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New fused dithiabicyclic compounds from the reaction of *N*,*N*-dialkyl perfluorothioamides with allylmagnesium halides

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ABSTRACT

Allylmagnesium reagents react with *N*,*N*-dialkylperfluorothioamide to give, at low temperature, an adduct stable enough to be trapped. At room temperature, this adduct can evolve by elimination of either a sulfide salt, leading to an iminium intermediate, and then an *N*,*N*-dialkyl-α,α-bis(allyl)-α-perfluoroalkylamine. This process is favoured if an excess of allyl magnesium is used. Alternatively, the adduct eliminates an aminyl moiety giving allyl(perfluoroalkyl)thioketone which is converted in situ into an unprecedented fused bis(perfluoroalkyl) bis(dihydrothiopyrane). A sequence deprotonation of the thioketone – oxidation of the resulting dienethiolate – dimerization of the dienethiyl radical is proposed to rationalize the formation of this unexpected bicyclic compound.

1. Introduction

The chemical reactivity of perfluorodithiocarboxylic acid derivatives with organometallic reagents is different from the one of their non-fluorinated analogues [1]. Perfluorodithioesters react with both alkyl and allyl magnesium and lithium reagents at sulfur [2], with subsequent fluoride elimination, leading to the corresponding perfluoroketene dithioacetal. Similarly perfluorothioamides are converted to *N*,*S*-ketene acetals under reaction with alkyllithium reagents [3,4]. We have reported the preliminary results regarding the reaction of perfluorothioamides with allymagnesium reagents (Scheme 1) [3]. This reaction proceeds, as in non-fluorinated series [5,6], via a carbophilic attack, probably because of the donating character of nitrogen which enhances the coordination of sulfur to magnesium, thus favouring a six member ring transition state. Thioamide **1** reacts cleanly with 1 equivalent of allylmagnesium halide at functional carbon at low temperature to give the thioaminal **3** after trapping of the salt adduct **2** by methyliodide. Compound **3** was transformed into 1-*F*-alkyl-1-amino diene **4** via oxidation to sulfoxide which induced spontaneous elimination of sulfenic acid [3]. We have since more deeply studied the behaviour of the intermediate adduct **2** under various conditions. We report now our complementary results, and in particular the formation of a new type of dithiabicyclic compounds.

2. Results and discussion

In non-fluorinated series, the product obtained after reaction of a thioamide with allylmagnesium halide was reported to be an α,α-diallylamine, the second allylation occurring on an intermediate iminium salt resulting from the elimination of a metal sulfide [5]. Because of the stabilization of the tetrahedral adduct by the withdrawing perfluoroalkyl group, the adduct obtained by nucleophilic allylation in fluorinated series was quantitatively trapped with methyl iodide, even if an excess of allylmagnesium halide was used [3]. We have now observed that bis(allylation) at carbon can occur if the reaction mixture was left to evolve several hours at room temperature under anaerobic conditions. As expected, this process was favoured when reaction was performed with an excess of allylmagnesium halide. Thus, using 3 equivalents of allylmagnesium bromide, thioamide **1b** was converted into the compound **5** in 81% isolated yield (Scheme 2).

On the other hand, unexpected results were observed when the mixture resulting from reaction performed with 1 equivalent of allylmagnesium reagent was directly submitted to a usual aqueous work-up or was left to evolve at −10 °C under air bubbling. After quenching the salt **2a** with water, a new compound **6a** was isolated

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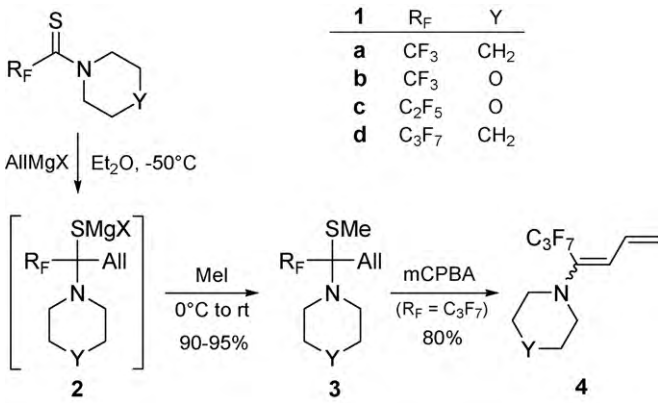
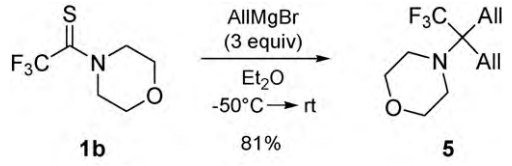
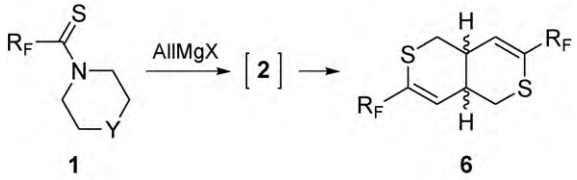


Scheme 1. Reaction of perfluorothioamides with allylmagnesium halide: preliminary results.



Scheme 2. Optimized preparation of the bis(allyl) compound **5**.



Scheme 3. Conversion of adducts **2** into dithiaheterocycles.

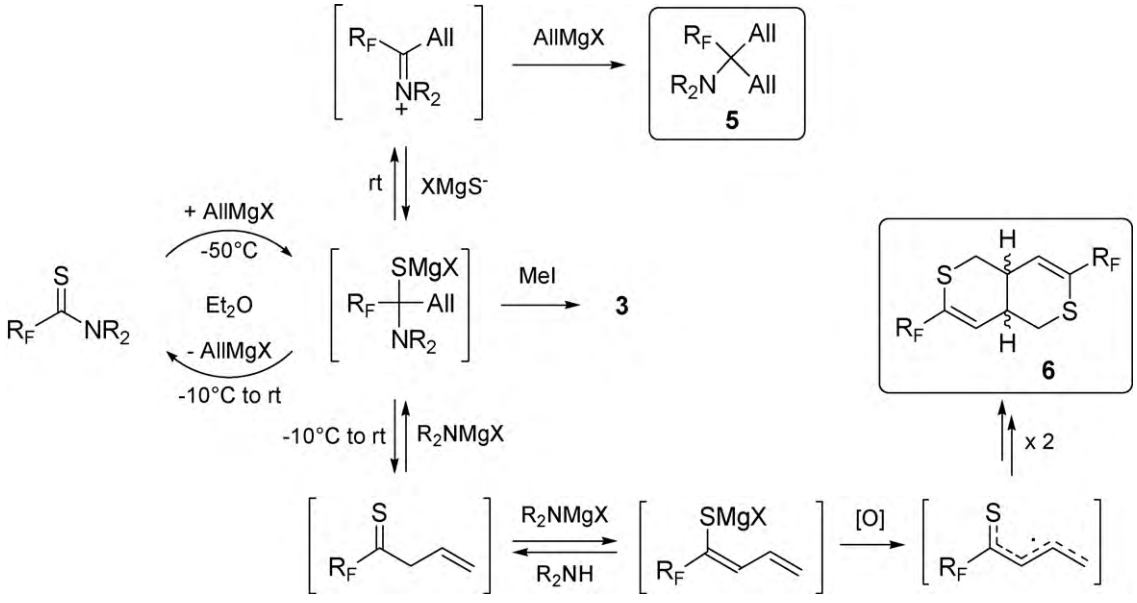
by crystallization in petroleum ether at −18 °C. The same behaviour was observed for piperidine and morpholine derivatives, as well as for various perfluoroalkyl chains (Scheme 3 and Table 1). The structure of compounds proved to be difficult to determine by NMR analysis except that the spectrum seemed to display two spin systems, possibly due to two isomers. Their molecular structure were studied by single-crystal X-ray diffraction (vide infra). This study confirmed the presence of two isomers and disclosed a very unexpected structure, corresponding to an unprecedented fused bis(dihydrothiopyrane). Compounds **6a–d** are yellowish crystalline products, well soluble in most organic solvents. Although they are isolated in 30–35% yields, they constitute the main component according to the NMR monitoring of the reaction mixture.

Table 1
Conversion of thioamides **1** into bicyclic compounds **6**.

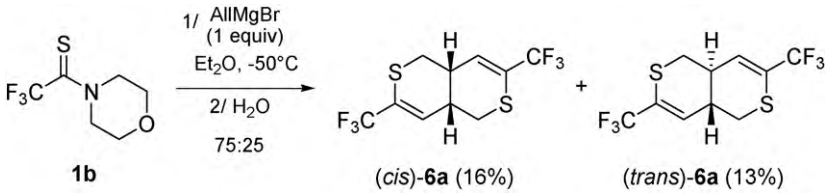
Starting material	R_F	X	Product	Yield (%) (isolated)	dr
1a	CF_3	CH_2	**6a**	30	71/29
1b	CF_3	O	**6a**	35	75/25
1c	C_2F_5	O	**6c**	30	67/33
1d	C_3F_7	CH_2	**6d**	35	56/44

Water seemed to have no role in the formation of compounds **6**, which prompted us to consider that an oxidation process would operate in place of an actual hydrolysis. The fused dihydrodithiopyranes **6** are formally the result of a dehydrodimerization of the thioketone resulting from a classical condensation process. This assumption was corroborated by the following qualitative experiments. The same bicyclic compound was obtained when, after completion of the addition of allylmagnesium chloride, temperature was raised to −10 °C and dry air was bubbled in the reaction medium for 6 h. The same effect was induced when TEMPO [7] was introduced [8].

This set of experimental results allows us to propose the reaction pathway depicted in Scheme 4 to rationalize the formation of different products according to the reaction conditions. The condensation process leading to the thioketone (and/or its enethiol tautomer) releases one equivalent of base, the corresponding amide (or hydroxide under aqueous work-up). Thus, deprotonation occurs to give the dienethiolate [9] which is oxidized into a highly delocalized thiyl radical [10]. A head-to-tail dimerization of this radical yields the final dithiabicyclic product **6**. The radical dimerization may also be viewed as a cascade reaction: addition of thiyl radical–6-exo-trig cyclisation–biradical coupling (Fig. 1).



Scheme 4. Proposed overall reaction pathway.



Scheme 5. Synthesis and separation of (*cis*)-**6a** and (*trans*)-**6a**.

The preferred formation of the bis(allyl) adduct under anaerobic conditions, even when only one equivalent of organometallic reagent was used, may be explained by the reversibility of all reactions in the range −10 °C to room temperature, except for the final steps. Under anaerobic conditions, under such thermodynamic control, all intermediates and the reactants are present and the iminium intermediate may be irreversibly trapped by allylmagnesium reagent. As expected, this trapping is more effective in the presence of an excess of allyl magnesium reagent. Under aerobic conditions, the fast oxidation step draws the equilibrium towards the formation of bicyclic compounds **6**. The low yield of the bicyclic products **6** is probably due to competitive reactions leading to unidentified products: (i) the amine released in the medium can react as base or nucleophile with the intermediate thioketone or the corresponding dienethiol, or with **6**; (ii) self [4 + 2] cycloaddition reactions of unsaturated thioketones and dithioesters were already observed [11]; (iii) unsaturated thiyl radicals were reported to cyclize [12].

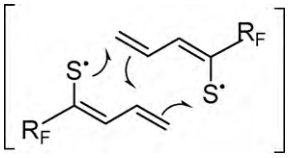


Fig. 1. Cascade mechanism for the dimerization of the dienethiyl radical.

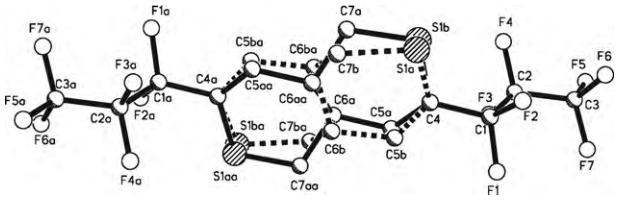


Fig. 2. X-Ray structure of compound 6d (mixture of diastereomers).

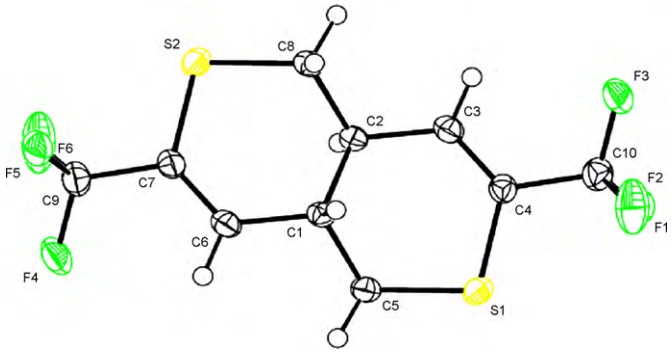


Fig. 3. X-Ray structure of compound 6a (minor isomer).

As mentioned above, the structure of **6** was approached by single-crystal X-ray diffraction analysis. Initially performed on compound **6d** as obtained by aqueous work-up, the analysis showed that the molecule occupies position on the centre of inversion and are disordered over two positions, disclosing that it contains two isomers in the unit cell [13]. The atoms of central bicyclic system (excluding carbons C-4) are disordered over two positions A and B with multiplicity 0.71 and 0.29, respectively. There are no strong distortion and disorder in the perfluoropropyl groups. The perspective view of molecule **6d** is given in Fig. 2. Atoms of position A are connected by solid line and position B by dashed line.

The precise geometry of the central bicyclic core being difficult to determine on such a mixture of diastereomers, we have carefully isolated and separated the two isomers of compound **6a**, from the reaction with trifluorothioacetamide **1b** (Scheme 5). Single crystals of the minor isomer were obtained for X-ray diffraction analysis [13], allowing to assign to him unambiguously the *trans* configuration (Fig. 3).

3. Conclusions

These complementary results confirm that fluorine substitution strongly modifies the electrophilic reactivity of thioamides. In contrast to organolithium reagents, allylmagnesium reacts at low temperature at carbon to give an adduct stable enough to be trapped, or which evolves either by a sulfide salt or an amide elimination at higher temperature. The chemoselectivity strongly depends on the reaction conditions. The results were rationalized assuming a reaction under thermodynamic control under anaerobic conditions, where an α,α-bis(allyl)-α-pefluoroalkylamine was formed in a process similar to the one reported for non-fluorinated analogues. The classical condensation process (amide elimination) leads to a thioketone converted in situ into a thioenolate which is easily oxidized under aerobic conditions. The resulting stabilized thiyl radical dimerizes to give a new type of fused bis(dihydrothiopyrane).

4. Experimental

4.1. General remarks

Diethyl ether was distilled from sodium-benzophenone. Silicagel (Macherey-Nagel GmbH & Co KG – 40–63 μm, ASTM for column chromatography) was used for flash chromatography. Melting points (mp) were determined on a Tottoli apparatus and were uncorrected. NMR spectra were recorded in $CDCl_3$, at frequencies of 250 or 500 MHz for ^1H, 235.3 MHz for ^{19}F and 62.9 or 125.8 MHz for ^{13}C NMR. Chemical shifts (δ) are reported in ppm relative to TMS for ^1H and ^{13}C NMR spectra and to $CFCl_3$ for ^{19}F NMR spectra. In the ^{13}C NMR data, reported signal multiplicities are related to C–F coupling. The following abbreviations are used to indicate the multiplicities: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br s (broad singlet). The progress of all reactions was monitored by ^{19}F NMR spectroscopy. Elemental

analysis were performed on a Perkin-Elmer CHN 2400 apparatus and analyses fell within ±0.4% of the calculated values. MS data were obtained on a Trace MS Thermoquest apparatus (GC–MS) at 70 eV in the electron impact mode.

4.2. Preparation of 2-allyl-2-morpholino-1,1,1-trifluoropent-4-ene (5)

To a solution of thioamide **1b** (150 mg, 0.75 mmol) in diethyl ether (5 mL) was added at −50 °C and under Ar, allylmagnesium bromide (0.87 M in Et_2O, 2.59 mL, 2.26 mmol, 3 equiv.). After 2 h of stirring at −50 °C and 5 h at room temperature, the reaction mixture was quenched with sat aq NH_4Cl and brine. The organic layer was dried with $MgSO_4$ and concentrated under reduced pressure. Chromatography of the residue on SiO_2 (PE:Et_2O 6:1 → 1:1) afforded the bisallyladduct **5** (151 mg, 81%) as a colourless oil. ^{19}F NMR ($CDCl_3$): δ −69.3 (s, CF_3). ^1H NMR ($CDCl_3$): δ 5.84 (m, 2H, 2 =CH), 5.15 (m, 2H, 2 =C*H*aHb), 5.10 (m, 2H, 2 =CHa*H*b), 3.62 (m, 4H, $2CH_2O$), 2.83 (m, 4H, $2CH_2N$), 2.55 (dd, *J* = 7.0, 15.5 Hz, 2C*H*aHb), 2.46 (dd, *J* = 7.0, 15.5 Hz, 2CHa*H*b). ^{13}C NMR ($CDCl_3$): δ 132.5 (q, *J* = 1.0 Hz, 2 =CH), 128.7 (q, *J* = 297.5 Hz, CF_3), 119.0 (2 $=CH_2$), 68.5 (q, *J* = 1.0 Hz, 2 OCH_2), 64.5 (q, *J* = 21.0 Hz, C–CF_3), 47.9 (q, *J* = 1.0 Hz, $2NCH_2$), 35.4 (q, *J* = 1.5 Hz, $2CH_2$). Anal. Calcd for $C_{12}H_{18}F_3NO$: C, 57.82; H, 7.28; N, 5.62. Found: C, 58.03; H, 7.56; N, 5.64.

4.3. Preparation and separation of both diastereomers of 3,7-bis(trifluoromethyl)-1,4a,5,8a-tetrahydro-thiopyrano[4,3-c]thiopyran (6a)

To a solution of thioamide **1b** (191 mg, 0.96 mmol) in diethyl ether (10 mL) was added at −50 °C and under Ar allylmagnesium bromide (0.87 M in ether, 1.10 mL, 0.96 mmol, 1 equiv.). After warming to 0 °C, the reaction mixture was quenched with water. The ethereal layer was washed with sat aq NH_4Cl, dried with $MgSO_4$ and the solvent was evaporated. The residue (mixture of two diastereomers cis:trans 75:25) was purified by chromatography on SiO_2 (pentane 100%, solid deposit) to afford (*trans*)-**6a** (38 mg, 13%) followed by (*cis*)-**6a** (47 mg, 16%) both as white solid.

(trans)-3,7-Bis(trifluoromethyl)-1,4a,5,8a-tetrahydro-thiopyrano[4,3-c]thiopyran (trans)-**6a** (*minor isomer*). mp 149 °C (Et_2O/petroleum ether). ^{19}F NMR ($CDCl_3$): δ −66.1 (q, *J* = 1.5 Hz, CF_3). ^1H NMR ($CDCl_3$): δ 6.18 (s, 2H, 2 =CH), 3.03 (m, 4H), 2.59 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 127.5 (q, *J* = 33.0 Hz, C–CF_3), 125.5 (q, *J* = 5.5 Hz, 2CH=), 122.0 (q, *J* = 273.5, $2CF_3$), 35.5 ($2CH_2S$), 31.1 (2CH). Anal. Calcd for $C_{10}H_8F_6S_2$: C, 39.21; H, 2.63. Found: C, 39.39; H, 2.68. A sample has been recrystallized in Et_2O/EP for X-ray analysis.

(cis)-3,7-Bis(trifluoromethyl)-1,4a,5,8a-tetrahydro-thiopyrano[4,3-c]thiopyran (cis)-**6a** (*major isomer*). mp 122 °C (petroleum ether at −18 °C). ^{19}F NMR ($CDCl_3$): δ −66.6 (t, *J* = 2.0 Hz, CF_3). ^1H NMR ($CDCl_3$): δ 6.27 (s, 2H, 2 =CH), 3.00 (d, *J* = 13.0 Hz, 2H), 2.92 (br s, 2H), 2.74 (dd, *J* = 9.0, 13.0 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 127.7 (q, *J* = 33.0 Hz, C–CF_3), 124.7 (q, *J* = 5.0 Hz, 2CH=), 122.0 (q, *J* = 273.5 Hz, $2CF_3$), 32.0 ($2CH_2S$), 28.3 (2CH). Anal. Calcd for $C_{10}H_8F_6S_2$: C, 39.21; H, 2.63. Found: C, 39.50; H, 2.69.

4.4. General procedure for the preparation of 6 as a mixture of diastereomers

To a solution of thioamide **1** (4 mmol) in diethyl ether (15 mL), an equimolar amount of allylmagnesium chloride (2 M solution in THF) or bromide (1 M solution in ether) was added at −50 °C. The mixture turns to colorless. After warming to 0 °C, the reaction mixture was quenched with water. The ethereal layer was washed with sat aq NH_4Cl, dried with $MgSO_4$ and the solvent was evaporated. The residue was dissolved in hot petroleum ether and allowed to crystallize at −18 °C. Crystals were filtered, washed with cold petroleum ether and dried.

*3,7-Bis(pentafluoroethyl)-1,4a,5,8a-tetrahydro-thiopyrano[4,3-c]thiopyran (***6c***).* Mixture of isomers, 1:0.5. Yield 30%, yellowish crystals. ^{19}F NMR ($CDCl_3$): δ −84.3 (s, CF_3 *minor isomer*), −84.4 (s, CF_3 *major isomer*), δ_A −112.9, δ_B −115.8 (J_{AB} = 269.0 Hz, CF_2 *minor isomer*), δ_A −114.5, δ_B −115.3 (J_{AB} = 268.0 Hz, CF_2 *major isomer*). ^1H NMR ($CDCl_3$): δ 6.14 (m, 2H, 2 =CH), 3.12 (d, *J* = 13.0 Hz, 2 SC*H*aHb *major isomer*), 3.07–2.92 (m, 2 SCH_2CH *major and minor isomers*, SC*H*aHb *minor isomer*), 2.78 (dd, *J* = 7.5, 13.0 Hz, SCHa*H*b *major isomer*), 2.62 (m, SCHa*H*b *minor isomer*). ^{13}C NMR ($CDCl_3$): δ 127.9 (t, *J* = 8.0 Hz, 2CH= *minor isomer*), 127.2 (t, *J* = 8.0 Hz, 2CH= *major isomer*), 126.7 (t, *J* = 24.0 Hz, 2C–CF_2 *major isomer*), 126.4 (t, *J* = 24.0 Hz, 2C–CF_2 *minor isomer*), 118.8 (qt, *J* = 288.0, 38.0 Hz, $2CF_3$ *major isomer*), 112.0 (tq, *J* = 256.0, 39.0 Hz, $2CF_2$ *minor isomer*), 111.9 (tq, *J* = 257.0, 38.5 Hz, $2CF_2$ *major isomer*), 36.0 (2CH *minor isomer*), 32.1 (2CH *major isomer*), 31.6 ($2CH_2S$ *minor isomer*), 29.2 ($2CH_2S$ *major isomer*). GC–MS 70 eV, *m*/*z* (rel. int.): 406 $[M]^+$ (70), 391 $[M-CH_3]^+$ (36), 229 $[M-C_2F_5CSCH_2]^+$ (100), 215 $[M-C_2F_5CSCH_2CH_2]^+$ (42), 203 $[M/2]^+$ (38), 133 (96).

*3,7-Bis(heptafluoropropyl)-1,4a,5,8a-tetrahydro-thiopyrano[4,3-c]thiopyran (***6d***).* Mixture of isomers, 1:0.8. Yield 35%, yellowish crystals. ^{19}F NMR ($CDCl_3$): δ −80.7 (t, *J* = 10.0 Hz, CF_3 *major isomer*), −80.8 (t, *J* = 10.0 Hz, CF_3 *minor isomer*), δ_A −109.8, δ_B −112.9 (AB of quartets, J_{AB} = 273.0 Hz, *J* = 10.0 Hz, CF_2 *major isomer*), δ_A −111.3, δ_B −112.4 (AB of quartets, J_{AB} = 273.0 Hz, *J* = 10.0 Hz, CF_2 *minor isomer*), −126.6 (s, CF_2 *major isomer*), −126.7 (s, CF_2 *minor isomer*). ^1H NMR ($CDCl_3$): δ 6.16 (m, 2 =CH *major isomer*), 6.12 (m, 2 =CH *minor isomer*), 3.07 (d, *J* = 12.5 Hz, 2H, SC*H*aHb *major isomer*), 3.04–2.95 (m, SCH_2CH *major and minor isomers*, SC*H*aHb *minor isomer*), 2.76 (dd, *J* = 12.5, 7.5 Hz, SCHa*H*b *major isomer*), 2.63 (m, SCHa*H*b *minor isomer*) ppm. ^{13}C NMR ($CDCl_3$): δ 128.3 (t, *J* = 8.0 Hz, 2CH= *minor isomer*), 127.7 (t, *J* = 8.0 Hz, 2CH= *major isomer*), 126.8 (t, *J* = 24.0 Hz, 2C–CF_2 *major isomer*), 126.6 (t, *J* = 24.0 Hz, 2C–CF_2 *minor isomer*), 118.1 (qt, *J* = 289.0, 35.0 Hz, CF_3 *major isomer*), 113.7 (tt, *J* = 258.0, 31.0 Hz, CF_2 *minor isomer*), 113.6 (tt, *J* = 258.0, 31.0 Hz, CF_2 *major isomer*), 108.8 (tq, *J* = 266.0, 39.0 Hz, CF_2 *minor isomer*), 35.8 (2CH *minor isomer*), 32.2 (2CH *major isomer*), 31.4 ($2CH_2S$ *minor isomer*), 29.1 ($2CH_2S$ *major isomer*). GC–MS 70 eV, *m*/*z* (rel. int.): 506 $[M]^+$ (28), 491 $[M-CH_3]^+$ (10), 279 $[M-C_3F_7CSCH_2]^+$ (100), 253 $[M/2]^+$ (42), 133 (84).

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References

[1] For reviews on thiocarboxylic derivatives, see:
(a) P. Metzner, Synthesis 12 (1992) 1185–1199;
(b) P. Metzner, A. Thuillier, Sulfur Reagents in Organic Synthesis, Academic Press, London, 1994, chap. 4, pp. 96–126;
(c) P. Metzner, in: P. Metzner (Ed.), Organosulfur Chemistry I, Topics in Current Chemistry, vol. 204, Springer-Verlag, Heidelberg, 1999, pp. 127–181;
(d) R.S. Glass, Science of Synthesis, vol. 22, Georg Thieme Verlag, 2005, pp. 75–132.
[2] (a) C. Portella, Y.G. Shermolovich, Tetrahedron Lett. 38 (1997) 4063–4064;
(b) F. Grellepois, V.M. Timoshenko, Y.G. Shermolovich, C. Portella, Org. Lett. 8 (2006) 4323–4326.
[3] V.M. Timoshenko, Y.G. Shermolovich, F. Grellepois, C. Portella, J. Fluorine Chem. 127 (2006) 471–475.
[4] S.S. Mikhailichenko, A.V. Rudnichenko, V.M. Timoshenko, A.N. Chernega, Y.G. Shermolovich, F. Grellepois, C. Portella, J. Fluorine Chem. 128 (2007) 703–709.

[5] Y. Tamaru, T. Harada, S. Nishi, Z. Yoshida, Tetrahedron Lett. 23 (1982) 2383–2386.
[6] T. Murai, K. Ui, Narengerile, J. Org. Chem. 74 (2009) 5703–5706.
[7] (a) P. Carloni, E. Damiani, M. Iacussi, L. Greci, P. Stipa, D. Cauzi, C. Rizzoli, P. Sgarabotto, Tetrahedron 51 (1995) 12445–12452;
(b) T. Vogler, A. Studer, Synthesis 13 (2008) 1979–1993.
[8] TEMPO (1 equivalent) was introduced once the reaction temperature had reached 0 °C. Compound 6a was observed as the major product according to the ^{19}F NMR spectrum recorded within 5 minutes.
[9] A.M. Le Nocher, P. Metzner, Tetrahedron Lett. 33 (1992) 6151–6154.
[10] A direct oxidation of the dienethiol may not be excluded.
[11] (a) P. Metzner, T.N. Pham, J. Vialle, Tetrahedron 42 (1986) 2025–2036;
(b) P. Gosselin, S. Masson, A. Thuillier, Tetrahedron Lett. 21 (1980) 2421–2424.
[12] (a) M. Dagonneau, J. Vialle, Tetrahedron 30 (1974) 415–418;
(b) O. Ito, S. Tamura, K. Murakami, M. Matsuda, J. Org. Chem. 53 (1988) 4758–4762.
[13] CCDC-768782 (compound (*trans*)-**6a**) and CCDC-286193 (compound **6d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.