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Short communication

Skeletal transformations of perfluorinated 2,2-diethyl- and 2-ethyl-2-phenyl-benzocyclobutenones under the action of antimony pentafluoride

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ABSTRACT

Perfluoro-2-ethyl-2-phenylbenzocyclobutenone heated with SbF_5 at 70 °C and then treated with water, forms perfluoro-3-ethyl-3-phenylphthalide. In contrast to this, heating of perfluoro-2,2-diethylbenzocyclobutenone with SbF_5 at 70 °C gives, after treatment of the reaction mixture with water, perfluoro-2-(pent-2-en-3-yl)benzoic acid. When the reaction temperature is raised to 125 °C, a solution of a salt of perfluoro-4-ethyl-3-methylisochromenyl cation is obtained. Hydrolysis of the solution of the salt gives perfluoro-4-ethyl-3-methylisochromen-1-one.

1. Introduction

Perfluorinated ketones and vinyl ketones having a CF_3 group in the position β to the carbonyl group are known to undergo intramolecular cyclisation on heating with antimony pentafluoride to give derivatives of oxolane and 2,5-dihydrofuran, respectively [1–3]. The carbon framework of the compounds in these reactions does not change. Recently, we have found carbocationoid skeletal rearrangements of carbonyl derivatives of perfluorinated benzocyclobutene [4], indan [5,6], tetralin [4] and 1-ethylindan [7] under the action of SbF_5 [4,5,7] or HF-SbF_5 [6], unknown for perfluoroketones. In the reactions of perfluorobenzocyclo-alken-1-ones with SbF_5 there occur skeletal transformations of ketones along with their disproportionation to benzocycloalkenes and benzocycloalkenediones. The latters undergo skeletal transformations under the reaction conditions [4,5]. Thus, perfluorobenzocyclobutenone heated with SbF_5 and then treated with water, gives perfluorobenzocyclobutene, perfluoro-2-methylbenzoic and tetrafluorophtalic acids as well as the products containing more complicated carbon frame [4]. Analogous reaction of perfluorotetralin-1-one leads to the mixture of perfluorinated tetralin, benzocondensed five- and six-membered oxygen-containing heterocyclic compounds and alkylbenzoic acids [4]. Perfluoroindan-1-one heated with SbF_5 and then treated with water, forms perfluorinated 2-ethylbenzoic acid, indan, 3-methylphthalide and 3-hydroxy-3-methylphthalide [5]. Perfluoro-3,4-dimethylisochromenyl cation is obtained in the reaction of perfluoro-3-ethylindan-1-one with SbF_5 at 125 °C. Hydrolysis of the cation gives perfluoro-3,4-dimethylisochromen-1-one [7].

In this connection it was worthwhile to study the behaviour of a number of carbonyl derivatives of perfluoroalkylbenzocycloalkenes under the action of antimony pentafluoride with the aim to study the possibility of their cationoid skeletal transformations. This work describes the reaction of perfluoro-2,2-diethylbenzocyclobutenone (**1**) and perfluoro-2-ethyl-2-phenylbenzocyclobutenone (**2**) with antimony pentafluoride.

2. Results and discussion

It has been shown that heating of ketone **1** with SbF_5 at 70 °C gives, after treatment of the reaction mixture with water, perfluoro-2-(pent-2-en-3-yl)benzoic acid (**3**) as a mixture of *E*- and *Z*-isomers. When the reaction temperature is raised to 125 °C, a solution of a salt of perfluoro-4-ethyl-3-methylisochromenyl cation (**4**) is obtained. Hydrolysis of the solution of the salt gives perfluoro-4-ethyl-3-methylisochromen-1-one (**5**) (Scheme 1).

The probable mechanism for the transformations of ketone **1** in the presence of SbF_5 can be formulated as shown in Scheme 1. At first compound **1** with SbF_5 seems to generate cation **6**, which undergoes four-membered ring opening, analogously to that for

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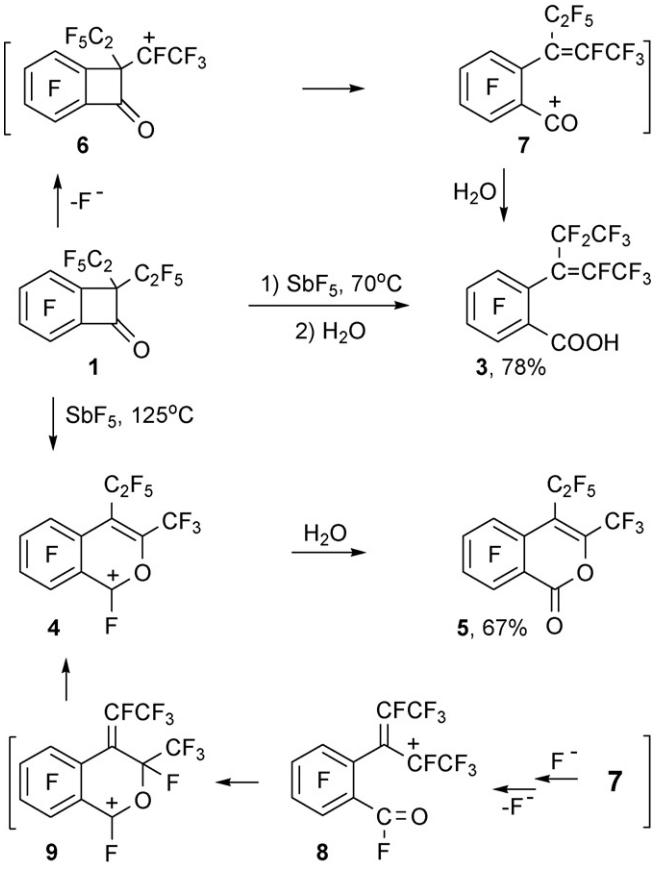
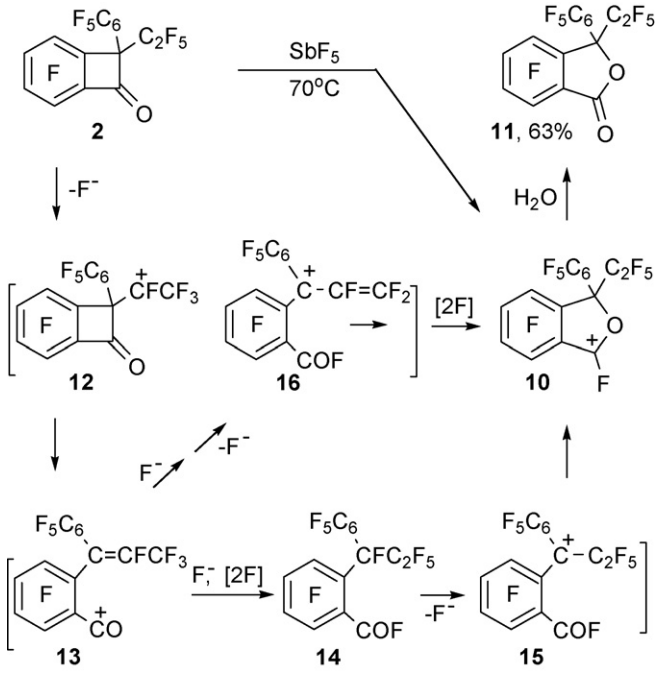


Scheme 1.



Scheme 2.

the reaction of perfluoro-1,1-diethylbenzocylobutene with SbF_5 [8], to give the benzoyl type ion **7**. Hydrolysis of the latter gives acid **3**. Cation **7** may isomerise to allyl type cation **8** by way of the fluoride anion addition–elimination (the lower row of the Scheme 1). An intramolecular attack of positively charged carbon atom of the allyl system of cation **8** at the fluorocarbonyl oxygen atom gives cation **9**. This ion undergoes isomerisation with a double bond migration to the thermodynamically more stable isomer **4**. The mechanism of the formation of isochromenyl cation **4** by cyclisation of ion **7** is similar to that for the formation of perfluoro-3,4-dimethylisochromenyl cation in the reaction of perfluoro-3-ethylindan-1-one with antimony pentafluoride [7].

In contrast to diethylbutenone **1**, heating ketone **2** with SbF_5 at 70 °C gives a salt of perfluoro-3-ethyl-3-phenylphthalan-1-yl cation (**10**). Hydrolysis of the salt leads to perfluoro-3-ethyl-3-phenylphthalide (**11**) (Scheme 2).

Transformation of ketone **2** to cation **10** in the presence of antimony pentafluoride possibly proceeds in the following way (Scheme 2). At first cation **12** is formed from ketone **2** and SbF_5. The four-membered cycle of the cation **12** may undergo ring opening to produce the intermediate **13**. The latter adds fluoride anion and the product obtained is further fluorinated to yield compound **14**, which seems to generate cation **15** under the action of SbF_5. Intramolecular cyclisation of ion **15** gives cation **10**. In addition, the possibility of transformation of cation **13** to **16** with further cyclisation and fluorination yielding cation **10** cannot be excluded.

The structures of the compounds were established by HRMS and spectral characteristics. Assignment of signals in the ^{19}F NMR spectra of the compounds and cations **4** and **10** was made on the basis of chemical shifts of the signals, their fine structure and integral intensities. The configurations of *E*- and *Z*-isomers of acid **3** were defined on the basis of through–space coupling constants of the – $C(CF_2CF_3)=CFCF_3$ group, similarly to that for *E*- and *Z*-isomers of perfluoro-2-(but-2-en-2-yl)benzoic acid [7] and (perfluorobut-2-en-2-yl)benzene [9]. The $J_{\alpha,\gamma}$, $J_{\gamma,A}$, $J_{\gamma,B}$ values are equal to 7, 12 and 23 Hz for *E*-**3** and less than 2 Hz for *Z*-**3** isomers. It should be noted nonequivalence of the CF_2-group fluorine atoms of acid **3**, which can be a result of restricted rotation of the group *ortho*-C_6F_4COOH around C–C-bond. Similar phenomenon was observed for perfluoro-2-(pent-2-en-3-yl)benzophenone [10].

3. Experimental

IR spectra were taken on a Bruker Vector 22 IR spectrophotometer. UV spectra were measured on a Hewlett Packard 8453 UV spectrophotometer. ^{19}F and ^{1}H NMR spectra were recorded on a Bruker AC 200 instrument (188.3 and 200 MHz, respectively), ^{19}F NMR spectrum of cation **10** – on a Bruker AV 300 instrument (282.4 MHz). Chemical shifts are given in δ ppm from CCl_3F (^{19}F) and TMS (^{1}H), *J* values in Hz; C_6F_6 and SO_2ClF (−162.9 and 99.9 ppm from CCl_3F) and $(Me_3Si)_2O$ (0.04 ppm from TMS) were used as internal standards. The molecular masses of the compounds were determined by high-resolution spectrometry on a Finnigan Mat 8200 instrument (EI 70 eV).

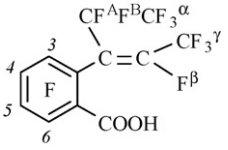
Antimony pentafluoride was obtained commercially; ketones **1** and **2** were synthesized according to Refs. [11] and [10], respectively.

3.1. Reaction of perfluoro-2,2-diethylbenzocyclobutenone (1) with SbF_5

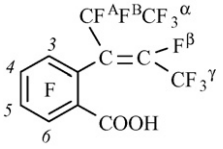
A mixture of compound **1** (0.54 g) and SbF_5 (3.06 g) (molar ratio, 1:11) in a nickel bomb (10 ml) was heated at 70 °C for 26 h. The mixture was treated with 5% hydrochloric acid and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. The solvent was distilled off and the residue was sublimed (90 °C, 5 Torr) to give 0.42 g (yield 78%) of acid **3**.

3.1.1. Perfluoro-2-(pent-2-en-3-yl)benzoic acid (3)

1. Mixture of two isomers, ratio *E*:*Z* = 13:87. IR (CCl_4) ν, cm^{-1}: 3516, 3024 (OH), 1753, 1718 (C=O); 1524, 1481 [fluorinated aromatic ring (FAR)]. ^1H NMR (CCl_4): δ 11.20 (s, OH).



E-isomer: ^{19}F NMR (CH_2Cl_2): δ −67.3 (3F, CF_3-γ), −83.9 (3F, CF_3-α), −95.8 (1F, F-β), −109.4 ($1F_A$) and −110.5 ($1F_B$, CF_2), −131.6 (1F, F-6), −134.5 (1F, F-3), −146.1 (1F, F-4), −148.9 (1F, F-5); $J_{\alpha,\gamma}$ = 7, $J_{\gamma,A}$ = 12, $J_{\gamma,B}$ = 23, $J_{A,B}$ = 284, $J_{3,4}$ = 22, $J_{3,5}$ = 6, $J_{3,6}$ = 11, $J_{4,5}$ = 20, $J_{4,6}$ = 10, $J_{5,6}$ = 21.



Z-isomer: ^{19}F NMR (CH_2Cl_2): δ −69.7 (3F, CF_3-γ), −84.6 (3F, CF_3-α), −105.4 (1F, F-β), −112.4 ($1F_A$) and −112.6 ($1F_B$, CF_2), −130.9 (1F, F-6), −133.7 (1F, F-3), −145.8 (1F, F-4), −148.3 (1F, F-5); $J_{\alpha,\beta}$ = 14, $J_{\alpha,3}$ = 9, $J_{\alpha,A}$ = 2, $J_{\alpha,B}$ = 2, $J_{\beta,\gamma}$ = 7, $J_{\beta,A}$ = 26, $J_{\beta,B}$ = 18, $J_{\beta,3}$ = 3, $J_{A,B}$ = 278, $J_{3,4}$ = 22, $J_{3,5}$ = 7, $J_{3,6}$ = 11, $J_{4,5}$ = 20, $J_{4,6}$ = 10, $J_{5,6}$ = 21. HRMS (mixture of *E*- and *Z*-isomers) *m/z*, 423.9765 (M^+). Calcd for $C_{12}HF_{13}O_2$ = 423.9769.

2. A mixture of compound **1** (0.17 g) and SbF_5 (1.04 g) (molar ratio, 1:12) in an ampoule with FEP inliner for recording of NMR spectra was heated at 70 °C for 17 h and then at 125 °C for 84 h. SO_2ClF (~0.2 g) was added to the resulting mixture and ^{19}F NMR spectrum of the solution was measured at ~20 °C. The spectrum contained signals of cation **4**.The solution was poured into 5% hydrochloric acid and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$. The solvent was evaporated to give a mixture contained (^{19}F NMR) 83% (yield 67%) of compound **5**. An analytical sample of compound **5** was prepared by crystallization.

3.1.2. Perfluoro-4-ethyl-3-methylisochromenyl cation (4)

^{19}F NMR (SbF_5–SO_2ClF): δ −9.5 (1F, F-1), −59.4 (3F, CF_3-3), −75.2 (3F, CF_3-4), −96.0 (2F, CF_2), −98.5 (1F, F-6), −107.4 (1F, F-8), −113.4 (1F, F-5), −130.8 (1F, F-7); $J_{1,5}$ = 4, $J_{1,6}$ = 9, $J_{1,8}$ = 96, $J_{CF_3(3)-CF_3(4)}$ = 8, $J_{CF_3(3)-CF_2}$ = 20, J = 29, $J_{CF_2-F(5)}$ = ~60, $J_{5,6}$ = 18, $J_{5,7}$ = 16, $J_{5,8}$ = 11, $J_{6,7}$ = 19, $J_{6,8}$ = 32, $J_{7,8}$ = 20.

3.1.3. Perfluoro-4-ethyl-3-methylisochromen-1-one (5)

mp 75.5–76.5 °C (hexane). UV (hexane) λ_{max}, nm (lg ε): 224 (4.36), 308 (3.59). IR (CCl_4) ν, cm^{-1}: 1795 (C=O); 1518, 1483 (FAR). ^{19}F NMR (CH_2Cl_2): δ −64.7 (3F, CF_3-3), −75.1 (3F, CF_3-4), −96.0 (3F, CF_2), −128.2 (1F, F-5), −130.6 (1F, F-8), −139.4 (1F, F-6), −147.3 (1F, F-7); $J_{CF_3(3)-CF_3(4)}$ = 8, $J_{CF_3-CF_2}$ = 18, $J_{CF_3(4)-F(5)}$ = 31, $J_{CF_2-F(5)}$ = 52, $J_{5,6}$ = 19, $J_{5,7}$ = 8, $J_{5,8}$ = 13, $J_{6,7}$ = 21, $J_{6,8}$ = 13, $J_{7,8}$ = 21. HRMS *m/z*, 403.9712 (M^+). Calcd for $C_{12}F_{12}O_2$ = 403.9707.

3.2. Reaction of perfluoro-2-ethyl-2-phenylbenzocyclobutenone (2) with SbF_5

Analogously to the previous experiment, the reaction of compound **2** (0.08 g) and SbF_5 (1.86 g) (molar ratio, 1:48) gave (70 °C, 14 h) a solution of a salt of cation **10** in SbF_5, which was diluted with SO_2ClF and ^{19}F NMR spectrum of the solution was measured at ~20 °C. The spectrum contained bad-resolved signals of cation **10**. Hydrolysis of the solution gave 0.06 g of a mixture contained (GLC) 87% (yield 63%) of compound **11**. An analytical sample of compound **11** was prepared by crystallization.

3.2.1. Perfluoro-3-ethyl-3-phenylphthalan-1-yl cation (10)

^{19}F NMR (SbF_5–SO_2ClF): δ −0.1 (1F, F-1), −77.6 (3F, CF_3), −100.9 (1F) and −105.5 (1F, F-5, F-7), −111.2 ($1F_A$) and −111.8 ($1F_B$, CF_2, $J_{A,B}$ = 291), −112.7 (1F, F-4), −132.0 (2F, F-*ortho*), −133.4 (1F, F-6), −138.8 (1F, F-*para*), −155.3 (2F, F-*meta*).

3.2.2. Perfluoro-3-ethyl-3-phenylphthalide (11)

mp 110–111 °C (hexane). UV (hexane) λ_{max}, nm (lg ε): 272 (3.45). IR (CCl_4) ν, cm^{-1}: 1831 (C=O); 1518, 1505 (FAR). ^{19}F NMR ($CHCl_3$): δ −78.5 (3F, s, CF_3), −115.5 ($1F_A$) and −116.7 ($1F_B$, CF_2), −134.2 (1F, F-4), −135.2 (2F, F-*ortho*), −136.1 (1F, F-7), −139.7 (1F, F-5), −145.5 (1F, F-6), −148.0 (1F, F-*para*), −159.5 (2F, F-*meta*); $J_{A,B}$ = 280, $J_{A,4}$ = 28, $J_{A,ortho}$ = 21, $J_{B,4}$ = 18, $J_{B,ortho}$ = 35, $J_{ortho,para}$ = 6, $J_{ortho,4}$ = 18, $J_{meta,para}$ = 22, $J_{4,5}$ = 20, $J_{4,6}$ = 8, $J_{4,7}$ = 18, $J_{5,6}$ = 18, $J_{5,7}$ = 11, $J_{6,7}$ = 21, $J_{6,7}$ = 21. HRMS *m/z*, 489.9671 (M^+). Calcd for $C_{16}F_{14}O_2$ = 489.9675.

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