Aliphatic Thiocarbonyl Ylides and Thiobenzophenone: Experimental Study of Regiochemistry and Methylene Transfer in Cycloadditions[‡]

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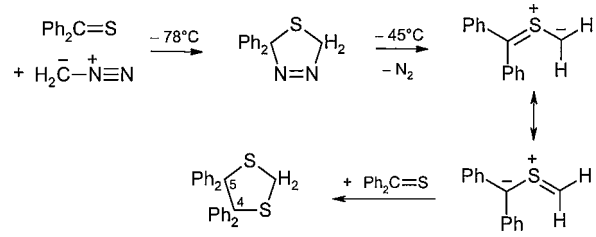
Dedicated to Gottfried Märkl, Regensburg, on the occasion of his 75th birthday

Keywords: Thiocarbonyl ylides / Cycloadditions / 1,3-Dithiolanes / Methylene transfer / Heterocycles

1,3-Dipolar cycloadditions of aliphatic or alicyclic thiocarbonyl ylides **3A-D** – sterically hindered at least at one terminus – with thiobenzophenone produce both regioisomeric 1,3-dithiolanes **4** and **5**. According to quantum-chemical calculations (preceding paper), a concerted cycloaddition furnishing 2,4-substituted dithiolanes **4** competes with the formation of an intermediate *C,C*-biradical **9** which cyclizes to the more crowded 4,5-substituted dithiolanes **5**. When steric hindrance of **3** increases, the cycloaddition is superseded by 'methylene transfer', i.e., the transfer of the less hindered terminus of **3E-J** to the S-atom of thiobenzophenone. The thiobenzophenone *S*-alkylide **11**, thus formed, rapidly reacts with a second molecule ofthiobenzophenone to generate the 4,4,5,5-tetraphenyl-1,3-dithiolane **12** via the highly stabilized *C,C*-biradical **10**. Methylene transfer occurs when the cyclization of the mixed *C,C*-biradical **9** requires a higher activation barrier than its dissociation to aliphatic thioketone + **11**; the threshold is surprisingly well reproduced by calculations. The structural assignment of sixteen 1,3-dithiolanes is based on their formation from corresponding reactant pairs as well as on ^{1}H and ^{13}C chemical shifts. X-ray diffraction analyses of three spiro-1,3-dithiolanes reveal the van der Waals strain in non-bonded interactions, folding angles, shearing forces, and bond lengths. Comparison of the mass spectra of many 1,3-dithiolanes allows the reconstruction of major fragmentation pathways.

Introduction

The 1,3-cycloaddition of thiocarbonyl ylides to thiones affords 1,3-dithiolanes. The first example was inadvertently discovered in 1930 and 1931 when thiobenzophenone was treated with diazomethane to give 4,4,5,5-tetraphenyl-1,3-dithiolane as a 2:1 product in high yield.[1,2] Fifty years later, the intermediacy of 2,2-diphenyl-2,5-dihydro-1,3,4-thiadiazole and thiobenzophenone *S*-methylide was established (Scheme 1).[3,4] The regiochemistry remained the same when the aromatic substituents of 1,3-dipole and dipolarophile were varied.[5,6]



Scheme 1. Formation of 4,4,5,5-tetraphenyl-1,3-dithiolane by cycloaddition of thiobenzophenone *S*-methylide to thiobenzophenone.

On the other hand, it was observed that thiocarbonyl ylides and thiones containing cycloaliphatic or aliphatic substituents furnished 2,4-substituted 1,3-dithiolanes exclusively;[7–10] an example is shown in Scheme 2. 2,4-Substituted 1,3-dithiolanes suffer much less from the van der Waals strain created by sterically demanding substituents than the 4,5-substituted regioisomers.

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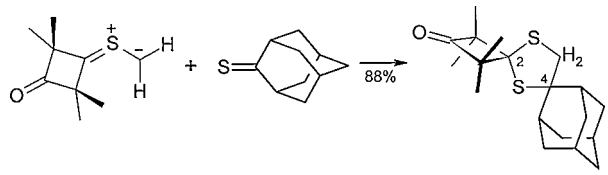


Scheme 2. Conversion of 2,2,4,4-tetramethyl-3-thioxocyclobutanone *S*-methylide and adamantanethione to a 2,4-substituted dispiro-1,3-dithiolane.

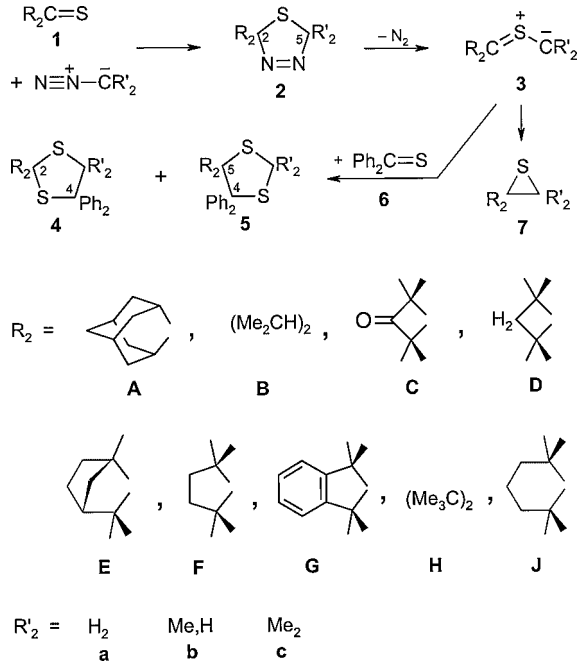
The suspected mechanistic dichotomy was confirmed by quantum-chemical calculations (restricted and unrestricted B3LYP/6-31G*). For the reaction of thioacetone *S*-methylide with thioacetone, the concerted formation of the 2,2,4,4-tetramethyl-1,3-dithiolane resulted as the preferred course; pathways via *C,S*- or *C,C*-biradicals had higher activation energies.[11] For the reaction of thiobenzophenone *S*-methylide with thiobenzophenone, the calculation (UB3-LYP/6-31G*//UHF/3-21G*) indicated a moderate barrier to the concerted process which leads to 2,2,4,4-tetraphenyl-1,3-dithiolane. However, this pathway had no chance because a *C,C*-biradical **10** (Scheme 4), stabilized by four phenyl groups and two thioether functions is exothermally formed with virtually no activation energy. The cyclization of this intermediate is geared to the 4,4,5,5-tetraphenyl-1,3-dithiolane which is in bond energy by 16.8 kcal mol^{-1} less favorable than the 2,4-substituted isomer.[12]

The calculations of the preceding paper deal with cycloadditions of aliphatic and cycloaliphatic thiocarbonyl ylides to thiobenzophenone. Here a *C,C*-biradical as intermediate can only profit from *one* benzhydryl-type stabilization. Activation barriers of comparable magnitude resulted for the concerted pathway which leads to the 2,4-substituted 1,3-dithiolanes, and for the two-step process to give the more hindered 4,5-substituted regioisomers.[13] Furthermore, the calculations provided the clue to the understanding of the 'methylene transfer' reaction and the nonequivalence of corresponding pairs of reactants. Theory and experiment will be compared here.

Results and Discussion

Competing Formation of Regioisomeric 1,3-Dithiolanes and the Methylene Transfer Reaction

The addition of diazomethane to thioketones **1** at 0 °C in pentane afforded the 2,5-dihydro-1,3,4-thiadiazoles **2a** as major or exclusive products; their thermolysis at 40–50 °C was the method of choice for the generation and in situ reaction of thiocarbonyl *S*-methylides **3a** (Scheme 3). On systematically varying the bulky residues R_2, the sequence **A**–**J** goes along with increasing steric hindrance in the interaction with thiobenzophenone (**6**).



Scheme 3. Preparation of thiocarbonyl ylides and formation of regioisomeric 1,3-dithiolanes by cycloaddition with thiobenzophenone; position numbering of monocyclic dithiolanes.

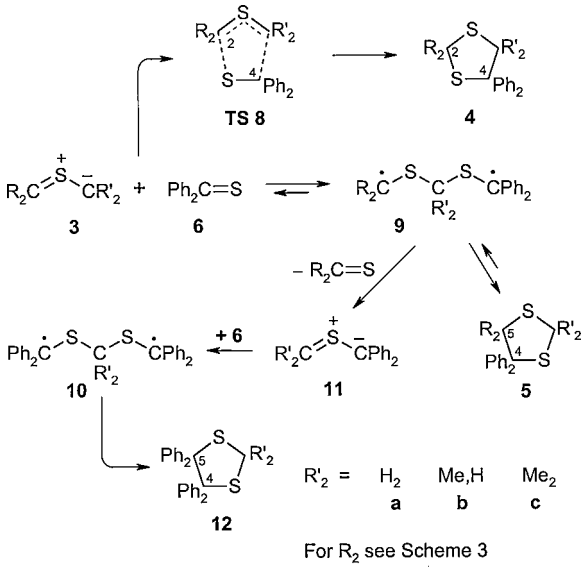
How will methyl substitution at the second terminus of **3** influence the reactivity? Analogous cycloadditions of **1** with diazoethane or 2-diazopropane provided the methylated 2,5-dihydro-1,3,4-thiadiazoles **2b** and **2c** which, in turn, furnish the tri- and tetra-substituted thiocarbonyl ylides **3b** and **3c** on thermal N_2 extrusion. The two manifolds of R_2 and R'_2 in Scheme 3 require double indices of formula numbers, e.g., **5Bb** is 5,5-diisopropyl-2-methyl-4,4-diphenyl-1,3-dithiolane.

When the adamantanethione *S*-methylide (**3Aa**) was generated in the presence of 1.1 equivalents of thiobenzophenone (**6**), quantitative ^{1}H NMR analysis with weights-standard revealed the regioisomeric 1,3-dithiolanes **4Aa** and **5Aa** in 42% and 50% yield, respectively.[8] Analogous experiments with the *S*-ethylide **3Ab** and *S*-isopropylide **3Ac** pointed to a modest shift towards the 2,4-substituted 1,3-dithiolanes **5Ab/5Ac** in the mixture of regioisomers. The N_2 elimination from the methylated precursors, **2Ab** and **2Ac**, proceeded somewhat slower than that of **2Aa**; the experimental conditions and products are listed in Table 1. The properties of the isolated cycloadducts and their structural assignment will be described in the next chapter.

The additional introduction of methyl groups into the second terminus of the thiocarbonyl ylide was not subject to calculations, and its effect on the competing pathways is interpreted with reserve. The dimethylated terminus of **3Ac** which is still less hindered than the one with the adamantylidene group, will attack the S-atom of **6,** and the formation of biradical **9c** will be sterically retarded; the methyl groups will not contribute to the radical stabilization (Scheme 4). The shifting of the regioselectivity towards 2,4-substitution suggests that the early TS **8c** of the concerted addition suf-

Table 1. In situ reactions of thiocarbonyl ylides **3** with thiobenzophenone (**6**); for R_2 and formula numbers see Scheme 3.

R'$_2$	Reaction conditions	% 1,3-Dithiolane 4	5	% Further products
Adamantanethione *S*-alkylide 3A				
H,H	THF, 40°C, 8 h [8]	42 **4Aa**,	50 **5Aa**	
Me,H	THF, 60°C, 6 h	57 **4Ab**	38 **5Ab**	
Me,Me	toluene, 80°C, 6 h	**4Ac** 65:35	**5Ac**	
Diisopropyl thioketone *S*-methylide (3Ba)				
H,H	THF, 65°C, 6 h [19]	22 **4Ba**	67 **5Ba**	
2,2,4,4-Tetramethyl-3-thioxocyclobutanone *S*-alkylide 3C				
H,H	THF, 40 °C, 8 h [20]	23 **4Ca**	56 **5Ca**	3 **12a**
H,H	$CDCl_3$, 80 °C, 10 min	20 **4Ca**	68 **5Ca**	9 **12a**
Me,H	THF, 45 °C, 6 h	57 **4Cb**	34 **5Cb**	
Me,H	$CDCl_3$, 80 °C, 10 min	37 **4Cb**	42 **5Cb**	9 **12b**, 11 **7Cb**
Me, Me	THF, 60 °C, 5 h	22 **4Cc**	23 **5Cc**	12 **12c**, 18 **7Cc**
2,2,4,4-Tetramethylcyclobutanethione *S*-methylide (3Da)				
H,H	THF, 40 °C, 12 h	18 **4Da**	62 **5Da**	
H,H	C_6D_6, 80 °C, 15 min	12 **4Da**	70 **5Da**	13 **12a**
Thiofenchone *S*-methylide (3Ea)				
H,H	THF, 50 °C, 2.5 h [18]			86 **12a**, 88 **1E**
2,2,5,5-Tetramethylcyclopentanethione *S*-alkylide 3F				
H,H	$CDCl_3$, 40 °C, 15 h			95 **12a**, 98 **1F**
Me, H	$CDCl_3$, 80 °C, 10 min			99 **12b**, **1F**
Me,Me	toluene, 100 °C, 1 h			90 **7Fc**
1,1,3,3-Tetramethylindan-2-thione *S*-alkylide 3G				
H,H	$CDCl_3$, 80 °C, 15 min			96 **12a**, **1G**
Me,H	C_6D_6, 80 °C, 15 min			98 **12b**, **1G**
Me,Me	toluene, 130 °C, 5 h			93 **7Gc**
Di-*tert*-butyl thioketone *S*-methylide (3Ha)				
H,H	toluene, 80 °C, 5 h [19]			67 **12a**, 75 **1H**, 13 **7Ha**
2,2,6,6-Tetramethylcyclohexanethione *S*-alkylide 3J				
H,H	octane, 130 °C, 15 min			73 **12a**, 18 **7Ja**
Me,H	octane, 130 °C, 10 min			61 **12b**, 28 **7Jb**



Scheme 4. Thiocarbonyl ylides and thiobenzophenone: competition of cycloaddition and methylene transfer reaction.

fers less from methyl substitution than the TS of biradical formation.

The reactions of thiocarbonyl *S*-methylides **3Ba**, **3Ca**, and **3Da** with **6** reveal increasing shares of 4,5-substituted dithiolanes **5** (Table 1). It is a sequence of growing steric demand of R_2. In cycloadditions to dimethyl 2,3-dicyanofumarate and dimethyl 2,3-dicyanomaleate, a high violation of stereoretention was observed for **3Ca** and **3Da** as a consequence of rotation in a zwitterionic intermediate;[14,15] on the other hand, the loss of stereochemical integrity was only modest for cycloadditions of **3Aa**.[16]

The emergence of a by-product in the reactions of **3Ca** and **3Da** with thiobenzophenone was most remarkable: 3–13% of 4,4,5,5-tetraphenyl-1,3-dithiolane (**12a**). Two molecules of thiobenzophenone are linked by a methylene group which is provided by the thiocarbonyl ylide **3**. By-product **12a** gained dominance, when the *S*-methylides of the increasingly hindered thioketones were reacted with thiobenzophenone (Table 1). The 'methylene transfer' reaction was first observed, when thiofenchone *S*-methylide (**3Ea**) was reacted with **6** and furnished 86% of **12a**; interestingly, the reaction with thioxanthione instead of **6** still provided some 4,5-substituted 1,3-dithiolane of type **5** besides the methylene transfer product.[17,18]

The methyl groups in the tetramethylcyclobutane ring are 'bent back' as a consequence of the intracyclic bond angle, thus reducing the van der Waals pressure in the spirodithiolanes **4C/5C** and **4D/5D** and diminishing the strain in the preceding TSs. This alleviation is no longer offered by the tetramethyl five-membered and six-membered rings of **F**, **G**, and **J** in the role of R_2 (Scheme 3). The reaction of tetramethylcyclopentanethione *S*-methylide (**3Fa**) with two equivalents of **6** (40 °C, 15 h) afforded 95% of the 1:2 product **12a** and 98% of thioketone **1F**. Thus, steric hindrance prevents the formation of cycloadducts. Finally, in the reaction of tetramethylcyclohexanethione *S*-methylide (**3Ja**) and **6**, the electrocyclization yielding thiirane **7Ja** (18%) began to compete with the methylene transfer (73% **12a**). The interaction of di-*tert*-butyl thioketone *S*-methylide (**3Ha**) with **6** met similar hindrance: methylene transfer and thiirane formation occurred side by side.

In the plausible mechanistic Scheme 4, the thiocarbonyl ylide **3** attacks **6** at the *S*-atom and forms the 'mixed' biradical **9**. The cyclization barrier of **9** on the way to the 4,5-substituted dithiolane **5** will rise with increasing volume of R_2. A competing dissociation to thione **1** and thiobenzophenone *S*-alkylide **11** takes control. The latter avidly picks up a second molecule of thiobenzophenone to produce the favored stabilized biradical **10**. In a subsequent step, **10** cyclizes to **12**, i.e., in the case of **12a**, the product of the 'Schönberg reaction'.[4,12] In summa: thiocarbonyl ylide **3** combines with two molecules of thiobenzophenone to give thione **1** + dithiolane **12**. In the most crowded ylides like **3Gc** and **3Jb**, electrocyclization leading to thiiranes **7** competes with alkylidene transfer.

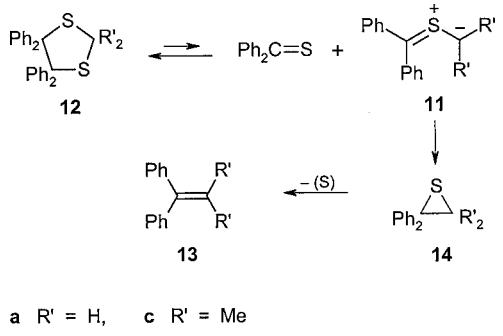
The data perfectly harmonize with the calculations.[13] The 'mixed' biradical **9Aa**, containing the adamantyl radical, cyclizes exothermally to 1,3-dithiolane **5Aa** via a barrier

of 6.6 kcal mol^{-1} whereas the dissociation to adamantanethione (**1A**) + **11A** requires an activation energy of 11.1 kcal mol^{-1}. On the other hand, the mixed biradical **9Fa** which is formed from tetramethylcyclopentanethione *S*-methylide (**3Fa**) and **6** will not pass the cyclization barrier of 23.9 kcal mol^{-1} leading to **5Fa**, but prefers the dissociation leading to thione **1F** + **11a** (barrier 8.3 kcal mol^{-1}) with subsequent interception of **11a** by **6** (Scheme 4).

Compared with the *S*-methylide **3Ca** of the tetramethyl-3-thioxocyclobutanone series, the *S*-ethylide **3Cb** and the *S*-isoproylide **3Cc** furnished slightly higher shares of dithiolanes **4Cb/4Cc**, and the products of ethylidene and isopropylidene transfer, **12b** (9%) and **12c** (10%), respectively, were likewise observed (Table 1). The occurrence of thiiranes (11% **7Cb**, 18% **7Cc**) indicated increasing steric hindrance in the interaction with **6**. Several examples of Table 1 suggest that, with rising temperature, the regioisomer ratio **4/5** shifts vs. **5**, and the share of **12**, the product ofmethylene transfer, is increased. That makes sense because a lower temperature coefficient is expected for the concerted cycloaddition (via TS **8**) than for the formation of inter-mediate **9** (Scheme 4). The thiocarbonyl ylides **3F** and **3G**, i.e., those derived from tetramethylcyclopentanethione and tetramethylindan-2-thione, ran parallel in their behavior: the *S*-ethylides furnished **12b** + thione **1** in virtuallyquantitative yields whereas the *S*-isopropylides no longer interacted with **6**, but rather furnished thiiranes **7Fc** and **7Gc**.

The 1,3-dithiolanes **5** suffer from van der Waals pressure caused by spiroanellation and the front strain of substituents in positions 4 and 5. The cycloaddition of thioformaldehyde *S*-methylide + $H_2C{=}S$ to afford the parent 1,3-dithiolane was calculated by (U)B3LYP/6-31G* to be exothermic with –76.0 kcal mol^{-1}.[11] This reaction heat shrinks for **3Aa** + **6** to –25.1 kcal mol^{-1} and for **3Fa** + **6** to a mere –4.8 kcal mol^{-1}.[13]

These data suggest another test for the mechanism of the methylene transfer reaction (Scheme 4). When dithiolane **5Da** – R_2 is the spiro-tetramethylcyclobutane residue – was heated with **6** in benzonitrile at 140 °C for 5 h, the ^{1}H NMR spectrum showed the emergence of tetraphenyldithiolane **12a**, thione **1D**, and 1,1-diphenylethylene (**13a**). This indicates equilibration of **5Da** with *C,C*-biradical **9Da**, dissociation of the latter into **1D** + thiobenzophenone *S*-methylide (**11a**), and capturing of **11a** by the added **6**. However, the cycloaddition which affords **12a** is likewise reversible, and



Scheme 5. Thermolysis of 4,4,5,5-tetraphenyl-1,3-dithiolanes.

the *S*-methylide **11a** occurring in the equilibrium at 140 °C enters the irreversible electrocyclization to give thiirane **14a**; subsequent sulfur loss leads to **13a** (Scheme 5).

The 2,2-dimethyl-4,4,5,5-tetraphenyl-1,3-dithiolane (**12c**) is more thermolabile than **12a**. After heating at 100 °C in $CDCl_3$ for 110 h, the conversion to 1,1-diphenylisobutene (**13c**) reached 99%. By-the-way, a *sulfur atom* is not involved in the desulfurization of thiiranes **14**. A kinetic study carried out in the Munich laboratory established the nucleophilic catalysis of such sulfur extrusions, and phenylated thiiranes served as models.[21]

Regiochemical Assignments of 1,3-Dithiolanes

Corresponding pairs of thiocarbonyl ylide + thioketone give rise to one and the same 4,5-substituted 1,3-dithiolane. Thus, the reactant pairs **3Ca** + **6** and **11a** + **1C** contain thiobenzophenone and tetramethyl-3-thioxocyclobutanone (**1C**) in exchanged functions. The common product must be **5Ca** whereas the 2,4-substituted regioisomers are different in the two systems. Similarly, it was shown that dithiolane **5Aa** resulted from corresponding reactant pairs.[6,8]

Reliable NMR criteria are based on the CH_2 group in the heterocycle and were recently employed to regioisomeric dithiolanes with aliphatic and cycloaliphatic substituents.[10] In the ^{13}C NMR spectra, the triplet for C-5 of **4a** (R'_2 = H,H) occurs at higher frequencies than that of C-2 in **5a**. The neighboring diphenyl-substituted C-4 deshields C-5 in **4a** to a higher extent than the second thioether function does on C-2 of **5a**; $\Delta\delta$ = 18.7–24.2 ppm was observed for four pertinent pairs (Table 2). The same criterion holds for the ^{13}C doublets in **4b** and **5b** (R'_2 = Me,H), and even for the singlets in dithiolanes **4c** and **5c** (R'_2 = Me,Me), albeit with smaller values of $\Delta\delta$. Since the multiplicities do not help in the recognition of C-5 in **4c** and of C-2 in **5c**, the assignment of **4Cc** was confirmed by an X-ray analysis (see below).

Table 2. 1,3-Dithiolanes prepared by cycloaddition of thiocarbonyl ylides to thiobenzophenone (see Scheme 3 for formula numbers).

Formula	M.p. [°C]	δ(1H)	δ(13C)	Ref.
4Aa	126–128	3.95 (5-H_2)	48.3 (C-5)	[8]
5Aa	203–205	3.28 (2-H_2)	28.0 (C-2)	[8]
4Ab	115–117	4.55 (5-H)	52.8 (C-5)	
5Ab	195–196	3.57 (2-H)	35.9 (C-2)	
4Ac	153–155		62.4 (C-5)	
5Ac	(not pure)		50.8 (C-2)	
4Ba	93–94	3.72 (5-H_2)	49.0 (C-5)	[19]
5Ba	138–140	3.63 (2-H_2)	30.3 (C-2)	[19]
4Ca	85–86	3.83 (5-H_2)	49.7 (C-5)	[20]
5Ca	124–126	3.34 (2-H_2)	25.5 (C-2)	[6,20]
4Cb	170–171	4.35 (5-H)	54.0 (C-5)	
5Cb	126–128	3.87 (2-H)	38.9 (C-2)	
4Cc	136–138		62.8 (C-5)	
5Cc	148–149		51.1 (C-2)	
4Da	51–52	3.69 (5-H_2)	49.6 (C-5)	
5Da	106–107	3.26 (2-H_2)	25.4 (C-2)	
12a	203–204	3.66 (2-H_2)	30.1 (C-2)	[1,2,4]
12b	172–174	4.09 (2-H)	42.7 (C-2)	[4]
12c	161–163		54.2 (C-2)	

The ^{1}H NMR shifts corroborate the structural attributions: the δ(5-H_2) of **4a** and the δ(5-H) of **4b** have higher values than the δ(2-H_2) of **5a** and the δ(2-H) of **5b**, respectively, although $\Delta\delta_H$ (0.09–0.98) varies more. Furthermore, the δ_H of the methyl pairs at C-2′ and C-4′ of the tetramethylcyclobutane (and, 1′-one) residues reveal stronger deshielding by the CPh_2 in 4-position of **5** than by the neighboring S-3 in **4**. E. g., the δ(Me_4) of **5Ca** at δ = 1.35 and 1.65 ppm are higher than 1.22 and 1.28 ppm observed for **4Ca**. This rule pertains to all **4/5** regioisomers of Table 2 (see Experimental).

The 1,3-dithiolanes with R′$_2$ = H,H (**a**) and Me,Me (**c**) display a σ-plane in their NMR spectra, i.e., a 'dynamic C_s symmetry' which results from the equilibrium of nonplanar enantiomeric conformations. The ratios of ^{13}C signals for CH and CH_2 groups in the adamantane systems of **4Aa/5Aa** and **4Ac/5Ac** mirror the σ–plane, as well as the methyl pairs do in **4Ca/5Ca** and **4Cc/5Cc**. The diisopropyl-1,3-dithiolanes **4Ba/5Ba** exhibit two ^{13}C signals for pairs of diastereotopic Me groups. On the other hand, dithiolanes with R′$_2$ = Me,H (**b**) are chiral and show the anticipated higher numbers of ^{1}H and ^{13}C signals.

It is only in the NMR spectra at 100 °C that the hexasubstituted dithiolanes **4Cc** and **5Cc** display sharp signals in accordance with the point group C_s. In the spectra at 32 °C, selected ^{1}H and ^{13}C signals of methyl and phenyl groups reveal beginning coalescence by line broadening (see Experimental). We suppose that hindered phenyl rotation is responsible, the more so, as we described such ^{13}C DNMR phenomena for 4,4,5,5-tetraphenyl-1,3-dithiolane (**12a**): coalescences of two *o*-CH (0 °C) and two aromatic C_q (15 °C) revealed a rate process with $\Delta G^{\neq}$ = 12.9 kcal mol^{-1}.[6]

Structure Analyses of Three 1,3-Dithiolanes

Single crystal X-ray analyses of **4Cc**, **5Ca**, and **5Da** supplement those of **4Aa** and **5Aa** published previously.[8] The spiroadamantane system of **4Aa** and **5Aa** is replaced by the sterically more demanding spiro-annulated tetramethylcyclobutanone in **4Cc** and **5Ca**, and by tetramethylcyclobutane in **5Da**. The compromise between the various steric constraints looks different in each examples.

In contrast to **4Aa** and **5Aa**, the three new structures contain the 1,3-dithiolane ring in an envelope conformation with the diphenyl-substituted C4 as the flap. The spiro-C-atom is C2 in **4Cc**, and C5 in **5Ca** and **5Da**. Would the envelope be regular, the intracyclic torsion angle at S1–C2 should be zero. The hexasubstituted dithiolane **4Cc** (Figure 1) comes close with a deviation of only 2.4°, vs. 6.5° and 3.8° in the tetra-substituted **5Ca** and **5Da**, respectively (Table 3).

In a regular envelope, the two bonds at the flap have the same torsion angle (opposite sign), e.g., 40.3° for cyclopentane.[22] The dithiolane **4Cc** (Figure 1) shows with 48.0° at C4–C5 and 46.7° at S3–C4 the best approximation, whereas **5Ca** with 61.0° and 52.4° is farer progressed towards the half-chair on the pseudorotational circuit.[23]

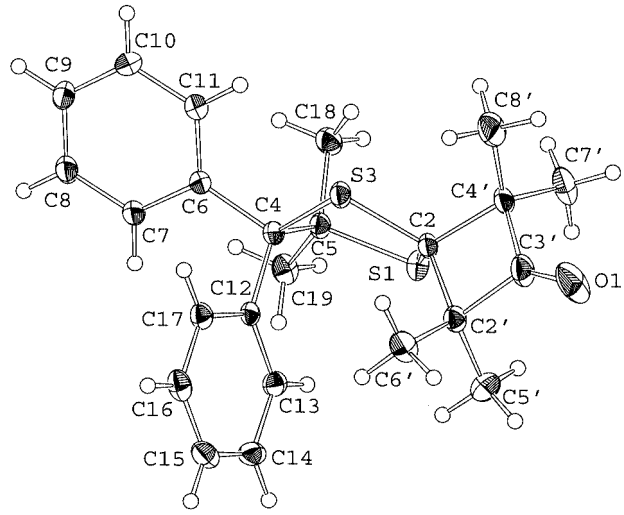


Figure 1. X-ray structure of 1,1,3,3,7,7-hexamethyl-6,6-diphenyl-5,8-dithiaspiro[3,4]octane-2-one (**4Cc**). ZORTEP plot (thermal ellipsoids at 30% probability level; position numbering of monocyclic dithiolanes).

Table 3. X-ray structures of some 1,3-dithiolanes; selected bond lengths and angles.

	4Cc	**5Ca**	**5Da**
Bond lengths [Å]			
S1–C2	1.827(3)	1.808 (3)	1.805(2)
C2–S3	1.818(3)	1.798(2)	1.790(2)
S3–C4	1.847(2)	1.847(2)	1.854(2)
C4–C5	1.577(4)	1.594(3)	1.601(2)
C5–S1	1.840(3)	1.835(2)	1.841(2)
Bond angles [°]			
S1–C2–S3	107.0(2)	109.8(1) 109.1(2)	
C2–S3–C4	98.1(1)	94.7(2)	94.1(1)
S3–C4–C5	104.0(2)	100.1(2)	101.1(1)
C4–C5–S1	106.5(2)	102.4(1)	103.5(1)
C5–S1–C2	100.8(2)	96.7(2)	98.7(1)
Intracyclic torsion angles [°]			
S1–C2–S3–S4	27.0(2)	–24.8(2)	–32.6(2)
C2–S3–C4–C5	–46.7(2)	52.4(2)	54.5(2)
S3–C4–C5–S1	48.0(2)	–61.0(1)	–56.0(1)
C4–C5–S1–C2	–28.7(2)	41.9(2)	32.7(2)
C5–S1–C2–S3	–2.4(2)	–6.5(2)	3.8(2)
Folding angle [°]			
Dithiolane	132.4	122.0	123.4
Cyclobutane	174.8	157.2	158.3

Closely connected is the folding angle, which varies from 122.0° to 132.3° in the three dithiolanes. The puckering of cyclopentane reduces the Pitzer strain of a planar five-membered ring. The non-bonded interactions should be lower in thiolanes and 1,3-dithiolanes than in the carbocycle. Characteristically, the torsion angle at C4–C5, the only C–C bond of the ring, has the highest value (Table 3).

Cyclobutane (gas phase) exhibits a puckering angle φ of 28°[24] and an inversion barrier of ca. 1.4 kcal mol^{-1};[25] in cyclobutanone the barrier is even lower, and φ is

10.4 ± 2.7°.[26] According to a survey, 20° < φ < 35° was observed for most substituted cyclobutanes, and crystal packing forces were made responsible for values of φ close to 0° which were found in a substantial number of crystal structures.[27]

The shallow puckering function of the four-membered ring is modified by various steric restraints in our examples, as suggested by folding angles of 174.8° (**4Cc**) and 157.2° (**5Ca**) for the two tetramethylcyclobutanones, and 158.3° for the tetramethylcyclobutane ring in **5Da**. In another dithiolane structure reported recently, the cyclobutanone ring was virtually planar.[10]

Both hexasubstituted dithiolanes, **4Cc** and **5Cc**, display hindered phenyl rotation in the NMR spectra at 32 °C (see above). Figure 1 illustrates the curbing of phenyl rotation by the methyl groups at C5 in **4Cc**: the closest distance of a methyl-H at C19 and the aromatic 13-H is 1.93 Å which is significantly below the sum of the van der Waals radii. The 4,5-tetrasubstituted dithiolanes **5Ca** and **5Da** likewise suffer from front strain, and the methyl groups at the cyclobutane ring interfere with phenyl rotation; one H,H distance of 1.96 Å in **5Da** (Figure 2) establishes the proximity. On the NMR time scale, however, phenyls in **5Ca** and **5Da** rotate still unrestricted at 32 °C.

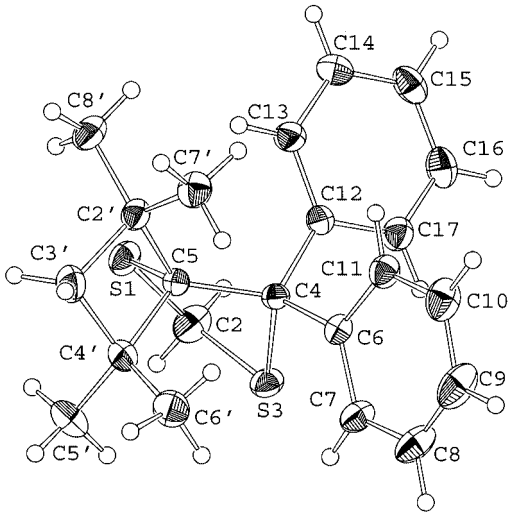


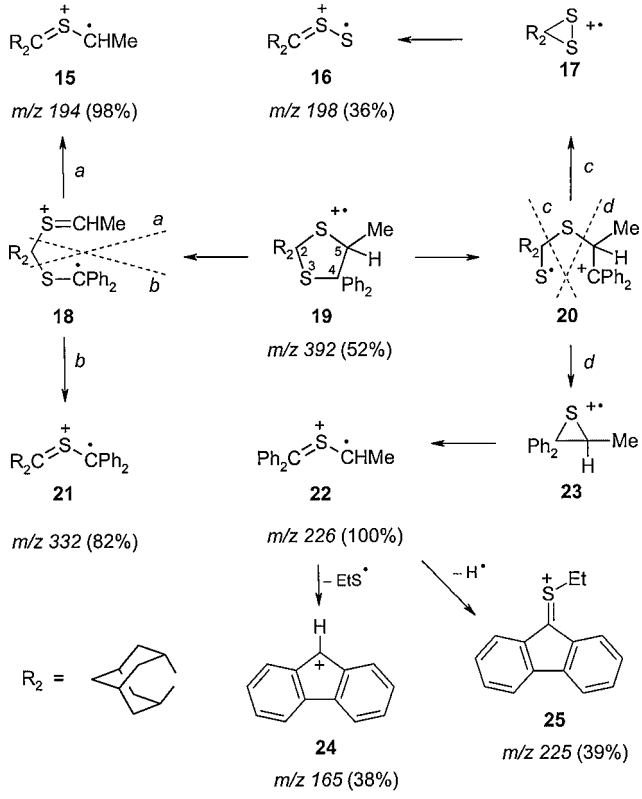
Figure 2. X-ray structure of 1,1,3,3-tetramethyl-8,8-diphenyl-5,7-dithiaspiro[3.4]octane (**5Da**); ZORTEP plot.

The bulky substituents exert shearing forces in our 1,3-dithiolanes, as exemplified with **4Cc** (Figure 1): C2′ and C4′ of the four-membered ring have different distances from the plane defined by S1–C2–S3, –1.08 and +1.17 Å, respectively. Similarly, the aromatic C-atoms C6 and C12 are located by +1.29 Å above and –1.19 Å below the plane S3–C4–C5.

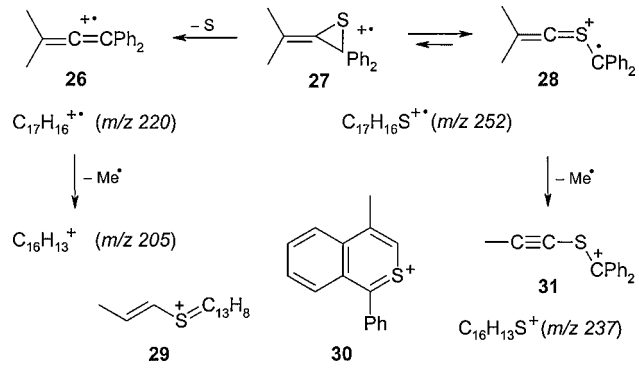
The bond lengths likewise demonstrate the van der Waals strain: **4Cc** shows 1.82–1.85 Å for all four C–S bonds, whereas the bonds S–CH_2 in **5Ca** and **5Da** are markedly shorter: 1.79–1.81 Å. The distances in the cyclobutane ring of **5Da** (Figure 2) differ even more: 1.53 Å for C2′–C3′(H_2) and C4′–C3′(H_2) vs. 1.61 and 1.62 Å for the bonds C2′–C5 and C4′–C5.

Mass Spectra of 1,3-Dithiolanes

The assignment of molecular formulae to mass peaks was supported by the intensities of ^{13}C and ^{34}S peaks and, in some examples, by high resolution. Many common features in the MSs of the dithiolanes (Table 2) invite to reconstructing sequences of fragmentation, although the structures in Schemes 6 and 7 remain speculative.



Scheme 6. Mass spectrum of the spiro[adamantane-2,2′-[1,3]dithiolane] **4Ab**: Supposed fragmentation pathways.



Scheme 7. Mass spectra of spiro-1,3-dithiolanes **5C** and **5D**: Section of fragmentation pathways.

The fragmentation process is dominated by 3+2 cycloreversions in concordance with previous discussions,[6,8] and the dithiolane **4Ab** may serve as a prototype. Whether its radical cation **19** preserves the heterocycle or consists of a mixture of open-chain species **18** and **20**, is uncertain. The

formulation as *distonic* species (separate centers of charge and spin density),[28] **18** and **20**, allows the substituents to contribute to cation and radical stabilization. The ionized thiocarbonyl ylides are allyl-type radicals with a sulfonium center in the middle. In calculations of related species, they rank in energy below the corresponding three-membered rings.[29]

The fragmentation pathways *a* and *b* of **18**, ring-opened at the bond C4–C5, mirror the 1,3-dipolar cycloadditions which start from two reactant pairs. In addition to **15** and **21**, also the mass peaks of the thioketones were observed.

Ring-opening of **19** at the bond S3–C4 likewise retains the superior benzhydryl-type stabilization. Intramolecular substitutions in **20** by paths *c* and *d* give rise to dithiirane **17** and thiirane **23** which, in turn, produce the distonic species **16** and **22**. Adamantanethione *S*-sulfide is a known 1,3-dipole,[30] and **16**, its radical cation, has been observed before.[8]

The base peak in the MS of **4Ab**, *m/z 226*, fits the radical cation **22** of thiobenzophenone *S*-ethylide. Generally, the radical cations of thiobenzophenone *S*-alkylides showed high intensities in the MS of 1,3-dithiolanes **4A/5A** and **4B/5B**, thus reflecting the diphenylmethyl-type stabilization.

In the MS of the dithiolanes described here, *m/z 165* occurs as a substantial peak. It was established by Schumann et al., that thiobenzophenone$^{+\cdot}$ (and related radical cations) break down into the 9-fluorenyl cation (**24**, *m/z 165*) + HS$^{\cdot}$, and a reasonable mechanism was proposed.[31] We observed that the peaks of thiobenzophenone *S*-alkylides$^{+\cdot}$ have a steady companion, which possesses one mass unit less, and a conversion of diphenylmethyl to fluorenyl is supposed. One of the two H-atoms set free reduces the alkylidene group, e.g., the sulfonium structure **25** is tentatively assigned to *m/z 225* (39%). The competing loss of EtS$^{\cdot}$ converted **22** to the fluorenyl cation **24** (38%).

In the MS of the positional isomer **5Ab**, *m/z 226* is likewise base peak (+ *m/z 225*, 40%), and radical cations **15** and **21** are also present. Despite having many peaks in common, different intensities and specific fragments support the non-identity of the MS of **4Ab** and **5Ab.** Some 'mixing' of fragments also appeared in the MS of **4Ba/5Ba**, but it is not general.

Radical cations of cyclobutanones and cyclobutanes undergo 2+2 cycloreversions. The loss of dimethylketene from the spiro-tetramethylcyclobutanones of type **4C/5C**$^{+\cdot}$ and isobutene elimination from **4D/5D**$^{+\cdot}$ are taking place side by side with the 3+2 cycloreversions. In the MS of **4C** and **4D**, a fragmentation is preferred which corresponds to path *c* of Scheme 6, whereas the radical cations of **5C/5D** favored initial expulsion of R′$_2$C=S, followed by 2+2 cycloreversion, to give thiirane **27** as product of an intramolecular substitution (Scheme 7).

Selected for discussion is the further degradation of **27** (*m/z 252*) which is a common fragment in the MS of all members of the **5C/5D** family. Either it forms **28** on ring-opening or loses a sulfur atom to give *m/z 220* which – formally – could be the allene derivative **26**. Even more populated were the products of further methyl loss, the cations *m/z 237* and *m/z 205* among which are the base peaks in the MS of **5Ca**, **5Cc** and **5Da**. Formula **31** for *m/z 237* illustrates the smallest structural change, but the fluorene-9-sulfonium structure **29** or the 2-thionianaphthalene derivative **30** appear more likely. For the cation $C_{16}H_{13}^+$ (*m/z 205*), the sulfur-free analogues of **29**–**31** can be considered: 9-(1-propenyl)fluorenyl$^+$, 1-phenyl-3-methylindenyl$^+$, or propynyl-diphenylmethyl$^+$ among others.

A closer study of the MSs of dithiolanes **4** and **5** (see Experimental) brings to light many more common features which reveal fragmentation sequences, but little structural evidence.

Experimental Section

General Remarks: ^{1}H NMR spectra were recorded on a Bruker WP80CW (80 MHz) for ^{1}H and WP80DS (20.15 MHz) for ^{13}C; some spectra were run on Varian XR400S. Solvent was acid-free $CDCl_3$, stored over dry K_2CO_3, if not stated otherwise. As weight standard for quantitative ^{1}H NMR analysis (usually ± 5%, relative), *sym*-tetrachloroethane (δ = 5.92 ppm), the *as*-isomer (δ = 4.28 ppm) or trichloroethylene (δ = 6.70 ppm) were used; 3–5 machine integrals of each signal were averaged. The multiplicities of the ^{13}C NMR signals were determined by comparison of H-decoupled with off-resonance spectra. The MS are EI spectra with 70 eV, recorded on a AET 909 or a Finnegan MAT90 instrument; intensities of isotope peaks are reported as, e.g., ^{13}C% calcd./% found, and in the same way for HR = high resolution. CC = column chromatography; PLC = preparative layer chromatography on 20 × 20 cm glass plates, usually with a 2 mm layer of Merck silica gel 60PF_{254}.

In the description of the NMR spectra, the structural assignments of the signals are based on a spectroscopic synopsis of numerous 2,5-dihydro-1,3,4-thiadiazoles, thiiranes, and 1,3-dithiolanes; those of this paper and preceding ones[6,8,10] were involved. To facilitate the comparison, the position numbering of the monocyclic heterorings is retained for the spiro-compounds. For each of the three heterocycles, one example shows the procedure, and the others follow with formula numbers and brief spectroscopic and analytical characterization. In the interpretation of the MS, the proposed formulae may not be the structures of the cationic fragments, but rather illustrate fragmentation pathways.

New 2,5-Dihydro-1,3,4-thiadiazoles and Thiiranes

2,5-Dihydro-5,5-dimethylspiro[(1,3,4)-thiadiazole-2,2′-adamantane] (2Ac): Freshly sublimed adamantanethione[32] (**1A**, 498 mg, 3.0 mmol) in pentane (5 mL) at 0 °C was dropwise treated with the red 2-diazopropane,[33] until the red color of **1A** just faded. After 1 h at –78°, the lustrous leaflets of **2Ac** were filtered: 634 mg (89%); the m.p. 59–60 °C (dec.) did not change after recryst. from pentane. ^{1}H NMR: δ = 1.72 (s, 2 Me), 1.77–2.2 (m, 12 H), 2.57–2.85 (m, 2 H) ppm. IR (KBr): $\tilde{\nu}$ = 990, 1449 cm^{-1} st; 1583 m (N=N) cm^{-1}. MS (30 °C), *m/z* (%): 2.35 (0.1) [M^+– 1], 208 (44) [M^+ – N_2], 176 (46) [208 – S]$^+$, 166 (100) [**1A**$^+$], 135 (40) [$C_{10}H_{15}^+$], 91 (50), 79 (34). $C_{13}H_{20}N_2S$ (236.37): calcd. C 66.05, H 8.53, N 11.85, S 13.57; found C 66.13, H 8.58, N 11.80, S 13.60.

2Ba: This dihydro-1,3,4-thiadiazole and is 1,2,3-regioisomer were formed in the ratio 87:13[34] by the reaction of diisopropyl thioketone (**1B**)[35] with gaseous diazomethane in pentane at 0 °C. M.p. –12 to –10 °C (MeOH). ^{1}H NMR: δ = 0.90, 0.97 (2 d, J = 6.5 Hz, 2 × 2 Me), 2.60 (sept, J = 6.5 Hz, 2 H of *i*Pr$_2$), 5.62 (s, 5-H$_2$) ppm. IR (KBr plates): $\tilde{\nu}$ = 1383 m, 1469 br.; 1577 m (N=N) cm^{-1}. MS

(30 °C), *m/z* (%): 172 (< 0.1) [M$^+$], 144 (100) [$M^+ - N_2$], 129 (14) [144 – Me]$^+$, 111 (32), 101 (57) [144 – *i*Pr]$^+$, 97 (45), 83 (50), 74 (50). $C_8H_{16}N_2S$ (172.29): calcd. C 55.77, H 9.36, N 16.26, S 18.61; found C 55.82, H 9.09, N 16.26, S 18.59.

2Fb: 2,2,5,5- Tetramethylcyclopentanethione (**1F**)[36,37] and diazoethane (1.4 equiv.) were reacted in Et_2O at –10 °C. The pale-yellow oil (74%) crystallized from pentane at –78 °C and was obtained as a colorless oil at room temp. ^{1}H NMR: δ = 0.65, 0.76, 1.13, 1.15 (4 s, 4 Me), 1.75 (d, *J* = 6.9 Hz, 5-Me), 1.90–2.20 (m, 3′-H_2, 4′-H_2), 5.77 (q, *J* = 6.9 Hz, 5-H) ppm. ^{13}C NMR: δ = 22.0, 24.8, 25.0, 29.8 (4 q, 1:1:1:2, 5 Me), 38.0, 38.2 (2 t, C-3′, C-4′), 46.8, 47.8 (2 s, C-2′, C-5′), 93.7 (d, C-5), 130.7 (s, C-2) ppm. IR (KBr plates): $\tilde{\nu}$ = 1015 s, 1366 s, 1381 s, 1465 br.; 1570 m, 1594 m (N=N) cm^{-1}. MS (90 °C), *m/z* (%): 212 (3.5) [M$^+$], 211 (10), 185 (38) [$C_{11}H_{21}S$; ^{13}C 4.7/4.7, $^{13}C_2$ + ^{34}S 1.7/1.7], 156 (16) [$C_9H_{16}S^+$, **1F**$^+$], 141 (26) [**1F**$^+$ – Me], 138 (30), 123 (100) [$C_9H_{15}^+$, probably tetramethylcyclopentenyl$^+$], 109 (31), 95 (12), 81 (22), 69 (35) [$C_5H_9^+$]. $C_{11}H_{20}N_2S$ (212.35): calcd. C 62.21, H 9.49, N 13.19; found C 62.72, H 9.64, N 12.97.

2Fc: The reaction of **1F** with 2-diazopropane in Et_2O furnished 67% of pure **2Fc**, crystalline in pentane at –78 °C, and at room temp. colorless oil. ^{1}H NMR: δ = 0.75, 1.10 (2 s, 2×2 Me at C-2′, C-5′), 1.75 (s, 2 Me at C-5), 1.88–2.31 (m, 3′-H_2, 4′-H_2) ppm. ^{13}C NMR: δ = 25.1, 29.9, 30.5 (3 q, 3×2 Me), ≈ 38.1 (11 lines, higher order, C-3′, C-4′), 47.4 (s, C-2′ + C-5′), 103.7 (s, C-5), 130.8 (s, C-2) ppm. IR (KBr plates): $\tilde{\nu}$ = 1365 s, 1381 s, 1457 s br.; 1588 m (N=N) cm^{-1}. MS (25 °C), *m/z* (%): 211 (19) [M^+ – Me], 198 (23) [$M^+ - N_2$], 183 (11) [198 – Me]$^+$ (^{13}C 1.4/1.2), 123 (55) [$C_9H_{15}^+$; ^{13}C 5.5/6.1, no S], 109 (100) [$C_8H_{13}^+$, probably trimethylcyclopentenyl$^+$], 107 (19), 95 (22), 81 (15), 67 (13). $C_{12}H_{22}N_2S$ (226.38): calcd. C 63.67, H 9.80, N 12.37, S 14.16; found C 64.15, H 9.54, N 12.20, S 14.21.

2Gb: Reaction of 1,1,3,3-tetramethylindanthione (**1G**)[36,38] with diazoethane in Et_2O at –10 °C, 78% yield. M.p. 64–66 °C (pentane). ^{1}H NMR: δ = 0.95, 1.06, 1.36, 1.39 (4 s, 4 Me), 1.81 (d, *J* = 6.8 Hz, 5-Me), 5.93 (q, *J* = 6.8 Hz, 5-H), 7.19 (br. s, 4 arom. H). ^{13}C NMR: δ = 22.0, 22.26, 22.41, 31.0, 31.3 (5 q, 5 Me), 50.0, 50.7 (2 s, C-1′, C-3′), 95.0 (d, C-5), 122.46, 122.55, 127.4 (3 d, 1:1:2, 4 arom. CH), 131.6 (s, C-2), 148.3 (s, 2 arom. C_q) ppm. IR (KBr): $\tilde{\nu}$ = 759 s (arom. out-of-plane deform.), 1454 m, 1468 m, 1479 m, 1574 w, 1581 w, 1604 w (arom. ring vibr., N=N) cm^{-1}. MS (40 °C), *m/z* (%): 245 (2) [M^+ – Me], 232 (16) [$M^+ - N_2$; $^{13}C_2$ + ^{34}S 0.9/0.8], 185 (20) [$C_{14}H_{17}^+$], 172 (100) [$C_{13}H_{16}^+$, probably tetramethylindene$^+$ or trimethylnaphthalene$^+$; ^{13}C 14/13, $^{13}C_2$ 1.0/0.7, no S], 171 (23), 157 (85) [$C_{12}H_{13}^+$], 155 (15), 141 (22), 128 (14) [$C_{10}H_8^+$, naphthalene$^+$], 115 (12). $C_{15}H_{20}N_2S$ (260.39): calcd. C 69.18, H 7.74, N 10.76, S 12.32; found C 69.33, H 7.74, N 10.89, S 12.31.

2Gc: Reaction of **1G** with 2-diazopropane in Et_2O at –10 °C gave 90% yield. M. p. 117–118 °C (pentane). ^{1}H NMR: δ = 1.03, 1.33, 1.81 (3 s, 3×2 Me), 7.18 (br. s, 4 arom. H) ppm. ^{13}C NMR: δ = 22.6, 30.6, 31.3 (3 q, 3×2 Me), 50.4 (s, C-1′ + C-3′), 105.3 (s, C-5), 122.5, 127.3 (2 d, 2×2 arom. CH), 131.8 (s, C-2), 148.3 (s, 2 arom. C_q) ppm. IR (KBr): $\tilde{\nu}$ = 765 + 768 s, 990 s, 1360 m, 1375 m, 1451 s, 1479 m, 1594 m cm^{-1}. MS (50 °C), *m/z* (%): 246 (11) [$M^+ - N_2$], 231 (8) [246 – Me]$^+$, 199 (16) [231 – S]$^+$, 189 (15) [**1G**$^+$ – Me, $C_{12}H_{13}S^+$], 172 (68) [$C_{13}H_{16}^+$], 157 (100) [$C_{12}H_{13}^+$, trimethylindenyl$^+$], 156 (28), 149 (15), 142 (27) [$C_{11}H_{10}^+$, methylnaphthalene$^+$], 115 (24), 111 (15). $C_{16}H_{22}N_2S$ (274.42): calcd. C 70.03, H 8.08, N 10.21, S 11.69; found C 70.32, H 7.96, N 10.44, S 11.72.

2Ha: Di-*tert*-butyl thioketone (**1H**)[39] (δ(^{1}H) = 1.45, s, 6 Me) and diazomethane in Et_2O at 0 °C. ^{1}H NMR analysis indicated 97% of **2Ha**. Colorless needles (MeOH), m.p. 64–65 °C. ^{1}H NMR: δ = 1.15 (s, 6 Me), 5.54 (s, 5-H_2) ppm. IR (KBr): $\tilde{\nu}$ = 946 br. m, 1368 s, 1391 s; 1576 m (N=N) cm^{-1}. MS (20 °C), *m/z* (%): 200 (0.2) [M$^+$], 172 (14) [$M^+ - N_2$], 143 (10) [M^+ – *t*Bu], 140 (2) [172 – S]$^+$, 111 (25) [143 – S]$^+$, 83 (31) [140 – *t*Bu]$^+$, 70 (57), 57 (100) [*t*Bu$^+$]. $C_{10}H_{20}N_2S$ (200.34): calcd. C 59.95, H 10.06, N 13.98, S 16.01; found C 60.22, H 9.99, N 13.96, S 16.05.

2Ja: 2,2,6,6-Tetramethylcyclohexanethione (**1J**)[38,40] and diazomethane in pentane at –10 °C; twice recryst. from pentane, **2Ja** (72%) showed m.p. 104–105 °C (dec.). ^{1}H NMR: δ = 0.54, 1.21 (2 s, 2×2 Me), 1.51–2.14 (m, 6 ring-H), 5.58 (s, 5-H_2) ppm. ^{13}C NMR: δ = 19.0 (t, C-4′), 27.2, 28.1 (2 q, 2×2 Me), 38.6 (t, C-3′ + C-5′), 41.1 (s, C-2′ + C-6′), 83.9 (t, C-5), 121.1 (s, C-2) ppm. IR (KBr): $\tilde{\nu}$ = 1379 s, 1385 s; 1578 m (N=N) cm^{-1}. MS (40 °C), *m/z* (%): 212 (3) [M$^+$], 184 (76) [$M^+ - N_2$], 169 (34) [184 – Me]$^+$, 152 (13) [184 – S, $C_{11}H_{20}^+$], 137 (93) [152 – Me]$^+$, 123 (84) [$C_9H_{15}^+$], 109 (47) [$C_8H_{13}^+$], 95 (82), 82 (100) [$C_6H_{10}^+$], 81 (77), 69 (62). $C_{11}H_{20}N_2S$ (212.34): calcd. C 62.21, H 9.49, N 13.19, S 15.10; found C 62.47, H 9.57, N 13.43, S 15.10.

2Jb: Thione **1J** and diazoethane in Et_2O at –10 °C; 70% of isolated **2Jb**, m.p. 71–72 °C (pentane). ^{1}H NMR: δ = 0.55, 0.64, 1.18, 1.23 (4 s, 4 Me), 1.79 (d, *J* = 6.9 Hz, 5-Me), 1.50–2.03 (m, 6 H), 5.69 (q, *J* = 6.9 Hz, 5-H) ppm. ^{13}C NMR: δ = 19.0 (t, C-4′), 20.6, 27.08, 27.23, 27.71, 29.0 (5 q, 5 Me), 38.2, 38.6 (2 t, C-3′, C-5′), 39.9, 41.4 (2 s, C-2′, C-6′), 94.3 (d, C-5), 130.0 (s, C-2) ppm. IR (KBr): $\tilde{\nu}$ = 1585 m (N=N) cm^{-1}. MS (40 °C), *m/z* (%): 211 (5) [M^+ – Me], 198 (28) [M^+ – S; ^{13}C 3.7/3.6, $^{13}C_2$ 0.23/0.26, no S], 169 (19), 137 (16), 123 (100) [$C_9H_{15}^+$, trimethylcyclohexenyl$^+$ or tetramethylcyclopentenyl$^+$], 121 (13) [$C_9H_{13}^+$], 95 (23), 81 (43) [$C_6H_9^+$], 79 (11), 69 (15), 67 (16). $C_{12}H_{22}N_2S$ (226.38):, calcd. C 63.67, H 9.80, N 12.37, S 14.16; found C 63.85, H 9.70, N 12.39, S 14.15.

Extrusion of N_2 from 2,5-Dihydro-1,3,4-thiadiazoles (2): The conditions for the in situ reactions of thiocarbonyl ylides **3** have to be adapted to the half-life of **2**. For studying cycloadditions of **3**, low stationary concentrations are desirable. A half-life of the precursor **2** in the range of 1 h and 6–8 half-lives as reaction time are fitting. The rate measurement by the nitrometric technique[4] is described and supplemented by a list of further half-lives.

2Ac: The vigorously stirred soln. of pure **2Ac** (472 mg, 2.00 mmol) in toluene (10 mL) was brought into a bath of 80 ± 1 °C and connected with a 100 mL nitrometer. Time and N_2 volume after 15 min are defined as zero values, and V_∞ was measured after 7 h. The first-order evaluation with $k_1 t = \ln (V_\infty/V_\infty - V_t)$ and linear regression of 17 volume readings (up to 83% reaction) afforded $10^4 k_1$ = 2.45 [s^{-1}] ($t_{½}$ = 47.2 min) and a correlation coefficient r = 0.9992; reproducibility ±4%.

Further Rate Data (often mean values of several determinations): Values below refer to the formula numbers in Scheme 3, $t_{½}$ in min (solvent, temp. in °C): **2Aa** 25.7 (xylene, 50), 77.5 (xylene, 40), 90.3 (THF, 40), 108 (MeCN, 40); **2Ab** 37.4 (xylene, 50); **2Ac** 124 (xylene, 50); **2Ba** 23.9 (toluene, 70); **2Ca** 17.8 (xylene, 50); **2Cb** 19.1 (xylene, 50); **2Cc** 120 (xylene, 50); **2Da** 97.1 (xylene, 40), 101 (THF, 40), 163 (MeCN, 40); **2Ea** 16.5 (toluene, 52); **2Fa** 111 (xylene, 40); **2Fb** 31.8 (xylene, 50); **2Fc** 91.7 (xylene, 100); **2Ga** 0.718 (xylene, 100), 68.4 (xylene, 50); **2Gb** 65.6 (xylene, 50); **2Gc** 20.0 (xylene, 100); **2Ha** 29.2 (xylene, 100); **2Ja** 15.6 (xylene, 100); **2Jb** 20.8 (xylene, 100).

Thiiranes 7 as Products of Electrocyclization of 2: With increasing steric demands of thiocarbonyl ylides **2**, the electrocyclization competes with the in situ cycloadditions, and the analysis of thiiranes in the reaction mixtures is required. The example of **7Fb** is supplemented by the brief description of further new thiiranes. Some-

times, a symmetry-allowed 1,4-H shift competes with the electrocyclization; the thioenol ethers formed will not be dealt with here.[34]

2,2,3′,5,5-Pentamethylspiro[cyclopentane-1,2′-thiirane] (7Fb): 2,5-Dihydro-1,3,4-thiadiazole **2Fb** (970 mg, 4.57 mmol) in benzene (5 mL) was refluxed for 2 h. After removal of the solvent, the ^{1}H NMR analysis with *sym*-$C_2H_2Cl_4$ in $CDCl_3$ indicated 100% of **7Fb** (q, 2.86). The thiirane crystallized from MeOH at –78 °C and was filtered at low temp., m.p. 58–60 °C. ^{1}H NMR: δ = 0.83, 1.06, 1.23 (3 s, 1:2:1, 4 Me), 1.55–1.64 (m, 3-H_2, 4-H_2), 1.60 (d, J = 6.0 Hz, 3′-Me), 2.86 (q, J = 6.0 Hz, 3′-H) ppm. ^{13}C NMR (100 MHz, DEPT): δ = 19.3, 27.3, 29.6, 31.3, 32.2 (5 Me), 38.2 (C-3′), 39.0, 41.7 (C-3, C-4), 43.5, 43.9 (C-2, C-5), 74.0 (C-2′) ppm. MS (25°), *m/z* (%): 184 (22) [M^+], 152 (10) [M^+ – S], 137 (54) [$C_{10}H_{17}^+$, 152 – Me], 123 (33) [$C_9H_{15}^+$], 109 (100) [$C_8H_{13}^+$, probably trimethylcyclopentenyl$^+$], 96 (33) [$C_7H_{12}^+$], 95 (42) [109 – Me]$^+$, 81 (55) [$C_6H_9^+$]. $C_{11}H_{20}S$ (184.34): calcd. C 71.76, H 10.94, S 17.39; found C 71.93, H 10.90, S 17.35.

7Cb: N_2 extrusion from **2Cb**[41] (toluene, 50 °C, 4 h) and distillation at 99–94 °C (bath)/12 mm furnished **7Cb** as colorless oil; yield 81% (^{1}H NMR analysis). ^{1}H NMR: δ = 1.07, 1.20, 1.25, 1.37 (4 s, 4 Me at C-2, C-4), 1.61 (d, J = 6.0 Hz, 3′-Me), 3.19 (q, J = 6.0 Hz, 3′-H) ppm. IR (NaCl plates): $\tilde{\nu}$ = 999, 1030, 1459; 1782 vs, 1810 m (C=O). $C_{10}H_{16}OS$ (184.29): calcd. C 65.17, H 8.75, S 17.40; found C 65.20, H 8.67, S 17.39.

7Fc: After N_2 elimination from **2Fc** (octane, 130°, 1 h), ^{1}H NMR analysis in $CDCl_3$ showed 85% of **7Fc**. M.p. 131–133 °C (MeOH). ^{1}H NMR: δ = 1.06, 1.29 (2 s, 4 Me at C-2, C-5), 1.68 (s, 2 Me at C-3′), 1.55–1.70 (br. s, 3-H_2, 4-H_2) ppm. MS: the fragmentation cascade is similar to that observed for the precursor **2Fc** (see above). $C_{12}H_{22}S$ (198.36): calcd. C 72.66, H 11.18, S 16.17; found C 72.09, H 11.03, S 16.02.

7Gb: After thermolysis in the closed NMR tube ($CDCl_3$, 80 °C, 1 h), ^{1}H NMR analysis indicated 94% of **7Gb**. M. p 53–54 °C (MeOH). ^{1}H NMR: δ = 1.11, 1.38, 1.40, 1.52 (4 s, 4 Me at C-1, C-3), 1.75 (d, J = 6.2 Hz, 3′-Me), 3.02 (q, J = 6.2 Hz, 3′-H), 7.15 (br. s, 4 arom. H) ppm. ^{13}C NMR: δ = 19.0, 28.3, 30.3, 32.1 (4 q, 1:1:1:2, 5 Me), 36.8 (d, C-3′), 46.9, 47.7 (2 s, C-1,C-3), 73.6 (s, C-2), 121.9, 122.2, 127.09, 127.27 (4 d, 4 arom. CH), 148.6, 150.3 (2 s, 2 arom. C_q) ppm. MS: similar to that of **2Gb** above. $C_{15}H_{20}S$ (232.38): calcd. C 77.52, H 8.68, S 13.80; found C 77.54, H 8.57, S 13.77.

7Gc: ^{1}H NMR analysis with *sym*-$C_2H_2Cl_4$ showed quantitat. formation of **7Gc** in the thermolysis of **2Gc** (toluene, 120 °C, 5 h). M.p. 93–94 °C (MeOH, 89%, colorless needles). ^{1}H NMR: δ = 1.41, 1.53 (2 s, 4 Me at C-1 and C-3), 1.85 (s, 2 Me at C-3′), 7.14 (s, 4 arom. H) ppm. ^{13}C NMR: δ = 28.4, 30.8, 31.3 (3 q, 3×2 Me), 48.6 (s, C-1 + C-3), 48.8 (s, C-3′), 78.5 (s, C-2), 121.9, 127.2 (2 d, 2×2 arom. CH), 149.9 (s, 2 arom. C_q) ppm. $C_{16}H_{22}S$ (246.40): calcd. C 77.99, H 9.00, S 13.01; found C 78.28, H 8.93, S 13.01.

7Ha: 73% (^{1}H NMR analysis). Distillation at 50 °C (bath)/10 mm and PLC (pentane) gave **7Ha** as colorless liquid. ^{1}H NMR: δ = 1.15 (s, 6 Me), 2.35 (s, 3′-H_2) ppm. $C_{10}H_{20}S$ (177.33): calcd. 69.69, H 11.70, S 18.61; found C 69.87, H 11.46, S 18.58.

7Ja: After N_2 elimination from **2Ja** (xylene, 100 °C, 2 h, 99%) and Kugelrohr distillation, **7Ja** crystallized from Et_2O. M.p. 77–78 °C. ^{1}H NMR: δ = 0.93, 1.15 (2 s, 2×2 Me), 1.30–1.75 (m, 6 ring-H), 2.43 (s, 3′-H_2) ppm. ^{13}C NMR: δ = 19.0 (t, C-4), 28.5, 30.4 (2 q, 2×2 Me), 29.1 (t, C-3′), 37.0 (s, C-2 + C-6), 41.7 (t, C-3 + C-5), 63.2 (t, C-1) ppm. $C_{11}H_{20}S$ (184.34): calcd. C 71.67, H 10.94, S 17.39; found C 71.66, H 10.80, S 17.45.

7Jb: N_2 elimination from **2Jb** (octane, 130 °C, 1 h) provided 89% of **7Jb** (^{1}H NMR analysis). M.p. 65–66 °C (pentane). ^{1}H NMR: δ = 0.86, 1.08, 1.22, 1.31 (4 s, 4 Me at C-2, C-6), 1.38–1.60 (m, 3×2 H), 1.73 (d, J = 6.4 Hz, 3′-Me), 2.94 (q, J = 6.4 Hz, 3′-H) ppm. ^{13}C NMR: δ = 19.0 (t, C-4), 17.7, 26.4, 28.7, 31.2, 36.1 (5 q, 5 Me), 36.8, 38.3 (2 s, C-2, C-6), 39.1 (d, C-3′), 40.3, 43.9 (2 t, C-3, C-5), 65.9 (s, C-1) ppm. $C_{12}H_{22}S$ (198.36): calcd. C 72.66, H 11.18, S 16.17; found C 72.35, H 11.03, S 16.17.

Reactions with Thiobenzophenone: Table 1 presents the reaction conditions for the thermolysis of dihydro-1,3,4-thiadiazoles **2** in the presence of thiobenzophenone as well as the product yields determined by ^{1}H NMR analysis with weight standard. The example **2Ab** (key to formula numbers in Scheme 3) illustrates the procedure.

Adamantanethione *S*-Ethylide (3Ab): Spiro compound **2Ab**[41] (444 mg, 2.00 mmol) and freshly distilled thiobenzophenone (**6**, 436 mg, 2.20 mmol) in abs. THF (4 mL) were magnetically stirred in a 60 °C bath for 6 h. After evaporation, quantitat. ^{1}H NMR analysis indicated 57% of **4Ab** (t δ = 4.55 ppm) and 38% of **5Ab** (t, 3.57). The solvent was removed, and the residue subjected to PLC (petroleum ether/CH_2Cl_2 8:2). The first fraction afforded **5Ab** (120 mg, 15%) from $CHCl_3$/acetone as colorless prisms. Renewed PLC of the second fraction gave **4Ab** as colorless oil (175 mg, 25%) which soon crystallized.

4Ab: M.p. 115–117 °C ($CHCl_3$/EtOH). ^{1}H NMR: δ = 1.17 (d, J = 6.5 Hz, Me), 1.42–2.42 (m, 14 H), 4.55 (q, J = 6.5 Hz, 5-H), 7.06–7.50 (m, 10 arom. H) ppm. ^{13}C NMR: δ = 19.3 (q, Me), 26.3, 26.4, 41.6, 42.9 (4 d, 4 CH of adamantane), 35.7, 35.9, 37.1, 37.4, 37.6 (5 t, 5 CH_2 of adamantane), 52.8 (d, great residual ^1J_R, C-5), 73.7, 75.9 (2 s, C-2, C-4), 126.3, 126.7, 127.3, 127.7, 127.8, 129.4 (6 d, 1:1:2:2:2:2, 10 arom. CH), 143.0, 146.2 (2 s, 2 arom. C_q) ppm. MS (EI, 100 °C), *m/z* (%): 392 (52) [M^+], 332 (82) [M^+ – MeCHS, **21**], 331 (12), 226 (100) [M^+ – **1A**, Ph_2C–S=CHMe$^+$, **22**], 225 (39) [$C_{15}H_{13}S^+$, **25**], 198 (27) [$C_{10}H_{14}S_2^+$; $^{13}C_2$ + $^{34}S_2$ calcd. 1.84/found 2.2], 194 (80) [$C_{10}H_{14}$–S=CHMe]$^+$, 166 (56) [$C_{10}H_{14}S^+$ = **1A**$^+$], 165 (38) [9-fluorenyl$^+$, **24**], 133 (31) [$C_{10}H_{13}^+$], 91 (41) [$C_7H_7^+$]. $C_{25}H_{28}S_2$ (392.61): calcd. C 76.48, H 7.19, S 16.34; found C 76.50, H 7.25, S 16.30.

5Ab: M.p. 195–196 °C (dec) (CH_2Cl_2/EtOH). ^{1}H NMR: δ = 1.47 (d, J = 6.3 Hz, Me), 1.0–3.45 (m, 14 H), 3.57 (q, J = 6.3 Hz, 2-H), 7.0–8.12 (3 m, 6:2:2, 10 arom. H) ppm. ^{13}C NMR: δ = 19.7 (q, Me), 26.4 (2 x), 38.9, 40.0 (3 d, 4 CH of $C_{10}H_{14}$), 33.3, 33.5, 37.6, 39.3, 42.1 (5 t, 5 CH_2), 35.9 (d, high ^1J_R, C-2), 78.5, 79.6 (2 s, C-4, C-5), 126.0, 127.6 (2 d, 2 arom. *p*-CH), 127.1, 127.6, 131.0, 132.3 (4 d, 8 arom. *o*-CH, *m*-CH), 143.0, 145.4 (2 s, 2 arom. C_q) ppm. MS (100 °C), *m/z* (%): 392 (3) [M^+], 332 (10) [M^+ – MeCHS, **21**], 300 (77) [Ph_2C=$C_{10}H_{14}$]$^+$, 226 (100) [Ph_2C=S–CHMe]$^+$, 225 (40) [$C_{15}H_{13}S^+$], 211 (32) [226 – Me]$^+$, 194 (18) [$C_{10}H_{14}$ = S–CHMe]$^+$, 166 (32) [**1A**$^+$], 165 (43) [9-fluorenyl$^+$], 91 (40) [$C_7H_7^+$], 77 (11) [$C_6H_5^+$]. $C_{25}H_{28}S_2$ (392.61): calcd. C 76.48, H 7.19, S 16.34; found C 76.54, H 7.22, S 16.36.

Adamantanethione *S*-Isopropylide (3Ac): The first fraction of PLC crystallized from EtOH: **4Ac** (55%). **5Ac** was enriched in the second fraction (separation failed).

4Ac: M.p. 153–155 °C. ^{1}H NMR: δ = 1.55 (s, 2 Me), 1.57–2.25 (m, 14 H), 7.0–7.25 (2 m, 6:4, 10 arom. H) ppm. ^{13}C NMR: δ = 28.9 (q, broadened, 2 Me), 26.0, 26.2, 42.4 (3 d, 1:1:2, 4 CH of $C_{10}H_{14}$), 36.3, 36.4, 37.5 (3 t, 2:2:1, 5 CH_2 of $C_{10}H_{14}$), 62.4 (s, C-5), 70.9, 77.6 (2 s, C-2, C-4), 126.2, 126.9, 130.1 (3 d, 1:2:2, 10 arom. CH), 145.6 (s, 2 arom. C_q) ppm. MS (100 °C), *m/z* (%): 406 (5) [M^+], 332 (100) [M^+ – Me_2CS, **21**], 331 (18), 240 (15) [$C_{16}H_{16}S^+$, Ph_2C–

S=CMe$_2^+$], 208 (42) [$C_{10}H_{14}$=S–CMe$_2$]$^+$, 193 (18) [$C_{15}H_{13}^+$], 166 (58) [$C_{10}H_{14}S^+$ = **1A**$^+$], 165 (35) [9-fluorenyl$^+$], 115 (25), 91 (46) [$C_7H_7^+$], 77 (13) [$C_6H_5^+$]. $C_{26}H_{30}S_2$ (406.63): calcd. C 76.79, H 7.44, S 15.77; found C 76.89, H 7.47, S 15.76.

5Ac: From spectrum of mixture by subtraction. ^{1}H NMR: δ = 1.42 (s, 2 Me) ppm. ^{13}C NMR: δ = 29.0 (q, br., 2 Me), 26.7, 27.0, 34.8 (3 d, 1:1:2, 4 CH of $C_{10}H_{14}$), 33.6, 39.2, 39.5 (3 t, 2:2:1, 5 CH_2 of $C_{10}H_{14}$), 50.8 (s, C-2), 80.7, 81.1 (2 s, C-4, C-5), 126.5, 132.6 (2 d, 8:2, 10 arom. CH), 146.8 (s, 2 arom. C_q) ppm.

Diisopropyl Thioketone *S*-Methylide (3Ba):[19] By-product (≈ 10%) was a thioenol ether formed from **3Ba** by 1,4-hydrogen shift.[34] From EtOH 50% of **5Ba;** PLC of the mother liquor (pentane/CH_2Cl_2 8:2) afforded **4Ba** (12%).

4Ba: M.p. 93–94 °C (MeOH). ^{1}H NMR: δ = 0.98 (d, J = 6.6 Hz, 4 Me), 2.20 (sept, J = 6.6 Hz, 2 H of *i*Pr$_2$), 3.72 (s, 5-H$_2$), 7.05–7.57 (2 m, 6:4, 2 Ph) ppm. ^{13}C NMR: δ = 19.7, 20.0 (2 q, 2×2 diastereotopic Me), 37.5 (d, 2 CH of *i*Pr$_2$), 49.0 (t, C-5), 74.1, 84.1 (2 s, C-2, C-4), 126.5, 127.9 (2 d, 4:1, 10 arom. CH), 145.8 (s, 2 arom. C_q) ppm. MS (60 °C), *m*/*z* (%): 342 (2) [M$^+$], 299 (100) [M^+ – *i*Pr], 211 (11) [$C_{14}H_{11}S^+$, 9-(methylsulfanyl)fluorenyl$^+$], 180 (13) [Ph$_2$C=CH$_2^+$], 87 (59) [*i*PrC≡S$^+$]. $C_{21}H_{26}S_2$ (342.55): calcd. C 73.63, H 7.65, S 18.72; found C 73.82, H 7.58, S 18.75.

5Ba: M.p. 138–140 °C (EtOH). ^{1}H NMR: δ = 0.92, 1.32 (2 d, J = 6.6 Hz, 2 × 2 diastereotopic Me), 2.60 (sept, J = 6.6 Hz, 2 H of *i*Pr$_2$), 3.63 (s, 2-H$_2$), 7.45–7.70 (2 m, 6:4, 2 Ph) ppm. ^{13}C NMR: δ = 22.1, 25.1 (2 q, 2 × 2 Me), 30.3 (t, C-2), 35.0 (d, 2 × CH of *i*Pr$_2$), 78.0, 80.0 (2 s, C-4, C-5), 126.5, 127.0, 129.9 (3 d, 1:2:2, 10 arom. CH), 144.4 (s, 2 arom. C_q) ppm. MS (80 °C), *m*/*z* (%): 342 (0.4) [M$^+$], 299 (10) [M^+ – *i*Pr; ^{13}C 2.0/2.1], 257 (21) [299 – C_3H_6]$^+$, 221 (11) [$C_{17}H_{17}^+$, probably 9-isobutylfluorenyl$^+$; HR 221.134/221.131], 212 (100) [Ph$_2$C–S=CH$_2^+$; $^{13}C_2$ + ^{34}S 5.6/6.1; HR 212.0657/212.0644], 211 (88) [$C_{14}H_{11}S^+$, 9-methylsulfanylfluorenyl$^+$; HR 211.0579/211.0574], 198 (61) [**6**$^+$; ^{13}C 8.9/9.6, $^{13}C_2$ + ^{34}S 3.3/3.2], 197 (21) [$C_{13}H_9S^+$], 180 (24) [Ph$_2$C=CH$_2^+$; ^{13}C 3.8/3.5], 179 (26) [$C_{14}H_{11}^+$, 9-methylfluorenyl$^+$], 165 (98) [fluorenyl$^+$; ^{13}C 14.1/15.1, HR 165.070/165.068], 152 (10) [$C_{12}H_8^+$, biphenylene$^+$; HR 152.0624/152.0623], 144 (18) [$C_8H_{16}S^+$, *i*Pr$_2$C=S–CH$_2^+$; $^{13}C_2$ + ^{34}S 0.87/0.86], 130 (13) [*i*Pr$_2$CS$^+$], 121 (49) [PhC≡S$^+$; $^{13}C_2$ + ^{34}S 2.3/2.7], 87 (23) [*i*PrC≡S$^+$], 77 (14) [Ph$^+$]. $C_{21}H_{26}S_2$ (342.55): calcd. C 73.63, H 7.65, S 18.72; found C 73.36, H 7.56, S 18.78.

2,2,4,4-Tetramethyl-3-thioxocyclobutanone *S*-Methylide (3Ca): (a) In addition to the 80 °C-experiment of Table 1, **2Ca**[42] and 2 equiv. of **6** in C_6D_6 were reacted in an NMR tube at 80 °C for 15 min and furnished 19% of **4Ca** (s, δ = 3.78 ppm), 70% of **5CA** (s, 3.33), and 10% of **12a** (s, 3.68). (b) The low solubility allowed isolation of **12a** from $CHCl_3$/MeOH, m.p. 198–200 °C (blue), identified with authentic **12a**[4] (m.p. 203–204 °C) by ^{1}H NMR and IR spectra. (c) The preparative experiment furnished **5Ca** (31%, m.p. 123–126 °C, from MeOH, identical with the product obtained from thiobenzophenone *S*-methylide + **1C**[6] in mixed m.p. and NMR spectra. The mother liquor contained **4Ca/5Ca** 7:3, and separation was achieved by PLC (petroleum ether/ethyl acetate, 98:2); the second fraction gave **4Ca** which crystallized from hexane and little CH_2Cl_2.

4Ca: M.p. 85–86 °C (CH_2Cl_2/hexane). ^{1}H NMR (400 MHz): δ = 1.21, 1.27 (2 s, 2 × 2 Me), 3.83 (s, 5-H$_2$), 7.23–7.32 (m, 6 arom. H), 7.46–7.48 (m, 4 arom. H) ppm. ^{13}C NMR (100 MHz, DEPT): δ = 22.7, 24.4 (2 × 2 Me), 49.7 (C-5), 66.7 (C-2′ + C-4′), 73.7, 77.2 (C-2, C-4), 127.1 (2 arom. *p*-CH), 127.87, 128.08 (4 *m*-CH, 4 *o*-CH), 144.1 (2 arom. C_q), 220.6 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 695 s, 748 m (arom. out-of-plane deform.), 1446, 1458, 1492 m, 1597 w (arom. ring vibr.), 1781 vs. (C=O) cm^{-1}. MS (20 °C, MAT 95Q, CMASS), *m*/*z* calcd./found (%): 368.1263/368.1276 (0.1) [M$^+$], 298.0846/298.0857 (43) [$C_{18}H_{18}S_2^+$, M^+ – C_4H_6O], 212.0657/212.0672 (13) [$C_{14}H_{12}S^+$, Ph$_2$C=S–CH$_2^+$], 211.0597/211.0586 (15) [$C_{14}H_{11}S^+$, 9-(methylsulfanyl)fluorenyl$^+$], 180.0936/180.0954 (100) [$C_{14}H_{12}^+$, Ph$_2$C=CH$_2^+$; ^{13}C 15.6/15.4; $^{13}C_2$ 1.14/1.15, no S], 179.0858/179.0864 (38) [$C_{14}H_{11}^+$], 178.0780/178.0796 (36) [$C_{14}H_{10}^+$], 165.0702/165.0704 (47) [$C_{13}H_9^+$, **24**), 152.0624/152.0629 (8) [$C_{12}H_8^+$], 86.0189/86.0189 (25) [Me$_2$C=C=S$^+$], 70.0417/70.0425 (9) [Me$_2$C=C=O$^+$]. $C_{22}H_{24}OS_2$ (368.54): calcd. C 71.69, H 6.56; found C 71.19, H 6.54.

2,2,4,4-Tetramethyl-3-thioxocyclobutanone *S*-Ethylide (3Cb): The dependence of the product composition on the reaction temp. (Table 1) is noteworthy. The 45 °C experiment afforded **4Cb** (40%) and 11% of **5Cb** by fractional crystallization from EtOH. Dithiolane **12b** (q, 4.09) was identified with the product obtained from thiobenzophenone *S*-ethylide and **6**.[4] Thiirane **7Cb** was analyzed by q at 3.19.

4Cb: M.p. 170–171 °C (CH_2Cl_2/EtOH), fine needles. ^{1}H NMR: δ = 0.92, 1.04, 1.32, 1.42 (4 s, 4 Me), 1.16 (d, J = 6.5 Hz, 5-Me), 4.35 (q, J = 6.5 Hz, 5-H), 7.0–7.5 (m, 2 Ph) ppm. ^{13}C NMR: δ = 20.2 (s, probably 5-Me), 22.6, 23.3, 24.1, 24.4 (4 q, 4 Me at C-2′, C-4′), 54.0 (d, C-5), 65.3, 67.7, 71.9 (3 s, C-2′, C-4′, C-2), 76.4 (s, C-4), 126.7, 127.0 (2 d, 2 arom. *p*-CH), 127.6, 127.7, 128.4, 128.8 (4 d, 8 arom. *o,m*-CH), 142.4, 145.8 (2 s, 2 arom. C_q), 220.6 (s, C=O) ppm. MS (30 °C), *m*/*z* (%): 382 (0.03) [M$^+$], 312 (37) [M^+ – C_4H_6O; ^{13}C 7.7/7.8], 226 (10) [Ph$_2$C=S–CHMe$^+$; $^{13}C_2$ + ^{34}S 0.59/0.51], 225 (9), 194 (100) [Ph$_2$C=CHMe$^+$; $^{13}C_2$ 1.3/1.1, no S], 193 (33) [$C_{15}H_{13}^+$, probably 9-(ethylsulfanyl)fluorenyl$^+$], 179 (14) [194 – Me]$^+$, 165 (13) [fluorenyl$^+$], 115 (15), 86 (13) [Me$_2$C=C=S]$^+$. $C_{23}H_{26}OS_2$ (382.57): calcd. C 72.20, H 6.85, S 16.76; found C 72.53, H 6.79, S 16.78.

5Cb: M.p. 126–128 °C (CH_2Cl_2/pentane). ^{1}H NMR: δ = 1.30, 1.37, 1.67 (3 s, 1:1:2, 4 Me), 1.35 (d, J = 6.5 Hz, 2-Me), 3.87 (q, J = 6.5 Hz, 2-H), 6.95–7.65 (2 m, 6:4, 10 arom. H) ppm. ^{13}C NMR: δ = 21.1 (d, 2-Me), 25.4, 26.0, 26.9 (3 q, 1:2:1, 4 Me), 38.9 (d, C-2), 68.0, 68.5 (2 s, C-2′, C-4′), 77.7, 79.7 (2 s, C-4, C-5), 126.76, 126.88 (2 d, 8 arom. *o,m*-CH), 130.5, 131.4 (2 d, 2 arom. *p*-CH), 144.6 (s, br., 2 arom. C_q), 220.5 (s, C=O) ppm. $C_{23}H_{26}OS_2$ (382.58): calcd. C 72.20, H 6.85, S 16.76; found C 72.04, H 6.93, S 16.77.

2,2,4,4-Tetramethyl-3-thioxocyclobutanone *S*-Isopropylide (3Cc): (a) After reaction (THF, 60 °C, 6 h) of **2Cc**[43] with 1.2 equiv. of **6**, ^{1}H NMR analysis in $CDCl_3$ at 102 °C (closed tube) with dibenzyl as weight standard indicated the 1,3-dithiolanes **4Cc**, **5Cc**, and **12c** (Table 1) as well as 18% of thiirane **7Cc** (s, 1.67),[43] and 18% of 2,2,4,4-tetramethyl-3-[(1-methylethenyl)sulfanyl]cyclobutanone (2 s, 3.35, 4.70) as product of 1,4-H shift.[43] (b) PLC (pentane/CH_2Cl_2, 7:3) gave the red thione **1C** (13%) from the first fraction and **12c** (12%) from the second fraction. Renewed PLC (pentane/Et_2O 95.5) of the third fraction furnished 18% each of pure **4Cc** and **5Cc**.

4Cc: M.p. 136–138 °C (MeOH). ^{1}H NMR (100 °C): δ = 1.03, 1.30, 1.58 (3 × 2 Me), 7.00–7.75 (2 m, 6:4, 2 Ph) ppm. ^{1}H NMR (30 °C): two signals are broadened by coalescence: 0.97 (half-width 16 Hz, 2 Me), 7.35–7.80 (4 arom. H) ppm. ^{13}C NMR (32 °C): δ = 22.7 (q, 4 Me), 24.3 (br., 2 Me), 62.8 (s, C-5), 66.8 (s, C-2′ + C-4′), 68.8 (s, C-2), 78.3 (s, C-4), 126.6 (d, 2 arom. CH), 127.1, 130.0 (2 d, 2 × 4 arom. CH), ≈ 145 (br., 2 arom. C_q), 221.3 (s, C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1779 cm^{-1} (C=O) cm^{-1}. MS (30 °C), *m*/*z* (%): 326 (65) [M^+ – C_4H_6O; $^{13}C_2$ + ^{34}S 7.3/7.0], 252 (20) [326$^+$ – Me$_2$CS, $C_{17}H_{16}S^+$, **28**], 251 (38) [$C_{17}H_{15}S^+$], 240 (7) [$C_{16}H_{16}S^+$, Ph$_2$C–S=CMe$_2^+$], 239 (14), 237 (65) [$C_{16}H_{13}S^+$; ^{13}C 11.6/12.0], 208 (100) [Ph$_2$C=CMe$_2^+$], 207 (14), 193 (31) [208 – Me]$^+$, 178 (31) [208 – 2 Me]$^+$, 165 (36) [fluorenyl$^+$], 159 (21), 129 (15), 115 (28), 86 (22) [Me$_2$C=C=S$^+$], 70

(14) [$Me_2C{=}C{=}O^+$]. $C_{24}H_{28}OS_2$ (396.60): calcd. C 72.68, H 7.12, S 16.17; found C 72.62, H 7.06, S 16.18.

5Cc: M.p. 148–149 °C (MeOH). ^{1}H NMR (100 °C): δ = 1.30, 1.37, 1.72 (3 s, 3 × 2 Me), 6.95–7.23, 7.37–7.63 (2 m, 6:4, 10 arom. H) ppm. ^{1}H NMR (30 °C): 1.30 (s, half-width 18 Hz, 4 Me), 1.71 (s, 2 Me), 7.03–7.23 (m, sharp, 6 arom. H), 7.33–7.67 (br. hump, 4 arom. H) ppm. ^{13}C NMR (32 °C): δ = 26.4, 26.8, 33.0 (slightly broadened, q not resolved, 3 × 2 Me), 51.1 (s, C-2), ≈ 69 (very br., C-2′ + C-4′), 79.9, 80.7 (2 s, C-4, C-5), 126.85 (d, sharp, 4 arom. CH), 127.06 (d, 2 arom. CH), 131.6 (br., d not resolved, 4 arom. CH), ≈ 147 (br., 2 arom. C_q), 220.9 (s, C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1779 cm^{-1} (C=O) cm^{-1}. MS (80 °C), *m/z* (%): 326 (34) [M^+ – C_4H_6O], 322 (48) [M^+ – Me_2CS; ^{13}C 11.2/11.6, $^{13}C_2$ + ^{34}S 3.4/3.7], 252 (67) [322 – C_4H_6O, $Me_2C{=}C{=}S{-}CPh_2^+$; $^{13}C_2$ + ^{34}S 4.1/4.3], 237 (100) [$C_{16}H_{13}S^+$, **29**, **30**, or **31**; ^{13}C 17.8/17.9], 220 (38) [$C_{17}H_{16}^+$, **26**], 205 (34) [$C_6H_{13}^+$, probably 9-(1-propenyl) fluorenyl$^+$], 165 (23) [fluorenyl$^+$], 111 (11). $C_{24}H_{28}OS_2$ (396.60): calcd. C 72.68, H 7.12, S 16.7; found C 72.71, H 7.11, S 16.17.

12c: M.p. 161–163 °C (blue). ^{1}H NMR: δ = 1.57 (br. s, 2 Me), 6.75–7.47 (2 m, 6:4, 4 Ph) ppm. ^{13}C NMR (32 °C, some signals broadened): δ = 32.8 (q, 2 Me), 54.2 (s, C-2), 81.7 (s, C-4 + C-5), 126.2, 132.1 (2 d, 16 arom. *o,m*-CH), 126.5 (d, 4 arom. *p*-CH), 144.0 (s, 4 arom. C_q) ppm. IR (KBr): $\tilde{\nu}$ = 699 s, 729 m (arom. out-of-plane deform.), 1441 m, 1490 m, 1597 w (arom. ring vibr.) cm^{-1}. MS (125 °C), *m/z* (%): 438 (< 1) [M^+], 332 (4) [$Ph_2C{=}CPh_2^+$], 240 (18) [$C_{16}H_{16}S^+$, $Ph_2C{=}S{-}CMe_2^+$], 239 (10), 225 (16) [240 – Me]$^+$, 208 (22) [$C_{16}H_{16}^+$, $Ph_2C{=}CMe_2^+$], 198 (22) [$Ph_2C{=}S^+$], 193 (11) [208 – Me]$^+$, 165 (100) [9-fluorenyl$^+$], 129 (12) [$C_{10}H_9^+$], 121 (84) [PhC≡S$^+$], 115 (48), 91 (27) [$C_7H_7^+$], 77 (59) [Ph$^+$]. $C_{29}H_{26}S_2$ (438.63): calcd. C 79.40, H 5.98, S 14.62; found C 79.25, H 5.87, S 14.61.

2,2,4,4-Tetramethylcyclobutanethione *S*-Methylide (3Da): After the reaction (40 °C, 12 h) of **2Da**[15] (13.7 mmol) with **6** (15.0 mmol) in THF (20 mL), **5Da** (38%) crystallized from EtOH; CC on silica gel (cyclohexane) afforded **5Da** (9%) as the first fraction and **4Da** (5%) as last fraction.

4Da: M.p. 52 °C (pentane). ^{1}H NMR: δ = 1.14, 1.28 (2 s, 2 × 2 Me), 1.60 (s, 3′-H_2), 3.69 (s, 5-H_2), 7.06–7.50 (m, 10 arom. H) ppm. ^{13}C NMR: δ = 28.8, 30.0 (2 q, 2 × 2 Me), 42.8 (s, C-2′ + C-4′), 47.4, 49.6 (2 t, C-3′, C-5), 73.1 (s, C-2), 80.9 (s, C-4), 126.6 (d, 2 arom. *p*-CH), 127.82, 127.88 (2 d, 8 arom. *o,p*-CH), 144.9 (s, 2 arom. C_q) ppm. MS (40 °C), *m/z* (%): 354 (0.6) [M^+], 298 (100) [M^+ – C_4H_8, $C_{18}H_{18}S_2^+$; ^{13}C 20/21, $^{13}C_2$ + $^{34}S_2$ 10.8/10.3], 212 (16) [$C_{14}H_{12}S^+$, $Ph_2C{-}S{=}CH_2^+$; ^{13}C 2.5/2.9], 211 (12), 180 (98) [$Ph_2C{=}CH_2^+$; ^{13}C 15/14, $^{13}C_2$ 1.1/1.2, no S], 179 (30) [$C_{14}H_{11}^+$], 178 (29), 174 (12) [probably $C_8H_{14}S_2^+$], 165 (32) [9-fluorenyl$^+$], 86 (20). $C_{22}H_{26}S_2$ (354.56): calcd. C 74.52, H 7.39, S 18.09; found C 74.90, H 7.31, S 18.11.

5Da: M.p. 106–107 °C (EtOH). ^{1}H NMR: δ = 1.26, 1.58 (2 s, 2 × 2 Me), 1.34, 1.80 (AB, J = 10.6 Hz, 3′-H_2), 3.26 (s, 2-H_2), 7.0–7.3 (m, 10 arom. H) ppm. ^{13}C NMR: δ = 25.4 (t, C-2), 30.2, 32.6 (2 q, 2 × 2 Me), 45.6 (s, C-2′ + C-4′), 47.9 (t, C-3′), 78.8, 79.2 (2 s, C-4, C-5), 126.2 (d, 2 arom. *p*-CH), 126.7, 130.8 (2 d, 8 arom. *o,m*-CH), 145.1 (s, 2 arom. C_q) ppm. MS (30 °C), *m/z* (%): 308 (8) [M^+ – CH_2S, $C_{21}H_{24}S^+$; ^{13}C 1.9/1.7, $^{13}C_2$ + ^{34}S 0.58/0.46], 298 (56) [M^+ – C_4H_8, $C_{18}H_{18}S_2^+$; ^{13}C 11.2/11.5], 276 (14) [308$^+$ – S, $C_8H_{14}{=}CPh_2^+$; $^{13}C_2$ 0.36/0.30, no S], 276 (14) [$C_{21}H_{24}^+$], 252 (9) [298$^+$ – CH_2S, **28**], 237 (32) [$C_{16}H_{13}S^+$], 233 (26) [$C_{18}H_{17}^+$], 220 (92) [276$^+$ – C_4H_8, **26**], 219 (31) [$C_{17}H_{15}^+$], 212 (23) [$Ph_2C{-}S{=}CH_2^+$], 211 (29), 205 (100) [$C_{16}H_{13}^+$; ^{13}C 17.8/18.0, $^{13}C_2$ 1.5/1.8, no S], 198 (22) [$Ph_2C{=}S^+$], 180 (34) [$Ph_2C{=}CH_2^+$], 179 (32) [$C_{14}H_{11}^+$], 178 (40), 165 (67) [fluorenyl$^+$], 121 (22) [Ph-C≡S$^+$], 86 (39) [$Me_2C{=}C{=}S^+$]. $C_{22}H_{26}S_2$ (354.56): calcd. C 74.52, H 7.39, S 18.09; found C 74.43, H 7.31, S 18.08.

2,2,5,5-Tetramethylcyclopentanethione *S*-Methylide (3Fa), Methylene Transfer: Dihydro-1,3,4-thiadiazole **2Fa**[37] (0.49 mmol) and **6** (0.99 mmol) in $CDCl_3$ (0.5 mL) were reacted in a NMR tube 15 h at 40 °C. After addition of *sym*-$C_2H_4Cl_2$, the ^{1}H NMR analysis revealed 98% of thione **1F** (s, 1.90, 4 H), and 95% of **12a** (s, 3.70, 2 H). In a preparative experiment, **12a** was isolated and identified.

2,2,5,5-Tetramethylcyclopentanethione *S*-Ethylide (3Fb): Reaction of **2Fb** with 2.6 equiv. of **6** in $CDCl_3$ (0.5 mL) in a closed NMR tube. ^{1}H NMR analysis as above indicated 99% of **12b** (d, 1.65; q, 4.09), and the signals of **1F** appeared.

2,2,5,5-Tetramethylcyclopentanethione *S*-Isopropylide (3Fc): The reaction of **2Fc** with 3.3 equiv. of **6** in toluene at 100 °C in 1 h provided thiirane **7Fc** (90%, s, 1.06).

1,1,3,3-Tetramethylindan-2-thione *S*-Methylide (3Ga): Methylene transfer was observed when dihydrothiadiazole **2Ga**[37] and 5 equiv. of **6** in $CDCl_3$ (1 mL) were reacted 15 min at 80 °C. ^{1}H NMR analysis indicated 96% of **12a** (s, 3.70) besides the signals of thione **1G**.

1,1,3,3-Tetramethylindan-2-thione *S*-Ethylide (3Gb): Dihydrothiadiazole **2Gb** and 2.1 equiv. of **6** were reacted under the same conditions and provided **12b** (98%, ^{1}H NMR analysis, s, 4.08). The isolated crystals, m.p. 174–176 °C (blue), were compared with authentic **12b**[4] (m.p. 172–174 °C, dec., blue).

1,1,3,3-Tetramethylindan-2-thione *S*-Isopropylide (3Gc): The N_2 extrusion from the more stable **2Gc** in the presence of 2.1 equiv. of **6** in toluene required 5 h at 130 °C. The ^{1}H NMR analysis ($CDCl_3$) disclosed 93% of thiirane **7Gc** (s, 1.84).

Di-*tert*-butyl Thioketone *S*-Methylide (3Ha):[19] The ^{1}H NMR analysis used s, 3.70 for **12a** (67%), s, 1.45 for thioketone **1H** (75%), and s, 2.34 for thiirane **7Ha** (13%); **12a** was isolated and identified.

2,2,6,6-Tetramethylcyclohexanethione *S*-Methylide (3Ja): After reaction of **2Ja** and 2.7 equiv. of **6** (Table 1), the analysis with *sym*-$C_2H_2Cl_4$ indicated 73% of **12a** (s, 3.68) and 18% of thiirane **7Ja** (s, 2.41).

2,2,5,5-Tetramethylcyclohexanethione *S*-Ethylide (3Jb): The conditions for N_2 extrusion from **2Jb** were the same as for **2Ja**. The analysis established **12b** (q, 4.09, 61%), thiirane **7Jb** (q, 2.90, 28%), and an unknown compound (q, 3.68, 8%). The isolated crystals of **12b**, m.p. 168–169 °C, were identified.

Thermolysis Reactions of Some 1,3-Dithiolanes

(a) 4,4,5,5-Tetraphenyl-1,3-dithiolane (12a): In a closed NMR tube, **12a** (46 μmol) in PhCN (0.4 mL) was heated to 140 °C for 110 min; the blue solution contained **12a** (s, 3.68) and 1,1-diphenylethylene (**13a**, s 5.38) in 1:1 ratio. After 12 h at 140 °C, **12a** had disappeared and 46% of **13a** were present; several signals of unknown products at δ = 1.98–2.63 were integrated and corresponded to 49% of CH_2 group of the initial concentration of **12a**. In a second experiment, **12a** (103 μmol) in $CDCl_3$ was heated to 135 °C for 35 h; besides **13a** (66%), again signals at 2.0–2.6 showed up. UV/Vis spectroscopy indicated **6** (103 μmol, 100%).

(b) 2,2-Dimethyl-4,4,5,5-tetraphenyl-1,3-dithiolane (12c): The more thermolabile **12c** (80 μmol) and *sym*-$C_2H_2Cl_4$ (116 μmol) in $CDCl_3$ (0.5 mL) were heated in a closed tube at 100 °C (bath). The smooth conversion of **12c** (s, 1.56) to 1,1-diphenylisobutene (**13c**, s, 1.79, no side products) amounted to% (after h): 6 (4), 28 (19.5), 42 (74), 91 (65), 99 (110); identification with an authentic specimen.

Table 4. X-ray crystallographic data of 1,3-dithiolanes.

Compound	**4Cc**	**5Ca**	**5Da**
Molecular formula	$C_{24}H_{28}OS_2$	$C_{22}H_{24}OS_2$	$C_{22}H_{26}S_2$
Molecular mass	396.58	368.53	354.55
Crystal size [mm]	0.10 × 0.17 × 0.26	0.53 × 0.40 × 0.20	0.50 × 0.40 × 0.23
Crystal system	monoclinic	monoclinic	monoclinic
Space group, Z	$P2_1/c$, 8	$P2_1/c$, 4	$P2_1/n$, 4
Unit cell parameters			
a [Å]	15.8285(4)	15.465(5)	10.775(2)
b [Å]	22.8286(4)	8.806(3)	16.174(3)
c [Å]	11.9030(2)	13.994(3)	11.052(2)
β [°]	101.0855(8)	96.86(2)	93.233(12)
Volume [Å^3]	4220.8(2)	1892.1(10)	1923.0(6)
$D_{calcd.}$ [g cm^{-3}]	1.248	1.294	1.225
F(000)	1696	784	760
Index range	$-17 \le h \le 18$	$0 \le h \le 17$	$0 \le h \le 12$
	$-26 \le k \le 26$	$-10 \le k \le 0$	$-18 \le k \le 0$
	$-12 \le l \le 13$	$-16 \le l \le 15$	$-12 \le l \le 12$
θ range [°]	3.17–24.06	2.65–23.97	2.23–23.97
Temperature [K]	200(2)	295(2)	295(2)
Reflections collected	39517	3072	3189
Reflections unique	6640	2953	3015
Reflections obsd. [$> 2\sigma(I)$]	5066	2511	2594
R_{int}	0.0621	0.0261	0.0082
Parameters	487	230	221
Final R [$I > 2\sigma(I)$]	0.0478	0.0352	0.0353
Final $wR2$	0.1077	0.0854	0.0880
Residual electron dens. [e/Å]	0.274, –0.292	0.165, –0.192	0.202, –0.209
Goodness of fit	1.059	1.077	1.098
CCDC deposition no.	249169	249170	249171

(c) Spiro Compound 5Da: When **5Da** (172 μmol) and **6** (187 mmol) in PhCN (0.5 mL) were heated at 140 °C for 5 h, the ^{1}H NMR spectrum indicated dithiolane **12a** (s, 3.68), 1,1-diphenylethylene (**13a**, s, 5.38), and unconsumed **5Da** (s, 3.13) in the ratio 39:25:36, and thione **1D** (s, 2.18) occurred in an amount equivalent to **12a** + **13a**. On further heating, **12a** and **5Da** disappeared; after 20 h at 140 °C, ^{1}H NMR analysis with *as*-$C_2H_2Cl_4$ provided **13a** (86 μmol) and **1D** (97 μmol); not identified signals pointed to side products.

X-ray Diffraction Analyses of 1,3-Dithiolanes (Table 4, Figure 1, Figure 2): All crystals were sealed in glass capillaries and mounted on the goniometer head of a Nonius KappaCCD aera detector (**4Cc**) or a Nonius MACH3 four-circle diffractometer (**5Ca** and **5Da**) operating with Mo-K_α radiation and a graphite monochromator. The unit cell dimensions were calculated using a least-squares refinement of a variable amount of setting angles. In case of the KappaCCD measurement a sphere was measured using a φ/ω scan with a scan step of 0.9° and a scan time of 60 s per degree. In the case of the MACH3 diffractometer, a quadrant was measured using an intensity-dependent ω/2Θ scan with a width of [0.81 + 0.47 tan Θ]° (**5Ca**) or [0.62 + 0.47 tan Θ]° (**5Da**). The usual corrections were applied. The structures were solved by SHELXS-86 and refined by SHELXL-93.[44] All non-hydrogen atoms were refined anisotropic, all hydrogen atoms were calculated as riding atoms with an isotropic temperature factor. The molecules were drawn using ZORTEP[45] on the basis of 30% probability ellipsoids. CCDC-249169 ... -249171 contain the supplementary crystallographic data (excluding structure factors) for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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