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Ambiguous Reactivity of a Fluorinated Thiocarbonyl *S*-Imide; Unprecedented Rearrangement under FVP Conditions

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Dedicated to Professor Rolf Huisgen on the occasion of his 80th birthday

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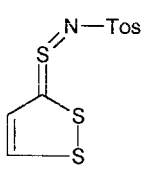
Abstract—Flash vacuum pyrolysis (FVP) of the *N*-(adamantan-1-yl)hexafluorothioacetone *S*-imide (**1b**) yielded an isomeric compound **4** without extrusion of the sulfur atom. On the other hand, thermolysis of the same *S*-imide in $CDCl_3$-solution afforded dithiazolidine **5** as the main product. Thermal cleavage of **1b** leading to in situ formation of hexafluorothioacetone is the primary reaction in solution. [3+2]-Cycloadditions of **1b** with strained *trans*-cyclooctene and dimethyl norbornenedicarboxylate occurred smoothly at ambient temperature with no decomposition and/or isomerisation. Reactions with less reactive cycloaliphatic thioketones **8a-b** were carried out at elevated temperature and gave products of multi-step processes. Isomerisation of **1b** which competes with the cleavage to hexafluorothioacetone, is postulated in order to explain the structures of the isolated products.

Introduction

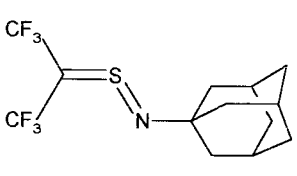
Thiocarbonyl *S*-imides **1** constitute a class of sulfur-centered three-atom systems which can be considered either as heterocumulenes or as 1,3-dipoles.[1] Like other species of similar nature, e.g. thiocarbonyl *S*-ylides or thiocarbonyl *S*-sulfides (thiosulfines) they usually appear as transient species and only in rare instances can they be isolated as storable compounds. Generally, the presence of electron-withdrawing groups at the carbon atom and/or a bulky substituent at the nitrogen atom contribute remarkably to the enhancement of the stability of compounds of type **1**. The first synthesis of a stable representative of **1** was described by Oae and Tamagaki[2] who succeeded in the preparation of a yellow coloured solid identified as **1a**. Some years later, Roesky et al., found that two CF_3-substituents and a bulky 1-adamantanyl moiety are sufficient to stabilise the *S*-imide system.[3]

The structure of the yellow-coloured, shelf stable *N*-(adamantan-1-yl)hexafluorothioacetone *S*-imide (**1b**) was confirmed by means of an X-ray crystallographic analysis.

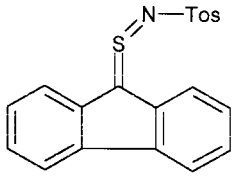
In contrast to thiocarbonyl *S*-ylides,[4] compounds of type **1** are not known nearly as well. Two review papers summarise the chemistry of thiocarbonyl *S*-imides up to the middle of the 1990s.[5] Thermal and photochemical reactions of **1** have been in the focus of attention for many years. Oae and Tamagaki studied the thermolysis of **1a** and found that the reaction proceeds with elimination of sulfur to give the imine compound **3a**.[6] However, increasing polarity of the solvent influenced the reaction course and in alcoholic solution cleavage of the thiocarbonyl *S*-imide occurred which led to the formation of the thiocarbonyl product. The mechanisms of both reactions, i.e. cleavage leading to the respective compound containing C=S group and



1a



1b



1c

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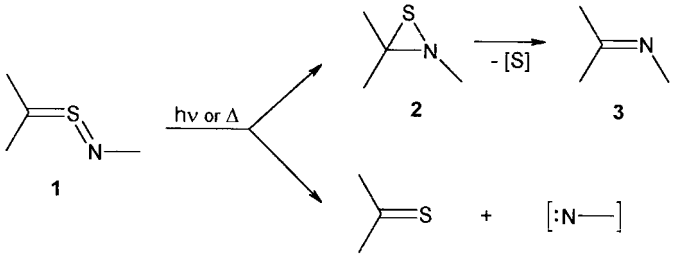
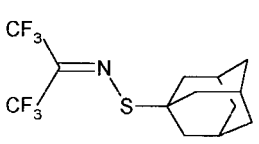


Scheme 1.



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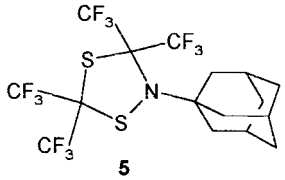

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desulfurisation yielding an imine product, were described as processes involving thiaziridines **2** as key intermediates (Scheme 1).[6]

Recent papers by Senning and coworkers reported on the thermolyses of some α-carbonyl substituted *S*-imides and, also in this case, explanation of the reaction pathway was based on the suggestion that thiaziridine derivatives are transient species.[7]

The aim of this paper is to compare the behaviour of the fluorinated thiocarbonyl *S*-imide **1b** in thermolyses performed in solution and in the gas-phase, respectively.

The reactivity of **1b** towards C=C dipolarophiles and a comparison with thiocarbonyl derivatives of 2,2,4,4-tetramethyl-cyclobutane-1,3-dione are also described.

Results and Discussion

The variable behaviour of **1a** in thermolyses performed in different solvents prompted us to compare the reactivities of **1b** in the gas-phase and in solution, respectively. The flash vacuum thermolysis (FVP) reaction of **1b** was carried out at 500°C/1.5×10^{-3} Torr and this was the lowest temperature which allowed complete conversion of the starting material. The product was condensed as a colourless, crystalline solid on the cold finger and no change was observed when the temperature was raised to 20°C. Analysis of the solid collected on the finger led to the conclusion that the FVP-reaction resulted in the formation of only one product which was isolated in high yield. After crystallisation, the elemental analysis of the colourless solid (mp 56–58°C) confirmed the molecular formula as $C_{13}H_{15}F_6NS$, which was identical with the starting material, and the MS spectrum confirmed the expected molecular weight (M=331). Thus, the gas-phase thermolysis of **1b** yielded in a smooth reaction a new product *without extrusion* of the sulfur atom. The ^{1}H NMR spectrum does not reveal signals relevant for the elucidation of the structure. The ^{19}F NMR spectrum showed two quartets (−68.26 and −67.83 ppm) with $^4J_{F,F}$=5.64 Hz. In the ^{13}C NMR spectrum, along with strong signals from the adamantane skeleton (Ad-skeleton), two non-equivalent quartets of the CF_3-groups appeared (117.2 and 117.8 ppm) with $^1J_{C,F}$=283.2 Hz and $^1J_{C,F}$=276.0 Hz, respectively.

An X-ray crystallographic analysis unambiguously confirmed this conclusion (Fig. 1). A characteristic pattern identified as a q,q-signal with two identical coupling constants calculated as $^2J_{C,F}$=36.67 Hz was found at 133.01 ppm. This value of the chemical shift suggested that the atom in question may be a sp^2-carbon atom. Based on this observation, the structure of a thiaziridine had to be excluded. Instead, all data available allowed its structure to be postulated as the hexafluoroacetone *S*-(adamantan-1-yl)thiooxime (**4**).

The unprecedented course of the gas-phase thermolysis which afforded **4** as the single product, prompted us to check the behaviour of the yellow **1b** when heated in solution. First tests carried out at 60°C showed that the reaction is rather slow and its completion could not be achieved even after 3 days. Therefore, a sealed tube containing **1b** dissolved in $CDCl_3$ was heated at 100°C and the

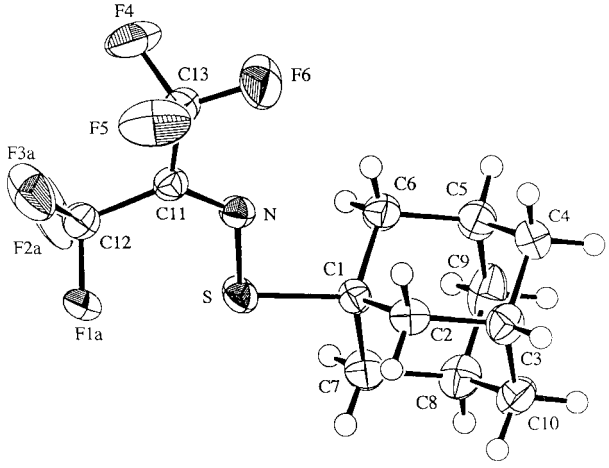
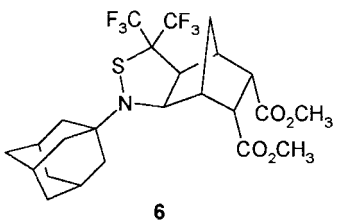


Figure 1. ORTEP[24] drawing of the molecular structure of **4** (50% probability ellipsoids).



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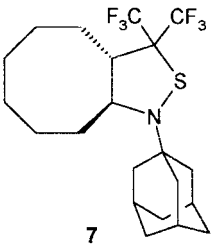

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yellow colour of the starting material disappeared after 12 h. The ^{13}C NMR spectrum of the crude reaction solution did not reveal known signals corresponding to either **1b** or **4**. Instead, signals registered (30.7, 35.8, 42.5 and 69.0 ppm) suggested that in this reaction the main product was 1,4,2-dithiazolidine **5** which has been fully characterised in one of our earlier papers.[8] Evaporation of the solvent and crystallisation of the oily residue afforded colourless needles which actually had identical properties as those of an original sample of **5**.

It is well established that thiocarbonyl *S*-imides **1** undergo [3+2]-dipolar cycloadditions to give five-membered heterocyclic products.[5] Whereas thiofluorenone *S*-(*N*-tosyl)-imide (**1c**) does not react with simple olefinic dipolarophiles,[9] **1b** reacts with styrene and its pyridine analogues.[10] We tested the reactivity of **1b** toward cyclohexene, dimethyl norbornenedicarboxylate and the strained *trans*-cyclooctene.

At ambient temperature, a solution of **1b** in cyclohexene did not change even after 7 d. When the same reaction mixture was heated in a sealed tube at 100°C for 4 h, the only identified product was again the known **5**.

Dimethyl norbornenedicarboxylate reacted slowly with **1b** at room temperature and the reaction was complete after 4 d. The cycloadduct **6** was formed in a smooth reaction in good yield. Its structure was established by means of spectral methods and unambiguously confirmed by an X-ray diffraction analysis (Fig. 2). The molecular structure shows that **1b** approaches the norbornene system from the more favourable *exo*-side and therefore avoids repulsion by the two ester groups. This preferable orientation results in the exclusive formation of the *exo*-product **6**.

A vigorous reaction was observed when **1b** dissolved in CH_2Cl_2 was treated with a 1.5 mol equiv. of *trans*-cyclooctene. After a few minutes at ambient temperature the reaction was complete and after evaporation of the solvent a crystalline product was isolated in practically quantitative yield. The spectral data were in good agreement with the postulated structure **7**.

Smooth reactions of 'superdipolarophilic' aromatic thioketones were described by us in an earlier paper.[8] 2,2,4,4-Tetramethyl-3-thioxocyclobutanone (**8a**) is one of only a few stable thioketones and its reactions with 1,3-dipoles have been studied extensively.[11] According to Huisgen's scale, aliphatic thioketones are less reactive than their aromatic counterparts.[12] The reaction of **1b** with **8a** was carried out in $CDCl_3$ solution and the progress of the reaction was monitored by ^1H NMR. At room temperature, the ^1H NMR spectrum remained unchanged even after 2 days. Therefore, the NMR tube was sealed off and the reaction mixture was subsequently heated at 100°C. After 3 h the reaction was complete and the solvent was removed under vacuum.

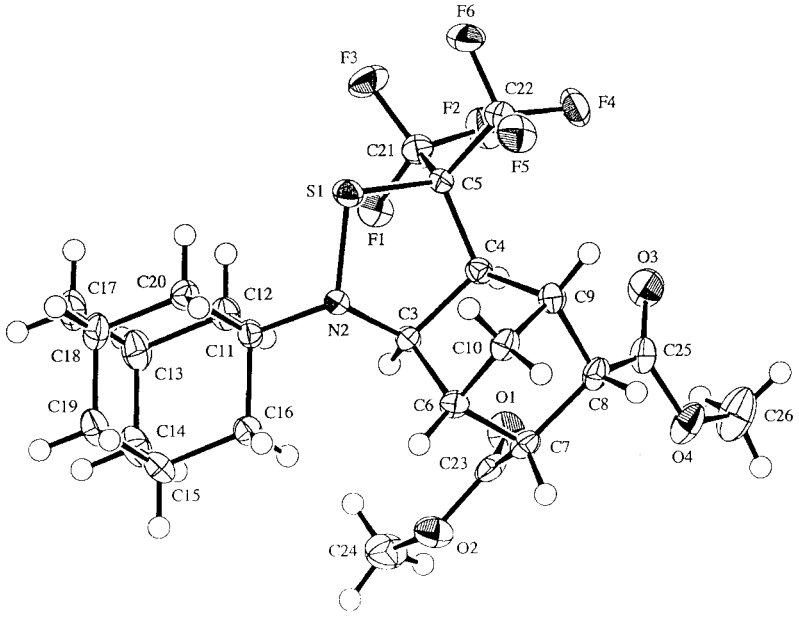


Figure 2. ORTEP drawing of the molecular structure of **6** (50% probability ellipsoids).

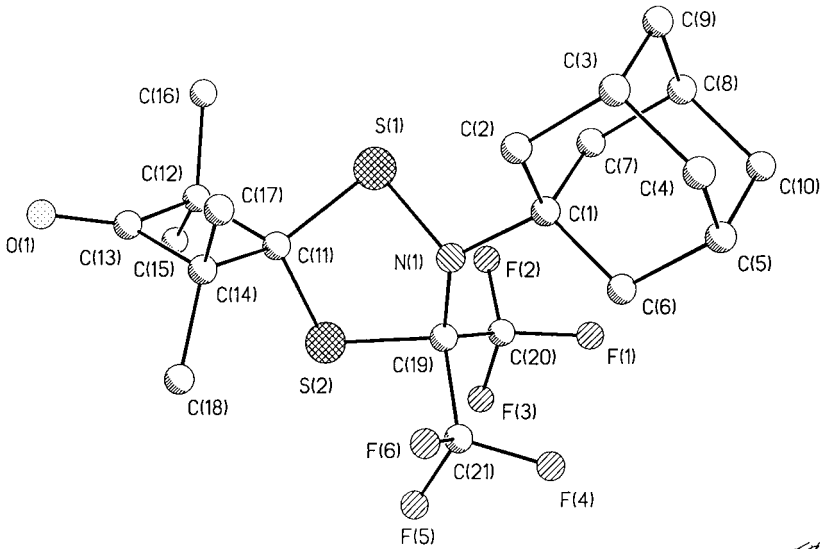
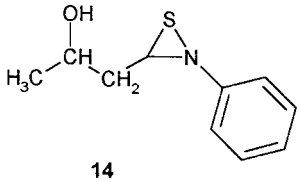


Figure 3. ORTEP drawing of the molecular structure of **11** (50% probability ellipsoids).

The oily residue, after treatment with methanol, afforded crystalline **5**, but two other products were also separated chromatographically from the mother liquor. Colourless crystals obtained from the fraction eluted with a mixture of dichloromethane and petroleum ether (25:75) showed signals in the ^{1}H NMR spectrum which corresponded with the Ad-skeleton and singlets from CH_3-groups linked to the cyclobutanone ring. Although all spectroscopic data and HRMS supported the molecular formula ($C_{21}H_{27}F_6NOS_2$) which is consistent with a 1:1 adduct of **1b** with **8a**, the actual structure of the product was uncertain. In order to solve the problem, an X-ray diffraction analysis was carried out and the result is presented in Fig. 3. It shows that the product is not a 1,3-cycloadduct of **1b** onto the C=S bond, i.e. **9** or **10**, but an isomeric compound **11**.

The heterocyclic ring of **11** does not reveal a structure fragment which might be attributed to **1b**. The result suggests that more complicated [3+2]-cycloaddition reaction pathway leads to **11**. The third component of the reaction mixture was eluted as the most polar fraction and by comparison with the authentic sample it was identified as the di-*spiro*-1,2,4-trithiolane **13**.[13]

Reaction of **1b** with a two-fold molar amount of the dithione **8b** was also carried out at 100°C. The product of the intermolecular reaction was isolated as red coloured crystals. The ^{13}C NMR spectrum revealed the signal of the C=S group at 265.2 ppm. Other signals appeared in regions very close to those found in the already described cycloadduct **11**. Thus, an analogous structure **12** is conceivable. Syntheses of thiaziridine derivatives have been attempted for many decades, but there is only one report in which the authors claim to have synthesised a stable compound of this type and which was believed to have the structure **14**.[14] Postulation of a three-membered heterocycle, which was based only on the result of elemental analysis, is a doubtful conclusion and the result is under investigation in our laboratory.[15] Later attempts to prepare an isolable thiaziridine by Quast and other authors were in vain.[16]



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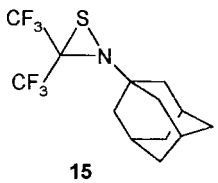

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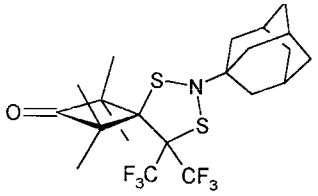

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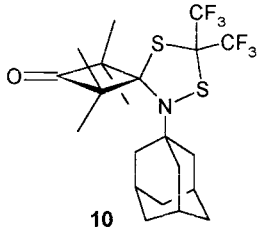

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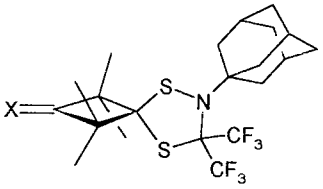
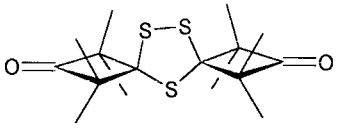


11 (X = O)
12 (X = S)



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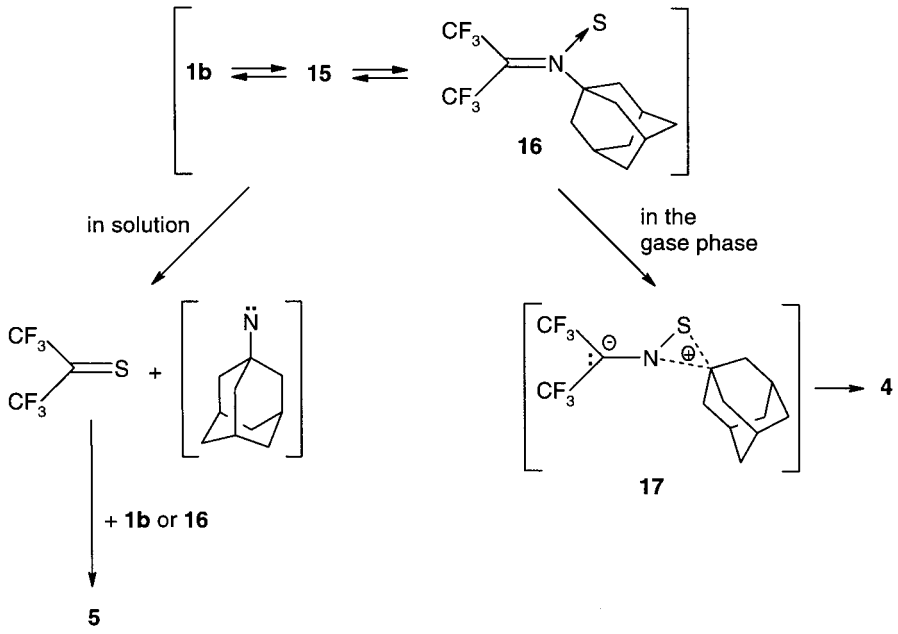

Scheme 2.

Bearing in mind all known factors which contribute to the stabilisation of small, strained rings (electron-withdrawing and/or bulky groups as substituents), the *S*-imide **1b** seemed to be an ideal starting material for a photochemically[17] or thermally mediated cyclisation to the thiaziridine derivative. In spite of the fact that we were not able to isolate 2-(adamantan-1-yl)-3,3-bis(trifluoromethyl)thiaziridine (**15**), we obtained strong evidence for its presence as an intermediate, which is crucial for the formation of the rearranged product **4** and the dithiazolidines **11**,**12**, respectively. Rearrangement of **1b** to **4** requires exchange of the positions of the sulfur and the nitrogen atoms, as well as migration of the bulky Ad moiety (Scheme 2).

In our interpretation, the pathway leading from **1b** to **4** is initiated with its cyclization to **15**, which subsequently opens the ring to afford thionitrone **16**.

Under FVP conditions, the latter intermediate undergoes an intramolecular rearrangement probably via a cyclic three-atom transition state **17**, which enables migration of the Ad-group from the nitrogen to the sulfur atom. Heating **1b** in solution probably affords a similar equilibrium mixture and its formation competes with the irreversible cleavage of the N–S bond, which leads to hexafluorothioacetone (and probably adamantan-1-yl nitrene[18]) a known and extremely reactive dieno- and dipolarophile.[19] Hexafluorothioacetone can subsequently react not only with **1b** but also with in situ generated thionitrone **16**; both reactions lead to the same dithiazolidine **5**. The thionitrone **16** is believed to react faster and this hypothesis is confirmed by the results of the reactions of **1b** with cycloaliphatic thioketones, e.g. the monothione **8a** is selectively intercepted by **16** to yield **11**, whereas hexafluorothioacetone can react with both **1b** and **16**, and both reactions result in the formation of **5**.

As indicated earlier, [3+2]-dipolar cycloadditions of **1b** with reactive, strained olefins could be performed at ambient temperature. Under these conditions the equilibrium shown in Scheme 2 is shifted to the left and the reaction solution essentially contains neither **15** nor **16**. Therefore, the formation of **6** and **7**, respectively, resulting from [3+2]-cycloadditons of **1b** to the C=C double bonds is observed.

In summary, the results presented in this paper show that the thiocarbonyl *S*-imide **1b** can be exploited as a reactive 1,3-dipole in reactions carried out at ambient temperature. After heating, however, it is likely that it undergoes a rearrangement to generate the elusive thionitrone **16** via a pathway which involves the thiaziridine **15**, or it cleaves to release reactive hexafluorothioacetone which undergoes fast reaction with the starting material to afford **5**. On the other hand, the only reaction observed under FVP conditions is the rearrangement to the thermodynamically more stable thiooxime ether **4**. To the best of our knowledge this is the first example of an intramolecular, thermal conversion of thiocarbonyl *S*-imide which does not result in the extrusion of the sulfur atom.

Experimental

General

Melting points were determined on a *Mel-Temp* (Aldrich) apparatus in a capillary and are uncorrected. ^{1}H (300 MHz), ^{13}C (75.5 MHz) NMR spectra were recorded on a Bruker ARX-300 using samples prepared as $CDCl_3$ solutions and TMS was used as a standard. ^{19}F NMR spectra were registered with a Bruker AMX-600 (564.7 MHz) instrument and trichlorofluoromethane was used as a standard. The IR spectra were taken with a Specord-75 spectrometer. Mass spectra were determined on a Finnigan MAT-90; CI-MS with NH_3. Column chromatography was performed with silica gel (Merck) and the eluent is shown in parentheses.

Starting materials

N-(adamantan-1-yl)hexafluorothioacetone *S*-imide (**1b**);[3,8] 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**8a**) and 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**8b**) were prepared according to cited protocols.[11] Other reagents were purchased from Aldrich or Fluka.

Flash vacuum thermolysis of 1b

The flash vacuum thermolysis was carried out in a 30×2.5 cm^2 electrically heated horizontal quartz tube packed with quartz rings at 1.5×10^{-3} Torr. The compound **1b** (2 mmol) was slowly sublimed from a flask held at 50°C into the thermolysis tube preheated to 500°C. The products were collected in a CO_2-acetone trap. After thermolysis, the system was brought to atmospheric pressure allowing a slow warm up to room temperature and the products were dissolved in CH_2Cl_2. The solvent was removed under reduced pressure and the crude product, obtained in practically quantitative yield, was purified by recrystallisation from methanol.

Hexafluoroacetone *S*-(adamantan-1-yl)thiooxime (4). Yield 530 mg (80%), colourless prisms, mp 56–57°C (methanol). ^{1}H NMR: 1.75, 1.96, 2.14 (3m, 15H). ^{13}C NMR: 29.4 (3 CH), 36.1 (3 CH_2), 40.7 (3 CH_2), 51.9 (C_q), 117.2 (CF_3, q, $^1J_{C-F}$=283.2 Hz), 117.75 (CF_3, q, $^1J_{C-F}$=276.0 Hz), 133.0 (C=N, q, $^2J_{C-F}$=36.4 Hz). ^{19}F NMR: −67.84 (q, *J*=5.64 Hz) and −68.26 (q, *J*=5.64 Hz) (2 CF_3). IR (KBr): ν 840 cm^{-1}, 980 s, 1060, 1120, 1180 vs, 1240 s, 1320, 1340 s, 1460, 1605, 2790, 2850 vs; MS *m/z* (%): 331 [M^+](<5), 135 [$C_{10}H_{15}^+$] (100). Anal. $C_{13}H_{15}F_6NS$ (331.33), calcd C 47.13; H 4.56; N 4.23; S 9.68; found: C 47.31; H 4.59; N 4.15; S 9.47.

X-Ray crystallographic details for compound 4. (Fig. 1)[22]: $C_{13}H_{15}F_6NS$, M_r=331.32, monoclinic, space group $P2_1/n$, a=13.542(2), b=7.913(2), c=13.946(2) Å, β=107.53(1)°, V=1424.9(4) Å^3, Z=4, D_c=1.544 Mg m^{-3}, F(000)=680, T=173(1) K, μ(MoKα)=0.286 mm^{-1}, colourless crystals, dimensions: 0.20×0.40×0.48 mm^3, Rigaku AFC5R diffractometer, graphite-monochromated MoKα radiation, λ=0.71073 Å, cell constants from 25 centred reflections, $\omega-2\theta$ scans, intensities of 3 standards checked after every 150 reflections: no decay, 2θ range 5–55°, 3666 measured reflections of which 3283 were unique (R_{int}=0.011). The intensities were corrected for *Lorentz* and polarization effects, but not for absorption. Structure solution by direct methods using SHELXS-86[20] and refined on F by full-matrix least-squares methods using TEXSAN,[23] non-H atoms refined anisotropically, H-atoms refined isotropically. Disorder is evident in the F atoms of the CF_3 groups. Two orientations with relative site occupation factors of 0.614:0.386 were defined for one of the CF_3 groups. The refinement of 279 parameters using 2481 observed reflections with $I>2\sigma(I)$ gave R=0.0442, wR=0.0405, S=1.918, weights: $[\sigma^2(F_o)+(0.005F_o)^2]^{-1}$, max and min residual electron density 0.29; −0.24 e Å^{-3}.

Thermolysis of 1b in $CDCl_3$ solution

165 mg (0.5 mmol) **1b** were dissolved in 0.5 ml $CDCl_3$ and the solution was placed in an NMR tube. The tube was sealed and heated in a 100°C oil bath. From time to time the tube was cooled to room temperature and the reaction progress was monitored by running a ^{1}H NMR spectrum. After 12 h the reaction was complete and the crude reaction mixture was analysed by means of a ^{13}C NMR spectrum. Signals registered (30.7, 35.8, 42.5 and 69.0 (s) ppm), matched well with the data described for **5**[8] and suggested that it is the main component of the reaction mixture. Other relatively strong signals found (29.6, 31.0, 36.1, 36.9 and 42.4 ppm), could not be attributed to any known structure. The solvent was evaporated and the residue, obtained as a thick oil, was recrystallised from methanol; 55 mg (43%) of colourless needles of **5** with mp 67–68°C (lit.[8] mp 65–67°C) were isolated. No other products were isolated from the mother liquor.

Reactions of 1b with dimethyl *(r-1)(t-2)(t-3)*-norborn-5-enedicarboxylate. 140 mg (0.7 mmol) of dimethyl 5-norbornenedicarboxylate and 165 mg (0.5 mmol) of **1b** were dissolved in 0.5 ml $CDCl_3$. This solution was stored at ambient temperature and the progress of the reaction was monitored from time to time by running a ^{1}H NMR spectrum. After 7 d the reaction was complete. The solvent was removed in vacuo and the oily residue was evaporated three times with small portions of hexane (ca 3 ml each). Colourless crystals (244 mg, 90%) of the crude product **6** were isolated and purified by recrystallisation.

Dimethyl *(r-1)(c-2)(c-5)(c-7)(t-8)(t-9)*-3-(adamantan-1-yl)-5,5-bis(trifluoromethyl)-3-aza-4-thiatricyclo-[5.2.1.0^{2,6}]-decane-8,9-dicarboxylate (6). Colourless crystals, yield after recrystallisation 184 mg (68%), mp 138–140°C (hexane). IR (KBr): (690 cm^{-1}, 920 s, 1050 s, 1080 s, 1130 s, 1190 vs, 1340, 1350, 1440 s, 1740 vs (C=O). ^{1}H NMR: 1.36–3.91 (m, 8H), 3.67, 3.68 (2s, 2OCH_3). ^{13}C NMR: 29.8, 36.4, 41.0, 68.8, 35.6, 36.4, 41.0, 41.5, 44.1, 46.8, 50.4, 51.6, 51.9, 68.9, 70.1 ($^2J_{C-F}$=27.7 Hz), 123.8 ($^1J_{C-F}$=284.2 Hz, CF_3), 124.9 ($^1J_{C-F}$=284.2 Hz, CF_3), 171.8, 172.3 (2s, 2C=O). ^{19}F NMR: −62.02 (broad, CF_3), −69.62 (q, J_{F-F}=11.85 Hz, CF_3). MS (CI); *m/z* (%): 542 (100) [M^++1], 510 (5) [M^++1S]. Anal. $C_{24}H_{29}F_6NO_4S$ (541.55): calcd C 53.22; H 5.39; N 2.58; found C 53.20; H 5.36; N 2.56.

X-Ray crystallographic details for compound 6. (Fig. 2)[22]: $C_{24}H_{29}F_6NO_4S$, M_r=541.55, monoclinic, space group $C2/c$, a=27.817(8), b=8.546(5), c=20.319(4) Å, β=95.27(2)°, V=4810(3) Å^3, Z=8, D_c=1.495 Mg m^{-3}, F(000)=2256, T=173(1) K, μ(Mo Kα)=0.214 mm^{-1}, colourless crystals, dimensions: 0.32×0.40×0.50 mm^3, Rigaku AFC5R diffractometer, graphite-monochromated MoKα radiation, λ=0.71073 Å, cell constants from 22 centred reflections, $\omega-2\theta$ scans, intensities of 3 standards checked after every 150 reflections: no decay, 2θ range 5–55°, 6014 measured reflections of which 5522 were unique (R_{int}=0.043). The intensities were corrected for Lorentz and polarization effects, but not for absorption. Structure solution by direct methods using SHELXS-86[20] and refined on F by full-matrix least-squares methods using TEXSAN,[23] none-H atoms refined anisotropically, H-atoms fixed in calculated positions. The refinement of 326 parameters using 3886 observed reflections with $I>2\sigma(I)$ gave R=0.0423,

wR=0.0371, S=1.795, weights: $[\sigma^2(F_o)+(0.005F_o)^2]^{-1}$, max and min residual electron density 0.43; −0.29 eÅ^{-3}.

Reactions of 1b with *trans*-cyclooctene. 100 mg (0.90 mmol) *trans*-cyclooctene were dissolved in 0.5 ml $CDCl_3$, placed in a 2 ml flask cooled in a water-ice bath. A solution of 220 mg (0.66 mmol) **1b** in 0.5 ml $CDCl_3$ was added in small portions. After 5 min at 0–5°C, the initially yellow colour of the solution completely disappeared and the ^{1}H NMR spectrum taken thereafter showed that the reaction was complete. The solvent and excess *trans*-cyclooctene were removed in vacuo. The residue was evaporated three times with small portions (3 ml each) of methanol to yield 277 mg (95%) of the crude, crystalline product. Recrystallisation from methanol afforded an analytically pure sample.

2-(Adamantan-1-yl)-5,5-bis(trifluoromethyl)cyclooctа[c]-(1,2)-thiazolidine (7). Colourless crystals, yield after recrystallisation 154 mg (53%), mp 77–79°C were obtained from methanol with a small amount of dichloromethane. IR (KBr): (710 cm^{-1}, 725, 920, 1080, 1100, 1140, 1185 vs, 1270 vs, 1470, 2920 vs. ^{1}H NMR: 1.47–2.00 (m, 27H), 2.94 (m, 1H), 3.76 (m, 1H). ^{13}C NMR: 24.5, 26.5 26.7, 26.9 36.7, 58.8 (6t, 6CH_2 cyclooctane ring), 36.4, 41.6 (2t, 6CH_2 adamantane), 30.0, 51.3, 66.7 (3d, 3CH), 70.8 (quintet, $^2J_{C-F}$=24.8 Hz, C-5), 124.6 (q, $^1J_{C-F}$=280.7 Hz, CF_3), 124.8 (q, $^1J_{C-F}$=284.3 Hz, CF_3). ^{19}F NMR: −61.70, −67.67 (2q with J_{F-F}=10.7 Hz, 2CF_3). MS(CI); m/z (%): 442 (100) [M^++1]. Anal. $C_{21}H_{29}F_6NS$ (441.52): calcd C 57.13; H 6.62; N 3.17; found C 57.03; H 6.57; N 3.15.

Reactions of 1b with 2,2,4,4-tetramethyl-3-thioxocyclobutanone (8a) and 2,2,4,4-tetramethylcyclobutane-1,3-dithione (8b)—a general procedure. 660 mg (2 mmol) **1b** and 1 mmol of the corresponding thione **8** were dissolved in 1 ml of $CDCl_3$ and the solution was placed in an NMR tube. The tube was sealed and the red-coloured solution was heated in a 100°C-oil bath. After 3 h, the reactions were complete; after cooling to room temperature, the tube was opened and the solvent removed in vacuo. The semi-solid residue was treated with 2 ml methanol and stored overnight in the refrigerator. The next day the colourless crystals, identified as **5**, were filtered off and the mother liquor was separated chromatographically on a SiO_2-column using petroleum ether with an increasing amount of dichloromethane as the eluent. An additional amount of **5** was isolated as the less polar fraction.

Reaction with 8a: 4-(Adamantan-1-yl)-2,2,5,5-tetrakis-(trifluoromethyl)-1,3,4-dithiazolidine (5). Yield 360 mg (70%), mp 64–66°C (lit.[8] mp 65–67°C).

1,1,3,3-Tetramethyl-5,8-dithia-6-azaspiro[3.4]octane-2-one (11). Isolated with a petroleum ether/dichloromethane mixture (75:25), colourless prisms, yield 130 mg (27%), mp 138–140°C, were obtained after recrystallisation from a hexane solution. IR (KBr): (695 cm^{-1}, 795, 905, 945, 1020, 1050, 1170 s, 1230 s, 1355, 1450, 1790 s. ^{1}H NMR: 1.35 (s, 6H), 1.42 (s, 6H), 1.60 (m, 6H), 2.09 (m, 9H). ^{13}C NMR: 21.1, 24.5, 30.6, 35.8, 41.9, 65.3, 66.1, 66.2, 87.2 (m, $^2J_{C-F}$=27.8 Hz, C-7), 124.0 (q, $^1J_{C-F}$=290.1 Hz, 2CF_3), 218.0 (s, C=O). ^{19}F NMR: −62.56 (s, 2CF_3). MS (EI); m/z (%): 487 (<5) [M^+], 135 (100). Anal. $C_{21}H_{27}F_6NOS_2$ (487.60): calcd C 51.73; H 5.58; N 2.87; found C 51.58; H 5.61; N 2.94.

X-Ray crystallographic details for compound 11. (Fig. 3)[25]: $C_{21}H_{27}F_6NOS_2$, M_r=487.60, triclinic, space group P-1, a=10.250(5), b=10.383(4), c=10.815(5) Å α=75.808(12), β=82.29(2), γ=75.33(2)°, V=1076.3(8) Å^3, Z=2, D_c=1.504 Mg m^{-3}, F(000)=508, T=193(2) K, μ(MoKα)=0.314 mm^{-1}, colourless crystals, dimensions: 0.60×0.50×0.35 mm^3, Stoe-Siemens AED four-circle diffractometer, graphite-monochromated MoKα radiation, λ=0.71073 Å, cell constants from 15 centred reflections, ω–2θ scans with profile fitting, intensities of three standard reflections checked every 90 min, 2θ range 6–45°, 4025 measured reflections of which 2797 were unique (R_{int}=0.1073). The intensities were corrected for Lorentz and polarization effects. Structure solution by direct methods using SHELXS-90[20] and refined on F^2 by full-matrix least-squares methods using SHELXL-93,[21] none-H atoms refined anisotropically, H-atoms included in calculated positions and refined using a riding model. Final $R1$=0.0537 and $R2$=0.0977 for 1834 reflections with $I>2\sigma(I)$, $R1$=0.1084 and $R2$=0.1194 for all data, weights: SHELXL-93, max and min residual electro-density 0.34; −0.28 eÅ^{-3}.

1,1,3,3,7,7,9,9-Octamethyl-5,10,11-trithiadispiro[3.1.3.2]-undecane-2,8-dione (13). Isolated with a 65:35 petroleum ether/dichloromethane mixture, yield 120 mg (70%), colourless needles, mp 98–100°C (lit.[13] mp 97–99°C). ^{1}H NMR: 1.39, 1.49 (2s, 4CH_3 each).

Reaction with 8b: 4-(Adamantan-1-yl)-2,2,5,5-tetrakis-(trifluoromethyl)-1,3,4-dithiazolidine (5). Yield 350 mg (68%).

1,1,3,3-Tetramethyl-5,8-dithia-6-azaspiro[3.4]octane-2-thione (12). Red crystals, yield 148 mg (29%), mp 147–149°C were obtained after crystallisation from methanol. IR (KBr): (700 cm^{-1}, 900, 940, 980, 1050, 1130 m (C=S), 1170 s, 1230 s, 1295, 1350, 1450. ^{1}H NMR: 1.45 (s, 6H), 1.52 (s, 6H), 1.63 (m, 6H), 2.13 (m, 9H). ^{13}C NMR: 25.2, 28.6, 30.6, 35.8, 41.9, 65.2, 68.9, 69.9, 87.2 (m, $^2J_{C-F}$=27.8 Hz), 123.8 (q, $^1J_{C-F}$=290.2 Hz, 2CF_3), 277.8 (s, C=S). ^{19}F NMR: −62.58 (s, 2CF_3). MS (CI); m/z (%): 504 (10) [M^++1], 152 (100). Anal. $C_{21}H_{27}F_6NS_3$ (503.64): calcd C 50.08; H 5.40; N 2.78; found C 50.32; H 5.44; N 2.78.

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