

Study of the nucleophilic reaction of 2-mercaptoethanol with 1-fluoroalkyl-2-iodo-alkenes

Hui-Ping Guan, Bing-Hao Luo, Chang-Ming Hu *

354 Fenglin Road, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, People's Republic of China

Received 18 December 1996; accepted 27 May 1997

Abstract

The stepwise nucleophilic addition of 2-mercaptoethanol (**2**) to 1-fluoroalkyl-2-iodo-alkenes (**1**) was studied. Fluorine-containing building blocks of a new type (**4**) containing a fluorine atom, a fluoroalkyl-substituted double bond and a latent carbonyl group were synthesized in good yield via the intermediate thioethers **3**. A reasonable pathway is suggested. © 1997 Elsevier Science S.A.

Keywords: 1-Fluoroalkyl-2-iodo-alkenes; 2-Mercaptoethanol; Nucleophilic reaction

1. Introduction

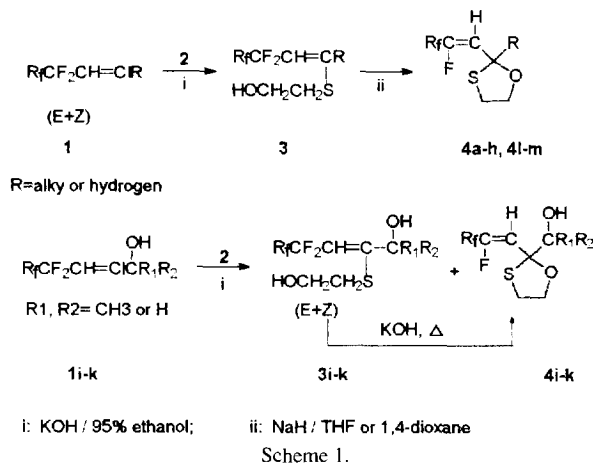
The chemistry of fluoro-olefins is one of the most extensively studied topics in organofluorine chemistry. 3,3,3-Tri-fluoropropylene has received considerable attention in recent years and several useful reactions have been reported [1]. Feiring et al. [2] studied the reaction of monofluoroalkyl-substituted alkenes with a series of nucleophiles and complicated results with modest target product yields were obtained. The low yield was attributed to the low reactivity of such compounds towards nucleophiles and the unfavourability of the intermolecular reaction.

With regard to fluoroalkyl-substituted alkenyl halides, elimination [3], electrophilic addition [2,4] and reactions via metal reagents [5] have been studied. 1-Fluoroalkyl-2-iodo-alkenes, formed from the direct addition of fluoroalkyl iodides to alkynes, are versatile fluorine-containing building blocks. Their dehydro-iodination to give fluoroalkyl alkynes [6] and cyclocondensation with hydrazine or hydroxylamine to give fluoroalkylated heterocyclic compounds [7] have been described.

In this paper, the stepwise reaction of 1-fluoroalkyl-2-iodo-alkenes (**1**) with 2-mercaptoethanol (**2**) is reported in detail.

2. Results and discussion

In the presence of potassium hydroxide, the nucleophilic reaction of 2-mercaptoethanol (**2**) with 1-fluoroalkyl-2-iodo-



alkenes (**1**) furnished a new type of alkene **3** in which the iodine atom was replaced by the group HOCH₂CH₂S. Such a reaction occurred smoothly in 95% aqueous ethanol at room temperature to give compound **3** in good yield (Scheme 1).

The product **3** was a mixture of *E* and *Z* isomers. The ratio did not depend on the proportion of *E* and *Z* isomers in the starting material **1**. The fluoroalkyl and alkyl groups had little effect on the reaction. However, compounds **1f** and **1i–1k**, which contained a free hydroxyl in the alkyl group, could accelerate the reaction. Such a reaction proceeded slowly when sodium carbonate or triethylamine was used as the base. A suitable temperature was about 50 °C. Dithiols or diols instead of reagent **2** gave complicated products. Results for the synthesis of compound **3** are listed in Table 1.

* Corresponding author. Fax: +86 21 64166128.

Table 1
Synthesis of compounds **3**^a and **4**^b from compound **1**

Entry	Substrate	R _f	R	E : Z ^c in 1	Time (h) for 3	Product 3 ^d	E : Z ^c in 3	Yield (%) ^e of 3	Product 4 ^f	Yield (%) ^g of 4
1	1a	CF ₃	Ph	10 : 1	10	3a	5 : 1	82	4a	65
2	1b	ClCF ₂	Ph	10 : 1	10	3b	6 : 1	85	4b	64
3	1c	CF ₃	C ₅ H ₁₁	8 : 1	8	3c [*]	6 : 1	87	4c	68
4	1d	CF ₃	CH ₂ OTHP	2 : 1	8	3d [*]	8 : 1	85	4d	66
5	1e	ClCF ₂	CH ₂ OTHP	2.5 : 1	8	3e [*]	7 : 1	84	4e	65
6	1f	CF ₃	CH ₂ OH	1.5 : 1	8	3f	5 : 1	45		
7	1g	F(CF ₂) ₃	Ph	7 : 1	10	3g [*]	7 : 1	80	4g	70
8	1h	Cl(CF ₂) ₃	Ph	8 : 1	10	3h	4 : 1	88	4h	68
9	1h	Cl(CF ₂) ₃	Ph	8 : 1	36	3h ^h	4 : 1	38	4h	68
10	1h	Cl(CF ₂) ₃	Ph	8 : 1	36	3h ⁱ	5 : 1	26	4h	68
11	1i	Cl(CF ₂) ₃	CH ₂ OH	2 : 1	6	3i	8 : 1	50	4i ^j	72
12	1j	Cl(CF ₂) ₃	CH(CH ₃)OH	1.5 : 1	8	3j [*]	9 : 1	48	4j ^j	70
13	1k	Cl(CF ₂) ₃	C(CH ₃) ₂ OH	1.2 : 1	8	3k [*]	6 : 1	43	4k ^j	66
14	1l	Br(CF ₂) ₃	H		8	3l [*]		75	4l	71
15	1m	Br(CF ₂) ₅	H		8	3m [*]		80	4m	68

^a Unless otherwise indicated, the base used in this reaction was KOH in 95% aqueous ethanol.

^b A two-step procedure was used unless otherwise indicated.

^c Ratio based on TLC and ¹H NMR.

^d The compounds with an asterisk were used without purification.

^e Overall isolated yields of E and Z isomers based on **1**.

^f All new products were characterized by ¹H NMR, ¹⁹F NMR, IR, MS and elemental analysis.

^g Overall isolated yield based on **1**.

^h Na₂CO₃ (3 eq.) in 95% aqueous ethanol was used.

ⁱ Et₃N (3 eq.) in acetonitrile was used.

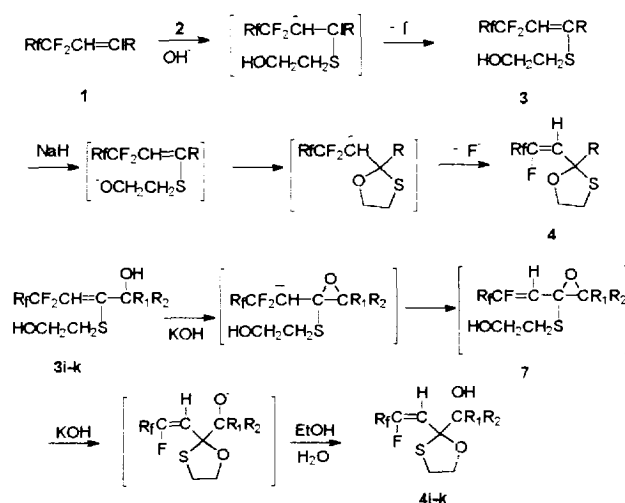
^j The one-pot reaction proceeded in KOH (3 eq.)–ethanol (95%) first at room temperature and then at 60 °C.

Further intramolecular nucleophilic reaction between the hydroxyl group and the fluoroalkylated double bond in compound **3** seemed to be possible. However, a base such as KOH could not facilitate such a reaction even at high temperature or prolonged reaction times. Such an addition–elimination reaction proceeded smoothly only when sodium hydride was used. In this case, compound **4** was formed in high yield.

The treatment of compound **3a** with sodium hydride in anhydrous tetrahydrofuran or 1,4-dioxane for about 6 h furnished compound **4a** as a colourless liquid in 80% yield. The ¹H nuclear magnetic resonance (NMR) spectrum revealed an olefinic hydrogen at the trans position to the fluorine atom on the double bond ($\delta = 6.06$ (1H, d, $J = 31$ Hz) ppm) [8], and the ¹⁹F NMR spectrum showed one olefinic fluorine (52.3 (1F, br) ppm) and a trifluoromethyl group (-5.0 (3F, s) ppm). The mass spectrum (MS) revealed 278 (35.61%) as the molecular ion peak. All spectral data indicated the formation of 2-phenyl-2-(2,3,3,3-tetrafluoro-1-propenyl)-1,3-oxathiolane (**4a**).

The reaction of **2** with compound **1** containing various fluoroalkyl and alkyl groups to produce compounds **3** and **4** is summarized in Table 1.

On the basis of the above results, a base-induced, multistep, nucleophilic addition–elimination process is suggested as a reasonable pathway (Scheme 2). For substrates **1i–1k**, the neighbouring group participation of the allylic hydroxyl may facilitate the nucleophilic addition of the other hydroxyl group to the double bond via the intermediate **7**, leading to the formation of product **4**.



In summary, the two-step, nucleophilic addition–elimination reaction of 2-mercaptoethanol **2** with 1-fluoroalkyl-2-iodoalkenes **1** has been studied, and a new type of fluorine-containing electrophilic compound **4** has been obtained in good yield. With the latent carbonyl group and the double bond, such compounds may be useful as fluorine-containing building blocks in organic synthesis.

3. Experimental details

All melting and boiling points are uncorrected. IR spectra were recorded pure as films for liquid and as KCl plates for

solid samples on a Shimadzu IR-440 spectrometer. The ^1H NMR spectra were measured with CDCl_3 as the solvent and tetramethylsilane (TMS) as internal standard on an FX-90Q spectrometer. The ^{19}F NMR spectra were measured with external CF_3COOH as standard and with upfield shifts positive using a Varian EM-360L spectrometer at 56.4 MHz. Mass spectra were recorded using an HP5989A mass spectrometer. Solvents and reactants were of reagent grade and were used without further purification. Light petroleum refers to the fraction boiling in the range 60–90 °C.

3.1. General method for the preparation of compound 3 from compound 1

A well-stirred mixture of compound **1** (10 mmol) and 2-mercaptoethanol **2** (12 mmol) in 95% aqueous ethanol (15 ml) was cooled in an ice–water bath; a solution of KOH (30 mmol in 4 ml of 95% ethanol) was added dropwise. The resultant mixture was stirred at room temperature for 8–10 h (monitored by thin layer chromatography (TLC)). The mixture was neutralized with saturated aqueous NH_4Cl , diluted with water and extracted with diethyl ether (3×30 ml). The combined extracts were dried (Na_2SO_4) and distilled to remove the solvent. The residue was purified by flash chromatography on silica gel and eluted with light petroleum–EtOAc (10 : 1–5 : 1, by volume) to give pure compound **3** in high yield. For compounds **3i–3k**, ethyl acetate was used to extract the organic compound and light petroleum–EtOAc (5 : 1–2 : 1, by volume) was used as eluent.

3.1.1. Hydroxyethyl-3,3,4,4,4-pentafluoro-1-phenyl-1-butenyl sulphide **3a**

^1H NMR δ (*E* isomer): 7.50 (5H, s), 5.90 (1H, t, $J=13$ Hz), 3.52 (2H, t, $J=6$ Hz), 2.60 (2H, t, $J=6$ Hz), 2.50 (1H, s) ppm; (*Z* isomer): 7.50 (5H, s, Ar-H), 5.90 (1H, t, $J=13$ Hz), 3.75 (2H, t, $J=6$ Hz), 2.80 (2H, t, $J=6$ Hz), 2.50 (1H, s) ppm. ^{19}F NMR δ (*E* isomer): 8.0 (3F, s), 31.6 (2F, m) ppm; (*Z* isomer): 8.0 (3F, s), 29.0 (2F, m) ppm. MS (*m/e*): 298 (M^+ , 53.45), 281 ($\text{M}^+ - \text{OH}$, 1.0), 253 ($\text{M}^+ - \text{HOCH}_2\text{CH}_2$, 34.34), 233 (253 – HF, 6.71), 183 (38.35), 135 (100).

3.1.2. Hydroxyethyl-4-chloro-3,3,4,4-tetrafluoro-1-phenyl-1-butenyl sulphide **3b** (*E* isomer)

IR ν_{max} (cm^{-1}): 3400, 1600, 1220, 1150, 1380. ^1H NMR δ : 7.63 (5H, s), 5.95 (1H, t, $J=12$ Hz), 3.9 (2H, t, $J=6$ Hz), 2.90 (2H, t, $J=6$ Hz), 2.50 (1H, s) ppm. ^{19}F NMR δ : –6.6 (2F, s), 25.0 (2F, s) ppm. MS (*m/e*): 314 (M^+ , 15.83), 297 ($\text{M}^+ - \text{OH}$, 12.99), 283 ($\text{M}^+ - \text{HOCH}_2$, 6.67), 270 ($\text{M}^+ - \text{OCH}_2\text{CH}_2$, 100), 237 ($\text{M}^+ - \text{Ph}$, 6.71), 185 (49.21), 151 (47.98), 121 (63.15).

3.1.3. Hydroxyethyl-4,4,5,5,5-pentafluoro-1-hydroxy-2-pentenyl sulphide **3f** (*E* isomer)

^1H NMR δ : 5.90 (1H, t, $J=15$ Hz), 4.40 (2H, s), 3.83 (2H, t, $J=6$ Hz), 3.30 (2H, s), 3.05 (2H, t, $J=6$ Hz) ppm.

^{19}F NMR δ : 7.3 (3F, s), 31.8 (2F, s) ppm. MS (*m/e*): 252 (M^+ , 16.72), 235 ($\text{M}^+ - \text{OH}$, 87.43), 222 ($\text{M}^+ - \text{CH}_2\text{O}$, 15.01), 206 ($\text{M}^+ - \text{CH}_2\text{CH}_2\text{OH}$, 75.48), 191 (97.31), 179 (80.66), 45 ($\text{CH}_2\text{CH}_2\text{OH}$, 100).

3.1.4. Hydroxyethyl-6-chloro-3,3,4,4,5,5,6,6-octafluoro-1-phenyl-1-hexenyl sulphide **3h**

IR ν_{max} (cm^{-1}): 3010, 2950, 1700, 1600, 1500, 1450, 1200, 1140. ^1H NMR δ (*E* isomer): 7.50 (5H, s), 5.86 (1H, t, $J=13.5$ Hz), 3.6 (2H, t, $J=6$ Hz), 2.64 (2H, t, $J=6$ Hz), 2.10 (1H, s) ppm; (*Z* isomer): 7.50 (5H, s), 5.86 (1H, t, $J=13.5$ Hz), 3.80 (2H, t, $J=6$ Hz), 2.86 (2H, t, $J=6$ Hz), 2.10 (1H, s) ppm. ^{19}F NMR δ (*E* isomer): –10.0 (2F, s, ClCF_2), 27.0 (2F, m), 41.7 (2F, s), 44.5 (2F, s) ppm; (*Z* isomer): –10.0 (2F, s, ClCF_2), 24.4 (2F, m), 41.7 (2F, s), 44.5 (2F, s) ppm. MS (*m/e*): 414 (M^+ , 8.05), 416 (3.25), 370 ($\text{M}^+ - \text{OCH}_2\text{CH}_2$, 14.99), 372 (5.44), 337 ($\text{M}^+ - \text{HOCH}_2\text{CH}_2\text{S}$, 6.18), 319 (4.02), 165 (43.04), 105 (60.24), 60 (100). HR MS: calculated for $\text{C}_{14}\text{H}_{11}\text{F}_8\text{OS}^{35}\text{Cl}$: 414.0092; found: 414.0078.

3.1.5. Hydroxyethyl-7-chloro-4,4,5,5,6,6,7,7-octafluoro-1-hydroxyl-2-heptenyl sulphide **3i** (*E* isomer)

^1H NMR δ : 6.0 (1H, t, $J=14$ Hz), 4.42 (2H, s), 3.87 (2H, t, $J=6$ Hz), 3.31 (2H, s), 3.0 (2H, t, $J=6$ Hz) ppm. ^{19}F NMR δ : –10.0 (2F, s, ClCF_2), 24.0 (2F, m), 42.0 (2F, s), 45.0 (2F, s) ppm. MS (*m/e*): 368 (M^+ , 5.10), 351 ($\text{M}^+ - \text{OH}$, 42.78), 333 ($\text{M}^+ - \text{Cl}$, 20.45), 223 ($\text{M}^+ - \text{CH}_2\text{CH}_2\text{OH}$, 15.28), 45 ($\text{CH}_2\text{CH}_2\text{OH}$, 100).

3.2. General method for the preparation of compound 4 from compound 3

NaH (0.24 g, 10 mmol) was added slowly to a well-stirred solution of compound **3** (5 mmol) in anhydrous tetrahydrofuran (THF) or 1,4-dioxane (8 ml) and the mixture was stirred at room temperature under nitrogen for 6 h (monitored by TLC or ^{19}F NMR). After the reaction was completed, glacial acetic acid (HOAc) was dropped in slowly to decompose the unreacted NaH. The mixture was then diluted with water and extracted with diethyl ether (3×30 ml). The combined extracts were washed, dried (Na_2SO_4) and distilled. The residue was purified by flash chromatography on silica gel and eluted with light petroleum to give pure compound **4**.

3.2.1. 2-Phenyl-2-(*Z*-2,3,3,3-tetrafluoro-1-propenyl)-1,3-oxathiolane **4a**

IR ν_{max} (cm^{-1}): 3030, 2950, 1710 ($\text{CF}=\text{C}$), 1280, 1150. ^1H NMR δ : 7.50 (5H, m), 6.06 (1H, d, $J=31$ Hz), 4.20 (2H, m), 3.25 (2H, m) ppm. ^{19}F NMR δ : –5.0 (3F, m), 52.3 (1F, br) ppm. MS (*m/e*): 278 (M^+ , 35.61), 258 ($\text{M}^+ - \text{HF}$, 8.29), 230 ($\text{M}^+ - \text{HF} - \text{CH}_2\text{CH}_2$, 26.75), 219 ($\text{M}^+ - \text{CF}_3$, 10.50), 202 ($\text{M}^+ - \text{Ph} + 1$, 42.76), 60 (SCH_2CH_2 , 100). Analysis: calculated for $\text{C}_{12}\text{H}_{10}\text{F}_4\text{OS}$: C, 51.80%; H, 3.60%; F, 27.34%; found: C, 51.51%; H, 3.38%; F, 27.58%.

3.2.2. 2-(Z-3-Chloro-2,3,3-trifluoro-1-propenyl)-2-phenyl-1,3-oxathiolane **4b**

IR ν_{\max} (cm⁻¹): 3010, 2900, 1700, 1500, 1140 (C–C, C–F). ¹H NMR δ : 7.53 (2H, m), 7.30 (3H, m), 6.08 (1H, d, $J=32$ Hz), 4.20 (2H, m), 3.20 (2H, m) ppm. ¹⁹F NMR δ : –18.0 (2F, s), 48.0 (1F, br) ppm. MS (m/e): 294 (M⁺, 29.78), 259 (M⁺ – Cl, 13.20), 235 (12.58), 209 (12.47), 105 (30.40), 60 (SCH₂CH₂, 100). Analysis: calculated for C₁₁H₁₀F₃OSCl: C, 48.90%; H, 3.39%; F, 19.35%; found: C, 49.25%; H, 3.16%; F, 19.36%.

3.2.3. 2-n-Pentyl-2-(Z-2,3,3,3-tetrafluoro-1-propenyl)-1,3-oxathiolane **4c**

IR ν_{\max} (cm⁻¹): 2950, 1710, 1360, 1300, 1200, 1150. ¹H NMR δ : 5.80 (1H, d, $J=43$ Hz), 4.30 (2H, m), 2.13 (2H, m), 2.06 (2H, m), 1.40 (6H, m), 0.95 (3H, t) ppm. ¹⁹F NMR δ : –5.0 (3F, m), 54.5 (1F, br) ppm. MS (m/e): 272 (M⁺, 1.58), 252 (M⁺ – HF, 4.10), 201 (M⁺ – C₅H₁₁, 100), 141 (37.74), 60 (99.27). Analysis: calculated for C₁₁H₁₆F₄OS: C, 48.53%; H, 5.88%; F, 27.94%; found: C, 48.61%; H, 5.82%; F, 27.67%.

3.2.4. 2-(2-Tetrahydropyranoxymethyl)-2-(Z-2,3,3,3-tetrafluoro-1-propenyl)-1,3-oxathiolane **4d**

¹H NMR δ : 6.74 (1H, d, $J=34$ Hz), 4.70 (1H, m), 4.20 (2H, m), 3.70 (4H, m), 3.0 (2H, m), 1.65 (6H, m) ppm. ¹⁹F NMR δ : –5.0 (3F, m), 53.0 (1F, br) ppm. MS (m/e): 316 (M⁺, 0.83), 215 (M⁺ – OTHP, 22.1), 201 (M⁺ – CH₂OTHP, 15.02), 85 (THP, 100). Analysis: calculated for C₁₂H₁₆F₄O₃S: C, 45.57%; H, 5.06%; F, 24.05%; found: C, 45.57%; H, 5.25%; F, 24.15%.

3.2.5. 2-(Z-3-Chloro-2,3,3-trifluoro-1-propenyl)-2-(2-tetrahydropyranoxymethyl)-1,3-oxathiolane **4e**

¹H NMR δ : 5.84 (1H, d, $J=51$ Hz), 4.66 (1H, m), 4.20 (2H, t, $J=9.0$ Hz), 3.70 (4H, m), 3.10 (2H, t, $J=9.0$ Hz), 1.63 (6H, m) ppm. ¹⁹F NMR δ : –5.0 (3F, m), 53.0 (1F, br) ppm. MS (m/e): 316 (M⁺, 0.83), 215 (M⁺ – OTHP, 22.1), 201 (M⁺ – CH₂OTHP, 15.02), 85 (THP, 100). Analysis: calculated for C₁₂H₁₆F₄O₃S: C, 45.57%; H, 5.06%; F, 24.05%; found: C, 45.57%; H, 5.25%; F, 24.15%.

3.2.6. 2-(Z-2,3,3,4,4,5,5-Octafluoro-1-pentenyl)-2-phenyl-1,3-oxathiolane **4g**

¹H NMR δ : 7.50 (5H, m), 6.10 (1H, d, $J=36$ Hz), 4.20 (2H, m), 3.20 (2H, m) ppm. ¹⁹F NMR δ : 3.0 (3F, s, CF₃), 40.2 (2F, s), 48.0 (1F, br), 49.3 (2F, s) ppm. MS (m/e): 378 (M⁺, 9.96), 358 (M⁺ – HF, 1.86), 319 (M⁺ – SCH₂CH₂ + 1, 6.29), 301 (M⁺ – Ph, 3.57), 241 (14.46), 60 (SCH₂CH₂, 100). Analysis: calculated for C₁₄H₁₀F₈OS: C, 44.44%; H, 2.65%; F, 40.21%; found: C, 44.44%; H, 2.77%; F, 40.98%.

3.2.7. 2-(Z-5-Chloro-2,3,3,4,4,5,5-heptafluoro-1-pentenyl)-2-phenyl-1,3-oxathiolane **4h**

IR ν_{\max} (cm⁻¹): 3050, 2900, 1600, 1450, 1340, 1180. ¹H NMR δ : 7.50 (2H, m), 7.33 (3H, m), 6.10 (1H, d, $J=33$

Hz), 4.17 (2H, m), 3.20 (2H, m) ppm. ¹⁹F NMR δ : –9.8 (2F, s, ClCF₂), 39.2 (2F, s), 43.6 (2F, s), 47.0 (1F, br) ppm. MS (m/e): 394 (M⁺, 14.27), 396 (5.93), 335 (M⁺ – SCH₂CH₂ + 1, 10.75), 337 (3.89), 317 (M⁺ – Ph, 3.99), 257 (14.46), 60 (SCH₂CH₂, 100). Analysis: calculated for C₁₄H₁₀F₇OSCl: C, 42.58%; H, 2.53%; F, 33.71%; found: C, 42.73%; H, 2.62%; F, 33.99%.

3.2.8. 2-(Z-5-Chloro-2,3,3,4,4,5,5-heptafluoro-1-pentenyl)-2-hydroxymethyl-1,3-oxathiolane **4i**

IR ν_{\max} (cm⁻¹): 3400 (O–H), 2930, 1700, 1180. ¹H NMR δ : 5.90 (1H, d, $J=35$ Hz), 4.30 (2H, m), 3.90 (2H, s), 3.23 (2H, m), 2.65 (1H, s) ppm. ¹⁹F NMR δ : –9.6 (2F, s, ClCF₂), 40.0 (2F, s), 44.0 (2F, s), 46.4 (1F, br) ppm. MS (m/e): 331 (M⁺ – OH, 30.84), 333 (12.56), 317 (M⁺ – CH₂OH, 100), 319 (41.73), 289 (317 + 1 – F, 13.58), 257 (M⁺ – SCH₂CH₂, 22.99). HR MS: calculated for C₉H₈F₇O₂S³⁵Cl: 347.9821; found: 347.9845.

3.2.9. 2-(Z-5-Chloro-2,3,3,4,4,5,5-heptafluoro-1-pentenyl)-2-(1-hydroxyethyl)-1,3-oxathiolane **4j**

IR ν_{\max} (cm⁻¹): 3420, 2950, 1700, 1150. ¹H NMR δ : 5.84 (1H, d, $J=35$ Hz), 4.40 (1H, m), 3.10 (2H, m), 3.06 (2H, m), 2.75 (1H, s), 1.24 (3H, d, $J=6.0$ Hz) ppm. ¹⁹F NMR δ : –10.0 (2F, s), 39.0 (2F, s), 43.5 (2F, s), 48.0 (1F, br) ppm. MS (m/e): 345 (M⁺ – OH, 51.56), 317 (M⁺ – CH(CH₃)OH, 100), 298 (317 – F, 13.58), 257 (317 – SCH₂CH₂, 41.12), 213 (15.32). HR MS: calculated for C₁₀H₁₀F₇O₂S³⁵Cl: 361.9638; found: 361.9665.

3.2.10. 2-(Z-5-Chloro-2,3,3,4,4,5,5-heptafluoro-1-pentenyl)-2-(1-hydroxyl-1-methyl-ethyl)-1,3-oxathiolane **4k**

IR ν_{\max} (cm⁻¹): 3450, 2980, 1710, 1340, 1180. ¹H NMR δ : 5.85 (1H, d, $J=33$ Hz), 4.50 (1H, m), 4.0 (1H, m), 3.08 (2H, m), 2.20 (1H, s), 1.38 (6H, s) ppm. ¹⁹F NMR δ : –9.6 (2F, s, ClCF₂), 39.0 (2F, s), 43.6 (2F, s), 51.5 (1F, br) ppm. MS (m/e): 359 (M⁺ – OH, 66.41), 361 (27.27), 317 (M⁺ – C(CH₃)₂OH, 17.47), 298 (M⁺ – SCH₂CH₂, 39.14), 257 (317 – SCH₂CH₂, 41.12), 213 (38.10), 59 (100). Analysis: calculated for C₁₁H₁₂F₇O₂S³⁵Cl: C, 35.06%; H, 3.18%; F, 35.35%; found: C, 35.00%; H, 3.27%; F, 35.48%.

3.2.11. 2-(Z-5-Bromo-2,3,3,4,4,5,5-heptafluoro-1-pentenyl)-1,3-oxathiolane **4l**

IR ν_{\max} (cm⁻¹): 2930, 1700, 1320, 1120. ¹H NMR δ : 6.0 (1H, s), 5.83 (1H, dd, $J=9$ and 36 Hz), 4.30 (1H, m), 4.0 (1H, m), 3.16 (2H, t) ppm. ¹⁹F NMR δ : –14.3 (2F, s, BrCF₂), 39.5 (2F, s), 41.0 (2F, s), 49.6 (1F, br) ppm. MS (m/e): 363 (M⁺ + H, 12.49), 365 (12.03), 343 (M⁺ – HF, 6.97), 345 (7.32), 317 (M⁺ – CH₂CH₂OH, 8.31), 60 (100). HR MS: calculated for C₈H₆F₇OS⁷⁹Br: 361.9211; found: 361.9219; calculated for C₈H₆F₇OS⁸¹Br: 363.9190; found: 363.9217.

3.2.12. 2-(Z-5-Bromo-2,3,3,4,4,5,5,6,6,7,7-undecafluoro-1-heptenyl)-1,3-oxathiolane **4m**

IR ν_{\max} (cm^{-1}): 2900, 1710, 1330, 1200, 1150. ^1H NMR δ : 6.02 (1H, s), 5.90 (1H, d, $J=34$ and 9 Hz), 4.30 (1H, m), 4.0 (1H, m), 3.20 (2H, m) ppm. ^{19}F NMR δ : -14.0 (2F, s, BrCF_2), 40.5 (4F, s), 44.0 (2F, s), 45.3 (2F, s), 50.5 (1F, br) ppm. MS (m/e): 462, 464 (M^+ , 1.59), 401, 403 ($\text{M}^+ - \text{CH}_2\text{CH}_2\text{SH}$, 1.78), 337 ($\text{M}^+ - \text{HBr} - \text{HOCH}_2\text{CH}_2$, 3.31), 317 (337 - HF, 15.28), 257 (13.67), 60 (100). Analysis: calculated for $\text{C}_{10}\text{H}_6\text{F}_{11}\text{OSBr}$: C, 25.86%; H, 1.29%; F, 45.40%; found: C, 25.59%; H, 1.02%; F, 45.32%.

Acknowledgements

We thank the National Natural Science Foundation (No. 29632003) for financial support.

References

- [1] I. Ojima, M. Yatabe, T. Fuchikami, J. Org. Chem. 47 (1982) 2051. A.E. Feiring, J. Org. Chem. 45 (1980) 1962. I. Ojima, K. Kato, M. Okabe, T. Fuchikami, J. Am. Chem. Soc. 109 (1987) 7714. W.A. Herrmann, S. Eder, W. Scherer, Angew. Chem. Int. Ed. Engl. 104 (1992) 1371.
- [2] A.E. Feiring, M.C. Hovey, S.D. Arthur, J. Fluorine Chem. 24 (1984) 125.
- [3] A.D. Berry, R.A. De Maroc, W.B. Fox, J. Am. Chem. Soc. 101 (1979) 737. P. Calas, P. Moreau, A. Commeyras, J. Chem. Soc. Chem. Commun. (1982) 433. P. Moreau, N. Naji, A. Commeyras, J. Fluorine Chem. 30 (1985) 315.
- [4] Yu.L. Ignatova, H.M. Karimova, O.V. Kildsheva, Izv. Akad. Nauk SSSR, Ser. Khim. (1986) 732. T. Fuchikami, A. Yamanouchi, I. Ojima, Synthesis (1984) 766. F. Hong, C.M. Hu, J. Chem. Soc. Chem. Commun. (1996) 57.
- [5] T. Fuchikami, I. Ojima, Tetrahedron Lett. 23 (1982) 4099. B. Jiang, Y.Y. Xu, J. Org. Chem. 56 (1991) 7336. C.M. Hu, F. Hong, Y.Y. Xu, J. Fluor. Chem. 64 (1993) 1. F. Hong, X.Q. Tang, C.M. Hu, J. Chem. Soc. Chem. Commun. (1994) 289.
- [6] R.N. Haszeldine, K. Leedham, J. Chem. Soc. (1952) 3483. M.L. Blanc, G. Santini, F. Jeanneaux, J.G. Riess, J. Fluorine Chem. 7 (1976) 525. R.N. Haszeldine, J. Chem. Soc. (1951) 588. R.N. Haszeldine, Nature 165 (1950) 152. W.R. Cullen, M.C. Waldman, Can. J. Chem. 47 (1969) 3093.
- [7] X.Q. Tang, C.-M. Hu, J. Chem. Soc. Chem. Commun. (1994) 631. X.Q. Tang, C.-M. Hu, J. Fluor. Chem. 73 (1994) 133.
- [8] J.W. Emsley, J. Feeney, L.H. Sutcliffe, High Resolution Nuclear Magnetic Resonance Spectroscopy, vol. 2, Pergamon, 1966, Chapter 11.