1,3-Dipolar Cycloadditions, 117[‡]

Reactions of Thiobenzophenone *S*-Methylide with Thiocarbonyl Compounds

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Dedicated to Professor M. V. George, Regional Research Laboratory, Trivandrum (CSIR), India, on the occasion of his 70th birthday

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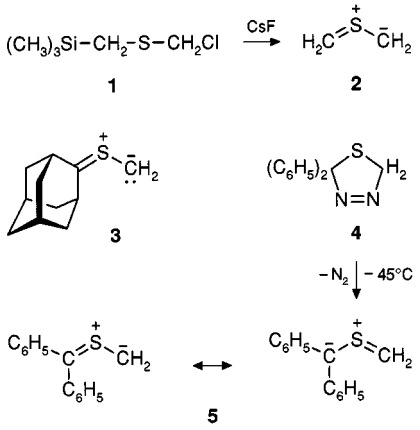
2,5-Dihydro-2,2-diphenyl-1,3,4-thiadiazole (**4**) eliminates N_2 at –45 °C and generates thiobenzophenone *S*-methylide (**5**), which is intercepted by dipolarophiles. The 1,3-cycloadditions of **5** with thiones (aromatic and aliphatic thioketones, dithioesters, trithiocarbonate) furnish 1,3-dithiolanes **7**, in which the substituents, even voluminous ones, appear in the proximal 4- and 5-positions. The reaction of **5** with adamantanethione furnishes **7h** and 4,4,5,5-tetraphenyl-1,3-dithiolane (**7a**) in a ratio of 4:1; a methylene transfer is involved, and the mechanistic pathways are discussed. The cycloadduct **7f** originating from **5** and diphenyl trithiocarbonate undergoes an isomerization which consists of ionization and ring-opening leading to a ketene dithioacetal structure.

Introduction

Thiocarbonyl ylides are active 1,3-dipoles in cycloadditions.[1] A general synthesis consists of the thermal elimination of N_2 from 2,5-dihydro-1,3,4-thiadiazoles, which, in turn, are accessible by 1,3-cycloadditions of diazoalkanes to C=S double bonds. The availability of thiones constitutes a limit; thioaldehydes cannot be prepared in substance, except for sterically hindered types.[2] This gap is filled by the preparation of thiocarbonyl ylides from silylated precursors. Even thioformaldehyde *S*-methylide (**2**), the parent compound, has been synthesized from **1** and was intercepted by CC multiple bonds furnishing high yields of cycloadducts (Scheme 1).[3] 1-Trimethylsilylated thioformaldehyde *S*-methylides are likewise available.[4]

1,3,4-Thiadiazolines, prepared from *aliphatic* thioketones and diazomethane, can be isolated and have some storage capacity. The extrusion of N_2 is carried out in the presence of a dipolarophile at controlled temperature. Recently, we described 1,3-cycloadditions of adamantanethione *S*-methylide (**3**).[5,6]

The rapid addition of diazomethane to thiobenzophenone *at −78 °C* furnishes quantitatively the 2,5-dihydro-2,2-diphenyl-1,3,4-thiadiazole (**4**) which is conveniently handled in solution, as described in the preceding paper.[7] The reaction **4** → **5** + N_2 proceeds in THF at −45 °C with



Scheme 1

$t_{1/2}$ = 56 min; a small stationary concentration of thiobenzophenone *S*-methylide (**5**) allows an efficient in situ capturing by reaction partners.

When diazomethane is introduced into a solution of thiobenzophenone *at room temperature*, the thiadiazoline **4** rapidly expels N_2 and the intermediate **5** adds to a second molecule of thiobenzophenone providing 4,4,5,5-tetraphenyl-1,3-dithiolane (**7a**) ("Schönberg reaction").[7]

Formation of "Mixed" 1,3-Dithiolanes

Thiobenzophenone (**6a**) fulfils a double role in the mentioned formation of **7a**: The first molecule interacts as a dipolarophile vs. diazomethane, whereas the second molecule captures the *S*-ylide **5**. The separation of the two roles is the basis of a general and convenient preparation of 1,3-

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dithiolanes.[8] This synthesis elegantly supplements the classic reaction of 1,2-dithiols with carbonyl compounds, known since 1887;[9] an abundance of 2-substituted 1,3-dithiolanes originates from the protection of carbonyl groups by dithioacetal formation with 1,2-dithiols.[10]

The solution of **4** in THF, prepared at −78 °C, was mixed with the precooled solution of a second thiocarbonyl reactant **6** (usually 1.2 equiv) and kept in a cold bath at about −45 °C, until the N_2 evolution ceased. The crystalline 1,3-dithiolanes, obtained from **5** and various thiocarbonyl compounds are listed in Table 1; aromatic thioketones provided high yields of cycloadducts. The procedure was adapted to other diarylthioketone *S*-methylides, which are analogously amenable from the thioketones and diazomethane *via* the 2,5-dihydro-1,3,4-thiadiazoles (Table 2, Scheme 2).

Apart from the conversion of **7a** to tetraphenylethylene, the ^{13}C NMR parameters reveal the C_{2v} symmetry of **7a** and other "Schönberg products", which bear identical substituents in 4- and 5-positions.[7] The symmetry is reduced to a σ plane in 1,3-dithiolanes **7b**−**7i**, and C-4 and C-5 have different δ_C values. The ^{13}C triplets of C-2 appear in the narrow range of δ_C = 25.7−32.2 for **7a**−**7i**, whereas the singlets of C-4 and C-5 lie in the likewise close range of δ_C = 70.0−82.4. The δ_H singlet of 2-H_2 (AB for **11**) was found at δ = 3.27−4.26 (Table 1).

Matched pairs of *S*-methylide A + thione B and *S*-methylide B + thione A afforded one and the same dithiolane; that demands the formation of 4,5-disubstituted thiolanes **7** and excludes the 2,4-regioisomers **8**. E.g., the cycloaddition of **5** with 4,4′-dimethoxythiobenzo-

Table 1. 1,3-Dithiolanes prepared from thiobenzophenone *S*-methylide (**5**) and thiones in THF at −45 °C

Thione	Formula	Dithiolane Yield (%)	m.p. (°C)	NMR Parameters ($CDCl_3$) δ(C-2)	δ(C-4/C-5)	δ_H(2-H_2)
Thiobenzophenone	**7a**	95	202−203	30.1	77.6	3.74
4,4′−Dimethoxythiobenzophenone	**7b**	86	181−183	30.0	76.8, 77.4	3.63
Fluorene-9-thione	**7c**	82	> 236	31.0	74.1, 76.3	4.26
Xanthione	**7d**	84	165−167	31.8	70.0, 80.2	4.08
Thioxanthione	**7e**	95	149−151	30.5	78.5, 79.8	4.08
Methyl 1-dithionaphthoate	**11**	87	151−153	30.6	80.9, 82.4	3.25,3.81
Diphenyl trithiocarbonate	**7f**	47	150−152	31.4	81.3, 89.5	3.82
2-Thioxo-1,3-dithiolane-4,5-dione	**7g**	75	198−199	32.2	75.9, 79.8	3.88
Adamantanethione	**7h**	27	201−203	28.0	76.6, 77.5	3.28
	+**7a**	8	203−204			3.74
2,2,4,4-Tetramethyl-3-thioxo-cyclobutanone	**7i**	62	124−126	25.7	75.3, 78.5	3.34

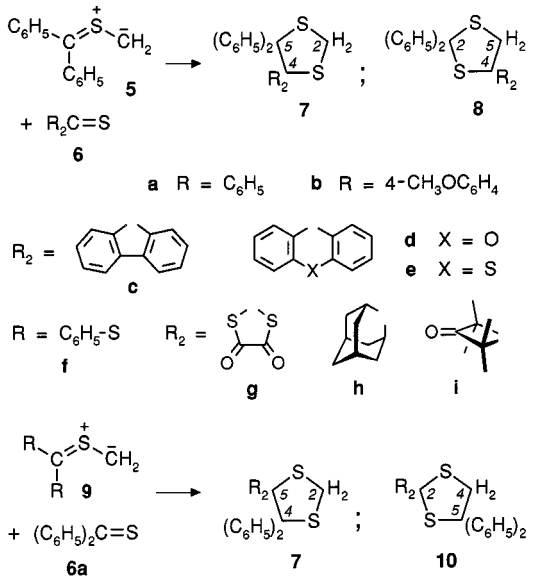
Table 2. 1,3-Dithiolanes from various thiocarbonyl ylides and thiobenzophenone in THF

Dipolarophilic thione	Formula	Dithiolane Yield (%)	m.p. (°C)
a. *4,4-Dimethoxythiobenzophenone S-methylide* (**9b**)			
Thiobenzophenone	**7b**	95	180−182
4,4′-Dimethoxythiobenzophenone[7]		98	161−162
b. *Fluorene-9-thione S-methylide* (**9c**)			
Thiobenzophenone	**7c**	86	> 232
Fluorene-9-thione[7]		94	259−262
c. *Thioxanthione S-methylide* (**9e**)			
Thiobenzophenone	**7e**	67	149−151
Thioxanthione[12]			168−170
e. *Adamantanethione S-methylide* (**9h**)			
Thiobenzophenone[7]	**7h**	50	197−199
	+**10h**	42	126−128
f. *2,2,4,4-Tetramethyl-3-thioxocyclobutanone S-methylide* (**9i**)			
Thiobenzophenone[15]	**7i**	68	122−125
	+**10i**	20	not isol.
	+**10a**	9	202−203

The regiochemistry of the cycloaddition deserves attention insofar as only the 4,4,5,5-tetrasubstituted 1,3-dithiolanes **7** were observed. Thus, the reactants combine in the sterically hard way by bond formation between the centers bearing the voluminous substituents. Apparently, other effects are controlling. According to Aono, Terao, and Achiwa, HO(**5**) − LU(**6a**) is the dominant interaction in the concerted addition, and the atomic orbital coefficients calculated by MNDO appear to favor the formation of **7a** over **8a**.[11]

phenone (**6b**) gave rise to **7b** (86% isolated), whereas the interaction of 4,4′-dimethoxythiobenzophenone *S*-methylide (**9b**) with thione **6a** produced the same **7b** in 98% yield (Table 2).

What are the limits in the choice of the thiocarbonyl compound in the role of the dipolarophile? Despite the dithioester resonance, methyl 1-dithionaphthoate accepted the *S*-methylide **5** to give 87% of **11**, which is lacking symmetry; the ^{13}C NMR parameters reveal diastereotopicity of the phenyl groups. However, *O*-methyl thiobenzoate, thio-



Scheme 2

benzamide, *O*-ethyl thiocarbamate, and phenyl isothiocyanate failed to react with **5**.

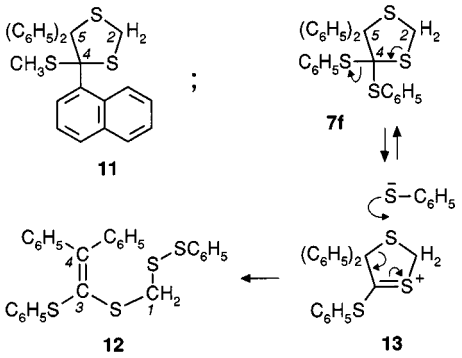
Diphenyl trithiocarbonate (**6f**) provided dithiolane **7f** in 47% yield. Besides the symmetry shown by the NMR parameters, the hydrogenolysis with Raney nickel in methanol furnished 1,1-diphenylethane in accordance with structure **7f**. 2-Thioxo-1,3-dithiolane-4,5-dione (**6g**) is a cyclic trithiocarbonate and an active dipolarophile vs. **5**; the somewhat odd choice stems from the fact that Schönberg et al. reacted it with diazoalkanes.[12]

Many of the dithiolanes turn blue on melting, suggesting some thiobenzophenone as dissociation product. The instability of dithiolane **7f** in solution has another reason. In acid-free $CDCl_3$ at room temp., cycloadduct **7f**, $\delta(2\text{-}H_2)$ = 3.82, slowly isomerized to a compound with $\delta(CH_2)$ = 3.99; the conversion reached 5% in 24 h, but was catalyzed by a trace of trifluoroacetic acid. The viscous oily product gave correct analytical data for an isomer of **7f**. The methylene protons remain equivalent, indicating a σ plane.

We first suspected a rearrangement of **7f** to **8f** by dissociation and recombination, but attempts of capturing the intermediate **5** by more active dipolarophiles failed. For both **7f** and **8f**, two pairs of equivalent phenyl groups are expected. The ^{13}C NMR spectra confirm the pairwise equivalence for **7f**. However, the new isomer shows four nonequivalent phenyls, i.e., eight signals for *o*- and *m*-CH, and four for *p*-CH. Five signals appear in the δ region of quaternary sp^2-hybridized C-atoms; at least one must be olefinic .

Structure **12** (Scheme 3) fits the spectroscopic properties. The C_q at highest frequency (δ = 153.8) could well be the C-3 of the ketene dithioacetal group, and the CH_2 group between sulfur functions appears at higher frequency (δ = 42.2) than in the 5-membered ring of **7f** (δ = 31.4). Whereas many ^1H and ^{13}C signals of **7f** are broadened, due to the hindered ring inversion (see below), the NMR absorptions of the open-chain compound **12** are sharp and well-defined.

The mass spectra of **7f** and **12** are similar; partial thermal isomerization (120−160 °C) of **7f** preceding ionization is

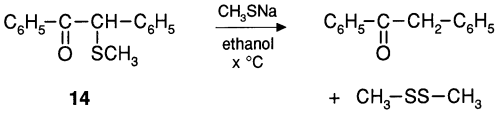


Scheme 3

probable. In both the MS, *m*/*z* 210 is the base peak, and $(C_6H_5)_2C{=}C{=}S^+$ is a likely candidate. For the ($^{34}S+^{13}C_2$) isotope peak (*m*/*z* 212), 5.6% is expected; only in the case of **7f**, the intensity of *m*/*z* 212 is by 18% greater, pointing to a second fragment $C_{14}H_{10}S^+$. The latter was found in the MS of most cycloadducts of **5** and is attributed to the radical cation of **5** (see below). The peaks *m*/*z* 110 ($C_6H_5SH^+$) and 109 ($C_6H_5S^+$) are highly populated in the MS of both **7f** and **12**.

Not only by acid catalysis, also by adsorption on silica gel the isomerization **7f** → **12** is accelerated. On the other hand, **7f** is stable in C_6D_6 at room temperature. These data point to an ionization process, **7f** → **13**. The subsequent attack of the thiophenolate on the resonance-stabilized dithiolanium cation is a ring-opening process.

The heterolysis of a C−S bond by substitution with thiolate at sulfur is unusual, but there are precedents. The acid-catalyzed reduction of acyloins to ketones by 1,3-propanedithiol, described by Cram and Cordon in 1955,[13] involves such a step with RSH as nucleophilic reagent. Methanethiolate is the reducing agent in the conversion of **14** to deoxybenzoin and dimethyl disulfide, according to Oki et al. (Scheme 4).[14]

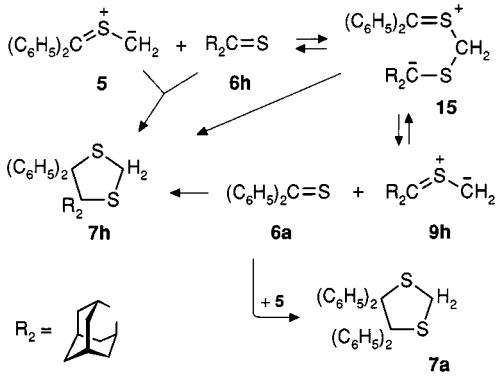


Scheme 4

Adamantanethione (**6h**) and 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**6i**) represent aliphatic thioketones in Table 1; both are sterically hindered. Nevertheless, both reacted with **5** furnishing the 4,5-disubstituted dithiolanes **7h** and **7i**, albeit in lower yield.

Some side reactions are noteworthy. The formation of 8% of 4,4,5,5-tetraphenyl-1,3-dithiolane (**7a**) besides 27% of **7h** in the reaction of adamantanethione (**6h**) with **5** has mechanistic implications. It is conceivable that a thiophilic attack of the 1,3-dipole **5** on **6h** gives rise to a zwitterionic intermediate **15**; the species can also be formulated as a diradical (Scheme 5). **15** could mediate a methylene transfer equilibrium, **5** + **6h** ⇄ **6a** + **9h**. Since **6a** is more reactive than **6h**,

it will capture **5** with preference. Thus, **7a** is formed besides the mixed dithiolane **7h**.



Scheme 5

Is the cyclization of type **15** intermediates the normal pathway to 1,3-dithiolanes? In the reactions of **5** with diarylthioketones **6b**−**6g** (Table 1), the formation of **7a** has not been observed. We favor a *concerted* mechanism as long as strong steric hindrance does not give the twostep pathway via **15** a chance. The formula scheme above records the concerted *and* stepwise paths giving **7h**. Calculations of the transition states for the concerted and twostep pathway would be highly desirable.

The C=S bond of 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**6i**) is screened by four methyl groups. The hindered interaction with **5** led to 62% of **7i**, and the regioisomer **8i** was not found.

When the *S*-ylide **5** is not intercepted, its dimer, the 2,2,3,3-tetraphenyl-1,4-dithiane, is usually formed in high yield.[7] In the reaction with **6h**, the dithiolane yields, 27% of **7h** and 8% of **7a**, account for 43% of the employed **5**, and 62% of **5** was consumed in the formation of **7i** from **6i**. In both reactions no dithiane, but substantial amounts of *benzophenone* were observed among the products.

The idea is not far-fetched that these cycloadditions of **5** could also furnish the sterically less hindered dithiolanes **8h** and **8i** besides **7h** and **7i**. A hydrolysis of the 2,2-diphenyl-1,3-dithiolanes **8** to give benzophenone during product separation by chromatography on silica gel would be conceivable. Furthermore, the hydrolysis of an *unknown intermediate* (e.g., **15** on the path to **7**) by traces of water during the interaction with **5** would constitute another possible source of benzophenone.

Recently we described that adamantanethione *S*-methylide (**3**), combined with thiobenzophenone affording 50% of **7h** and 42% of the regioisomer **10h**; the structure of the latter was confirmed by X-ray analysis.[6] It is worth mentioning that **8h** and **10h** *cannot be formed* via a type **15** intermediate. Similarly, the product of 2,2,4,4-tetramethyl-3-thioxocyclobutanone *S*-methylide (**9i**) with thiobenzophenone contained 68% of **7i** and 20% of **10i**; in addition, 9% of the tetraphenyl-1,3-dithiolane (**7a**) was formed.[15]

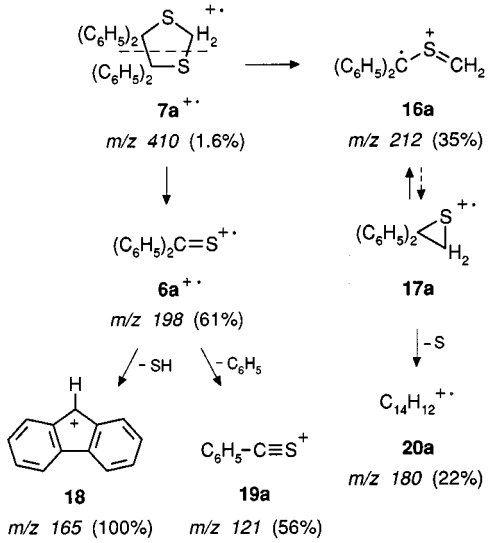
It is noteworthy that the cycloadditions of *S*-methylides **9h** and **9i** with thiones **6h** and **6i** afforded *only* the 2,4-substituted 1,3-dithiolanes;[16] here, finally, the steric interaction appears to surpass the electronic preference.

The cyclohexane-like chair conformations of 1,4-dithianes are located in pronounced energy troughs,[7] whereas the pseudorotation circuit of the 5-membered 1,3-dithiolanes usually involves small barriers to ring inversion. However, the NMR signals of 1,3-dithiolanes, which contain voluminous groups in 4- and 5-position, show a distinct broadening which can be ascribed to dynamic processes at room temperature.

The tetraphenyl compound **7a** was chosen as an example. The ^{13}C NMR spectrum (100 MHz, $CDCl_3$) reveals at −44 °C two sets of phenyl groups, each consisting of four sharp signals, one corresponding to *pseudo-axial* and the other to *pseudo-equatorial* pairs of phenyl groups in a frozen 1,3-dithiolane conformation; the C−C_6H_5 rotation must still be rapid. A pseudorotation barrier for the heteroring, $\Delta G^{\neq} = 13.0 \pm 0.2$ kcal mol^{-1}, was evaluated from coalescence data of the *ortho*-C (T_C = 0 °C) and the *quaternary* phenyl−C (T_C = +15 °C). The same barrier height resulted from the temperature dependence of the ^1H NMR spectrum (400 MHz, $Cl_2CD-CDCl_2$). The doublet of the eight *o*-H at 45 °C (δ = 7.31) coalesces at 1 °C and splits into two 4H-doublets at −44 °C (δ = 7.20, 7.43).

The Mass Spectra of the 1,3-Dithiolanes

Some general features will be discussed using C_{2v}-symmetric dithiolane **7a** as an example. The stepwise degradations sketched out are formal, and the same reserve concerns the structures of the fragments. Very often, *molecular formulae* were confirmed by the intensities of isotope peaks for ^{13}C and ($^{34}S+^{13}C_2$), and sometimes by high resolution; however, the *structures* proposed are not more than a kind of bookkeeping on the basis of smallest structural changes (Scheme 6).



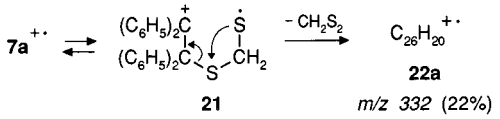
Scheme 6

The major splitting pathway of the radical cation **7a**$^+$ is the 1,3-cycloreversion rendering back thiocarbonyl ylide and thione. Each of the two fragments can accommodate the radical cation character suggesting that the ionization

potentials of the neutral species are not grossly different. The radical cation of **5**, present in the MS of nearly all dithiolanes of type **7**, appears in **7a** with a peak intensity of 35%. We favor a description as *distonic* radical ion **16a** in which charge and spin density have different centers.[17] Perhaps **16a** occurs in an equilibrium with the thiirane radical cation **17a**. Species **17a** is a likely candidate for the loss of sulfur, and the peak *m/z 180* (22%) corresponds to $C_{14}H_{12}^{+}$ and could be the radical cation of 1,1-diphenylethylene, methylfluorene, or 9,10-dihydrophenanthrene, etc.; the condensed systems would explain the appearance of a cascade with *m/z 179* (18%) and *178* (20%). It is worth mentioning, that the bonded groups $(C_6H_5)_2C$ and CH_2 of **20a** were separated by sulfur in the dithiolane; they become connected by the electrocyclic ring closure, **16a** → **17a**.

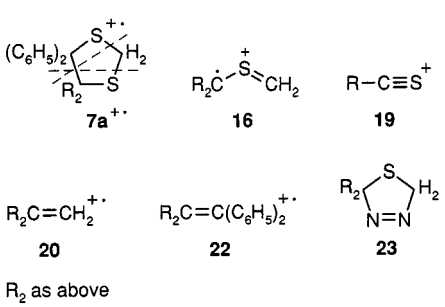
Thiobenzophenone, i.e., the second fragment of $\mathbf{7a}^{+}$, also appeared as radical cation ($\mathbf{6a}^{+}$), *m/z 198* (61%), and was confirmed by the intensities of isotope peaks. Fragments $[M^{+} - SH]$ are generally found in the MS of aliphatic and aromatic thioketones.[18] Here, as in the MS of thiobenzophenone itself, $C_{13}H_9^{+}$ is the base peak and was identified with the 9-fluorenyl cation (**18**) by Schumann et al. in 1969.[19] The cation **18** and the thiobenzoyl cation **19a** (*m/z 121*) are kind of leading fossils in the MS reported here .

The fragment *m/z 332*, free of sulfur, is $C_{26}H_{20}^{+}$ and complies with $[M^{+} - CH_2S_2]$. More probable than a onestep elimination of CH_2S_2 is a ring opening to give **21**, and an intramolecular radical substitution. Formally, **22a** could be the radical cation of tetraphenylethylene, but nonolefinic isomers are also conceivable (Scheme 7).



Scheme 7

Matched pairs of [3+2] cycloadditions afford the same 1,3-dithiolanes **7**. In concordance, two cycloreversion routes of $\mathbf{7}^{+}$ are open and provide double the manifold of fragments which were so far discussed. E.g., in the MS of **7b** (two 4-methoxyphenyl groups in 4 position), the distonic ions **16b** (*m/z 272*, 14%) and **16a** (*m/z 212*, 15%) are found, and so are the thione radical cations **6b** (*m/z 258*, 19%) and **6a** (*m/z 198,* 47%). The fluorenyl cation **18** (*m/z 165,* 100%) dominates over its dimethoxy derivative (*m/z 225*, 16%), and the thioacylium ions **19b** (*m/z 151*, 16%) and **19a** (*m/z 121*, 53%) appear side by side (Scheme 8). Since the population of a MS peak depends on the rate ratio of formation and breakdown of a fragment, the conclusion from peak intensities on major or minor degradation paths is often fallacious.



Scheme 8

Experimental Section

General:[7] CC is column chromatography on silica gel.

4,4,5,5-Tetraphenyl-1,3-dithiolane (7a).[7] **– (a):** ^{1}H NMR (400 MHz, 25 °C): δ = 3.74 (s, 2-H_2), 7.05 (nearly tt, 8 *m*-H), 7.12 (tt, $J \approx 7.2$, 1.2 Hz, 4 *p*-H), 7.34 (d, $J = 6.4$ Hz, 8 *o*-H, broad, approaching coalescence). – ^{13}C (100 MHz, DEPT, 25 °C): δ = 30.1 (C-2), 77.6 (C-4/5), 126.3, 126.5, 131.7 (the latter broadened, 2:1:2 for arom. *m*/*p*/*o*-CH), 143.2 (very broad, 4 arom. C_q); much less line broadening in the 20 MHz spectrum. – MS (70 eV, 110 °C); *m/z* (%): 410 (1.6) [M^{+}; ^{13}C 0.47/0.50, (^{34}S+$^{13}C_2$) 0.21/0.19], 332 (18) [$M^{+} - CH_2S_2$, $C_{26}H_{20}^{+}$, **22a**; ^{13}C 5.3/5.2, no ^{34}S peak], 255 (2.5) [$C_{20}H_{15}^{+}$, 332 – C_6H_5), 254 (3.2), 253 (5.9), 252 (5.5), 212 (35) [$C_{14}H_{12}S^{+}$, **16a**], 211 (28) [212^{+} – H], 198 (61) [$C_{13}H_{10}S^{+}$, $(C_6H_5)_2C{=}S^{+}$; ^{13}C 8.8/9.2, (^{34}S+$^{13}C_2$) 3.3/3.3], 197 (21), 180 (22) [$C_{14}H_{12}^{+}$, **20a**], 179 (18) [$C_{14}H_{11}^{+}$], 178 (20), 167 (19) [$(C_6H_5)_2CH^{+}$], 166 (6), 165 (100) [fluorenyl^{+}, **18**; ^{13}C 15/16], 152 (10) [$C_{12}H_8^{+}$, biphenylene], 121 (56) [$C_6H_5{-}C{\equiv}S^{+}$; ^{13}C 4.3/4.8; (^{34}S+$^{13}C_2$) 2.6/2.7], 77 (17) [$C_6H_5^{+}$]. – **(b) ^{1}H NMR Evidence for Dynamic Process:** The 400 MHz spectrum at 40 °C in $Cl_2CD{-}CDCl_2$ shows the 8 arom. *o*-H as a slightly broadened d at δ = 7.31. On cooling, the signal reaches coalescence at +1 °C and splits into two d at lower temp.; at −44 °C they are still somewhat broad, δ = 7.20 and 7.43, $^3J = 6.8$ Hz. The low-frequency branch partially overlaps with the t of the 4 *p*-H at δ = 7.11. The Δν of the two d for the 2 × 4 *o*-H shows only a small temp. dependence and allows an extrapolation to Δν = 89 Hz at T_C +1 °C. From $k = 198\ s^{-1}$, $\Delta G_C^{\neq} = 13.1$ kcal mol^{-1} at +1 °C is calculated. The s of 2-H_2 at δ = 3.74 reveals at −44 °C a slight broadening; due to the presence of a *quasi*-C_2 axis, no splitting is expected. – **(c) ^{13}C DNMR:** A HETCOR experiment connected ^{1}H and ^{13}C chemical shifts and confirmed the assignments. The 100 MHz spectrum ($CDCl_3$) displays at −44 °C a double set of phenyl signals for *pseudo-e* and *pseudo-a* positions: δ = 125.73, 126.83 (2 × 4 *m*-C), 126.20, 126.72 (2 × 2 *p*-C), 130.75, 132.01 (2 × 4 *o*-C). On raising the temp., the signals of *p*-C and *m*-C merge, thwarting an evaluation. The two *o*-C signals coalesce at 0 °C, and those of C_q at 15 °C. The temp. dependence of $\nu(^{13}C)$ allows a linear extrapolation of Δν to T_C: 127 Hz for *o*-C and 395 Hz for C_q. *k* values of 283 s^{-1} at 0 °C and 877 at 15 °C lead to $\Delta G^{\neq} = 12.9$ and 13.0 kcal mol^{-1}, respectively.

4,4-Bis(4-methoxyphenyl)-5,5-diphenyl-1,3-dithiolane (7b). – (a): Thiobenzophenone (**6a**, 665 mg, 3.35 mmol) in 5 mL of THF, cooled to −78 °C, was reacted with 1.0 equiv. of diazomethane in about 5 mL of THF, precooled to −78 °C, until the dark-blue color turned light-blue (see ref.[7]). *4,4′-Dimethoxythiobenzophenone* (**6b**, 1.14 g, 4.42 mmol) in 8 mL of THF at −78 °C was mixed with the above solution of **5** and kept in a −40 °C bath (thermostated) for 3 h and at −20 °C for 1 h. After the solution reached room temp., the solvent was removed at the rotary evaporator, and the residue crystallized from ether/pentane; 1.35 g (86%) of **7b** was obtained, m.p. 181−183 °C (blue melt) after recrystallization. – ^{1}H NMR: δ = 3.63 (s, 2-H_2), 3.70 (s, 2 OCH_3), 6.43−6.72 (m, 4 arom. H), 6.90−7.47 (m, 14 arom. H). – ^{13}C NMR (20.2 MHz, H-decoupled and off-resonance): Table 1; further absorptions: δ = 55.1 (q, 2 OCH_3), 111.5 (d, C-3′/5′ of 2 *p*-methoxyphenyl), 126.4, 131.6, 132.8 (3 d, 14 arom. CH), 134.8, 143.5 (2 s, C-1′ of 4 aryl), 157.9

(s, C-4′ of 2 *p*-methoxyphenyl). − MS (120 °C); *m/z* (%): 470 (1.5) [M^+], 392 (63) [$C_{28}H_{24}O_2^+$, $M^+ - CH_2S_2$, **22b**; ^{13}C 20/19, $^{13}C_2$ 3.2/3.0, no S], 272 (14) [$C_{16}H_{16}O_2S^+$, **16b**], 258 (19) [$C_{16}H_{16}O_2S^+$, **6b**$^+$; ^{13}C 3.2/3.7, ($^{34}S+^{13}C_2$) 1.1/1.4], 241 (10), 240 (12) [$C_{16}H_{16}O_2^+$, **20b**], 225 (16) [**6b**$^+$ − SH, 3,6-dimethoxyfluorenyl$^+$], 212 (15) [$C_{14}H_{12}S^+$, **16a**], 211 (14) [$C_{14}H_{11}S^+$], 198 (47) [**6a**$^+$; ^{13}C 6.8/7.1], 180 (82) [$C_{14}H_{12}^+$, **20a**, ^{13}C 13/15], 165 (100) [9-fluorenyl$^+$, **18**], 151 (16) [$C_8H_7OS^+$, **19b**], 121 (53) [$C_7H_5S^+$, **19a**; ^{13}C 4.1/4.7, ($^{34}S+^{13}C_2$) 2.5/2.6], 105 (42) [$C_8H_9^+$, no ^{34}S peak], 77 (62) [$C_6H_5^+$]. − $C_{29}H_{26}O_2S_2$ (470.6): calcd. C 74.01, H 5.57, S 13.63; found C 73.90, H 5.54, S 13.65. − **(b):** *4,4′-Dimethoxythiobenzophenone* (**9b**, 816 mg, 3.16 mmol) in 10 mL THF was reacted with 1 equiv. of diazomethane in ≈ 5 mL THF affording a solution of the thiadiazoline **23b**[7] (−78 °C, 8 h). After mixing with 805 mg (4.06 mmol) of **6a** in 5 mL of THF, the N_2 evolution took place within 5 h at −45 °C. Workup as above and trituration with ether gave 1.42 g (95%) of **7b** in two fractions. Recrystallized from $CHCl_3$/diethyl ether, the m.p. 180−182 °C; mixed m.p., and the NMR spectra confirmed the identity.

5′5′-Diphenylspiro[fluorene-9,4′-[1,3]dithiolane] (7c). − (a): The solution of 3.02 mmol of thiadiazoline **4** in THF at −78 °C was mixed with the THF solution of 4.17 mmol of *9-fluorenethione* (**6c**)[20] and kept for 5 h at −45 °C. 1.011 g (82%) of **7c**, m.p. 230−233 °C (dec.) was isolated. Recrystallization from benzene gave colorless needles with m.p. > 236 °C (blue black). − ^1H NMR: Table 1; δ = 6.8−7.8 (m, 18 arom. H). − ^{13}C NMR: Table 1; δ = 120.0, 126.3, 2 × 126.8, 127.4, 128.2, 130.5 (7 d, 18 arom. CH), 139.5, 144.2, 144.9 (3 s, 6 arom. C_q). − MS (120 °C); *m/z* (%): 408 (25) [M^+], 362 (2) [$M^+ - CH_2S$], 330 (100) [$C_{26}H_{18}^+$, $M^+ - CH_2S_2$, **22c**; ^{13}C 29/26; $^{13}C_2$ 4.1/3.6, no S], 329 (40), 328 (13), 327 (16), 326 (16), 253 (37) [330 − C_6H_5, $C_{20}H_{13}^+$; ^{13}C 8.2/7.2, $^{13}C_2$ 0.9/0.7, no S], 252 (35) [$C_{20}H_{12}^+$], 212 (80) [$C_{14}H_{12}S^+$, **16a**; ^{13}C 12.4/13.8, ($^{34}S+^{13}C_2$) 4.5/4.2], 211 (53) [$C_{14}H_{11}S^+$], 210 (26) [$C_{14}H_{10}S^+$, **16c**$^+$], 198 (6) [**6a**$^+$], 196 (6) [**6c**$^+$], 178 (16), 165 (51) [**18**], 163 (11), 121 (6) [**19a**], 85 (61), 77 (2) [$C_6H_5^+$]. − $C_{27}H_{20}S_2$ (408.6): calcd. C 79.37, H 4.93, S 15.70; found C 79.64, H 4.87, S 15.65. − **(b):** The thiadiazoline **23c**[7] was prepared from 2.76 mmol of 9-fluorenethione (**6c**) and 1 equiv. of diazomethane in THF at −78 °C and reacted with 4.16 mmol of **6a** at −45 °C for 2 h. 971 mg (86%) of **7c** crystallized from $CHCl_3$/diethyl ether, m.p. > 232 °C (dec.). The ^1H and ^{13}C NMR spectra were identical with those of the above sample. − $C_{27}H_{20}S_2$ (408.6): found C 79.61, H 4.91, S 15.69.

5′5′-Diphenylspiro[xanthene-9,4′-[1,3]dithiolane] (7d):[21] **4** (10.0 mmol) was reacted with 2.12 g (10.0 mmol) of *xanthione* (**6d**) in THF at −45 °C; 3.57 g (84%) of **7d** was isolated, m.p. 160−164 °C (dec.). The analytical specimen (CH_2Cl_2) showed m.p. 165−167 °C (green melt). − ^1H NMR: (Table 1). − ^{13}C NMR: Table 1; δ = 115.8, 121.8, 126.7, 2 × 126.9, 128.9, 131.9 (7 d, 18 arom. CH), 123.4, 140.6, 152.5 (3 s, 6 arom. C_q). − MS (120 °C); *m/z* (%): 424 (2.2) [M^+], 346 (4.6) [$M^+ - CH_2S_2$, **22d**], 212 (69) [xanthione$^+$, $C_{13}H_8OS$, **6d**$^+$, or M^+ − xanthione, $C_{14}H_{12}S^+$, **16a**; ^{13}C 10 or 11/12; ($^{34}S+^{13}C_2$) 3.8 or 3.9/4.5], 198 (2) [**6a**$^+$], 180 (100) [$C_{14}H_{12}^+$, **20a**; ^{13}C 16/13], 179 (50) [$C_{14}H_{11}^+$], 178 (12), 168 (11), 165 (57) [**18**; ^{13}C 8.2/8.9], 152 (8) [$C_{12}H_8^+$, biphenylene$^+$], 89 (22), 77 (15) [$C_6H_5^+$]. − $C_{27}H_{20}OS_2$ (424.6): calcd. C 76.38, H 4.75, S 15.11; found C 76.25, H 4.99, S 15.01.

5′5′-Diphenylspiro[thioxanthene-9,4′-[1,3]dithiolane] (7e). − (a): Thiadiazoline **4** (3.02 mmol) and 753 mg (3.30 mmol) of *thioxanthione* (**6e**) in 20 mL of THF were magnetically stirred at −45 °C, whereby the crystalline **6e** slowly dissolved. After 5 h, the solvent was removed at room temp., and the residue triturated with ether: 1.02 g of **7e** as yellow crystals, m.p. 149−151 °C (dec.), were obtained. The mother liquor provided 292 mg of green solid, which contained 251 mg of **7e** (^1H NMR analysis with weight standard), bringing the total yield to 95%. Recrystallization from $CHCl_3$/ether furnished a light-yellow specimen, m.p. 149−151 °C (green black). − ^1H NMR: Table 1. − ^{13}C NMR: Table 1; δ = 125.3, 126.1, 126.3, 127.3, 127.6, 130.9, 132.9 (7 d, 18 arom. CH), 134.7, 135.8, 136.7 (3 s, 6 arom. C_q). − MS (120 °C); *m/z* (%): 440 (0.76) [M^+; ^{13}C 0.23/0.22, ($^{34}S+^{13}C_2$) 0.13/0.11], 362 (1.7) [$C_{26}H_{18}S^+$, $M^+ - CH_2S_2$, **22e**; ^{13}C 0.48/0.48, ($^{34}S+^{13}C_2$) 0.14/0.13], 228 (100) [$C_{13}H_8S_2^+$, **6e**$^+$; ($^{34}S+^{13}C_2$) 9.9/9.7], 227 (42), 212 (23) [$C_{14}H_{12}S^+$, **16a**], 211 (11) [$C_{14}H_{11}S^+$], 198 (10) [$C_{13}H_{10}S^+$, **6a**$^+$; ^{13}C 1.4/1.5, ($^{34}S+^{13}C_2$) 0.54/0.52], 197 (6) [$C_{13}H_9S^+$, thioxanthylium$^+$], 184 (25) [$C_{12}H_8S^+$, **6e**$^+$ − CS, dibenzothiophene; ^{13}C 3.4/3.6, ($^{34}S+^{13}C_2$) 1.3/1.3], 180 (39) [$C_{14}H_{12}^+$, **20a**; ^{13}C 6.2/6.7], 179 (30), 178 (26), 165 (44) [$C_{13}H_9^+$, **18**; ^{13}C 6.3/6.9], 152 (10) [$C_{12}H_8^+$, biphenylene$^+$], 121 (8) [**19a**], 105 (10) [$C_8H_9^+$], 77 (10) [$C_6H_5^+$]. − $C_{27}H_{20}S_3$ (440.6): calcd. C 73.59, H 4.58, S 21.83; found C 73.50, H 4.44, S 21.82. − **(b):** *Thioxanthion* (**6e**, 571 mg, 2.50 mmol) was stirred with 1.0 equiv. of diazomethane in 15 mL of THF at −78 °C for 5 h, until it had dissolved. **6a** (3.30 mmol) was added, and the mixture was kept at −55 °C for 5 h and at −20 °C overnight. Workup afforded 742 mg (67%) of **7e** as light-green prisms, m.p. 149−151 °C (dec); ^1H and ^{13}C spectra confirmed the structure. − $C_{27}H_{20}S_3$ (440.6): found C 73.54, H 4.51, S 21.84.

(c) 6e (4.88 mmol) and 1.2 equiv. of diazomethane in 18 mL of THF was stirred at −78 °C for 20 h, until the violet needles had dissolved and the colorless precipitate of **23e** appeared. The N_2 evolution at −20 °C required 3 h. 652 mg of a yellow powder was filtered; the ^1H NMR spectrum suggested a mixture of *spiro[thioxanthene-9,2′-thiirane]* (δ = 3.35, s, 3′-H_2) and *9-methylenethioxanthene* (δ = 5.48, s, CH_2). In a separate experiment, the rate of N_2 extrusion from *spiro[thioxanthene-9,2′-[1,3,4]thiadiazoline*] (**23e**) was measured by volumetry in THF at −44 °C: $k_1 = 1.23\ 10^{-4}$ s^{-1}, i.e., lower than that of **4** by a factor of 1.7.

4-Methylthio-4-(1-naphthyl)-5,5-diphenyl-1,3-dithiolane (11): **4** (3.32 mmol) and 4.09 mmol of *methyl 1-dithionaphthoate*[22] were mixed in 15 mL of THF at −78 °C. Workup after 5 h at −45 °C furnished 1.25 g (87%) of **11** as colorless crystals, m.p. 151−153 °C (reddish melt). − ^1H NMR: δ = 0.83 (s, SCH_3), 3.25, 3.81 (AB, J_{gem} = 9.3 Hz, 2-H_2), 6.9−8.4 (m, 17 arom. H). − ^{13}C NMR: δ = 17.3 (q, SCH_3), 30.6 (t, C-2), 80.9, 82.4 (2 s, C-4, C-5), 122.5, 124.6, 125.5, 126.1, 127.0, 127.8, 127.9, 128.6, 129.1, 129.5, 131.9, 132.7 (12 d, 17 arom. CH), 132.2, 133.8, 134.5, 141.5 (4 s, 5 arom. C_q). − MS (120 °C); *m/z* (%): 430 (0.7) [M^+], 353 (2.3), 352 (2.5) [$C_{25}H_{20}S^+$, $M^+ - CH_2S_2$], 218 (31) [$C_{12}H_{10}S_2^+$, methyl dithionaphthoate$^+$; ^{13}C 4.1/5.3, ($^{34}S+^{13}C_2$) 3.0/3.1], 212 (11) [$C_{14}H_{12}S^+$, **16a**], 180 (100) [$C_{14}H_{12}^+$, **20a**], 179 (83) [$C_{14}H_{11}^+$], 178 (57), 171 (76) [$C_{10}H_7-C{\equiv}S^+$], 165 (99) [9-fluorenyl$^+$, **18**; ^{13}C 14/15], 152 (20), [$C_{12}H_8^+$, biphenylene$^+$], 127 (20) [$C_{10}H_7^+$, naphthyl$^+$], 121 (5) [**19a**], 89 (40), 77 (32) [$C_6H_5^+$]. − $C_{26}H_{22}S_3$ (430.6): calcd. C 72.51, H 5.15, S 22.34; found C 72.71, H 5.33, S 22.28.

5,5-Diphenyl-4,4-bis(phenylthio)-1,3-dithiolane (7f). − (a): **4** (2.00 mmol) and 550 mg (2.10 mmol) of *diphenyl trithiocarbonate*[23] in 12 mL of THF were reacted for 6 h at −45 °C. In the workup, room temp. was not exceeded; after evaporation, the residue was dissolved in little of acid-free CH_2Cl_2. Careful addition of hexane gave 450 mg (47%) of **7f**, m.p. 150−152 °C. − ^1H NMR (400 MHz): δ = 3.82 (s, 2-H_2), br m 7.02−7.42 (16 arom. H), 7.76 (broadened s, due to beginning coalescence, 4 arom. CH); the 60 MHz spectrum shows dd at δ = 7.7−7.9 with $J \approx 6.5$ Hz as larger coupling, probably corresponding to 4 *o*-H. − ^{13}C NMR

(20.2 MHz): Table 1; δ = 126.9, 127.3, 128.0, 129.6, 131.5, 137.9 (6 d, 20 arom. CH), 132.9 (s, 2 C_q of SC_6H_5), 142.7 (br s, C_q of 2 C−C_6H_5); in the 100.6 MHz spectrum, the line broadening of the CH signals at δ = 126.9, 131.5, and 137.9 is strong; the C_q signals at 132.9 is hardly observable and that at 142.7 has disappeared in coalescence. − MS (160 °C); *m/z* (%): 474 (1.1) [M^+; ^{13}C 0.23/0.23], 396 (1.8) [$C_{26}H_{20}S_2^+$, $M^+ - CH_2S_2$, **22f**; ^{13}C 0.52/0.47, ($^{34}S+^{13}C_2$) 0.23/0.20], 365 (8.4) [$C_{21}H_{17}S_3^+$, $M^+ - SC_6H_5$; ^{13}C 1.9/2.4, ($^{34}S+^{13}C_2$) 1.3/1.3], 287 (11) [$C_{20}H_{14}S^+$, $(C_6H_5)_2C{=}C{=}SC_6H_5^+$; ^{13}C 2.4/3.1], 256 (8.2)[$C_{15}H_{12}S_2^+$, $M^+ - 2\ C_6H_5S$; ^{13}C 1.4/1.6, ($^{34}S+^{13}C_2$) 0.83/1.03], 255 (9), 254 (8), 253 (12), 218 (12) [$C_{12}H_{10}S_2^+$, diphenyl disulfide ?; ^{13}C 1.6/1.6, ($^{34}S+^{13}C_2$) 1.2/1.0], 212 (23) [$C_{14}H_{12}S_2^+$, **16a**; peak contains 5.6% ($^{34}S+^{13}C_2$) of *m/z* 210], 211 (32), 210 (100) [$C_{14}H_{10}S^+$, $(C_6H_5)_2C{=}C{=}S^+$], 209 (10), 208 (12), 198 (5) [**6a**$^+$], 178 (21), 165 (50) [$C_{13}H_9^+$, fluorenyl$^+$], 121 (7) [$C_7H_5S^+$, **19a**], 110 (42) [$C_6H_5SH^+$], 109 (19) [$C_6H_5S^+$], 77 (9) [$C_6H_5^+$]. − $C_{27}H_{22}S_4$ (474.7): calcd. C 68.31, H 4.67, S 27.02; found C 68.35, H 4.52, S 27.03. − **(b) Hydrogenolysis:** 300 mg of **7f** and 3 g of freshly prepared Raney nickel in 30 mL of methanol were stirred for 4 d at 45 ± 5 °C. Workup afforded 48 mg (42%) of *1,1-diphenylethane* as a colorless oil. − ^1H NMR: δ = 1.63 (d, *J* = 7.1 Hz, CH_3), 4.13 (q, 1-H), 7.23 (s, 2 C_6H_5).

[(1-Phenylthio-2,2-diphenylvinyl)thio]methyl Phenyl Disulfide (12). − (a): **7f** (400 mg, 0.84 mmol) was subjected to CC with CH_2Cl_2/petroleum ether (2:8) as mobile phase. The first fraction contained **6f**, which solidified at room temp. and was identified by its ^1H NMR spectrum. The second, major fraction, 320 mg (80%) of **12**, was isolated as a pale-yellow viscous, resin-like oil. The crude product turned yellow on exposure to air, but, after repeated CC, was nearly colorless and insensitive to air. − IR (neat): $\tilde{\nu}$ = 710 cm^{-1}, 755 st (arom. CH out-of-plane deform.), 1040, 1090, 1200 m; 1445, 1470 st; 1585 m (C=C). − ^1H NMR ($CDCl_3$, 400 MHz, $CDCl_3$): δ = 3.99 (s, CH_2), 7.17−7.39 (complex m of 18 arom. H), 7.51, 7.53 (2 dd, 2 arom. H); (C_6D_6): 3.81 (s, CH_2); arom. H: 6.89 (m, 2 H), 6.93−7.06 (m, 8 H), 7.13 (tt, 2 H), 7.29−7.31 (m, 4 H), 7.37−7.41 (m, 4 H). − ^{13}C NMR ($CDCl_3$, 100 MHz, DEPT): δ = 42.21 (CH_2), 126.51, 127.04, 127.68, 127.81 (4 arom. *p*-CH); 127.85, 128.02, 128.13, 128.86, 128.96, 129.22, 129.27, 129.63 (*m*- and *o*-CH of 4 different C_6H_5), 135.3, 136.9, 141.6, 142.1, 153.8 (5 signals for 2 olefinic and 4 arom. C_q). − MS (70 eV, 120 °C); *m/z* (%): 474 (0.6) [M^+; ^{13}C 0.19/0.18, ($^{34}S+^{13}C_2$) 0.14/0.11], 365 (1.6) [$M^+ - SC_6H_5$; ($^{34}S+^{13}C_2$) 0.25/0.33], 318 (10) [$C_{20}H_{14}S_2^+$, ^{13}C 2.3/2.9], 287 (7), 218 (18) [$C_{12}H_{10}S_2^+$, diphenyl disulfide$^+$; ^{13}C 2.3/2.5, ($^{34}S+^{13}C_2$) 1.5/1.5], 210 (100) [$C_{14}H_{10}S^+$, $(C_6H_5)_2C{=}C{=}S^+$], 208 (12) ($C_{14}H_8S^+$, probably biphenylenethioketene$^+$], 186 (17) [$C_6H_5SC_6H_5^+$; ^{13}C 2.2/2.4], 185 (10), 178 (22) [$C_{14}H_{10}^+$], 165 (41) [fluorenyl$^+$], 110 (78) [C_6H_5SH; ($^{34}S+^{13}C_2$) 3.6/3.5], 109 (34) [$C_6H_5S^+$], 77 (15) [$C_6H_5^+$]. − $C_{27}H_{22}S_4$ (474.7): calcd. C 68.31, H 4.67, S 27.02; found C 68.51, H 4.74, S 27.33. − **(b):** The ^1H NMR spectrum of the fresh solution of **7f** was free of **12**, but after 24 h at room temp. the conversion reached 4.5%; it was complete after several weeks. In a further experiment in $CDCl_3$, a trace of trifluoroacetic acid accelerated the conversion into **12**; after 4 h, the signal of **7f** at δ = 3.82 had disappeared, and **12** was quantitatively formed. The CH_2 signal of **12** at δ = 3.99 is much sharper than that of **7f** (hindered ring inversion).

5,5-Diphenyl-4,2′-spirobi[1,3-dithiolane]-4′,5′-dione (7g): **4** (3.11 mmol) and 547 mg (3.33 mmol) of *2-thioxo-1,3-dithiolane-4,5-dione* (**6g**)[24] interacted in THF at −45 °C; 874 mg (75%) of **7g** was isolated as light-yellow crystals, m.p. 198−199 °C (dec.). − IR (KBr): $\tilde{\nu}$ = 699 cm^{-1}, 720, 752 m (C_6H_5 out-of-plane deform.), 1026 br; 1446, 1497 m (arom. ring vibr.), 1690, 1706 st (C=O). − ^{13}C NMR: Table 1; δ = 127.8, 128.7, 129.5 (3 d, 10 arom. H), 128.3, 139 br (2 s, 2 arom. C_q), 185.9 (s, 2 C=O). − MS (130 °C); *m/z* (%): 376 (0.4) [M^+], 298 (1.5) [$M^+ - CH_2S_2$, **22g**], 288 (1.7) [$C_{15}H_{12}S_3^+$, $M^+ - S - 2\ CO$; ($^{34}S+^{13}C_2$) 0.25/0.22], 212 (76) [$C_{14}H_{12}S^+$, **16a**], 211 (56), 210 (100) [$C_{14}H_{10}S^+$, diphenylthioketene$^+$], 198 (1.2) [**6a**$^+$], 178 (20), 165 (61) [**18**], 164 (7) [**6g**$^+$], 121 (6) [**19a**], 89 (10), 77 (10) [$C_6H_5^+$]. − $C_{17}H_{12}O_2S_4$ (376.5): calcd. C 54.22, H 3.21, S 34.06; found C 54.13, H 3.12, S 34.82.

Reaction of 5 with Adamantanethione (6h): 6a (396 mg, 2.00 mmol; freshly purified by chromatography and recrystallization) in abs. THF was converted into **5** at −78 °C as usual. After addition of 4.00 mmol of **6h**,[25] the temp. was adjusted to −45 °C; the N_2 evolution was finished after 5 h. The solvent was removed at room temp., the residue treated with 5 mL of CCl_4, and again evaporated. ^1H NMR analysis in $CDCl_3$ with *sym*-tetrachloroethane as weight standard indicated 27% of **7h** (δ = 3.27) and 8% of **7a** (δ = 3.74). Separation was achieved by CC with petroleum ether and increasing amounts of CH_2Cl_2; the first fraction (220 mg) was trimeric **6h**, and the second fraction (260 mg) was recrystallized from methanol/CH_2Cl_2 giving 180 mg (22%) of *5′,5′-diphenylspiro[adamantane-2,4′-[1,3]dithiolane]* (**7h**), m.p. 201−203 °C [dec., 203−205 °C[6]]. The third fraction was treated with methanol, and 25 mg (6%) of **7a**, m.p. 203−205 °C, was obtained; **7h** and **7a** were identified by their NMR spectra. The oily last fraction, eluted by petroleum ether/CH_2Cl_2 7:3, contained benzophenone (TLC and IR comparison) and some unidentified side products.

2,2,4,4-Tetramethyl-5′,5′-diphenylspiro[cyclobutane-3,4′-[1,3]dithiolane]-1-one (7i): 2.00 mmol of **4** interacted with 328 mg (2.10 mmol) of *2,2,4,4-tetramethyl-3-thioxocyclobutanone* (**6i**)[26] in 15 mL of THF 4 h at −45 °C and overnight at −27 °C. After evaporation of the solvent, the ^1H NMR analysis with weight standard revealed 62% of **7i** (δ = 3.28), but no other dithiolane. Purification by CC (CH_2Cl_2/petroleum ether) gave 310 mg (42%) of **7i**, m.p. 124−126 °C after recrystallization from methanol. Benzophenone was found in the mother liquor. − ^1H NMR: δ = 1.37 (s, 2 CH_3), 1.67 (s, 2 CH_3), 3.34 (s, 2-H_2), 7.0−7.2 (m, 6 arom. H), 7.4−7.6 (m, 4 arom. H). − ^{13}C NMR ($CDCl_3$): δ = 25.47 (t, C-2′), 25.62, 25.75 (2 q, 4 CH_3), 68.1, 75.3, 78.5 (3 s, C-2/4, C-4′, C-5′), 126.8 (d, 2 arom. *p*-CH), 127.0, 130.6 (2 d, 4 *o*-CH, 4 *m*-CH), 144.0 (s, 2 arom. C_q), 220.1 (s, C=O). − MS (110 °C); *m/z* (%): 368 (1) [M^+], 322 (50) [$M^+ - CH_2S$, $C_{21}H_{22}OS^+$], 298 (100) [M^+ − dimethylketene, $C_{18}H_{18}S_2^+$], 262 (30) [$C_{20}H_{22}^+$], 247 (20) [$C_{19}H_{19}^+$], 237 (25), 220 (100) [$C_{17}H_{16}^+$, $(C_6H_5)_2C{=}C{=}C(CH_3)_2$?], 205 (25) [$C_{16}H_{13}^+$], 165 (10) [**18**], 91 (10) [$C_7H_7^+$]. − $C_{22}H_{24}OS_2$ (368.5): calcd. C 71.69, H 6.56, S 17.40; found C 71.92, H 6.40, S 17.42.

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