Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Fluorine Chemistry 125 (2004) 49–53
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/jfluchem

The alicyclic ring contraction of perfluoro-1-phenyltetralin in reaction with antimony pentafluoride

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

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

Received 10 July 2003; received in revised form 24 September 2003; accepted 26 September 2003

Abstract

Perfluoro-1-phenyltetralin (**1**) heated with antimony pentafluoride at 130 °C, then treated with water, gave a mixture of perfluorinated 3-methyl-2-phenylindenone (**3**), 3-methyl-2-phenylindene (**4**), 3-hydroxy-1-methyl-3-phenylindan (**5**), 1-methyl-3-phenylindan (**6**), 9-methyl-1,2,3,4,5,6,7,8-octahydroanthracene (**7**), and 1,9-dimethyl-5,6,7,8-tetrahydro-β-naphthindan (**8**). When heated with SbF_5 in the presence of HF, then treated with water, compound **1** is transformed to a mixture of products **3–6**. The reaction at 170 and 200 °C forms compounds **3–6** together with perfluoro-2-(cyclohexen-1-yl)-3-methylindene (**10**).

Keywords: Skeletal transformations; Perfluorophenyltetralin; Alicyclic ring contraction; Antimony pentafluoride; NMR spectroscopy

1. Introduction

Among the chemical transformations of perfluorocarbons of special interest are the skeletal rearrangements proceeding under the action of Lewis acids. They are interesting largely due to the fact that in the hydrocarbon series, cationoid rearrangements are widespread, whereas in the series of perfluorinated compounds, they occur very rarely. Thus, the alicyclic ring contraction of 2-halopolyfluorotetralins in the reaction with SbF_5 [1] and the ring opening of perfluorocyclopropane derivatives under the action of antimony pentafluoride [2,3] or aluminium chlorofluoride [4] are both known. Skeletal transformations of the four-, five- and six-membered alicyclic fragments of perfluorinated benzocyclobutene, indan, tetralin, and their perfluoroalkyl derivatives in an SbF_5 medium have been investigated, see for example [1–7] cited in our previous work [5].

Recently, we have found that the carbon framework in perfluoro-1-phenylindan changes under the action of SbF_5 to give perfluoro-9-methylfluorene and perfluorinated di-, tetra- or octa-hydro derivatives of anthracene and β-naphthindan [5]. When heated with antimony pentafluoride, perfluoro-1-(2-ethylphenyl)benzocyclobutene is converted to perfluoro-8,9-dimethyl-1,2,3,4-tetrahydrofluorene while perfluoro-1-(4-ethylphenyl)benzocyclobutene gives 2-ethyl-9,10-dihydroanthracene and perfluoro-6-ethyl-1,2,3,4-tetrahydroanthracene [6]. In contrast to this, perfluoro-1-phenylbenzocyclobutene does not undergo skeletal transformations under the same conditions [6].

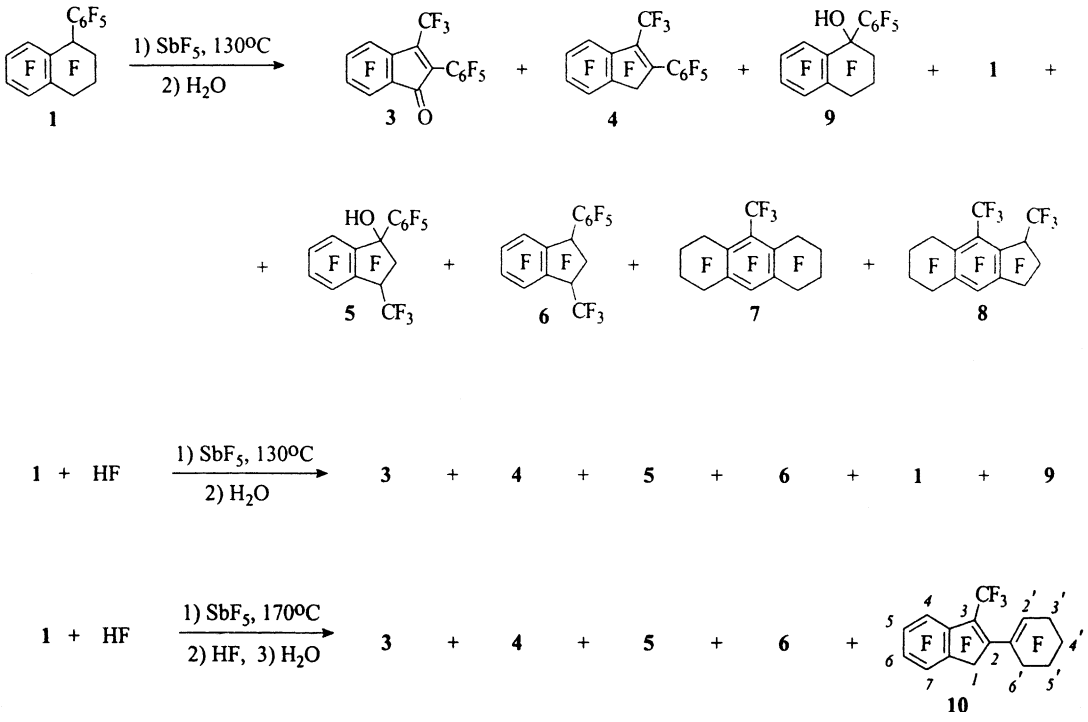
The aim of this paper is to investigate the behavior of perfluoro-1-phenyltetralin (**1**) under the action of antimony pentafluoride in order to study the effect of the perfluoroaryl group and the size of the alicycle on the route of the skeletal transformations of polyfluorobenzocycloalkenes.

2. Results and discussion

Compound **1** was obtained by electrophilic alkylation of pentafluorobenzene by perfluorotetralin (**2**) in the presence of antimony pentafluoride [7]. It has been shown that compound **1** undergoes skeletal transformations under the action of SbF_5 at high temperature. Thus, tetralin **1**, heated with antimony pentafluoride at 130 °C (15 h) and then treated with water, gives a mixture of perfluoro-3-methyl-2-phenylindenone (**3**) and small amounts of perfluoro-3-methyl-2-phenylindene (**4**), 3-hydroxy-perfluoro-1-methyl-3-phenylindan (**5**) in addition to perfluoro-1-methyl-3-phenylindan (**6**), perfluoro-9-methyl-1,2,3,4,5,6,7,8-octahydroanthracene (**7**), and perfluoro-1,9-dimethyl-5,6,7,8-tetrahydro-β-naphthindan (**8**). The reaction mixture also contains unchanged compound **1** together with 1-hydroxy-perfluoro-1-phenyltetralin (**9**) (Scheme 1).

* Corresponding author. Fax: +7-3832-34-4752.
E-mail address: karpov@nioch.nsc.ru (V.M. Karpov).

0022-1139/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2003.09.006

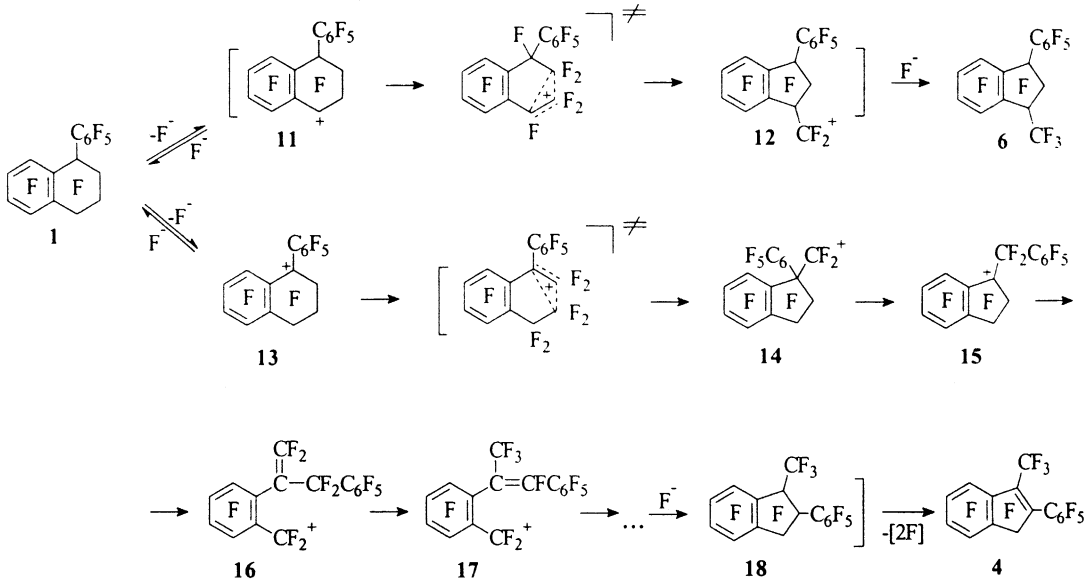


Scheme 1.

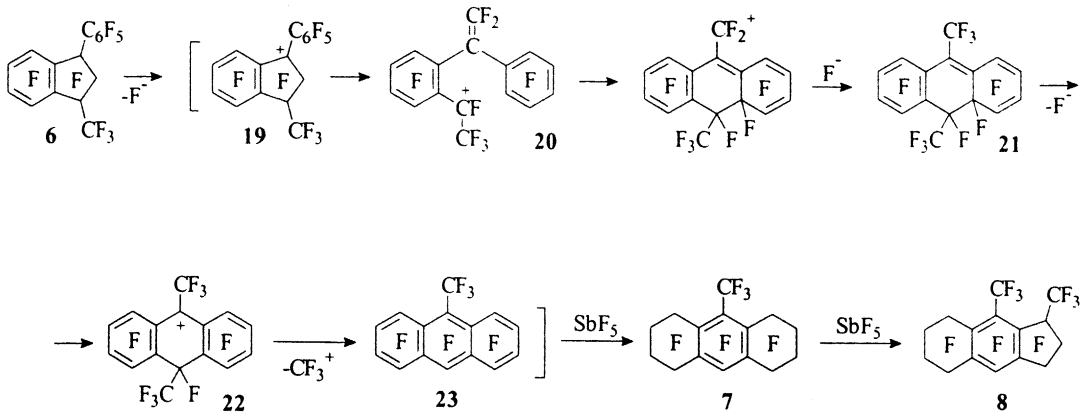
Heating at 130 °C (15 h) a solution of tetralin **1** (obtained in the reaction of compound **2** with C_6F_5H in SbF_5) and HF in antimony pentafluoride and subsequent treatment of the reaction mixture with water, leads to compounds **1**, **3–6**, and **9** but not compounds **7** and **8** (Scheme 1). It should be noted that compounds **7** and **8** were obtained in the reaction of perfluoro-1-phenylindan with SbF_5 in the absence of HF [5].

Prolonged heating of equimolar amounts of tetralin **1** and HF with excess of antimony pentafluoride at 130 °C (60 h), with further treatment of the reaction mixture with anhydrous HF and then with water, leads to compounds **3–6** and a small amount of perfluoro-2-(cyclohexen-1-yl)-3-methylindene (**10**). The reaction at 170 °C (14.5 h) or at 200 °C (10 h) forms compounds **3–6**, **10**, the yield of indene **10** increased while the yield of compounds **3** and **4** decreased as compared with the reaction at 130 °C (Scheme 1).

Isomerization of tetralin **1** to indan **6** under the action of SbF_5 possibly, proceeds analogously to the transformations of perfluoroethyltetralins [8,9] (Scheme 2). At first, the perfluoro-4-phenyl-1-tetralinyl cation (**11**) could be generated



Scheme 2.



Scheme 3.

from compound **1**. Cation **11** will be transformed, presumably, by the 1,2-shift of the perfluoroalkyl fragment, to cation **12**, which adds the fluoride ion to give indan **6**. Cation **11** is not the most stable one generated from tetralin **1**, but its concentration is apparently sufficient for the reaction.

A possible route for the formation of compound **4** is also presented in Scheme 2. The perfluoro-1-phenyl-1-tetralinyl cation (**13**) generated from compound **1** in an SbF_5 medium is the most stable [7]. Cation **13** apparently undergoes an intramolecular rearrangement, as a result of which it isomerizes into cation **14**. The latter is transformed into the perfluoro-1-benzyl-1-indanyl cation (**15**) which isomerizes to the benzyl type ion **16**. The double bond in the latter evidently moves inside the chain. The intramolecular cyclization of the vinylbenzyl cation **17** leads to the perfluoro-1-methyl-2-phenyl-1-indanyl cation which adds fluoride ion to produce perfluoro-1-methyl-2-phenylindan (**18**). A similar transformation of perfluoro-1-alkyl-1-indanyl cations was proposed for reactions of perfluoro-1-alkylindans with SbF_5 [10,11]. Defluorination and/or disproportionation of compound **18** gives indene **4**. It should be noted that the formation of perfluoro-2,3-dimethylindene from perfluoro-1,2-dimethylindan [11,12] and disproportionation of polyfluorocyclohexadienes in an SbF_5 medium are known [13,14]. Fluorination of compound **4** with SbF_5 leads to indene **10**.

It may be suggested that compounds **4** and **6** exist in an SbF_5 medium as salts of perfluoro-1-methyl-2-phenylindenyl and perfluoro-3-methyl-1-phenyl-1-indanyl (**19**) cations (cf. [7,10,15]); hydrolysis of these salts leads to the formation of products **3** and **5**, respectively.

Compounds **7** and **8** are possibly formed from indan **6**. The process may be represented, for example, by Scheme 3, similar to that for skeletal transformations of perfluoro-1-phenylindan under the action of antimony pentafluoride [5].

Cation **19**, generated from compound **6**, possibly undergoes cleavage of the five-membered ring to give cation **20**. Intramolecular attack at the *ortho*-position of the pentafluorophenyl ring by the benzyl carbon atom in cation **20** seems to give compound **21** after fluoride ion addition. It may be suggested that in ion **22** generated from compound **21**, elimination of CF_3^+ occurs to give perfluoro-9-methylanthracene (**23**). The latter then undergoes fluorination to form compound **7**, which isomerizes to product **8**. Transformation of compound **7** to product **8** was found by us earlier [5].

The structures of the compounds were established by HRMS 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. Patterns observed in the spectra of compounds **3**, **4**, and **10** are in agreement with those for perfluoro-2,3-dimethylindenone, perfluoro-2,3-dimethylindene, and other polyfluoroindenes [10,16]. Compounds **7** and **8** were identified by comparison of the ^{19}F NMR data with data for authentic samples [5].

Compounds **5** and **6** were obtained as *E*,*Z*-isomers. Their ^{19}F NMR spectra are in agreement with those for other polyfluoroindans [1,8–11]. An *E*-configuration was attributed to isomers of compounds **5** and **6**, for which signals of *tert*-F(1) atoms in ^{19}F NMR spectra are located at −7.3 and −9.0 ppm, and the *Z*-configuration, for which *tert*-F(1) signals have chemical shifts 5.0 and 2.4 ppm, respectively.

3. Experimental

The ^{19}F NMR spectra of $CHCl_3$ solutions of the reaction mixtures and individual compounds were recorded on a Bruker WP-200 SY instrument (188.3 MHz). Chemical shifts are given in δ (ppm) downfield from C_6F_6 (−162.9 ppm from CCl_3F) as internal standard. GC-MS: Hewlett Packard G1081A, combined with Hewlett Packard 5890 with mass selective detector HP 5971 (EI 70 eV). The molecular masses of the compounds were determined by

high-resolution spectrometry on a Finnigan Mat 8200 instrument. Contents (yields) of products in the reaction mixtures were established by GLC and GC-MS methods and ^{19}F NMR spectroscopic data.

3.1. Reaction of perfluoro-1-phenyltetralin (*1*) with antimony pentafluoride

Phenyltetralin **1** (1.44 g) and SbF_5 (3.78 g) (molar ratio, 1:6) were heated in a nickel bomb (10 ml) for 15 h at 130 °C. The mixture was poured into an ice-water and extracted with $CHCl_3$. The extract was dried over $MgSO_4$. The solvent was distilled off to give 1.24 g of the product, containing 17% (yield 15%) of **1**, 25% (25%) of **3**, 2% (2%) of **4**, 6% (5%) of **5**, 6% (5%) of **6**, 5% (4%) of **7**, 5% (4%) of **8**, and 16% (14%) of **9**. The yields of compounds **3**–**8** for converted phenyltetralin **1** are 34, 3, 7, 7, 5, and 5%, respectively. The individual compound **3** (0.17 g) was isolated by silica gel column chromatography (CCl_4 as eluent).

Perfluoro-3-*methyl*-2-*phenylindenone* (**3**): m.p. 79.5–81 °C (from hexane). HRMS *m/z*, 435.9769 (M^+). Calcd. for $C_{16}F_{12}O = 435.9757$. ^{19}F NMR δ: 96.1 (3F, CF_3); 29.7 (1F, F-7); 28.6 (1F, F-4); 20.8 (1F, F-5); 13.1 (1F, F-6); 25.5 (2F, F-*o*); 14.7 (1F, F-*p*); 1.6 (2F, F-*m*) ppm; $J_{CF_3\text{-}F(4)} = 21$ Hz, $J_{4,5} = 20$ Hz, $J_{4,6} = 6.5$ Hz, $J_{4,7} = 14$ Hz, $J_{5,6} = 16$ Hz, $J_{5,7} = 11$ Hz, and $J_{6,7} = 21$ Hz.

3.2. Reaction of perfluoro-1-phenyltetralin (*1*) + HF with antimony pentafluoride

1. Pentafluorobenzene (0.78 g) was added at room temperature to a solution of 1.47 g of perfluorotetralin (**2**) in 6.4 g of SbF_5 (molar ratio, 1.1:1:7) in a nickel bomb (10 ml). The mixture was heated at 50 °C for 5 h (preparation of **1** + HF), then at 130 °C for 15 h and treated as in the previous experiment to give 1.89 g of the product, containing 14% (yield 13%) of **1**, 16% (16%) of **3**, 2% (2%) of **4**, 19% (17%) of **5**, 10% (9%) of **6**, and 20% (18%) of **9**. The yields of compounds **3**–**6** for converted phenyltetralin **1** are 24, 3, 25, and 13%, respectively. In this and the previous experiment, the ratio of *E*:*Z* isomers is ~15:85 for **5** and ~40:60 for **6**.
2. A mixture of phenyltetralin **1** + HF and SbF_5 prepared from 0.87 g of C_6F_5H, 1.63 g of tetralin **2**, and 7.11 g of SbF_5 (molar ratio, 1.1:1:7) was heated at 130 °C for 59.5 h. The mixture was diluted with anhydrous HF (2.5–3 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 (2.2 g), containing 4% (yield 4%) of **3**, 13% (13%) of **4**, 22% (21%) of **5**, 27% (26%) of **6**, and 3% (3%) of **10**.
3. Analogously to the previous procedure, the reaction of C_6F_5H (0.82 g), tetralin **2** (1.54 g) and SbF_5 (7.26 g) (molar ratio, 1.1:1:7.6) gave (170 °C, 14.5 h) a mixture (1.94 g), containing 3% (yield 3%) of **3**, 8% (8%) of **4**, 23% (20%) of **5**, 28% (25%) of **6**, and 10% (8%) of **10**.
4. Analogously to procedure (2), the reaction of C_6F_5H (1.24 g), tetralin **2** (2.34 g), and SbF_5 (10.22 g) (1.1:1:7) gave (200 °C, 10 h) a mixture (3.28 g), containing 4% (yield 4%) of **4**, 23% (23%) of **5**, 22% (22%) of **6**, and 12% (11%) of **10**. Compounds **4**, **5** (*E*:*Z* ~ 25:75), **6** (*E*:*Z* ~ 15:85), and **10** were isolated by preparative GLC (200 °C, SKTFT-50 on Chromaton N-AW-DMCS, N_2) from the combined products obtained from experiments (2)–(4). Individual compound *Z*-**5** (m.p. 70–71.5 °C) was isolated by crystallization of **5** from hexane.

Perfluoro-3-*methyl*-2-*phenylindene* (**4**) (contaminated with about 10% of **6**): HRMS *m/z*, 457.9757 (M^+). Calcd. for $C_{16}F_{14} = 457.9776$. ^{19}F NMR δ: 96.9 (d, 3F, $J_{CF_3\text{-}F(4)} = 21$ Hz, CF_3); 43.0 (2F, F-1); 26.6 (1F, F-4); 23.9 (1F, F-7); 16.2 (1F) and 13.3 (1F, F-5, F-6); 24.7 (2F, F-*o*); 13.3 (1F, F-*p*); 2.0 (2F, F-*m*) ppm.

3-*Hydroxy*-*perfluoro*-1-*methyl*-3-*phenylindan* (**5**): HRMS *m/z*, 493.9774 (M^+). Calcd. for $C_{16}HF_{15}O = 493.9788$. GC-MS *m/z*, 494 ($M^+$) for *Z*-**5** and for *E*-**5** as well. *Compound Z*-**5**: ^{19}F NMR δ: 88.0 (3F, CF_3); 46.4 ($1F_A$) and 38.7 ($1F_B$, $J_{A,B} = 250$ Hz, CF_2-2); 28.5 (1F, F-7); 22.3 (1F, F-4), 18.0 (1F, F-5); 14.8 (1F, F-6); 24.0 (1F, F-*o*); 20.2 (1F, F-*o*); 12.7 (1F, F-*p*); 2.5 (1F, F-*m*); 2.0 (1F, F-*m*); 5.0 (1F, F-1) ppm. *Compound E*-**5**: ^{19}F NMR δ: 86.8 (3F, CF_3); 51.0 ($1F_A$) and 38.2 ($1F_B$, $J_{A,B} = 245$ Hz, CF_2-2); 27.4 (1F, F-7); 21.9 (1F, F-4), 17.7 (1F, F-5); 14.9 (1F, F-6); 24.1 (1F, F-*o*); 20.2 (1F, F-*o*); 12.6 (1F, F-*p*); 2.6-1.9 (2F, F-*m*); −7.3 (1F, F-1) ppm.

Perfluoro-1-*methyl*-3-*phenylindan* (**6**): HRMS *m/z*, 495.9718 (M^+). Calcd. for $C_{16}F_{16} = 495.9744$. GC-MS *m/z*, 496 (M^+) for *Z*-**6** and for *E*-**6**. *Compound Z*-**6**: ^{19}F NMR δ: 87.7 (3F, CF_3); 46.0 ($1F_A$) and 40.6 ($1F_B$, $J_{A,B} = 255$ Hz, CF_2-2); 29.2 (1F, F-7); 24.2 (1F, F-4), 19.0 (1F, F-5); 18.3 (1F, F-6); 26.3 (dm, 1F, $J_{F(o)\text{-}F(3)} = 60$ Hz, F-*o*); 22.5 (1F, F-*o*); 14.6 (1F, F-*p*); 3.2 (1F, F-*m*); 1.6 (1F, F-*m*); 24.0 (dm, 1F, $J_{F(3)\text{-}F(o)} = 60$ Hz, F-3); 2.4 (1F, F-1) ppm. *Compound E*-**6**: ^{19}F NMR δ: 86.4 (3F, CF_3); 49.5 ($1F_A$) and 38.1 ($1F_B$, $J_{A,B} = 250$ Hz, CF_2-2); 28.4 (1F, F-7); 26.4–22.5 (4F, F-3, F-4, 2F-*o*), 19.0 (1F, F-5); 18.3 (1F, F-6); 14.4 (1F, F-*p*); 3.2–1.6 (2F, F-*m*); −9.0(1F, F-1) ppm. Exact identification of some *E*-**6** signals was difficult since they overlap with signals of the isomer *Z*-**6**.

Perfluoro-2-(*cyclohexen*-1-*yl*)-3-*methylindene* (**10**): HRMS *m/z*, 533.9717 (M^+). Calcd. for $C_{16}F_{18} = 533.9712$. ^{19}F NMR δ: 96.6 (d, 3F, $J_{CF_3\text{-}F(4)} = 21$ Hz, CF_3); 48.2 (2F, F-1); 27.7 (1F, F-4); 24.4 (1F, F-7); 16.3 (1F) and 14.7 (1F, F-5, F-6); 46.6 (1F, F-2′); 43.7 (dm, 2F, $J_{F(3')\text{-}F(2')} = 20$ Hz, F-3′); 34.2 ($1F_A$) and 22.3 ($1F_B$, $J_{A,B} = 280$ Hz), 32.7 ($1F_A$) and 22.3 ($1F_B$, $J_{A,B} = 280$ Hz, CF_2-4′, CF_2-5′); 60.9 ($1F_A$) and 37.1 ($1F_B$, $J_{A,B} = 290$ Hz, CF_2-6′) ppm.

Acknowledgements

We gratefully acknowledge the Russian Foundation for Basic Researches (project no. 99-03-32876a) for financial support.

References

[1] V.V. Bardin, G.G. Furin, G.G. Yakobson, J. Fluorine Chem. 14 (1979) 455.
[2] S.D. Chepik, V.A. Petrov, M.V. Galakhov, G.G. Belen'kii, L.S. German, Izv. Akad. Nauk SSSR Ser. Khim. (1990) 1844.
[3] V.M. Karpov, V.E. Platonov, Izv. Akad. Nauk Ser. Khim. (1998) 1666.
[4] V.A. Petrov, C.G. Krespan, B.E. Smart, J. Fluorine Chem. 77 (1996) 139.
[5] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, V.R. Sinyakov, J. Fluorine Chem. 107 (2001) 53.
[6] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, V.R. Sinyakov, J. Fluorine Chem. 117 (2002) 73.
[7] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, V.R. Sinyakov, L.N. Shchegoleva, Zh. Org. Khim. 38 (2002) 1210.
[8] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, J. Fluorine Chem. 77 (1996) 101.
[9] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, Zh. Org. Khim. 33 (1997) 755.
[10] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, Izv. Akad. Nauk SSSR Ser. Khim. (1990) 645.
[11] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, Izv. Akad. Nauk Ser. Khim. (1992) 1419.
[12] V.M. Karpov, T.V. Mezhenkova, V.E. Platonov, Izv. Akad. Nauk SSSR Ser. Khim. (1990) 645.
[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] V.M. Karpov, V.E. Platonov, G.G. Yakobson, Tetrahedron 34 (1978) 3215.
[16] R.S. Matthews, W.E. Preston, Org. Magn. Reson. 14 (1980) 258.