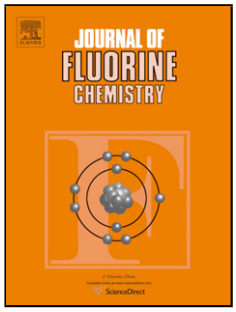

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Author: Volodymyr M. Ogurok Sergiy A. Siry Eduard B. Rusanov Yuriy G. Shermolovych

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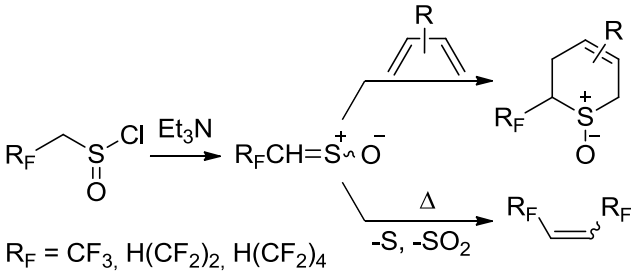
Polyfluoroalkyl sulfines derived from 1,1-dihydropolyfluoroalkanesulfinyl chlorides: decomposition and [4+2]-cycloaddition reactions

Volodymyr M. Ogurok, Sergiy A. Siry, Eduard B. Rusanov, Yuriy G. Shermolovych*

Institute of Organic Chemistry, National Academy of Science of Ukraine, Murmans'ka str, 5, 02094, Kyiv, Ukraine

* Corresponding author. Tel.: +380 44 2928312; fax: +380 44 573 2643. E-mail address: sherm@ioch.kiev.ua (Yu.G. Schermolovich).

Graphical Abstract



1,1-Dihydropolyfluoroalkanesulfinyl chlorides were prepared by the oxidative chlorination of 1,1-dihydropolyfluoroalkyl thioacetates. The dehydrochlorination of the sulfinyl chlorides produced unstable polyfluoroalkanethial-S-oxides. The decomposition of the fluorinated thioaldehyde-S-oxides and their [4+2]-cycloaddition with dienes were studied.

Highlights

- 1,1-Dihydropolyfluoroalkanesulfinyl chlorides were prepared by the oxidative chlorination of polyfluoroalkyl thioacetates.
- The dehydrochlorination of these chlorides produced new polyfluoroalkanethial-S-oxides.
- Internal fluorinated alkenes were prepared by the thermal decomposition of sulfines.
- Convenient preparation of 2-(polyfluoroalkyl)-3,6-dihydro-2*H*-thiopyran-1-oxides was elaborated.

Abstract

A convenient method for the preparation of 1,1-dihydropolyfluoroalkanesulfinyl chlorides has been developed basing on the oxidative chlorination of 1,1-dihydropolyfluoroalkyl thioacetates. The dehydrochlorination of the sulfinyl chlorides leads to the formation of new polyfluoroalkylsulfines (fluorinated thioaldehyde-S-oxides). The thermal decomposition of the sulfines results in formation of the symmetrical polyfluorinated alkenes, whereas the reactions of the sulfines with 1,3-dienes afford 2-(polyfluoroalkyl)-3,6-dihydro-2*H*-thiopyran-1-oxides.

Keywords: sulfinyl chloride, sulfine, polyfluorinated alkene, thiopyran, sulfoxide.

1. Introduction

Sulfines (thiocarbonyl S-oxides, fig. 1) are extensively studied as synthetically useful organosulfur reagents. General synthetic routes to sulfines, their properties and application in the organic synthesis were outlined in the reviews [1,2,3].

Due to the high reactivity sulfines with per- or polyfluoroalkylated substituents at the carbon atom of the C=S=O heterocumulene fragment are of interest as building blocks for the preparation of various types of fluorinated organosulfur compounds (R^1 = CF_3, R^2 = H [4], R^1 = $H(CF_2)_6$, R^2 = H [5], R^1 = R^2 = CF_3 [6,7], R^1 = CF_3, CF_2Cl, CF_2Br, R^2 = F [8], R^1 = CF_3, R^2 = Cl [9], R^1 = CF_3, R^2 = Me, Ph [10]). Most existing methods of their preparation are based on high-temperature reactions of the corresponding precursors and are not very suitable for the preparative chemistry.

Dehydrochlorination of 1,1-dihydropolyfluoroalkanesulfinyl chlorides seems to be more convenient approach towards polyfluoroalkylsulfines (fig. 1, R^1 = H, R^2 = R_F). The main advantage of this approach is that the preparation or *in situ* generation of potentially unstable polyfluoroalkanethial-S-oxides can be realized in mild conditions and does not require special equipment. To date, the utility of this method has been practically not explored, since the necessary fluorinated sulfinyl chlorides could be prepared only by the oxidative chlorination of poorly available 1,1-dihydropolyfluoroalkanethiols [11]. The aim of the present work consisted in the development of more convenient synthetic route to fluorinated sulfinyl chlorides, preparation of the corresponding sulfines by the dehydrochlorination and studies of their properties and synthetic utility.

2. Results and discussion

In order to prepare fluorinated sulfinyl chlorides we studied the oxidative chlorination of the polyfluoroalkyl thioacetates **1a-c**, which are readily obtainable by the reaction of potassium thioacetate with the corresponding fluoroalkyl tosylates [12]. We have found, that treatment of the equimolar mixtures of thioacetates **1a-c** and acetic acid with the excess of chlorine without solvent produced sulfinyl chlorides **2a-c** (scheme 1). Fluorinated sulfinyl chlorides **2a-c** were isolated in good yields by the distillation of the reactive mixtures and appeared as colorless liquids, which are stable for weeks if kept under inert atmosphere.

Treatment of the sulfinyl chlorides **2a-c** with equimolar amount of triethylamine in inert solvents led to the formation of the corresponding sulfines **3a-c**. Sulfines appeared to be unstable and could not be isolated, that is why they could be only roughly characterized by ^{19}F NMR and ^{1}H NMR spectroscopy in $CDCl_3$ solutions. The signals in the NMR spectra of sulfine **3a** were well-defined, whereas only ^{1}H NMR signals of CH=S=O moieties and ^{19}F NMR signals of the adjacent CF_2 groups could be distinguished in the spectra of the sulfines **3b,c**, other signals overlapped badly with the signals of the decomposition products.

Chemical shifts of the protons of sulfine moieties of the compounds **3a-c** are close to the shifts of the protons of their non-fluorinated analogs [13,14]. In all the spectra double sets of signals corresponding to sulfines were observed due to the formation of the mixtures of (*E*)- and (*Z*)-isomers. Stereochemistry of the sulfines **3a-c** was deduced basing on known observations that the signals of (*E*)-isomers are downfielded with respect to the signals of (*Z*)-isomers [13,15] (table 1). (*Z*)-Isomer prevailed slightly in the mixture of sulfines **3a**, whereas in diastereomeric mixtures of the sulfines **3b,c** (*E*)-isomers predominated. It is noteworthy, that the relation between ^{19}F NMR shifts and configuration of sulfine moiety is opposite to that between ^{1}H NMR shift and configuration: (*E*)-isomers give signals in higher field than (*Z*)-isomers do.

[a] Triethylamine (0.1 mmol) in $CDCl_3$ (0.3 mL) was added to a cooled (–10°C) solution of sulfinyl chloride (0.1 mmol) in $CDCl_3$ (0.3 mL) in NMR tube, and the mixture was shaken at room temperature for few seconds. The NMR measurements were carried out immediately after mixing.
[b] Signal of CF_3 group.
[c] Signal of 2-CF_2 group.
[d] Established by the integration of ^{1}H NMR signals.

Even in solutions the sulfines **3a-c** decomposed gradually, and after 48 h at room temperature they could not be detected by the NMR spectroscopy. Sulfine **3a** decomposed giving complex mixture of the products. The decomposition of the sulfines **3b,c** produced mainly symmetrical fluorinated alkenes **4b,c** (scheme 2). The formation of the symmetrical alkenes from fluorinated [4,16] and non-fluorinated [14,17,18] sulfines has already been reported. A plausible mechanism of the reaction includes dimerization of the sulfines with the formation of 3,4-bis(polyfluoroalkyl)-1,2,5-oxadithiolan-2-oxides followed by the extrusion of SO_2 and S to give final products (scheme 2). Compound **4b** appeared as the mixture of two diastereomers in ratio 1:1.1, whereas compound **4c** was formed as single diastereomer. In the ^{1}H NMR spectra of the alkenes **4b,c** complex signals of $X_2AA'X_2'$ systems corresponding to $CF_2CH{=}CHCF_2$ moieties were observed, based on this data the stereochemistry of the alkenes could not be established unequivocally.

Compounds **4b** and **4c** were isolated by the distillation of the reactive mixtures obtained by the treatment of sulfinyl chlorides **2b** and **2c** with triethylamine in diethyl ether. Alkene **4b** was obtained as *ca* 65% solution in diethyl ether. Less volatile compound **4c** was obtained in pure form in 80% yield. Most known methods of the preparation of internal fluorinated alkenes of such type are based on high-temperature catalytic transformations of polyfluorochloroalkanes [19,20] or reactions involving perfluoroalkyl iodides [21] or perfluoroorganocopper reagents [22]. The preparation of the symmetrical polyfluoroalkenes by decomposition of sulfines may be of certain interest, since it does not require special equipment and expensive or unstable starting materials.

It is obvious, that if sulfines **3a-c** are to be used for other synthetic purposes, they should be generated *in situ* in the presence of trapping reagents. As highly reactive heterodienophiles, fluorinated sulfines are useful precursors for the preparation of 3,6-dihydro-2*H*-thiopyran-1-oxides by the reactions with 1,3-dienes [23], however only one example of the reaction of polyfluoroalkanethial-S-oxides with 1,3-diene has been described to date [5].

We studied the cycloaddition of the sulfines **3a-c** with 1,3-butadiene, 2,3-dimethyl-1,3-butadiene and (*E*)-1-acetoxybutadiene. The reactions were carried out by the addition of triethylamine to the solutions of the sulfinyl chlorides **2a-c** and excess of diene in dichloromethane at –70°C. All the reactions produced diastereomeric mixtures of 2-(polyfluoroalkyl)-3,6-dihydro-2*H*-thiopyran-1-oxides **5-10**, which were isolated after work-up and flash chromatography in satisfactory yields (table 2). Reactions involving 1-acetoxy-1,3-butadiene proceeded regioselectively with the formation of 6-acetoxy derivatives **7** and **9**. The mixtures of the sulfoxides

could not be separated by chromatography. Major component of the mixture of the diastereomers **8a,b** was partially isolated by crystallization.

According to the ^{1}H NMR data, the molecules of all the sulfoxides adopt preferably *half-chair* conformation in $CDCl_3$ solutions, which is in accordance with the values of the vicinal coupling constants. In the ^{1}H NMR spectra of all the sulfoxides two well-different vicinal coupling constants were observed between the protons H-2 and diastereotopic protons of the methylene group in the positions 3. Their values ($J_{H2,H3ax}$ = 8.4–14.1 Hz, $J_{H2,H3eq}$ = 3.9–5.3 Hz) indicated the axial orientation of the protons H-2, thus, polyfluoroalkyl groups being equatorial. These data also fit well with the known tendency of polyfluoroalkyl groups to adopt equatorial positions in cyclohexane [24] and other thiopyran derivatives [25].

The reactions involving symmetrical dienes produced the mixtures of two diastereomeric sulfoxides **5a,b**, **6a,b**, **8a,b** and **10a,b** (table 2, entries 1, 2, 4, 6). Since the molecules of all these compounds contain equatorially oriented fluorinated substituents, in each pair the diastereomers differ in orientation of the sulfinyl groups. It is known, that chemical shifts of the axial protons in the positions 3 (5) of the 6-membered sulfoxides with the axial S=O groups are downfielded and the shifts of the axial protons in the positions 2 (6) are upfielded if compared with the shifts of the corresponding protons of the sulfoxides with the equatorial S=O groups [26,27,28]. Shifts of the pseudoaxial protons H-3 of the minor components of the diastereomeric mixtures **5a,b**, **6a,b**, **8a,b** and **10a,b** are 0.10 – 0.60 ppm downfielded with respect to the shifts of the pseudoaxial protons H-3 of major components. In contrast, shifts of the axial protons H-2 and pseudoaxial protons H-6 are 0.32 – 0.50 ppm upfielded, indicating equatorial orientation of S=O groups in the molecules of the major sulfoxides. Therefore, we assigned the structures **5a**, **6a**, **8a** and **10a** with *trans*-orientation of the oxygen atoms to the fluoroalkyl substituents for the major isomers, whereas the structures **5b**, **6b**, **8b** and **10b** with the relative *cis*-orientation of S=O and polyfluoroalkyl groups for minor ones.

Our suggestions on the stereochemistry of the sulfoxides were additionally supported by the x-ray study of the major component of the mixture of the cycloadducts **8a,b** (fig. 2). According to x-ray data, both fluorinated substituent and oxygen atom are equatorial, thus having relative *trans*-configuration.

In the solid state structure **8a** the six-membered S1C1-C5 cycle (see the numbering in fig. 2) is non-planar and has *half-boat* conformation. Atoms C1 – C5 lies in plane (mean deviation atoms from plane is 0.044 Å) and S1 atoms vary from that plane to 1.0405(25) Å, thus the dihedral angle between C1-C5 and C1S1C5 planes is 56.60(8)º. C1-S1 and C5-S1 bonds are slightly non equivalent (1.819(2) and 1.796(2) Å). All C-C bond lengths and bond angles are in usual range. HCF_2CF_2 group is oriented in such a manner that the stabilization of the intramolecular C7-H···O1 interaction is possible (C···O 2.992(4) Å, CHO angle is 124.0º).

Dehydrochlorination of sulfinyl chloride **2a** in the presence of 1-acetoxybutadiene produced the mixture of three diastereomeric sulfoxides in ratio 6.6:1.3:1 (table 2, entry 3), whereas from chloride **2b** the mixture of two isomers in ratio 7.5:1 was obtained (table 2, entry 5). The chemical shifts of the pseudoaxial protons H-3 of the major sulfoxides were close to the shifts of the corresponding protons of the sulfoxides **5a**, **6a**, **8a** and **10a** indicating the equatorial orientation of S=O groups. The values of the vicinal coupling constants between the protons H6 and H5 of the major products (6.3 Hz for the major product from chloride **2a** and 6.4 Hz for the product from chloride **2b**) correspond to the pseudo-equatorial orientation of the protons H-6, acetoxy groups being pseudo-axial. As a conclusion, structures **7a** and **9a** were suggested for the major components of the mixtures. Besides sulfoxide **7a**, the mixture derived from sulfinyl chloride **2a** contained two minor products. The majority of their signals in the ^{1}H NMR spectrum were hindered by the signals of compound **7a**, however, the chemical shifts and splitting patterns of some well-distinguished ones revealed the stereochemistry of the sulfoxides. Small values of the constants between the

protons H-5 and H-6 (2.5 Hz for minor isomer and 2.6 Hz for the minutest one) indicated pseudo-axial orientation of the protons H-6. Chemical shift due to the proton H-2 of minor isomer was downfielded (3.99 ppm) with respect to the proton H-2 of minutest isomer (3.54 ppm). Basing on these data, structure **7b** with equatorial S=O group was suggested for minor isomer, minutest isomer was identified as compound **7c** with the axial S=O group. The constants due to the H-H coupling in the ^{1}H NMR spectrum of the minor counterpart of sulfoxide **9a** were of close values to the corresponding constants in the spectra of the sulfoxides **7b,c** indicating the same relative configuration at the positions 2 and 6. The orientation of the S=O group could not be established unequivocally, that is why the structure **9b** with uncertain relative configuration at the sulfur atom was suggested.

It is noteworthy, that the ratios of the diastereomeric sulfoxides formed upon the cycloaddition (see table 2) are different considerably from the ratios of the sulfines **3a-c** produced by the dehydrochlorination of the sulfinyl chlorides (see table 1). The stereoselectivity of the cycloaddition was not dependent on the temperature, in particular, the addition of 2,3-dimethyl-1,3-butadiene to the solutions of preformed sulfines **3a-3c** in $CDCl_3$ at room temperature (see the (*E*)/(*Z*) ratios in table 1) resulted in the formation of the sulfoxides **6a,b**, **8a,b**, **10a,b** almost in the same ratios as at –70°C, however, the larger proportions of the by-products due to the thermal decomposition of the sulfines were formed. Similar phenomenon has already been observed during the cycloaddition of the aromatic thioaldehyde-S-oxides with dienes [17]. It has been explained by the existence of the rapid interconversion between (*Z*)- and (*E*)-sulfines along with lower activation energy for the cycloaddition between diene and one of the diastereomeric sulfines. The predominant formation of the sulfoxides with *trans* relation between sulfinyl oxygen and fluorinated substituent (compounds **5a** – **10a**) in our experiments may be due to the low activation energy for the cycloaddition of (*E*)-sulfines if compared with their (*Z*)-counterparts.

3. Conclusion

In conclusion, we have developed a simple procedure for the preparation of the 1,1-dihydropolyfluoroalkanesulfinyl chlorides and have found them to be useful precursors for the poorly studied unstable polyfluorothioalkanethial-S-oxides. Synthetic potential of the fluorinated thioaldehyde-S-oxides has been demonstrated by their spontaneous dimerization followed by the elimination of SO_2 and S, which gives symmetrical polyfluorinated alkenes, and by their reactions of [4+2]-cycloaddition with 1,3-dienes, which produce 2-(polyfluoroalkyl)-3,6-dihydro-2*H*-thiopyran-1-oxides.

4. Experimental

4.1. General

All solvents were purified according to the standard procedures. Column chromatography was performed on silica gel Merck 60–260 (micrometers). TLC was performed on Silufol plates. ^{1}H NMR spectra were recorded on Varian VXR-300 spectrometer (299.9 MHz) or on Bruker Avance 400 spectrometer (400.1 MHz). ^{19}F NMR spectra were obtained on a Varian VXR-300 spectrometer (282.2 MHz) or on a Varian Gemini-200 spectrometer (188.1 MHz) with C_6F_6 (δ = –162.9 ppm with respect to $CFCl_3$) as internal standard. ^{13}C NMR spectra (100.6 MHz) were measured on Bruker Avance 400 spectrometer. All ^{1}H NMR and ^{13}C NMR chemical shift data were given in ppm in δ scale with tetramethylsilane as internal standard (0 ppm). GC/MS data were obtained on the Hewlett- Packard 5890\5972 apparatus (GC/MS) at 70 eV in the electron impact mode.

In the description of the NMR spectra of the mixtures of isomers the nuclei of the major isomers are marked with asterisk*. In the description of the spectra of the diastereomeric mixtures **7a,b,c** and **9a,b** only NMR data of major isomers **7a** and **9a** are given in full, for minor isomers only well-distinguished signals are given as selected NMR data. Separated GC/MS data for each component of the mixtures are given only when possible.

*4.2. 1,1-Dihydropolyfluoroalkyl thioacetates (**1a-c**).*

The preparation of 2,2,3,3-tetrafluoropropyl thioacetate **1b** was described in the previous paper [12]. Thioacetates **1a,c** were prepared by the similar procedure. The synthesis was carried out in argon atmosphere. To a stirred suspension of finely powdered anhydrous K_2CO_3 (84.17 g, 609 mmol) in DMSO (300 mL) thioacetic acid (92.71 g, 1218 mmol) was added dropwise. Stirring was continued until CO_2 evolution ceased, and corresponding polyfluorinated tosylate (406 mmol) was added. The mixture was stirred for 15 h at 40 – 44°C, cooled to 10 ºC and diluted with water (350 mL). The product was extracted by CH_2Cl_2 (4×100 mL). The combined organic layers were washed with water (5×100 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The residue was distilled giving thioacetates as yellow liquids.

*4.2.1. 2,2,2-Trifluoroethyl thioacetate (**1a**).*

Yield 76%, bp 108–110 °C (atmospheric pressure). ^{1}H NMR (400 MHz, $CDCl_3$): 2.43 (s, 3H, CH_3), 3.59 (q, 2H, $^3J_{HF}$ = 10.0 Hz, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 30.2 (s, CH_3), 31.0 (q, $^2J_{CF}$ = 34 Hz, CH_2), 124.8 (q, $^1J_{CF}$ = 276 Hz, CF_3), 191.9 (s, C=O). ^{19}F NMR (188 MHz, $CDCl_3$): –67.57 (t, 3F, $^3J_{FH}$ = 10.0 Hz, CF_3). GC/MS, m/z (rel. int.): 158 (2) $[M]^+$, 143 (3) $[M\text{-}CH_3]^+$, 83 (3) $[CF_3CH_2]^+$, 69 (3) $[CF_3]^+$, 43 (100) $[AcO]^+$. Anal. calcd. for $C_4H_5F_3OS$: C, 30.38; H, 3.19; S, 20.28; found: C, 30.45; H, 3.20; S, 20.18.

*4.2.2. 2,2,3,3,4,4,5,5-Octafluoropentyl thioacetate (**1c**).*

Yield 84%, bp 84-85°C/ 19 torr. ^{1}H NMR (400 MHz, $CDCl_3$): 2.43 (s, 3H, CH_3), 3.64 (tt, 2H, $^3J_{HF}$ = 17.5 Hz, $^4J_{HF}$ = 1.3 Hz, CH_2), 6.05 (tt, 1H, $^2J_{HF}$ = 52.1 Hz, $^3J_{HF}$ = 5.5 Hz, HCF_2). ^{13}C NMR (100 MHz, $CDCl_3$): 29.3 (t, $^2J_{CF}$ = 24 Hz, CH_2), 30.15 (s, CH_3), 107.8 (tt, $^1J_{CF}$ = 255 Hz, $^2J_{CF}$ = 31 Hz, HCF_2), 107.0÷116.0 (m, $HCF_2(\underline{CF_2})_2CF_2$), 115.7 (tt, $^1J_{CF}$ = 254 Hz, $^2J_{CF}$ = 32 Hz, $CH_2\underline{CF_2}$), 192.1 (s, C=O). ^{19}F NMR (188 MHz, $CDCl_3$): –113.24 ÷ –113.50 (m, 2F, CF_2CH_2), –125.56 ÷ –125.76 (m, 2F, $HCF_2CF_2\underline{CF_2}$), –130.55÷ –130.77 (m, 2F, $HCF_2C\underline{F_2}CF_2$), –138.20 (dm, 2F, $^2J_{FH}$ = 52.1 Hz, HCF_2). GC/MS, m/z (rel. int.): 290 (0.5) $[M]^+$, 275 (1) $[M\text{-}CH_3]^+$, 101 (1) $[HCF_2CF_2]^+$, 51 (4) $[HCF_2]^+$, 43 (100) $[AcO]^+$. Anal. calcd. for $C_7H_6F_8OS$: C, 28.97; H, 2.08; S, 11.05; found: C, 28.90; H, 2.10; S, 11.15.

*4.3. General procedure for the preparation of the sulfinyl chlorides (**2a-c**).*

The equimolar mixture or thioacetate **1a-c** and glacial acetic acid was stirred and cooled in the ice bath and dry chlorine was bubbled at the temperature not exceeding 20°C. After the initial exotherm corresponding to the absorption of 1 mole of Cl_2 per mole of thioacetate subsided, cooling bath was removed and chlorine was bubbled slowly at room temperature until saturation occurred (6–10 h) and the NMR analysis revealed full conversion. Then the mixture was distilled at reduced pressure giving corresponding sulfinyl chloride.

*4.3.1. 2,2,2-trifluoroethane-1-sulfinyl chloride (**2a**).*

Colorless liquid, b.p. 19-20 °C/9-10 torr, yield 65%. ^{1}H NMR (400 MHz, $CDCl_3$): 4.14-4.3 (m, 2H, $^2J_{HH}$ = 14.5 Hz, $^3J_{HF}$ = 9.5 CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): 66.5 (q, $^2J_{CF}$ = 39.3 Hz, CH_2), 122.02 (q, $^1J_{CF}$ = 279.3 Hz, CF_3). ^{19}F NMR (282 MHz, $CDCl_3$): –61.30 (t, 3F, $^2J_{FH}$ = 9.5 Hz, CF_3). GC/MS, m/z (rel. int.): 131 (6) $[M\text{-}Cl]^+$, 79 (100), 69 (10) $[CF_3]^+$, 67 (21), 48 (9) $[SO]^+$. Anal. calcd. for $C_2H_2ClF_3OS$: C, 14.42; H, 1.21; Cl, 21.29; S, 19.25; found: C, 14.12; H, 1.08; Cl, 20.86; S, 19.02.

*4.3.2. 2,2,3,3-tetrafluoropropane-1-sulfinyl chloride (**2b**).*

Colorless liquid, b.p. 48-49.5 °C/10-11 torr, yield 85%. ^{1}H NMR (300 MHz, $CDCl_3$): 4.04-4.25 (m, 2H, $^3J_{HF}$ = 16.5 Hz, CH_2), 6.90 (tt, 1H, $^2J_{HF}$ = 53.6 Hz, $^3J_{HF}$ = 2.2 Hz, HCF_2). ^{13}C NMR (100 MHz, $CDCl_3$): 109.4 (tt, $^1J_{CF}$ = 251.3 Hz, $^2J_{CF}$ = 39.3 Hz, HCF_2), 114.7 (tt, $^1J_{CF}$ = 251.3 Hz, $^2J_{CF}$ = 31.1 Hz, CF_2). ^{19}F NMR (282 MHz, $CDCl_3$): –112.00 (AB, 1F, $^2J_{FF}$ = 284.9 Hz, CF_2), –112.90 (AB, 1F, $^2J_{FF}$ = 284.9 Hz, CF_2), –135.35 (AB, 1F, $^2J_{FF}$ = 304.9 Hz, $^2J_{FH}$ = 53.6 Hz, HCF_2), –136.33 (AB, 1F, $^2J_{FF}$ = 304.9 Hz, $^2J_{FH}$ = 53.6 Hz, HCF_2). GC/MS, m/z (rel. int.): 163 (39) $[M\text{-}Cl]^+$,

117 (19), 79 (37), 51 (16) $[HCF_2]^+$, 44 (97) $[CS]^+$, 40 (100). Anal. calcd. for $C_3H_3ClF_4OS$: C, 18.15; H, 1.52; Cl, 17.85; S, 16.15; found: C, 17.89; H, 1.43; Cl, 17.51; S, 16.22.

*4.3.3. 2,2,3,3,4,4,5,5-octafluoropentane-1-sulfinyl chloride (**2c**).*

Colorless liquid, b.p. 71 °C/9-10 torr, yield 65%. ^{1}H NMR (300 MHz, $CDCl_3$): 4.09÷4.34 (m, 2H, CH_2), 6.06 (tt, 1H, $^2J_{HF}$ = 51.8 Hz, $^3J_{HF}$ = 5.2 Hz, HCF_2). ^{13}C NMR (100 MHz, $CDCl_3$): 65.2 (t, $^2J_{CF}$ = 22.0 Hz, CH_2), 107.7 (tt, $^1J_{CF}$ = 254.8 Hz, $^2J_{CF}$ = 30.8 Hz, HCF_2), 107.3÷113.3 (m, $HCF_2\underline{CF_2}CF_2CF_2$), 115.3 (tt, $^1J_{CF}$ = 259.4 Hz, $^2J_{CF}$ = 33.3 Hz, $HCF_2CF_2CF_2\underline{CF_2}$). ^{19}F NMR ($CDCl_3$): –109.67÷–112.00 (m, 2F, CH_2CF_2), –125.44÷–125.90 (m, 2F, CF_2), –129.90÷–130.23 (m, 2F, CF_2), –138.11 (dm, 2F, $^2J_{FH}$ = 51.8 Hz, HCF_2). GC/MS, m/z (rel. int.): 263 (1) $[M\text{-}Cl]^+$, 177 (3) $[M\text{-}HCF_2CF_2\text{-}HF]^+$, 101 (2) $[HCF_2CF_2]^+$, 79 (100), 51 (10) $[HCF_2]^+$. Anal. calcd. for $C_5H_3ClF_8OS$: C, 20.11; H, 1.01; Cl, 11.87; S, 10.74; found: C, 19.84; H, 1.12; Cl, 11.52; S, 10.23.

*4.4. 1,1,2,2,5,5,6,6-Octafluorohex-3-en (**4b**).*

To the stirred solution of sulfinyl chloride **2b** (0.9 g, 4.5 mmol) in Et_2O (8 mL) a solution of Et_3N (0.45 g, 4.5 mmol) in Et_2O (8 mL) was added dropwise at –35°C. After addition of the base the mixture was allowed to reach room temperature slowly and was stirred until sulfine **3b** disappeared (*ca* 48 h, established by the ^{19}F NMR measurements). The mixture was distilled at 0.05 torr at room temperature, and volatile products were collected in a receiver cooled in liquid nitrogen bath. The bulk of Et_2O from condensate was removed by the distillation at the atmospheric pressure until vapor temperature reached 40°C. The colorless liquid in the distilling flask being *ca* 65% mass solution of compound **4b** in Et_2O, yield 0.58 g (74%), further separation was unsuccessful. Mixture of two diastereomers in ratio 1:1.1. ^{1}H NMR (400 MHz, $CDCl_3$): 5.84 (tm, 1H, $^2J_{HF}$ = 53.7 Hz, HCF_2), 5.88 (tm, 1.1H, $^2J_{HF}$ = 53.6 Hz, HCF_2*), 6.18 (m, 1H, CH), 6.40 (m, 1.1H, CH*). ^{13}C NMR (100 MHz, $CDCl_3$): 109.7 (tt, $^1J_{CF}$ = 251 Hz, $^2J_{CF}$ = 42 Hz, HCF_2*), 109.9 (tt, $^1J_{CF}$ = 252 Hz, $^2J_{CF}$ = 42 Hz, HCF_2), 110.0÷116.0 (m, CF_2 of both isomers), 127.6 (m, HC=CH), 128.9 (t, $^2J_{CF}$ = 33 Hz, HC=CH*). ^{19}F NMR (282 MHz, $CDCl_3$): –112.37 (s, 2F, CF_2), –116.61 (s, 2.2F, CF_2*), –135.47 (d, 2.2F, $^2J_{FH}$ = 53.6 Hz, HCF_2*), –135.82 (d, 2F, $^2J_{FH}$ = 53.7 Hz, HCF_2).

*4.5. 1,1,2,2,3,3,4,4,7,7,8,8,9,9,10,10-Hexadecafluorodec-5-ene (**4c**).*

To the stirred solution of sulfinyl chloride **2c** (2.5 g, 8.4 mmol) in Et_2O (8 mL) a solution of Et_3N (0.84 g, 8.4 mmol) in Et_2O (8 mL) was added dropwise at –35°C. Following treatment was the same as for preparation of compound **4b** except the volatile material from the reactive mixture was concentrated at 20 torr at room temperature until constant weight was achieved giving pure alkene **4c** as colorless liquid. Yield 1.42 g (80%). ^{1}H NMR (400 MHz, $CDCl_3$): 6.03 (tt, 1H, $^2J_{HH}$ = 52.0 Hz, $^3J_{HH}$ = 5.0 Hz, HCF_2), 6.49 (m, 1H, CH). ^{13}C NMR (100 MHz, $CDCl_3$): 107.8 (tt, $^1J_{CF}$ = 255 Hz, $^2J_{CF}$ = 32 Hz, HCF_2), 108.2÷114.0 (m, $HCF_2\underline{CF_2}\underline{CF_2}CF_2$), 113.49 (tt, $^1J_{CF}$ = 256 Hz, $^2J_{CF}$ = 32 Hz, $\underline{CF_2}CH$), 128.1 (tt, $^2J_{CF}$ = 25 Hz, $^3J_{CF}$ = 9 Hz, CH=CH). ^{19}F NMR (282 MHz, $CDCl_3$): –115.11 (s, 2F, $HCF_2CF_2CF_2\underline{CF_2}$), –126.18 (s, 2F, $HCF_2CF_2\underline{C}F_2CF_2$), –130.21 (s, 2F, $HCF_2\underline{C}F_2CF_2CF_2$), –138.23 (d, 2F, $^2J_{FH}$ = 52.0 Hz, HCF_2). GC/MS, m/z (rel. int.): 277 (100) $[M\text{-}HCF_2CF_2CF_2]^+$, 227 (3) $[M\text{-}HCF_2(CF_2)_3]^+$, 207 (61), 151 (10) $[HCF_2(CF_2)_2]^+$, 101 (67) $[HCF_2CF_2]^+$, 51 (70) $[HCF_2]^+$ Anal. calcd. for $C_{10}H_4F_{16}$: C, 28.06; H, 0.94; found: : C, 27.85; H, 0.76.

*4.6. General procedure of the preparation of 2-(polyfluoroalkyl)-3,6-dihydro-2H-thiopyran-1-oxides **5-10**.*

To a stirred solution of the corresponding sulfinyl chloride (10 mmol) and 1,3-diene (11 mmol) in CH_2Cl_2 (5 ml) a solution of Et_3N (10 mmol) in CH_2Cl_2 (5 ml) was added dropwise at –70°C. After addition of Et_3N the reactive reaction mixture was allowed to reach room temperature (3 h) and washed with water (2×10 ml). Organic layer was dried over Na_2SO_4 and evaporated under reduced pressure. Crude products were purified by the column chromatography on silica gel.

*4.6.1. (1RS,2SR)-2-(Trifluoromethyl)-3,6-dihydro-2H-thiopyran 1-oxide (**5a**) and (1RS,2RS)-2-(trifluoromethyl)-3,6-dihydro-2H-thiopyran 1-oxide (**5b**).*

Pale brown oil, yield 50 %, R_f = 0.15 (hexane–EtOAc, 2:1). Mixture of the diastereomeric sulfoxides **5a** and **5b** in ratio 4.5:1. ^{1}H NMR (400MHz, $CDCl_3$): 2.46÷2.57 (m, 5.5H, H-3*eq* + H-3*ax**), 2.79–2.94 (m, 5.5H, H-3*ax* + H-3*eq**), 3.17 (ddq, 1H, $^3J_{HH}$ = 12.5 Hz, 4.1 Hz, $^3J_{HF}$ = 8.5 Hz, H-2), 3.35 (dm, 1H, $^2J_{HH}$ = 18.1 Hz, H-6*ax*), 3.51÷3.56 (m, 5.5H, H-6*eq*+H-6*ax**), 3.64 (ddq, 4.5H, $^3J_{HH}$ = 10.1 Hz, 5.3 Hz, $^3J_{HF}$ = 8.4 Hz, H-2*), 3.83 (dd, 4.5H, $^2J_{HH}$ = 16.0 Hz, $^3J_{HH}$ = 5.9 Hz, H-6*eq**), 5.63-6.73 (m, 5.5H, H-5 + H-5*), 5.85–5.95 (m, 4.5H, H-4*), 6.02–6.09 (m, 1H, H-4). ^{13}C NMR (100 MHz, $CDCl_3$): 16.3 (q, $^3J_{CF}$ = 2.0 Hz, C-3), 23.6 (q, $^3J_{CF}$ = 3.0 Hz, C-3*), 47.2 (s, C-6), 49.4 (s, C-6*), 55.7 (q, $^2J_{CF}$ = 27 Hz, C-2), 60.8 (q, $^2J_{CF}$ = 26 Hz, C-2*), 115.6 (s, C-5), 118.0 (s, C-5*), 124.7 (q, $^1J_{CF}$ = 281 Hz, CF_3*), 124.9 (q, $^1J_{CF}$ = 280 Hz, CF_3), 126.5 (s, C-4), 126.9 (s, C-4*).^{19}F NMR (188 MHz, $CDCl_3$): –67.36 (d, 13.5F, $^3J_{HF}$ = 8.4 Hz, CF_3*), –69.37 (d, 3F, $^3J_{HF}$ = 8.5 Hz, CF_3). GC/MS, m/z (rel. int.): 184 (13) $[M]^+$, 164 (11) $[M\text{-}HF]^+$, 135 (18), 115 (100) $[M\text{-}CF_3]^+$, 95 (30), 69 (16) $[CF_3]^+$, 39 (49). Anal. calcd. for $C_6H_7F_3OS$: C, 39.13; H, 3.83; S, 17.41; found: C, 39.20; H, 3.88; S, 17.35.

*4.6.2. (1RS,2SR)-4,5-dimethyl-2-(trifluoromethyl)-3,6-dihydro-2H-thiopyran-1-oxide **6a** and (1RS,2RS)-4,5-dimethyl-2-(trifluoromethyl)-3,6-dihydro-2H-thiopyran-1-oxide **6b***

Light brown oil, yield 53%, R_f = 0.18 (CCl_4 – EtOAc, 5:2). Mixture of the diastereomers **6a** and **6b** in ratio 4:1. Data for isomer **6a**. ^{1}H NMR (400MHz, $CDCl_3$): 1.75 (s, 3H, CH_3), 1.78 (s, 3H, CH_3), 2.41 (dd, 1H, $^2J_{HH}$ = 17.8 Hz, $^3J_{HH}$ = 9.7 Hz, H-3*ax*), 2.72 (dd, 1H, $^2J_{HH}$ = 17.8 Hz, $^3J_{HH}$ = 5.6 Hz, H-3*eq*), 3.48 (ddq, 1H, $^3J_{HH}$ = 9.7 Hz, 5.6 Hz, $^3J_{HF}$ = 8.5 Hz, H-2), 3.55 (AB, 1H, $^2J_{HH}$ = 15.0 Hz, H-6$_A$), 3.59 (AB, 1H, $^2J_{HH}$ = 15.0 Hz, H-6$_B$). ^{13}C NMR ($CDCl_3$): 19.1 (s, CH_3), 19.7 (s, CH_3), 29.2 (q, $^3J_{CF}$ = 2 Hz, C-3), 54.6 (s, C-6), 63.1 (q, $^2J_{CF}$ = 26 Hz,C-2), 118.7 (s, C-5), 124.9 (q, $^1J_{CF}$ = 281 Hz, CF_3), 127.6, (s, C-4). ^{19}F NMR (282 MHz, $CDCl_3$): –67.69 (d, 3F, $^3J_{FH}$ = 8.5 Hz). GC/MS, m/z (rel. int.): 212 (100) $[M]^+$, 196 (6) $[M\text{-}O]^+$, 163 (96) $[M\text{-}H\text{-}SO]^+$, 143 (37) $[M\text{-}CF_3]^+$, 123 (57), 79 (52), 69 (28)$[CF_3]^+$, 39 (87). Data for isomer **6b**. ^{1}H NMR (400 MHz, $CDCl_3$): 1.76 (s, 3H, CH_3), 1.81, (s, 3H, CH_3), 2.33 (dd, 1H, $^2J_{HH}$ = 16.5 Hz, $^3J_{HH}$ = 3.5 Hz, H-3*eq*), 2.91 (dd, 1H, $^2J_{HH}$ = 16.5 Hz, $^3J_{HH}$ = 11.8 Hz, H-3*eq*), 3.12 (ddq, 1H, $^3J_{HH}$ = 11.8 Hz, 3.5 Hz, $^3J_{HF}$ = 7.9 Hz, H-2), 3.31÷3.34 (m, 2H, 2H-6). ^{13}C NMR (100 MHz, $CDCl_3$): 19.5 (s, CH_3), 19.8 (s, CH_3), 22.0 (q, $^3J_{CF}$ = 2.2 Hz, C-3), 52.3 (s, C-6), 56.1 (q, $^2J_{HH}$ = 27.5 Hz, C-2), 115.1 (s, C-5), 125.2 (q, $^1J_{CF}$ = 281 Hz, CF_3), 125.9 (s, C-4). ^{19}F NMR (282 MHz, $CDCl_3$): –69.15 (d, 2F, $^3J_{FH}$ = 7.9 Hz). GC/MS, m/z (rel. int.): 212 (100) $[M]^+$, 196 (6) $[M\text{-}O]^+$, 163 (87) $[M\text{-}H\text{-}SO]^+$, 143 (28) $[M\text{-}CF_3]^+$, 123 (43), 79 (44), 69 (20)$[CF_3]^+$, 39 (57). Anal. calcd. for $C_8H_{11}F_3OS$: C, 45.28; H, 5.22; S, 15.11; found: C, 45.12; H, 5.02; S, 14.93.

*4.6.3. (1RS,2RS,6RS)-6-acetoxy-2-(trifluoromethyl)-3,6- dihydro-2H-thiopyran-1-oxide **7a**, (1RS,2SR,6RS)-6-acetoxy-2-(trifluoromethyl)-3,6- dihydro-2H-thiopyran-1-oxide **7b** and (1RS,2SR,6RS)- 6-acetoxy-2-(trifluoromethyl)-3,6- dihydro-2H-thiopyran-1-oxide **7c**.*

Yellow oil, 52%, R_f = 0.18 (CCl_4 – ethyl acetate 5:2). Mixture of isomers **7a**, **7b**, **7c** in ratio 6.6:1.3:1. NMR data for isomer **7a**. ^{1}H NMR (400 MHz, $CDCl_3$): 2.25 (s, 3H, CH_3), 2.53 (AB, $^2J_{HH}$ = 19.4 Hz, $^3J_{HH}$ =11.9 Hz, 2.7 Hz, $^4J_{HH}$ = 2.5 Hz, H-3*ax*), 2.86 (AB, $^2J_{HH}$ = 19.4 Hz, $^3J_{HH}$ = 5.0 Hz, 5.1 Hz, $^4J_{HH}$ = 1.5 Hz, H-3*eq*), 3.94 (ddq, 1H, $^3J_{HH}$ = 11.9 Hz, $^3J_{HH}$ = 5.0 Hz, $^3J_{HF}$ = 8.3 Hz, H-2), 5.88 (dddd,1H, $^3J_{HH}$ = 6.2 Hz, 10.4 Hz, $^4J_{HH}$ = 2.5 Hz, 1.5 Hz, H-5), 6.13 (ddd, 1H, $^3J_{HH}$ = 10.4 Hz, 5.1 Hz, 2.7 Hz, H-4), 6.45 (d, 1H, $^3J_{HH}$ = 6.2 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$): 20.3 (s, CH_3), 24.5 (q, $^3J_{CF}$ = 3 Hz, 3-CH_2), 55.1 (q, $^2J_{CF}$ = 26.7 Hz, 2-CH), 75.2 (s, 6-CH), 119.9 (s,C-5), 124.8 (q, $^1J_{CF}$ = 280.6 Hz, CF_3) 132.5 (s, C-4), 169.1 (s, C=O). ^{19}F NMR(282 MHz, $CDCl_3$): –66.61 (d, 3F, $^3J_{HH}$ = 8.3 Hz, CF_3). Selected NMR data for isomer **7b**. ^{1}H NMR (400 MHz, $CDCl_3$): 3.99 (ddq, 1H, $^3J_{HH}$ = 9.8 Hz, 5.1 Hz, $^3J_{HF}$ = 8.4 Hz, H-2), 5.57 (dddd, 1H, $^3J_{HH}$ = 10.7 Hz, 2.5 Hz, $^4J_{HH}$ = 2.5 Hz, 2.5 Hz, H-5), 5.94 (ddd, $^3J_{HH}$ = 10.7 Hz, 5.1 Hz, $^4J_{HH}$ = 2.5 Hz, H-4) 6.49÷6.52 (m, 1H, H-6). ^{13}C NMR (100 MHz, $CDCl_3$): 20.1 (s, CH_3), 24.5 (q, $^3J_{CF}$ = 2 Hz, C-3), 60.2 (q, $^2J_{CF}$ = 27 Hz, C-2), 87.5 (s, C-6), 122.3 (s,C-5), 128.2 (s, C-4), 169.5 (s, C=O). ^{19}F NMR(282 MHz, $CDCl_3$): –66.85 (d,

3F, $^3J_{HH}$ = 8.4 Hz, CF_3). Selected NMR data for isomer **7c**. ^{1}H NMR (400 MHz, $CDCl_3$): 3.54 (ddq, 1H, $^3J_{HH}$ = 8.5 Hz, 4.1 Hz, $^3J_{HF}$ = 8.5 Hz, H-2), 5.50 (dddd, 1H, $^3J_{HH}$ = 11.0 Hz, 2.6 Hz, $^4J_{HH}$ = 1.7 Hz, 1.7 Hz, H-5). ^{13}C NMR (100 MHz, $CDCl_3$): 56.7 (q, $^2J_{CF}$ = 28 Hz, C-2), 82.3 (s, C-6), 118.9 (s, C-5), 129.3 (s, C-4), 169.6 (s, C=O). ^{19}F NMR (282 MHz, $CDCl_3$): –69.19 (d, 3F, $^3J_{HH}$ = 8.5 Hz, CF_3). GC/MS, m/z (rel. int.): 182 (7) $[M\text{-}AcOH]^+$, 166 (3) $[M\text{-}AcOH\text{-}O]^+$, 69 (7) $[CF_3]^+$, 43 (100) $[CH_3CO]^+$. Anal. calcd. for $C_8H_9F_3O_3S$: C, 39.67; H, 3.75; S, 13.24; found: C, 39.23; H, 3.56; S, 13.08.

4.6.4. (1RS,2SR)-4,5-dimethyl-2-(1,1,2,2-tetrafluoroethyl)-3,6-dihydro-2H-thiopyran-1-oxide ***8a*** *and (1RS,2RS)-4,5-dimethyl-2-(1,1,2,2-tetrafluoroethyl)-3,6-dihydro-2H-thiopyran-1-oxide* ***8b****.*

Brownish semisolid, yield 55%, R_f = 0.27 (hexane – EtOAc, 5:1). Mixture of the isomers **8a** and **8b** in ratio 6:1. By the crystallization from hexane – CH_2Cl_2 major isomer **8a** was obtained in 23% yield as colorless crystals, m.p. 104-105°C. NMR data for isomer **8a**. ^{1}H NMR (400 MHz, $CDCl_3$): 1.72 (s, 3H, CH_3),. 1.76 (s, 3H, CH_3), 2.52 (dd, 1H, $^2J_{HH}$ = 18.0 Hz, $^3J_{HH}$ = 11.5 Hz, H-3*ax*), 2.66 (dd, 1H, $^2J_{HH}$ = 18.0 Hz, $^3J_{HH}$ = 4.0 Hz, H-3*eq*), 3.48÷3.63 (m, 2H, H-2 + H-6$_A$), 3.67 (d, 1H, H-6$_B$), 6.33 (ddd, 1H, $^2J_{HF}$ = 54.4 Hz, 51.4 Hz, $^3J_{HF}$ = 12.5 Hz, HCF_2). ^{13}C NMR (100 MHz, $CDCl_3$): 19.2 (s, CH_3), 19.8 (s, CH_3), 28.7 (d, $^3J_{CF}$ = 6 Hz, C-3), 55.5 (s, C-6), 60.8 (t, $^2J_{CF}$ = 20.5 Hz, C-2), 106.0÷120.0 (m, HCF_2CF_2), 118.2 (s, C-5), 127.6 (s, C-4). ^{19}F NMR (282 MHz, $CDCl_3$): –124.14 (AB, $^2J_{FF}$ = 273.6 Hz, $^3J_{FH}$ = 2.8 Hz, 12.5 Hz, $^3J_{FF}$ = 12.0 Hz, 10.5 Hz, F$_B$ from $\underline{CF_2}CH_2H$), –125.62 (AB, $^2J_{FF}$ = 273.6 Hz, $^3J_{FH}$ = 23.8 Hz, $^3J_{FF}$ = 10.5 Hz, 12.5 Hz, F$_B$ from $\underline{CF_2}CH_2H$), –136.66 (AB, $^2J_{FH}$ = 54.7 Hz, $^2J_{FF}$ = 297.4 Hz, $^3J_{FF}$ = 10.5 Hz, $^3J_{FF}$ = 10.5 Hz, F$_B$ from HCF_2), –142.90 (AB, $^2J_{FH}$ = 51.6 Hz, $^2J_{FF}$ = 297.4 Hz, $^3J_{FF}$ = 12.0 Hz, $^3J_{FF}$ = 3.9 Hz, F$_A$ from HCF_2). GC/MS, m/z (rel. int.): 244 (40) $[M]^+$, 228 (39) $[M\text{-}O]^+$, 195 (100) $[M\text{-}SO\text{-}H]^+$, 143 (7) $[M\text{-}HCF_2CF_2]^+$, 125 (48), 101 (11) $[HCF_2CF_2]^+$, 51 (30) $[HCF_2]^+$. Data for isomer **8b**. ^{1}H NMR (400 MHz, $CDCl_3$): 1.76 (s, 3H, CH_3), 1.81 (s, 3H, CH_3), 2.33 (dd, 1H, $^2J_{HH}$ = 18.0 Hz, $^3J_{HH}$ = 4.0 Hz, H-3*eq*), 2.94 (dd, 1H, $^2J_{HH}$ = 18.0 Hz, $^3J_{HH}$ = 12.0 Hz, H-3*ax*), 3.11 (dddd, 1H, $^3J_{HH}$ = 12.0 Hz, 4.0 Hz, $^3J_{HF}$ = 13.9 Hz, 12.7 Hz, H-2), 3.31÷3.34 (m, 2H, 2H-6), 6.02 (tdd, 1H, $^2J_{HF}$ = 53.4 Hz, $^3J_{HF}$ = 4.5 Hz, 3.5 Hz, HCF_2). ^{13}C NMR (100 MHz, $CDCl_3$): 19.6 (s, CH_3), 20.0 (s, CH_3), 21.8 (d, $^3J_{CF}$ = 4.0 Hz, C-3), 52.2 (s, C-6), 54.7 (t, $^2J_{CF}$ = 20 Hz, C-2), 106.0÷120.0 (m, HCF_2CF_2), 115.1 (s, C-5), 126.6 (s, C-4). ^{19}F NMR (282 MHz, $CDCl_3$): –117.20÷–117.53 (m, 2F, CF_2), –135.20÷–135.94 (m, 2F, HCF_2). GC/MS, m/z (rel. int.):244 (33) $[M]^+$, 228 (29) $[M\text{-}O]^+$, 195 (51) $[M\text{-}SO\text{-}H]^+$, 143 (7) $[M\text{-}HCF_2CF_2]^+$, 125 (100), 101 (12) $[HCF_2CF_2]^+$, 51 (26) $[HCF_2]^+$. Anal. calcd. for $C_9H_{12}F_4OS$ (mixture): C, 44.26; H, 4.95; S, 13.13; found: C, 44.30; H, 4.68; S, 13.01.

4.6.5. (1RS,2RS,6RS)-6-acetoxy-2-(1,1,2,2-tetrafluoroethyl)-3,6- dihydro-2H-thiopyran-1-oxide ***9a*** *and (2RS,6SR)-6-acetoxy-2-(1,1,2,2-tetrafluoroethyl)-3,6- dihydro-2H-thiopyran-1-oxide* ***9b****.*

Yellow oil, yield 49%, R_f = 0.28 (CCl_4 –EtOAc 5:1). Mixture of the isomers **9a** and **9b** in ratio 7.5:1. NMR data for isomer **9a**. ^{1}H NMR (400 MHz, $CDCl_3$): 2.23 (s, 3H, CH_3), 2.59 ($^2J_{HH}$ = 19.3 Hz, $^3J_{HH}$ = 12.2 Hz, 2.4 Hz, H-3*ax*), 2.84 (ddd, 1H, $^2J_{HH}$ = 19.3 Hz, $^3J_{HH}$ = 5.3 Hz, 4.3 Hz, H-3*eq*), 4.00 (ddddd, 1H, $^3J_{HH}$ = 12.2 Hz, 4.3 Hz, $^3J_{HF}$ = 26.5 Hz, $^4J_{HF}$ = 2.5 Hz, $^5J_{HH}$ = 2.0 Hz, H-2), 5.87 (ddd, 1H, $^3J_{HH}$ = 10.5 Hz, $^3J_{HH}$ = 6.5 Hz, $^5J_{HH}$ = 2.0 Hz, H-5), 6.17 (ddd, 1H, $^3J_{HH}$ = 10.5 Hz, 5.3 Hz, 2.4 Hz, H-4), 6.29 (ddd, 1H, $^2J_{HF}$ = 54.6 Hz, $^2J_{HF}$ = 51.2 Hz, $^3J_{HF}$ = 13.8 Hz, HCF_2), 6.49 (dd, 1H, $^3J_{HH}$ = 6.5 Hz, $^5J_{HF}$ = 2.8 Hz, H-6). ^{13}C NMR (100 MHz, $CDCl_3$): 20.4 (s, CH_3), 23.4 (d, $^3J_{CF}$ = 8.1 Hz, C-3), 53.1 (td, $^2J_{CF}$ = 22 Hz, $^3J_{CF}$ = 2 Hz, C-2), 75.1 (s, C-6), 109.8 (dddd, $^1J_{CF}$ = 255 Hz, 247 Hz, $^2J_{CF}$ = 39 Hz, 24 Hz, HCF_2), 113.2÷118.8 (m, $\underline{CF_2}CF_2H$) 119.7 (s, C-5), 133.9 (s, C-5), 169.1 (s, C=O). ^{19}F NMR (282 MHz, $CDCl_3$): –122.75 (AB, 1F, $^2J_{FF}$ = 273.4 Hz, $^3J_{FF}$ = 15.0 Hz, 9.2 Hz, $^3J_{FH}$ = 13.8 Hz, $^5J_{FH}$ = 2.8 Hz, F$_B$ from $\underline{CF_2}CF_2H$), –125.75 (AB, 1F, J_{FF} = 273.4 Hz, $^3J_{FF}$ = 6.8 Hz, 12.1 Hz, $^3J_{FH}$ = 26.5 Hz, F$_A$ from $\underline{CF_2}CF_2H$), –136.92 (AB, 1F, $^2J_{FF}$ = 299.0 Hz, $^3J_{FF}$ = 9.2 Hz, 12.1 Hz, $^2J_{FH}$ = 54.6 Hz, F$_B$ from HCF_2), –143.40 (AB, 1F, $^2J_{FF}$ = 299.0 Hz, $^3J_{FF}$ = 6.8 Hz, 15.0, $^2J_{FH}$ = 51.2 Hz, $^4J_{FH}$ = 2.5 Hz, F$_A$ from HCF_2). Selected NMR data for isomer **9b**. ^{1}H NMR (400

MHz, $CDCl_3$): 2.24 (s, 3H, CH_3), 2.66÷2.74 (m, 1H, H-3), 5.49 (dddd, 1H, $^3J_{HH}$ = 10.7 Hz, 2.2 Hz, $^4J_{HH}$ = 1.9 Hz, 1.9 Hz, H-5), 6.33 (ddd, 1H, $^2J_{HF}$ = 54.4 Hz, 51.3 Hz, $^3J_{HF}$ = 12.5 Hz, HCF_2), 6.55÷6.58 (m, 1H, H-6). ^{19}F NMR ($CDCl_3$): –124.11÷–124.80 (m, 2F, $\underline{CF_2}CF_2H$). ^{13}C NMR ($CDCl_3$): 20.8 (s, CH_3), 23.7 (d, $^3J_{CF}$ = 8 Hz, C-3), 58.4 (t, $^2J_{CF}$ = 22 Hz, C-2), 89.1 (s, C-6), 107.9÷119.1 (m, HCF_2CF_2), 122.4 (s, C-5), 128.7 (s, C-4), 169.6 (s, C=O). GC/MS, m/z (rel. int.): 274 (1) $[M]^+$, 232 (4) $[M\text{-}C_2H_2O]^+$, 214 (9) $[M\text{-AcOH}]^+$, 183 (17), 115 (12), 97 (11), 43 (100) $[AcO]^+$. Anal. calcd. for $C_9H_{10}F_4O_3S$: C, 39.42; H, 3.68; S, 11.69; found: C, 39.18; H, 3.62; S, 11.42.

4.6.6. (1RS,2SR)-4,5-dimethyl-2-(1,1,2,2,3,3,4,4-octafluorobutyl)-3,6-dihydro-2H-thiopyran 1-oxide ***10a*** *and (1RS,2RS)-4,5-dimethyl-2-(1,1,2,2,3,3,4,4-octafluorobutyl)-3,6-dihydro-2H-thiopyran 1-oxide* ***10b****.*

Brown oil, yield 55%, R_f = 0.48 (hexane–EtOAc, 1:1). Mixture of isomers **10a** and **10b** in ratio 3.5:1. ^{1}H NMR (400 MHz, $CDCl_3$): 1.77 (s, 3H, CH_3), 1.78÷1.84 (m, 24H, CH_3 of both isomers), 2.36 (dd, 1H, $^2J_{HH}$ = 19.0 Hz, $^3J_{HH}$ = 4.0 Hz, H-3*eq*), 2.39 (dd, 3.5 H, $^2J_{HH}$ = 17.3 Hz, $^3J_{HH}$ = 8.4 Hz, H-3*ax**), 2.79 (dd, 3.5H, $^2J_{HH}$ = 17.3 Hz, $^3J_{HH}$ = 5.3 Hz, H-3*eq**), 2.98 (dd, 1H, $^2J_{HH}$ = 19.0 Hz, $^3J_{HH}$ = 12.8 Hz, H-3*ax*), 3.20 (dddd, $^3J_{HH}$ = 12.8 Hz, 4.0 Hz, $^3J_{HF}$ = 15.6 Hz, 13.3 Hz, H-2), 3.30÷3.36 (m, 2H, 2H-6), 3.43÷3.58 (m, 10.5H, 2H-6* + H-2*), 6.08 (tt, 13.5H, $^2J_{HF}$ = 52.1Hz, $^3J_{HF}$ = 5.5 Hz, HCF_2 of both isomers). ^{13}C NMR (100 MHz, $CDCl_3$): 19.3 (s, CH_3*), 19.5 (s, CH_3), 19.9 (s, CH_3*), 20.0 (s, CH_3), 21.9 (s, C-3), 27.5 (s, C-3*), 52.6 (s, C-6), 53.6 (s, C-6*), 54.9 (t, $^2J_{CF}$ = 21 Hz, C-2), 62.3 (t, $^2J_{CF}$ = 20 Hz, C-2*), 107.7 (tt, $^1J_{CF}$ = 253 Hz, $^2J_{CF}$ = 32 Hz, HCF_2*), 104÷121 (m, HCF_2 and $HCF_2(\underline{CF_2})_3$ of both isomers), 115.0 (s, C-5), 118.93 (s, C-5*), 126.4 (s, C-4), 127.7 (s, C-4*).^{19}F NMR (282 MHz, $CDCl_3$): –110.29 (AB, 3.5F, J = 285.1 Hz, F_B from $\underline{CF_2}(CF_2)_3H$*), –113.73 (AB, 1F, J = 289.2 Hz, F_B from $\underline{CF_2}(CF_2)_3H$), –114.87 (AB, 3.5F, J = 285.1 Hz, F_A from $\underline{CF_2}(CF_2)_3H$*), –115.68 (AB, 1F, J = 289.2 Hz, F_A from $\underline{CF_2}(CF_2)_3H$), –122.97 (AB, 3.5F, J = 296.7 Hz, F_B from $CF_2\underline{CF_2}(CF_2)_2H$*), –123.93 (AB, 3.5F, J = 296.7 Hz, F_A from $CF_2\underline{CF_2}(CF_2)_2H$*), –123.92÷–124.17 (m, 2F, $CF_2\underline{CF_2}(CF_2)_2H$), –130.45÷–131.07 (m, 9F, $(CF_2)_2\underline{CF_2}CF_2H$ of both isomers), –136.92÷–139.49 (m, 9F, HCF_2 of both isomers). GC/MS for **10a**, m/z (rel. int.):.344 (42) $[M]^+$, 295 (100) $[M\text{-SO-H}]^+$, 125 (42), 101 (13) $[HCF_2CF_2]^+$, 51 (52) $[HCF_2]^+$. GC/MS for **10b**, m/z (rel. int.):. 344 (100) $[M]^+$, 295 (30) $[M\text{-SO-H}]^+$, 145 (88) $[M\text{-}HCF_2(CF_2)_2\text{-SO}]^+$, 125 (57), 51 (41) $[HCF_2]^+$. Anal. calcd. for $C_{11}H_{12}F_8OS$: C, 38.38; H, 3.51; S, 9.31; found: C, 38.13; H, 3.14; S, 9.18.

4.7. X-Ray structure determination for compound ***8a****.*

Crystals, suitable for the X-Ray analysis, were obtained by the crystallization of compound **8a** from hexane – CH_2Cl_2. Crystal data: $C_9H_{12}F_4OS$, M 244.25, monoclinic, space group $P2_1/c$, a = 9.790(3), b = 15.830(5), c = 7.100(2)Å, β = 102.597(7), V = 1073.8(5)Å^3, Z = 4, d_c = 1.511 g·cm^{-3}, μ = 0.328 mm^{-1}, F(000) = 504, crystal size ca. 0.13 × 0.24 × 0.41 mm. All crystallographic measurements were performed at room temperature on a Bruker Smart Apex II diffractometer operating in the ω and φ scans mode. The intensity data were collected within the range of $2.13 \le \theta \le 26.46°$ using Mo-K_α radiation (λ = 0.71078 Å). The intensities of 10561 reflections were collected (2212 unique reflections, R_{merg} = 0.0683). The structure was solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms using the Bruker SHELXTL program package [29]. All hydrogen atoms were refined as 'riding' model. In the refinement 2212 independent reflections were used. Convergence was obtained at R1 = 0.0691 and wR2 = 0.1165 for all reflection and R1 = 0.0434 and wR2 = 0.1019, GOF = 1.031 for 1568 observed reflections with $I \ge 2\sigma(I)$, 138 parameters; the largest and minimal peaks in the final difference map 0.26 and –0.27 e/Å^3, weighting scheme is as follows: $\omega = 1/[\sigma^2(Fo^2) + (0.0499P)^2+0.3289P]$, where $P = (Fo^2 + 2Fc^2)/3$), Full crystallographic details have been deposited at Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for these materials should quote the full literature citation and reference number CCDC 1483266.

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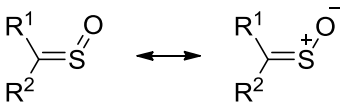


R^1, R^2 = Alk, Ar, H, Hal, SAlk, SAr, $NAlk_2$

Fig. 1. General structure of sulfines.

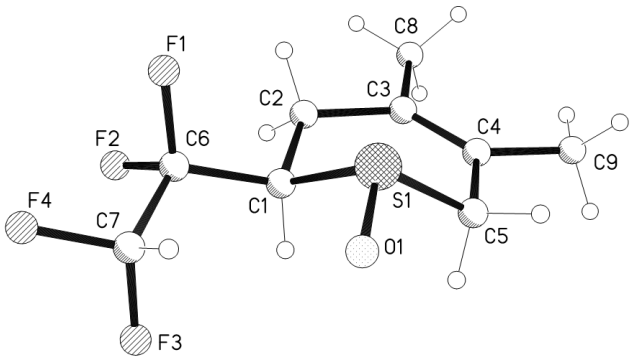
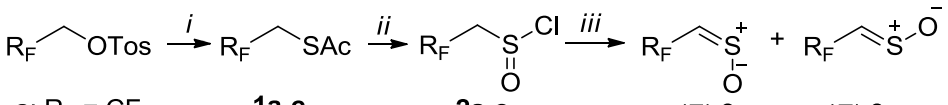
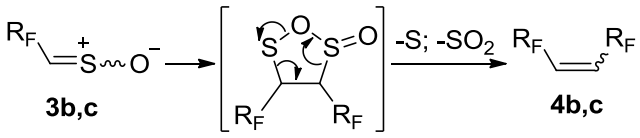


Fig. 2. General view of the molecule of sulfoxide **8a** in the solid state.



a: $R_F = CF_3$ **1a-c** **2a-c** *(Z)*-**3a-c** *(E)*-**3a-c**
b: $R_F = H(CF_2)_2$
c: $R_F = H(CF_2)_4$

Scheme 1. Reagents and conditions: (*i*)AcSK, DMSO, 45°C; (*ii*) Cl_2, AcOH, rt; (*iii*) Et_3N, $CDCl_3$, –10°C to rt.



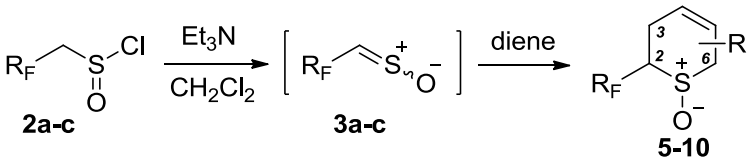
a: $R_F = H(CF_2)_2$;
b: $R_F = H(CF_2)_4$

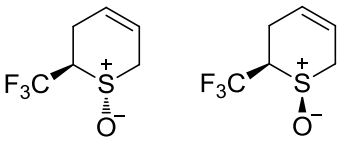
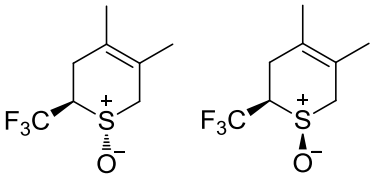
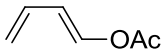
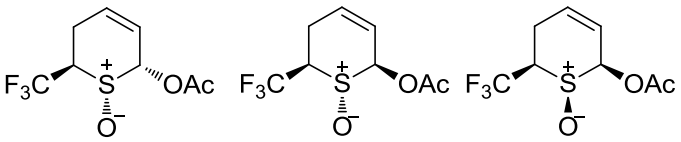
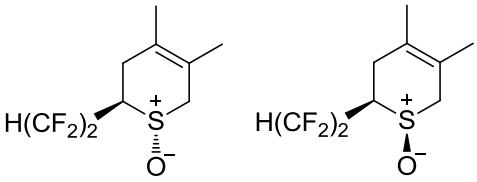
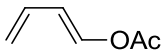
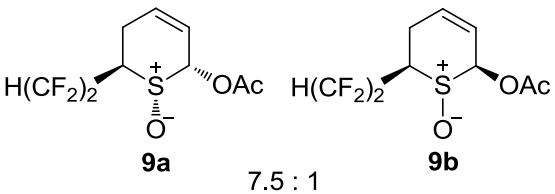
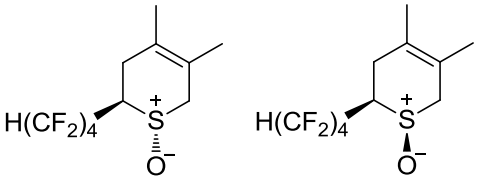
Scheme 2. Decomposition of polyfluoroalkylsulfines **3b,c**.

Table 1
NMR parameters of the sulfines **3a-c**[a]

Entry	Sulfine	$\delta_{HC=S=O}$, ppm ($^3J_{HF}$, Hz)		δ_F, ppm		Ratio (*E*)/(*Z*)[d]
		(*E*)	(*Z*)	(*E*)	(*Z*)	
1	**3a**	8.58 (8.2)	8.44 (7.7)	–60.26[b]	–59.01[b]	1 : 1.1
2	**3b**	8.57 (14.2)	8.27 (11.3)	–111.10[c]	–110.52[c]	1.1 : 1
3	**3c**	8.55 (14.3)	8.26 (13.7)	–114.13[c]	–111.94[c]	1.3 : 1

Table 2
Preparation of 2-(polyfluoroalkyl)-3,6-dihydro-2*H*-thiopyran-1-oxides by the dehydrochlorination of sulfinyl chlorides **3a-c** in the presence of diene.



Entry	Sulfinyl chloride	Diene	Products and their ratios[a]	Yield, %[b]
1	**2a**		 **5a** : **5b** = 4.5 : 1	50
2	**2a**		 **6a** : **6b** = 4 : 1	53
3	**2a**		 **7a** : **7b** : **7c** = 6.6 : 1.3 : 1	52
4	**2b**		 **8a** : **8b** = 6 : 1	55
5	**2b**		 **9a** : **9b** = 7.5 : 1	49
6	**2c**		 **10a** : **10b** = 3.5 : 1	55

[a] Established by the integration of ^{1}H NMR signals.
[b] Isolated yield of the mixtures.