Reactions of Thioketones with a Fluorinated Thione *S*-Imide☆

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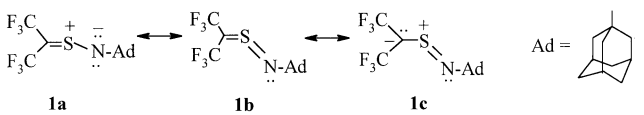
N-(1-Adamantyl)hexafluorothioacetone *S*-imide (**1**) reacts readily with aromatic thioketones **4a**−**e** to afford 1,4,2-dithiazolidines **5a**−**e** as products of [3 + 2] dipolar cycloadditions. Unexpectedly, cycloadducts **5d** and **5e**, obtained from thioxanthione (**4d**) and 4,4′-(dimethoxy)thiobenzophenone (**4e**), respectively, are found to decompose at room temperature and could not be isolated as pure compounds. Unlike aromatic thiones, adamantanethione (**4f**) did not react with **1** at ambient temperature. However, reaction did occur upon heating in a sealed tube, and the new 1,4,2-dithiazolidine **9**, bearing two adamantyl moieties, was isolated as the major product. The structure of **9** has been determined by X-ray diffraction analysis. The connectivity of the heterocyclic ring in this product indicates that the mechanism of its formation must proceed by a different route involving another in situ generated sulfur-centered 1,3-dipole. Retrocycloaddition of the primary adamantanethione cycloadduct **13** liberates hexafluorothioacetone, which is subsequently captured by *S*-imide **1** to give tetrakis(trifluoromethyl)-1,4,2-dithiazolidine **8** as a crystalline product. The structure of **8** has also been confirmed by X-ray diffraction analysis.

Introduction

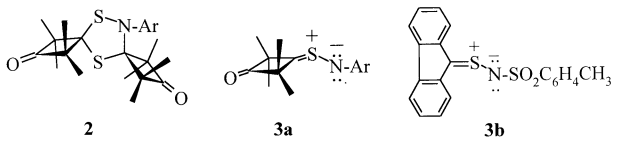
Thiones have generally been regarded as being rather unstable compounds that are difficult to obtain and have been dismissed as being of limited importance in organic synthesis[1]. In recent years, however, the situation has changed and several papers concerning new, convenient preparative methods involving thioketones have been published[2]. Particularly important were the findings of Huisgen et al. that thiones are superdipolarophilic and that they are more reactive towards 1,3-dipoles than other, well-known electron-poor dipolarophiles such as tetracyanoethylene (TCNE), dimethyl acetylenedicarboxylate (DMAD), dimethyl azodicarboxylate, etc.[2a][3]. Furthermore, Sauer et al. recently reported a high dienophilic reactivity of thiones, which may be of importance with regard to new applications in hetero Diels-Alder chemistry[4].

Reactions of thiones with 1,3-dipoles are now attracting the attention of many groups. In the last few years, their reactions with diazoalkanes[5], nitrones[6], azides[7], and azomethine ylides[8] have been described. The reaction using organic azides, which was first reported by Schönberg in the mid-1930′s[9], merits special attention. This little known conversion of thioketones has recently been shown to offer a completely new approach to the in situ preparation of highly reactive, sulfur-centered 1,3-dipoles, such as thione *S*-sulfide (thiosulfine) and thione *S*-imide[7].



1a **1b** **1c**

The aim of this paper is to present new reactions of aromatic and cycloaliphatic thiones using fluorinated thione *S*-imide **1**, which represents a rare example of an isolable and storable sulfur-centered 1,3-dipole (thiocumulene). The synthesis of **1** has recently been described[10] and its reactions with some C=C, C=N, and C=P dipolarophiles have already been studied[11]. Generally, however, the reactions of thione *S*-imides are not widely reported in the literature and their chemistry is still less well known than that of other sulfur-centered 1,3-dipoles[12]. To the best of our knowledge, there have been only a few accounts of reactions of thiocarbonyl *S*-imides with thiocarbonyl compounds. One of these deals with sterically crowded 1,4,2-dithiazolidines **2**, isolated in reactions of 2,2,4,4-tetramethyl-3-thioxocyclobutanone with aromatic azides. Here, a plausible interpretation of the mechanism of their formation centred on the intermediacy of an in situ generated thione *S*-imide **3a**[7b].



2 **3a** **3b**

In 1980, Saito et al.[13] reported on an attempted synthesis of similar systems, but the primary [3 + 2] cycloadducts, formed by reaction of *N*-tosyl-substituted *S*-imide **3b** with thioketones, were found to be very unstable and underwent complete dissociation within a short period of time at room temperature. The proposed structures of the unstable products were deduced solely on the basis of spectroscopic data, without their isolation from the reaction mixtures[13].

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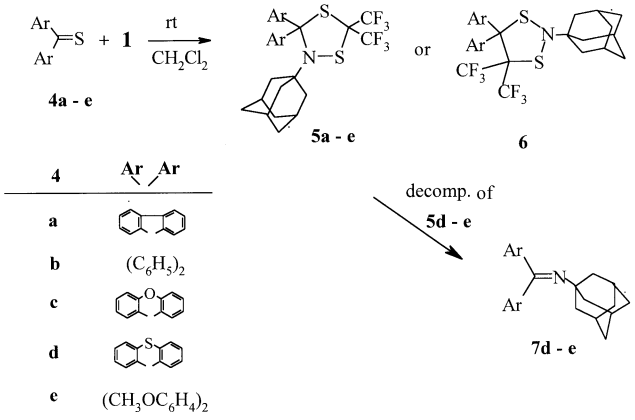
Results and Discussion

The reactions of aromatic thiones **4a**−**e** with **1** described in this paper were performed at ambient temperature and decolorizations of reaction solutions were observed after a short period of time depending on the specific thione used. Generally, the observed reactivity of **4** was in agreement with the data reported by Huisgen et al.[3], the reaction with thiofluorenone (**4a**) proceeding most rapidly (< 1 min.), followed by those with thiobenzophenone (**4b**) and xanthione (**4c**). In contrast to the findings of Saito et al.[13] (but in accordance with Huisgen′s scale of thione reactivity), 4,4′-(dimethoxy)thiobenzophenone (**4e**) was found to be the least reactive of the thioketones used in this study.

The ^{19}F-NMR spectra of the crude reaction mixtures indicated the formation of only one regioisomer of the expected [3 + 2] cycloadducts of types **5** or **6**. The products obtained with thiones **4a**−**c** were sufficiently stable to be isolated in an analytically pure form and could be stored indefinitely at room temperature without significant decomposition. On the other hand, the products isolated from reactions using thioxanthione (**4d**) and 4,4′-(dimethoxy)-thiobenzophenone (**4e**) decomposed during recrystallization at room temperature and only the corresponding imines **7d**−**e** could be isolated as analytically pure compounds.

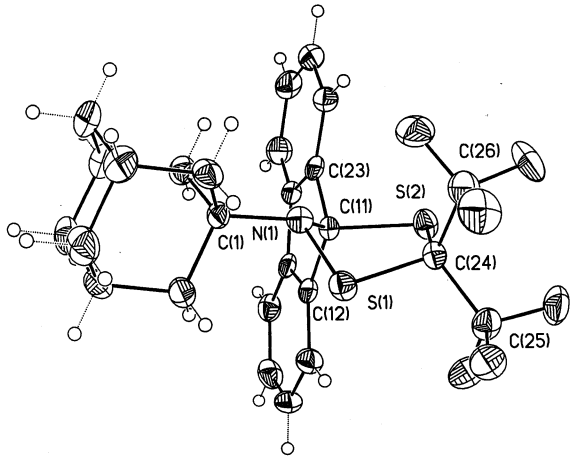
Scheme 1



In order to establish the regiochemistry of the cycloaddition of **1** to aromatic thiones, the structure of 1,4,2-dithiazolidine **5a**, formed as a single product after a fast reaction of **1** with **4a**, was determined by X-ray diffraction analysis (Figure 1). The structure of the heterocyclic ring is confirmed as corresponding to 1,4,2- (**5a**) and not to the isomeric 1,3,2-dithiazolidine **6a**. Thus, the regiochemical course of the [3 + 2] cycloaddition of **1** with the thione group C=S is similar to that observed in the previously studied reaction involving the in situ generated *S*-imide of 2,2,4,4-tetramethyl-3-thioxocyclobutanone[7b]. Figure 1 shows that the nitrogen atom of the *S*-imide system binds the carbon atom of the C=S bond. The conformation of **5a** can be described as being of envelope-form, with the nitrogen atom at the flap position, and corresponds to the conformation of other stable 1,4,2-dithiazolidines recently described by one of us[7b].

The crystal structure of compound **5a** is shown in Figure 1. This species crystallizes in the monoclinic space group $P2_1/c$, with two molecules in the asymmetric unit. The five-membered rings, forming the cores of the structures in the two independent molecules, show deviations from planarity of 0.208 and 0.201 Å, respectively. If we ignore the N atom in the rings, the remaining C and S atoms show only very slight deviation from planarity (average 0.049 Å for the two independent molecules).

Figure 1. Crystal structure of **5a** with anisotropic displacement parameters depicting 50% probability; only one of the two molecules present in the asymmetric unit is shown for the sake of clarity[a]



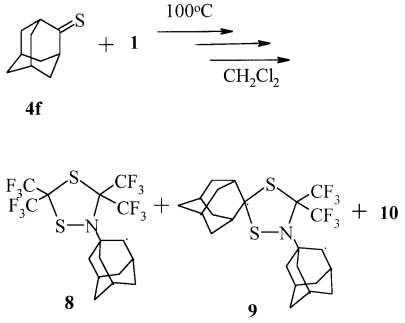
[a] Selected bond lengths [Å] and angles [°] (all the values averaged over the two crystallographically independent molecules): N(1)−C(11) 1.470(6), C(11)−S(2) 1.864(5), S(2)−C(24) 1.805(6), C(24)−S(1) 1.804(6), S(1)−N(1) 1.733(4), N(1)−C(1) 1.517(6); N(1)−C(11)−S(2) 104.3(3), C(11)−S(2)−C(24) 97.7(3), S(2)−C(24)−S(1) 107.7(3), C(24)−S(1)−N(1) 93.9(2), S(1)−N(1)−C(11) 109.2(3), C(12)−C(11)−C(23) 102.0(4), C(25)−C(24)−C(26) 111.0(5).

Decomposition of the unstable cycloadducts **5d**−**e**, obtained from the reactions of **1** with thioxanthione (**4d**) and 4,4′-(dimethoxy)thiobenzophenone (**4e**), respectively, afforded *N*-(1-adamantyl)-substituted imines **7d**−**e**. The direct bond between the nitrogen and the substituted sp^2-carbon atom of the aromatic system may be viewed as supporting evidence for the same regiochemical course as that for the formation of the initial 1:1 products. Apparently, the cycloaddition step is controlled by electronic factors, while the steric hindrance resulting from the presence of the bulky adamantyl skeleton at the carbon atom adjacent to the aromatic rings does not influence the course of the formation of **5**.

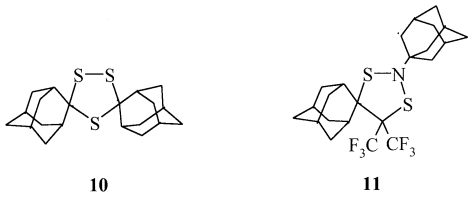
In the ^{13}C-NMR spectra of **5a**−**c**, the signals of the C atoms bearing two trifluoromethyl groups appear as septuplets, with typically low intensity and coupling constants $^2J_{C-F}$ = 29.0 Hz. These signals are seen at chemical shifts in the range $\delta(^{13}C)$ = 66.2−75.2 and are invariably upfield-shifted compared to the singlets attributable to the C-3 atoms. The differences in the chemical shifts of the C-3 and C-5 atoms were typically found to be around 20 ppm; only in the case of the thiobenzophenone adduct **5b** was a markedly larger difference observed (ca. 32 ppm).

Mass spectra recorded for dithiazolidines **5a**−**d** were in accordance with the proposed structures of the heterocyclic rings. The radical cation of adamantane (*m*/*z* = 135) was always found as the parent peak. In the MS of **5b**, the fragment with *m*/*z* = 315 (88) was identified as the radical cation of the imine fragment $[(C_6H_5)_2C{=}N{-}Ad]^+$ and its formation is further evidence supporting the structure of the product derived from **1** and **4b**.

Scheme 2



Adamantanethione (**4f**) is a quite stable cycloaliphatic thione, which has been used in many reactions as a moderately reactive dipolarophile[14][15]. In a preliminary experiment, performed at ambient temperature, **4f** was found not to react with *S*-imide **1**, even after several days. This observation is consistent with Huisgen's scale of thione reactivities towards 1,3-dipoles; in all known cases, cycloaliphatic thiones were found to react more slowly than their aromatic counterparts[2a][3]. Therefore, we changed the reaction conditions and after heating equimolar amounts of **4f** and **1** in chloroform solution in a sealed tube at 80°C for 2 h, the orange color of the reaction mixture had disappeared and TLC analysis indicated complete consumption of **1**. However, a small amount of **4f** was still present in the reaction solution. Chromatographic work-up resulted in the isolation of two major fluorinated products **8** and **9**, and a third component, which was found to be the well-known dispiro(2-adamantyl)]-1,2,4-trithiolane **10** (Scheme 2)[15]. The ^{19}F-NMR spectra of **8** and **9** differed substantially; in the case of **8**, the spectrum revealed the presence of two non-equivalent CF_3 groups giving rise to signals at $\delta(^{19}F) = -63.44$ and -67.07, respectively, whereas for **9** only one signal was seen at $\delta(^{19}F) = -63.95$. The ^{1}H- and ^{13}C-NMR spectra suggested that only product **9** contains two distinct adamantyl moieties as substituents on the heterocyclic ring. Elemental analyses confirmed the formulae $C_{16}H_{15}F_{12}NS_2$ for the less polar **8**, and $C_{23}H_{29}F_6NS_2$ for **9**. On the basis of these data, one might conclude that **9** is the expected [3 + 2] cycloadduct of **1** with **4f**. In the ^{13}C-NMR spectrum of **9**, however, characteristic signals identified as a septuplet [$\delta(^{13}C) = 87.5$, $^2J_{C-F} = 28.1$ Hz] and a singlet [$\delta(^{13}C) = 64.0$] appeared in a reverse order compared with the corresponding signals in the series of 1,4,2-dithiazolidines **5** produced in the reactions of **1** with aromatic thiones. In the case of **9**, the characteristic septuplet was downfield-shifted, suggesting a different structure of the heterocyclic ring. In order to establish the molecular structure of **9**, a single-crystal X-ray diffraction analysis was performed (Figure 3). The structure is indeed different from the expected product **11**, in fact it corresponds to one of its possible isomeric forms.

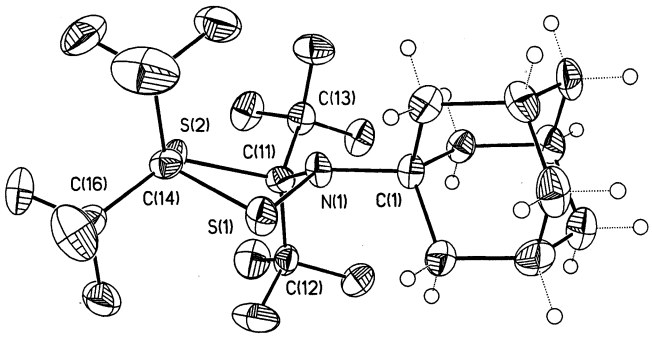


The position of the substituents on the dithiazolidine ring indicates that **9** does not contain the structural motif of the thione *S*-imide **1**. Therefore, this product must have resulted from a cascade of reactions involving a new 1,3-dipole generated in situ in the reaction mixture.

Compound **8** was first identified as an interception product of hexafluorothioacetone with *S*-imide **1** on the basis of spectroscopic data. Its structure was finally confirmed by a single-crystal X-ray diffraction analysis (Figure 2). It is noteworthy that the ^{13}C-NMR-chemical shifts of C-3 [$\delta(^{13}C) = 89.0$ (sept)] and C-5 [$\delta(^{13}C) = 64.6$ (sept)] correspond very closely to those found in the spectrum of **9**.

The crystal structure of compound **8** is shown in Figure 2. This species crystallizes in the triclinic space group $P\bar{1}$, with two independent molecules in the asymmetric unit. The deviation from planarity shown by the five-membered rings forming the core of the two crystallographically independent molecules is 0.202 Å in both cases, and is thus of the same order as that observed in the case of **5a**. Again, the two C and the two S atoms in the ring lie approximately in the same plane (mean deviation 0.093 Å for the two independent molecules).

Figure 2. Crystal structure of **8** with anisotropic displacement parameters depicting 50% probability; only one of the two molecules present in the asymmetric unit is shown for the sake of clarity[a]

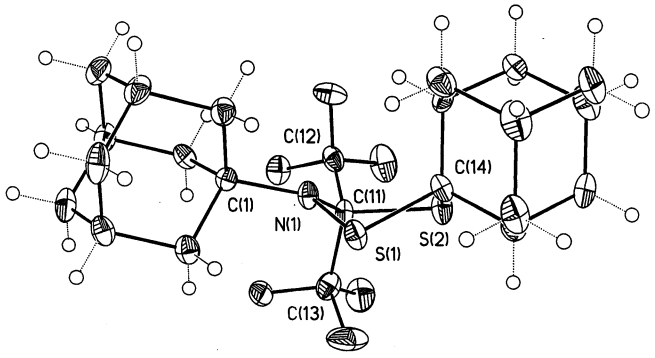


[a] Selected bond lengths [Å] and angles [°] (all the values averaged over the two crystallographically independent molecules): N(1)−C(11) 1.456(9), C(11)−S(2) 1.871(7), S(2)−C(14) 1.797(7), C(14)−S(1) 1.795(7), S(1)−N(1) 1.726(6), N(1)−C(1) 1.531(9); N(1)−C(11)−S(2) 106.3(4), C(11)−S(2)−C(14) 97.5(3), S(2)−C(14)−S(1) 107.5(4), C(14)−S(1)−N(1) 94.1(3), S(1)−N(1)−C(11) 11.1(4), C(12)−C(11)−C(13) 110.0(6), C(15)−C(14)−C(16) 110.9(6).

The crystal structure of compound **9** is shown in Figure 3. This species crystallizes in the monoclinic space group

$P2_1/c$. The shape of the five-membered ring at the core of the structure looks different to that in compounds **5a** and **8** described above, in that the two carbon atoms and the two sulfur atoms do not lie in the same plane. The ring carbon atom that is also part of the adamantane skeleton shows a marked deviation from the plane, allowing its coordination geometry to become regular tetrahedral. The mean deviation from planarity in the case of the five-membered ring is significantly larger than that for the two previously discussed structures (0.246 Å), with the four non-nitrogen atoms in the ring deviating from their mean plane by 0.187 Å.

Figure 3. Crystal structure of **9** with anisotropic displacement parameters depicting 50% probability[a]



[a] Selected bond lengths [Å] and angles [°]: N(1)−C(11) 1.450(6), C(11)−S(2) 1.865(5), S(2)−C(14) 1.840(5), C(14)−S(1) 1.797(5), S(1)−N(1) 1.728(4), N(1)−C(1) 1.527(6); N(1)−C(11)−S(2) 106.3(3), C(11)−S(2)−C(14) 97.6(2), S(2)−C(14)−S(1) 101.9(2), C(14)−S(1)−N(1) 92.7(2), S(1)−N(1)−C(11) 111.1(3), C(12)−C(11)−C(13) 109.0(4).

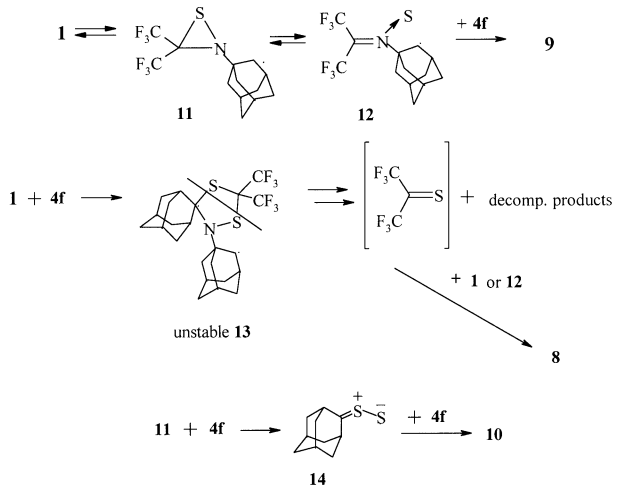
The mechanism of the cycloaddition of **1** to aromatic thiones is probably a one-step, concerted process, leading directly to formation of the products **5a**−**e**. No evidence has been found to suggest any violation of this classical interpretation. The substitution pattern seemingly has an influence on the stability of the primary cycloadducts. Unexpectedly, decomposition of the 1,4,2-dithiazolidines **5d**−**e** to afford the corresponding imines was found to occur quite readily. The difference in stability of **5c** and **5d** is particularly noteworthy and we do not as yet have a plausible explanation for this observation.

The interpretation of the reaction of **1** with adamantanethione (**4f**), which afforded a mixture of the three products **8**, **9**, and **10**, is more complicated (Scheme 3). Thione *S*-imides are known to undergo intramolecular cyclization under thermal and photochemical conditions[12]. One possible interpretation is based on the assumption that thiaziridine **11**, formed by cyclization of **1**, can exist in equilibrium with the thionitrone **12**, which in turn is intercepted by adamantanethione to give **9**.

Dithiazolidine **8** is the product of the reaction of **1** with hexafluorothioacetone, which is formed in the [3 + 2] cycloreversion of **13**. Similar reactions, which involve the release of thioketone as a product of cycloreversion processes, are well documented in the literature[16a][16b].

The formation of dispiro(2-adamantyl)]-1,2,4-trithiolane (**10**) has also been reported previously[15][16a]. Thiaziridine

Scheme 3



11 can be regarded as a possible source of atomic sulfur, which might then be transferred to the thiocarbonyl group with the formation of the very reactive adamantanethione *S*-sulfide (thiosulfine) (**14**). This would be rapidly trapped by the adamantanethione to afford **10**[15].

In summary, fast [3 + 2] cycloaddition of the fluorinated *S*-imide **1** with aromatic thioketones results in the formation of the 1,4,2-dithiazolidines **5**, which show different stabilities depending on the type of aromatic substituents attached to the heterocyclic ring. The regiochemistry of the cycloaddition step reflects formation of the stronger nitrogen−carbon instead of a nitrogen−sulfur bond in the final product. The less reactive adamantanethione (**4f**) only reacts with **1** at elevated temperature. A cascade of reactions affords two different 1,4,2-dithiazolidines **8** and **9**, as well as a small amount of 1,2,4-trithiolane **10**.

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Experimental Section

General: NMR: Bruker WP 80 SY, Bruker AM 250 or Bruker AS 400; solvent $CDCl_3$; standards: tetramethylsilane (TMS) for ^{1}H-, and ^{13}C-NMR spectra and trichlorofluoromethane (Freon 11) for ^{19}F-NMR spectra. − IR: Specord 71-IR as KBr pellets. − MS: Finnigan MAT system 8230 and Finnigan MAT 95. − Melting points were determined in capillaries (Büchi SMP-20 apparatus) and are uncorrected.

Thiofluorenone (**4a**) was synthesized using a modified literature procedure[17]. 3.0 g (16.6 mmol) of fluorenone and 2.6 g (24.5 mmol) of trimethyl orthoformate were dissolved in ethanol (100 ml) and the solution was placed in a three-necked round-bottomed flask equipped with a magnetic stirring bar and two glass tubes, through which streams of hydrogen sulfide and hydrogen chloride were introduced. The reaction flask was cooled in an iced-water bath and the progress of the reaction was monitored by TLC (SiO_2, petroleum ether/dichloromethane, 7:3). After 3 h, the olive-green reaction mixture was poured into iced water and crude thiofluorenone was filtered off and washed several times with cold water.

Chromatographic purification on an SiO_2 column (petroleum ether with increasing amounts of dichloromethane) afforded analytically pure thiofluorenone as olive-green needles (2.3 g, 71%), m.p. 73−75°C (ref.[17] m.p. 75−76°C).

Thioketones **4b**−**f** were prepared according to known literature procedures: Thiobenzophenone (**4b**), xanthione (**4c**), thioxanthione (**4d**), and 4,4′-(dimethoxy)thiobenzophenone (**4e**) from the corresponding ketones by treatment with Lawesson′s reagent (LR) according to literature protocol[18], while adamantanethione (**4f**) was synthesized by the reaction of adamantanone with phosphorus pentasulfide according to Greidanus[19]. Hexafluorothioacetone *S*-(1-adamantyl)imide (**1**) was synthesized by treatment of 1-chloro-1,1-bis(trifluoromethyl)methanesulfenamide with lithium hexamethyldisilazanide in ethereal solution, as described in an earlier paper[10].

General Procedure for the Reaction of S-Imide **1** *with Aromatic Thioketones* **4a**−**e**: A solution of 2 mmol of the appropriate thioketone **4** in dichloromethane (2 ml) was stirred magnetically at room temp. and 704 mg (2.0 mmol) of **1** dissolved in dichloromethane (1 ml) was added dropwise over a period of 2−3 min. The intensely colored thioketone solutions were decolorized after the periods of time quoted at the beginning of each of the following sets of experimental data. After complete decolorization, the solvent was removed in vacuo in a rotary evaporator and the crystalline residues were triturated with a small amount of methanol; after 1 h in a refrigerator, the crude products were filtered off. Recrystallization from methanol or methanol/dichloromethane mixture afforded analytically pure samples.

2-(1-Adamantyl)-5,5-bis(trifluoromethyl)spiro[1,4,2]dithiazolidine-3,9′-[9H]fluorene (**5a**): Fast decolorization after ca. 30 s, colorless prisms (770 mg, 73%), m.p. 135−137°C (decomp., brown) ($MeOH/CH_2Cl_2$). − IR (KBr): $\tilde{\nu}$ = 2890 cm^{-1}, 1460, 1195 and 1250 (CF_3), 1080, 950, 930, 760, 740, 710. − ^1H NMR: δ = 1.20−1.44, 1.46−1.55, 1.75−1.92 (m, 15 H, Ad), 7.24−7.42, 7.57−7.62, 8.06−8.12 (m, 8 H, Ar). − ^{13}C NMR: δ = 30.1 (t), 35.8 (t), 43.0 (d) and 63.7 (s) (all Ad), 66.2 (sept, $^2J_{C-F}$ = 29.5 Hz, C-5), 88.9 (s, C-3), 120.1, 127.1, 128.1, 129.7 (4 d), 138.6 (s) and 146.0 (s) (all Ar), 124.2 (q, $^1J_{C-F}$ = 284.3 Hz, CF_3). − ^{19}F NMR: δ = −67.50 (2 CF_3). − MS; *m/z* (%): 527 (5) [M^+], 392 (2) [M^+ − Ad], 313 (4), 256 (10), 210 (10), 135 (100) [Ad^+], 107 (10), 93 (16), 79 (16). − HRMS for $C_{26}H_{23}F_6NS_2$: calcd. 527.1176; found 527.1176.

X-ray Data of Dithiazolidine **5a**[20]: $C_{26}H_{23}F_6NS_2$, M_r 527.57, monoclinic, space group $P2_1/c$ (No.14). Unit cell dimensions: a = 11.094(2), b = 19.350(4), c = 22.269(5) Å, β = 101.18(3)°, V = 4690(2) Å^3, Z = 8; $D_{calcd.}$ = 1.494 mg/ml; $F(000)$ = 2176; T = 193(2) K; μ(Mo-K_α) = 0.291 mm^{-1}. Data collection: Stoe-Siemens AED four-circle diffractometer, colorless crystal (size 0.35 × 0.20 × 0.20 mm) mounted on a glass fibre, cell constants from 15 centered reflections. Mo-K_α radiation, graphite monochromator, λ = 0.71073 Å, ω-2θ scan with profile fitting. Intensity of three standard reflections checked every 90 min, 2θ range 5−45°, 6295 reflections measured, 6155 unique and observed (R_{int} = 0.2184), and 4025 with $I > 2\sigma(I)$. Structure solution by SHELXS-90[20] and refinement by SHELXL-93[21], non-hydrogen atoms refined anisotropically, hydrogen atoms included in calculated positions and refined using a riding model. Full-matrix refinement against F^2. Final $R1$ = 0.0639 and $wR2$ = 0.1152 for 4025 reflections with $I > 2\sigma(I)$. $R1$ = 0.1174 and $wR2$ = 0.1428 for all data. Weights: SHELXL-93. Maximum and minimum peak and hole in the Fourier synthesis 0.305 and −0.317 eÅ^{-3}.

2-(1-Adamantyl)-5,5-bis(trifluoromethyl)-3,3-diphenyl-1,4,2-dithiazolidine (**5b**): 10 min, colorless prisms (805 mg, 76%), m.p. 105−107°C (decomp., blue) (MeOH). − IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1}, 1445, 1305, 1240 and 1180 (br., CF_3), 1070, 955, 740, 700. − ^1H NMR: δ = 0.80−0.95 and 1.20−2.00 (m, 15 H, Ad), 7.10−7.40 and 7.45−7.62 (m, 2 C_6H_5). − ^{13}C NMR: δ = 30.7 (t), 35.8 (t), 43.2 (d) and 66.3 (s) (all Ad), 75.2 (sept, $^2J_{C-F}$ = 31.0 Hz, C-5), 107.8 (s, C-3), 127.4, 128.2, 130.6 (br.) (3 d) and 143.5 (br. s) (all C_6H_5), 124.4 (q, $^1J_{C-F}$ = 283.7 Hz, 2 CF_3). − ^{19}F NMR: δ = −65.2 (2 CF_3). − MS; *m/z* (%): 529 (1) [M^+], 396 (4), 315 (88) [$(C_6H_5)_2C{=}N{-}Ad^+$], 258 (46), 214 (10), 180 (24), 165 (28), 135 (100) [Ad^+], 113 (15), 93 (18), 77 (20), 69 (12) [CF_3^+]. − HRMS for $C_{26}H_{25}F_6NS_2$: calcd. 529.1333; found 529.1333.

2-(1-Adamantyl)-5,5-bis(trifluoromethyl)spiro[1,4,2]dithiazolidine-3,9′-[9H]xanthene (**5c**): 50 min, colorless prisms (707 mg, 65%), m.p. 146−148°C (decomp., green), (hexane). − IR (KBr): $\tilde{\nu}$ = 2930 cm^{-1}, 1600, 1480, 1450, 1330, 1250 (s) and 1195 (s, CF_3), 1070, 950, 760, 710. − ^1H NMR: δ = 1.20−1.50, 1.50−1.75 and 1.75−1.82 (m, 15 H, Ad), 6.98−7.40 and 8.50−8.90 (m, 8 H, Ar). − ^{13}C NMR: δ = 30.1 (t), 35.8 (t), 42.4 (d) and 63.5 (s) (all Ad), 66.3 (sept, $^2J_{C-F}$ = 31.0 Hz, C-5), 81.9 (s, C-3), 116.3, 123.0, 130.3, 134.8 (4 d) and 123.9, 149.6 (2 s) (all Ar), 124.7 (q, $^1J_{C-F}$ = 252.0 Hz, 2 CF_3). − ^{19}F NMR: δ = −67.0 (2 CF_3). − MS; *m/z* (%): 543 (10) [M^+], 361 (20) [$M^+ - (CF_3)_2C{=}S$], 330 (10), [xanthene=$C(CF_3)_2$], 272 (40), 329 (32) [(xanthene=N−Ad)$^+$], 212 (76) [xanthione$^+$], 168 (10), 149 (14), 135 (100) [Ad^+], 107 (8), 93 (18), 79 (19). − HRMS for $C_{26}H_{23}F_6NOS_2$: calcd. 543.1125; found 543.1125.

2-(1-Adamantyl)-5,5-bis(trifluoromethyl)spiro[1,4,2]dithiazolidine-3,9′-[9H]thioxanthene (**5d**): 50 min, colorless crystals could not be obtained in an analytically pure state (decomposition upon attempted purification by recrystallization or column chromatography); crude yield 873 mg (78%), m.p. 129−135°C (decomp.). − ^{13}C NMR: δ = 30.2 (t), 35.8 (d), 42.5 (d) and 63.5 (s) (all Ad), 66.4 (sept, C-5), 87.6 (s, C-3), 124.5, 125.3, 128.3, 129.1, 132.9 and 134.6 (all Ar). − ^{19}F NMR: δ = −66.8 (2 CF_3).

1-[(9H-Thioxanthen-9-ylidene)amino]adamantane (**7d**): Isolated from hexane solution after attempted crystallization of crude **5d**; colorless prisms (435 mg, 63%), m.p. 181−183°C. − IR (KBr): $\tilde{\nu}$ = 2840 cm^{-1}, 1620 (s, C=N), 1580, 1450, 1430, 1300, 1095, 1070, 790, 750. − ^1H NMR: δ = 1.60−1.67 (m, 6 H), 1.82−1.92 (m, 6 H) and 1.97−2.10 (m, 3 H) (all Ad), 7.20−7.32 (m, 4 H), 7.35−7.47 (m, 2 H) and 7.50−7.80 (br. m, 2 H) (all Ar). − ^{13}C NMR: δ = 29.9 (t), 36.6 (d), 44.5 (d) and 58.5 (s) (all Ad), 126.0, 126.4, 126.6 (br.), 127.9, 130.0 and 134.2 (all Ar), 157.0 (s, C=N). − MS; *m/z* (%): 345 (58) [M^+], 288 (100), 236 (10), 196 (9), 152 (22), 135 (13) [Ad^+], 93 (8), 79 (12). − HRMS for $C_{23}H_{23}NS$: calcd. 345.1551; found 345.1557.

2-(1-Adamantyl)-3,3-bis(4-methoxyphenyl)-2,2-bis(trifluoromethyl)-1,4,2-dithiazolidine (**5e**): 4 h, isolated as colorless crystals after treatment of the crude reaction mixture with hexane, m.p. 95−101°C; could not be obtained in analytically pure form and decomposed upon attempted recrystallization; crude yield 895 mg (76%). − ^1H NMR: δ = 1.53−1.63 (m, 6 H), 1.63−1.80 (m, 6 H) and 1.80−2.00 (br. m, 3 H) (all Ad), 3.75 (3 H, OCH_3), 3.83 (3 H, OCH_3), 6.75 and 7.45 (AB system with J = 8.5 Hz, 8 H, Ar).

1-{[Bis(4-methoxyphenyl)methylidene]amino}adamantane (**7e**): Isolated after attempted crystallization of crude **5e** from methanolic solution; yield 365 mg (49%), m.p. 130−132°C. − IR (KBr): $\tilde{\nu}$ = 1630 cm^{-1} (s, C=N), 1600 (s), 1510, 1320, 1310, 1300, 1260 (vs, O−C), 1180, 1040. − ^1H NMR: δ = 1.50−1.60 (6 H), 1.65−1.75 (6 H), 1.80−2.00 (3 H) (all Ad), 3.77 (3 H, OCH_3), 3.85 (3 H,

OCH_3), 6.75/7.43 (AB system, 4 H), and 6.83/7.05 (AB system, 4 H). – ^{13}C NMR: δ = 29.8 (t), 36.5 (d), 44.3 (d) and 57.6 (s) (all Ad), 55.2 and 55.3 (2 OCH_3), 113.0, 113.1, 129.4, 129.5 (CH of Ar ring), 132.7, 135.6 (C_q, Ar), 159.0, 160.6 (C_q–OCH_3), 162.3 (C=N). – MS; *m/z* (%): 375 (49) [M^+], 242 (48), 135 (100) [Ad^+]. – HRMS for $C_{25}H_{29}NO_2$: calcd. 375.2198; found 375.2175.

Reaction of **1** *with Adamantanethione* (**4f**): An orange-colored solution of 329 mg (2 mmol) of **4f** and 588 mg (1.8 mmol) of **1** in $CDCl_3$ (1.5 ml) was sealed in a glass tube and heated at 100°C for 2 h. After this time, the solution had turned yellow and the ^1H-NMR spectrum of the reaction mixture no longer indicated the presence of **1**. After cooling in an acetone/dry ice bath, the tube was opened and the reaction mixture was diluted with ethanol (2 ml). The clear solution thus obtained was stored for about 12 h in a refrigerator, after which a portion of colorless needles (242 mg) with m.p. 185–189°C was filtered off. The mother liquor was concentrated and chromatographed on a silica gel column. Pentane with increasing amounts of dichloromethane was used as the eluent. First, the interception product **8** was isolated as colorless crystals using pentane as the eluent; the next fraction contained 1,4,2-dithiazolidine **9** (pentane/dichloromethane, 9:1), and finally dispiro-trithiolane **10** was isolated upon elution with pentane/dichloromethane (8:2).

2-(1-Adamantyl)-3,3,5,5-tetrakis(trifluoromethyl)-1,4,2-dithiazolidine (**8**): Yield 71 mg (8%), m.p. 65–66°C (from methanol). – IR (KBr): $\tilde{\nu}$ = 2860 cm^{-1}, 1240 (br., s) and 1180 (vs) (CF_3), 1090 (s), 955, 705. – ^1H NMR: δ = 1.55–1.75 (br.) and 2.05–2.20 (br. m, 15 H, Ad). – ^{13}C NMR: δ = 30.8, 35.6 (2 t), 42.2 (d) and 68.7 (s) (all Ad), 64.6 (sept, $^2J_{C-F}$ = 30.1 Hz, C-5), 89.0 (sept, $^2J_{C-F}$ = 30.0 Hz, C-3), 122.7 (q, $^1J_{C-F}$ = 291.1 Hz, 2 CF_3) and 123.0 (q, $^1J_{C-F}$ = 285.5 Hz, 2 CF_3). – ^{19}F NMR: δ = −63.44 (br. s) and −67.07 (s). – MS; *m/z* (%): 378 (36) [M^+ – Ad], 135 (100) [Ad^+]. – HRMS: $C_{16}H_{15}F_{12}NS_2$: calcd. 513.0454; found 513.0376.

X-ray Data of Dithiazolidine **8**[20]: $C_{16}H_{15}F_{12}NS_2$, M_r = 513.41, triclinic, space group $P\bar{1}$ (No.2). Unit cell dimensions: a = 6.988(1), b = 9.732(2), c = 28.990(6) Å, α = 91.10(3), β = 92.14(3), γ = 107.33(3)°, V = 1880(1) Å^3, Z = 4; $D_{calcd.}$ = 1.814 mg/ml; $F(000)$ = 1032; T = 193(2) K; μ(Mo-K_α) = 0.403 mm^{-1}. Data collection: Stoe-Siemens AED four-circle diffractometer, colorless crystal (size 0.60 × 0.40 × 0.30 mm) mounted on a glass fibre, cell constants from 18 centered reflections. Mo-K_α radiation, graphite monochromator, λ = 0.71073 Å, ω-2θ scan with profile fitting. Intensity of three standard reflections checked every 90 min, 2θ range 7–45°, 6381 reflections measured, 4914 unique and observed (R_{int} = 0.0605), and 3587 with $I > 2\sigma(I)$. Structure solution by SHELXS-90[20] and refinement by SHELXL-93[21], non-hydrogen atoms refined anisotropically, hydrogen atoms included in calculated positions and refined using a riding model. Full-matrix refinement against F^2. Final $R1$ = 0.0663 and $wR2$ = 0.1492 for 3587 reflections with $I > 2\sigma(I)$. $R1$ = 0.0996 and $wR2$ = 0.1707 for all data. Weights: SHELXL-93. Maximum and minimum peak and hole in the Fourier synthesis 0.447 and −0.424 eÅ^{-3}.

2-(1-Adamantyl)-3,3-bis(trifluoromethyl)spiro[(1,4,2)-dithiazolidine-5,2′-adamantane] (**9**): Overall yield after filtration and chromatography 478 mg (53%), m.p. 184–186°C (from methanol/dichloromethane). – IR (KBr): $\tilde{\nu}$ = 2860 cm^{-1}, 1450 (s), 1240 (s), and 1180 (vs) (all CF_3), 1100, 1060, 920, 715. – ^1H NMR: δ = 1.58–2.12 (m) and 2.36 (br.) (all Ad). – ^{13}C NMR: δ = 26.4, 26.8, 35.8, 36.0, 36.5, 36.6, 37.3 and 42.2 [all Ad (×2)], 64.0 (s, C-5), 69.6 (s, Ad), 87.5 (sept, $^2J_{C-F}$ = 28.1 Hz, C-3), 123.8 (q, $^1J_{C-F}$ = 290.0 Hz, 2 CF_3). – ^{19}F NMR: δ = −63.95 (s, 2 CF_3). – MS; *m/z* (%): 497 (2) [M^+], 364 (< 1) [M^+ – Ad], 166 (6) [Ad=$S^{+\bullet}$], 135 (100) [$Ad^{+\bullet}$], 107 (6), 93 (10), 79 (12). – $C_{23}H_{29}F_6NS_2$: calcd. 497.1646; found 497.1646 (MS).

X-ray Data of Dithiazolidine **9**[20]: $C_{23}H_{29}F_6NS_2$, M_r = 497.59, monoclinic, space group $P2_1/c$ (No.14). Unit cell dimensions: a = 6.853(1), b = 12.568(3), c = 24.908(5) Å, β = 95.90(3)°, V = 2133.9(7) Å^3, Z = 4; $D_{calcd.}$ = 1.549 mg/ml; $F(000)$ = 1040; T = 193(2) K; μ(Mo-K_α) = 0.314 mm^{-1}. Data collection: Stoe-Siemens AED four-circle diffractometer, colorless crystal (size 0.40 × 0.25 × 0.20 mm) mounted on a glass fibre, cell constants from 15 centered reflections. Mo-K_α radiation, graphite monochromator, λ = 0.71073 Å, ω-2θ scan with profile fitting. Intensity of three standard reflections checked every 90 min, 2θ range 6–45°, 4025 reflections measured, 2797 unique and observed (R_{int} = 0.1073), and 1834 with $I > 2\sigma(I)$. Structure solution by SHELXS-90[20] and refinement by SHELXL-93[21], non-hydrogen atoms refined anisotropically, hydrogen atoms included in calculated positions and refined using a riding model. Full-matrix refinement against F^2. Final $R1$ = 0.0537 and $wR2$ = 0.0977 for 1834 reflections with $I > 2\sigma(I)$. $R1$ = 0.1084 and $wR2$ = 0.1194 for all data. Weights: SHELXL-93. Maximum and minimum peak and hole in the Fourier synthesis 0.338 and −0.284 eÅ^{-3}.

Dispiro[adamantane-2,5′-(1,2,4)-trithiolane-3′,2′′-adamantane] (**10**): Yield 71 mg (20%), m.p. 189–191°C (ref.[15]: m.p. 193–195°C). The IR spectrum of this product matched that of the previously obtained sample of **10**.

☆ Dedicated to Professor *Günter Siegemund* on the occasion of his 60th birthday.

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[22] Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-100325. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk].

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