio of **1**:HF:SbF_5 = 1:1:7) [11] was heated at 90 °C for 15 h. The mixture was poured into 5% hydrochloric acid and extracted with $CHCl_3$. The extract was dried over $MgSO_4$. The solvent was distilled of to give 0.64 g of the product, containing (GLC, ^{19}F NMR spectrum) 23% of compound **3**, 14% of **4** and 12% of **5** along with unidentified compounds. Ketones **3** (0.1 g), **4** (0.08 g) and **5** (0.04 g) were isolated by silica gel column chromatography (CCl_4 and then $CHCl_3$ as eluent).

3.1.1. Perfluoro-4-[1-(6-propylphenyl)propylidene]cyclohexa-2,5-dienone (*3*)



Liquid. NMR ^{19}F ($CHCl_3$): δ −79.2 (3F, CF_3-10), −81.1 (3F, CF_3-13), −100.66 (1F, F-9), −100.70 (1F, F-9′), −104.2 (1F, F_A) and −105.2 (1F, F_B, CF_2-11), −125.5 (2F, CF_2-12), −128.1 (1F, F-5), −131.2 (2F, F-1, F-8), −133.6 (1F, F-4), −145.6 (2F, F-3, F-6 (or F-7)), −146.5 (1F, F-7 (or F-6)), −147.7 (1F, F-2). J_{AB} = 290, J_{A1} = 30, J_{12} = 20, J_{23} = 21, J_{34} = 22, J_{13} = 10, $J_{14} \sim 10$, J_{24} = 7, $J_{F(4)–CF3(10)}$ = 12, J_{59} = 62, $J_{59'}$ = 79, $J_{F(5)–CF3(10)}$ = 26, $J_{89} = J_{89'}$ = 11, $J_{56} = J_{78}$ = 7. HRMS *m/z*, 611.9617 (M^+). Calcd for $C_{18}F_{20}O$ = 611.9630.

3.1.2. Perfluoro-4b,10-diethylbenzo[a]azulen-7(4bH)-one (*4*)

mp 71–73 °C (hexane–CH_2Cl_2). HRMS *m/z*, 573.9665 (M^+). Calcd for $C_{18}F_{18}O$ = 573.9661.

3.1.3. Perfluoro-10-ethylbenzo[a]azulen-6(10H)-one (*5*)

mp 185–188 °C (hexane–benzene, in a sealed capillary). HRMS *m/z*, 473.9040 (M^+). Calcd for $C_{16}F_{14}O$ = 473.9725.

3.2. X-ray crystallography

Single crystals of compounds **4** and **5** were grown by slow evaporation of solvents from hexane–CH_2Cl_2 and hexane–benzene solutions, respectively.

The X-ray diffraction experiments were carried out on a Bruker P4 diffractometer (graphite-monochromated Mo Kα radiation) at room temperature. Intensity data were collected using $\theta/2\theta$-scan, $2\theta < 52°$ and $2\theta < 48°$ for **4** and **5** accordingly. Reflection intensities of **4** were corrected for absorption by integration method. The structures were solved by direct methods, using SHELXS-97 program [14] and refined by anisotropic full-matrix least squares against F^2 of all reflections using SHELXL-97 program [14]. Crystallographic data for the structures of **4** and **5** in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 654119 and 654120. Copy of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 122 3336033; e-mail: deposit @ccdc.cam.ac.uk; internet: http://www.ccdc.cam.ac.uk).

3.2.1. Crystallographic data and refinement parameters for *4*

$C_{18}F_{18}O$, M = 574.18, monoclinic, space group $P2_1/c$, a = 9.270(1), b = 13.974(2), c = 29.635(4) Å, β = 96.990(9)°, V = 3810.4(9) Å^3, Z = 8, D_{calc} = 2.002 g cm^{-3}, μ = 0.245 mm^{-1}, 7446 total reflexions, 6957 unique reflexions (R_{int} = 0.0329), R = 0.0525 for 4149 $I > 2\sigma(I)$, 667 parameters, wR_2 = 0.1484 and GOF = 1.013 for all data, max/min $\Delta\rho$ 0.29/−0.34.

3.2.2. Crystallographic data and refinement parameters for *5*

$C_{16}F_{14}O$, M = 474.16, orthorhombic, space group *Pbca*, a = 5.914(1), b = 22.591(3), c = 23.417(3) Å, V = 3128.7(9) Å^3, Z = 8, D_{calc} = 2.013 g cm^{-3}, μ = 0.240 mm^{-1}, 2443 unique reflexions, R = 0.0950 for 1047 $I > 2\sigma(I)$, 280 parameters, wR_2 = 0.3367 and GOF = 1.043 for all data, max/min $\Delta\rho$ 0.51/−0.41.

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