Journal of Fluorine Chemistry 162 (2014) 71–77

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

The first carbonylation of perfluoroorganic compounds: The reactions of perfluorobenzocyclobutene and its perfluoroalkyl and pentafluorophenyl derivatives with CO in SbF_5 medium

Yaroslav V. Zonov [a,b], Victor M. Karpov [a,*], Vyacheslav E. Platonov [a]

[a] N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry, Novosibirsk 630090, Russia
[b] Novosibirsk State University, Novosibirsk 630090, Russia

ARTICLE INFO

Article history:
Received 14 February 2014
Received in revised form 20 March 2014
Accepted 22 March 2014
Available online 13 April 2014

Keywords:
Carbonylation
Carbocations
Perfluorinated benzocyclobutenes
Antimony pentafluoride

ABSTRACT

Carbonylation of polyfluorinated benzocyclobutenes with CO in an SbF_5 medium readily proceeds at room temperature and atmospheric pressure and it is followed by four-membered ring transformations. Perfluorinated benzocyclobutene, 3- and 4-methyl-benzocyclobutenes add two CO molecules to form, after ring opening and following heterocyclization, isochromene derivatives. Hydrolysis of the reaction mixtures gives corresponding 4-carboxy-1*H*-isochromenes and 2-(carboxymethyl)benzoic acids. The carbonylation of perfluorinated 1-methyl-, 1-ethyl- and 1-isopropyl-benzocyclobutene gives salts of 2-(2-methylphenyl)alk-2-enoyl cations and the corresponding acids after hydrolysis of the latters. Perfluoro-1-phenylbenzocyclobutene in the reaction with CO–SbF_5 transforms into a salt of perfluro-4-phenylisochromenyl cation, its hydrolysis gives perfluro-4-phenylisochromen-1-one.

1. Introduction

Fluorinated organic compounds are important to fundamental organic chemistry [1] and its applications, particularly to materials science, biomedicine and agriculture [1–3]. Of obvious interest are comparative studies of fluorocarbon derivatives and their hydrocarbon congeners.

Many examples of carbonylation reactions of hydrocarbon alcohols, alkyl halides, alkenes etc. proceeding by the addition of CO to the cations generated from these compounds in acid systems are known [4–6]. At the same time, even though there is a wide variety of fluorinated cation reactions in the literature, there are no examples of carbon monoxide addition to these fluoro-cations. Decarbonylation of fluorinated acyl halides in the presence of Lewis acids are the only known examples [7–9]; and they may be influenced by thermodynamic factors that shift the equilibrium of the carbonylation reactions to starting compounds.

Polyfluorinated benzocyclobutenes appear to be a promising study of carbonylation reactions with carbon monoxide in the presence of SbF_5. For example, carbonylation of cation **A** would give **B** leading to four-membered ring opening (Scheme 1) as reported for cation reactions of polyfluorinated benzocyclobutenes [10,11]. Irreversible ring opening would lead to complete conversion of starting benzocyclobutene even if the concentration of **B** in the equilibrium is quite low. Therefore, a study into the behavior of polyfluorinated benzocyclobutenes in the CO–SbF_5 system seemed worthwhile.

In this work, we report on the carbonylation of perfluorinated benzocyclobutene and a number of its perfluoroalkyl and pentafluorophenyl derivatives under the action of carbon monoxide in the presence of SbF_5.

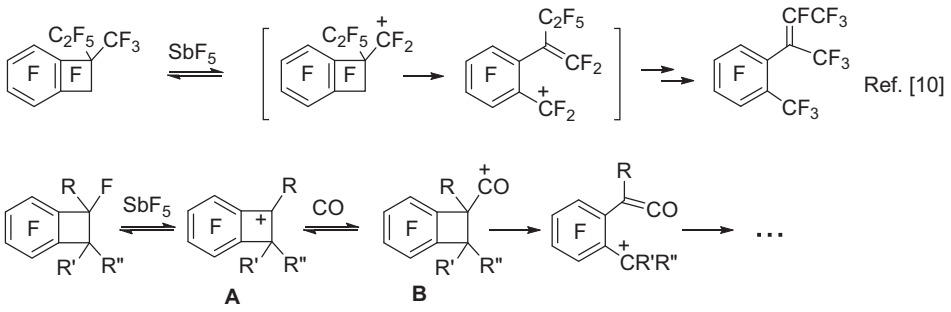
2. Results and discussion

2.1. Reactions of polyfluorobenzocyclobutenes with CO–SbF_5

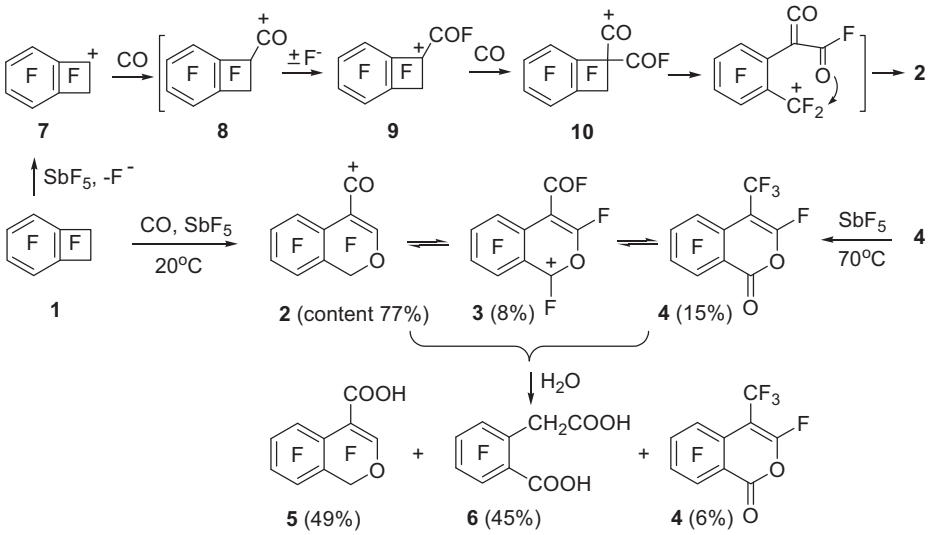
We have found that carbonylation of polyfluorinated benzocyclobutenes in an SbF_5 medium readily proceeds at room temperature and atmospheric pressure and it is followed by four-membered ring transformations. Thus, perfluorobenzocyclobutene (**1**) reacts with CO in the presence of SbF_5 to form a solution of salts of perfluorinated (1*H*-isochromen-4-yl)(oxo)methyl (**2**) and 4-fluorocarbonylisochromenyl (**3**) cations and perfluoro-4-methylisochromen-1-one (**4**). Hydrolysis of the reaction mixture gives perfluoro-4-carboxy-1*H*-isochromene (**5**) and 2-(carboxymethyl)-3,4,5,6-tetrafluorobenzoic acid (**6**) with admixture of compound **4** (Scheme 2).

* Corresponding author. Tel.: +7 3833 30 6943; fax: +7 3832 34 4752.
E-mail address: karpov@nioch.nsc.ru (V.M. Karpov).

http://dx.doi.org/10.1016/j.jfluchem.2014.03.008
0022-1139/



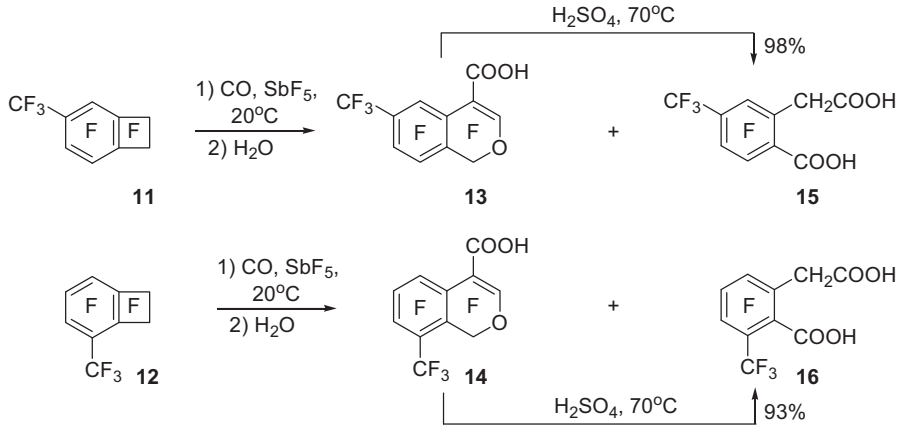
Scheme 1. Cationic ring opening of polyfluorobenzocyclobutenes.



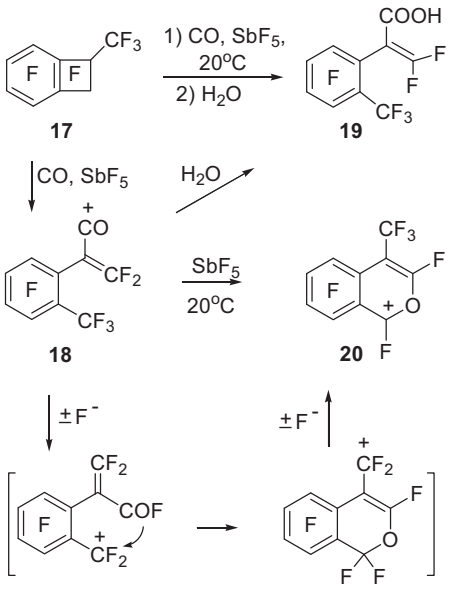
Scheme 2. Carbonylation reaction of perfluorobenzocyclobutene (**1**).

The transformations of compound **1** can be rationalized by Scheme 2. At first, compound **1** with SbF_5 generates cation **7** [12] which adds a molecule of CO to form acyl cation **8**. The latter isomerizes to benzocyclobutenyl cation **9** which adds a second molecule of CO to form cation **10**. Opening of the four-membered ring in cation **10** followed by heterocyclization gives cation **2**. Compounds **2**–**4** in the SbF_5 solution appear to be in equilibrium. This assumption is confirmed by formation of similar mixture of the products in the reaction of individual compound **4** with SbF_5.

The reactions of perfluorinated 4-methyl- and 3-methylbenzocyclobutenes (**11**) and (**12**) with CO–SbF_5 proceed regioselectively and result in the formation of perfluorinated 6-methyl- and 8-methyl-4-carboxy-1*H*-isochromenes (**13**) and (**14**) together with 4-trifluoromethyl- and 6-trifluoromethyl-2-(carboxymethyl)-trifluorobenzoic acids (**15**) and (**16**), respectively (Scheme 3). Thus, the carbonylation occurs at the CF_2 group in meta-position to the CF_3 group. This selectively arises from a higher relative stability of the corresponding perfluoromethylbenzocyclobuten-1-yl cations without electron withdrawing CF_3 group in



Scheme 3. Regioselectiv carbonylation of perfluoromethylbenzocyclobutenes **11** and **12**.



Scheme 4. Carbonylation reaction of perfluoro-1-methylbenzocyclobutene (**17**).

the resonance positions [13,14]. When heated with sulfuric acid, isochromenes **13** and **14** are converted into homophthalic acids **15** and **16** in a high yield.

Perfluoro-1-methylbenzocyclobutene (**17**) in the reaction with CO–SbF_5 transforms into a salt of perfluoro-2-(2-methylphenyl)-propenoyl cation (**18**) (Scheme 4). Its hydrolysis gives perfluoro-2-(2-methylphenyl)propenoic acid (**19**). At room temperature cation **18** gradually undergoes heterocyclization to form perfluoro-4-methylisochromenyl cation (**20**).

Perfluoro-1-ethylbenzocyclobutene (**21**) reacts with CO–SbF_5 in a similar way to form a solution of a salt of perfluoro-2-(2-methylphenyl)but-2-enoyl cation (**22**) (Scheme 5). The latter in contrast to cation **18** does not undergo the cyclization at room temperature. However, hydrolysis of the reaction mixture gives not only perfluoro-2-(2-methylphenyl)but-2-enoic acid (**23**), but also small amounts of perfluorinated 4-fluorocarbonyl-3-methylisochromen-1-one (**24**) and 4-carboxy-3-methylisochromen-1-one (**25**) as by-products of hydrolysis. Methanolysis of the solution of the salt of cation **22** gives methyl perfluoro-2-(2-methylphenyl)but-2-enoate (**26**) together with methyl 3,4,4,4-tetrafluoro-2-(3,4,5,6-tetrafluoro-2-methoxycarbonylphenyl)but-2-enoate (**27**) and 5,6,7,8-tetrafluoro-4-methoxycarbonyl-3-trifluoromethylisochromen-1-one (**28**).

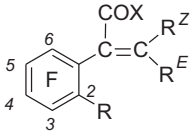
Despite the bulky perfluoroisopropyl group perfluoro-1-isopropylbenzocyclobutene (**29**) also readily reacts with CO–SbF_5 to form perfluoro-2-(2-methylphenyl)isopent-2-enoic acid (**30**), after hydrolysis (Scheme 6).

Perfluoro-1-phenylbenzocyclobutene (**31**) in the reaction with CO–SbF_5 forms a salt of perfluoro-4-phenylisochromenyl cation (**32**) (Scheme 6), acyclic products of the four-membered ring opening were not found. Hydrolysis of the reaction mixture gives mainly perfluoro-4-phenylisochromen-1-one (**33**). Transformation of compound **31** into **32** apparently proceeds via addition of CO molecule to perfluoro-1-phenylbenzocyclobutenyl cation (**34**) [21] with subsequent formation of cation **35** after the ring opening. Its further intramolecular cyclization gives isochromenyl cation **32**. The reaction of compound **31** with CO–SbF_5 readily proceeds at room temperature but elevation of the reaction temperature up to 70 °C allows by-products formation to be decreased.

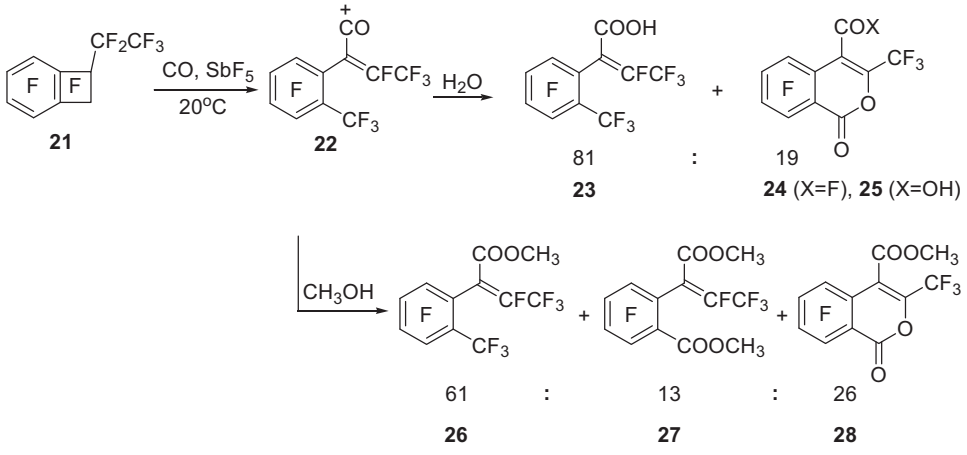
2.2. Structure of compounds

The structures of the compounds were established by HRMS, elemental analysis and 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. Compounds **4**, **6**, **20** [15], **24**, **25** [16] were identified by comparison of the ^{19}F NMR data with data for authentic samples.

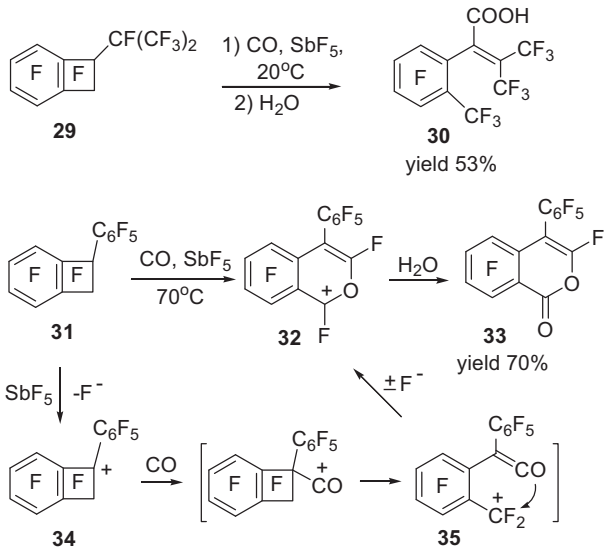
The structures of *E*- and *Z*-isomers of compounds **23**, **26** and **27** were defined on the base of through-space *J*(F,F) values between closely located fluorine atoms. Thus, $J_{CF3(E)-F(6)}$, $J_{CF3(E)-CF3(2)}$ in the *Z*-isomers are equal to 2 Hz whereas in the ^{19}F NMR spectra of the *E*-isomers $J_{CF3(Z)-F(6)}$, $J_{CF3(Z)-CF3(2)}$ are not observed. On the other hand, $J_{F(E)-CF3(2)}$ = 3–3.5 Hz are measured in the ^{19}F NMR spectra of the *E*-isomers.



Assignment of signals in the ^{19}F NMR spectra of isochromenyl cations **3** and **32** was made by analogy with that for cation **20** [15]. Chemical shifts and *J*(F,F) values in the ^{19}F NMR spectra of acyl cations **2**, **18** and **22** are in agreement with those for perfluoro-2-methylpropenoyl cation [17]; the structures of these cations are additionally confirmed by isolation of the corresponding hydrolysis or metanolysis products.



Scheme 5. Reaction of perfluoro-1-ethylbenzocyclobutene (**21**) with CO.



Scheme 6. Carbonylation reaction of perfluorinated 1-isopropyl- and 1-phenylbenzocyclobutenes **29** and **31**.

3. Conclusion

The behaviour of perfluorinated benzocyclobutene and a number of its alkyl and phenyl derivatives under the action of carbon monoxide in the presence of SbF_5 was investigated. It was found that these compounds undergo carbonylation/four-membered ring opening tandem reactions and this is the first example of carbonylation of perfluorinated compounds. Benzocyclobutenes, which do not contain substituents in the aliphatic cycle, add two CO molecules to form, after ring opening and following heterocyclization, isochromene derivatives. Carbonylation of 3- and 4-methyl-benzocyclobutenes occurs regioselectively at the CF_2 group in meta-position to the CF_3 group. 1-Alkyl- and 1-phenyl-benzocyclobutenes undergo monocarbonylation at the substituted position of the four-membered ring to form finally salts of 2-(2-methylphenyl)alk-2-enoyl and 4-phenylisochromenyl cations, respectively.

4. Experimental

Analytical and spectral measurements were carried out in the Collective Chemical Service Center of SB RAS. IR spectra were taken on a Bruker Vector 22 IR spectrophotometer. ^{19}F and ^{1}H NMR spectra were recorded on a Bruker AV 300 instrument (282.4 MHz and 300 MHz, respectively). 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), $CHCl_3$ and acetone-d_5 (7.24 and 2.04 ppm from TMS) were used as internal standards. The molecular masses of the compounds were determined by high-resolution mass-spectrometry on a Thermo Electron Corporation DFS instrument (EI 70 eV). Contents of products in the reaction mixtures were established by ^{19}F NMR spectroscopic data.

Antimony pentafluoride was distilled at atmospheric pressure (*bp* 142–143 °C); carbon monoxide was prepared by decomposition of formic acid in concentrated sulfuric acid and it was additionally dried with the latter. The starting compounds were obtained according to Refs.: **1** and **17** [18]; **21** [12]; **29** [19]; mixture of isomers **11** and **12** [18,20]. The reactions were carried out in glassware at atmospheric pressure.

4.1. Reaction of perfluorobenzocyclobutene (*1*) with CO–SbF_5

(1). A mixture of compound **1** (0.558 g) and SbF_5 (3.323 g) (molar ratio, 1:6.8) was intensively stirred under CO atmosphere at room temperature for 2.5 h. The mixture was treated with cold 5% hydrochloric acid, extracted with mixture CH_2Cl_2–Et_2O (4:1) and dried over $MgSO_4$. The extract contained compounds **4**, **5** and **6** in the ratio 6:49:45. The solvents were distilled off, the residue was dissolved in CH_2Cl_2 and extracted with aqueous solution of $NaHCO_3$. The aqueous extract was acidified with HCl, extracted with CH_2Cl_2 and then with Et_2O. The extracts were dried over $MgSO_4$. The solvents were distilled off to give 0.231 g (yield 34%) of acid **5** (from CH_2Cl_2 extract) and 0.199 g (yield 35%) of acid **6** (from Et_2O extract).

(2). A mixture of compound 1 (0.365 g) and SbF_5 (2.553 g) (molar ratio, 1:8) was intensively stirred under CO atmosphere at room temperature for 3 h. ^{19}F NMR spectrum of the resulting solution contained signals of compound 4 and cations 2 and 3 in the ratio 15:77:8.

4.1.1. Perfluoro-4-carboxy-1H-isochromene (*5*)

mp 125–126 °C (CCl_4). IR (KBr) ν, cm^{-1}: 1737, 1717, 1684 (O=C–C=C); 1527, 1500 [fluorinated aromatic ring (FAR)]. ^{1}H NMR ($CDCl_3$): δ 9.7 (bs, COOH). ^{19}F NMR ($CDCl_3$): δ −51.8 (d, 2F, F-1), −76.8 (ddddt, 1F, F-3), −135.8 (ddddt, 1F, F-5), −139.6 (dtddd, 1F, F-8),−147.7 (ddddt, 1F, F-6), −153.4 (ddddt, 1F, F-7); $J_{1,3}$ = 1, $J_{1,5}$ = 1.5, $J_{1,6}$ = 1.5, $J_{1,7}$ = 1, $J_{1,8}$ = 21, $J_{3,5}$ = 3.5, $J_{3,6}$ = 1.5, $J_{3,7}$ = 4.5, $J_{3,8}$ = 2.5, $J_{5,6}$ = 20.5, $J_{5,7}$ = 5, $J_{5,8}$ = 12.5, $J_{6,7}$ = 20, $J_{6,8}$ = 8, $J_{7,8}$ = 21.5. HRMS *m/z*, 301.9809 (M^+). Calcd. for $C_{10}HF_7O_3$ = 301.9808.

4.2. Reaction of perfluoro-4-methylisochromen-1-one (*4*) with SbF_5

A solution of compound **4** (0.364 g) in SbF_5 (1.592 g) (molar ratio, 1:6.1) was heated at 70 °C for 5 h, then SO_2ClF (0.2 g) was added at 0 °C and ^{19}F NMR spectrum of the solution was measured at 20 °C. The spectrum contained signals of compound **4** and cations **2** and **3** in the ratio 11:80:9. The solution was poured into 5% hydrochloric acid and extracted with mixture CH_2Cl_2–Et_2O (4:1). The extract was dried over $MgSO_4$. Distillation of the solvent gave 0.280 g of a mixture of compounds **4**, **5** and **6** in the ratio 8:36:56.

4.2.1. Perfluoro(1H-isochromen-4-yl)(oxo)methyl cation (*2*)

^{19}F NMR (SbF_5–SO_2ClF): δ −16.7 (s, 1F, F-3), −38.1 (d, 2F, F-1, $J_{1,8}$ = 14), −131.1 (m, 1F, F-8 or F-5), −131.3 (m, 1F, F-5 or F-8), −138.9 (m, 1F, F-6 or F-7), −143.1 (m, 1F, F-7 or F-6).

4.2.2. 4-Fluorocarbonyl-perfluoroisochromenyl cation (*3*)

^{19}F NMR (SbF_5–SO_2ClF): δ 56.0 (dd, 1F, COF, $J_{COF-F(5)}$ = 33, $J_{COF-F(3)}$ = 18,), −20.0 (d, 1F, F-1, $J_{1,8}$ = 80), −64.1 (m, 1F, F-3), −99.0 (m, 1F, F-6), −111.3 (dm, 1F, F-8, $J_{1,8}$ = 80), −126.8 (m, 1F, F-5), −135.6 (m, 1F, F-7).

4.3. Reaction of perfluorinated 4-methyl- and 3- methylbenzocyclobutenes (*11*) and (*12*) with CO–SbF_5

(1). Analogously to procedure 4.1. a mixture of compounds **11** and **12** (0.667 g) and SbF_5 (3.403 g) (molar ratio, 0.92:0.08:6.9) gave mixtures of compounds **13** and **14** in the ratio 92:8 (0.430 g, yield 55%) and compounds 15 and 16 in the ratio 93:7 (0.100 g, yield 15%). The former mixture was sublimed (125 °C, 3 Torr), subsequent recrystallization from CCl_4 gave 0.185 g of acid **13**.

(2). Analogously to procedure 4.1. a mixture of compounds **11** and **12** (0.540 g) and SbF_5 (3.088 g) (molar ratio, 0.23:0.77:7.8) gave mixtures of compounds **13** and **14** in the ratio 26:74

(0.250 g, yield 39%) and compounds **15** and **16** in the ratio 30:70 (0.166 g, yield 30%). The former mixture was sublimed (115 °C, 3 Torr), subsequent recrystallization from CCl_4 gave 0.056 g of acid **14**.

*4.3.1. Perfluoro-4-carboxy-6-methyl-1*H*-isochromene (**13**)*

mp 107.5–109.5 °C (CCl_4). IR (KBr) ν, cm^{-1}: 1740, 1720, 1680, 1649 (O=C–C=C); 1500, 1427 (FAR). ^1H NMR ($CDCl_3$): δ 9.3 (bs, COOH). ^{19}F NMR ($CDCl_3$): δ −53.6 (d, 2F, F-1), −58.0 (t, 3F, CF_3-6), −77.2 (m, 1F, F-3), −112.7 (qdm, 1F, F-5), −132.0 (qdd, 1F, F-7), −140.3 (dtdd, 1F, F-8); $J_{CF3(6)–F(5)}$ = 23, $J_{CF3(6)–F(7)}$ = 23, $J_{1,8}$ = 21, $J_{3,7}$ = 5, $J_{3,8}$ = 2.5, $J_{5,8}$ = 16.5, $J_{7,8}$ = 21. HRMS *m/z*, 351.9775 (M^+). Calcd. for C_{11} HF_9O = 351.9777. Anal. Calcd for $C_{11}HF_9O_3$: C, 37.5; H, 0.3; F, 48.6%. Found: C, 37.5; H, 0.4; F, 48.3%.

*4.3.2. Perfluoro-4-carboxy-8-methyl-1*H*-isochromene (**14**)*

mp 138–141 °C (CCl_4). IR (KBr) ν, cm^{-1}: 1742, 1651, 1630 (O=C–C=C); 1509, 1479 (FAR). ^1H NMR ($CDCl_3$): δ 8.5 (bs, COOH). ^{19}F NMR [$CO(CD_3)_2$]: δ −52.7 (q, 2F, F-1), −53.9 (dt, 3F, CF_3-8), −80.1 (m, 1F, F-3), −123.1 (ddm, 1F, F-5), −128.8 (qddd, 1F, F-7), −147.7 (ddm, 1F, F-6); $J_{CF3(8)–F(1)}$ = 21, $J_{CF3(8)–F(7)}$ = 31, $J_{3,7}$ = 3.5, $J_{5,6}$ = 20, $J_{5,7}$ = 15, $J_{6,7}$ = 20. HRMS *m/z*, 351.9779 (M^+). Calcd. for C_{11} HF_9O_3 = 351.9777. Anal. Calcd for $C_{11}HF_9O_3$: C, 37.5; H, 0.3; F, 48.6%. Found: C, 37.2; H, 0.3; F, 49.0%.

*4.4. Reaction of perfluorinated 4-carboxy-6-methyl-1*H*-isochromene (**13**) and 4-carboxy-8-methyl-1*H*-isochromene (**14**) with H_2SO_4*

(1). A mixture of compound **13** (0.085 g) and 90% sulfuric acid (3.4 g) was heated at 70 °C for 5 h. The mixture was poured into water, extracted with Et_2O and dried over $MgSO_4$. The solvent was distilled off and the residue was sublimed (150 °C, 3 Torr) to give 0.072 g (yield 98%) of acid **15**.

(2). Analogously to previous procedure compound **14** (0.020 g) gave acid **16** (0.016 g, yield 93%).

*4.4.1. 2-(Carboxymethyl)-3,5,6-trifluoro-4-trifluoromethylbenzoic acid (**15**)*

mp 174–176.5 °C. IR (KBr) ν, cm^{-1}: 1726, 1695 (C=O); 1489, 1472, 1433 (FAR). ^1H NMR [$CO(CD_3)_2$]: δ 9.3 (bs, 2*H*, COOH), 3.94 (d, 2*H*, CH_2). ^{19}F NMR [$CO(CD_3)_2$]: δ −55.8 (t, 3F, CF_3-4), −117.0 (qdm, 1F, F-3), −135.2 (qd, 1F, F-5), −139.8 (dd, 1F, F-6); $J_{CH2–F(3)}$ = 2, $J_{CF3(4)–F(3)}$ = 22, $J_{CF3(4)–F(5)}$ = 23.5, $J_{3,6}$ = 15, $J_{5,6}$ = 20.5. Anal. Calcd for C_{10} $H_4F_6O_4$: F, 37.7%. Found: F, 37.8%.

*4.4.2. 2-(Carboxymethyl)-3,4,5-trifluoro-6-trifluoromethylbenzoic acid (**16**)*

mp 169–171 °C. IR (KBr) ν, cm^{-1}: 1724, 1697, 1664 (C=O); 1516, 1475 (FAR). ^1H NMR [$CO(CD_3)_2$]: δ 9.3 (bs, 2*H*, COOH), 3.83 (d, 2*H*, CH_2). ^{19}F NMR [$CO(CD_3)_2$]: δ −55.6 (d, 3F, CF_3-6), −126.1 (ddm, 1F, F-3), −133.7 (dqd, 1F, F-5), −156.4 (dd, 1F, F-4); $J_{CH2–F(3)}$ = 2, $J_{CF3(6)–F(5)}$ = 19.5, $J_{3,4}$ = 20, $J_{3,5}$ = 13.5, $J_{4,5}$ = 20. HRMS *m/z*, 302.0002 (M^+). Calcd. for C_{10} $H_4F_6O_4$ = 302.0008.

*4.5. Reaction of perfluoro-1-methylbenzocyclobutene (**17**) with CO–SbF_5*

(1). A mixture of compound **17** (0.580 g) and SbF_5 (2.356 g) (molar ratio, 1:5.6) was intensively stirred under CO atmosphere at room temperature for 1 h. The mixture was treated with cold 5% hydrochloric acid, extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was distilled off to give 0.525 g of a product containing ~85% of acid 19. It was dissolved in hexane (5 ml) and filtrated, subsequent sublimation (110 °C, 10 Torr) and recrystallization from hexane gave 0.188 g (yield 30%) of acid **19**.

(2). A mixture of compound **17** (0.430 g) and SbF_5 (2.500 g) (molar ratio, 1:8) was intensively stirred under CO atmosphere at room temperature for 1 h and then kept at this temperature. ^{19}F NMR spectrum of the resulting solution contained signals of cations **18** and **20** in the ratio 68:32 (after 6 h) and 25:75 (after 24 h).

*4.5.1. Perfluoro-2-(2-methylphenyl)propenoyl cation (**18**)*

^{19}F NMR (SbF_5): δ 5.7 (d, 1F, F-*Z* or F-*E*, $J_{Z,E}$ = 158), −5.1 (d, 1F, F-*Z* or F-*E*, $J_{Z,E}$ = 158), −53.9 (d, 3F, CF_3-2, $J_{CF3(2)–F(3)}$ = 24), −125.2 (m, 1F, F-6), −128.7 (m, 1F, F-3), −136.2 (m, 1F, F-4 or F-5), −140.5 (m, 1F, F-5 or F-4).

*4.5.2. Perfluoro-2-(2-methylphenyl)propenoic acid (**19**)*

mp 66.5–68 °C. IR (CCl_4) ν, cm^{-1}: 1742, 1707, 1680 (O=C–C=C); 1526, 1485 (FAR). ^1H NMR ($CDCl_3$): δ 11.6 (bs, COOH). ^{19}F NMR ($CDCl_3$): δ −57.7 (dd, 3F, CF_3-2), −60.4 (d, 1F, F-*Z*), −60.6 (ddq, 1F, F-*E*), −135.0 (dm, 1F, F-6), −137.3 (qddd, 1F, F-3), −148.2 (ddd, 1F, F-5), −150.5 (ddd, 1F, F-4); $J_{Z,E}$ = 33.5, $J_{E,6}$ = 3, $J_{CF3(2)–F(E)}$ = 3, $J_{CF3(2)–F(3)}$ = 23, $J_{3,4}$ = 21, $J_{3,5}$ = 8, $J_{3,6}$ = 11, $J_{4,5}$ = 20, $J_{4,6}$ = 6, $J_{5,6}$ = 22. HRMS *m/z*, 323.9831 (M^+). Calcd. for $C_{10}HF_9O_2$ = 323.9827. Anal. Calcd for $C_{10}HF_9O_2$: C, 37.1; H, 0.3; F, 52.8%. Found: C, 37.0; H, 0.5; F, 52.8%.

*4.6. Reaction of perfluoro-1-ethylbenzocyclobutene (**21**) with CO–SbF_5*

(1). A mixture of compound **21** (0.515 g) and SbF_5 (2.543 g) (molar ratio, 1:8) was intensively stirred under CO atmosphere at room temperature for 3 h. ^{19}F NMR spectrum of the resulting solution contained signals of cation **22** (*E*:*Z* = 92:8). The solution was kept at room temperature for 46 h but no significant changes in the spectrum were observed. The mixture was treated with cold 5% hydrochloric acid, extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was distilled off to give 0.483 g of a product containing ~85% of compounds **23** (*E*:*Z* = 82:18), **24** and **25** in the ratio 81:7:12. The product was dissolved in CH_2Cl_2 and extracted with aqueous solution of $NaHCO_3$. The aqueous extract was acidified with HCl, extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was distilled off, and recrystallization of a residue from hexane gave 0.098 g of a mixture of compounds **23** (*E*:*Z* = 99:1), **25** and 5,6,7,8-tetrafluoro-3-hydroxy-3-trifluoromethyl-3,4-dihydroisochromen-1-one [16] in the ratio 84:2:14.

(2). A mixture of compound **21** (0.548 g) and SbF_5 (2.050 g) (molar ratio, 1:6) was intensively stirred under CO atmosphere at room temperature for 2 h. The mixture was poured into CH_3OH (20 ml) at 0 °C, then treated with cold 5% hydrochloric acid (200 ml), extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was distilled off to give 0.570 g of a product containing ~85% of compounds **26** (*E*:*Z* = 86:14), **27** (*E*:*Z* = 62:38) and **28** in the ratio 61:13:26. Silica gel column chromatography ($CHCl_3$ as eluent) gave 0.275 g (yield 45%) of compound **26** (*E*:*Z* = 88:12), 0.040 g (yield 7%) of compound **27** (*E*:*Z* = 81:19), 0.054 g (yield 10%) of compound **28**.

*4.6.1. Perfluoro-2-(2-methylphenyl)but-2-enoyl cation (**22**)*

Mixture of two isomers, ratio *E*:*Z* = 92:8.

E-**22**: ^{19}F NMR (SbF_5): δ −21.6 (s, 1F, F-*E*), −53.7 (d, 3F, CF_3-2, $J_{CF3(2)–F(3)}$ = 22,), −68.93 (d, 3F, CF_3-*Z*, $J_{CF3(Z)–F(E)}$ = 7), −124.3 (m, 1F, F-6), −127.1 (m, 1F, F-3), −134.3 (m, 1F, F-4 or F-5), −139.5 (m, 1F, F-5 or F-4).

Z-**22** ^{19}F NMR (SbF_5): δ −31.2 (s, 1F, F-*Z*), −52.8 (d, 3F, CF_3-2, $J_{CF3(2)–F(3)}$ = 24,), −66.9 (bs, 3F, CF_3-*E*), −123.7 (m, 1F, F-6), −127.9 (m, 1F, F-3), −134.1 (m, 1F, F-4 or F-5), −139.6 (m, 1F, F-5 or F-4).

*4.6.2. Perfluoro-2-(2-methylphenyl)but-2-enoic acid (**23**)*

Mixture of acid **23** (two isomers, *E*:*Z* = 99:1) with compounds **25** and 5,6,7,8-tetrafluoro-3-hydroxy-3-trifluoromethyl-3,4-dihydroisochromen-1-one in the ratio 84:2:14. ^{1}H NMR ($CDCl_3$): δ 8.6 (bs, COOH).

E-**23**: ^{19}F NMR ($CDCl_3$): δ −57.5 (dd, 3F, CF_3-2), −67.6 (d, 3F, CF_3-*Z*), −97.7 (qdq, 1F, F-*E*), −135.3 (dddd, 1F, F-6), −136.6 (qddd, 1F, F-3), −147.2 (ddd, 1F, F-5), −149.7 (ddd, 1F, F-4); $J_{CF3(Z)-F(E)}$ = 5.5, $J_{E,6}$ = 5, $J_{CF3(2)-F(E)}$ = 3.5, $J_{CF3(2)-F(3)}$ = 21.5, $J_{3,4}$ = 20.5, $J_{3,5}$ = 8.5, $J_{3,6}$ = 10.5, $J_{4,5}$ = 20.5, $J_{4,6}$ = 6, $J_{5,6}$ = 21.5.

Z-**23**: ^{19}F NMR ($CDCl_3$): δ −56.9 (d, 3F, CF_3-2), −69.8 (dqd, 3F, CF_3-*E*), −100.0 (q, 1F, F-*Z*) −135.0 (m, 1F, F-6), −136.9 (m, 1F, F-3), −147.5 (m, 1F, F-5), −149.5 (m, 1F, F-4); $J_{CF3(E)-F(Z)}$ = 7.5, $J_{CF3(E)-F(6)}$ = 2, $J_{CF3(E)-CF3(2)}$ = 2, $J_{CF3(2)-F(3)}$ = 21.

*4.6.3. Methyl perfluoro-2-(2-methylphenyl)but-2-enoate (**26**)*

Mixture of two isomers, ratio *E*:*Z* = 88:12, liquid. IR (CCl_4) ν, cm^{-1}: 2957 (CH); 1759, 1742 (C=O); 1526, 1485 (FAR).

E-**26**: ^{1}H NMR ($CDCl_3$): δ 3.81 (s, CH_3).^{19}F NMR ($CDCl_3$): δ −57.4 (dd, 3F, CF_3-2), −67.6 (d, 3F, CF_3-*Z*), −103.2 (qdq, 1F, F-*E*), −135.3 (dddd, 1F, F-6), −136.9 (qddd, 1F, F-3), −147.6 (ddd, 1F, F-5), −150.2 (ddd, 1F, F-4); $J_{CF3(Z)-F(E)}$ = 6, $J_{E,6}$ = 5, $J_{CF3(2)-F(E)}$ = 3, $J_{CF3(2)-F(3)}$ = 21.5, $J_{3,4}$ = 20.5, $J_{3,5}$ = 8.5, $J_{3,6}$ = 11, $J_{4,5}$ = 20.5, $J_{4,6}$ = 6, $J_{5,6}$ = 21.5.

Z-**26**: ^{1}H NMR ($CDCl_3$): δ 3.83 (s, CH_3). ^{19}F NMR ($CDCl_3$): δ −56.9 (d, 3F, CF_3-2), −69.7 (dqd, 3F, CF_3-*E*), −104.3 (q, 1F, F-*Z*) −135.1 (m, 1F, F-6), −137.3 (qddd, 1F, F-3), −148.0 (ddd, 1F, F-5), −150.1 (ddd, 1F, F-4); $J_{CF3(E)-F(Z)}$ = 8, $J_{CF3(E)-F(6)}$ = 2, $J_{CF3(E)-CF3(2)}$ = 2, $J_{CF3(2)-F(3)}$ = 21.5, $J_{3,4}$ = 20.5, $J_{3,5}$ = 8, $J_{3,6}$ = 11, $J_{4,5}$ = 20.5, $J_{4,6}$ = 6, $J_{5,6}$ = 21.5. HRMS (mixture of two isomers) *m/z*, 387.9948 (M^+). Calcd. for $C_{12}H_3F_{11}O_2$ = 387.9952.

*4.6.4. Methyl 3,4,4,4-tetrafluoro-2-(3,4,5,6-tetrafluoro-2-methoxycarbonylphenyl)but-2-enoate (**27**)*

Mixture of two isomers, ratio *E*:*Z* = 81:19, liquid. IR (CCl_4) ν, cm^{-1}: 2957 (CH); 1751, 1738 (C=O); 1517, 1481 (FAR).

E-**27**: ^{1}H NMR ($CDCl_3$): δ 3.89 (s, 3*H*, CH_3), 3.79 (s, 3*H*, CH_3).^{19}F NMR ($CDCl_3$): δ −67.6 (d, 3F, CF_3-*Z*), −107.4 (dq, 1F, F-*E*), −135.3 (ddd, 1F, F-3), −136.3 (dddd, 1F, F-6), −148.8 (ddd, 1F, F-5), −151.2 (ddd, 1F, F-4); $J_{CF3(Z)-F(E)}$ = 6.5, $J_{E,6}$ = 7, $J_{3,4}$ = 21.5, $J_{3,5}$ = 8, $J_{3,6}$ = 11.5, $J_{4,5}$ = 21.5, $J_{4,6}$ = 5.5, $J_{5,6}$ = 21.5.

Z-**27**: ^{1}H NMR ($CDCl_3$): δ 3.89 (s, 3*H*, CH_3), 3.81 (s, 3*H*, CH_3). ^{19}F NMR ($CDCl_3$): δ −69.2 (dd, 3F, CF_3-*E*), −107.3 (qd, 1F, F-*E*), −135.0 (ddd, 1F, F-3), −136.5 (ddddq, 1F, F-6), −148.9 (ddd, 1F, F-5), −151.1 (ddd, 1F, F-4); $J_{CF3(E)-F(Z)}$ = 8, $J_{CF3(E)-F(6)}$ = 2, $J_{Z,6}$ = 3, $J_{3,4}$ = 21.5, $J_{3,5}$ = 8, $J_{3,6}$ = 11.5, $J_{4,5}$ = 20, $J_{4,6}$ = 5.5, $J_{5,6}$ = 22. HRMS (mixture of two isomers) *m/z*, 378.0127 (M^+). Calcd. for $C_{13}H_6F_8O_4$ = 378.0133.

*4.6.5. 5,6,7,8-tetrafluoro-4-methoxycarbonyl-3-trifluoromethylisochromen-1-one (**28**)*

mp 88–89 °C (hexane). IR (CCl_4) ν, cm^{-1}: 2957 (CH), 1787, 1757 (C=O); 1636 (C=C); 1508 (FAR). ^{1}H NMR ($CDCl_3$): δ 3.95 (s, CH_3). ^{19}F NMR ($CDCl_3$): δ −68.5 (s, 3F, CF_3), −129.8 (ddd, 1F, F-8), −138.4 (ddd, 1F, F-5), −140.7 (ddd, 1F, F-6), −147.7 (ddd, 1F, F-7); $J_{5,6}$ = 20, $J_{5,7}$ = 5, $J_{5,8}$ = 14, $J_{6,7}$ = 20.5, $J_{6,8}$ = 13, $J_{7,8}$ = 20. HRMS *m/z*, 343.9905 (M^+). Calcd. for $C_{12}H_3F_7O_4$ = 343.9914. Anal. Calcd for $C_{12}H_3F_7O_4$: C, 41.9; H, 0.9; F, 38.6%. Found: C, 41.5; H, 1.2; F, 38.3%.

*4.7. Reaction of perfluoro-1-isopropylbenzocyclobutene (**29**) with CO–SbF_5*

A mixture of compound **29** (0.848 g) and SbF_5 (2.922 g) (molar ratio, 1:6.3) was intensively stirred under CO atmosphere at room temperature for 2 h. The mixture was treated with cold 5% hydrochloric acid, extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was distilled off to give 0.751 g of a product containing ~70% of acid **30**. The product was dissolved in CH_2Cl_2 extracted with aqueous solution of $NaHCO_3$. The aqueous extract was acidified with HCl, extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was distilled off and the residue was sublimed (90 °C, 3 Torr) to give 0.483 g (yield 53%) of acid **30**.

*4.7.1. Perfluoro-2-(2-methylphenyl)isopent-2-enoic acid (**30**)*

mp 59–62 °C. IR (CCl_4) ν, cm^{-1}: 1732 (C=O); 1528, 1481 (FAR). ^{1}H NMR ($CDCl_3$): δ 11.0 (bs, COOH). ^{19}F NMR ($CDCl_3$): δ −56.8 (d, 3F, CF_3-2), −61.1 (qm, 3F, CF_3-*E*), −61.3 (q, 3F, CF_3-*Z*), −134.2 (dm, 1F, F-6), −135.4 (dqdd, 1F, F-3), −146.4 (ddd, 1F, F-5), −148.4 (ddd, 1F, F-4); $J_{CF3(E)-CF3(Z)}$ = 8, $J_{CF3(2)-F(3)}$ = 17.5, $J_{3,4}$ = 20.5, $J_{3,5}$ = 9, $J_{3,6}$ = 11, $J_{4,5}$ = 20.5, $J_{4,6}$ = 6.5, $J_{5,6}$ = 21.5. HRMS *m/z*, 423.9759 (M^+). Calcd. for $C_{12}HF_{13}O_2$ = 423.9763. Anal. Calcd for $C_{12}HF_{13}O_2$: C, 34.0; H, 0.2; F, 58.2%. Found: C, 33.8; H, 0.5; F, 58.2%.

*4.8. Reaction of perfluoro-1-phenylbenzocyclobutene (**31**) with CO–SbF_5*

(1). A solution of compound **31** in SbF_5 was prepared by the reaction of benzocyclobutene 1 (0.518 g) with C_6F_5H (0.361 g) in SbF_5 (3.152 g) (molar ratio, 1:1:7) [21]. The solution was intensively stirred under CO atmosphere at 70 °C for 4 h, then SO_2ClF (0.4 g) was added at 0 °C and ^{19}F NMR spectrum of the resulting solution was measured at 20 °C. The spectrum contained signals of cation **32**. The mixture was treated with cold 5% hydrochloric acid, extracted with CH_2Cl_2 and dried over $MgSO_4$. The solvent was distilled off to give 0.852 g of a residue containing ~90% of compound **33**. Sublimation (110 °C, 3 Torr) and subsequent recrystallization of the residue from hexane gave 0.588 g (yield 70%) of compound **33**.

(2). Analogously to previous procedure the reaction of compound **31**, prepared from benzocyclobutene 1 (0.530 g), C_6F_5H (0.370 g) and SbF_5 (3.159 g) (molar ratio, 1:1:6.8), with CO at room temperature (4 h) gave 0.890 g of a product, which contained ~60% of compound **33** together with unidentified impurities.

*4.8.1. Perfluoro-4-phenylisochromenyl cation (**32**)*

^{19}F NMR (SbF_5–SO_2ClF): δ −19.5 (dm, 1F, F-1, $J_{1,8}$ = 78), −68.2 (m, 1F, F-3), −103.4 (m, 1F, F-6), −114.7 (dm, 1F, F-8, $J_{1,8}$ = 78), −134.2 (m, 1F, F-5), −136.4 (m, 2F, F-*ortho*), −137.6 (m, 1F, F-7), −144.8 (tm, 1F, F-*para*, $J_{para,meta}$ = 19), −158.7 (m, 2F, F-*meta*).

*4.8.2. Perfluoro-4-phenylisochromen-1-one (**33**)*

mp 76–77 °C (hexane). IR (CCl_4) ν, cm^{-1}: 1798 (C=O); 1681 (C=C); 1508 (FAR). ^{19}F NMR ($CDCl_3$): δ −76.1 (ddtdd, 1F, F-3), −131.4 (dddd, 1F, F-8), −139.5 (m, 2F, F-*ortho*), −141.2 (dddd, 1F, F-6), −145.8 (ddddt, 1F, F-5), −151.6 (tt, 1F, F-*para*), −153.9 (dddd, 1F, F-7), −161.9 (m, 2F, F-*meta*); $J_{para,meta}$ = 21, $J_{para,ortho}$ = 2.5, $J_{ortho,3}$ = 4, $J_{ortho,5}$ = 2, $J_{3,5}$ = 4.5, $J_{3,6}$ = 2, $J_{3,7}$ = 5.5, $J_{3,8}$ = 3, $J_{5,6}$ = 20, $J_{5,7}$ = 2.5, $J_{5,8}$ = 14, $J_{6,7}$ = 20.5, $J_{6,8}$ = 13.5, $J_{7,8}$ = 20.5. HRMS *m/z*, 401.9734 (M^+). Calcd. for $C_{15}F_{10}O_2$ = 401.9733.

Acknowledgments

We gratefully acknowledge the Russian Foundation for Basic Researches (project no. 10-03-00120) for financial support.

References

[1] (a) R.D. Chambers, Fluorine in Organic Chemistry, Blackwell Publishing, Oxford, 2004;
(b) P. Kirsch, Modern Fluoroorganic Chemistry. Synthesis, Reactivity, Applications, Wiley-VCH, Weinheim, 2004;

(c) R.E. Banks, B.E. Smart, J.C. Tatlow (Eds.), Organofluorine Chemistry: Principles and Commercial Applications, Plenum, New York, NY, 1994.
[2] (a) M.L. Tang, Z. Bao, Chem. Mater. 23 (2011) 446–455;
(b) F. Babudri, G.M. Farinola, F. Naso, R. Ragni, Chem. Commun. (2007) 1003–1022.
[3] (a) I. Ojima (Ed.), Fluorine in Medicinal Chemistry and Chemical Biology, Wiley-Blackwell, Oxford, UK, 2009, pp. 291–311;
(b) J.-P. Begue, D. Bonnet-Delpon, Bioorganic and Medicinal Chemistry of Fluorine, Wiley, Hoboken, 2008;
(c) S. Purser, P.R. Moore, S. Swallow, V. Gouverneur, Chem. Soc. Rev. 37 (2008) 320–330;
(d) F. Leroux, P. Jeschke, M. Schlosser, Chem. Rev. 105 (2005) 827–856;
(e) C.D. Hewitt, M.J. Silvester, Aldrichim. Acta 21 (1988) 3–10.
[4] Ya.T. Eidus, A.L. Lapidus, K.V. Puzitskii, B.K. Nefedov, Usp. Khim. 42 (1973) 442–470;
Ya.T. Eidus, A.L. Lapidus, K.V. Puzitskii, B.K. Nefedov, Russ. Chem. Rev. 42 (1973) 199–213 (English translation).
[5] J.A. Falbe (Ed.), New Syntheses with Carbon Monoxide, Springer, New York, NY, 1980.
[6] O. Farooq, M. Marcelli, G.K.S. Prakash, G.A. Olah, J. Am. Chem. Soc. 110 (1988) 864–867.
[7] G.A. Olah, P.v.R. Schleyer (Eds.), Carbonium Ions, vol. 5, Wiley-Interscience, New York, NY, 1976.
[8] C.G. Krespan, V.A. Petrov, Chem. Rev. 96 (1996) 3269–3301.
[9] V.V. Bardin, G.G. Furin, G.G. Yakobson, Zh. Org. Khim. 20 (1984) 567–573;
V.V. Bardin, G.G. Furin, G.G. Yakobson, Russ. J. Org. Chem. 20 (1984) 514–519 (English translation).
[10] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, G.G. Yakobson, Izv. Akad, Nauk SSSR Ser. Khim. (1990) 1114–1120;
V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, G.G. Yakobson, Bull. Acad. Sci. USSR, Div. Chem. Sci. 39 (1990) 1000–1004 (English translation).
[11] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, V.R. Sinyakov, J. Fluorine Chem. 117 (2002) 73–81.
[12] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, G.G. Yakobson, J. Fluorine Chem. 28 (1985) 121–137.
[13] G.A. Olah, C.U. Pittman, J. Am. Chem. Soc. 88 (1966) 3310–3313.
[14] Yu.V. Pozdnyakovich, V.D. Shteingarts, J. Fluorine Chem. 4 (1974) 283–296.
[15] Ya.V. Zonov, T.V. Mezhenkova, V.M. Karpov, V.E. Platonov, Zh. Org. Khim. 44 (2008) 1675–1679;
Ya.V. Zonov, T.V. Mezhenkova, V.M. Karpov, V.E. Platonov, Russ. J. Org. Chem. 44 (2008) 1652–1656 (English translation).
[16] Ya.V. Zonov, V.M. Karpov, V.E. Platonov, J. Fluorine Chem. 128 (2007) 1065–1073.
[17] V.F. Snegirev, M.V. Galakhov, V.A. Petrov, K.N. Makarov, V.I. Bakhmutov, Izv. Akad, Nauk SSSR Ser. Khim. (1986) 1318–1325;
V.F. Snegirev, M.V. Galakhov, V.A. Petrov, K.N. Makarov, V.I. Bakhmutov, Bull. Acad. Sci. USSR, Div. Chem. Sci. 35 (1986) 1194–1200 (English translation).
[18] V.E. Platonov, T.V. Senchenko, G.G. Yakobson, Zh. Org. Khim. 12 (1976) 816–821;
V.E. Platonov, T.V. Senchenko, G.G. Yakobson, J. Org. Chem. USSR 12 (1976) 818–823 (English translation).
[19] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, G.G. Yakobson, Izv. Akad Nauk SSSR Ser. Khim. (1985) 2315–2323;
V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, G.G. Yakobson, Bull. Acad. Sci. USSR, Div. Chem. Sci. 34 (1985) 2143–2150 (English translation).
[20] V.R. Sinyakov, Ya.V. Zonov, V.M. Karpov, I.V. Beregovaya, V.E. Platonov, Zh. Org. Khim. 49 (2013) 1026–1034;
V.R. Sinyakov, Ya.V. Zonov, V.M. Karpov, I.V. Beregovaya, V.E. Platonov, Russ. J. Org. Chem. 49 (2013) 1010–1018 (English translation).
[21] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, V.R. Sinyakov, L.N. Shchegoleva, Zh. Org. Khim. 38 (2002) 1210–1217;
V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, V.R. Sinyakov, L.N. Shchegoleva, Russ. J. Org. Chem. 38 (2002) 1158–1165 (English translation).