

1,3-Dipolar Cycloadditions, 117^[†]Reactions of Thiobenzophenone *S*-Methylide with Thiocarbonyl CompoundsRolf Huisgen,^{*,[a]} Xingya Li,^{[a][†]} Grzegorz Mloston,^{[a][†]} and Claudia Fulka^[a]*Dedicated to Professor M. V. George, Regional Research Laboratory, Trivandrum (CSIR), India, on the occasion of his 70th birthday***Keywords:** Thiocarbonyl ylides / Cycloadditions / 1,3-Dithiolanes / Sulfur heterocycles / Thioketones

2,5-Dihydro-2,2-diphenyl-1,3,4-thiadiazole (**4**) eliminates N₂ 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 adamant-

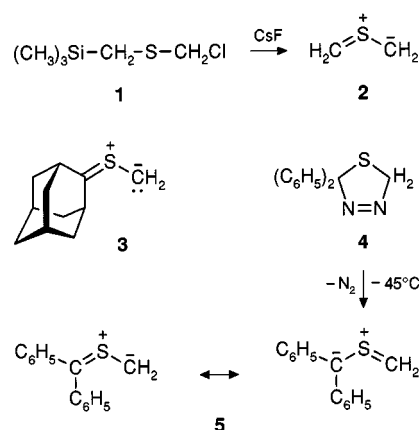
anethione furnishes **7h** and 4,4,5,5-tetraphenyl-1,3-dithiolane (**7a**) in a ratio of 4:1; a methylene transfer is involved, and the mechanistic pathways are discussed. The cycloadduct **7f** originating from **5** and diphenyl trithiocarbonate undergoes an isomerization which consists of ionization 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 N₂ 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 N₂ 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** + N₂ 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 N₂ 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-

[†] Part 116; Ref.[7]

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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 $-78\text{ }^{\circ}\text{C}$, was mixed with the precooled solution of a second thiocarbonyl reactant **6** (usually 1.2 equiv) and kept in a cold bath at about $-45\text{ }^{\circ}\text{C}$, 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 $\delta_{\text{C}} = 25.7\text{--}32.2$ for **7a–7i**, whereas the singlets of C-4 and C-5 lie in the likewise close range of $\delta_{\text{C}} = 70.0\text{--}82.4$. The δ_{H} singlet of 2- H_2 (AB for **11**) was found at $\delta = 3.27\text{--}4.26$ (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 $-45\text{ }^{\circ}\text{C}$

Thione	Formula	Dithiolane Yield (%)	m.p. ($^{\circ}\text{C}$)	NMR Parameters (CDCl_3)		
				$\delta(\text{C-2})$	$\delta(\text{C-4/C-5})$	$\delta_{\text{H}}(2\text{-H}_2)$
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

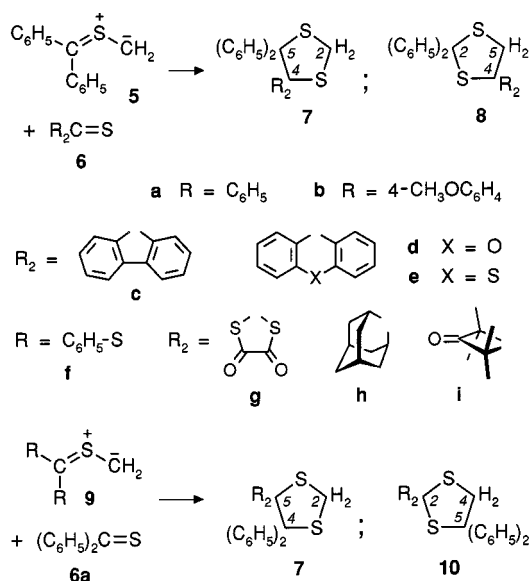
Table 2. 1,3-Dithiolanes from various thiocarbonyl ylides and thiobenzophenone in THF

Dipolarophilic thione	Formula	Dithiolane Yield (%)	m.p. ($^{\circ}\text{C}$)
a. 4,4'-Dimethoxythiobenzophenone <i>S</i> -methylide (9b)			
Thiobenzophenone	7b	95	180–182
4,4'-Dimethoxythiobenzophenone ^[7]		98	161–162
b. Fluorene-9-thione <i>S</i> -methylide (9c)			
Thiobenzophenone	7c	86	> 232
Fluorene-9-thione ^[7]		94	259–262
c. Thioxanthione <i>S</i> -methylide (9e)			
Thiobenzophenone	7e	67	149–151
Thioxanthione ^[12]			168–170
e. Adamantanethione <i>S</i> -methylide (9h)			
Thiobenzophenone ^[7]	7h	50	197–199
	+ 10h	42	126–128
f. 2,2,4,4-Tetramethyl-3-thioxocyclobutanone <i>S</i> -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, $\text{HO}(\mathbf{5}) - \text{LU}(\mathbf{6a})$ 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**.

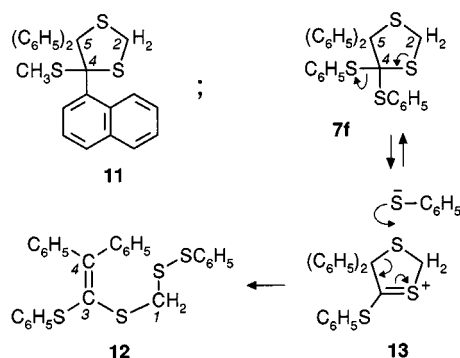
Diphenyl trithiocarbonate (**6f**) provided dithiolane **7f** in 47% yield. Besides the symmetry shown by the NMR parameters, the hydrogenolysis with Raney nickel in methanol furnished 1,1-diphenylethane in accordance with structure **7f**. 2-Thioxo-1,3-dithiolane-4,5-dione (**6g**) is a cyclic trithiocarbonate 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 $\delta(\text{CH}_2) = 3.99$; 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 ($\delta = 153.8$) could well be the C-3 of the ketene dithioacetal group, and the CH_2 group between sulfur functions appears at higher frequency ($\delta = 42.2$) than in the 5-membered ring of **7f** ($\delta = 31.4$). 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

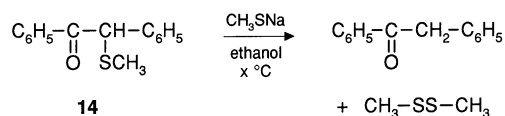


Scheme 3

probable. In both the MS, m/z 210 is the base peak, and $(\text{C}_6\text{H}_5)_2\text{C}=\text{C}=\text{S}^+$ is a likely candidate. For the ($^{34}\text{S}+^{13}\text{C}_2$) 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 $\text{C}_{14}\text{H}_{10}\text{S}^+$. 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 ($\text{C}_6\text{H}_5\text{SH}^+$) and 109 ($\text{C}_6\text{H}_5\text{S}^+$) 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]

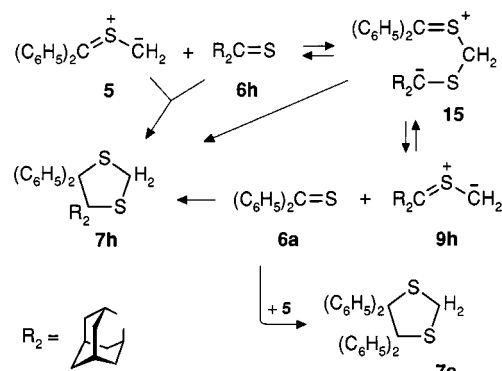


Scheme 4

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, $\text{5} + \text{6h} \rightleftharpoons \text{6a} + \text{9h}$. 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 diarylthio ketones **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]

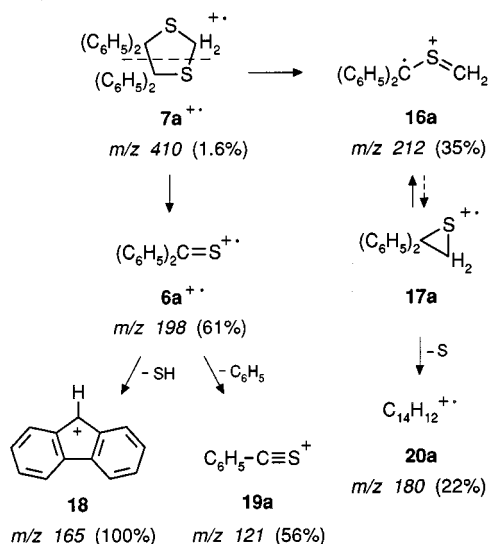
It is noteworthy that the cycloadditions of *S*-methylides **9h** and **9i** with thiones **6h** and **6i** afforded *only* the 2,4-substituted 1,3-dithiolanes,^[16] here, finally, the steric interaction appears to surpass the electronic preference.

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 ¹³C NMR spectrum (100 MHz, CDCl₃) 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–C₆H₅ rotation must still be rapid. A pseudorotation barrier for the heteroring, Δ*G*[‡] = 13.0 ± 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, Cl₂CD–CDCl₂). 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 ¹³C and (³⁴S+¹³C₂), 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).



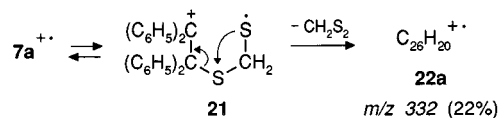
Scheme 6

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 C₁₄H₁₂⁺ 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 (C₆H₅)₂C and CH₂ of **20a** were separated by sulfur in the dithiolane; they become connected by the electrocyclic ring closure, **16a** → **17a**.

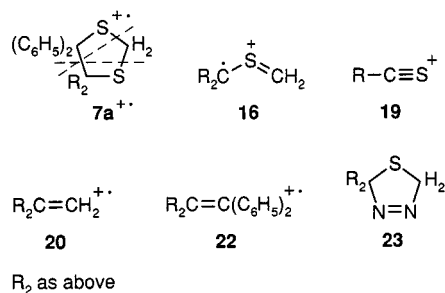
Thiobenzophenone, i.e., the second fragment of **7a**⁺, also appeared as radical cation (**6a**⁺), *m/z* 198 (61%), and was confirmed by the intensities of isotope peaks. Fragments [M⁺ – SH] are generally found in the MS of aliphatic and aromatic thioketones.^[18] Here, as in the MS of thiobenzophenone itself, C₁₃H₉⁺ 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 C₂₆H₂₀⁺ and complies with [M⁺ – CH₂S₂]. More probable than a onestep elimination of CH₂S₂ 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 **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 popula-



Scheme 8

tion 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.

Experimental Section

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

4,4,5,5-Tetraphenyl-1,3-dithiolane (7a).^[7] – (a): ¹H NMR (400 MHz, 25 °C): δ = 3.74 (s, 2-H₂), 7.05 (nearly tt, 8 *m*-H), 7.12 (tt, *J* ≈ 7.2, 1.2 Hz, 4 *p*-H), 7.34 (d, *J* = 6.4 Hz, 8 *o*-H, broad, approaching coalescence). – ¹³C (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⁺; ¹³C 0.47/0.50, (³⁴S+¹³C₂) 0.21/0.19], 332 (18) [M⁺ – CH₂S₂, C₂₆H₂₀⁺, **22a**; ¹³C 5.3/5.2, no ³⁴S peak], 255 (2.5) [C₂₆H₁₅⁺, 332 – C₆H₅], 254 (3.2), 253 (5.9), 252 (5.5), 212 (35) [C₁₄H₁₂S⁺, **16a**], 211 (28) [212⁺ – H], 198 (61) [C₁₃H₁₀S⁺, (C₆H₅)₂C=S⁺; ¹³C 8.8/9.2, (³⁴S+¹³C₂) 3.3/3.3], 197 (21), 180 (22) [C₁₄H₁₂⁺, **20a**], 179 (18) [C₁₄H₁₁⁺], 178 (20), 167 (19) [(C₆H₅)₂CH⁺], 166 (6), 165 (100) [fluorenyl⁺, **18**; ¹³C 15/16], 152 (10) [C₁₂H₈⁺, biphenylene], 121 (56) [C₆H₅–C≡S⁺; ¹³C 4.3/4.8; (³⁴S+¹³C₂) 2.6/2.7], 77 (17) [C₆H₅⁺]. – (b) ¹H NMR Evidence for Dynamic Process: The 400 MHz spectrum at 40 °C in Cl₂CD–CDCl₂ 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, ³*J* = 6.8 Hz. The low-frequency branch partially overlaps with the t of the 4 *p*-H at δ = 7.11. The Δ*v* of the two d for the 2 × 4 *o*-H shows only a small temp. dependence and allows an extrapolation to Δ*v* = 89 Hz at *T*_C + 1 °C. From *k* = 198 s^{–1}, Δ*G*_C[‡] = 13.1 kcal mol^{–1} at +1 °C is calculated. The s of 2-H₂ at δ = 3.74 reveals at –44 °C a slight broadening; due to the presence of a *quasi*-C₂ axis, no splitting is expected. – (c) ¹³C DNMR: A HETCOR experiment connected ¹H and ¹³C chemical shifts and confirmed the assignments. The 100 MHz spectrum (CDCl₃) 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 *ν*(¹³C) allows a linear extrapolation of Δ*v* 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 Δ*G*[‡] = 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. – ¹H NMR: δ = 3.63 (s, 2-H₂), 3.70 (s, 2 OCH₃), 6.43–6.72 (m, 4 arom. H), 6.90–7.47 (m, 14 arom. H). – ¹³C NMR (20.2 MHz, H-decoupled and off-resonance): Table 1; further absorptions: δ = 55.1 (q, 2 OCH₃), 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) [$C_8H_5^+$, 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 $\approx$ 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-fluoreneethione (**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-fluoreneethione (**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) [$C_{13}H_9S^+$, thioxanthylum $^+$], 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) [$C_8H_5^+$], 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: $k_1 = 1.23 \cdot 10^{-4} s^{-1}$, 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 SC₆H₅), 142.7 (br s, C_q of 2 C–C₆H₅); 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⁺; ¹³C 0.23/0.23], 396 (1.8) [C₂₆H₂₀S₂⁺, M⁺ – CH₂S₂, **22f**; ¹³C 0.52/0.47, (³⁴S+¹³C₂) 0.23/0.20], 365 (8.4) [C₂₁H₁₇S₃⁺, M⁺ – SC₆H₅; ¹³C 1.9/2.4, (³⁴S+¹³C₂) 1.3/1.3], 287 (11) [C₂₀H₁₄S⁺, (C₆H₅)₂C=C=SC₆H₅⁺; ¹³C 2.4/3.1], 256 (8.2) [C₁₅H₁₂S₂⁺, M⁺ – 2 C₆H₅S; ¹³C 1.4/1.6, (³⁴S+¹³C₂) 0.83/1.03], 255 (9), 254 (8), 253 (12), 218 (12) [C₁₂H₁₀S₂⁺, diphenyl disulfide?; ¹³C 1.6/1.6, (³⁴S+¹³C₂) 1.2/1.0], 212 (23) [C₁₄H₁₂S₂⁺, **16a**; peak contains 5.6% (³⁴S+¹³C₂) of m/z 210], 211 (32), 210 (100) [C₁₄H₁₀S⁺, (C₆H₅)₂C=C=S⁺], 209 (10), 208 (12), 198 (5) [**6a**⁺], 178 (21), 165 (50) [C₁₃H₉⁺, fluorenyl⁺], 121 (7) [C₇H₅S⁺, **19a**], 110 (42) [C₆H₅SH⁺], 109 (19) [C₆H₅S⁺], 77 (9) [C₆H₅⁺]. – C₂₇H₂₂S₄ (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, CH₃), 4.13 (q, 1-H), 7.23 (s, 2 C₆H₅).

[(1-Phenylthio-2,2-diphenylvinyl)thio]methyl Phenyl Disulfide (12). – (a): **7f** (400 mg, 0.84 mmol) was subjected to CC with CH₂Cl₂/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 (CDCl₃, 400 MHz, CDCl₃): δ = 3.99 (s, CH₂), 7.17–7.39 (complex m of 18 arom. H), 7.51, 7.53 (2 dd, 2 arom. H); (C₆D₆): 3.81 (s, CH₂); 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). – ¹³C NMR (CDCl₃, 100 MHz, DEPT): δ = 42.21 (CH₂), 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 C₆H₅), 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⁺; ¹³C 0.19/0.18, (³⁴S+¹³C₂) 0.14/0.11], 365 (1.6) [M⁺ – SC₆H₅; (³⁴S+¹³C₂) 0.25/0.33], 318 (10) [C₂₀H₁₄S₂⁺, ¹³C 2.3/2.9], 287 (7), 218 (18) [C₁₂H₁₀S₂⁺, diphenyl disulfide⁺; ¹³C 2.3/2.5, (³⁴S+¹³C₂) 1.5/1.5], 210 (100) [C₁₄H₁₀S⁺, (C₆H₅)₂C=C=S⁺], 208 (12) (C₁₄H₈S⁺, probably biphenylenethioketene⁺), 186 (17) [C₆H₅SC₆H₅⁺; ¹³C 2.2/2.4], 185 (10), 178 (22) [C₁₄H₁₀⁺], 165 (41) [fluorenyl⁺], 110 (78) [C₆H₅SH; (³⁴S+¹³C₂) 3.6/3.5], 109 (34) [C₆H₅S⁺], 77 (15) [C₆H₅⁺]. – C₂₇H₂₂S₄ (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 CDCl₃, 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 CH₂ signal of **12** at δ = 3.99 is much sharper than that of **7f** (hindered ring inversion).

5,5-Diphenyl-4,2'-spiro[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 (C₆H₅ out-of-plane deform.), 1026 br; 1446, 1497 m (arom. ring vibr.), 1690, 1706 st (C=O). – ¹³C 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⁺ – CH₂S₂, **22g**], 288 (1.7) [C₁₅H₁₂S₃⁺, M⁺ – S – 2 CO; (³⁴S+¹³C₂) 0.25/0.22], 212 (76) [C₁₄H₁₂S⁺, **16a**], 211 (56), 210 (100) [C₁₄H₁₀S⁺, diphenylthioketene⁺], 198 (1.2) [**6a**⁺], 178 (20), 165 (61) [**18**], 164 (7) [**6g**⁺], 121 (6) [**19a**], 89 (10), 77 (10) [C₆H₅⁺]. – C₁₇H₁₂O₂S₄ (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 N₂ evolution was finished after 5 h. The solvent was removed at room temp., the residue treated with 5 mL of CCl₄, and again evaporated. ¹H NMR analysis in CDCl₃ 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 CH₂Cl₂; the first fraction (220 mg) was trimeric **6h**, and the second fraction (260 mg) was recrystallized from methanol/CH₂Cl₂ 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/CH₂Cl₂ 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 (CH₂Cl₂/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 CH₃), 1.67 (s, 2 CH₃), 3.34 (s, 2-H₂), 7.0–7.2 (m, 6 arom. H), 7.4–7.6 (m, 4 arom. H). – ¹³C NMR (CDCl₃): δ = 25.47 (t, C-2'), 25.62, 25.75 (2 q, 4 CH₃), 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⁺ – CH₂S, C₂₁H₂₅OS⁺], 298 (100) [M⁺ – dimethylketene, C₁₈H₁₈S₂⁺], 262 (30) [C₂₀H₂₂⁺], 247 (20) [C₁₉H₁₉⁺], 237 (25), 220 (100) [C₁₇H₁₆⁺, (C₆H₅)₂C=C=C(CH₃)₂⁺], 205 (25) [C₁₆H₁₃⁺], 165 (10) [**18**], 91 (10) [C₇H₇⁺]. – C₂₂H₂₄OS₂ (368.5): calcd. C 71.69, H 6.56, S 17.40; found C 71.92, H 6.40, S 17.42.

Acknowledgments

Our thanks are going to the Fonds der Chemischen Industrie, Frankfurt, for the continued support of our research program. G.M. expresses his gratitude to the Alexander von Humboldt Foundation for a fellowship. We are greatly indebted to Reinhard Seidl for his competence in recording the MS, to Helmut Huber for many of the NMR spectra, to Dr. David S. Stephenson for a DNMR study, and to Helmut Schulz and Magdalena Schwarz for taking care of the elemental analyses. We thank cand. chem. Christian Leyh and cand. chem. Wolfgang Sieß for help in the cycloaddition experiments. Part of the experiments (1998/99) were carried out at the Institute of Organic and Applied Chemistry, University of Lodz, Poland; the technical assistance by Ms. M. Celeda is gratefully acknowledged.

- [1] Reviews: ^[1a] R. M. Kellogg, *Tetrahedron* **1976**, 32, 2165; ^[1b] R. Huisgen, C. Fulka, I. Kalwisch, X. Li, G. Mloston, J. R. Moran, A. Pröbstl, *Bull. Soc. Chim. Belg.* **1984**, 93, 511–532.
- [2] R. Okazaki, The Chemistry of Thioaldehydes. In *Organosulfur Chemistry*; Academic Press, New York, **1995**; Chapter 5.
- [3] A. Hosomi, Y. Matsuyama, H. Sakurai, *J.C.S., Chem. Commun.* **1986**, 1073–1074.
- [4] Review: Y. Terao, M. Aono, K. Achiwa, *Heterocycles* **1988**, 27, 981–1008.
- [5] G. Mloston, R. Huisgen, H. Huber, D. S. Stephenson, *J. Heterocyclic Chem.*, **1999**, 36, 959–968.
- [6] G. Mloston, R. Huisgen, K. Polborn, *Tetrahedron* **1999**, 55, 12783–12796.
- [7] R. Huisgen, I. Kalwisch, X. Li, G. Mloston, *Eur. J. Org. Chem.* **2000**, 1685–1694, preceding paper.
- [8] Preliminary account: X. Li, R. Huisgen, *Tetrahedron Lett.* **1983**, 24, 4181–4184.
- [9] H. Fasbender, *Ber. Dtsch. Chem. Ges.* **1887**, 20, 460–465; **1888**, 21, 1473–1477.
- [10] Reviews: ^[10a] D. S. Breslow, H. Skolnik, Multi-Sulfur and Sulfur and Oxygen Five- and Six-Membered Heterocycles. In *The Chemistry of Heterocyclic Compounds*; (Ed.: A. Weissberger); Interscience Publ., New York; Vol. 21, **1966**, pp 447–467; ^[10b] R. Csuk, B. I. Glänzer, 1,3-Dithiolanes. In *Comprehensive Heterocyclic Chemistry II*; (Eds.: A. R. Katritzky, C. W. Rees, V. Scriven); Pergamon, Elsevier Science, New York, Vol 3, **1966**, pp 642–648.
- [11] M. Aono, Y. Terao, K. Achiwa, *Chem. Lett.* **1987**, 1851–1852.
- [12] A. Schönberg, B. König, E. Singer, *Chem. Ber.* **1967**, 100, 767–777.
- [13] D. J. Cram, M. Cordon, *J. Am. Chem. Soc.* **1955**, 77, 1810–1811. Further examples: D. J. Cram, L. K. Gaston, *J. Am. Chem. Soc.* **1960**, 82, 6386–6389. M. Braun, D. Seebach, *Chem. Ber.* **1976**, 109, 669–691.
- [14] ^[14a] M. Oki, W. Fukunoshi, A. Nakamura, *Bull. Chem. Soc. Jap.* **1971**, 44, 828–832; ^[14b] M. Oki, W. Fukunoshi, *ibid.* **1971**, 44, 832–835.
- [15] H. Giera, Ph. D. Thesis, Univ. of Munich, **1991**, pp 74, 183.
- [16] G. Mloston and R. Huisgen, unpublished.
- [17] Definition: B. F. Yates, W. J. Bouma, L. Radom, *Tetrahedron* **1986**, 42, 6225–6234.
- [18] D. Paquer, L. Morin, M. Vazeux, C. G. Andrieu, *Rec. Trav. Chim. Pays-Bas* **1981**, 100, 36–40, 52–58.
- [19] D. Schumann, E. Frese, A. Schönberg, *Chem. Ber.* **1969**, 102, 3192–3204.
- [20] E. Campaigne, W. B. Reid, *J. Am. Chem. Soc.* **1946**, 68, 769–770.
- [21] Experiment by I. Kalwisch, University of Munich, **1980**.
- [22] J. Houben, K. M. L. Schultze, *Ber. Dtsch. Chem. Ges.* **1911**, 44, 3226–3234.
- [23] W. Autenrieth, H. Hefner, *Ber. Dtsch. Chem. Ges.* **1925**, 58, 2151–2156.
- [24] A. Schönberg, B. König, E. Frese, *Chem. Ber.* **1965**, 98, 3303–3310.
- [25] J. W. Greidanus, *Can. J. Chem.* **1970**, 48, 3530–3536.
- [26] E. U. Elam, H. E. Davis, *J. Org. Chem.* **1967**, 32, 1562–1565.

Received October 1, 1999

[O99552]