ELSEVIER

Journal of Fluorine Chemistry 77 (1996) 183–191

JOURNAL OF FLUORINE CHEMISTRY

Functionalization of alkenes by polyfluorinated α,β-unsaturated sulphenyl chlorides [1] Dual reactivity of perfluoro-2-methyl-2-penten-3-yl sulphenyl chloride in reactions with activated olefins

V.Ya. Popkova [a,*], V.K. Osmanov [b], A.V. Borisov [b], B.I. Ugrak [a], I.V. Bodrikov [b]

[a] *A.N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov str. 28, Moscow 117813, Russian Federation*

[b] *Nizhegorodskii State Technical University, Minin str. 24, Nizhnii Novgorod, Russian Federation*

Abstract

A dual reactivity of perfluoro-2-methyl-2-penten-3-yl sulphenyl chloride (**1**) in reactions with alkenes is described. Whereas **1** interacts with 3,3-dimethyl-1-butene and styrene in nitromethane solution in the sulphenyl chloride form, reactions with olefins that have mobile hydrogen atoms in an allylic position (e.g. allyl- and *p*-methoxyallyl-benzenes) occur through the tautomeric thioketone form – 2-chloroperfluoro-2-methylpentanethione-3 (**3**) – with the formation of products by ene rearrangement. Chlorotropism in the system **1** ⇌ **3** in the presence of nucleophilic solvents or catalysts is responsible for the dual reactivity of **1** in the above reactions.

Keywords: Alkene functionalization; Polyfluorinated α,β-unsaturated sulphenyl chloride; Dual reactivity; Activated olefins; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

The ability of sulphenyl chlorides to add to double bonds is widely used for the functionalization of alkenes. In this article and previously [1] it was shown that α,β-unsaturated polyfluorinated sulphenyl chlorides of the aliphatic and alicyclic series first reported in our papers [2–4] possess this property as well, and undergo electrophilic addition reactions with olefins easily and with high yield, providing an opportunity to introduce versatile fluorine- and sulphur-containing multifunctional building blocks into various types of olefins.

Along with the mentioned practical significance, these transformations undoubtedly present a theoretical interest, because the highly electrophilic character of polyfluorinated α,β-unsaturated sulphenyl chlorides, the utilization of activated olefins (styrene, 3,3-dimethyl-1-butene, allyl- and *p*-methoxyallylbenzenes), polar solvents (CH_2Cl_2, CH_3NO_2, $CHCl_3$) and salt additives ($LiClO_4$, Bu_4NClO_4) permitted us not only to realise the additive reactions, but also to stimulate the substitution of vinylic hydrogen in olefins or skeletal rearrangements.

2. Results and discussion

Present work is focused on the studies of the interaction of perfluorinated α,β-unsaturated sulphenyl chlorides of the aliphatic series – perfluoro-2-methyl-2-penten-3-yl sulphenyl chloride (**1**) [2] – with 3,3-dimethyl-1-butene, styrene, allyl- and *p*-methoxyallyl-benzenes in nitromethane solution, as well as in the $LiClO_4/CH_3NO_2$ and Bu_4NClO_4/CH_3NO_2 systems[2].

Sulphenyl chloride **1** is a very interesting compound both from its synthetic and theoretical aspects. The phenomenon of chlorotropism in the 'carbon–carbon–sulphur' triad occurring with nucleophilic solvent or catalyst assistance in polyfluorinated α,β-unsaturated sulphenyl chlorides as first reported by us [5] is most clearly observed with **1**. That is why we hoped to obtain significant results upon the introduction of **1** in the aforementioned reactions.

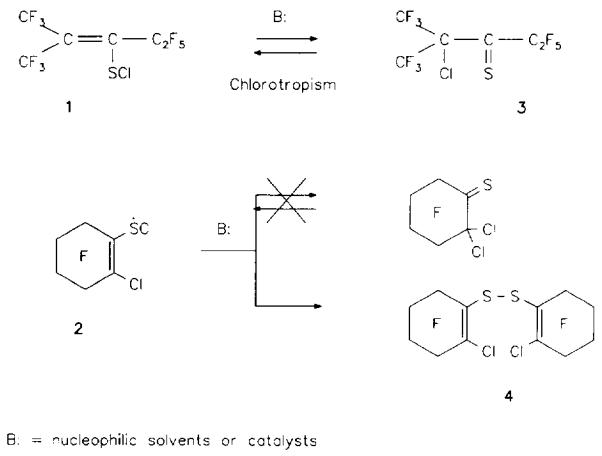
In a nucleophilic medium (nitromethane in the present instance), **1** is in mobile equilibrium with its tautomeric thioketone form – 2-chloroperfluoro-2-methylpentane-3-

* Corresponding author.

[1] See Ref. [1].

[2] Similar interactions in the alicyclic series have been investigated by us previously using, in particular, 2-chloroperfluoro-1-cyclohexenylsulphenyl chloride (**2**) [1].

PII S0022-1139(96)03425-2

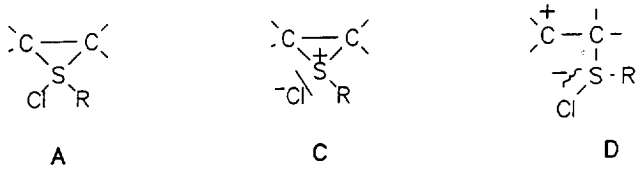


Scheme 1.

thione (**3**) (chlorotropism) (Scheme 1). In this case the solution is coloured dark green because the individual sulphenyl chloride (**1**) is orange whereas thioketone **3** is bright blue [5]. On addition of alkene the green colour of the reaction solution disappears, and this can be used for the determination of the end-point of the reaction. Unsaturated alicyclic sulphenyl chlorides (in particular compound **2**) do not isomerize to the corresponding α-chlorothioketones under the above-mentioned conditions. In contrast to **1**, they are dechlorinated to the disulphides (**2**→**4**) (see also Ref. [2a]). The latter process is much faster in the presence of stronger (than nitromethane) nucleophiles (for instance, *N*-methylpyrrolidone or $BF_3 \cdot NEt_3$) (Scheme 1).

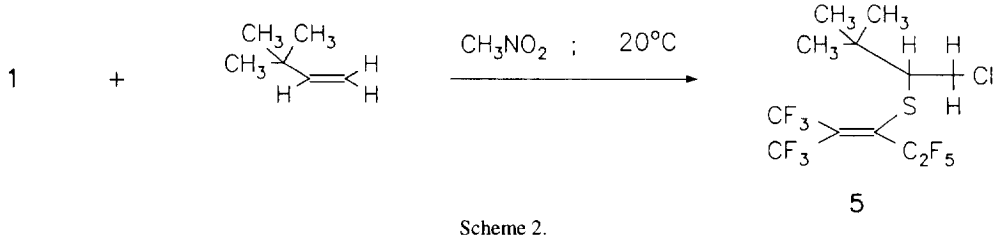
When 3,3-dimethyl-1-butene is added to a solution of **1** in nitromethane at 20 °C, the anti-Markovnikov isomer (AM) **5** is formed, which means that the reaction proceeds similarly to that of the saturated unfluorinated sulphenyl chloride [6] and its cyclic analogue **2** [1], i.e. exclusively regiospecifically by an electrophilic addition mechanism (Ad_E) (Scheme 2).

The intermediate formation of episulphurane A or a close ion-pair C is postulated in similar reactions of an Ad_E-type [7].

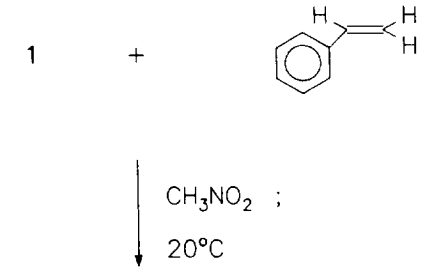


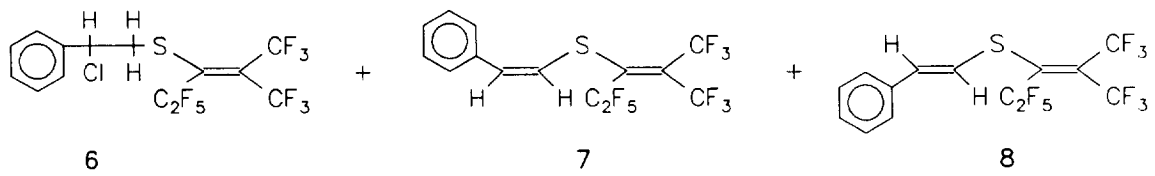
The reaction of **1** with styrene in nitromethane gives a mixture consisting of about 80% arising by an Ad_E mechanism with the formation of the Markovnikov isomer (M) **6** and about 20% arising by substitution with the formation of vinyl sulphides with a *cis*-(**7**) and *trans*-(**8**) configuration (Scheme 3).

Compound **6** and the mixture of isomers **7** and **8** can be easily separated by column chromatography, while the cyclic sulphenyl chloride **2** reacts with styrene to give the Markovnikov isomer exclusively [1]. The substitution of a vinylic hydrogen in styrene by reaction with sulphenyl chlorides was

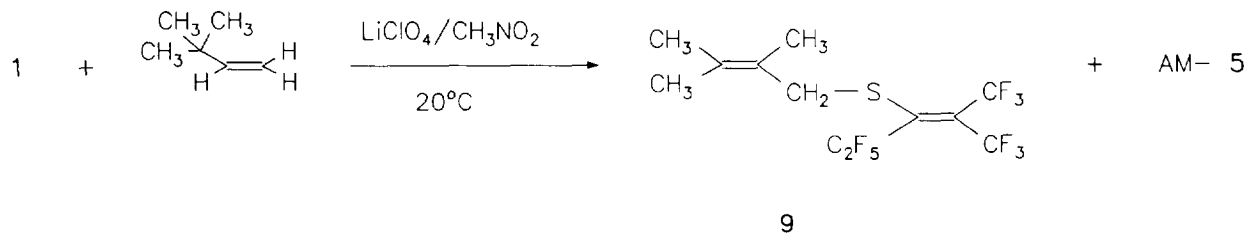


Scheme 2.

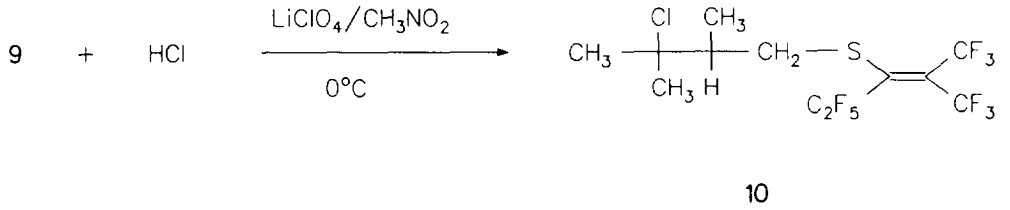




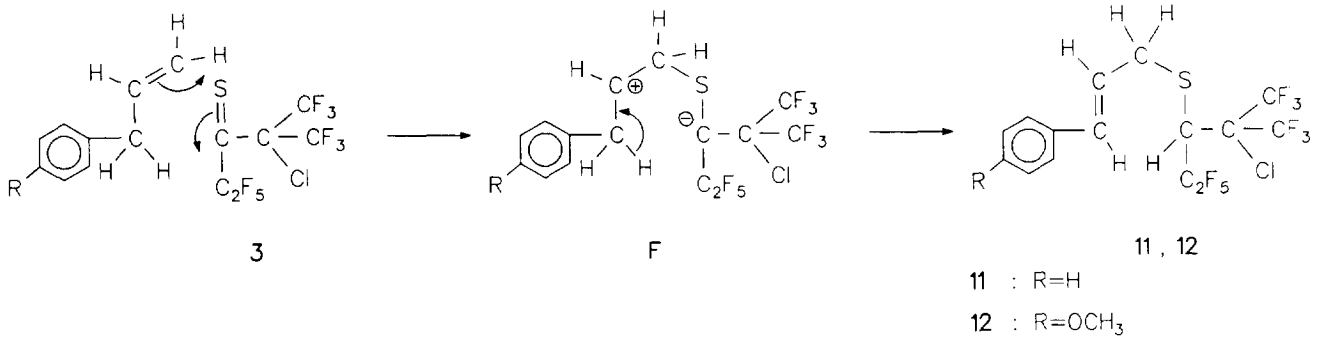
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

observed previously in the case of 2,4-dinitrobenzenesulphenyl chloride and *p*-methoxysterene [8].

These results show that **1** has a higher electrophilicity than **2** and also indicate the contribution of polar intermediate of open type D along with the less polar A or C in the transition state of this reaction.

The formation of **9** (a product of the 1,2-migration of the methyl group) is the main route of the reaction of **1** with 3,3-dimethyl-1-butene in the $LiClO_4/CH_3NO_2$ system at 20 °C. Adduct AM-**5** is also present in the reaction mixture but in small quantity, the ratio of **9**/AM-**5** being 4:1 (Scheme 4). The mixture is easily separated by column chromatography.

It is known that the $LiCO_4/CH_3NO_2$ system enhances the polarization of intermediates in the reaction of sulphenyl chlorides with alkenes [9]. Hence the difference in the results obtained in Schemes 2 and 4 becomes clear when account is taken of the predominant formation of zwitterions of type D as intermediates in the latter case. We also observed similar transformations in case of the cyclic analogue **2** [1].

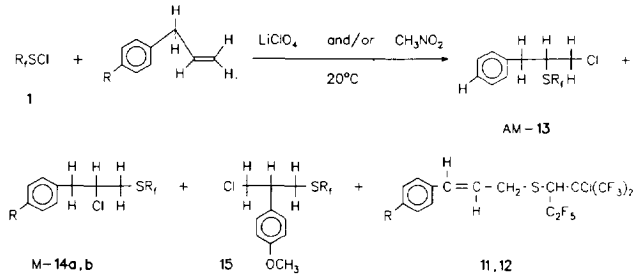
The kinetically-controlled product AM-**5** does not undergo any transformation (data from GLC and ^1H NMR analysis) on standing under the same conditions ($LiClO_4$, CH_3NO_2). Thus, the formation of **9** and AM-**5** are parallel processes and the rearrangement is realized directly in the Ad_E reaction.

At 0 °C in the $LiClO_4/CH_3NO_2$ system the unsaturated sulphide **9** adds HCl with the formation of γ-chlorothioether **10** in nearly quantitative yield (Scheme 5).

Thus, in the aforementioned examples (Schemes 2, 3 and 4) the interaction of **1** with alkenes takes place via reaction of the sulphenyl chloride form leading to the corresponding products **5–9**. However, the picture changes dramatically when olefins that have mobile hydrogen atoms in an allylic position, e.g. allyl- and *p*-methoxyallyl-benzenes, are used in the reaction in nitromethane. In this case, the alternative reaction involving the thione form **3** in an allylic addition process appears (Scheme 6).

This type of addition, with the formation of the corresponding products **11** and **12** arising from an ene rearrangement, occurs up to 80%–90% depending on the alkene employed. The reaction proceeds under mild conditions at room temperature. The results of these transformations are summarized in Table 1. The products of the reaction of the sulphenyl chloride form, i.e. isomers **13–15**, are present in the reaction mixture in amounts of 18% and 10%, respectively, depending on the starting alkene. They can be easily separated by column chromatography. The ratio of products in the reaction mixture indicates that the rate of the ene reaction of **3** is higher than the rate of electrophilic addition of **1**. The latter fact is advan-

Table 1
Results of the interaction of sulphenyl chlorides **1** with allyl- and *p*-methoxy allyl-benzenes under various reaction conditions at 20°C



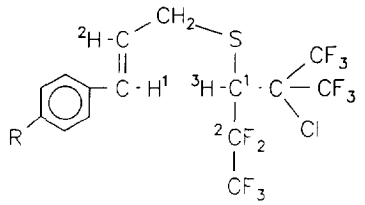
R_fSCl	Reaction conditions	R	Ratio of components in reaction mixture (%) [a]				
			AM (**13**)	M (**14**)	**15**	**11**	**12**
1	CH_3NO_2 [b]	H	5	5	–	90	–
		OCH_3	–	6	12	–	82
1	$LiClO_4$/ CH_3NO_2	H	55	45	–	–	–
		OCH_3	–	20	80	–	–

[a] The ratio of reaction products is based on GLC and NMR data for the reaction mixtures.
[b] Or Bu_4NClO_4/CH_3NO_2 for R = OCH_3.

tageous in the sense that for the synthesis of the products of ene reaction there is no necessity to work with pure thioketone **3**, which at present can only be isolated in the individual state by preparative GLC [5a] whereas sulphenyl chloride **1** is much more readily available.

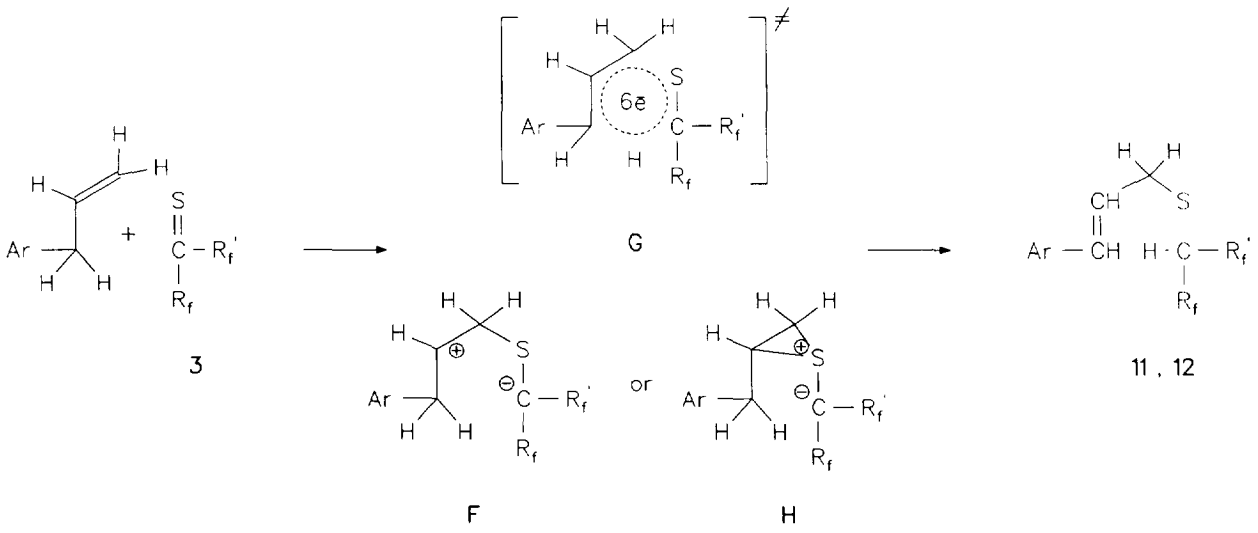
The analogous ene reaction with different olefins was observed in the early 1960s by Middleton during investigations of the properties of hexafluorothioacetone [10]. Diene polymers such as polyisoprene (crepe rubber) are modified by a similar reaction with hexafluorothioacetone [11]. However, as the latter only exists in an individual state at −78 °C, such reactions are only possible at low temperature [10]. The transformations found by us are preparatively much more simple and allow work to be undertaken at room temperature.

Investigation of the NMR spectra of **11** and **12**, the products of the ene reactions, has shown that these materials have a *trans* configuration. The coupling constants $^3J_{HH} \approx 15$ Hz for the olefinic protons in the ^1H NMR spectra demonstrate the *trans* sub-structure of **11** and **12**.



In the case of the *cis* isomer, the $^3J_{HH}$ coupling constant for the olefinic protons must not exceed 11 Hz [12]. The differential spectra of the nuclear Overhauser effect (NOE) also demonstrates the *trans* configuration of the products of the ene reactions, since during irradiation of the H^1 proton of sulphide **11** NOE enhancement was observed for the protons of the CH_2- and phenyl groups and for the H^3 proton. However, there was no influence on the peak intensities in the case of the H^2 proton. The peculiarities of the NMR spectra of sulphides **11** and **12** may be explained via coupling of the H^3 proton signal to only one fluorine atom of the CF_2 group, which as expected produces the AB system. This may be the result of inhibited rotation of the C_2F_5 group about the C(1)–C(2) σ-bond.

The mechanism of the ene reaction is usually discussed in terms of two limiting possibilities [13]. In one, an ene reac-



Scheme 7.

tion is considered to proceed by a concerted process via a cyclic 6e-transition state G. In the other, the mechanism can be considered to be stepwise via an intermediate, which can be either a zwitterion or a diradical with either free or restricted rotation (see G, F and H in Scheme 7) [13a].

The exclusive formation of *trans* isomers demonstrates the stepwise mechanism of the ene reactions observed by us, which are likely to proceed through an intermediate having a zwitterion structure of type F (see Schemes 6 and 7). Stabilization of intermediate F may be explained by the donor character of the benzyl group and electron–acceptor properties of the perfluoroalkyl substituents [14].

In the $LiClO_4/CH_3NO_2$ medium, the tautomeric process **1** ⇌ **3** is completely inhibited and it is the pure sulphenyl chloride form **1** which actually reacts with allyl- and *p*-methoxyallyl-benzenes. Inhibition of chlorotropism in the presence of $LiClO_4$ may also be observed visually, because the reaction mixture in this case is coloured yellow rather than green as in case of the **1** ⇌ **3** tautomerism (see Experimental details). It is quite possible that this phenomenon is associated with the more complicated process of complex formation involving participation of the alkaline metal cation (Li^+)[3].

In contrast to the reaction with styrene, the interaction of **1** with allylbenzene does not occur regiospecifically, but rather regioselectively with the formation of adducts AM-**13** and M-**14a** in a ratio of 55% and 45%, respectively (compare Scheme 3 and Table 1). The isomers can be separated by column chromatography. The unambiguous assignment of the ^1H NMR signals for adduct AM-**13** was achieved using heteronuclear resonance (^{13}C-{H}). Suppression of the protons at 3.64 ppm in the ^1H NMR spectra provides the 'answer' to the behaviour of the carbon atoms of the CH_2Cl group in the ^{13}C NMR spectra. Thus, in the ^1H NMR spectra the doublet at 3.64 ppm is associated with the protons of the CH_2Cl group, whereas the protons of the CH_2Ph group give rise to the AB system (see Experimental details).

When *p*-methoxyallylbenzene is introduced into the above reaction (Table 1), a product arising from a skeletal rearrangement with 1,2-migration of the *p*-methoxyphenyl group, i.e. sulphide **15** (80%), is formed along with a small quantity (20%) of adduct M-**14b** (GS–MS and ^1H NMR analysis). Attempts at the complete chromatographic separation of isomers **15** and M-**14b** were unsuccessful, but one of the isomers was enriched. Thus, an unambiguous assignment of the ^1H NMR signals was possible.

Alicyclic sulphenyl chloride **2** reacts in a similar manner with allyl- and *p*-methoxyallyl-benzenes, the presence or the absence of salt additives ($LiClO_4$) having no influence either on the composition or the ratio of the reaction products [1]. The skeletal rearrangement observed in the reactions of **1** and **2** with *p*-methoxyallylbenzene requires the considerable involvement of the open-type intermediate D in the process. The percentage of rearrangement product in the reaction mixture produced from **1** is much higher than that obtained from **2** (80% and 25% [1], respectively), which can be explained by the higher electrophilicity of **1** in comparison with that of **2**. Similar migrations of aryl groups have been reported [15] (see also review in Ref. [6]), but somewhat infrequently.

[3] Bu_4NClO_4 does not inhibit the chlorotropism and does not influence the composition or the ratio of products in the reaction mixture (see Table 1).

3. Experimental details

3.1. General methods

^1H NMR spectra were obtained with Bruker WM-250 and AM-300 spectrometers (250.1 and 300.1 MHz), and ^{13}C NMR spectra with a Bruker AM-300 (75.47 MHz) spectrometer. TMS was used as a reference standard (for ^1H and ^{13}C). Chemical shifts are referenced internally to solvent peaks ($CDCl_3$: ^1H, 7.24 ppm; ^{13}C, 77.00 ppm). ^{19}F NMR spectra were recorded on Bruker AC-200 (188.3 MHz) and Perkin-Elmer R-32 (84.6 MHz) spectrometers, in both cases using CF_3COOH as external standard. IR spectra were recorded on a Zeiss UR-20 spectrophotometer. KR spectra were obtained with a Ramanor-HG-2S instrument (excitation being provided by the 5145 Å line of a CR-8 laser, power 100 mW). Mass spectra were measured on a VG 7070E instrument operating in the EI mode at 70 eV with a (25 m) capillary column containing OV-101; *m/z* values, proposed assignment and relative intensity (%) for ^{32}S and ^{35}Cl isotopes are listed. The purity of the compounds was monitored by GLC methods on an LKhM-8 MD (model 3) chromatograph using a column (3 m × 4 mm) packed with 20% QF on Chromaton, a Zvet-530 chromatograph using a column (3 m × 4 mm) packed with 10% SKTF-50 on Chromaton and by TLC on 'Silufol UV-254' plates. Column chromatography was performed on silica gel L5/40 and L40/100 (Chemapol). Lithium perchlorate was desiccated by heating up to the melting point in vacuo for 2 h. The ^{19}F NMR spectra of compounds **5–10** and **13–15** are listed in Table 2.

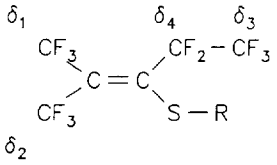
3.2. Di(2-chloroperfluoro-1-cyclohexenyl) disulphide (4)

Compound **2** (1.50 g, 4.59 mmol) was added dropwise with stirring to 3 ml of abs. *N*-methylpyrrolidone, maintaining the temperature at 20 °C. When the exothermic reaction had ceased, the mixture was poured into water. The organic layer was separated, dried over $MgSO_4$ and distilled to give 1.00 g (74.6%) of **4**, b.p. 89–90 °C/2 mmHg. The spectra of **4** were in good agreement with those published in Ref. [4] for ^{19}F NMR and IR spectra and in Ref. [1]a for the MS spectra.

3.3. 1-Chloro-3,3-dimethylbut-2-yl-perfluoro-2'-methyl-2'-penten-3'-yl sulphide (5)

3,3-dimethyl-1-butene (0.65 g, 1 ml, 7.72 mmol) in 1 ml of abs. nitromethane was added dropwise at 0–5 °C to a stirred green-coloured solution consisting of 1.04 g (2.98 mmol) of **1** in 2 ml of abs. nitromethane. The mixture was warmed up

Table 2
^{19}F NMR spectral data [($CDCl_3$) δ (ppm), J (Hz)] for compounds of the general formula:



Comp. No.	δ_1	δ_2	δ_3	δ_4	J_{1-2}	J_{1-3}	J_{1-4}
5	20.60 (tqq)	18.75 (q)	0.25 (q)	−23.0 (q)	10.0	10.0	21.0
6 [a]	21.33 (tqq)	18.67 (q)	1.11 (q)	−24.67 (q)	10.0	10.0	20.0
7	21.00 (tqq)	18.00 (q)	1.00 (q)	−26.50 (q)	10.0	10.0	18.0
8	21.00 (tqq)	18.63 (q)	1.00 (q)	−26.50 (q)	10.0	10.0	18.0
9	19.56 (tqq)	17.33 (q)	0.67 (q)	−25.78 (q)	10.0	10.0	20.0
10	21.00 (tqq)	17.50 (q)	1.00 (q)	−25.25 (q)	10.0	9.0	19.0
13	20.50 (tqq)	18.00 (q)	0.50 (q)	−24.50 (q)	10.0	9.0	19.0
14a	20.50 (tqq)	17.50 (q)	1.00 (q)	−25.00 (q)	10.0	10.0	20.0
14b	20.75 (tqq)	17.54 (q)	0.81 (q)	−25.50 (q)	10.0	9.0	20.0
15	20.75 (tqq)	17.54 (q)	0.81 (q)	−25.50 (q)	10.0	9.0	20.0

[a] Neat.

to room temperature and stirred for 1.5 h. After this time the green colour of the mixture had disappeared. The solvent was then evaporated in vacuo and the residue distilled to give 0.58 g (44.7%) of **5**, b.p. 55–56 °C/12 mmHg. ^1H NMR ($CDCl_3$) δ: 1.16 [s, 9H, (CH_3)$_3$]; 3.71 (H_A); 3.99 (H_B); 3.79 (H_X) [3H, CH_2Cl, CHS–ABX system, $^2J(H_A–H_B) = 11.74$ Hz, $^3J(H_A–H_X) = 6.94$ Hz, $^3J(H_B–H_X) = 3.73$ Hz]. ^{13}C NMR ($CDCl_3$) δ: 27.96 (CH_3); 36.17 [$C(CH_3)_3$]; 46.05 (CH_2 Cl); 64.12 (CHS). IR (film) (υ_{max} cm^{-1}): 1590 [C=C(CF_3)$_2$]. MS *m/z*: 417 [M–CH_3]$^+$ (3.3); 340 [$C_8H_3F_{11}S$]$^+$ (17.4); 119 [$C_6H_{12}Cl$]$^+$ (4.1); 83 [C_6H_{11}]$^+$ (42.5); 69 [CF_3]$^+$ (14.4); 69 [C_5H_9]$^+$ (7.0); 57 [C_4H_9]$^+$, (100.0); 55 [C_4H_7]$^+$ (21.5); 42 [C_3H_6]$^+$ (26.5). Analysis: Calc. for $C_{12}H_{12}F_{11}SCl$ (432.44): C, 33.33; H, 2.80; F, 48.33; S, 7.42%. Found: C, 33.39; H, 2.83; F, 48.49; S, 7.34%.

3.4. 2-Chloro-2-phenylethylperfluoro-2'-methyl-2'-penten-3'-yl sulphide (6), Z-styrylperfluoro-2-methyl-2-penten-3-yl sulphide (7) and E-styrylperfluoro-2-methyl-2-penten-3-yl sulphide (8)

Styrene (0.80 g, 7.68 mmol) in 2 ml of abs. nitromethane was added dropwise at 20 °C to a stirred green-coloured solution consisting of 2.68 g (7.68 mmol) of **1** in 10 ml of abs. nitromethane. The mixture was stirred for 15 h at room temperature when the green colour of the mixture had disappeared. The solvent was then evaporated in vacuo and the residue consisting of 80% **6**, 7% **7** and 13% **8** (GLC, ^1H and ^{19}F NMR analysis) was separated by column chromatography on 120 g of silica gel (eluent: hexane) to give 1.01 g (29.0%) of **6**, b.p. 93–95 °C/3 mmHg and 0.26 g (8.0%) of the mixture of **7** and **8** (ratio **7**/**8** = 1:2; GLC and ^1H NMR analysis), b.p. 75 °C/1 mmHg.

Compound **6**: ^1H NMR ($CDCl_3$) δ: 3.63 (H_A); 3.74 (H_B); 5.02 (H_X) [2H, CH_2S; 1H, $CHCl$–ABX system, $^2J(H_A–H_B) = 12.5$ Hz, $^3J(H_A–H_X) = 7.0$ Hz, $^3J(H_B–H_X) = 8.0$ Hz]; 7.4 (m, 5H, phenyl H). ^{13}C NMR ($CDCl_3$) δ: 46.47 (CH_2S); 60.18 ($CHCl$); 126.95, 129.01, 129.50 (phenyl C). IR (film) (υ_{max} cm^{-1}): 1600 [C=C(CF_3)$_2$, Ph]. Analysis: Calc. for $C_{14}H_8F_{11}SCl$ (452.727): C, 37.14; H, 1.78; F, 46.16; S, 7.08%. Found: C, 37.25; H, 1.79; F, 45.86; S, 7.06%.

Mixture of isomers **7** and **8**: IR (film) (υ_{max} cm^{-1}): 1590 [C=C(CF_3)$_2$, C=C, Ph]. KR (υ_{max} cm^{-1}): 1576.5, 1605.5 [C=C(CF_3)$_2$, C=C, Ph]. Analysis: Calc. for $C_{14}H_7F_{11}S$ (416.26): C, 40.39; H, 1.70; F, 50.20; S, 7.70%. Found: C, 40.43; H, 1.80; F, 49.73; S, 7.0%.

Compound **7**: ^1H NMR ($CDCl_3$) δ: 6.23 (dq, 1H, =CHS, $^3J_{HH} = 10.0$ Hz, $^6J_{HF} = 1.5$ Hz); 6.84 (d, 1H, Ph–CH=, $^3J_{HH} = 10.0$ Hz); 7.40 (m, 5H, phenyl H).

Compound **8**: ^1H NMR ($CDCl_3$) δ: 6.63 (dq, 1H, =CHS, $^3J_{HH} = 15.0$ Hz, $^6J_{HF} = 1.5$ Hz); 7.00 (d, 1H, Ph–CH=, $^3J_{HH} = 15.0$ Hz); 7.40 (m, 5H, phenyl H).

3.5. 2,3-Dimethyl-2-butenylperfluoro-2'-methyl-2'-penten-3'-yl sulphide (9)

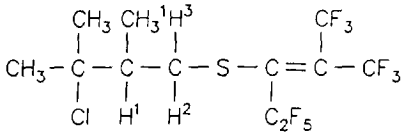
Compound **1** (4.18 g, 12.00 mmol) was added to a stirred solution consisting of 6.38 g (60 mmol) of desiccated $LiClO_4$ in 40 ml of abs. nitromethane. The reaction mixture was coloured yellow. Then 1.30 g (2 ml, 15.44 mmol) of 3,3-dimethyl-1-butene in 4 ml of abs. nitromethane were added dropwise at 20 °C. The yellow-coloured reaction mixture was stirred for 5 h at room temperature. The solvent was then evaporated in vacuo and the residue washed with water and extracted with dichloromethane. The organic layer was separated, dried ($MgSO_4$)$_2$ and evaporated to dryness. The crude material consisting of 80% **9** and 20% **5** (GLC and ^1H NMR analysis) was separated by column chromatography on 60 g

of silica gel (eluent: hexane) to give 1.95 g (41.0%) of **9**, b.p. 85–86 °C/16 mmHg and 0.62 g (12.0%) of **5**.

Compound **9**: ^{1}H NMR ($CDCl_3$) δ: 1.73 (s, 3H, CH_3^1); 1.77 [s, 6H (CH_3^2, CH_3^3)]; 3.75 (s, 2H, CH_2S). IR (film) (υ_{max} cm^{-1}): 1590 [C=C(CF_3)$_2$, C=C]. MS *m/z*: 396 [M]$^+$ (1.7); 381 [M–CH_3]$^+$ (1.2); 327 [M–CF_3]$^+$ (2.0); 232 [$C_7H_2F_6S$]$^+$ (6.5); 115 [$C_6H_{11}S$]$^+$ (32.0); 83 [C_6H_{11}]$^+$ (28.2); 82 [C_6H_{10}]$^+$ (12.3); 69 [CF_3]$^+$ (100.0); 67 [C_5H_7]$^+$ (13.1); 55 [C_4H_7]$^+$ (64.9); 53 [C_4H_5]$^+$ (6.5); 42 [C_3H_6]$^+$ (10.3). Analysis: Calc. for $C_{12}H_{11}F_{11}S$ (396.274): C, 36.37; H, 2.80; F, 52.74; S, 8.09%. Found: C, 35.94; H, 2.79; F, 53.01; S, 8.33%.

3.6. 3-Chloro-2,3-dimethylbutylperfluoro-2'-methyl-2'-penten-3'-yl sulphide (10)

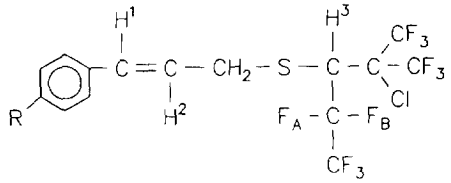
Dry HCl gas was passed through a stirred mixture consisting of 0.37 g (0.93 mmol) of **9** and 0.42 g (3.95 mmol) of desiccated $LiClO_4$ in 5 ml of abs. nitromethane at 0 °C; the progress of the reaction was monitored by GLC methods. The solvent was then evaporated in vacuo, the residue washed with water and extracted with dichloromethane. The organic layer was separated, dried ($MgSO_4$) and evaporated to dryness. The crude material was purified by column chromatography on 10 g of silica gel (eluent: hexane) to give 0.20 g (49.7%) of **10**, b.p. 58–60 °C/12 mmHg. ^{1}H NMR ($CDCl_3$) δ: 1.15 (d, 3H, CH_3^1, $^3J_{HH}$ = 7.0 Hz); 1.55 (s, 3H, CH_3^2); 1.63 (s, 3H, CH_3^3); 1.94 (dqd, 1H, H^1, ^3J(H^1–H^2) = 11.5 Hz, ^3J(H^1–CH_3^1) = 7.0 Hz, ^3J(H^1–H^3) = 3.0 Hz); 2.85 (dd, 1H, H^2, $^2J_{HH}$=$^3J_{HH}$ = 11.5 Hz); 3.51 (dd, 1H, H^3, $^2J_{HH}$ = 11.5 Hz, $^3J_{HH}$ = 3.0 Hz). IR (film) (υ_{max} cm^{-1}): 1590 [C=C(CF_3)$_2$]. MS *m/z*: 432 [M]$^+$ (3.2); 396 [M–HCl]$^+$ (3.5); 355 [M–$(CH_3)_2CCl$]$^+$ (12.0); 327 [$C_7H_2F_{11}S$]$^+$ (5.5); 175 [$C_8H_{12}ClS$]$^+$ (6.1); 118 [$C_6H_{11}Cl$]$^+$ (9.6); 115 [$C_6H_{11}S$]$^+$ (17.4); 83 [C_6H_{11}]$^+$ (100.0); 77 [$(CH_3)_2CCl$]$^+$ (19.4); 69 [CF_3]$^+$ (55.9); 69 [C_5H_9]$^+$ (15.2); 67 [C_5H_7]$^+$ (9.9); 55 [C_4H_7]$^+$ (57.4); 53 [C_4H_5]$^+$ (6.3); 43 [C_3H_7]$^+$ (26.7); 42 [C_3H_6]$^+$ (8.6).



3.7. E-3-Phenyl-2-propenylperfluoro-2'-methylpent-3'-yl sulphide (11)

Allylbenzene (0.20 g, 1.70 mmol) in 3 ml of abs. nitromethane was added dropwise at 20 °C to a stirred green-coloured solution consisting of 0.62 g (1.70 mmol) of **1** in 7 ml of abs. nitromethane. The mixture was stirred for 15 h at room temperature when the green colour of the mixture disappeared. The solvent was then evaporated in vacuo and the residue consisting of 90% **11**, 5% **13** and 5% **14a** (GLC, ^{1}H NMR analysis) was separated by column chromatography on 60 g of silica gel (eluent: hexane/dichloromethane 12:1) to give 0.51 g (64.0%) of **11**, b.p. 102–104 °C/0.5 mmHg and 0.05 g (6.0%) of the mixture of **13** and **14a** (ratio **13**/**14a** = 1:1; GLC and ^{1}H NMR analysis).

Compound **11**: ^{1}H NMR ($CDCl_3$) δ: 3.61 (H_A); 3.65 (H_B) [2H, CH_2S–AB system, with additional doubling of each component, ^2J(H_A–H_B) = 12.5 Hz, ^3J(H_A–H^2) = 7.5 Hz, ^3J(H_B–H^2) = 8.5 Hz]; 4.00 (d, 1H, H^3, $^3J_{HF}$ = 25.0 Hz); 6.18 [ddd, 1H, H^2, $^3JH_2$–H^1) = 16.0 Hz); ^3J(H^2–H_B) = 8.5 Hz, ^3J(H^2–H_A) = 7.5 Hz]; 6.60 (d, 1H, H^1, $^3J_{HH}$ = 16.0 Hz); 7.42 (m, 5H, phenyl H). ^{13}C NMR ($CDCl_3$) δ: 38.76 (CH_2S); 49.69 (t, $CHCF_2$, $^2J_{CF}$ = 18.92 Hz); 121.80 (=$CHCH_2S$); 126.71 (PhCH=); 128.55, 128.87, 135.95, 136.36 (phenyl C). ^{19}F NMR ($CDCl_3$) δ: 11.58 (m, 3F, CF_3^1); 11.14 (m, 3F, CF_3^2); −1.71 (s, 3F, CF_3CF_2); −27.47 (F_A); −37.30 (F_B) [2F, CF_2 – AB system with additional coupling of each component, ^2J(F_A–F_B) = 270.0 Hz, ^5J(F_A–CF_3^1) = 25.0 Hz, ^5J(F_B–CF_3^1) = 9.0 Hz, ^3J(F_B–H^3) = 25.0 Hz]. IR (film) (ν_{max} cm^{-1}): 1520, 1600 (C=C, Ph). Analysis: Calc. for $C_{15}H_{10}F_{11}SCl$ (466.67): C, 38.60; H, 2.14; F, 44.79; S, 6.87%. Found: C, 38.35; H, 2.17; F, 44.58; S, 6.86%.



R = H (11), OCH_3 (12)

3.8. E-3-(P-Methoxyphenyl)-2-propenylperfluoro-2'-methylpent-3'-yl sulphide (12)

P-Methoxyallylbenzene (0.49 g, 3.30 mmol) in 3 ml of abs. nitromethane was added dropwise at 20 °C to a stirred green-coloured solution consisting of 1.15 g (3.30 mmol) of **1** in 7 ml of abs. nitromethane. The mixture was stirred for 15 h at room temperature when the green colour of the mixture disappeared. The solvent was then evaporated in vacuo and the residue consisting of 82% **12**, 6% **14b** and 12% **15** (GLC, ^{1}H NMR analysis) was separated by column chromatography on 60 g of silica gel (eluent: hexane/dichloromethane 12:1) to give 0.68 g (41.5%) of **12**, b.p. 110–115 °C/1 mmHg and 0.07 g (4.0%) of the mixture of **14b** and **15** (ratio **14b**/**15** = 1:2; GLC and ^{1}H NMR analysis).

Compound **12**: ^{1}H NMR ($CDCl_3$) δ: 3.58 (m, 2H, CH_2S); 3.83 (s, 3H, OCH_3); 3.94 (d, 1H, H^3, $^3J_{HF}$ = 27.5 Hz); 5.97 [dt, 1H, H^2, ^3J(H^1–H^2) = 16.0 Hz, ^3J(H^2–CH_2) = 8.0 Hz]; 6.48 (d, 1H, H^1, $^3J_{HH}$ = 16.0 Hz); 6.88 (m, 2H, aryl H); 7.32 (m, 2H, aryl H). ^{13}C NMR ($CDCl_3$) δ: 38.90 (CH_2S); 48.90 (t, $CHCF_2$, $^2J_{CF}$ = 17.57 Hz); 55.26 (OCH_3); 114.13 (–$CHCH_2S$); 119.18 (PhCH=); 127.78, 128.39, 135.68, 159.82 (aryl C) ppm. ^{19}F NMR ($CDCl_3$) δ: 11.20 (m, 3F, CF_3^1); 11.00 (m, 3F, CF_3^2); −1.75 (s, 3F, CF_3CF_2); −27.38

(F_A); −37.00 (F_B) [2F, CF_2–AB system with additional coupling of each component, $^2J(F_A–F_B) = 270.0$ Hz, $^5J(F_A–CF_3^1) = 26.0$ Hz, $^5J(F_B–CF_3^1) = 9.0$ Hz, $^3J(F_B–H^3) = 27.51$ Hz]. IR (film) (ν_{max} cm^{-1}): 1520, 1615 (C=C, Ar). Analysis: Calc. for $C_{16}H_{12}F_{11}OSCl$ (496.779): C, 38.68; H, 2.44; F, 42.07; S, 6.45; Cl, 6.86%. Found: C, 39.26; H, 2.45; F, 42.47; S, 6.83; Cl, 7.14%.

*3.9. 1-Chloro-3-phenylprop-2-ylperfluoro-2'-methyl-2'-penten-3'-yl sulphide (**13**) and 2-chloro-3-phenylpropylperfluoro-2'-methyl-2'-penten-3'-yl sulphide (**14a**)*

Compound **1** (2.11 g, 5.78 mmol) was added to a stirred solution consisting of 3.06 g (28.78 mmol) of desiccated $LiClO_4$ in 20 ml of abs. nitromethane. The reaction mixture was coloured yellow. Then 0.68 g (5.78 mmol) of allylbenzene in 2 ml of abs. nitromethane were added dropwise at 20 °C. The yellow-coloured reaction mixture was stirred for 15 h at room temperature. The solvent was then evaporated in vacuo and the residue washed with water and extracted with dichloromethane. The organic layer was separated, dried ($MgSO_4$) and evaporated to dryness. The crude material consisting of 55% **13** and 45% **14a** (GLC, ^{1}H and ^{19}F NMR analysis) was separated by column chromatography on 90 g of silica gel (eluent: hexane) to give 0.62 g (23.0%) of **13**, b.p. 105–110 °C/1 mmHg and 0.43 g (16.0%) of **14a**, b.p. 105–110 °C/1 mmHg.

Compound **13**: ^{1}H NMR ($CDCl_3$) δ: 2.95 (H_A); 3.26 (H_B) [2H, CH_2Ph – AB system with additional doubling of each component, $^2J(H_A–H_B) = 14.24$ Hz, $^3J(H_A–H) = 6.63$ Hz, $^3J(H_B–H) = 7.68$ Hz; 3.62 (d, 2H, CH_2Cl, $^3J_{HH} = 5.34$ Hz); 3.95 [ddt, 1H, CH, $^3J(H–H_B) = 7.68$ Hz, $^3J(H–H_A) = 6.63$ Hz, $^3J_{HH} = 5.34$ Hz]; 7.30 (m, 5H, phenyl H). IR (film) (ν_{max} cm^{-1}): 1590 [C=C(CF_3)$_2$, Ph]. Analysis: Calc. for $C_{15}H_{10}F_{11}SCl$ (466.67): C, 38.60; H, 2.14; F, 44.79; S, 6.87%. Found: C, 38.35; H, 2.13; F, 44.66; S, 6.85%.

Compound **14a**: ^{1}H NMR ($CDCl_3$) δ: 3.15 (d, 2H, CH_2, $^3J_{HH} = 7.0$ Hz); 3.36 (H_A); 3.39 (H_B) [2H, CH_2S–AB system with additional doubling of each component, $^2J(H_A–H_B) = 13.0$ Hz, $^3J(H_A–H) = 5.5$ Hz, $^3J(H_B–H) = 6.5$ Hz]; 4.26 [tdd, 1H, CH, $^3J_{HH} = 7.0$ Hz, $^3J(H–H_B) = 6.5$ Hz, $^3J(H–H_A) = 5.5$ Hz]; 7.30 (m, 5H, phenyl H). Analysis: Calc. for $C_{15}H_{10}F_{11}SCl$ (466.67): C, 38.60; H, 2.14; F, 44.79; S, 6.87%. Found: C, 38.42; H, 2.14; F, 44.86; S, 6.79%.

*3.10. 2-Chloro-3-(p-methoxyphenyl)propylperfluoro-2'-methyl-2'-penten-3'-yl sulphide (**14b**) and 2-(p-methoxyphenyl)-3-chloropropylperfluoro-2'-methyl-2'-penten-3'-yl sulphide (**15**)*

Compound **1** (1.03 g, 2.82 mmol) was added to a stirred solution of 1.75 g (16.46 mmol) of desiccated $LiClO_4$ in 15 ml of abs. nitromethane. The reaction mixture was coloured yellow. Then 0.42 g (2.82 mmol) of *p*-methoxyallylbenzene in 2 ml of abs. nitromethane were added dropwise at 20 °C. The yellow-coloured reaction mixture was stirred for 15 h at room temperature. The solvent was then evaporated in vacuo and the residue washed with water and extracted with dichloromethane. The organic layer was separated, dried ($MgSO_4$) and distilled to give 0.73 g (52.0%) of a mixture consisting of 20% **14b** and 80% **15** (GLC, GC–MS, ^{1}H and ^{19}F NMR analysis), b.p. 115–116 °C/1 mmHg. IR (film) (ν_{max} cm^{-1}): 1660 [C=C(CF_3)$_2$, Ar]. Analysis: Calc. for $C_{16}H_{12}F_{11}OSCl$ (496.779): C, 38.68; H, 2.44; F, 42.07; S, 6.45; Cl, 6.86%. Found: C, 39.03; H, 2.47; F, 42.24; S, 6.57%.

Compound **14b**: ^{1}H NMR ($CDCl_3$) δ: 3.07 (d, 2H, CH_2, $^3J_{HH} = 7.0$ Hz); 3.35 (m, 2H, CH_2S); 3.84 (s, 3H, OCH_3); 4.20 [quin, 1H, CH, $^3J(H–CH_2) = {}^3J(H–CH_2S) = 7.0$ Hz]; 6.90 (m, 2H, aryl H); 7.13 (m, 2H, aryl H). MS *m/z*: 496 [M]$^+$ (11.18); 183 [$CH_3OC_6H_4C_3H_5Cl$]$^+$ (3.00); 147 [$CH_3OC_6H_4C_3H_4$]$^+$ (6.59); 121 [$CH_3OC_6H_4CH_2$]$^+$ (100.00); 77 [C_6H_5]$^+$ (3.43); 69 [CF_3]$^+$ (3.32).

Compound **15**: ^{1}H NMR ($CDCl_3$) δ: 3.22 [dddd, 1H, CH, $^3J(H–H_A) = 9.0$ Hz, $^3J(H–H_{A'}) = 7.8$ Hz, $^3J(H–H_B) = {}^3J(H–H_{B'}) = 5.5$ Hz]; 3.48 (H_A); 3.54 (H_B) [2H, CH_2S–AB system with additional doubling of each component, $^2J(H_A–H_B) = 12.0$ Hz, $^3J(H_A–H) = 9.0$ Hz, $^3J(H_B–H) = 5.5$ Hz]; 3.70 ($H_{A'}$); 3.74 ($H_{B'}$) [2H, CH_2Cl–AB system with additional doubling of each component, $^2J(H_{A'}–H_{B'}) = 11.0$ Hz, $^3J(H_{A'}–H) = 7.8$ Hz, $^3J(H_{B'}–H) = 5.5$ Hz]; 3.83 (s, 3H, OCH_3); 6.92 (m, 2H, aryl H); 7.14 (m, 2H, aryl H). ^{13}C NMR ($CDCl_3$) δ: 41.63 (CH_2S); 46.94 (CH); 47.51 (CH_2Cl); 55.25 (CH_3O); 114.29, 128.69, 130.37, 159.60 (aryl C). MS *m/z*: 496 [M]$^+$ (15.97); 447 [M–CH_2Cl]$^+$ (4.37); 183 [$CH_3OC_6H_4C_3H_5Cl$]$^+$ (12.67); 169 [$CH_3OC_6H_4C_2H_3Cl$]$^+$ (100.00); 134 [$CH_3OC_6H_4C_2H_3$]$^+$ (38.16); 121 [$CH_3OC_6H_4CH_2$]$^+$ (18.80); 119 [C_8H_7O]$^+$ (6.20); 91 [$C_6H_4CH_3$]$^+$ (7.94); 77 [C_6H_5]$^+$ (5.24); 69 [CF_3]$^+$ (5.92).

References

[1] For previous communication, see: (a) V.Ya. Popkova, V K. Osmanov, A.V. Borisov, A.I. Lutsenko, A.F. Aerov, E.I. Mysov, M.V. Galachov and I.V. Bodrikov, *J. Fluorine Chem., 65* (1993) 181; (b) V.K. Osmanov, *Ph.D. Thesis*, Nizhegorodskii State Technical University, Nizhnii Novgorod, 1993; (c) V.Ya. Popkova, *Professor Thesis*, INEOS, Russian Academy of Science, Moscow, 1995.

[2] (a) R.A. Bekker and V.Ya. Popkova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1982) 1123; *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, (1982) 1001; (b) V.Ya. Popkova, M.V. Galakhov and I.L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1989) 116; *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, (1989) 104.

[3] V.Ya. Popkova, V.F. Snegirev, M.Yu. Antipin and Yu.T. Struchkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1989) 1123; *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, (1989) 1019.

[4] R.A. Bekker, V.Ya. Popkova and I.L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1980) 2175; [*Chem. Abs., 94* (1981) 30 232k] – incorrect information, see correction in the CA File on STN International in 1993.

[5] (a) R.A. Bekker, V.Ya. Popkova, V.F. Snegirev and I.L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1981) 2167; *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, (1981) 1782; (b) V.Ya. Popkova, V.M. Anisimov,

G.N. Dolenko, M.N. Semenenko and V.M. Fedoseev, *J. Chem. Soc., Perkin Trans., 2* (1995) 1375, and literature cited therein.

[6] L.P. Rasteikiene, D.I. Greiciute, M.G. Lin'kova and I.L. Knunyants, *Usp. Khim., 46* (1977) 1041; *Russ. Chem. Rev., 46* (1977) 548, and literature cited therein.

[7] I.V. Bodrikov, A.V. Borisov, W.A. Smit and A.I. Lutsenko, *Tetrahedron Lett., 25* (1984) 4983, and literature cited therein.

[8] W.L. Orr and N. Kharasch, *J. Am. Chem. Soc., 78* (1956) 1201, and literature cited therein.

[9] A.V. Borisov, G.N. Borisova, A.I. Lutsenko, V.A. Smit and I.V. Bodrikov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1988) 1194; *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, (1988) 1054.

[10] W.J. Middleton, *J. Org. Chem., 30* (1965) 1395.

[11] W.J. Middleton, US Pat. 3 012 995, 1961; [*Chem. Abs., 56* (1962) 6141g].

[12] J.W. Emsley, J. Feeney and L.H. Sutcliffe, *High Resolution NMR Spectroscopy*, Pergamon Press, Oxford/London/Edinburgh/New York/Paris/Frankfurt, 1966, Vol. 2; V.F. Bistrov and Yu.N. Cheynker (eds.), *Spektroskopiya yadernogo magnitnogo rezonansa visokogo razrecheniya*, Mir, Moscow, 1969, Vol. 2, p. 60 (Russ. edn.).

[13] (a) Z. Song and P. Beak, *J. Am. Chem. Soc., 112* (1990) 8126, and literature cited therein; (b) E.L. Clennan and J.J. Koola, *J. Am. Chem. Soc., 115* (1993) 3802, and literature cited therein.

[14] C. Hansch, A. Leo and R.W. Taft, *Chem. Rev., 91* (1991) 165.

[15] N.R. Slobodkin and N. Kharasch, *J. Am. Chem. Soc., 82* (1960) 866.