

Cycloadditions of Adamantanethione *S*-Methylide to Heteromultiple Bonds ¹

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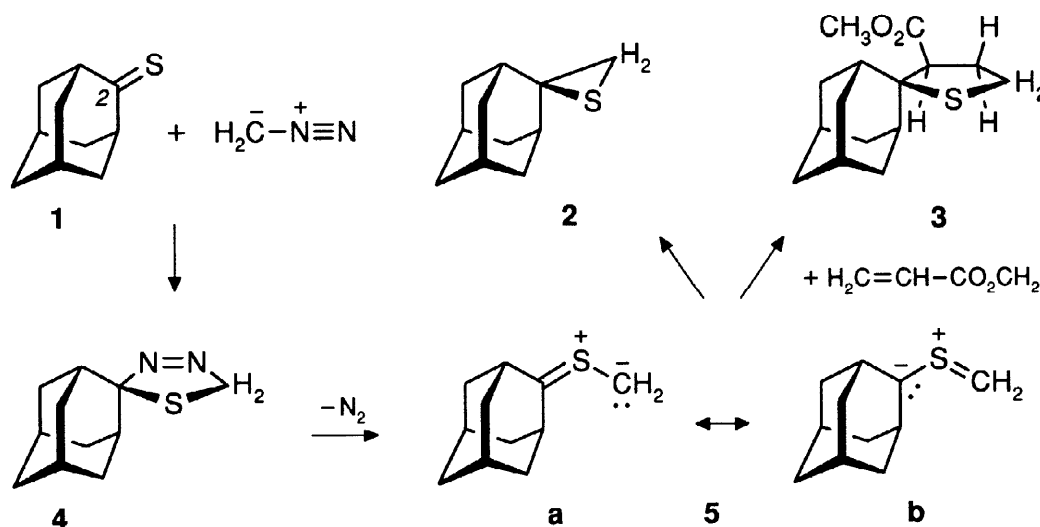
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Abstract: Adamantanethione *S*-methylide (**5**) is an easily accessible thiocarbonyl *S*-ylide. Generated by N₂ elimination from the cycloadduct of adamantanethione and diazomethane, the nucleophilic 1,3-dipole **5** reacts in situ with thiocarbonyl compounds furnishing 1,3-dithiolanes. **5** and carbon disulfide afford 1:1 and 2:1 cycloadducts. The structures are assessed by NMR spectra, a X-ray analysis, and C-S hydrogenolyses. The C=S group is an ambident electrophile; the ratios of regioisomeric adducts suggest that electronic effects favor the 4',5'-substituted 1,3-dithiolanes, whereas steric effects support the 2',4'-substituted systems. Electrophilic carbonyl compounds and **5** regiospecifically provide 2,4-disubstituted 1,3-oxathiolanes. Imines appear to be weak dipolarophiles vs. **5**. © 1999 Elsevier Science Ltd. All rights reserved.

Introduction

The thermal elimination of N₂ from 2,5-dihydro-1,3,4-thiadiazoles provides a convenient and variable access to thiocarbonyl ylides.³ The 2',5'-dihydrospiro[adamantane-2,2'-(1,3,4)-thiadiazole] (**4**) is easily available by addition of diazomethane to adamantanethione (**1**),⁴ which, in turn, is prepared from commercial adamantanone by reaction with P₄S₁₀ in 75–80% yield.⁵ The extrusion of N₂ from thiadiazole **4** proceeds as a first-order reaction with a half-life of 90 min in THF at 40°C.⁴ The adamantanethione *S*-methylide (**5**), formulated by its resonance structures of allyl anion type, is not isolable, but enters an irreversible



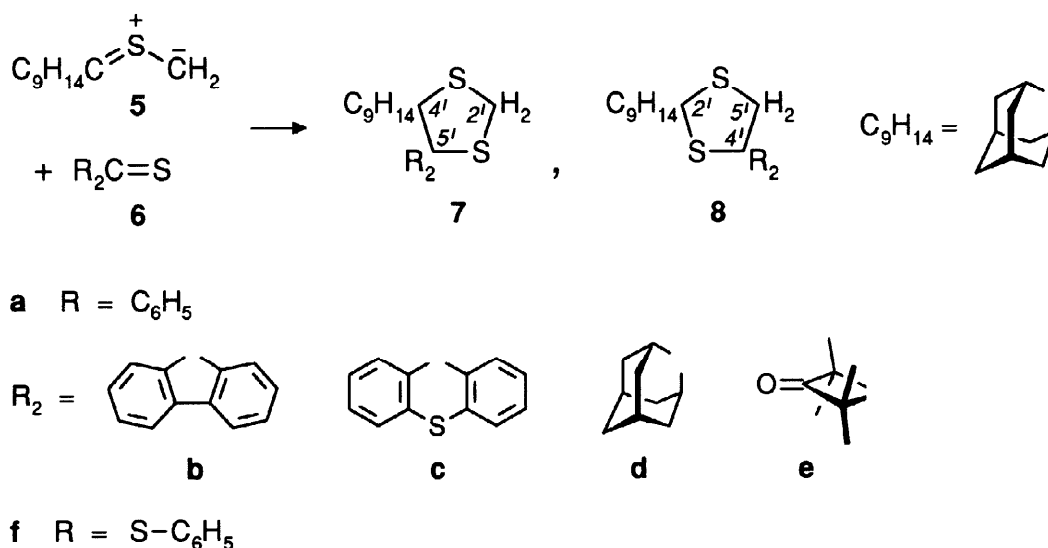
electrocyclic ring closure to give the spirothiirane **2**. However, thiocarbonyl ylide **5** can be intercepted *in situ* by electrophilic C=C bonds, *e.g.*, furnishing **3** (89%) by reaction with methyl acrylate.⁶ Also acids HX are suitable trapping reagents.⁷ It should be noticed that the N₂ elimination from **4** is a 1,3-dipolar cycloreversion, and the sequence $1 + \text{CH}_2\text{N}_2 \rightarrow 5 + \text{N}_2$ constitutes a 1,3-dipole metathesis.

Due to its easy access, **5** is a fitting test system for the 1,3-dipolar reactivity of thiocarbonyl ylides. It has been shown for the related thiobenzophenone *S*-methylide (**9**),⁸ that the C=S bond exceeds the C=C bond in dipolarophilic activity by far, *e.g.*, the reaction of **9** with thiobenzophenone is 4100 times faster than that with methyl acrylate.⁹ This superiority of thiones as dipolarophiles¹⁰ and dienophiles¹¹ turned out to be a general phenomenon of concerted [$\pi 4_s + \pi 2_s$] cycloadditions. MO calculations (MP2/6-31G*, Becke-3LYP) revealed, that the low π -HOMO-LUMO energy distance of the C=S bond, compared with the C=C bond, is responsible.¹²

The cycloadditions of **5** with aromatic and aliphatic thioketones, dithiocarboxylic esters, carbon disulfide, and other thiones are described here,¹³ and the dipolarophilic activity of carbonyl compounds and imines *vs.* **5** is tested.

Cycloadditions to Thioketones and Dithioesters

The 1,3-dipole **5** was generated by warming the THF solution of thiadiazoline **4** in the presence of 1.1 equiv of the thione for 8 h at 40°C. After removal of the solvent, a standard was weighed to the residue; the quantitative ¹H NMR analysis was based on the comparison of the integrals. Subsequently, the cycloadducts were separated and purified by chromatography or fractional crystallization. Table 1 provides the yields and some NMR parameters.



Thiobenzophenone (**6a**), thiofluorenone (**6b**), and thioxanthione (**6c**) as aromatic thioketones furnished pairs of regioisomeric 1,3-dithiolanes, *e.g.*, **6a** gave rise to 50% of **7a** and 42% of **8a**. **7a** bears the substituents in positions 4' and 5'. The same dithiolane, **10d** = **7a**, was obtained by the cycloaddition of the matched pair, thiobenzophenone *S*-methylide (**9**) and adamantanethione **1**.¹⁴ That establishes the regiochemistry of **7a** unambiguously. Only the dithiolane with 2'-H₂ can occur as common product from matched

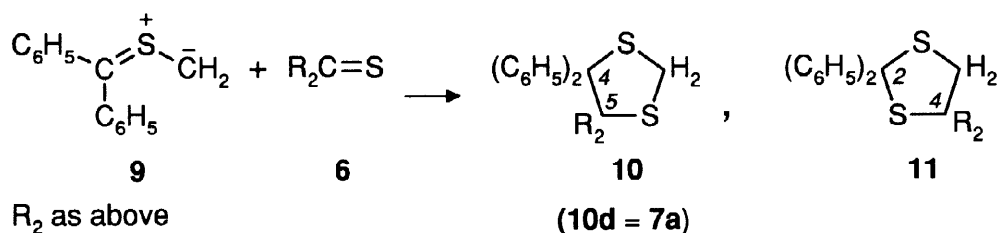


Table 1. Cycloadditions of Adamantanethione *S*-Methylide (**5**) with Thiones in THF at 40°C. (The yields refer to ¹H NMR analyses, those in brackets to isolation; for %¹J_R (¹³C,H) see text).

| Dipolarophile | 1,3-Dithiolane | | | Methylene Group | | |
|---|----------------|---------|---------|-----------------|----------------|--------------------------------------|
| | Formula | % Yield | mp (°C) | δ _H | δ _C | %J _R (¹³ C-H) |
| Thiobenzophenone | 7a | 50(28) | 197-199 | 3.28 | 28.0 | 35 |
| | + 8a | 42(18) | 126-128 | 3.95 | 48.3 | 25 |
| Thiofluorenone | 7b | 60(44) | 173-176 | 3.92 | 29.6 | 39 |
| | + 8b | 18 | | 3.42 | | |
| Thioxanthione | 7c | 41(25) | 183-185 | 4.07 | 30.8 | 41 |
| | + 8c | 34(27) | 237-239 | 3.59 | 44.2 | 26 |
| Adamantanethione | 8d | 86(76) | 165-166 | 3.25 | 45.5 | 24 |
| 2,2,4,4-Tetramethyl- 3-thioxocyclobutanone | 8e | 80(58) | 128-129 | 3.30 | 41.9 | 25 |
| Methyl dithioacetate | 16 | 64(44) | 43-45 | 3.02, 3.30 | 48.2 | 24 |
| Methyl dithiobenzoate | 15 | 51(28) | 166-168 | 3.45, 3.94 | 28.1 | 41 |
| | + 17 | 45(23) | 109-111 | 3.64, 3.73 | 47.3 | 23 |
| Diphenyl trithiocarbonate | 18 | 85(55) | 122-124 | 3.12 | 45.9 | 25 |
| Carbon disulfide (1:1) | 19 | 89(82) | 108-110 | 4.17 | 55.9 | |
| Dithiolactone 19 | 22 | (81) | 230-231 | 3.42, 3.62 | 48.2 | 32 |
| Phenyl isothiocyanate | 21 | 91(70) | 77-79 | 4.05 | 43.3 | 34 |

pairs of thione *S*-methylide + thione.

By-the-way, the third conceivable isomer, **11d**, was not found in the reaction of **9** + **1**. The mixtures of **7** and **8** in the cycloadditions of **5** could well originate from competing electronic and steric effects as controlling forces.

The regiochemistry of the methyl acrylate adduct **3** revealed that the CH₂ group is the nucleophilic terminus of **5**, symbolized by resonance structure **5a**.⁶ The thiocarbonyl group is an ambident electrophile. Organometallic reagents may attack thiones at sulfur (thiophilic route) or carbon atom; the ratio depends on the nature of the reactants and the conditions.^{15,16} The formation of **7** and **10** would correspond to the thiophilic attack of the nucleophilic 1,3-dipole - also in the framework of a concerted cycloaddition.

Additional structural evidence came from the hydrogenolysis of the C-S bonds by Raney nickel in refluxing alcohol. All three S functions were removed from the thioxanthione adduct **7c**, and 2-benzhydryladamantane (**12**, 91%) was formed. Incidentally, considering the easy hydrogenolysis, cycloadditions of

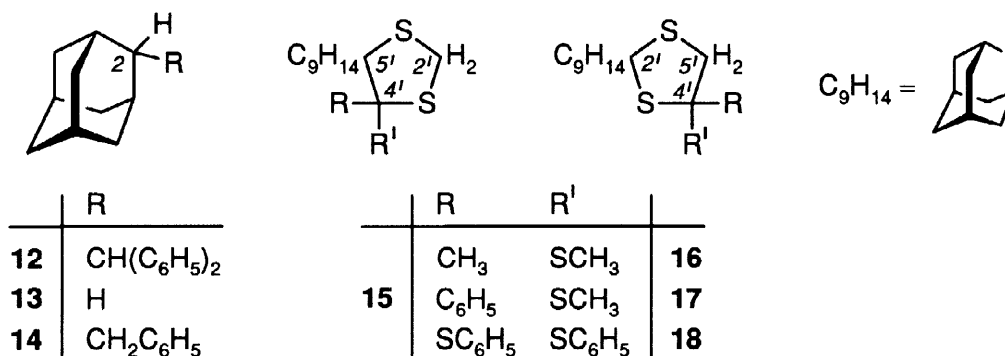
thiocarbonyl ylides to CC-double bonds and subsequent removal of sulfur may constitute a useful method for carbon-carbon bond formation.

The cycloadditions of **5** with adamantanethione (**1**) and 2,2,4,4-tetramethyl-3-thioxo-cyclobutanone (**6e**), *i.e.*, thioketones with high steric demand, afforded *only* the dithiolanes **8d** and **8e**. Steric hindrance on the pathway to **7d** and **7e** is probably responsible.

NMR criteria confirm the assignments. The singlets due to 2'-H₂ of **7** and 5'-H₂ of **8** are observed at δ 3.12 - 4.17, but do not allow the differentiation of **7** and **8**. However, the ¹³C chemical shifts of the dithiolane-CH₂ fall into two groups: δ_c 28.0 - 30.8 due to C-2' of **7** and 41.9 - 48.3 due to C-5' of **8** (Table 1). Obviously, the deshielding of the CH₂ in the heteroring by the adjacent quaternary C-atom in **8** is greater than the effect of the second sulfur function in **7**; this is in accordance with literature experience.¹⁷

How are the pertinent δ_c parameters distinguished from those of the five CH₂ groups of the adamantane system? The δ_c triplets which appear in the off-resonance decoupled spectrum show rather constant values of ¹J_R(¹³C,H) for the adamantane methylene groups; the residual splitting in the individual spectrum is related to the frequency offset $\Delta\nu$. The residual coupling constant, ¹J_R(¹³C,H), is significantly greater for the CH₂ of the five-membered dithiolane ring than for those of the adamantane part; greater by 38-41% for the 2'-CH₂ of **7**, and by 23-26% for the 5'-CH₂ of **8** (Table 1).

The ¹J(¹³C,H) for the CH₂ of adamantane (125.9 Hz), cyclopentane (128.5 Hz), and the α -H of tetrahydrothiophene (142.1 Hz)¹⁸ demonstrate that the vicinal sulfur atom increases the coupling constant.



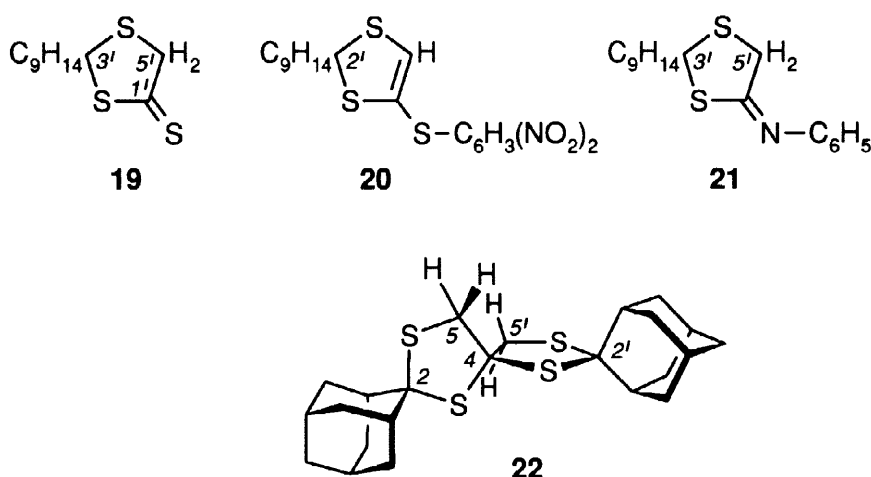
The 1,3-dithiolanes so far discussed have a σ plane as symmetry element. This is the reason for ¹H singlets due to the CH₂ group in the five-membered ring. The reduction of the number of ¹³C signals for the adamantane part likewise mirrors the point group C_s, *i.e.*, 3 d for the four CH in the ratio 1:1:2, 3 t for five CH₂ in the ratio 1:2:2, apart from the s for the quaternary C-2. Two such sets of ¹³C-signals appeared for the dispiro[(1,3)-dithiolane-2',2;4',2''-bis-adamantane] (**8d**); the two adamantane groups are in different environments.

Even the thione groups of dithioesters and trithiocarbonate are sufficiently dipolarophilic for adding the *S*-methylide **5**. Whereas methyl dithiobenzoate produced the two regioisomers (51% of **15** and 45% of **17**), only the cycloadduct corresponding to type **8** was observed for methyl dithioacetate (64% of **16**) and diphenyl trithiocarbonate (85% of **18**). Besides the ¹³C NMR parameters (Table 1), the hydrogenolysis with nickel aided again in the elucidation of the structures: **15** gave rise to 2-benzyladamantane (**14**), while adamantane (**13**) was formed from **16** and **18**.

Cycloadducts **15-17** are chiral and show in their ^{13}C NMR spectra the undiminished set of adamantane signals. The $2'\text{-H}_2$ of **15** and the $5'\text{-H}_2$ of **16** and **17** appear as AB spectra.

Cumulated C=S Bonds as Dipolarophiles

When the thermolysis (40°C) of 1.0 mmol of **4** was run in 200 ml of carbon disulfide (0.005 M), *i.e.*, in dilute solution, the ^1H NMR analysis established 89% of the 1:1-adduct **19**; 82% of the dithiolactone was isolated as brick-red crystals. Due to the adjacent thione function, $\delta(\text{C-}5')$ 55.9 was higher than usual. The reduced set of adamantane ^{13}C -signals and the singlet at δ 4.17 due to $5'\text{-H}_2$ testified to the σ plane. The central dithioester C-atom resonates at δ 239.2. The acidity of the $5'\text{-H}_2$ was demonstrated by reaction with 2,4-dinitrochlorobenzene in alkaline medium furnishing the ketene dithioacetal **20**.



As a cyclic dithioester, **19** still contains a thione function. It was not unexpected that **19** overcame carbon disulfide in dipolarophilic activity. The N_2 elimination from **4** in 0.2 M solution in CS_2 (0.005 M in the experiment above) led to 41% of the 1:1-adduct **19** and 40% of the 2:1-adduct **22**. When we assume in a rough estimate 0.05 M as medium concentration of **19**, then the dithiolactone **19** would be 330 times more reactive than carbon disulfide vs. **5**. Of course, the isolated **19** smoothly combined with the *S*-methylide **5** in cyclohexane giving **22** (81%).

The trispiro compound **22**, isolated in colorless crystals, possesses a C_2 axis which cuts the dithiolane plane at the spiro center 4,4' at an angle of 45°C ; the 180° rotation shows the two adamantanyl residues being equivalent. As a consequence of the chirality of **22**, *one* full set of ^{13}C parameters (5 t, 4 d, 1 s) was observed for the two adamantane systems. As expected, 5-H_2 and $5'\text{-H}_2$ are equivalent and generate *one* AB spectrum.

The N_2 extrusion from **4** in neat phenyl isothiocyanate led to the cycloaddition of **5** to the C=S bond. The ^1H NMR analysis indicated 91% of the colorless cyclic thioimide **21**. The δ 43.3 due to C-5' and a $^1J_{\text{R}}(^{13}\text{C},\text{H})$ which was greater by 34% than that of adamantyl- CH_2 established the regiochemistry. The dithiolactone **19** was converted to **21** (81%) by aniline at room temp., thus connecting the two cycloadducts.

Structure Analyses of 1,3-Dithiolanes 7a and 8a

The crystal analysis of 2,2'-bis(1,3-dithiolane) disclosed a half-chair conformation.¹⁹ The NMR parameters of alkylated 1,3-dithiolanes were also well accommodated by assuming half-chairs.²⁰ However, steric effects may change the conformational preference of a 1,3-dithiolane ring in the presence of voluminous substituents.

The conformation of the dithiolane ring in **8a** which bears adamantyl at C2' and two phenyl groups at C4' comes close to a perfect envelope with the methylene group (C5') as the flap (Fig. 1, Table 2). The dihedral angle S1'-C2'-S3'-C4' amounts to only 3.0°, and the intracyclic torsion angles at C4'-C5' (-52.2°) and C5'-S1' (51.5°) are the largest. The folding angle of the heteroring is 53°, and C5' is located 0.78 Å above the quasi-plane of the other ring members. This puckering displacement amounts to 0.43 Å for the envelope form of cyclopentane (electron diffraction in gas phase).²¹ Previously, NMR parameters led to the assumption, that 1,4-dithianes²² and 1,3-dithiolanes^{20a} are more strongly puckered than their oxygen analogues; it was based on the *vic*-H,H coupling, $J_{trans} > J_{cis}$, and finds confirmation in our X-ray data.

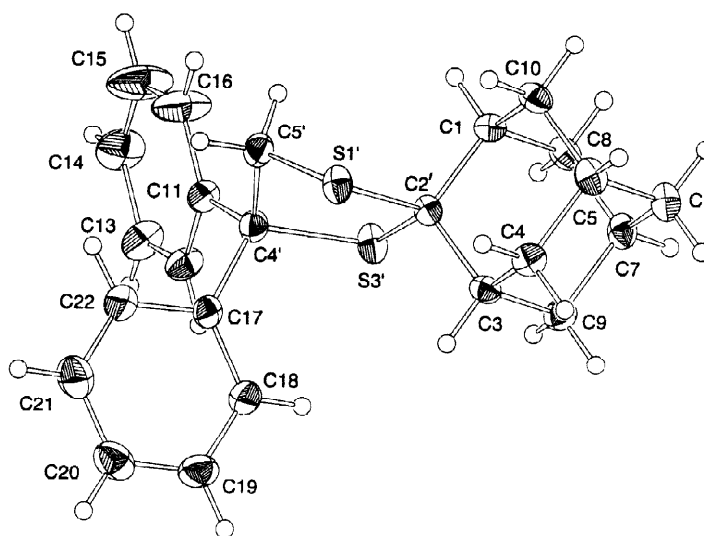


Figure 1. X-Ray Structure of 4',4'-Diphenylspiro[adamantane-2,2'-(1,3)-dithiolane] (**8a**); ZORTEP Plot (thermal ellipsoids represent 30% probability).

In the envelope conformation, the big substituents avoid crowding. The closest distance is that between 18-H and 3-H, 2.87 Å, somewhat less than the sum of the van der Waals radii (3.24 Å).²³

The lengths of the four C-S bonds in the dithiolane ring stretch from 1.80 to 1.86 Å. The bond angles at sulfur are 95.3° for S1' and 100.2° for S3'. The phenyl groups at C4' are twisted to a different degree; the phenyl hexagons cut the plane C4'-C5'-S1' at angles of 20.5° and 88.5°.

The van der Waals interaction of phenyl groups and adamantane system in adjacent positions of the 1,3-dithiolane **7a** causes much stronger deviations from an ideal envelope conformation than observed for **8a**. The X-ray analysis reveals an irregular shape (Fig. 2, Table 2), a kind of distorted envelope with S1' as the flap and a dihedral angle C2'-S3'-C4'C5' of 16.1°. S1' is out of the planes C2'-S3'-C4' by 0.55 Å and S3'-C4'-C5' by 1.25 Å, thus making one phenyl *quasi-axial* and the other *quasi-equatorial*.

Table 2. Bond Lengths, Angles and Dihedral Angles in the 1,3-Dithiolane Rings of **8a** and **7a**
(In parentheses standard deviations on the last decimal)

| Bond lengths (Å) | 8a | 7a | | 8a | 7a |
|---------------------|-----------|-----------|-----------------|-----------|-----------|
| S1'-C2' | 1.829(2) | 1.777(3) | C4'-C5' | 1.534(3) | 1.617(3) |
| C2'-S3' | 1.857(2) | 1.802(3) | C5'-S1' | 1.796(3) | 1.853(3) |
| S3'-C4' | 1.844(2) | 1.883(3) | | | |
| Bond angles (°) | | | | | |
| C5'-S1'-C2' | 95.3(1) | 93.5(1) | S3'-C4'-C5' | 103.4(2) | 103.7(2) |
| S1'-C2'-S3' | 106.2(2) | 108.0(2) | C4'-C5'-S1' | 107.7(2) | 105.3(2) |
| C2'-S3'-C4' | 100.2(1) | 100.5(1) | | | |
| Dihedral angles (°) | | | | | |
| S1'-C2'-S3'-C4' | 3.0(2) | 19.1(2) | C4'-C5'-S1'-C2' | 51.5(2) | 54.1(2) |
| C2'-S3'-C4'-C5' | 28.8(2) | 16.1(2) | C5'-S1'-C2'-S3' | -28.2(2) | -41.7(2) |
| S3'-C4'-C5'-S1' | -52.2(2) | -44.5(2) | | | |

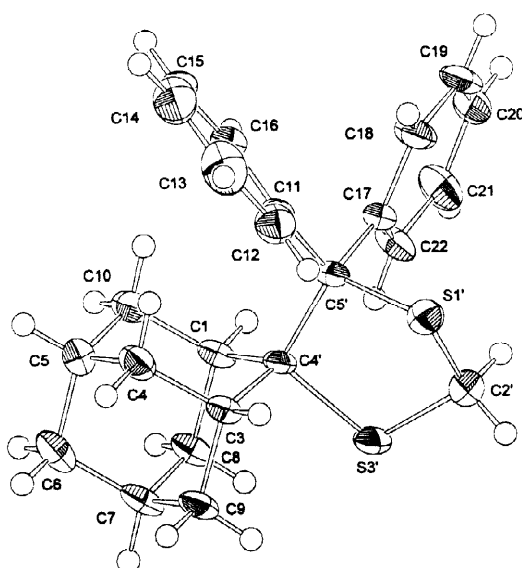


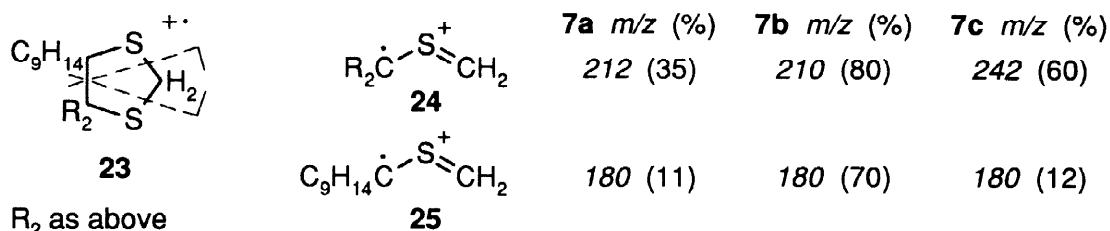
Figure 2. X-Ray Structure of 5',5'-Diphenylspiro[adamantane-2,4'-(1,3)-dithiolane] (**7a**);
ZORTEP Plot (thermal ellipsoids refer to 40% probability).

The distance between H3 of adamantane and H12 of the *quasi-axial* phenyl amounts to 1.96 Å. It is significantly less than the sum of the van der Waals radii and should not be taken at face value, because the H-atoms are located by the computer program regardless of van der Waals pressure. Nevertheless, the push by the phenyl is reflected in the structural parameters of the spiro annulation. The plane S3'-C4'-C5' should bisect the adamantane system. However, the distances of C1 and C3 from the mentioned plane are 1.21 and -1.27 Å. In a regular spiro structure the angles C5'-C4'-C1 and C5'-C4'-C3 should be identical; 118.7° and 113.7° again reveal the push by the phenyl group.

Our expectation that **7a** would assume a half-chair conformation with C4' and C5' above and below the plane S1'-C2'-S3' was not fulfilled. It may well be that lattice forces are responsible for generating a distorted envelope.

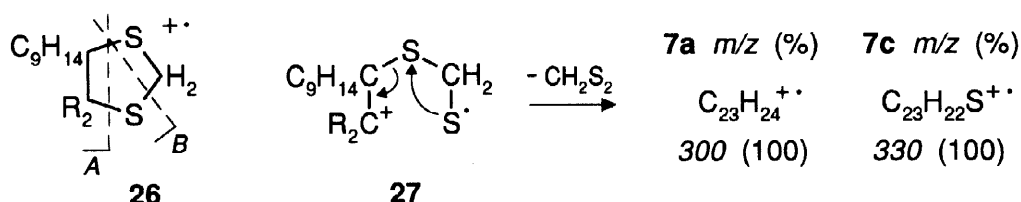
Mass Spectra of 1,3-Dithiolanes

Two matching pairs of thione *S*-methylide + thione lead to cycloadducts **7**. The two corresponding fragmentation pathways are illustrated in **23**; the *m/z* and peak intensities of the radical cations **24** and **25** which appear in the MS of **7a-c** are listed. The radical cations of the thiones are found to a minor extent. The ratios of the radical cationic fragments are influenced by their ionization potentials.



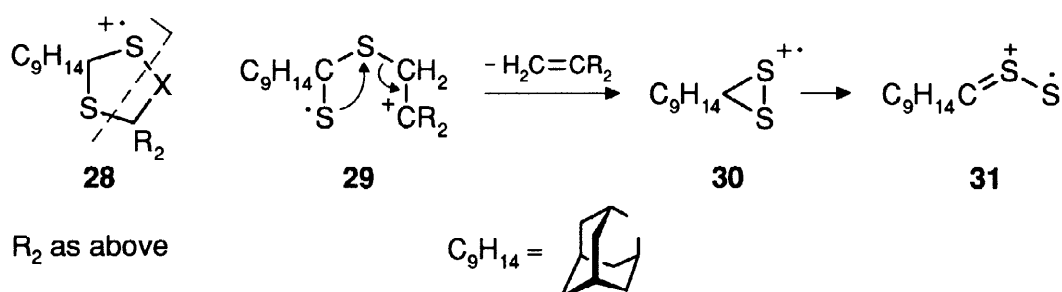
The ionized 1,3-dipoles are formulated in **24,25** as *distonic* radical cations, *i.e.*, a species in which the centers of charge and spin density are separated.²⁴ Fast electrocyclic ring openings have been observed for the radical cations of oxiranes.²⁵ According to calculations (MP4/6-311G**), H₂C=O⁺-CH₂ lies 20 kcal mol⁻¹ below the energy level of the oxirane radical cation.²⁶ Species **24,25** are the analogous allyl type radicals with a sulfonium function in the middle. Equilibria with thiirane radical cations are conceivable.

The molecular formulae of the fragments were confirmed by the intensities of ³⁴S and ¹³C isotope peaks, and in the case of **8a** by high resolution. In the following, we will discuss further splitting pathways of M⁺ rather than speculate about the structures of the fragments.



The breaking of M⁺ along the lines of the original cycloaddition is not as prevalent here as it is for the cycloadducts of **5** with electrophilic ethylenes.⁶ High populations of [M⁺ - CH₂S₂] appear in the MS of all dithiolanes of type **7** (path *A* in **26**), even as base peaks for **7a** and **7c**. A ring opening to the intermediate **27** and an intramolecular radical substitution looks attractive for the loss of CH₂S₂. Whether [M⁺ - CH₂S₂] is an olefin, *e.g.*, 2-(diphenylmethylene)adamantane in the case of **7a**, or (more probable) an isomerization product, is an open question. The minor fragmentation *B*, shown in **26**, consists of the elimination of CH₂S.

A strong peak *m/z* 198, confirmed as C₁₀H₁₄S₂⁺, appears in the MS of type **8** dithiolanes. Previously, this fragment was found in the MS of spiroadamantane derivatives of 1,2,4-trithiolanes (**28**, X = S)²⁷ or



1,2,4-oxadithiolanes (**28**, X = O),²⁸ and the structure **31** of the distonic radical ion was attributed to it. The M^+ of type **8** dithiolanes corresponds to **28**, X = CH_2 , and its fragmentation is similar to path **A** for **26**. In the dissociation of intermediate **29** (in contrast to **27**), the positive charge remains on the S-containing fragment. The assumption of **30** occurring on the pathway to **31** is no longer daring, since dithiiranes **29** and their relation to thiocarbonyl S-sulfides **27** became recently known.

The radical ion **31** appears as the base peak in the MS of **8a** and **8d**, and to a notable extent in those of **8c**, **19**, **21**, **22**. The latter cases take an intermediate position insofar as the positive charge can appear on each of the two fragments; **8c**, **21**, and **22** show $[M^+ - \text{C}_{10}\text{H}_{14}\text{S}_2]$ as base peaks, accompanied by $[\text{C}_{10}\text{H}_{14}\text{S}_2^+]$ (**31**) in lower population. Adamantanethione⁺ (**1**⁺), likewise established by the intensities of isotope peaks, is a steady companion of **31** and suggests the loss of a sulfur atom. A further sequential product is $\text{C}_{10}\text{H}_{13}^+$ (m/z 133); all thioketones studied show the fragment $[M^+ - \text{SH}]$.³⁰

By-the-way, M^+ of the CS_2 adduct **19** occurs as base peak; even in the MS of the bisadduct **22**, m/z 436 (M^+) is populated with 41%. Several cycloadducts of Table 1 reveal special fragmentations in their MS, *e.g.*, $15^+ - 17^+$ lose CH_3S , and $[\text{C}_6\text{H}_5\text{-SH}^+]$ is the base peak for **18**⁺. The experimental part may be consulted.

Cycloadditions to C=O and C=N Bonds

After **4** was reacted with benzaldehyde at 40°C for 8 h, the ¹H NMR analysis indicated 90% of the spiro-1,3-oxathiolane **32**. Chloral in bulk was polymerized in the reaction with **4**, but when 1.05 equiv was used in THF, a high yield of adduct **33** was obtained. Butyl glyoxylate and diethyl mesoxalate likewise contain very electrophilic carbonyl groups and smoothly combined with **5** affording the oxathiolanes **34** and **35** (Table 3).

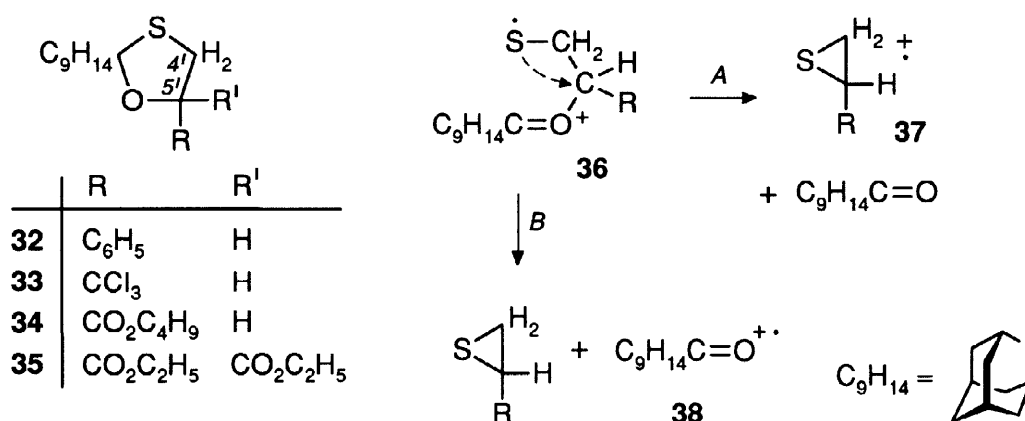


Table 3. Cycloadditions of Adamantanethione *S*-Methylide (**5**) with C=O and C=N Bonds in THF at 40°C (the yields refer to ¹H NMR analyses, those in brackets to isolation)

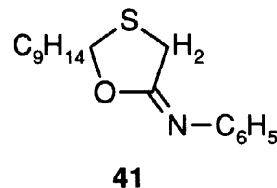
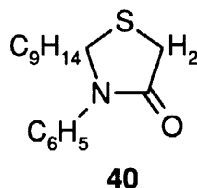
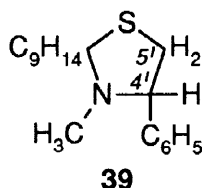
| Dipolarophile | Formula | Cycloadduct | | NMR Parameter | |
|----------------------------------|--------------|-------------|--------|---------------|-----------------------|
| | | %Yield | mp(°C) | δ(4'-H) | δ(5'-H ₂) |
| Benzaldehyde | 32 | 90 (82) | oil | dd 5.13 | 2.90,3.22 |
| Chloral | 33 | 91 (81) | oil | dd 4.69 | m 3.20 |
| Butyl glyoxylate | 34 | 98 (74) | 35-37 | dd 4.71 | m 3.19 |
| Diethyl mesoxalate | 35 | 87 (68) | oil | - | s 3.53 |
| <i>N</i> -Benzylidenemethylamine | 39 | 13 (7) | 97-99 | dd 4.68 | m 3.20 |
| Phenyl isocyanate | 40,41 | | oil | | s 3.77 |

Acetone did not interact with **5**, nor did non-activated carboxylic esters; ethyl acetate can be used as solvent. However, the keto group of methyl 3,3,3-trifluoropyruvate accepted **5** and other thiocarbonyl ylides, as recently reported.³¹

The ¹H NMR spectra of **32** - **34** showed ABX type coupling pattern of 5'-H₂ and 4'-H (Table 3), thus establishing the addition direction. The NMR spectra of the crude products did not offer evidence for the presence of regioisomers. Thus, the CH₂ group of **5** is the superior nucleophile among the two allylic centers of the 1,3-dipole, as observed in the cycloadditions with acrylic ester and acrylonitrile.

The major fragments in the MS of **32-35** can be explained *via* a 1,2-fission which allows an oxonium stabilization in **36**. In the breakdown of **36**, the radical cation character may reside on each of the two fragments (pathways *A* and *B*). The MS of **32** shows *m/z* 136 as the base peak; C₈H₈S⁺ was confirmed by the intensities of isotope peaks and could well be the thiirane radical cation **37**, R = C₆H₅, or the ring-opened distonic ion analogous to **24,25**. Adamantanone radical cation (**37**, *m/z* 150) comes from path *B* and is populated with 20%. The *m/z* 104 (27%) is attributed to styrene⁺ (loss of sulfur from **37**).

In the MS of **33** and **34**, radical cation **38** (*m/z* 150) is the base peak, and **37**, R = CCl₃ or CO₂C₄H₉, is missing; the electron-attracting groups increase the ionization potential.



Yields are not a measure of rate constants. Since the cycloaddition competes with the electrocyclization **5** → **2**, the meager yield of 13% for the cycloadduct **39** of *N*-benzylidenemethylamine speaks for low dipolarophilic activity. Indeed, the interaction of **4** with the 9:1 mixture of *N*-benzylidenemethylamine and benzaldehyde gave rise only to **32**, as established by the ¹H NMR signals of the crude product. The 4'-H of isolated **39** appeared as dd at δ 4.68 with *J*_{vic} = 10.4 and 6.6 Hz; thus, the NCH₃ group must be in position 3'.

Phenyl isocyanate reacts with **5**, but the adduct could not be obtained pure. Tentative experiments did not allow to distinguish between **40** and **41**, or a mixture of the two. The broad IR absorption at 1690 cm^{-1} would be compatible with both of the structures. When the crude adduct was dissolved in ethanol, a crystalline compound precipitated (53%) which was richer by $\text{C}_2\text{H}_5\text{OH}$ than the 1:1-adduct. The ethanolysis product could be an *N,S*-acetal or a *S,O*-acetal, as the conversion to adamantanone 2,4-dinitrophenylhydrazone suggests. Further experiments are required.

EXPERIMENTAL

General. IR spectra were recorded with a Perkin-Elmer 125 instrument or a Beckmann FT model IFS 45. - ^1H NMR spectra were obtained with a Bruker instrument WP80CW (80 MHz), and ^{13}C NMR spectra with Bruker WP80DS (20 MHz); comparison of the ^1H -decoupled with the off-resonance ^{13}C spectra provided the multiplicities. Spectra which were repeated with a Varian XR 400S instrument are marked. All NMR spectra were taken in acid-free CDCl_3 , if not mentioned otherwise, with TMS as internal standard. Quantitative ^1H NMR analysis (CDCl_3) was routinely applied to the crude products after evaporation of the solvent: a weighed standard (*sym*-tetrachloroethane δ 5.92, *as*-tetrachloroethane δ 4.28, or trichloroethylene δ 6.70) was added in an amount which made the integrals to be analyzed comparable with the s of the standard. - Mass spectra (EI, 70 eV) were run on a AET 902 instrument or a Finnigan MAT 90; the latter printed peak intensities with precision. Intensities of isotope peaks are given in the form, *e.g.*, ^{13}C % calcd/ % found. For high resolution (HR) the program CMASS on MAT 95Q ($R \geq 5000$) was used; small distortions of m/z can result from insufficient separation. - PLC is preparative thick-layer chromatography: 2 mm of silica gel 60 PF (Merck) on glass plates. Column chromatography (CC) was carried out on silica gel 60-200 (Merck). - Melting points are uncorrected.

Cycloadditions to C=S Bonds

Reaction with Thiobenzophenone (6a):³² Thiadiazoline **4** (417 mg, 2.00 mmol) and 436 mg (2.20 mmol) of **6a** in 10 ml of absol. THF were heated for 8 h in a 40°C bath. After removal of the solvent at the rotary evaporator, the residue was dissolved in CDCl_3 , and a weighed amount of standard was added; the ^1H NMR analysis of an aliquot, using machine integrals, indicated 50% of **7a** (δ 3.28) and 42% of **8a** (δ 3.95). The separation required repeated PLC with petroleum ether/ CH_2Cl_2 (8:2); 212 mg (28%) of **7a** and 134 mg (18%) of **8a** were isolated pure.

5',5'-Diphenylspiro[adamantane-2,4'-(1,3)-dithiolane] (7a): Recrystallized from CH_2Cl_2 /methanol, the colorless **7a** showed mp $203\text{--}205^\circ\text{C}$ (dec., blue). - IR (KBr): $\tilde{\nu}$ 701 cm^{-1} , 722, 749 st (C_6H_5 out-of-plane deform.), 1438, 1453, 1494 m, 1598 w (arom. ring vibr.), 2855, 2910 st (C-H). - ^1H NMR (400 MHz): δ 1.20 - 2.00 (structured m, 10 H of adamantyl), 2.55 - 3.10 (m, 4 H of adamantyl), 3.28 (s, 2'- H_2), 7.11 - 7.20 (m, 2 arom. H), 7.21 - 7.29 (m, 6 arom. H), 7.90 (s br, 2 arom. H). - ^{13}C NMR: δ 26.30, 26.32, 37.0 (3 d, 1:1:2, 4 CH), and 33.3, 39.2, 39.9 (3 t, 2:1:2, 5 CH_2 of adamantane part), 28.0 (t, C-2'; $^1J_{\text{R}}(^{13}\text{C},\text{H})$ is in the off-resonance spectrum by 35% greater than the values for adamantyl- CH_2), 76.6, 77.2 (2 s, C-4', C-5'), 126.8, 126.9, 131.6 (3 d, 10 arom. CH), 143.4 (s, 2 arom. C_q). - MS (110°C); m/z (%): 378 (2) [M^+], 332 (22) [$\text{M}^+ - \text{CH}_2\text{S}$, $\text{C}_{23}\text{H}_{24}\text{S}^+$; ^{13}C 5.5/5.5, ($^{34}\text{S} + ^{13}\text{C}_2$) 1.6/1.4], 300 (100) [$\text{M}^+ - \text{CH}_2\text{S}_2$, $\text{C}_{23}\text{H}_{24}^+$; ^{13}C 26/24, $^{13}\text{C}_2$ 3.2/3.7, no ^{34}S], 243 (8) [$\text{C}_{14}\text{H}_{11}\text{S}_2^+$], 212 (35)

[C₁₄H₁₂S⁺, **24a**; ¹³C 5.5/6.2, (³⁴S+¹³C₂) 2.0/1.8], 211 (31) [C₁₄H₁₁S⁺], 198 (5) [**6a**⁺; ¹³C 0.77/0.85], 180 (11) [C₁₁H₁₆S⁺, **25**, or C₁₄H₁₂⁺], 179 (11) [9-methylfluorenyl⁺ ?], 167 (12), 165 (27) [fluorenyl⁺], 121 (5) [C₆H₅-C≡S⁺], 91 (10) [C₇H₇⁺], 77 (5) [C₆H₅⁺]. - Anal. for C₂₄H₂₆S₂ (378.6): calcd C 76.14, H 6.92, S 16.94; found C 76.10, H 6.95, S 16.88.

X-Ray Diffraction Analysis of 7a (Fig. 2, Table 2):³³ Triclinic. Space group P1, No.2. Unit cell dimensions: $a = 8.306(4)$, $b = 9.394(5)$, $c = 12.798(7)$ Å, $\alpha = 73.60(4)^\circ$, $\beta = 80.99(4)^\circ$, $\gamma = 85.77(4)^\circ$, volume 945.7(8) Å³, $Z = 2$, $D_C = 1.329$ g/ml; $F(000) = 404$, $T = 293(2)$ K, $\mu(\text{Mo-K}\alpha) = 0.287$ mm⁻¹. Data collection: CAD4 Diffractometer, colorless rod (.53 x .43 x .23 mm), mounted in a glass capillary, cell constants from 25 centered reflexions. Mo-K α radiation, $\lambda = 0.71073$ Å, graphite monochromator, $\omega - 2\Theta$ scan, scan width $(0.90 + 0.45 \tan \Theta)^\circ$, maximum measuring time 60 sec, intensity of three standard reflections checked every 2 h, Θ range 2.26 - 23.95° for all $-h$, $\pm k$, $\pm l$ reflexions, 3192 reflexions measured, 2958 unique, and 2578 with $I > 2\sigma(I)$. Structure solution by SHELXS-86 and refinement by SHELXL-93,³⁴ non-hydrogen atoms refined anisotropically, hydrogens with $U_i = 1.2 \times U_{\text{eq}}$ of the adjacent carbon atom. Full matrix refinement against F^2 . Final $R1 = 0.0508$ and $wR2 = 0.1417$ for 2578 reflexions with $I > 2\sigma(I)$ and 235 variables and 0 restraints. $R1 = 0.0508$ and $wR2 = 0.1475$ for all data. Weight SHELXL-93. Maximum and minimum of the final difference Fourier synthesis 0.445 and -0.486 eÅ⁻³. ZORTEP plot.³⁵

4',4'-Diphenylspiro[adamantane-2,2'-(1,3)-dithiolane] (8a): mp 126-128°C after recrystallization from CH₂Cl₂/ethanol. - IR (KBr): $\tilde{\nu}$ 698 cm⁻¹, 743, 750 st (C₆H₅ out-of-plane deform.), 1452 st, 1491 m, 1499 st, 1593 w (arom. ring vibr.), 2855, 2905, 2924 st (C-H). - ¹H NMR (400 MHz): δ 1.67 - 1.87 (m, 8 H), 2.05 - 2.26 (m, 6 H), 3.95 (s, 5'-H₂), 7.19 (tt, 2 arom. *p*-H), 7.27 (tt, 4 arom. *m*-H), 7.47 (dt, 4 arom. *o*-H). - ¹³C NMR (100 MHz, DEPT): δ 26.3, 26.5, 42.1 (1:1:2, 4 CH), 36.5, 36.8, 37.6 (2:2:1, 5 CH₂ of adamantyl), 48.3 (C-5'; assignment based on 25% increase of $^1J_{\text{R}}(^{13}\text{C},\text{H})$ in off-resonance spectrum), 73.7, 77.7 (C-2', C-4'), 126.8, 127.7, 128.1 (1:2:2, 10 arom. CH), 144.8 (2 arom. C_q). - MS (140°C, MAT 95Q); m/z (%): 378.1470/.1489 (15) [M⁺], 212.0657/.0628 (15) [C₁₄H₁₂S⁺, **24a**], 211.0579/.0573 (12) [C₁₄H₁₁S⁺], 198.0501/.0493 (100) [C₁₃H₁₀S⁺, **6a**⁺] or 198.0534/.0493 [C₁₀H₁₄S₂⁺, **31**], 180.0936/.0955 (15) [C₁₄H₁₂⁺; likewise reconcilable is C₁₁H₁₆S⁺, **25**: 180.0969/.0955], 165.0702/.0728 (16) [C₁₃H₉⁺, fluorenyl⁺], 133.1014/.0977 (20) [C₁₀H₁₃⁺, 1⁺-SH]; in the presence of 2 peaks of similar m/z , the program CMASS averages. - Anal. for C₂₄H₂₆S₂ (378.6): calcd C 76.14, H 6.92, S 16.94; found C 76.27, H 6.87, S 16.90.

X-Ray Diffraction Analysis of 8a (Fig. 1, Table 2):³³ Triclinic, space group P1, No.2. Unit cell dimensions: $a = 6.475(2)$, $b = 10.983(2)$, $c = 14.875(2)$ Å, $\alpha = 68.282(13)^\circ$, $\beta = 87.25(2)^\circ$, $\gamma = 88.28(2)^\circ$, volume 981.6(4) Å³, $Z = 2$, $D_C = 1.284$ g/ml; $F(000) = 404$, $T = 295(2)$ K, $\mu(\text{Mo-K}\alpha) = 0.276$ mm⁻¹. Data collection: CAD4 Diffractometer, colorless rod (.33 x .50 x .53 mm), mounted in a glass capillary, cell constants from 25 centered reflexions. Mo-K α radiation, $\lambda = 0.71073$ Å, graphite monochromator, $\omega - 2\Theta$ scan, scan width $(0.90 + 0.45 \tan \Theta)^\circ$, maximum measuring time 60 sec, intensity of three standard reflections checked every 2 h, Θ range 2.89 - 23.97° for all $-h$, $\pm k$, $\pm l$ reflexions, 3382 reflexions measured, 3076 unique, and 2740 with $I > 2\sigma(I)$. Structure solution by the same methods as described above. Final $R1 = 0.0401$ and $wR2 = 0.1014$ for 2740 reflexions with $I > 2\sigma(I)$ and 255 variables and 2 restraints. $R1 = 0.0462$ and $wR2 = 0.1172$ for all data. Weight SHELXL-93. Maximum and minimum of the final difference Fourier synthesis 0.379 and -0.350 eÅ⁻³. One of the phenyl groups is disordered, and the signals are split in the ratio of 82:18.

Reaction with Thiofluorenone (6b): The reaction of 2.00 mmol of **4** with 2.20 mmol of **6b**³⁶ followed the same protocol. The ¹H NMR analysis revealed 60% of **7b** (δ 3.92, 5'-H₂) and 18% of **8b** (δ 3.42, 2'-H₂). After removal of the CDCl₃, the residue was dissolved in 5 ml of CH₂Cl₂, and 5 ml of ethanol was added. In 2 h at r.t. 330 mg (44%) of **7b** crystallized, mp 173–176°C. The mother liquor contained a ~ 1:1 mixture of **7b** and **8b**; the latter could not be obtained pure.

Dispiro[adamantane-2,5'-(1,3)-dithiolane-4'-9"-fluorene] (7b): IR (KBr): $\tilde{\nu}$ 709 cm⁻¹, 716, 720 st, 732 m (arom. CH out-of-plane deform.), 1413 st br, 1575 m br. - ¹H NMR: δ 1.0 - 1.8 (m, 10 H), 2.25 - 2.62 (s br, 4 H), 3.92 (s, 5'-H₂), 7.0 - 8.0 (m, 8 arom. H). - ¹³C NMR: adamantane signals at δ 26.4, 26.5, 37.3 (3 d, 1:1:2, 4 CH), 33.6, 38.3, 38.9 (3 t, 2:1:2, 5 CH₂); 29.6 (t, C-2'), 72.7, 77.4 (2 s, C-4', C-5'), 119.9, 126.6, 127.9, 128.2 (4 d, 8 arom. CH), 139.6, 145.7 (2 s, 4 arom. C_q). - MS (100°C); *m/z* (%): 376 (100) [M⁺], 330 (7) [C₂₃H₂₂S⁺, M⁺- CH₂S], 298 (50) [C₂₃H₂₂⁺, M⁺- CH₂S₂], 210 (80) [C₁₄H₁₀S⁺, **24b**], 180 (70) [C₁₁H₁₆S⁺, **25**], 165 (30) [C₁₃H₉⁺, fluorenyl⁺]. - Anal. for C₂₄H₂₄S₂ (376.6): calcd C 76.54, H 6.42, S 17.03; found C 76.32, H 6.66, S 17.06.

Reaction with Thioxanthione (6c): The same procedure gave a crude product, which contained 41% of **7c** (δ 4.07, 2'-H₂) and 34% of **8c** (δ 3.59, 5'-H₂). After evaporation of the solvent, the residue was triturated with 2 ml of CHCl₃; 208 mg (25%) of **8c** remained undissolved, mp 233–236°C. Methanol (3 ml) was added to the mother liquor; within 10 min at r.t. 219 mg (27%) of **7c** crystallized, mp 180–184°C. Both isomers were purified by recrystallization.

Dispiro[adamantane-2,4'-(1,3)-dithiolane-5',10''-thioxanthene] (7c): Colorless leaflets, mp 183–185°C, were obtained from CH₂Cl₂/methanol. - IR (KBr): $\tilde{\nu}$ 717 cm⁻¹ m, 758 st, 766, 789 (arom. out-of-plane deform.), 1054, 1096, 1270 m; 1441, 1462 st. - ¹H NMR: 1.2 - 2.0 (m, 12 H), 2.35 - 2.75 (m, 2 H), 4.07 (s, 2'-H₂), 7.0 - 7.2 (m, 6 arom. H), 8.32 - 8.62 (m, 2 arom. H). - ¹³C NMR: δ of adamantane signals: 26.5, 26.7, 35.4 (3 d, 1:1:2, 4 CH), 34.1, 38.9, 39.6 (3 t, 2:2:1, 5 CH₂); 30.8 (t, C-2'; increase of *J_R*(¹³C,H) by 41%), 74.8, 81.9 (2 s, C-4', C-5'), 124.5, 124.8, 127.2, 135.3 (4 d, 8 arom. CH), 130.4, 134.7 (2 s, 4 arom. C_q). - MS (110°C); *m/z* (%): 408 (20) [M⁺], 362 (45), [C₂₃H₂₂S₂⁺, M⁺- CH₂S], 330 (100) [C₂₃H₂₂S⁺, M⁺- CH₂S₂], 242 (60) [C₁₄H₁₀S₂⁺, M⁺- **1**, **24c**], 228 (10) [C₁₃H₁₈S₂⁺, **6c**⁺], 196 (17) [C₁₃H₈S⁺], 180 (12) [C₁₁H₁₆S⁺, **25**], 152 (10) [C₁₂H₈⁺, biphenylene], 78 (15) [CH₂S₂⁺ ?]. - Anal. for C₂₄H₂₄S₃ (408.6): calcd. C 70.54, H 5.92, S 23.54; found C 70.36, H 6.01, S 23.53.

Hydrogenolysis of 7c: 250 mg (0.61 mmol) of **7c** and ~ 3 g of fresh Raney nickel (W7)³⁷ were refluxed in 30 ml of methanol for 15 h. Hot filtering, washing with 3 x 15 ml of hot methanol, concentrating, and working up with water/CH₂Cl₂ furnished 168 mg (91%) of **2-diphenylmethyladamantane (12)** as colorless needles, mp 138–140°C (ethanol). - ¹H NMR: δ 1.3 - 2.2 (m, 14 H), 2.5 (d br, *J* = 12.0 Hz, 2-H), 4.12 (d, *J* = 12.0 Hz, benzyl-H), 7.0 - 7.4 (m, 2 C₆H₅). - Anal. for C₂₃H₂₆ (302.5): calcd C 91.33, H 8.67; found C 91.34, H 8.59.

Dispiro[adamantane-2,2'-(1,3)-dithiolane-4',10''-thioxanthene] (8c): mp 237–239°C (dec.) after recrystallization from CHCl₃. - IR (KBr): $\tilde{\nu}$ 749 cm⁻¹ st, 1439 m, 1450 st. - ¹H NMR: δ 1.4 - 2.5 (m, 14 H), 3.59 (s, 5'-H₂), 7.0 - 7.5 (m, 6 arom. H), 8.1 - 8.3 (m, 2 arom. H). - ¹³C NMR: δ 26.8, 27.1, 41.4 (3 d, 1:1:2, 4 CH), 36.7, 36.8, 37.8 (3 t, 2:2:1, 5 CH₂) for adamantane system; 44.2 (t, C-5'), 73.3, 77.1 (2 s, C-2', C-4'), 125.8, 126.82, 126.88, 128.8 (4 d, 8 arom. CH), 132.2, 138.1 (2 s, 4 arom. C_q). - MS (140°C); *m/z* (%): 408 (< 5) [M⁺], 242 (11) [C₁₄H₁₀S₂⁺, **24c**], 241 (13) [C₁₄H₉S₂⁺], 210 (100) [C₁₄H₁₀S⁺, M⁺- **31**], 198 (25) [C₁₀H₁₄S₂⁺, **31**], 166 (15) [C₁₀H₁₄S, **1**⁺], 91 (8%). - Anal. for C₂₄H₂₄S₃

(408.6): calcd C 70.54, H 5.92, S 23.54; found C 70.47, H 5.91, S 23.61.

Dispiro[(1,3)-dithiolane-2',2';4',2''-bis(adamantane)] (8d): Freshly sublimed *adamantanethione*⁵ (1, 2.20 mmol) was used in the same procedure. The ¹H NMR analysis indicated 1.71 mmol (86%) of **8d** (δ 3.25, 5-H₂); no other dithiolane was detectable. After removal of the solvent, trituration with 3 ml of ethanol afforded 525 mg (76%) of **8d** as colorless crystals, mp 165–166°C (2-propanol). - IR (KBr): $\tilde{\nu}$ 966 cm⁻¹, 1095, 1452 m; 2850, 3005 st (C-H). - ¹H NMR: δ 1.45 - 2.45 (m, 28 H), 3.25 (s, 5-H₂). - ¹³C NMR: δ 26.4, 26.7, 27.0, 27.7, 38.2, 42.8 (6 d, 1:1:1:1:2:2, 8 CH), 34.8, 36.6, 37.9, 38.4 (4 t, 2:6:1:1), 45.5 (t, C-5), 73.1, 76.0 (2 s, C-2', C-4). - MS (70°C); *m/z* (%): 346 (24) [M⁺; ¹³C 5.6/5.4, (³⁴S+¹³C₂) 2.7/2.6], 198 (100) [C₁₀H₁₄S₂⁺, **31**; ¹³C 11.1/10.5, (³⁴S+¹³C₂) 9.4/7.7], 166 (18) [C₁₀H₁₄S⁺, 1⁺; (³⁴S+¹³C₂) 0.9/0.9], 148 (14), 133 (21) [C₁₀H₁₃⁺, 1⁺- SH], 91 (12) [C₇H₇⁺]. - Anal. for C₂₁H₃₀S₂ (346.6): calcd C 72.77, H 8.73, S 18.50; found C 72.44, H 8.93, S 18.53.

2'',2'',4'',4''-Tetramethyldispiro[adamantane-2,2'-(1,3)-dithiolane-4',3''-cyclobutane]-1''-one (8e): The reaction of 2.00 mmol of **4** with 2.20 mmol of 2,2,4,4-tetramethyl-3-thioxocyclobutanone³⁸ provided 80% of **8e** (δ 3.30, 5'-H₂); no second dithiolane appeared. From ethanol crystallized 393 mg (58%) of **8e**, mp 128–129°C. - IR (KBr): $\tilde{\nu}$ 970 cm⁻¹, 1032, 1101, 1158, 1455, 1469 m; 1780 st (C=O). - ¹H NMR: δ 1.25 (s, 2 CH₃), 1.35 (s, 2 CH₃), 1.55 - 2.35 (m, 14 H), 3.30 (s, 5'-H₂). - ¹³C NMR: δ 19.4, 25.3 (2 q, 4 CH₃), 26.3, 26.5, 42.4 (3 d, 1:1:2, 4 CH), 36.6, 36.8, 37.7 (3 t, 2:2:1, 5 CH₂), 41.9 (t, C-5'), 63.2 (s, C-2'', C-4''), 70.8, 75.2 (2 s, C-2, C-4'), 221.0 (s, C=O). - MS (60°C); *m/z* (%): 336 (14) [M⁺; ¹³C 3.0/3.1, (³⁴S+¹³C₂) 1.6/1.5], 266 (100) [C₁₅H₂₂S₂⁺, M⁺- dimethylketene; ¹³C 17/15, (³⁴S+¹³C₂) 10/8], 198 (5) [C₁₀H₁₄S₂⁺, **31**; (³⁴S+¹³C₂) 0.47/0.52], 166 (29) [C₁₀H₁₄S⁺, 1⁺], 133 (4) [1⁺- SH], 100 (13) [C₅H₈S⁺; (³⁴S+¹³C₂) 0.60/0.59], 91 (6) [C₇H₇⁺]. - Anal. for C₁₉H₂₈OS₂ (336.5): calcd C 67.80, H 8.39, S 19.06; found C 67.47, H 8.22, S 19.04.

4'-Methyl-4'-(methylthio)spiro[adamantane-2,2'-(1,3)-dithiolane] (16): The reaction of **4** (2.00 mmol) with 2.20 mmol of *methyl dithioacetate*³⁹ furnished a crude product which contained 64% of **16** (AB at δ 3.02, 3.30). By PLC with petroleum ether/CH₂Cl₂ (8:2), 253 mg (44%) of **16** was obtained as a colorless oil which crystallized from ethanol, mp 43–45°C. - IR (film): $\tilde{\nu}$ 985 cm⁻¹, 1072, 1098, 1350, 1388, 1420 m, 1450 st; 2854, 2912 vst (C-H). - ¹H NMR: δ 1.5 - 2.3 (m, 14 H), superimposed by 1.82 (s, 4'-CH₃) and 2.17 (s, SCH₃), 3.02, 3.30 (AB, ²J = 12.5 Hz, 5'-H₂). - ¹³C NMR: δ 19.5 (q, SCH₃), 30.3 (q, CH₃); the adamantane signals indicate chirality: 26.2, 26.5, 41.6, 42.6 (4 d, 4 CH), 36.0, 36.1, 36.4, 37.3, 37.7 (5 t, 5 CH₂), 78.7 (s, C-2); 48.2 (t, C-5'), 69.3 (C-4'). - MS (30°C); *m/z* (%): 286 (18) [M⁺; ¹³C 3.0/3.1], 239 (100) [C₁₃H₁₉S₂⁺, M⁺- SCH₃], 198 (4) [C₁₀H₁₄S₂⁺, **31**], 181 (10) [C₁₁H₁₇S⁺], 167 (9), 166 (10) [C₁₀H₁₄S⁺, 1⁺], 133 (9) [C₁₀H₁₃⁺, 1⁺- SH], 117 (11), 91 (20) [C₇H₇⁺], 79 (12), 73 (13), 59 (7) [CH₃C≡S⁺]. - Anal. for C₁₄H₂₂S₃ (286.5): calcd C 58.68, H 7.74, S 33.58; found C 58.85, H 7.70, S 33.45.

Hydrogenolysis: **16** (250 mg, 0.87 mmol) and 3 g Raney nickel in 30 ml of ethanol were refluxed for 15 h. Workup, as described above, gave 98 mg (82%) of *adamantane* (**13**), mp 264–267°C (closed tube) after recrystallization from ethanol; the ¹H and ¹³C NMR spectra⁴⁰ established the identity.

Reaction with Methyl Dithiobenzoate:³⁹ The ¹H NMR analysis indicated 51% of **15** (AB at δ 3.45, 3.94) and 45% of **17** (AB at δ 3.64, 3.73). PLC with petroleum ether/CH₂Cl₂ (8:2) furnished 198 mg

(28%) of pure **15** as the first fraction. The second fraction (245 mg, **15/17** 1:6) was subjected to another separation by PLC and yielded pure **17** as a colorless oil (162 mg, 23%) which solidified.

4'-Methylthio-4'-phenylspiro[adamantane-2,5'-(1,3)-dithiolane] (15), mp 166–168°C (ethanol). - IR (KBr): $\tilde{\nu}$ 713 cm⁻¹, 722 st, 774, 792 m (C₆H₅ out-of-plane deform.), 1096 w; 1317 w, 1443 m (S-CH₃), 1474, 1481 m (C₆H₅ ring vibr.). - ¹H NMR: δ 0.6 - 2.8 (m, 14 H), superposed by 1.92 (s, SCH₃); 3.45, 3.94 (AB, ²J = 8.8 Hz, 2'-H₂), 7.2 - 7.4, 7.9 - 8.1 (2 m, C₆H₅). - ¹³C NMR: δ 14.4 (q, SCH₃); adamantane signals: 26.5, 26.7, 37.2, 38.1 (4 d, 4 CH), 32.7, 33.3, 37.4, 38.8, 41.4 (5 t, 5 CH₂), 78.8 (s, C-2); 28.1 (t, C-2'), 84.3 (C-4'), 127.9, 128.2, 131.2 (3 d, 5 arom. CH), 137.4 (s, arom. C_q). - MS (90°C); *m/z* (%): 348 (15) [M⁺], 301 (100) [C₁₈H₂₁S₂⁺, M⁺-SCH₃], 287 (11) [C₁₇H₁₉S₂⁺], 270 (95) [C₁₈H₂₂S⁺, M⁺-CH₂S₂], 255 (35) [C₁₇H₁₉S⁺, 301 - CH₂S], 223 (16), 180 (58) [C₁₁H₁₆S⁺, **25**], 168 (10), 166 (10) [C₁₀H₁₄S⁺, **1**], 121 (51) [C₆H₅C≡S⁺], 91 (29) [C₇H₇⁺], 84 (13), 79 (13), 78 (8), 77 (12) [C₆H₅⁺]. - Anal. for C₁₉H₂₄S₃ (348.6): calcd C 65.46, H 6.94, S 27.60; found C 65.48, H 7.02, S 27.66.

Hydrogenolysis: The usual procedure with 65 mg (0.19 mmol) of **15** and 3 g Raney nickel in 20 ml of methanol furnished **2-benzyladamantane (14)**, 36 mg, 84%), bp 135–136°C/0.7 mm.⁴¹ - ¹H NMR: δ 1.25 - 2.25 (m, 15 H), 2.71 (d, ³J = 7.5 Hz, benzylic CH₂), 7.1 (s, C₆H₅). - MS (180°C); *m/z* (%): 226 (23) [M⁺], 135 (100) [C₁₀H₁₅⁺], 91 (11) [C₇H₇⁺]. - Anal. for C₁₇H₂₂ (226.4): calcd C 90.20, H 9.80; found C 89.99, H 9.95.

4'-Methylthio-4'-phenylspiro[adamantane-2,2'-(1,3)-dithiolane] (17): mp 109–111°C (ethanol). - IR (KBr): $\tilde{\nu}$ 690 cm⁻¹, 705, 723 st (C₆H₅ out-of-plane deform.), 965, 1097 m; 1453 m, 1472, 1490 w (arom. ring vibr.); 2852, 2912 vst (C-H). - ¹H NMR: δ 1.5 - 2.5 (m, 14 H), 1.95 (s, SCH₃), 3.64, 3.73 (AB, ²J = 12.5 Hz, 5'-H₂), 7.0 - 7.6 (m, C₆H₅). - ¹³C NMR: δ 15.5 (q, SCH₃); adamantane system: 26.2, 26.4, 42.1, 42.3 (4 d, 4 CH), 36.3, 36.5, 2 x 36.7, 37.6 (5 t, 5 CH₂), 75.5 (s, C-2); 47.3 (t, C-5'), 78.3 (s, C-4'), 2 x 127.5, 128.0 (3 d, 5 arom. CH), 142.1 (s, arom. C_q). - MS (70°C); *m/z* (%): 348 (2.2) [M⁺], 301 (71) [C₁₈H₂₁S₂⁺, M⁺-SCH₃], 198 (4), 179 (22) [C₁₁H₁₅S⁺], 166 (12) [C₁₀H₁₄S⁺, **1**], 150 (9), 135 (35), 121 (7) [C₆H₅-C≡S⁺], 103 (10), 91 (24) [C₇H₇⁺], 79 (12), 77 (10) [C₆H₅⁺], 48 (89), 47 (100) [CH₃S⁺]. - Anal. for C₁₉H₂₄S₃ (348.6): calcd C 65.46, H 6.94, S 27.60; found C 65.25, H 6.89, S 27.61.

4',4'-Bis(phenylthio)spiro[adamantane-2,2'-(1,3)-dithiolane] (18): The experiment with 2.00 mmol of **4** and 2.20 mmol of *diphenyl trithiocarbonate*⁴² gave 85% of **18** (s, δ 3.12); no other dithiolane was found. 488 mg (55%) crystallized from ethanol, mp 122–124°C. - IR (KBr): $\tilde{\nu}$ 693 cm⁻¹, 704, 754 st (C₆H₅ out-of-plane deform.), 933, 971, 1026, 1102 m; 1441, 1455, 1473 st, 1572, 1582 w (arom. ring vibr.). - ¹H NMR: δ 1.50 - 2.25 (m, 14 H), 3.12 (s, 5'-H₂), 7.0 - 7.75 (m, 2 C₆H₅). - ¹³C NMR: δ 26.2, 26.4, 41.6 (3 d, 1:1:2, 4 CH), 36.1, 36.6, 37.6 (3 t, 2:2:1, 5 CH₂), 45.9 (t, C-5'), 80.0, 82.0 (2 s, C-2, C-4'); 128.6, 129.5, 137.1 (3 d, 2:1:2, 10 arom. CH), 132.5 (s, 2 arom. C_q). - MS (120°C); *m/z* (%): 332 (26) [C₁₈H₂₀S₃⁺, M⁺-C₆H₅SH; ¹³C 5/7, (³⁴S+¹³C₂) 4.0/4.5], 243 (9) [(C₆H₅S)₂CH⁺], 166 (10) [C₁₀H₁₄S⁺, **1**], 147 (5), 119 (5), 110 (100) [C₆H₅SH⁺; (³⁴S+¹³C₂) 4.6/4.9], 109 (24) [C₆H₅S⁺], 91 (15) [C₇H₇⁺], 84 (18), 77 (18) [C₆H₅⁺]. - Anal. for C₂₄H₂₆S₄ (442.7): calcd C 65.11, H 5.92, S 28.97; found C 65.04, H 5.65, S 28.88.

Hydrogenolysis: **18** (442 mg, 1.00 mmol) and 5 g Raney nickel in 30 ml of ethanol were reacted as usual and gave 85 mg (63%) of **13**, mp 262–264°C (closed tube), identified as above.

Spiro[adamantane-2,3'-(1,3)-dithiolane]-2'-thione (19): (a) **4** (208 mg, 1.00 mmol) in 200 ml (3.32 mol) of carbon disulfide were heated in a 40°C bath for 8 h, whereby the solution turned brick-red. After evaporation of CS₂, the ¹H NMR analysis showed 89% of **19** (s δ 4.17) and no **22**. PLC with hexane/CH₂Cl₂ afforded 210 mg (82%) of brick red needles, mp 108–110°C (tube put in bath at 100°C). - IR (KBr): ν 1010 cm⁻¹ st, 1099, 1145, 1450 m; 2855, 2910 st (C-H). - ¹H NMR: δ 1.35 - 2.55 (m, 14 H), 4.17 (s, 5'-H₂). - ¹³C NMR: adamantane signals, δ 26.3, 26.5, 39.6 (3 d, 1:1:2, 4 CH), 35.4, 36.4, 37.4 (3 t, 2:2:1, 5 CH₂), 84.2 (s, C-2); 55.9 (t, C-5'), 239.2 (s, C=S). - MS (60°C); *m/z* (%): 256 (100) [M⁺], 198 (25) [C₁₀H₁₄S₂⁺, **31**], 180 (95) [C₁₁H₁₆S⁺, M⁺- CS₂, **25**], 166 (70) [C₁₀H₁₄S⁺, 1⁺], 133 (35) [C₁₀H₁₃⁺, 1⁺- SH], 91 (76) [C₇H₇⁺], 78 (38). - Anal. for C₁₂H₁₆S₃ (256.4): calcd C 56.20, H 6.29, S 37.51; found C 56.23, H 6.32, S 37.47.

(b) **4,4'-Spirobis[adamantane-2''-spiro-2-(1,3)-dithiolane] (22):** The thermolysis of 208 mg (1.00) mmol of **4** was repeated in 5.0 ml (83 mmol) of CS₂, and the ¹H NMR analysis indicated 41% of **19** and 40% of **22**, the latter by the AB system at δ 3.42, 3.62. When the residue was dissolved in 5 ml of diethyl ether, the 2:1 adduct (**22**, 72 mg, 33%) crystallized in several h at 5°C. From CH₂Cl₂/methanol came colorless prisms of **22**, mp 230–231°C. - ¹H NMR: δ 1.45 - 2.50 (m, 28 H), 3.42, 3.62 (AB, ²J = 12.0 Hz, 5-H₂ + 5'-H₂). - ¹³C NMR (CS₂/CDCl₃): adamantane, δ 26.6, 26.8, 41.4, 42.8 (4 d, 8 CH), 35.5, 36.1, 36.6, 37.8, 38.0 (5 t, 10 CH₂), 77.1 (s, 2 C-2''); coincides with middle line of CDCl₃ and increases integral); 48.2 (t, C-5/C-5'), 82.1 (s, C-4 = C-4'). - MS (140°C); *m/z* (%): 436 (41) [M⁺; ¹³C 11/13, (³⁴S + ¹³C₂) 8.6/8.8], 270 (21) [C₁₃H₁₈S₃⁺, M⁺- 1], 238 (100) [C₁₃H₁₈S₂⁺, M⁺- **31**; (³⁴S + ¹³C₂) 9.8/10.0], 198 (11) [C₁₀H₁₄S₂⁺, **31**], 166 (46) [C₁₀H₁₄S⁺, 1⁺], 133 (16) [1⁺- SH], 104 (15), 91 (24) [C₇H₇⁺]. - Anal. for C₂₃H₃₂S₄ (436.6): calcd C 63.85, H 7.46, S 28.69; found C 63.48, H 7.33, S 29.34.

(c) *Hydrogenolysis of 22:* 1.00 mmol of **22** and 3 g of Raney nickel in 30 ml of ethanol reacted as before and afforded 128 mg (47%) of **13**, mp 264–267°C (closed tube), identified as above.

(d) **4'-(2,4-Dinitrophenylthio)spiro[adamantane-2,2'-(1,3)-2H-dithiole] (20):** **19** (128 mg, 0.050 mmol) in 10 ml of ethanol was reacted with 0.5 mmol of NaOH and 112 mg (0.50 mmol) of 2,4-dinitrochlorobenzene. After refluxing for 1.5 min, 175 mg (83%) of **20** crystallized as yellow needles, mp 207–209°C (dec.; CH₂Cl₂/ethanol). - IR (KBr): ν̃ 1339 cm⁻¹, 1528 vst (NO₂); 1450 w, 1586 vst (arom. ring vibr. and C=C). - ¹H NMR: δ 1.50 - 2.75 (m, 14 H), 6.62 (s, 5'-H), 7.65 (d, ³J = 9.4 Hz, 6''-H), 8.33 (dd, J = 9.4, 2.2 Hz, 5''-H), 8.97 (d, ⁴J = 2.2 Hz, 3''-H). - MS (150°C); *m/z* (%): 422 (100) [M⁺], 301 (10), 239 (9), 166 (25) [C₁₀H₁₄S⁺, 1⁺], 119 (19), 105 (24), 91 (64), 86 (98), 84 (99). - Anal. for C₁₈H₁₈N₂O₄S₃ (422.5): calcd C 51.16, H 4.29, N 6.63, S 22.77; found C 50.88, H 4.34, N 6.48, S 23.03.

(e) **4** (0.50 mmol) and 130 mg (0.51 mmol) of **19** in 5 ml of cyclohexane were heated at 40°C for 8 h. After evaporation and dissolving in CDCl₃, the ¹H NMR analysis with weight standard showed 81% of **22**.

N-Phenylspiro[adamantane-2,2'-(1,3)-dithiolane]-1'-imine (21): (a) **4** (416 mg, 2.00 mmol) in 5 ml of freshly distilled phenyl isothiocyanate was stirred at 40°C (oil bath); the nitrometer indicated 47 ml of N₂ (94%) after 5 h. The excess of the dipolarophile was distilled at 50–55°C/0.2 mm, and the residue subjected to ¹H NMR analysis (as-C₂H₂Cl₄ as standard); the integral of the s at δ 4.05 showed 91% of **21**. Trituration of the residue with 4 ml of ethanol and storage at +5°C for 20 h afforded 443 mg (70%) of **21** as colorless needles, mp 78–80°C. - IR (KBr): ν̃ 694 cm⁻¹, 768 st (C₆H₅ out-of-plane deform.); 1091, 1098 m; 1458, 1485 m, 1591 st (C₆H₅ ring vibr.), 1631 vst (C=N). - ¹H NMR: δ 1.57 - 2.00 (m, 10 H), 2.07 - 2.45 (m,

4 H), 4.05 (s, 5'-H₂), 6.75 - 7.37 (m, C₆H₅). - ¹³C NMR: adamantane part, δ 26.3, 26.7, 40.0 (3 d, 1:1:2, 4 CH), 35.4, 36.3, 37.7 (3 t, 2:2:1, 5 CH₂), 77.9 (s, C-2); 43.3 (t, C-5'; ¹J_R(¹³C,H) by 34% increased), 120.0, 129.0 (2 d, 4 arom. H), 124.5 (d, 2 arom. H), 151.7 (s, arom. C_q), 172.6 (s, C=N). - MS (70°C); *m/z* (%): 315 (86) [M⁺], 225 (9), 198 (22) [C₁₀H₁₄S₂⁺, 31], 180 (46) [C₁₁H₁₆S⁺, 25], 166 (22) [C₁₀H₁₄S⁺, 1⁺], 149 (66) [C₈H₇NS⁺], 133 (27) [C₁₀H₁₃⁺, 1⁺- SH], 117 (100) [C₈H₇N⁺, M⁺- 31, C₆H₅-N=C=CH₂⁺; no ³⁴S peak], 91 (38) [C₇H₇⁺], 77 (43) [C₆H₅⁺]. - Anal. for C₁₈H₂₁NS₂ (315.5): calcd C 68.52, H 6.71, N 4.44, S 20.33; found C 68.33, H 6.64, N 4.14, S 20.30.

(b) **19** (165 mg, 0.64 mmol) in 4 ml of freshly distilled aniline was kept for 4 h at r.t. (smell of H₂S). After distillation of the excess of aniline at 0.1 mm, the crude **21** was recrystallized from ethanol: 118 mg (58%) of the anil **21**, mp 78-80°C, was obtained and identified by mixed mp and ¹H NMR spectrum.

Cycloadditions with Carbonyl Compounds and Imines

5'-Phenylspiro[adamantane-2,2'-(1,3)-oxathiolane] (32). The reaction of 2.00 mmol of **4** with 5 ml of freshly distilled *benzaldehyde*, was carried out in 8 h at 40°C. The excess of aldehyde was distilled *in vacuo* and the ¹H NMR-analysis indicated 90% of **32** (δ 5.13). PLC (CH₂Cl₂/petroleum ether 3:7) afforded 470 mg (82%) of **32** as a colorless oil. IR (film): $\tilde{\nu}$ 696 cm⁻¹, 738, 764 (arom. CH out-of-plane deform.), 1070, 1080, 1104 st (C-O), 1453 st, 1468, 1490 (C₆H₅ ring vibr.), 2858, 2905 st (C-H). - ¹H NMR: δ 1.5 - 2.0 (m, 10 H), 2.0 - 2.45 (m, 4 H), ABX at 2.90 (t, 4'-H_A), 3.22 (dd, 4'-H_B), and 5.13 (dd, 5'-H) with *J*_{4'A,5'} = *J*_{4'A,4'B} = 10.0 Hz, *J*_{4'B,5'} = 4.7 Hz), 7.2 - 7.5 (m, C₆H₅). - MS (40°C); *m/z* (%): 286 (4) [M⁺; ¹³C 0.84/0.79; (³⁴S+¹³C₂) 0.22/0.26], 180 (3) [25], 166 (1) [1⁺], 150 (20) [C₁₀H₁₄O⁺, 38], 136 (100) [C₈H₈S⁺; 37, R = C₆H₅; ¹³C 9/11; (³⁴S+¹³C₂) 4.8/5.6], 104 (27) [C₈H₈⁺, styrene⁺], 91 (15) [C₇H₇⁺], 79 (18) [C₆H₇⁺], 78 (11) [C₆H₆⁺], 77 (10) [C₆H₅⁺]. - Anal. for C₁₈H₂₂OS (286.4): calcd C 75.48, H 7.74, S 11.20; found C 75.40, H 7.76, S 11.05.

5'-Trichloromethylspiro[adamantane-2,2'-(1,3)-oxathiolane] (33): *Chloral* (2.10 mmol, freshly prepared from chloral hydrate and distilled) was reacted with 2.00 mmol of **4** in 3 ml of abs. THF at 40°C for 8 h. The ¹H NMR integral at 4.69 indicated 1.82 mmol (91%) of **33**. After removal of impurities by PLC, 532 mg (81%) of **33** was isolated as a colorless oil. In a preceding experiment, chloral polymerized when it was used in excess as solvent. - IR (film): $\tilde{\nu}$ 800 cm⁻¹, 812 st (CCl₃), 1010, 1103 st (C-O). - ¹H NMR: δ 1.5 - 2.0 (m, 10 H), 2.0 - 2.5 (m, 4 H), 3.20 (mc, AB of ABX, 4'-H₂), 4.69 (dd + satellites, X of ABX, 5'-H) with *J*_{AB} - 11 Hz, *J*_{AX} - 6 Hz, *J*_{BX} - 8 Hz. - MS (30°C): Of the four isotope peaks for Cl₃ (100:96:30.7:3.3 with increasing mass) the lowest is quoted; *m/z* (%): 326 (51) [M⁺], 291 (15) [M⁺- Cl], 209 (54) [M⁺- CCl₃], 182 (95) [C₁₁H₁₈S⁺; ¹³C 11.6/12.3; (³⁴S+¹³C₂) 4.9/5.8], 166 (5) [C₁₀H₁₄S⁺, 1⁺], 154 (32), 150 (100) [C₁₀H₁₄O⁺, 38], 133 (6) [1⁺- SH], 121 (17), 117 (8) [CCl₃⁺], 91 (26) [C₇H₇⁺]. - Anal. for C₁₃H₁₇Cl₃OS (327.7): calcd C 47.64, H 5.23, S 9.79; found C 47.73, H 5.22, S 9.79.

Butyl Spiro[adamantane-2,2'-(1,3)-oxathiolane]-5'-carboxylate (34). *Butyl glyoxylate* ⁴³ (2.20 mmol) reacted with 2.00 mmol of **4** in 4 ml of abs. THF; the t at δ 4.69 analyzed for 98% of **34**. PLC (petroleum ether/acetone 95:5) gave 460 mg (74%) of a colorless oil which solidified, mp 35-37°C. - IR (film): $\tilde{\nu}$ 1103 cm⁻¹, 1149, 1195 st (C-O), 1734, 1761 st (C=O). - ¹H NMR: δ 0.82 (t, CH₃), 1.1 - 2.5 (m, 18 H), 3.19 (pseudo-d, *J*_{4',5'} = 6.5 Hz, 4'-H₂), 4.12 (t, *J* = 6.4 Hz, OCH₂), 4.71 (pseudo-t, *J* = 6.5 Hz, 5'-H). - MS (20-30°C); *m/z* (%): 310 (18) [M⁺; ¹³C 3.4/3.5], 209 (9) [M⁺- CO₂C₄H₉], 166 (9)

[C₁₀H₁₄S⁺, 1⁺], 150 (100) [C₁₀H₁₄O⁺, 38], 91 (10) [C₇H₇⁺]. - Anal. for C₁₇H₂₆O₃S (310.4): calcd C 65.77, H 8.44, S 10.33; found C 65.92, H 8.69, S 10.36.

Diethyl Spiro[adamantane-2,2'-(1,3)-oxathiolane]-5',5'-dicarboxylate (35). Diethyl mesoxalate (2.20 mmol) and 2.00 mmol of **4** were reacted as usual. The d at δ 3.52 indicated 87% of **35**. PLC as above gave 480 mg (68%) of a colorless oil. - IR (film): $\tilde{\nu}$ 1035 cm⁻¹ m, 1068 st, 1159, 1161, 1220 m, 1278 st br (C-O); 1748 vst, 1765 m (C=O). - ¹H NMR: δ 1.27 (t, 2 CH₃), 1.5 - 2.7 (m, 14 H), 3.53 (s, 4'-H₂), 4.15, 4.23 (2 t, diastereotopic OCH₂). - MS (40-50°C); *m/z* (%): 354 (28) [M⁺], 281 (100) [C₁₅H₂₁O₃S⁺, M⁺- CO₂C₂H₅; ¹³C 17/18; (³⁴S+¹³C₂) 5.8/7.0], 204 (61) [C₈H₁₂O₄S⁺, M⁺- adamantanone; ¹³C 5.4/6.5; (³⁴S+¹³C₂) 2.9/3.8], 166 (7) [1⁺], 158 (13) [C₇H₁₀O₄⁺], 150 (55) [C₁₀H₁₄O⁺, 38], 133 (8) [1⁺- SH], 91 (24) [C₇H₇⁺]. - Anal. for C₁₈H₂₆O₅S (354.5): calcd C 60.99, H 7.39, S 9.05; found C 60.80, H 7.27, S 9.03.

3'-Methyl-4'-phenylspiro[adamantane-2,2'-(1,3)-thiazolidine] (39). The *N*-benzylidenemethylamine must be free of benzaldehyde, because the latter reacts much faster with **5**. The aldimine was kept over KOH pellets in THF solution containing an excess of methylamine for several days, then distilled over a 30 cm column under argon, and immediately used. **4** (2 mmol) in 5 ml of *N*-benzylidenemethylamine was heated to 40°C for 8 h. After distilling the excess of dipolarophile *in vacuo*, the NMR analysis (δ 4.68) revealed 13% of **39**. PLC afforded a fraction which crystallized from ethanol: 43 mg (7%) of **39**, mp 97-99. - ¹H NMR: δ 1.3 - 2.6 (m, 14 H), superimposed by 1.93 (s, NCH₃), 2.95 - 3.40 (m, AB of ABX, 5'-H₂), 4.68 (dd, *J*_{4',5'A} = 10.4 Hz, *J*_{4',5'B} = 6.6 Hz, 4'-H). - Anal. for C₁₉H₂₅NS (299.5): calcd C 76.20, H 8.42, N 4.68, S 10.71; found: C 76.55, H 8.16, N 4.41, S 10.69.

3'-Phenylspiro[adamantane-2,2'-(1,3)-thiazolidine]-4'-one (40): (a) 2.00 mmol of **4** and 10 ml of freshly distilled *phenyl isocyanate*, magnetically stirred, were warmed to 40°C for 8 h (96% N₂). The excess of dipolarophile was distilled at 0.1 torr (40°C-bath). **14** could not be obtained pure. - IR (film): $\tilde{\nu}$ 1690 cm⁻¹ st br (C=O or C=N). - ¹H NMR: δ 3.77 (s, 5'-H₂), smaller s at 3.61, 4.90 are unexplained. - MS (40°C); *m/z* (%): 299 (19) [M⁺; ¹³C 3.8/4.1; (³⁴S+¹³C₂) 1.2/1.4], 266 (13) [no S, M⁺- SH; ¹³C 2.5/2.5], 225 (26), 180 (32) [C₁₁H₁₆S⁺, 25], 176 (33), 151 (82) [C₁₀H₁₅O⁺], 150 (100) [C₁₀H₁₄O⁺, 38], 167 (11), 166 (9), 133 (11), 104 (21), 93 (41) [C₆H₅NH₂⁺], 91 (37) [C₇H₇⁺].

(b) When 150 mg of the crude product was dissolved in 2 ml of ethanol, 130 mg precipitated in 5 min and was recrystallized from ethanol: 93 mg (54%), mp 157-159°C. - IR (KBr): $\tilde{\nu}$ 1727 cm⁻¹ st br (C=O), 3345 w (N-H). - ¹H NMR: δ 1.17 (t, *J* = 7.0 Hz, CH₃), 1.4 - 2.4 (m, 14 H), 3.32 (s, SCH₂), 3.55 (q, *J* = 7.0 Hz, CH₂ of ethoxy), 6.9 - 7.6 (m, C₆H₅). - MS (120°C); *m/z* (%): 345 (0.2) [M⁺], 299 (2) [M⁺- C₂H₅OH], 179 (100) [no ³⁴S peak, C₁₂H₁₉O⁺; ¹³C 13/15], 151 (27) [C₁₀H₁₅O⁺], 150 (8) [C₁₀H₁₄O⁺, 38], 93 (9) [C₆H₅NH₂⁺], 91 (8) [C₇H₇⁺], 79 (8), 77 (6) [C₆H₅⁺]. - Anal. for C₂₀H₂₇NO₂S (345.5): calcd C 69.52, H 7.88, N 4.05, S 9.28; found: C 69.31, H 7.80, N 3.94, S 9.32. In accordance with the structure of an acetal, the specimen was converted to adamantanone 2,4-dinitrophenylhydrazone, mp 214-217°C (ethanol), mixed m.p. with authentic material.

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This paper is dedicated to Professor *Wilhelm Bartmann*, Hoechst A.G., Frankfurt, on the occasion of his 70th birthday.

- 1,3-Dipolar Cycloadditions, 113; Part 112, see ref. 6.
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