Reaction of perfluoro-2-methylpent-2-en-3-yl isothiocyanate with ethyl and isopropyl alcohols

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Perfluoro-2-methylpent-2-en-3-yl isothiocyanate reacts with ethyl or isopropyl alcohols in the presence of NEt_3 to give derivatives of 4,5-dihydrothiazole and ethoxy(ethylthio)methylene-(1,1,1,4,4,5,5,5-octafluoro-2-trifluoromethylpent-2-en-3-yl)amine and isopropoxy(isopropylthio)methylene-(1,1,1,4,4,5,5,5-octafluoro-2-trifluoromethylpent-2-en-3-yl)amine, respectively. Heating of ethyl or isopropyl *N*-(perfluoro-2-methyl-2*H*-pentylidene-3-amino)thiocarbamate with potassium carbonate in DMF yields the same products plus 3-tetrafluoroethylidene-5,5-bis(trifluoromethyl)thiazolidin-2-one. The structure of the latter was confirmed by X-ray diffraction analysis. The IR spectroscopy data for this compound in solution (CCl_4) and in the solid state (KBr) suggest the formation of the intermolecular NH...O=C hydrogen bond between the NH group and the oxygen atom of the heterocycle.

Key words: perfluoro-2-methylpent-2-en-3-yl isothiocyanate, NMR spectroscopy, nucleophilic addition and intramolecular cyclization, derivatives of 4,5-dihydrothiazole, alkoxy(alkylthio)methylene-(1,1,1,4,4,5,5,5-octafluoro-2-trifluoromethylpent-2-en-3-yl)amines; 3-tetrafluoroethylidene-5,5-bis(trifluoromethyl)thiazolidin-2-one, X-ray diffraction analysis, intermolecular hydrogen bond, IR spectra, alkyl thiocarbamates.

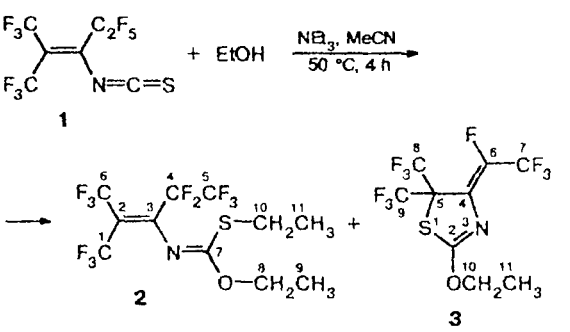
An important aspect of the chemistry of fluorine-containing compounds is extended studies in the field of fluorine-containing heterocylic compounds. Some of them have been found to be biologically active, in particular as pesticides.[1] Of special importance are heterocylic compounds with perfluoroalkyl groups. Their synthesis is based on derivatives of internal perfluorolefins and reactions of intramolecular nucleophilic cyclization yielding heterocylic systems.[2]

Earlier, perfluoroalkyl derivatives of 6*H*-1,3-thiazine and 4,5-dihydrothiazole have been synthesized by the reaction of perfluoro-2-methylpent-2-en-3-yl isothiocyanate (**1**) with secondary amines[3–6] and *C*-nucleophiles.[7,8] Using derivatives of internal perfluorolefins containing an N=C=S group linked directly to the double bond and capable of reacting with nucleophilic agents we have studied other mononucleophilic agents, *e.g.*, *O*-nucleophiles. It has been shown[9] that the action of alcohols on compound **1** results in derivatives of alkyl thiocarbamates, 1,4-addition products.

In continuation of these studies, the present work is devoted to more detailed investigations of the reaction of compound **1** with ethyl and isopropyl alcohols under different conditions, including interaction in the presence of bases (triethylamine and potassium carbonate).

It was found that compound **1** reacts smoothly with ethanol in the presence of triethylamine in acetonitrile to give compounds **2** and **3** (Scheme 1).

Scheme 1



A more complex picture is observed in the reaction of compound **1** with isopropyl alcohol in the presence of triethylamine. In this case, there was obtained a mixture of products where two derivatives of dihydrothiazole (compounds **4** and **5**) and compound **6** are the main ones (Scheme 2).

Apparently, the reaction of **1** with these alcohols begins with an attack of *O*-nucleophile at the C atom of the isothiocyanate group to produce anion **A**, whose further transformations can follow several pathways. According to one pathway, intramolecular nucleophilic cyclization involving the *S*-nucleophilic center and the double C=C bond yields 2-alkoxyderivatives of 4,5-di-

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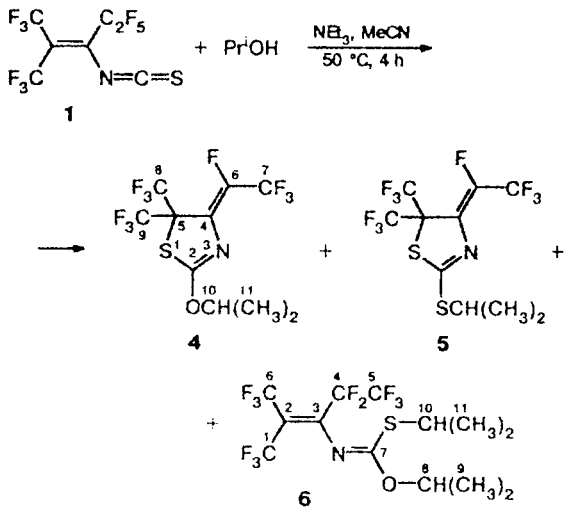
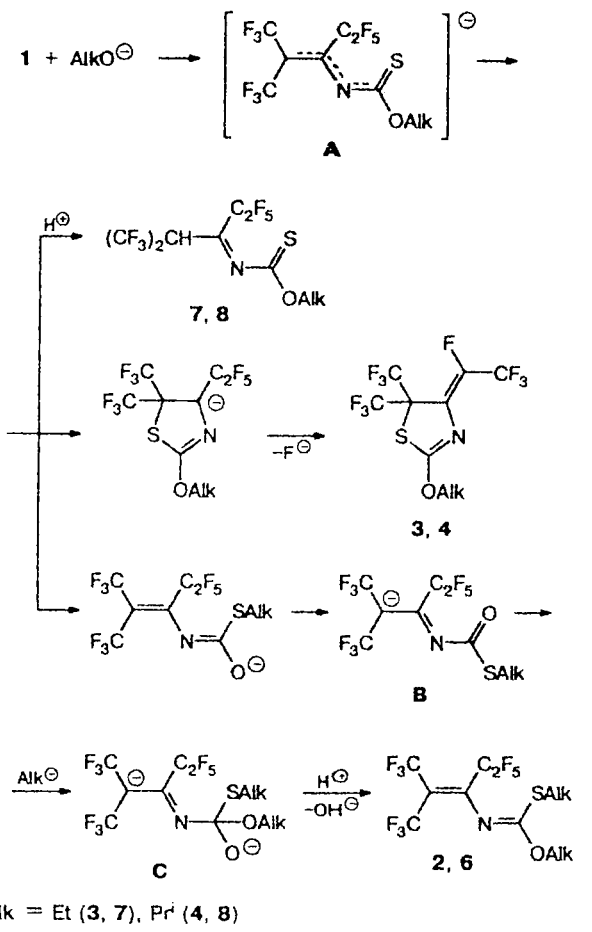
Scheme 2



Scheme 3



Alk = Et (**3**, **7**), Pr^i (**4**, **8**)

hydrothiazole (compounds **3** and **4**). Another pathway, because of migration of ethyl or propyl cations towards the negatively charged S atom, results in anion **B**. A subsequent attack of the alkoxide anion at the C=O group of anion **B** leads to the intermediate anion **C**, which, upon elimination of the OH^- anion, is transformed into compounds **2** and **6**. It cannot be excluded that the $AlkS^-$ anion is also detached from anion **C**, which makes it capable of attacking the C atom of the isothiocyanate group of the initial compound **1** to give compound **5**.

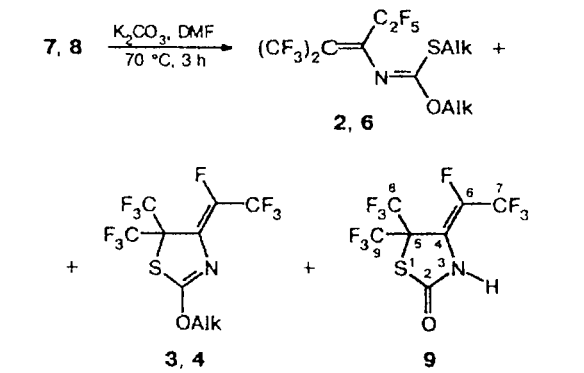
The reaction of the protons present in the system with anions **A** might also yield compounds **7** and **8**. Thus, one can assume that the action of bases on compounds **7** and **8** should result in the same products as the reaction of compound **1** with alcohols in the presence of triethylamine (Scheme 3).

To check this assumption, we obtained compounds **7** and **8** (for procedure see Ref. 9). It turned out that the action of potassium carbonate in DMF on compounds **7** and **8** affords mixtures of compounds where compound **9**, along with expected **2** (**6**) and **3** (**4**), was isolated in both the reactions (Scheme 4).

Earlier, compound **9** was obtained upon hydrolysis of compound **1**. In our case, its formation suggests cleavage of the O—Alk bond in compounds **7** and **8** and generation of the alkyl cation, which can react with anion **A** to give compounds **2** and **6**.

According to X-ray data, the thiazolidine fragment in the molecule **9** is nearly planar (Fig. 1), *viz.*, the S(1), C(2), N(3), C(4), C(5), C(6), and O(2) atoms lie in the same plane within ±0.085(2) Å. The bond lengths of this fragment, except the C(2)—N(3) and N(3)—C(4) bonds, correspond to the known mean values.[14] That the C(2)—N(3) and N(3)—C(4) bond lengths (see Fig. 1) are close to 1.372(16) Å (the mean value for 1*H*-pyrrole derivatives[14]) suggests a conjugation between the double

Scheme 4



bonds of the molecule (for comparison, the mean C—N bond length in tetrahydropyrrole is equal to 1.475(16) Å). We did not find compounds containing the 2-oxo-4-methylenethiazolidine fragment in the Cambridge Structural Data Bank.[15] However, it contains the structural data for compounds with the 2-oxo-5-methylene-

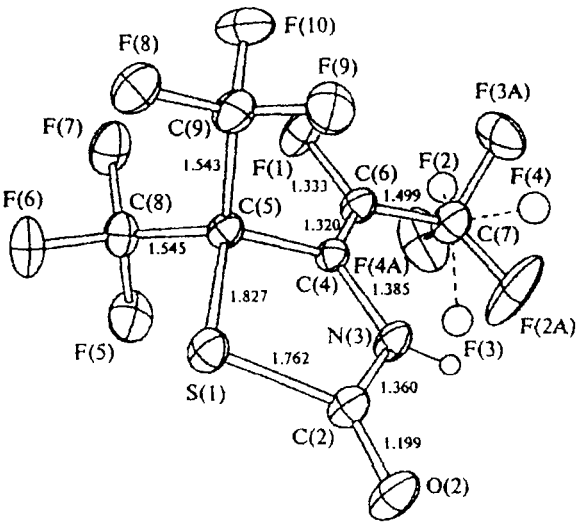


Fig. 1. The structure and selected bond lengths (the error 0.004—0.009 Å) of molecule **9** according to X-ray diffraction analysis.

tetrahydropyrrole fragment, and the geometry of the O=C—NH—C=C fragment we established is close, for example, to the corresponding data for a chloroform solvate of 3,3-dimethyl-2,3-dihydrobilatriene-abc.[16] In crystal, the molecules **9** form centrosymmetric dimers through the N(3)—H...O(2) hydrogen bonds (N(3)...O(2) 2.88(4), N(3)—H 0.80(4), H...O(2) 2.11(4) Å, and N(3)—H...O(2) 160(4)°). The shortened O(2)...F(2A) contact (2.722 Å) of the fluorine atom of the disordered CF_3 group should also be noted. A dimer-shape structure occurs in the crystal of the molecule **9** owing to the intermolecular NH...C=O hydrogen bond between the NH group and the oxygen atom of the C=O group of another molecule (see Fig. 1). The data from X-ray diffraction analysis suggest the *E*-configuration of the ethylidene fragment.

The presence of the hydrogen bond in the centrosymmetric dimers of compound **9** in the crystalline state can be detected by IR spectroscopy. Thus, the IR spectrum of a solid sample of compound **9** in KBr (Fig. 2, spectrum *1*) exhibits a set of bands in the range 3000—3500 cm^{-1} that can be assigned to the vibration of both "free" N—H bond (3429 cm^{-1}, the free NH group of the *trans*-isomer and 3249 cm^{-1}, the free NH group of the *cis*-isomer) and the N—H bond with the intermolecular hydrogen bond (3128 cm^{-1}, bonded NH group of the *cis*-isomer). To assign the vibrational bands of the NH bonds, we studied the IR spectra of solutions of compound **9** in CCl_4 at different concentrations (0.25, 0.11, and 0.026 mol L^{-1}) (see Fig. 2, spectra *2*—*4*). In the vibrational spectrum of a dilute solution of compound **9** in CCl_4 (C = 0.026 mol L^{-1}, spectrum *4*), the two NH absorption bands observed can be assigned to the *cis*-isomer [stretching vibrations of the free (3429 cm^{-1}) and bonded (3254 cm^{-1}) NH groups of the *cis*-configuration of the centrosymmetric dimers of compound **9**, respectively; the frequencies of the NH bond stretching vibrations should decrease upon formation of a hydrogen bond[10]]. However, the spectra of solutions of compound **9** in CCl_4 (C = 0.25 and 0.11 mol L^{-1}, see Fig. 2, spectra *2* and *3*) exhibit in

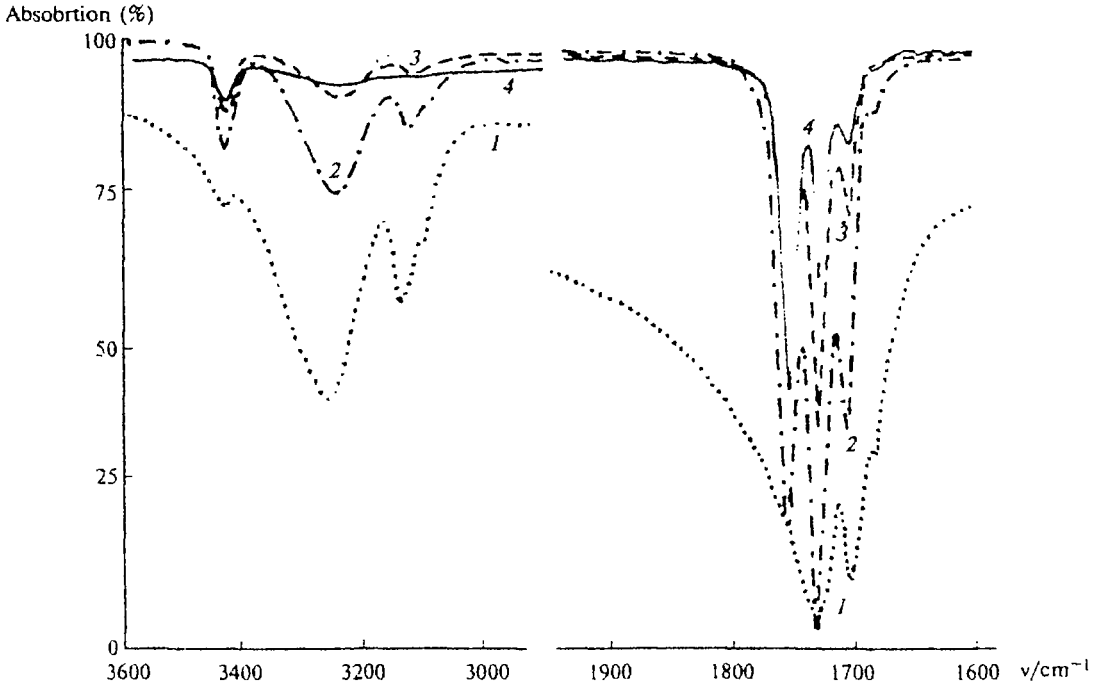
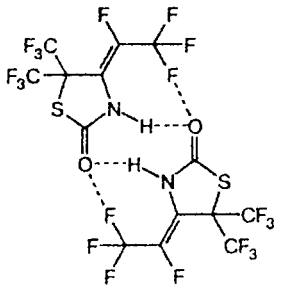


Fig. 2. The IR spectra of compound **9** in KBr (*1*) and CCl_4 (C = 0.25 (*2*), 0.11 (*3*), and 0.26 (*4*) mol L^{-1}).

this frequency range (3000—3500 cm^{-1}) not only bands at 3429 and 3249 cm^{-1} but also an absorption vibrational band at 3128 cm^{-1}, which suggests other intermolecular interactions between the atoms in the cyclic dimers of compound **9** (see Fig. 2, spectrum *2*). As the concentration of the compound in CCl_4 increases from 0.026 to 0.25 mol L^{-1}, the intensity of the vibrational bands of the NH group at 3249 and 3128 cm^{-1} begins to increase, the latter virtually disappearing in a dilute (C = 0.026 mol L^{-1}) solution in CCl_4. This may be explained by the presence of a molecular association formed by the F...O=C bond between the oxygen atom and fluorine of the CF_3 group (^{2A}F) (*e.g.*, structure **D**). This is also indicated by X-ray data.



D

The conjugation between the double C=C and C=O bonds in compound **9** occurs through the NH group. In accordance with this, the formation of the intermolecular NH...O=C hydrogen bond has to influence the stretching vibrations of the C=C and C=O bonds in the range 1700—1800 cm^{-1}. Thus, for a dilute solution of compound **9** in CCl_4, there are observed two bands, which can be attributed to the antisymmetrical (1705 cm^{-1}) and symmetrical (1730 cm^{-1}) stretching vibrations of the C=C bond. Along with these bands, there is an intense absorption band at 1753 cm^{-1}, which corresponds to the stretching vibrations of the C=O bond. As the concentration of compound **9** in CCl_4 increases, the vibrational frequencies of these groups remain unchanged, but their intensity sharply changes, which is probably due to the formation of the intermolecular hydrogen bond. In this case, an increase in the conjugation in the C=C—NH—O=C fragment leads to a decrease in the stretching vibration frequencies of the system (1753 → 1730 and 1730 → 1705 cm^{-1}). The picture observed in the IR spectra of compound **9** in KBr (see Fig. 2, spectrum *1*) is much like that in CCl_4 (C = 0.25 mol L^{-1}, see Fig. 2, spectrum *2*), which allows interpreting these spectra with consideration of X-ray data.

The structures of the compounds obtained were confirmed by data from IR and ^1H, ^{13}C, and ^{19}F NMR spectroscopy and mass spectrometry (Table 1). Analysis of the NMR spectra shows that they follow the same regularities for shielding the nuclei and have the same spin-spin coupling constant values observed earlier for similar compounds. The positions of the F and CF_3 substituents at the C=C double bond in compounds **3**, **4**, **5**, and **9** seem to be determined by steric factors. It should be noted that the following spin-spin coupling constant values for the fluorine atoms of the substituents at the C=C double bond are observed in the ^{19}F NMR spectra of these compounds: CF_3 (doublet, J_{FF} = 8 Hz, splitting on the F atom at this bond), *CF* (quartet (J_{FF} ~ 7—8 Hz, interaction with the fluorine atoms of CF_3 in position 7) of septets (J_{FF} ~ 22—25 Hz, interaction with the fluorine atoms of two CF_3 groups in position 5). Insofar as the C atom in position 5 is bonded with two CF_3 groups, less strained is the isomer with the *E*-ethylidene fragment. It is worthy of note that the similar arrangement of the F atom at the double bond in 2-aminoperfluoro-4,4-dimethyl-5-ethylidenedihydrothiazole was confirmed by X-ray analysis.[11,12]

Table 1. The atomic coordinates (×10^4) and equivalent isotropic thermal factors (×10^3) for compound **9**

Atom	*x/a*	*y/b*	*z/c*	U_{eq}/Å^2
S(1)	3722(1)	3741(1)	1655(1)	53(1)
C(2)	4272(5)	1915(4)	971(3)	50(1)
N(3)	5990(4)	751(3)	1433(3)	50(1)
C(4)	7063(5)	1152(3)	2275(3)	41(1)
C(5)	5831(4)	2848(3)	2701(3)	42(1)
C(6)	8883(5)	196(4)	2668(3)	51(1)
C(7)	10155(6)	−1483(5)	2331(4)	65(1)
C(8)	7221(5)	4063(4)	2441(4)	55(1)
C(9)	4684(6)	2668(4)	4171(4)	58(1)
O(2)	3217(4)	1762(3)	219(3)	71(1)
F(1)	9840(4)	659(3)	3477(3)	83(1)
F(2)[a]	11946(19)	−1942(16)	2582(18)	208(6)
F(2A)[b]	9408(12)	−2058(8)	1573(10)	163(3)
F(3)[a]	10447(17)	−1390(9)	1006(8)	94(3)
F(3A)[b]	10402(10)	−2565(5)	3437(5)	99(2)
F(4)[a]	8997(21)	−2455(10)	2681(13)	136(5)
F(4A)[b]	12164(9)	−1539(7)	1835(7)	124(3)
F(5)	8486(4)	3967(3)	1257(3)	83(1)
F(6)	5968(4)	5598(2)	2433(3)	80(1)
F(7)	8448(4)	3817(3)	3348(3)	81(1)
F(8)	3426(4)	4101(3)	4496(2)	83(1)
F(9)	3432(4)	1668(3)	4341(2)	79(1)
F(10)	6049(4)	2038(3)	5026(2)	86(1)
H(3)	6405(60)	−84(46)	1105(39)	63(11)

[a] The occupancy of the position is equal to 0.370(6).
[b] The occupancy of the position is equal to 0.630(6).

Experimental

^1H, ^{13}C, and ^{19}F NMR spectra were recorded on a Bruker WP 200 SY spectrometer (200, 50, and 188 MHz, respectively, spin-spin coupling constant J_{CH} was not measured) with respect to tetramethylsilane and C_6F_6 as the internal standards. The IR spectra of new compounds were recorded on an IFS66 IR-Fourier-spectrometer (Bruker) (CCl_4, KBr). Mass spectra were obtained on a VG 707 OE GC-/MS spectrometer (ionizing radiation energy 70 eV). The m/z, assumed assignments, and intensity (%) values are given. Mixtures were separated by preparative GLC on a Prepakhrom II-2 chromatograph (Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences), 15%—25% SKTFT-50 on Chromaton W, fraction 0.315—0.4 mm, evaporator temperature 220 °C, column temperature 175 °C, column 5600×14 mm, p 1.2 atm, nitrogen as carrier gas, flow velocity 200 mL min^{-1}.

Table 2. The mass spectrometry data for the compounds obtained

Compound	m/z (I_{rel} (%))
2	413 $[M]^+$ (5.52), 394 $[M-F]^+$ (2.53), 384 $[M-C_2H_5]^+$ (14.30), 368 $[M-OC_2H_5]^+$ (1.26), 356 $[M-C-OC_2H_5]^+$ (28.60), 294 $[M-C_2F_5]^+$ (11.20), 119 $[C_2F_5]^+$ (1.69), 69 $[CF_3]^+$ (5.33), 61 $[SC_2H_5]^+$ (13.98), 45 $[OC_2H_5]^+$ (1.81), 29 $[C_2H_5]^+$ (100)
4	379 $[M]^+$ (5.40), 337 $[M-CH_3C=CH_2]^+$ (58.82), 320 $[M-OCH(CH_3)_2]^+$ (0.63), 270 $[M-OCH(CH_3)_2-CF_2]^+$ (1.82), 268 $[M-CH_3C=CH_2,CF_3]^+$ (32.89), 240 $[M-CH_3C=CH_2,CF_3,CO]^+$ (9.44), 220 $[M-OCH(CH_3)_2$, $[CF_2=CF_2]^+$ (4.87), 119 $[C_2F_5]^+$ (2.76), 100 $[CF_2=CF_2]^+$ (1.43), 69 $[CF_3]^+$ (11.11), 60 $[SCN]^+$ (0.61), 43 $[CH(CH_3)_2]^+$ (100), 41 $[CH_3C=CH_2]^+$ (32.05)
8	399 $[M]^+$ (0.47), 358 $[M-C(CH_3)CH_2]^+$ (4.88), 357 $[M-C(CH_3)_2]^+$ (8.18), 340 $[M-OCH(CH_3)_2]^+$ (10.74), 119 $[C_2F_5]^+$ (3.63), 69 $[CF_3]^+$ (16.33), 61 $[HSC=O]^+$ (10.18), 59 $[HOC(CH_3)_2]^+$ (60.07), 43 $[O=C-CH_3]^+$ (100), 41 $(O=C=CH]^+$ (30.5)
9	337 $[M]^+$ (100), 318 $[M-F]^+$ (16.78), 309 $[M-CO]^+$ (8.34), 268 $[M-CF_3]^+$ (43.67), 248 $[M-CF_3,HF]^+$ (10.82), 240 $[M-CO-CF_3]^+$ (39.66), 220 $[M-CO-CF_3-HF]^+$ (26.41), 198 (16.59), 138 $[C_2F_6]^+$ (15.36), 119 $[C_2F_5]^+$ (3.81), 100 $[CF_2=CF_2]^+$ (13.74), 70 $[COS]^+$ (4.72), 69 $[CF_3]^+$ (46.40), 28 $[CO]^+$ (26.15)

The three-dimensional structure of the monocrystal of molecule **9** was determined on a Syntex $P2_1$ diffractometer (Cu-Kα-radiation, graphite monochromator). In the experiment, the monocrystal was placed into a polyethylene capillary to prevent its destruction. The crystals of compound **9** are triclinic, a = 6.585(1), b = 8.632(1), c = 10.331(2) Å, α = 78.29(1), β = 77.45(1), γ = 71.90(1)°, V = 539.0(2) Å^3, space group $P\bar{1}$, Z = 2, $C_7HF_{10}NOS$, μ = 4.103 mm^{-1}, d_{calc} = 2.077 g cm^{-3}. The intensity data from 1607 independent reflections with $2\theta < 120°$ were measured by $\theta/2\theta$ scanning. A correction was made for absorption on the crystal faces (transmission 0.22—0.69). The structure was solved by the direct method with the SHELX-86 program. The final least-squares refinement of the structural parameters was performed in the full-matrix anisotropic (isotropic for the H atom) approximation with the SHELXL-93 program to wR_2 = 0.1418 for all F^2 (R = 0.0480 for 1354 $F_0 > 4\sigma$, 214 parameters). The coordinates and equivalent thermal factors of nonhydrogen atoms are listed in Table 1. Because of the high thermal anisotropy of the fluorine atoms of the CF_3 group at the C(7) atom, the refinement used a model where each fluorine atom in this group occupies two positions.

The reaction of isothiocyanate 1 with ethanol and Et_3N. A mixture of compound **1** (6.8 g, 0.02 mol) (obtained according to the known procedure[13]), ethanol (0.8 g, 0.02 mol), and triethylamine (2.1 g, 0.02 mol) in 15 mL of acetonitrile was heated at 50 °C for 4 h, poured into water, and extracted with ether. The ethereal extract was dried with $CaCl_2$. The solvent was removed on a rotary evaporator, and the residue was distilled. The fraction (5.4 g) with b.p. 56—59 °C (0.4 Torr) was isolated (**2** (35.6%), **3** (18.9%), **1** (14%), and unidentified products (31.5%) (GLC and ^{19}F NMR)). Compounds **2** and **3** were isolated by preparative GLC.

Ethoxy(ethylthio)methylene-(1,1,1,4,4,5,5,5-octafluoropenten-3-yl)amine (2). Yield 2.8 g (33.8%). IR (5% CCl_4), ν/cm^{-1}: 2980 (C—H); 1680 (C=C); 1640 (C=C); 1450 (N=C); 1350 (N—C); 1180—1240 (C—F).[10] ^1H NMR ($CDCl_3$), δ: 4.34 (q, H(8), J = 7 Hz); 2.95 (q, H(10), J = 7 Hz); 1.34 (t, H(9), J = 7 Hz); 1.30 (t, H(11), J = 7 Hz). ^{13}C NMR ($CDCl_3$), δ: 163.0 (C(7)); 145.6 (C(3), $^2J_{CF}$ = 27.7 Hz); 120.1 (C(1), $^1J_{CF}$ = 276.1 Hz); 119.3 (C(6), $^1J_{CF}$ = 273.5 Hz); 117.0 (C(5), $^1J_{CF}$ = 287.4 Hz; $^2J_{CF}$ = 35.7 Hz); 109.1 (C(4), $^1J_{CF}$ = 264.2 Hz; $^2J_{C-F}$ = 38.2 Hz); 108.9 (C(2), $^2J_{CF}$ = 31.6 Hz); 65.1 (C(10)); 23.8 (C(8)); 12.4 (C(11)); 11.1 (C(9)). ^{19}F NMR ($CDCl_3$), δ: 108.3 (F(1), CF_3); 104.7 (F(6), CF_3); 82.6 (F(5), CF_3); 53.0 (F(4), CF_2). Found, m/z: 413.0314. $C_{11}H_{10}F_{11}NOS$. Calculated, m/z: 413.0307. Found (%): C, 32.02; H, 2.14; F, 50.50; N, 3.33; S, 7.96. Calculated (%): C, 31.96; H, 2.42; F, 50.61; N, 3.39; S, 7.75.

2-Ethoxy-4-(1,2,2,2-tetrafluoroethylidene)-5,5-bis(trifluoromethyl)-4,5-dihydrothiazole (3). Yield 2.2 g (40%), b.p. 60—61 °C (0.2 Torr). ^1H NMR ($CDCl_3$), δ: 4.50 (q, 2 H, CH_2); 1.34 (t, 3 H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 167. (C(2)); 142.7 (C(6), $^2J_{CF}$ = 29.1 Hz); 121.8 (C(8, 9), $^1J_{CF}$ = 282.1 Hz); 119.1 (C(7), $^1J_{CF}$ = 269.5 Hz, $^2J_{CF}$ = 36.5 Hz); 70.1 (C(10)); 63.8 (C(5), $^2J_{CF}$ = 33 Hz); 13.2 (C(11)). ^{19}F NMR ($CDCl_3$), δ: 95.3 (d, 3 F, F(7), J = 7 Hz); 96.1 (d, 6 F, F(8, 9), J = 22 Hz); 23.4 (q of septets, 1 F, F(6), J = 7 and 22 Hz). Found (%): C, 29.96; H, 1.42; F, 51.87; N, 4.04; S, 8.80. $C_9H_5F_{10}NOS$. Calculated (%): C, 29.59; H, 1.37; F, 52.05; N, 3.84; S, 8.77.

The reaction of isothiocyanate 1 with Pr^iOH and Et_3N. A mixture of compound **1** (10.17 g, 0.03 mol), isopropyl alcohol (1.8 g, 0.03 mol), and triethylamine (3.03 g, 0.03 mol) in 20 mL of acetonitrile was stirred at 50 °C for 4 h, cooled, poured into water, and extracted with ether. The ethereal extract was dried with $CaCl_2$. The reaction mixture contained compounds **1**, **4**, **5**, and **6** in the ratio 6.7 : 24.2 : 23.6 : 32.5 and unidentified products (13%) (^{19}F NMR and GLC). The solvent was removed on a rotary evaporator, and the residue was distilled *in vacuo*. The fractions with b.p. 66—70 and 84—95 °C (both 0.5 Torr) were isolated (6 and 4 g, respectively). Preparative GLC was used for isolation of the compounds in the individual state.

2-Isopropoxy-4-(1',2',2',2'-tetrafluoroethylidene)-5,5-bis(trifluoromethyl)-4,5-dihydrothiazole (4). Yield 2.3 g (20%), b.p. 46—47 °C (0.08 Torr). IR (5% CCl_4), ν/cm^{-1}: 2980 (C—H); 1690 (C=C); 1360, 1350 (N=C); 1200—1300 (C—F).[10] ^1H NMR ($CDCl_3$), δ: 5.23 (m, 1 H, C—H); 1.35 (d, 6 H, CH_3). ^{13}C NMR ($CDCl_3$), δ: 167.6 (C(2)); 142.9 (C(6), $^1J_{CF}$ = 262 Hz, $^2J_{CF}$ = 37 Hz); 132 (C(4), $^2J_{CF}$ = 27.9 Hz); 121.9 (C(8, 9), $^1J_{CF}$ = 283.8 Hz); 119.3 (C(7), $^1J_{CF}$ = 273.1 Hz, $^2J_{CF}$ = 37.1 Hz); 79.1 (C(10)); 74.5 (C(5), $^2J_{CF}$ = 32.5 Hz); 19.6 (C(11)). ^{19}F NMR ($CDCl_3$), δ: 95.4 (d, 6 F, F(8, 9), J = 24 Hz); 95.3 (d, 3 F, F(7), J = 10 Hz); 23.5 (q of septets, 1 F, F(6), J = 24 and 10 Hz). Found, m/z: 379.0086. $C_{10}H_7F_{10}NOS$. Calculated, m/z: 379.0088. Found (%): C, 31.00; H, 1.82; F, 50.97; N, 3.54; S, 8.67. Calculated (%): C, 31.66; H, 1.85; F, 50.13; N, 3.69; S, 8.44.

2-Isopropylthio-4-(1,2,2,2-tetrafluoroethylidene)-5,5-bis(trifluoromethyl)-4,5-dihydrothiazole (5). Yield 2.2 g (18%), b.p. 72—73 °C (13 Torr). ^{13}C NMR (CD_2Cl_2), δ: 165.8 (C(2)); 144.3 (C(6), $^1J_{CF}$ = 268.8 Hz, $^2J_{CF}$ = 40.1 Hz); 121.9 (C(8, 9), $^1J_{CF}$ = 238.6 Hz); 123.3 (C(4), $^2J_{CF}$ = 32.1 Hz); 118.3 (C(7), $^1J_{CF}$ = 267.1 Hz, $^2J_{CF}$ = 36.8 Hz); 75.3 (C(5), $^2J_{CF}$ = 29.6 Hz); 40.3 (C(10)); 21.1 (C(11)). ^{19}F NMR

($CDCl_3$), δ: 96.6 (d, 3 F, F(7), J = 7 Hz); 96.5 (d, 6 F, F(8, 9), J = 22 Hz); 25.9 (q of septets, 1 F, F(6), J = 7 and 22 Hz). Found (%): C, 30.52; H, 1.77; F, 47.98; N, 3.32; S, 16.20. $C_{10}H_7F_{10}NS_2$. Calculated (%): C, 30.38; H, 1.77; F, 48.10; N, 3.54; S, 16.20.

Isopropoxy(isopropylthio)methylene-(1,1,1,4,4,5,5,5-octafluoro-2-trifluoromethylpenten-3-yl)amine (6). Yield 3 g (23%), b.p. 69—70 °C (0.5 Torr). IR (CCl_4), ν/cm^{-1}: 3000 (C—H); 1600 (C=C); 1445 (N=C); 1350 (N—C); 1190—1250 (C—F).[10] ^{1}H NMR ($CDCl_3$), δ: 5.25 (septet, 1 H, H(8), J = 6 Hz); 3.75 (septet, 1 H, H(10), J = 7 Hz); 1.19 (d, 6 H, H(9), J = 6 Hz); 1.14 (d, 6 H, H(11), J = 7 Hz). ^{13}C NMR ($CDCl_3$), δ: 161.1 (C(7)); 141.2 (C(3), $^2J_{CF}$ = 28.1 Hz); 119.6 (C(1), $^1J_{CF}$ = 271.7 Hz); 119.5 (C(6), $^1J_{CF}$ = 280.3 Hz); 115.8 (C(5), $^1J_{CF}$ = 286.6 Hz, $^2J_{CF}$ = 35.8 Hz); 108.2 (C(4), $^1J_{CF}$ = 260.5 Hz, $^2J_{CF}$ = 37.3 Hz); 105.2 (C(2), $^2J_{CF}$ = 35.5 Hz); 74.3 (C(8)); 37.6 (C(10)); 18.7 (C(9)); 17.5 (C(11)). ^{19}F NMR ($CDCl_3$), δ: 114.7 (q, 3 F, F(1), J = 12 Hz); 110.6 (qqt, 3 F, F(6), J = 3, 12, and 21 Hz); 82.9 (q, 3 F, F(5), J = 21 Hz); 51.8 (q, 2 F, F(4), J = 3 Hz). Found (%): C, 35.34; H, 3.12; F, 47.36; N, 3.05. $C_{13}H_{14}F_{11}NOS$. Calculated (%): C, 35.37; H, 3.17; F, 47.39; N, 3.17.

Isopropyl *N*-(perfluoro-2-methyl-2*H*-pentylidene-3-amino)-thiocarbamate (8). A mixture of compound **1** (33.9 g, 0.1 mol) and isopropyl alcohol (6 g, 0.1 mol) in 50 mL of acetonitrile was stirred at 50 °C for 4 h, cooled, and poured into water. The organic layer was separated and dried with $MgSO_4$. Distillation gave compound **8** (3 g, 80%), b.p. 67—68 °C (25 Torr). IR (5% CCl_4), ν/cm^{-1}: 2980 (C—H); 1690, 1450 (N—C=S); 1360, 1350 (N—C); 1100—1250 (C—F).[10] ^{1}H NMR ($CDCl_3$), δ: 4.48 (m, 1 H, H(2)); 5.62 (m, 1 H, H(8), J = 6.3 Hz); 1.35 (d, 6 H, H(9, 10), J = 6 Hz). ^{13}C NMR ($CDCl_3$), δ: 192.0 (C(7)); 140 (C(3), $^2J_{CF}$ = 29 Hz); 119.1 (C(1, 6), $^1J_{CF}$ = 285.3 Hz); 116.8 (C(5), $^1J_{CF}$ = 286.8 Hz, $^2J_{CF}$ = 34.9 Hz); 108.9 (C(4), $^1J_{CF}$ = 264.7 Hz; $^2J_{CF}$ = 40 Hz); 77 (C(8)); 50.3 (C(2), $^2J_{CF}$ = 31.6 Hz); 19.3 (C(9, 10)). ^{19}F NMR ($CDCl_3$), δ: 100.1 (6 F, F(1, 6)); 81.9 (3 F, F(5)); 47.8 (2 F, F(4)). Found, m/z: 399.0143. $C_{10}H_8F_{19}NOS$. Calculated, m/z: 399.0150. Found (%): C, 30.21; H, 2.04; F, 52.51; N, 3.24; S, 8.10. Calculated (%): C, 30.07; H, 2.01; F, 52.38; N, 3.51; S, 8.02.

Ethyl *N*-(perfluoro-2-methyl-2*H*-pentylidene-3-amino)thiocarbamate (7). Compound **7** was obtained from compound **1** (20.34 g, 0.06 mol) and ethanol (3.3 g). Yield 19.5 g (84.4%), b.p. 77—78 °C (20 Torr). IR (5% CCl_4), ν/cm^{-1}: 3000 (C—H); 1450 (N=C); 1350 (N—C); 1200—1300 (C—F).[10] ^{1}H NMR ($CDCl_3$), δ: 4.50 (m, 1 H, C—H, H(2)); 4.61 (q, 2 H, CH_2, H(8)); 1.38 (t, 3 H, CH_3, H(9)). ^{13}C NMR ($CDCl_3$), δ: 193.4 (C(7)); 140.8 (C(3), $^2J_{CF}$ = 10 Hz); 120.9 (C(1, 6), $^1J_{CF}$ = 282.3 Hz); 117.8 (C(5), $^1J_{CF}$ = 287 Hz, $^2J_{CF}$ = 34.9 Hz); 109.5 (C(4), $^1J_{CF}$ = 265 Hz, $^2J_{CF}$ = 40.3 Hz); 68.9 (C(8)); 51.0 (C(2), $^2J_{CF}$ = 31.4 Hz); 12.4 (C(9)). ^{19}F NMR ($CDCl_3$), δ: 100.1 (6 F, F(1, 6)); 82 (3 F, F(5)); 47.4 (2 F, F(4)). Found, m/z: 384.9991. $C_9H_6F_{11}NOS$. Calculated, m/z: 384.9994.

The reaction of ester 8 with the base. A mixture of compound **8** (18 g, 0.045 mol) and K_2CO_3 (12.42 g, 0.12 mol) (or triethylamine (9 g, 0.09 mol)) in 60 mL of dry DMF was stirred at 70 °C for 3 h, cooled, worked up with 5% HCl and water, and dried with $MgSO_4$ to give a mixture of compounds **4** and **9** (16.5 g, b.p. 47—52 °C (0.08 Torr). **3-(1,2,2,2-Tetrafluoroethylidene)-5,5-bistrifluoromethylthiazolidin-2-one (9)** was crystallized from this mixture, m.p. 90—91 °C (from hexane). IR (5% CCl_4), ν/cm^{-1}: 1720 (C=O); 1700 (C=C); 1430 (N—C); 1370 (N—C); 1150—1300 (C—F).[10] ^{1}H NMR ($CDCl_3$), δ: 8.50 (N—H). ^{13}C NMR ($CDCl_3$), δ: 163.4 (C(2)); 133.5 (C(6), $^1J_{CF}$ = 250.7 Hz; $^2J_{CF}$ = 41.7 Hz); 121.5 (C(8, 9), $^1J_{CF}$ = 284.2 Hz); 118.9 (C(7), $^1J_{CF}$ = 233.4 Hz, $^2J_{CF}$ = 38.4 Hz); 118.4 (C(4), $^2J_{CF}$ = 30.9 Hz); 65.6 (C(5), $^2J_{CF}$ = 32.8 Hz). ^{19}F NMR ($CDCl_3$), δ: 96.1 (d, 6 F, F(8, 9), J = 25 Hz); 96.0 (d, 3 F, F(7), J = 10 Hz); 12.0 (q of septets, 1 F, F(6), J = 25 and 10 Hz). Found, m/z: 336.9614. $C_7H_1F_{10}NOS$. Calculated, m/z: 336.9619.

Distillation of the residue of this fraction gave compound **4**.

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