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N-Alkyl-C-polyfluoroalkyl-C-chlorosulfinimides $R_FC(Cl)=S=N-R$

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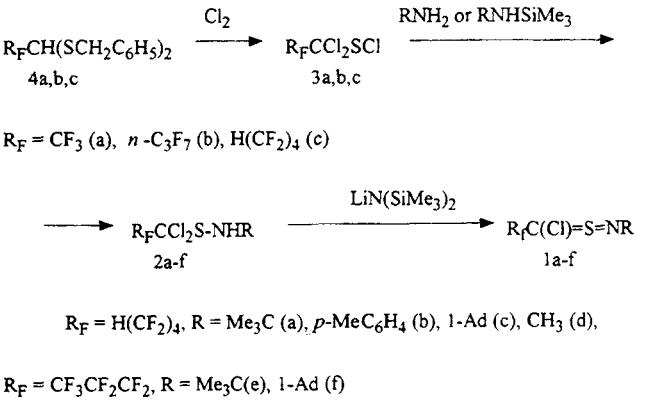
ABSTRACT

The N-alkyl-C-polyfluoroalkyl-C-chlorosulfinimides $R_FC(Cl)=S=N-R$ have been investigated. Some aspects of their thermal stability and their [3+2] and [3+1] cycloaddition reactions have been examined.

INTRODUCTION

Sulfinimides represent a comparatively new class of organic heterocumulenes [1,2]. At present, several sulfinimides are known in which the ylidic carbon atom is incorporated into aromatic, heterocyclic, or acyclic systems [3–5], while the iminic nitrogen atom is bound to an arylsulfonyl group [6].

Sulfinimides having fluoroalkyl substituents are well known and have been studied in detail [7,8] in [3+1] and [3+2] cycloaddition reactions. Also, we have synthesized polyfluoroalkylsulfinimides (**1**) containing an α-chlorine atom, which is potentially capable of nucleophilic substitutions [9], and have studied their reactions with olefins and germanium dichloride.



SCHEME 1

RESULTS AND DISCUSSION

Sulfinimides (**1a–f**) are formed in the reaction between lithium hexamethyldisilazane and sulfenamides (**2a–f**) [10]. The latter, in turn, are prepared by the reaction of 1,1-dichloropolyfluoroalkylsulfenyl chlorides (**3**) with the appropriate amines. To synthesize sulfenyl chlorides (**3**), we used the previously developed [11] method of chlorination of S,S-dibenzyldithioacetals of polyfluorinated aliphatic aldehydes (**4**).

Sulfinimides (**1a–f**) are thermally stable up to 100°C. The bulk of an alkyl substituent at the nitrogen atom seems to exert no appreciable effect on the thermal stability of each compound (**1**). Thus, N-methylsulfinimide (**1d**) is vacuum distillable, in

Dedicated to Prof. Shigeru Oae on the occasion of his seventy-fifth birthday.

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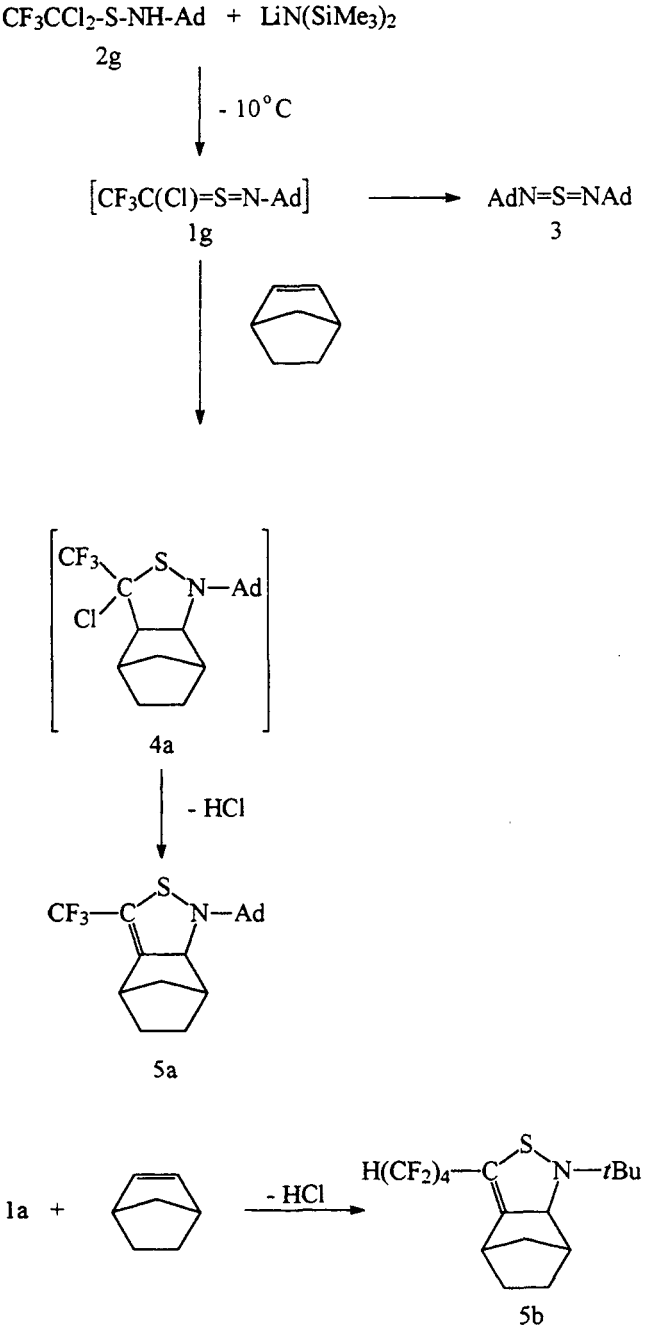
contrast to related sulfur-containing heterocumulenes Alk–N=S=X (X = O, NR), which are thermally unstable in compounds even having a normal alkyl substituent at the nitrogen atom [12]. On the other hand, polyfluoroalkyl substituents appeared to increase the thermal stability of compounds (**1**). This tentative conclusion resulted from the fact that the attempt to prepare the sulfinimide (**1g**) by treating N-1-adamantyl-1,1-dichloro-2,2,2-trifluoroethylsulfenamide (**2g**) with lithium hexamethyldisilylamide failed. (The apparent instability of sulfinimide (**1g**) can be associated with special features of the trifluoromethyl group which should be thoroughly studied.) The reaction actually produced N,N'-bis(adamantyl)sulfur diimide (**3**) in a good yield along with sulfur and a mixture of organofluorine compounds containing no sulfur.

In the ^{19}F NMR spectrum of the reaction mixture, six singlet signals were observed in the range of δ −56 to −72 from the fluorine nuclei of CF_3 groups, which is typical of compounds containing the CF_3 group at an sp^2 carbon atom [13].

Nevertheless, sulfinimide (**1g**) is apparently rather stable at low temperatures, as indicated by the reaction of sufenamide (**2g**) with lithium hexamethyldisilazane in the presence of norbornene conducted at −10°C. In this case, the [3+2] cycloaddition product (**5a**) was formed, along with sulfur diimide (**3**). The stable sulfinimide (**1a**) also reacted with norbornene to form the tricyclic compound (**5b**). The 4-thia-3-azatricyclo-[5.2.1.$0^{2,6}$]decan-5-ene derivatives (**5**) are formed as a result of HCl elimination from the primary adduct (**4**). The maximal yields of compounds (**5**) were obtained when triethylamine was used to bind the evolving hydrogen chloride.

The reaction of the sulfinimide (**1a**) with styrene led to the cycloadduct (**6**) containing no chlorine. It is evident that, also in this case, elimination of HCl from the primary isothiazolidine (**7**) took place. The ^{19}F NMR spectra of (**5**) and (**6**) showed that only one regioisomer was formed in each case. This is typical of the reaction of [1,3] dipolar compounds with olefins [7,14].

Compounds (**1**) may also react with electrophiles in a [3+1] cycloaddition reaction in a manner similar to that previously observed for bis(trifluoromethyl)sulfinimides [15]. Thus, the reaction of compounds (**1a, e**) with the dioxane adduct of germanium dichloride produced 1,2,3-thiazagermetidines (**8**).



SCHEME 2

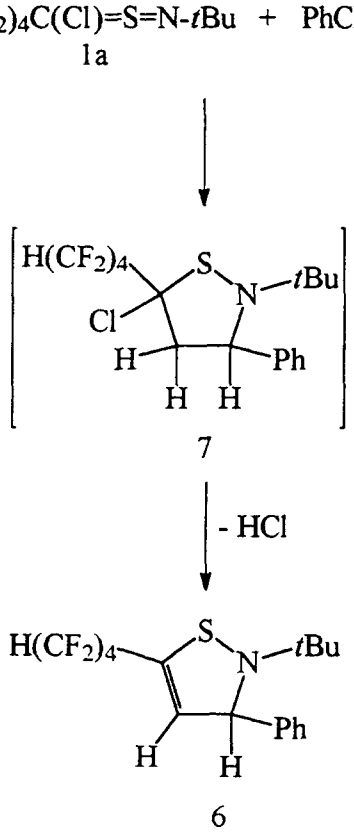
EXPERIMENTAL

All the reactions were performed in a flow of dry nitrogen using dry solvents. NMR: Bruker WP 80 SY, AM 250; Varian VXR-300, chemical shifts quoted being from TMS for ^1H and ^{13}C NMR, from $CFCl_3$ for ^{19}F NMR. MS: Finnigan MAT 8230 and Varian MAT CH 5.

Preparations of the compounds (**1a, b**), (**2a, b**), (**3c**), and (**4c**) were described in Ref. [10].

General Procedure for the Synthesis of S,S-Dibenzyldithioacetals of Polyfluorinated Aliphatic Aldehydes (**4a, b**)

A mixture of phosphoric anhydride (0.073 mol) and hexamethyldisiloxane (0.055 mol) in trichloro-

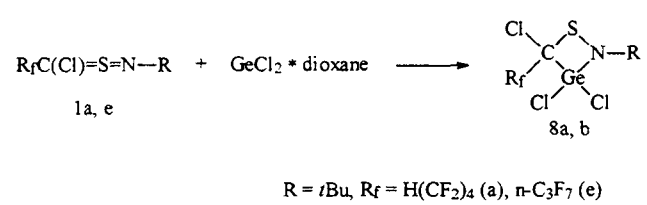


SCHEME 3

methane (200 mL) was refluxed with stirring for 3 hours. Either heptafluoropropanal (0.0184 mol) or trifluoroacetaldehyde ethyl hemiacetal (0.0184 mol) and benzylthiol (0.0368 mol) were added to the reaction mixture at 20°C. The mixture was refluxed for 12 hours with stirring. The cooled (20°C) reaction mixture was poured into a 1 N aqueous solution of NaOH (740 mL) with stirring, the organic layer was separated, and the water layer was extracted with $CHCl_3$ (3 × 50 mL). The organic layers were combined and dried over sodium sulfate. The solvent was distilled off at atmospheric pressure and the residue fractionated in vacuo.

1,1-Bis(benzylthio)-2,2,2-trifluoroethane (**4a**), yield 74%, bp 142–144°C/0.1 mm Hg. ^1H NMR ($CDCl_3$) δ: 3.84 (s, CH_2); 3.90 (tt, $^3J_{HF}$ = 14.8 Hz, $^4J_{HF}$ = 1.2 Hz, CH); 7.25 (m, C_6H_5). ^{19}F NMR ($CDCl_3$) δ: −70.01 (s). MS: m/z = 328 M^+. Anal. found: C, 58.4; H, 4.2; S, 19.1%. $C_{16}H_{15}F_3S_2$ requires C, 58.51; H, 4.60; S, 19.52%; M, 328.42.

1,1-Bis(benzylthio)-2,2,3,3,4,4,4-heptafluorobutane (**4b**), yield 78%, bp 150–152°C/0.05 mm Hg. ^1H NMR ($CDCl_3$) δ: 3.90 (s, CH_2); 3.99 (tt, $^3J_{HF}$ = 14.6 Hz, $^4J_{HF}$ = 1.0 Hz, CH); 7.20 (m, C_6H_5). ^{19}F NMR ($CDCl_3$) δ: −123.72 (m, CF_2); −108.73 (m, CF_2); −81.20 (t, $^3J_{FF}$ = 10.7 Hz, CF_3). MS: m/z = 428 M^+. Anal. found: C, 50.7; H, 3.6; S, 14.5%. $C_{18}H_{15}F_7S_2$ requires C, 50.46; H, 3.52; S, 14.97%; M, 428.43.



SCHEME 4

General Procedure for the Synthesis of 1,1-Dichloropolyfluoroalkylsulfenyl Chlorides (**3a, b**)

To a solution of dithioacetal (**4a, b**) (0.05 mol) in $CHCl_3$ (70 mL), chlorine (0.15 mol) was added with stirring for 1 hour. The solvent was distilled off, and the residue was fractionated at atmospheric pressure.

1,1-Dichloro-2,2,2-trifluoroethylsulfenyl chloride (**3a**), yield 80%, bp 93°C. (Ref. [16] data, bp 76°C). ^{19}F NMR ($CDCl_3$) δ: −76.58 (s, CF_3). MS: m/z 218 M^+. Anal. found: C, 11.0; Cl, 48.3%. $C_2Cl_3F_3S$ requires C, 10.95; Cl, 48.47%; M, 219.44.

1,1-Dichloro-2,2,3,3,4,4,4-heptafluorobutylsulfenyl chloride (**3b**), yield 81%, bp 153–155°C. ^{19}F NMR ($CDCl_3$) δ: −121.40 (m, CF_2); −107.34 (m, CF_2); −82.01 (t, $^3J_{FF}$ = 5.9 Hz, CF_3). ^{13}C NMR ($CDCl_3$) δ: 87.87 (tm, $^2J_{CF}$ = 31.2. Hz, CCl_2); 109.83 (tqt, $^1J_{CF}$ = 271.8 Hz, $^2J_{CF}$ = 38.5 Hz, CF_2-CF_3); 113.17 (ttq, $^1J_{CF}$ = 278.6 Hz, $^2J_{CF}$ = 29.4 Hz, $^3J_{CF}$ = 0.6 Hz, CF_2CCl_2); 117.59 (qtt, $^1J_{CF}$ = 288.8 Hz, $^2J_{CF}$ = 33.7 Hz, $^3J_{CF}$ = 2.1 Hz, CF_3). MS: m/z = 318 M^+. Anal. found: C, 15.2; Cl, 31.2; S, 9.1%. $C_4Cl_3F_7S$ requires C, 15.04; Cl, 33.29; S, 10.04%; M, 319.46.

General Procedure of the Synthesis of 1,1-Dichloropolyfluoroalkylsulfenamides (**2c–g**)

To a solution of a suitable amine (0.2 mol) or N-trimethylsilyladamantylamine (0.1 mol) in diethyl ether (50 mL) a solution of sulfenyl chloride (**3**) in ether (20 mL) was slowly added with stirring at 20°C. After additional stirring of the reaction mixture for 1 hour at 20°C, the alkylammonium chloride was filtered off, the solvent distilled off in vacuo (10–20 mm Hg), and finally, the residue distilled; compound (**2g**) was sublimed in vacuo (0.05 mm Hg).

N-1-Adamantyl-1,1-dichloro-2,2,3,3,4,4,5,5-octafluoropentylsulfenamide (**2c**), yield 70%, bp 145–148°C/0.05 mm Hg. ^1H NMR ($CDCl_3$) δ: 1.63, 1.71, 2.09 (m, Ad); 3.39 (s, NH); 6.03 (tt, $^2J_{HF}$ = 52.1 Hz, $^3J_{HF}$ = 5.5 Hz, CHF_2). ^{19}F NMR ($CDCl_3$) δ: −137.56 (dm, $^2J_{FH}$ = 52.0 Hz, CF_2H); −130.62, −118.31 (m, CF_2CF_2); −107.51 (tm, $^2J_{FF}$ = 24 Hz, $^3J_{FF}$ = 11.0 Hz, CF_2CCl_2). ^{13}C NMR ($CDCl_3$) δ: 29.91, 36.12, 43.83, 54.76 (s, Ad); 90.90 (tt, $^2J_{CF}$ = 27.9 Hz, $^3J_{CF}$ = 3.4

Hz, CCl_2); 114.34 (tt, $^1J_{CF}$ = 254.7 Hz, $^2J_{CF}$ = 30.9 Hz, HCF_2); 112.50, 109.00 (m, CF_2CF_2); 107.65 (tt, $^1J_{CF}$ = 252.4 Hz, $^2J_{CF}$ = 30.0 Hz, CF_2CCl_2). MS: m/z = 465 M^+. Anal. found: C, 38.2; H, 3.5; Cl, 15.1; S, 6.5%. $C_{15}H_{17}Cl_2F_8NS$ requires C, 38.64; H, 3.67; Cl, 15.21; S, 6.88%; M, 466.26.

N-1-Methyl-1, 1-dichloro-2, 2, 3, 3, 4, 4,5,5-octafluoropentylsulfenamide (**2d**), yield 64%, bp 96–98°C/10 mm Hg. ^1H NMR (C_6D_6) δ: 2.40 (d, $^2J_{HH}$ = 4.6 Hz, CH_3); 2.75 (s br, NH); 5.33 (tt, $^2J_{HF}$ = 51.8 Hz, $^3J_{HF}$ = 5.4 Hz, CHF_2). ^{19}F NMR ($CDCl_3$) δ: −136.51 (dm, $^2J_{FH}$ = 51.8 Hz, CF_2H); −129.60, −117.05, −107.61 (m, $CF_2CF_2CF_2$). Anal. found: C, 20.9; H, 1.4; Cl, 20.0; S, 9.4%. $C_6H_5Cl_2F_8NS$ requires C, 20.82; H, 1.46; Cl, 20.49; S, 9.27%.

N-*t*-Butyl-1,1-dichloro-2,2,3,3,4,4,4-heptafluorobutylsulfenamide (**2e**), yield 72%, bp 38–39°C/0.05 mm Hg. ^1H NMR ($CDCl_3$) δ: 1.23 (s, CH_3); 3.46 (s, NH). ^{19}F NMR ($CDCl_3$) δ: −120.81, −108.10 (m, CF_2CF_2); −81.80 (m, CF_3). ^{13}C NMR ($CDCl_3$) δ: 30.17 (s, CH_3); 55.17 (s, C (CH_3)$_3$); 90.66 (tt, $^2J_{CF}$ = 28.0 Hz, $^3J_{CF}$ = 3.4 Hz, CCl_2); 110.03 (tq, $^1J_{CF}$ = 271.1 Hz, $^2J_{CF}$ = 34.0 Hz, CF_2-CF_3); 113.71 (ttq, $^1J_{CF}$ = 267.3 Hz, $^2J_{CF}$ = 29.2 Hz, $^3J_{CF}$ = 1.9 Hz, CF_2CCl_2); 117.77 (qtt, $^1J_{CF}$ = 288.8 Hz, $^2J_{CF}$ = 34.0 Hz, $^3J_{CF}$ = 1.9 Hz, CF_3). MS: m/z = 355 M^+. Anal. found: C, 27.3; H, 2.8; Cl, 19.7, N, 3.8; S, 8.9%. $C_8H_{10}Cl_2F_7NS$ requires C, 27.55; H, 2.83; Cl, 19.91; N, 3.93; S, 9.00%; M, 356.13.

N-1-Adamantyl-1, 1-dichloro-2,2, 3, 3, 4,4,4-heptafluorobutylsulfenamide (**2f**), yield 70%, bp 118–120°C/0.05 mm Hg. ^1H NMR ($CDCl_3$) δ: 1.52, 1.69, 2.04 (m, Ad); 3.34 (s, NH). ^{19}F NMR ($CDCl_3$) δ: −120.91, −108.30 (m, CF_2CF_2); −81.87 (t, $^3J_{FF}$ = 11.5 Hz, CF_3). ^{13}C NMR ($CDCl_3$) δ: 30.11, 36.14, 43.84, 54.76 (s, Ad); 90.68 (tt, $^2J_{CF}$ = 47.8 Hz, $^3J_{CF}$ = 3.3 Hz, CCl_2); 109.96 (tq, $^1J_{CF}$ = 271.1 Hz, $^2J_{CF}$ = 37.9 Hz, CF_2-CF_3); 113.39 (ttq, $^1J_{CF}$ = 272.2 Hz, $^2J_{CF}$ = 48.0 Hz, $^3J_{CF}$ = 2.0 Hz, CF_2CCl_2); 119.54 (qtt, $^1J_{CF}$ = 288.9 Hz, $^2J_{CF}$ = 34.1 Hz, $^3J_{CF}$ = 1.9 Hz, CF_3). MS: m/z = 433 M^+. Anal. found: C, 39.4; H, 3.8; N, 3.2; S, 8.9%. $C_{14}H_{16}Cl_2F_7NS$ requires C, 38.72; H, 3.71; N, 3.22; S, 7.38%; M, 434.25.

N-1-Adamantyl - 1, 1-dichloro - 2, 2, 2 - trifluoroethylsulfenamide (**2g**), yield 71%, mp 75–77°C. ^1H NMR ($CDCl_3$) δ: 1.54, 1.65, 2.04 (m, Ad); 3.40 (s, NH). ^{19}F NMR ($CDCl_3$) δ: −76.34 (s, CF_3). MS: m/z = 333 M^+. Anal. found: C, 43.8; H, 4.8; Cl, 21.1; S, 9.9%. $C_{12}H_{16}Cl_2F_3NS$ requires C, 43.12; H, 4.82; Cl, 21.21; S, 9.59%; M, 334.23.

General Procedure for the Synthesis of Sulfinimides (**1c–f**)

To a solution of sulfenamide (**2c–f**) (0.01 mol) in hexane (25 mL) a solution of lithium hexamethylsilylamide (0.01 mol) in hexane (40 mL) was slowly added with stirring at 20°C. The mixture was stirred for 3 hours at 20°C, the precipitated solid was filtered off, and the filtrate was fractionated in vacuo.

N-1-Adamantyl-1,1,2,2,3,3,4,4-octafluorobutylchlorosulfinimide (**1c**), yield 40%, bp 115–120°C/0.05 mm Hg. (**1c**) decomposes partly at distillation. ^1H NMR ($CDCl_3$) δ: 1.63, 1.72, 2.10 (m, Ad); 6.03 (tt, $^2J_{HF}$ = 51.9 Hz, $^3J_{HF}$ = 5.5 Hz, CHF_2). ^{19}F NMR ($CDCl_3$) δ: −137.52 (qm, $^2J_{FH}$ = 52.0 Hz, CF_2H;) −130.00, 123.10 (m, CF_2CF_2); −105.20 (m, CF_2CCl). MS: m/z = 429 M^+. Anal. found: C, 41.0; H, 3.8; Cl, 9.0; S, 8.0%. $C_{15}H_{16}ClF_8NS$ requires C, 41.92; H, 3.75; Cl, 8.25; S, 7.46%; M, 429.80.

N-Methyl-1, 1, 2,2,3,3,4,4-octafluorobutylchlorosulfinimide (**1d**), yield 47%, bp 56–58°C/10 mm Hg. ^1H NMR (C_6D_6) δ: 2.52 (s, CH_3); 5.20 (tt, $^2J_{HF}$ = 52.0 Hz, $^3J_{HF}$ = 5.2 Hz, CHF_2). ^{19}F NMR ($CDCl_3$) δ: −137.01 (dm, $^2J_{FH}$ = 52.0 Hz, CF_2H); −128.02, −118.91, −105.90 (m, $CF_2CF_2CF_2$). Anal. found: C, 23.9; H, 1.3; Cl, 11.6%. $C_6H_4ClF_8NS$ requires C, 23.27; H, 1.30; Cl, 11.45%.

N-*t*-Butyl-1,1,2,2,3,3,3-heptafluoropropylchlorosulfinimide (**1e**) yield 70%, bp 85°C/15 mm Hg. ^1H NMR ($CDCl_3$) δ: 1.42 (s, CH_3). ^{19}F NMR ($CDCl_3$) δ: −125.20 (m, CF_2); −106.10 (m, CF_2CCl), −80.81 (tt, $^3J_{FF}$ = 9.9 Hz, $^4J_{FF}$ = 0.9 Hz, CF_3). MS: m/z = 319 M^+. Anal. found: C, 30.8; H, 2.7; Cl, 11.5; S, 10.8%. $C_8H_9ClF_7NS$ requires C, 30.06; H, 2.84; Cl, 11.09; S, 10.03%; M, 319.67.

N-1-Adamantyl-1, 1,2, 2,3, 3, 3-heptafluoropropylchlorosulfinimide (**1f**), yield 50%, bp 95–100°C/0.05 mm Hg). (**1f**) decomposes partly at distillation. ^1H NMR ($CDCl_3$) δ: 1.65, 1.85, 2.21 (m, Ad). ^{19}F NMR ($CDCl_3$) δ: −125.50, −106.10 (m, CF_2CF_2); −80.90 (m, CF_3). ^{13}C NMR ($CDCl_3$) δ: 29.95, 35.90, 45.81, 62.41 (s, Ad); 108.74 (tqt, $^1J_{CF}$ = 266.7 Hz, $^2J_{CF}$ = 38.1 Hz, $^3J_{CF}$ = 1.7 Hz, CF_2CF_3); 114.53 (tt, $^1J_{CF}$ = 258.9 Hz, $^2J_{CF}$ = 31.3 Hz, CF_2CCl); 117.79 (qtt, $^1J_{CF}$ = 287.8 Hz, $^2J_{CF}$ = 32.8 Hz, $^3J_{CF}$ = 2.0 Hz, CF_3); 117.80 (t, $^2J_{CF}$ = 25.9 Hz, CCl). MS: m/z = 397 M^+. Anal. found: C, 42.7; H, 4.2; N, 3.9; Cl, 7.3%. $C_{14}H_{15}ClF_7NS$ requires C, 42.27; H, 3.80; N, 3.52; Cl, 8.91%; M, 397.78.

3-Adamantyl-5-trifluoromethyl-4-thia-3-azatricyclo[5,2,1,$0^{2,6}$]decan-5-ene (**5a**), yield 53%, mp 180°C. ^1H NMR ($CDCl_3$) δ: 1.80, 2.50 (m, CH_2 + CH); 3.80 (m, CH-CH-N); 4.52 (d, $^3J_{HH}$ = 4.0 Hz, CH–N). ^{19}F NMR ($CDCl_3$) δ: −55.34 (s, CF_3). MS: m/z = 355 M^+. Anal. found: C, 64.4; H, 6.5; N, 4.4; S, 8.5%. $C_{19}H_{24}F_3NS$ requires C, 64.20; H, 6.80; N, 3.94; S, 9.02%; M, 355.47.

N,N'-Bis(1-adamantyl)sulfur diimide (**3**), yield 80%, mp 280°C (decomp). ^1H NMR ($CDCl_3$) δ: 1.65, 1.99, 2.07 (m, Ad). MS: m/z = 330 M^+. Anal. found: C, 72.7; H, 9.1; N, 8.5; S, 10.1%. $C_{20}H_{30}N_2S$ requires C, 72.67; H, 9.15; N, 8.48; S, 9.70%; M, 330.54.

3-*t*-Butyl-5-(1, 1, 2, 2, 3,3,4,4-octafluorobutyl)-4-thia-3-azatricyclo[5,2,1,$0^{2,6}$]decan-5-ene (**5b**), yield 51%, bp 113°C/0.05 mm Hg. ^1H NMR ($CDCl_3$) δ: 1.20 (s, CH_3); 1.60 (m, CH_2); 2.46 (m, CH); 3.02 (m, CH); 3.75 (m, CH-N); 6.05 (tt, $^2J_{HF}$ = 52.0 Hz, $^3J_{HF}$ = 5.6 Hz, CHF_2). ^{19}F NMR ($CDCl_3$) δ: −137.88 (dm, $^2J_{FH}$ = 52.0 Hz, CF_2H); −130.52, −124.50 (m,

CF_2CF_2); −105.59 (tm, $^3J_{FF}$ = 11.4 Hz, $\underline{C}F_2$-C). ^{13}C NMR ($CDCl_3$) δ: 23.91, 28.10, 40.53 (s, $\underline{C}H_2$); 28.42 (s, CH_3); 40.31, 42.22, 77.61 (s, CH); 108.12 (tt, $^1J_{CF}$ = 254.0 Hz, $^2J_{CF}$ = 30.4 Hz, CF_2H); 110.50, 114.50, (m, $\underline{C}F_2CF_2$); 114.58 (tt, $^1J_{CF}$ = 254.2 Hz, $^2J_{CF}$ = 32.7 Hz, $\underline{C}F_2C$=); 116.94 (t, $^2J_{CF}$ = 37.4 Hz, CF_2-$\underline{C}$=); 152.88 (t, $^3J_{CF}$ = 5.5 Hz, $\underline{C}$=C-CF_2). MS: m/z = 409 M^+. Anal. found: C, 45.2; H, 4.5; N, 3.6; S, 8.4%. $C_{16}H_{19}F_8NS$ requires C, 46.94; H, 4.68; N, 3.42; S, 7.83%; M, 409.38.

2-*t*-Butyl-3-phenyl-5-(1,1,2,2,3,3,4,4-octafluorobutyl)-isothiazol-4-in (**6**), yield 87%, bp 103–105°C/0.05 mm Hg. ^1H NMR ($CDCl_3$) δ: 1.20 (s, CH_3); 5.44 (m, $C\underline{H}$-Ph); 6.05 (tt, $^2J_{HF}$ = 52.0 Hz, $^3J_{HF}$ = 5.4 Hz, CHF_2); 6.29 (m, CH=); 7.25 (m, C_6H_5). ^{19}F NMR ($CDCl_3$) δ: −137.77 (dm, $^2J_{FH}$ = 52.0 Hz, CF_2H); −130.24, −124.08 (m, CF_2CF_2); −107.96, −103.84 (AB, J_{AB} = 281.6 Hz, CF_AF_B-C=). ^{13}C NMR ($CDCl_3$) δ: 26.31 (s, CH_3); 60.51 (s, $\underline{C}(CH_3)_3$); 71.98 (s, $\underline{C}$-Ph); 104.00–112.00 (m, $CF_2\underline{C}F_2CF_2$); 126.52, 128.08, 129.06, 139.20 (s, C_6H_5); 134.01 (t, $^2J_{CF}$ = 30.0 Hz, C-S). MS: m/z = 419 M^+. Anal. found: C, 48.8; H, 4.5; S, 8.0%. $C_{17}H_{17}F_8NS$ requires C, 48.69; H, 4.09; S, 7.65; M, 419.39.

2-*t*-Butyl-3,3,4-trichloro-4-(1,1,2,2,3,3,4,4-octafluorobutyl)-1,2,3-thiazagermetidine (**8a**), yield 68%, bp 75–78°C/0.05 mm Hg. ^1H NMR ($CDCl_3$) δ: 1.42 (s, CH_3); 6.04 (tt, $^2J_{HF}$ = 52.0 Hz, $^3J_{HF}$ = 5.4 Hz, CHF_2). ^{19}F NMR ($CDCl_3$) δ: −137.68 (dm, $^2J_{FH}$ = 52.0 Hz, CF_2H); −129.85, −121.33 (m, CF_2CF_2); −94.35 (tt, $^3J_{FF}$ = 12.4 Hz, $^4J_{FF}$ = 2.7 Hz, $\underline{C}F_2CCl$). MS: m/z = 495 M^+. Anal. found: C, 22.2; H, 2.1; Cl, 19.9; Ge, 14.2%. N, 2.9; $C_9H_{10}Cl_3F_8GeNS$ requires C, 21.83; H, 2.13; Cl, 21.48; Ge, 14.66%; N, 2.83; M, 495.21.

2-*t*-Butyl-3,3,4-trichloro - 4 -n-heptafluoropropyl-1,2,3-thiazagermetidine (**8b**), yield 64%, bp 60–62°C/0.05 mm Hg. ^1H NMR ($CDCl_3$) δ: 1.44 (s, CH_3). ^{19}F NMR ($CDCl_3$) δ: −123.91, −94.94 (m, CF_2CF_2); −80.21 (tt, $^3J_{FF}$ = 10.2 Hz, $^4J_{FF}$ = 1.2 Hz, CF_3). MS: m/z = 463 M^+. Anal. found: C, 21.6; H, 2.2; Cl, 25.0; Ge, 17.0% N, 3.5. S, 7.0; $C_8H_9Cl_3F_7GeNS$ requires C, 20.74; H, 1.96; Cl, 22.96; Ge, 15.68%; N, 3.02; S, 6.92; M, 463.19.

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