Reversible intramolecular 1,3-chlorine migration in the triad 'carbon–carbon–sulfur'

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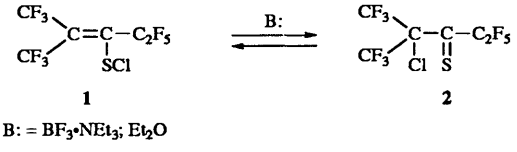
An intramolecular 1,3-chlorine migration in the triad 'carbon–carbon–sulfur' with nucleophilic solvent or catalyst assistance is proposed as a mechanism for the perfluoro-2-methylpent-2-ene-3-sulfenyl chloride **1** ⇌ 2-chloroperfluoro-2-methylpentane-3-thione **2** tautomerism. The data from radionuclidic investigations were used to elucidate the aforementioned mechanism. The results of MNDO calculations showed that the solvation lowers the height of the reaction barriers of both direct and reverse reactions and brings about different reaction pathways for these two processes, providing greater assistance to the **1** ⟶ **2** than to the **2** ⟶ **1** reaction.

Introduction

One of the fundamental problems of organic chemistry is that of tautomerism.[1] Therefore, the discovery of a new tautomeric system is of current interest. In the early 1980s, during an investigation of the properties of polyfluorinated α,β-unsaturated sulfenyl chlorides,[2,3] we found that perfluoro-2-methylpent-2-ene-3-sulfenyl chloride **1** was converted into a mixture of itself (20%) and 2-chloroperfluoro-2-methylpentane-3-thione **2** (80%) at 20 °C in the presence of basic catalysts (BF_3·NEt_3) or solvents (Et_2O)[3,4] (Scheme 1).

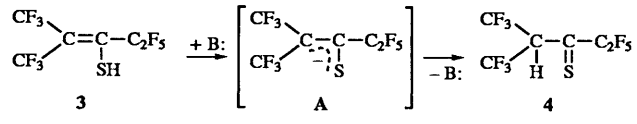


Scheme 1

It was shown that compounds **1** and **2** are in mobile equilibrium with each other. When the thioketone **2**, isolated by preparative GLC, was treated under the same conditions the same equilibrium mixture (**2**:**1** = 4:1) was obtained. It should be noted that sulfenyl chloride **1** is an orange substance whereas thione **2** is bright blue. It is therefore possible to judge the extent of the tautomeric conversion directly from the colour of the reaction mixture which becomes dark green (mixture of colours) when the equilibrium between **1** and **2** is established. These results show that under the reaction conditions applied a reversible migration of chlorine in the triad 'carbon–carbon–sulfur' takes place. That is why we named this tautomeric process chlorotropism. In the absence of basic catalysts or solvents both forms are completely stable and show no tautomerism even on prolonged storage.

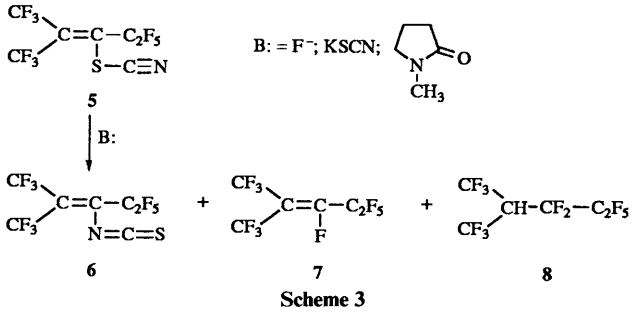
Originally[3,4] we supposed that this rearrangement is of a cationotropic nature. The reaction was assumed to proceed by initial halogenophilic attack of the base (BF_3·NEt_3, Et_2O) at the chlorine, *via* formation of an anion of type **A**, analogously to the proton displacement **3** ⟶ **4**, which we observed in the same system by the action of the same catalysts in the course of irreversible isomerization of enethiol **3** into the thioketone **4** reported in ref. 5 (Scheme 2).

Further systematic investigations in the field of polyfluorinated organic derivatives of bivalent sulfur, and in particular of the intermolecular isomerization of perfluorinated α,β-



Scheme 2

unsaturated thiocyanate **5** into isothiocyanate **6** by the action of nucleophiles, which proceeds as a nucleophilic substitution[6,7] (Scheme 3),† have led us to the conclusion that the migration



Scheme 3

of chlorine in the system **1** ⇌ **2** is intra-, rather than intermolecular. Therefore an anion of type **A** cannot be an intermediate in the process **1** ⇌ **2**.

Results and discussion

In the present work, in order to elucidate the mechanism of chlorotropism **1** ⇌ **2**, we have attempted isomerization of sulfenyl chloride **1** in the presence of various solvents and catalysts. The experimental conditions and the ratio of isomers **1** and **2** in the reaction mixture (according to GLC and ^{19}F NMR data) are given in Table 1.

We found that it is not only weak bases (BF_3·NEt_3, Et_2O)

† The presence of perfluoroalkene **7** in the reaction products is due to the parallel nucleophilic substitution reaction **5** ⟶ **7** performed with F^- as a nucleophilic agent. The latter is always present in the reaction mixture as a result of fluoride elimination from mobile fluorine atoms in the allylic position.[7]

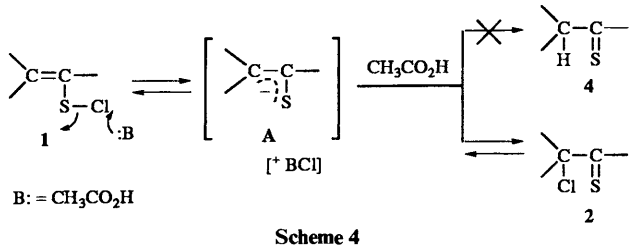
Table 1 Tautomeric ratio **1**:**2** in the reaction mixture of isomerization of sulfenyl chloride **1** in various solvents and/or with catalysts at 20 °C (according to GLC and ^{19}F NMR data)

Reaction conditions		Ratio of tautomers (%)	
Solvent or catalyst	Time (t/h)	**1**	**2**
Hexane	24	100	
$SbCl_5$	24	100	
$BF_3{\cdot}Et_2O$	8	100	
Et_2O	24	20	80
$BF_3{\cdot}NEt_3$	1.5	20	80
$BF_3{\cdot}NEt_3$/hexane	1.5	20	80
AcOH	17	43	57
$MeNO_2$	1.5	34	66
PhCN	0.16	28	72
PhCN	4	26	74
CsF/PhCN	1	15	85
LiCl/PhCN	0.5	17	83

that catalyse the above transformation. From Table 1 one can see that, in general, a nucleophilic medium is an absolutely indispensable prerequisite for the process. In pure sulfenyl chloride **1** or in non-nucleophilic solvents (*e.g.*, in hexane), or in the presence of Lewis acids ($BF_3{\cdot}Et_2O$, $SbCl_5$) no isomerization was observed. It is necessary to emphasize that the term nucleophile is restricted to reagents that supply a pair of electrons in a substitution or combination process.[8] Solvent nucleophilicity of Et_2O and acetic acid is known,[8] as are the weak nucleophilic properties of $MeNO_2$ and PhCN.[9] The basic character of $BF_3{\cdot}NEt_3$ is well documented.[10]

What is the role of a nucleophilic catalyst or nucleophilic solvent in the process of chlorotropism? Is this process inter- or intra-molecular?

The experiment in the presence of $MeCO_2H$ rules out our earlier [3,4] idea about chlorotropism as being an intermolecular reaction, where the solvent plays the role of halogenophile. In such a case one might have expected the formation of a product of protonation of intermediate **A**—thioketone **4** (see ref. 5 for its synthesis)—at least as a by-product, when the reaction is carried out in the presence of AcOH (Scheme 4). However, there were no indications of the presence of compound **4** in the reaction mixture.

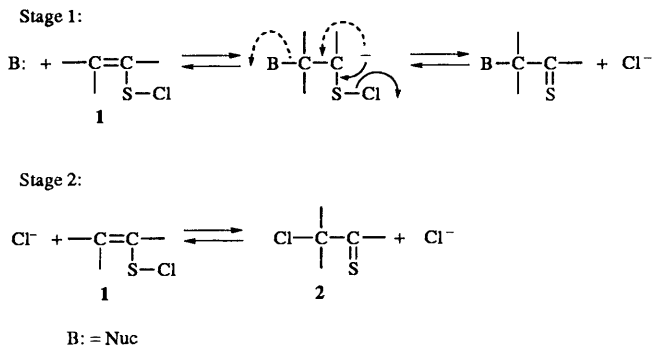


Scheme 4

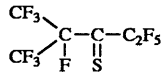
Theoretically, it is possible to treat the tautomerism **1** ⇌ **2** as an intermolecular reaction, which proceeds like a nucleophilic substitution according to Scheme 5, analogously to the **5** ⟶ **6** isomerization [7] (Scheme 3).

In this case, when the reaction is carried out in the presence of F^-, we should observe the formation of perfluoro-2-methylpentane-3-thione **9**—perfluorinated analogue of α-chloro thioketone **2**—as one of the products of the reaction. However, not even traces of compound **9** were found among the reaction products of sulfenyl chloride **1** with CsF in PhCN.

In order to confirm the mechanism of the reversible isomerization **1** ⇌ **2** we undertook the labelling studies. Starting from sulfenyl chloride **1** labelled with ^{36}Cl, we carried out its isomerization in PhCN in the presence of LiCl. In two



Scheme 5



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separate experiments, the reaction was allowed to take place over periods of 30 min and 1 h, respectively. The products of isomerization were then isolated (17% **1** and 83% **2**) and the specific radioactivity of the resulting mixtures was measured. In both cases, the specific radioactivity of the products was almost equal (12 065 and 11 228 dpm mg^{-1}, respectively) to that of the starting material (12 415 dpm mg^{-1}). This result showed that there was no exchange between sulfenyl chloride halogen (^{36}Cl) and the external chloride ions of the solution of LiCl in PhCN.‡

On the basis of all these results we concluded that the tautomeric process **1** ⇌ **2** proceeds intramolecularly *via* a four-membered cyclic transition state (see Fig. 2, below).

The fact that the isomerization process occurs also in PhCN solution in the absence of LiCl (see Table 1) may, however, raise some doubts in respect to our conclusions based on the labelling studies. Nevertheless, the examination of quantitative data given in Table 1 makes it clear that LiCl does have an influence on the quantitative ratio of isomers: the composition of the mixture in PhCN is 28 and 72% (**1**:**2**) after 10 min, and 26 and 74% (**1**:**2**) after 4 h; the addition of LiCl to PhCN changes the composition of the mixture (**1**:**2**) after 30 min to 17 and 83% respectively.

As mentioned at the beginning of this article it is possible to observe the tautomeric process **1** ⇌ **2** only in the presence of nucleophilic medium. That is why we suggest that the external nucleophilic solvent or catalyst causes the lowering of a reaction barrier **1** ⇌ **2**. The presence of electron-accepting perfluoroalkyl groups in the molecules **1** and **2** gives rise to a number of atomic centres with a lack of electron density. That is why these molecules readily form some sort of solvated complexes with the nucleophiles, which act as electron-pair donors. It should be noted that Table 1 certainly does not give an exhaustive list of nucleophiles capable of promoting the isomerization.

It is well known that the formation of a solvated complex always causes a lowering of the potential energy of interacting particles, but for the lowering of the height of the reaction barrier it is important that the transition state be solvated more strongly than the initial molecule. Only in this case will solvation decrease the ration barrier. In order to show that such solvation cases may be involved in reaction **1** ⇌ **2** we carried out semiempirical quantum chemical computations of com-

‡ The labelling studies were carried out by us in the Radiochemistry Laboratories of the Chemical Department of M. V. Lomonosov Moscow State University.

Table 2 Total energies (E_{tot}) of molecules **1**, **10** and **2** according MNDO and *ab initio* (in STO-3G basis)[12] calculations

Molecule	E_{tot} (eV) by MNDO	E_{tot} (eV) by *ab initio*
1	−6 633.898	−58 522.495
10	−6 631.490	
2	−6 633.092	−58 522.519

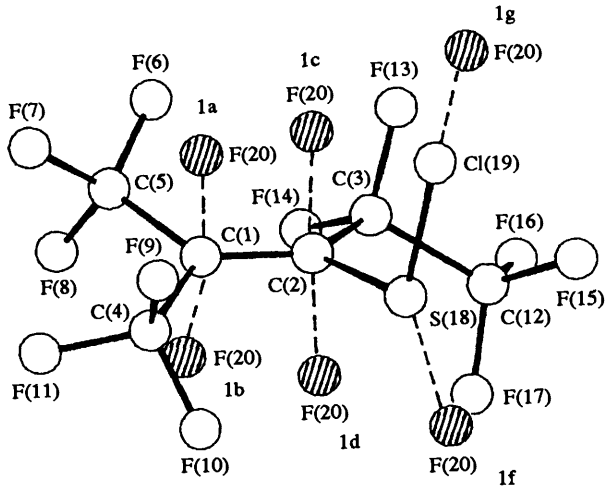
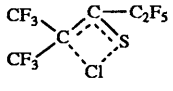


Fig. 1 ORTEP[13] representation of MNDO-optimized molecular geometry of sulfenyl chloride **1** and its possible modes of solvation by anion F^-, denoted by F(20)

pounds **1**, **2** and probable transition state **10**—corresponding to the transition state at the barrier to the reaction—and their various solvated complexes by an MNDO program.[11] We examined the influence of the position of solvent near molecules on the value of the reaction barrier. We considered the solvation of the aforementioned molecules only by one solvent particle. The latter has been modelled by the F^- anion.



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The geometry of species **1**, **2** and **10** was fully optimized, and their total energies are shown in Table 2. Only the position of F^- in the solvated complexes was optimized, since the geometry of compounds **1**, **2** and **10** was accepted to be the same as in the isolated molecules. Owing to the aforementioned approximations we expect to get only a qualitative picture of the role of the solvent in the intramolecular chlorine-atom transfer.

From Table 2 one can see that MNDO and *ab initio* calculations yield opposite results in respect to the relative thermodynamic stability of forms **1** and **2**. Our experimental data (see Table 1) show that thioketone form **2** is thermodynamically more stable than the sulfenyl chloride form **1**, so only *ab initio* calculations give correct values of total energies. That is why in our further discussions based on the results of MNDO calculations, we will use the direct and reverse reaction-barrier changes on solvation rather than their absolute values.

Possible modes of solvation of species **1**, **10** and **2** are shown in Figs. 1, 2 and 3, respectively; the gains of energies on solvation (ΔE_{solv}) for these molecules for different modes of solvation are listed in Table 3.

Solvation at the sulfur atom for all three molecules, **1**, **10** and

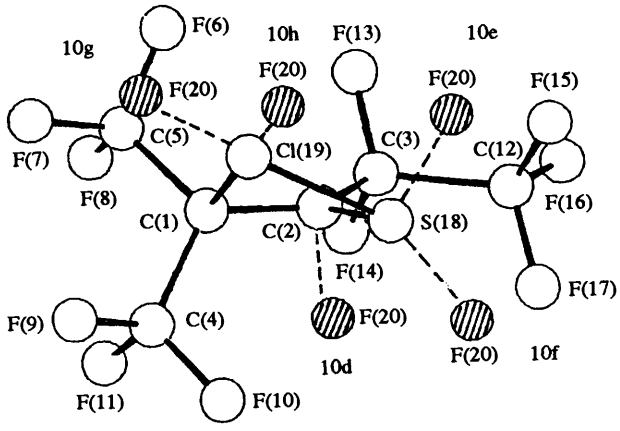


Fig. 2 ORTEP representation of MNDO-optimized molecular geometry of transition state **10** and its possible modes of solvation (by anion F^-)

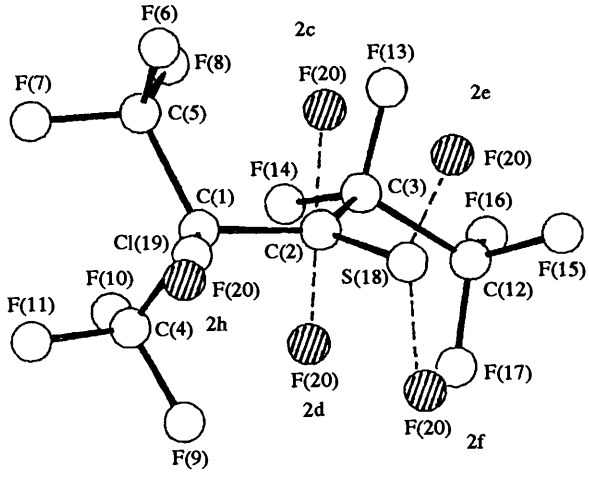


Fig. 3 ORTEP representation of MNDO-optimized molecular geometry of thione **2** and its possible modes of solvation (by anion F^-)

2 (see Table 3), gives the maximum gain of energy. The disposition of solvent particles under the plane C(1)–C(2)–S(18) is more preferable due to the steric factors associated with the presence of Cl(19) atom and favourable F(20)–C and S(18)–Cl(19) bond dipole-vector orientations (compare **b** with **a** and **d** with **c** in Table 3).

In order to answer the question as to which mode of solvation plays the most important role in the process being discussed we calculated the change in energy of the reaction barrier on solvation (ΔE) of both the direct and reverse reactions for each mode of solvation, using eqn. (1).§

$$\Delta E = E_2 - E_1 = \Delta E_{solv.10_m} - \Delta E_{solv.X_n} \qquad (1)$$

where E_1 = the energy of the reaction barrier of the direct (**1** ⟶ **2**) or reverse (**2** ⟶ **1**) reaction, E_2 = the energy of the reaction barrier on solvation of the direct or reverse reaction, $\Delta E_{solv.10_m}$ = the gain in energy on solvation for transition state **10**, $\Delta E_{solv.X_n}$ = the gain in energy on solvation for compounds **1** or **2**

X = **1**, **2**: **n**, **m** are different modes of solvation (see the Figures).

§ From the simple arithmetical solution of equation (1) it is clear that the E_{tot} of molecules **1**, **2** and **10** are not included in this equation, so the error in MNDO calculations of E_{tot} has no influence on the change in the reaction barrier on solvation.

Table 3 The gain in energy under solvation [$\Delta E_{solv.}$ (eV)] for molecules **1**, **10** and **2** in their various modes of solvation (by anion F^-)

$$\Delta E_{solv} = E_{tot.X_m} - E_{tot.X} - E_{tot.F^-}$$
$$E_{tot.F^-} = -478.245 \text{ eV}$$

	Modes of solvation with different positions of F^- near the atoms[a]							
	Near C(1)		Near C(2)		Near S(18)		Near Cl(19)	
m / X	a	b	c	d	e	f	g	h
1	−1.672	−2.016	−0.465	−1.568		−3.203	−2.733	
10				−1.737	−2.597	−3.812	−2.201	−2.095
2			−0.523	−1.098	−4.008	−3.958		−2.290

[a] Position of F^- anion: above the plane C(1)–C(2)–S(18)—**a**, **c**, **e**; along the line S(18)–Cl(19)—**g**; under the plane C(1)–C(2)–S)18)—**b**, **d**, **f**; along the line C(1)–Cl(19)—**h**.

Table 4 The change in energy of the reaction barrier under solvation (ΔE) for direct and reverse reactions of process **1** ⇌ **2**

Reaction **1** ⟶ **10**	ΔE (eV)	Reaction **2** ⟶ **10**	ΔE (eV)
1a ⟶ **10g**	−0.529	**2d** ⟶ **10d**	−0.639
1d ⟶ **10d**	−0.169	**2e** ⟶ **10e**	+1.411
1f ⟶ **10f**	−0.609	**2f** ⟶ **10f**	+0.146
1g ⟶ **10g**	+0.532	**2h** ⟶ **10h**	+0.089

We assumed that the change in position of the solvent particle is consistent with chlorine-atom transfer, so that each solvation mode of the starting molecule will go to the only definite mode of solvation of the resulting system. The most important possible pathways are shown in Table 4. A negative sign of ΔE indicates a lowering of the reaction barrier, and a positive sign corresponds to its increase.

From Table 4 one can see that the solvation of sulfenyl chloride **1** promotes the reaction in all cases with the exception of solvation at the chlorine atom (mode of solvation **1g**), as in this case compound **1** is solvated more strongly than is transition state **10**.

The major reaction path for the reaction **1** ⟶ **10** is **1f** ⟶ **10f** (the sulfur atom is solvated). It gives the most significant decrease in the reaction barrier. This mode of solvation of substrate **1** is predominant since it results in the largest energy gain: −3.203 eV (see Table 3). The reaction **1a** ⟶ **10g** with the F^- anion migration from C(1) to Cl(19) during the chlorine-atom transfer is also possible. However, it is less probable than the previously mentioned process, because of the low gain in energy on solvation of system **1a** (−1.672 eV, see Table 3), and the necessity of the F^- anion migration.

The **1b** and **1c** modes of solvation cannot initiate direct reaction at all, because they do not correspond to any possible mode of solvation of transition state **10**, therefore the solvation particle will have to leave the solvated molecule during the chlorine-atom transfer, thus making such a process energetically unfavourable. The **1d** mode of solvation would produce only a small decrease of the reaction barrier and there is but a small probability of its contributing to the reaction process.

Let us consider now the reaction **2** ⟶ **10**. From Table 4 we can see that solvation of thione **2** only at the C(2) atom (mode of solvation **2d**) decreases the reaction barrier, whereas solvation at all other centres increases the reaction barrier. Therefore, there is only one reaction path for the reverse reaction, namely the process **2d** ⟶ **10d**. The **2c** mode of solvation was not included in Table 4 because it cannot directly go to one of the modes of solvation of transition state **10**.

Comparison of the role of the nucleophilic solvent for the direct (**1** ⟶ **2**) and the reverse (**2** ⟶ **1**) reactions led to the following conclusions:

(i) Solvation brings different reaction pathways for the direct and reverse reactions, which are characterized by different modes of solvation for the initial and the final states of the reactions. The **1** ⟶ **2** process involves solvation at the sulfur atom, while the reaction **2** ⟶ **1** solvation occurs at the C(2) atom;

(ii) Solvation provides greater assistance to the direct (**1** ⟶ **2**) than to the reverse reaction (**2** ⟶ **1**). In the case of compound **1** the reaction starts from mode of solvation **1f**, which has a maximum concentration in the solution and gives a maximum decrease of the reaction barrier. The reverse reaction, starting from thione **2d**, gives a maximum decrease of the reaction barrier too, but the **2d** mode of solvation will be at low concentration in the solution, since its solvation energy is very small.

It is our belief that different solvation assistances for the direct and reverse reactions, as well as a higher thermodynamic stability for thione **2** as compared with that of sulfenyl chloride **1**, are the most important reasons for the smaller concentration of sulfenyl chloride **1** than that of thione **2** at the equilibrium (see Table 1). The concentration of compound **1** and **2** at equilibrium depends on the nature of the solvent, not only on the thermodynamic stability of compounds **1** and **2**.

Experimental

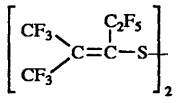
^{19}F and ^1H NMR spectra were obtained with a Bruker AC-200 spectrometer (188 and 200 MHz, respectively), with CF_3CO_2H and $SiMe_4$ as external standards. IR spectra were measured on a Zeiss UR-20 spectrophotometer. Mass spectra were measured on a VG 7070E instrument operating in the EI mode at 70 eV, with a capillary column OV-101 (25 m). The values for *m/z*, relative intensity (%) and proposed assignment for ^{32}S and ^{35}Cl isotopes are given. The purity of the compounds was monitored by GLC on a LKhM-8 MD (model 3) chromatograph using a column (3 m × 4 mm) packed with 20% QF on Chromaton.

Perfluoro-2-methylpent-2-ene-3-sulfenyl chloride **1** with isotopically labelled chlorine (^{36}Cl) was prepared by bubbling of radioactive chlorine ($^{36}Cl_2$) through perfluoro-2-methylpent-2-ene-3-thiol **3**, by analogy to ref. 5. $^{36}Cl_2$ Was obtained according to the method in ref. 14. Radioactivity measurements were performed by using the liquid scintillator counter 'Mark-III.'

Reaction of perfluoro-2-methylpent-2-ene-3-sulfenyl chloride 1 with PhCN

Absolute PhCN (4 cm^3) was added to stirred compound **1**[15] (1.58 g, 4.5 mmol) at 20 °C. After 10 min the mixture contained substrate (28% recovery) and 2-chloroperfluoro-2-methylpentane-3-thione **2** (72%; monitored by ^{19}F NMR spectro-

scopy). After 4 h the volatile products were collected under reduced pressure (0.5 mmHg) in a trap (−78 °C). A mixture (1.39 g, 88.0%) was obtained, containing substrate **1** (26% recovery) and thione **2** (74%; ^{19}F NMR analysis[3,4]). In the residue, trace quantities of bis(perfluoro-1-ethyl-2-methylprop-1-enyl) disulfide **11**[15,¶] were found, whose mass spectrum was identical with that of an authentic sample. For disulfide **11**: *m/z* (EI, 70 eV) 626 (M^+, 21%) 313 ($C_6F_{11}S^+$, 100), 213 ($C_4F_7S^+$, 6), 175 ($C_4F_5S^+$, 26), 163 ($C_3F_5S^+$, 32), 113 ($C_2F_3S^+$, 9) and 69 (CF_3^+, 52). Distillation of the volatile products collected in the trap (−78 °C) gave the same mixture (0.95 g, 60.1%), bp 109–115 °C.



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Reaction of sulfenyl chloride 1 with LiCl in PhCN

(*a*) Compound **1** (2.23 g, 6.4 mmol) was added dropwise at 20 °C to a stirred mixture of dry LiCl (0.44 g, 10.4 mmol) and abs. PhCN (6 cm^3). The mixture was stirred for 30 min and then evaporated at 20 °C under reduced pressure (0.5 mmHg), collecting the volatile products in a trap (−78 °C). A mixture (1.5 g, 67.3%) was obtained, containing substrate **1** (17%) and thione **2** (83%; ^{19}F NMR analysis). The lower (fluoroorganic) layer of the residue was separated to give a mixture (0.28 g), 56% of which was disulfide **11** (according to GLC and ^{19}F NMR spectroscopy), which was identical with an authentic sample.[15] This mixture therefore contains compound **11** to the extent of 0.16 g, which accounts for a yield of 8% from the starting sulfenyl chloride **1**. Distillation of the volatile products collected in the trap (−78 °C) gave the same mixture **1**:**2** (1.0 g, 44.8%), bp 109–115 °C.

(*b*) By use of an analogous procedure, compound **1** (2.13 g, 6.1 mmol) and dry LiCl (0.44 g, 10.4 mmol) in abs. PhCN (6 cm^3) gave, after 1 h, a volatile product (1.48 g, 69.5%) as a mixture of substrate **1** (17%) and thione **2** (83%). Distillation gave the same mixture (1.14 g, 53.5%), bp 109–115 °C. A mixture of fluoroorganic products (0.33 g) was isolated from the residue, 43% of which was found to be the disulfide **11**. This mixture therefore contains disulfide **11** to the extent of 0.14 g, which accounts for 7.4% of the starting sulfenyl chloride **1**.

Reaction of sulfenyl chloride 1 with CsF in PhCN

Compound **1** (2.55 g, 7.3 mmol) was added dropwise to a stirred mixture of well dried CsF (1.2 g, 7.9 mmol) in abs. PhCN (4 cm^3). After complete addition, the mixture was stirred for 1.5 h, then evaporated at 20 °C under reduced pressure (0.5 mmHg), collecting the volatile products in a trap (−78 °C). A mixture (1.79 g, 70.2%) was obtained, containing compound **1** (15% recovery) and thione **2** (85%; ^{19}F NMR analysis). Distillation gave the same mixture (1.23 g, 48.2%), bp 109–115 °C.

Reaction of sulfenyl chloride 1 with AcOH

A mixture of compound **1** and freshly distilled glacial acetic acid was sealed in a glass ampoule and was kept for 17 h at 20 °C. The reaction mixture was found to consist of substrate **1** (43% recovery) and thione **2** (57%; ^{19}F NMR analysis).

Reaction of perfluoro-2-methylpent-2-en-3-yl thiocyanate 5 with CsF in PhCN

A mixture of compound **5**[7] (3.5 g, 10.3 mmol), well dried CsF (0.5 g, 3.3 mmol) and abs. PhCN (5 cm^3) was stirred at room temp. for 2 h and then evaporated at 20 °C under reduced pressure (1 mmHg), collecting the volatile products in a trap (−78 °C). A mixture (1.63 g) was obtained, containing (according to ^{19}F NMR spectroscopy) perfluoro-2-methylpent-2-en-3-yl isothiocyanate **6**, perfluoro-2-methylpent-2-ene **7** and 2*H*-perfluoro-2-methylpentane **8**[‖] with the proportions 1:1:0.9, respectively. The ^{19}F NMR spectra were in good agreement with those published in ref. 7 for **6** and in ref. 17 for compounds **7** and **8**.

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¶ The formation of compound **11** may be explained by the parallel process of reduction of sulfenyl chloride **1** resulting from single-electron transfer under the reaction conditions. The amount of disulfide **11** formed in the isomerization varies from trace quantities to a few percent (see the experiment below).

‖ The presence of compound **8** is readily explained by the addition of HF to the double bond of compound **7** as reported in ref. 16.

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