Massive Steric Hindrance in Two 'Thiocarbonyl Ylides': Cycloadditions with Tetra-Acceptor-Substituted Ethylenes *via* Zwitterionic Intermediates[1])

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Dedicated to the memory of *Günther Seidl*, formerly *Hoechst AG*

The switch from a concerted to a two-step pathway of 1,3-dipolar cycloadditions was recently established for the reactions of sterically hindered 'thiocarbonyl ylides' with acceptor ethylenes. This mechanism *via* zwitterionic intermediates is studied here for 1,3-dipoles **5A** and **5B**, which are derived from 2,2,5,5-tetramethylcyclopentanethione and 1,1,3,3-tetramethylindan-2-thione, respectively, and contain a highly screened reaction center. In the reactions of **8A** and **8B** (the precursors of **5A** and **5B**) with dimethyl 2,3-dicyanofumarate (**15**) and 2,3-dicyanomaleate (**16**), virtually identical ratios of *cis*- and *trans*-thiolanes were observed (**17**/**18** 93:7 for **5a** and 94:6 for **5B**). Thus, full equilibration of rotameric zwitterions precedes cyclization; an anteceding disturbing isomerization **15** ⇌ **16** had to be circumvented. The *cis*,*trans* assignment of the cycloadducts rests on three X-ray analyses. The kinetically favored *cis*-thiolanes **17** isomerize at $>80°$ to **18** (*trans*), and irreversible cleavage leads to thione **7** and *trans*,*cis* isomeric dimethyl 1,2-dicyanocyclopropane-1,2-dicarboxylates (**27** and **28**, resp.). Furthermore, the zwitterionic intermediates equilibrate with the cyclic seven-membered ketene imine **21**, which was intercepted under conditions where the solvent contained 2 vol-% of H_2O or MeOH. Lactams **22** were obtained with H_2O in high yields, and the primary products of capturing by MeOH were the cyclic ketene *O*,*N*-acetals **23**, which subsequently tautomerized to the lactim methyl ethers **24**. When **5B** was reacted with ethenetetracarbonitrile in $CDCl_3$/MeOH (98:2 vol-%), the analogous cyclic ketene imine **13B** was trapped to the extent of 93%.

1. Introduction. – 1,3-Dipoles are ambivalent species, but their nucleophilic or electrophilic character can predominate to variable degrees [2][3]. Their 1,3-cycloadditions are described by pairs of π-HOMO-LUMO interactions, which are located on a continuum between HOMO(1,3-dipole) – LUMO(dipolarophile) control and LUMO(1,3-dipole) – HOMO(dipolarophile) control [2][4]. It is at the two extremes of this scale that a mechanistic switch from a concerted to a two-step pathway *via* zwitterionic intermediate is to be expected. Both of these borderline crossings have been experimentally verified [5][6].

The indirect evidence for the concertedness of the majority of 1,3-dipolar cycloadditions is manifold [4]. The switch to a two-step mechanism is revealed by interception of the zwitterionic intermediates as well as by the loss of stereoretention in additions to *cis,trans*-isomeric dipolarophiles. The isolation of such zwitterions in suitable systems, as reported by *Quast et al.* [6], is especially convincing.

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[1]) 1,3-Dipolar Cycloadditions, Part 125; Part 124: [1].

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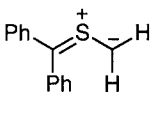
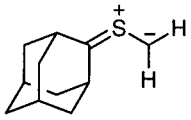
The π-HOMO and LUMO energies of 1,3-dipoles are determined by the nature and number of heteroatoms as well as by substituents. Since carbon and sulfur have the same electronegativity [7], thiocarbonyl ylides (=sulfonioalkylides) are located at the upper end of the energy scale, but still below the allyl anion that lacks the onium charge.

The first switch of mechanisms was observed for cycloadditions of electron-rich thiocarbonyl ylides with electron-deficient tetra-acceptor-substituted ethylenes [5][8][9]. Besides high HOMO-LUMO energies, strong steric hindrance – at least at one terminus of the 1,3-dipole – turned out to be indispensable for the two-step pathway. In the sequence **1** < **2** < **3**, **4**, the steric encumbrance of the thiocarbonyl ylide increases. The reactions of **3** (not those of **1** and **2**) with ethenetetracarbonitrile (TCNE) [8] or with dimethyl 2,3-dicyanofumarate and dimethyl 2,3-dicyanomaleate [10] reveal the involvement of zwitterionic intermediates by the above-mentioned criteria. Two electron-attracting substituents at one C-atom of the dipolarophile are mandatory for stabilization of the anionic terminus of the intermediate zwitterion. This condition is also fulfilled by the cycloaddition of **3** to benzylidenemalononitrile and related dipolarophiles [11].



1



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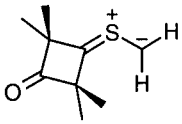

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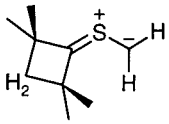

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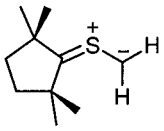
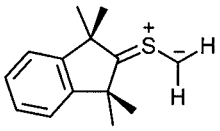


5A

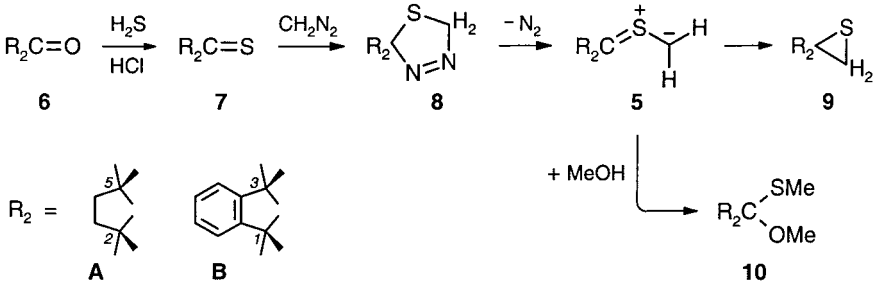


5B

We report here the reactions of two thiocarbonyl ylides that even exceed **3** and **4** in steric demand: (2,2,5,5-tetramethylcyclopentylidenesulfonio)methanide (**5A**) and (1,1,3,3-tetramethylindanylidenesulfonio)methanide (**5B**). The backbending of the Me-bearing C-atoms in the four-membered rings of **3** and **4** relieves some steric pressure, whereas the bond angles in the nonplanar five-membered rings of **5A** and **5B** are close to tetrahedral. Rate constants for nitrone cycloadditions to the corresponding alicyclic thiones indeed confirm the steric relief by backbending [12].

2. Results and Discussion. – 2.1. *2,5-Dihydro-1,3,4-thiadiazoles as Precursors of* **5A** *and* **5B**. The 1,3-cycloadditions of CH_2N_2 to thiones **7** in pentane at $-10°$ to $-20°$ furnished **8** (*Scheme 1*), and the regioisomeric 4,5-dihydro-1,2,3-thiadiazoles were not observed.

Scheme 1



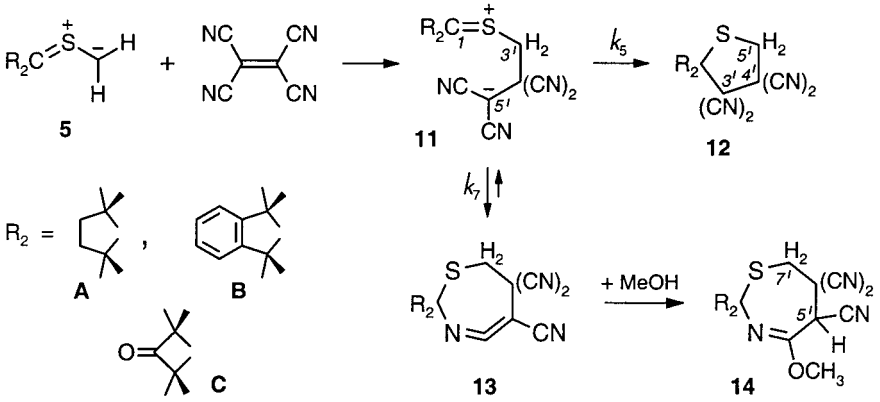
In the first-order elimination of N_2 from **8**, the thiocarbonyl ylides **5** are generated. The half-life in xylene at 50° amounts to 37 min for **8A** and 92 min for **8B**. The half-life of N_2 extrusion from **8A** in xylene or THF at 40° was only insignificantly changed in experiments performed in the presence of 1.1 equiv. of TCNE, and the rates were still first-order. The interaction with TCNE (see below) begins *after* the liberation of **5A**.

In inert solvents, the electrocyclization of the thiocarbonyl ylides **5A** and **5B** provided the thiiranes **9A** and **9B** (*Scheme 1*). When the N_2 extrusion from **8** was carried out in MeOH, the *O*,*S*-dimethyl acetals **10A** and **10B** were obtained nearly quantitatively. This type of acid-base reaction was extensively studied for thiocarbonyl ylide **2** [13].

The NMR parameters of **8**–**10** unequivocally confirmed the structures. The pairwise identity of the four C–Me groups revealed the presence of a σ-plane. In the MS of the thiiranes **9A** and **9B**, the signals of M^+, $[M-\mathrm{Me}]^+$, and $[M-\mathrm{S}]^+$ occur, but the base peaks are $[M-\mathrm{S}-\mathrm{Me}]^+$, indicating the trimethylcyclopentenyl cation and trimethylindenyl cation, respectively, as probable structures. Methylated cyclopentenyl cations are preferred species in the chemistry of alkanes in conc. H_2SO_4 [14], and the conversion of cyclohexane to the methylcyclopentyl cation by superacid [15] may likewise be mentioned in this context. In the MS of *O*,*S*-dimethyl acetal **10B**, the molecular peak is missing, and the carboxonium ion $[M-\mathrm{SMe}]^+$ appears as the strongest signal. The cascade of methylated indenyl cations from $C_{13}H_{15}^+$ (*m*/*z* 171, 61%) to $C_9H_7^+$ (*m*/*z* 115, 13%) as well as the naphthalene radical cation (*m*/*z* 128, 17%) result from further fragmentation.

2.2. *Reactions with Ethenetetracarbonitrile.* The elimination of N_2 from **8A** and **8B** at 65° allowed to study the *in situ* cycloadditions of **5A** and **5B** with TCNE, which afforded good yields of cycloadducts **12A** and **12B** (*Scheme 2*). However, when the reaction was carried out in $CDCl_3$ that contained 2 vol-% of MeOH, crystalline 1:1:1 products of **5**, TCNE, and MeOH (**14A**, **14B**) were isolated. Recently, we described this deflection from the normal course of (3+2) cycloaddition for the reaction of thiocarbonyl ylide **5C** with TCNE in the presence of MeOH [8]. The zwitterion **11** reversibly forms the cyclic seven-membered ketene imine **13**, which is intercepted by MeOH (or H_2O) to give the lactim methyl ether **14** (or lactam). The structural and mechanistic evidence [8] will not be repeated here.

Scheme 2



No intermediate was captured with MeOH or H_2O in the reactions of thiocarbonyl ylides **1** and **2** [16][17]. The trapping reaction requires the sterically more demanding thiocarbonyl ylides **5A**–**5C**. The ratio of **12C**/**14C** 65:35 reflects the rate ratio of cyclizations of zwitterion **11C**, k_7/k_5, and is not increased by an excess of MeOH [8].

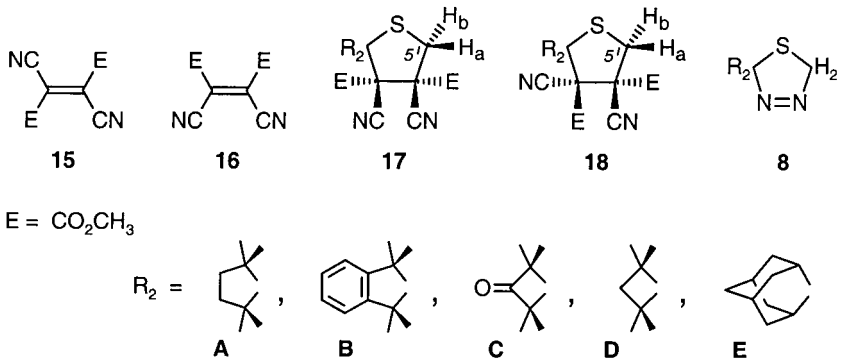
An ^{1}H-NMR analysis (with weight standard) of the product, obtained from **8B** and TCNE in $CDCl_3$/MeOH (98:2 vol-%), revealed 3% of thiolane **12B**, 82% of lactim ether **14B**, and 11% of a ketene *O,N*-acetal, an isomer of **14B**, which was not isolated here (*cf. Sect. 2.3.5*). Irrespective of ring strain, **13** > **12**, the N-atom of the linear CN group more easily passes the grid of the two pairs of geminal dimethyl groups in the cyclization **11** → **13** than the carbanion C(5′) does in the C–C ring closure, **11** → **12**. We conclude from the experimental ratio of **14B**/**12B** = k_7/k_5 = 97:3 that steric hindrance at C(1) of **11B** exceeds that of **11C**.

The presence of a σ-plane in thiolanes **12** leads to pairwise NMR identity of the four CN and four Me groups. The lactim ethers **14** are chiral (C(5′) is a stereogenic center), and the mentioned groups appear with different chemical shifts. The *singlets* of CH_2(5′) in **12** become *AB* spectra of CH_2(7′) in **14**.

2.3. *Cycloadditions with Dimethyl 2,3-Dicyanofumarate and Dimethyl 2,3-Dicyanomaleate*. 2.3.1. *Nonstereospecificity at 40°*. Generation of **5A** from **8A** in the presence of 1.1 equiv. of dimethyl 2,3-dicyanofumarate (**15**) in refluxing CH_2Cl_2 (12 h) afforded the *cis*-cycloadduct **17A** and the *trans*-isomer **18A** in 90 and 7% yield, respectively (^{1}H-NMR analysis). The corresponding reaction of ylide **5B** with **15** in CH_2Cl_2 (48 h) provided the spiroindan derivatives **17B** (92%) and **18B** (6%). The *cis,trans*-isomeric thiolanes **17A** and **18A**, as well as **17B** and **18B**, were separated and purified.

Thus, the overall cycloadditions of **5A** and **5B** to **15** proceeded nonstereospecifically, and – against our expectations – it was the *cis*-adduct **17** that predominated in the experiments with the *trans*-dicarboxylate **15**. Before we discuss the steric course, the configurational assignment must be clarified.

2.3.2. *NMR-Spectroscopic* cis,trans *Assignment*. The ^{1}H- and ^{13}C-NMR parameters demonstrate the chirality of the spirothiolanes, but only the ^{1}H signals of H_a–C(5′) and H_b–C(5′) allowed a distinction of **17** (*cis*) and **18** (*trans*). The CH_2(5′) appear at 400 MHz as *AX* spectra for the *cis*-adducts **17A** and **17B**, and as *AB* (or *AM*) spectra



for the *trans*-compounds **18A** and **18B**. As shown in a preceding paper [10], the cycloadducts **17C** and **18C** share this feature with several further adducts of thiocarbonyl ylides with **15** and **16**. According to *Table 1*, the chemical-shift difference of $H_a-C(5')$ and $H_b-C(5')$ amounts to 0.41 – 0.46 ppm for **17A** – **17E** (*cis*) and to 0.08 – 0.17 ppm for **18A** to **18E** (*trans*). The coupling constants (11.5 – 12.8 Hz) and the chemical shifts of the MeO groups are without diagnostic value.

Table 1. *Chemical Shifts* [ppm] *of* $H_a-C(5')$ *and* $H_b-C(5')$ *in Spirothiolanes* **17** *and* **18** [$CDCl_3$]

cis-Cycloadducts				*trans*-Cycloadducts			
No.	H_a	H_b	Δ [ppm]	No.	H_a	H_b	Δ [ppm]
17A	3.50	3.91	0.41	**18A**	3.47	3.61	0.14
17B	3.51	3.96	0.45	**18B**	3.43	3.60	0.17
17C	3.43	3.87	0.44	**18C**	3.56	3.64	0.08
17D	3.39	3.85	0.46	**18D**	3.51	3.59	0.08
17E	3.40	3.84	0.44	**18E**	3.37	3.53	0.16

The *cis,trans* assignment by this empirical NMR criterion needed calibration, which was provided by the X-ray analyses of two *trans*- and one *cis*-adduct.

2.3.3. *X-Ray Structures of Cycloadducts* **17** *and* **18**. In the spirothiolanes **17B** and **18B**, the envelope conformation of the five-membered carbocyclic ring is rigidified by the fusion with the benzene ring. The atoms C(2′) are located above the best planes of C(3)–C(3A)–C(7A)–C(1) by 0.51 Å for **17B** and 0.60 Å for **18B**, according to folding angles of 31° and 37°, respectively (*Figs. 1* and *2*). The saturated cyclopentane ring of **18A** (*Fig. 3*) has greater conformational freedom and assumes another envelope form with C(5) as the flap (0.72 Å above the quasi-plane of C(2′)–C(2)–C(3)–C(4), folding angle 45°). These displacements of the flap exceed that observed for the envelope conformation of the parent cyclopentane (0.43 Å, electron diffraction in gas phase [18]).

In contrast to cyclopentane, the parent thiolane prefers a half-chair form with C(1)–S(1)–C(5) in a plane, and C(3) and C(4) above and below (electron diffraction in the gas phase [19]). *Fig. 1* reveals that the thiolane ring in the crystalline *cis*-adduct **17B** approximates an envelope conformation with C(2′), the spiro center, as the flap

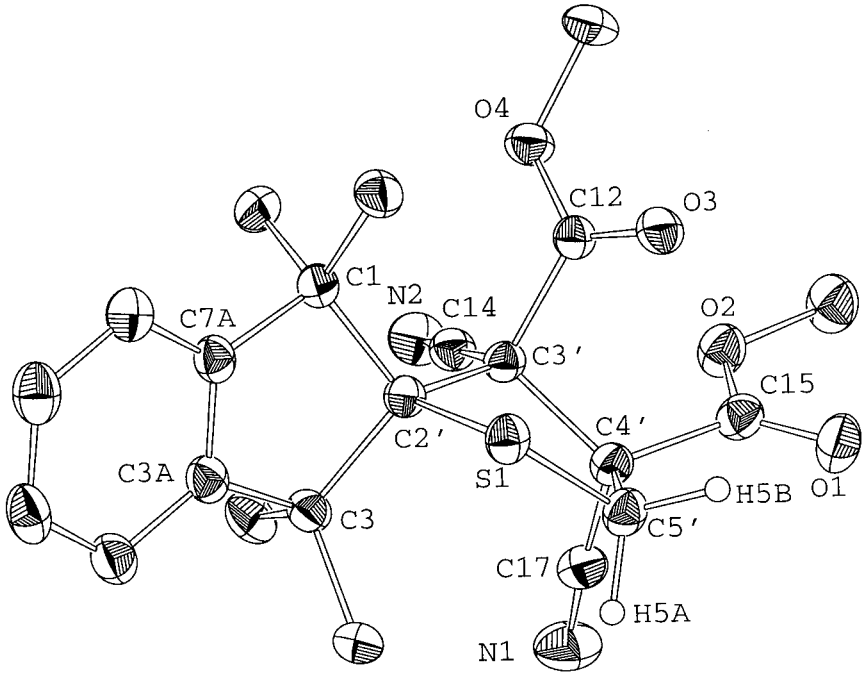


Fig. 1. *X-Ray structure of* cis-*thiolane* **17B**, *ZORTEP plot* (thermal ellipsoids represent 30% probability)

with a folding angle of 41°. The two CO_2Me and the two CN groups form torsion angles at C(3′)–C(4′) of 35° and 34°, respectively, thus diminishing ecliptic strain.

In the *trans*-stereoisomer **18B** (*Fig. 2*), another fairly good envelope conformation of the thiolane ring is found, now with C(5′) as the flap and a folding angle of 48°. The greater conformational flexibility of the *trans*-cycloadduct **18A** allows the thiolane ring to assume a nearly perfect half-chair form (*Fig. 3*) with C(4′) and C(5′) equidistant below (−0.38 Å) and above (0.37 Å) the plane of S(1)–C(2′)–C(3′). Amusingly, the thiolane rings in all three analyzed cycloadducts show different conformations.

The bond lengths of the spirothiolane rings (*Table 2*) are discussed for **18B** as an example. The C–C bonds of the parent thiolane (1.54 Å [19]) correspond to that of diamond. This normal value is observed for the C(4′)–C(5′) bond (1.53 Å) of **18B**. The longer bonds, 1.58 Å for C(3′)–C(4′) and even 1.61 Å for C(2′)–C(3′) and C(2′)–C(3), reflect the increasing *Van der Waals* strain to which the geminal dimethyl groups strongly contribute. A nearly linear dependence of C–C bond length on strain enthalpy has been well documented by *Rüchardt* and *Beckhaus* [20]. The two C–S bond lengths allow the same conclusions: 1.79 Å for S–C(5′) and 1.87 Å for S–C(2′).

The intracyclic bond angles at the S-atom (94–96°) for the three spirothiolanes insignificantly differ from 93.4° for the parent thiolane [19]. The intracyclic torsion angles (*Table 2*) define the ring conformations. Here, the two *trans*-adducts, **18A** and **18B**, are somewhat closer related than the spiroindans **17B** (*cis*) and **18B** (*trans*) among themselves. The exocyclic torsion angles allow the same conclusion.

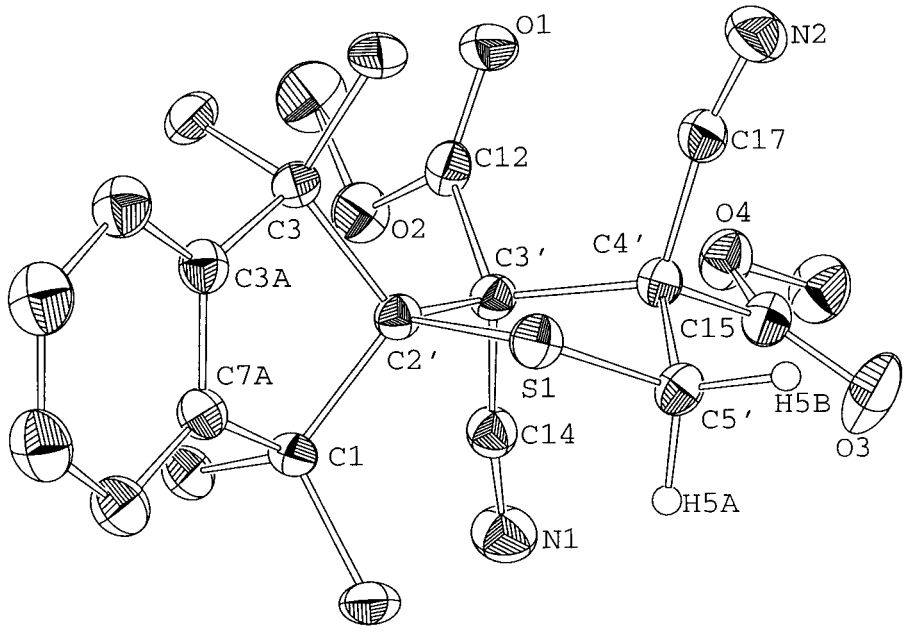


Fig. 2. *X-Ray structure of* trans-*thiolane* **18B**, *ZORTEP plot*

Do the thiolane conformations in the solid state offer a clue to the understanding of the diagnostic ^{1}H-NMR criterion for *cis*- and *trans*-cycloadducts (*Sect. 2.3.2*)? The ZORTEP plots [21] of *Figs. 1–3* show an axial and an equatorial H-atom at C(5) (H5A and H5B), both of which are located in the deshielding cones of the CN and MeOCO groups. The atomic coordinates provide eight values each for the distances of H5A and H5B to C- and N-atom of the two CN groups as well as to the estercarbonyl C- and O-atoms. Distances of 2–3 Å are defined as strong interactions, those of 3–4 Å as weak ones. In the case of the *cis*-adduct **17B**, the data allows us to expect for the axial H–C(5′) one strong and three weak interactions, and for the equatorial H–C(5′) three strong and two weak interactions, suggesting a notable difference in chemical shifts. In the *trans*-adducts **18B** and **18A**, however, both H_{ax}–C(5′) and H_{eq}–C(5′) are influenced by three strong and two weak deshielding contributions, and small shift differences might be the consequence.

It is not rewarding to go beyond this qualitative reasoning. Conformational equilibria of the thiolane rings, established in solution by pseudorotation, offer a tough obstacle to quantitative treatment.

2.3.4. *Stereochemistry of Cycloaddition*. Dimethyl 2,3-dicyanofumarate (**15**) and 2,3-dicyanomaleate (**16**) are rather stable in neutral medium, but equilibrate by nucleophilic catalysis, and **15**/**16** 88 : 12 is established in $CDCl_3$ at 25° [16]. As reported for the cycloadditions of **3** and **4** to **15** and **16**, the thiadiazoline precursors **8** are efficient catalysts of the isomerization **15** ⇌ **16** [10]. The thiadiazolines **8A** and **8B** are likewise active catalysts, and it has to be examined, whether the mentioned loss of stereochemical integrity in the cycloadditions of **5A** and **5B** with **15** (**17A**/**18A** 93 : 7 and **17B**/**18B** 94 : 6) occurred *before*, *during*, or/and *after* the cycloaddition.

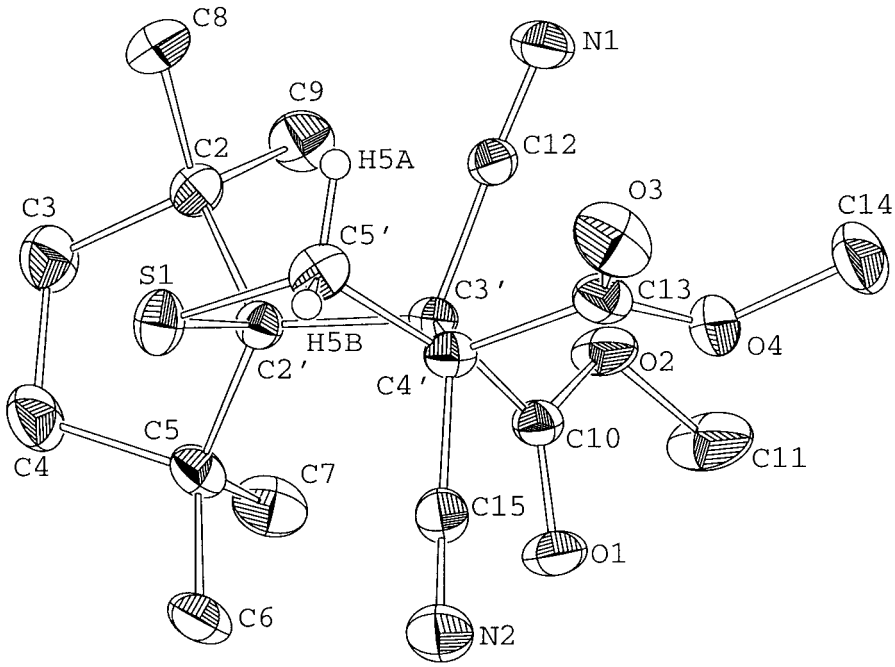


Fig. 3. *X-Ray structure of* trans-*thiolane* **18A**, *ZORTEP plot*

Table 2. *X-Ray Structures of Cycloadducts* **17B** (*cis*), **18B** (*trans*), *and* **18A** (*trans*): *Selected Bond Lengths and Angles*

	17B	**18B**	**18A**		**17B**	**18B**	**18A**
Bond lengths [Å]							
S–C(2′)	1.834	1.865	1.868	C(4′)–C(5′)	1.547	1.531	1.530
C(2′)–C(3′)	1.590	1.606	1.604	C(5′)–S	1.799	1.786	1.785
C(3′)–C(4′)	1.590	1.579	1.583	C(2′)–C(3)	1.624	1.609	1.604
Bond angles [°]							
S–C(2′)–C(3′)	100.9	104.2	103.2	C(4′)–C(5′)–S	109.0	103.6	104.3
C(2′)–C(3′)–C(4′)	107.8	109.1	109.8	C(5′)–S–C(2′)	95.5	94.1	96.2
C(3′)–C(4′)–C(5′)	108.5	104.2	104.6				
Intracyclic torsion angles [°]							
C(5′)–S–C(2′)–C(3′)	−36.7	18.8	12.1	C(3′)–C(4′)–C(5′)–S	3.6	51.7	48.5
S–C(2′)–C(3′)–C(4′)	43.4	8.7	14.7	C(4′)–C(5′)–S–C(1′)	20.4	−42.0	−36.2
C(2′)–C(3′)–C(4′)–C(5′)	−31.3	−38.5	−41.0				
Some exocyclic torsion angles [°] (E = CO_2Me)							
S–C(2′)–C(3′)–CN	167.0	103.8	98.0	NC–C(3′)–C(4′)–CN	34.4	162.9	159.5
S–C(2′)–C(3′)–E	70.7	132.6	138.0	E–C(3′)–C(4′)–E	34.9	74.3	73.0
C(2′)–C(3′)–C(4′)–CN	91.5	79.0	78.4	C(1)–C(2′)–C(3′)–C(4′)	158.6	125.9	
C(2′)–C(3′)–C(4′)–E	154.1	158.6	160.6	C(2)–C(2′)–C(3′)–C(4′)			134.0

The thiadiazoline catalysis by **8C**, but not that by **8D**, could be suppressed by a small amount of strong acid, thus allowing us to study the steric course of cycloadditions of **3** with **15** and **16** [10]. As shown in *Sect. 5.4.1* of *Exper. Part*, the isomerization catalysis

by **8A** and **8B** was fairly well curbed by employing of 0.0076M H_2SO_4 in $CDCl_3$ as solvent.

The reactions of thiadiazoline **8A** with 1.1 equiv. of **15** and **16** (5–10 min at 80°) were performed in NMR tubes, and the ^{1}H-NMR analyses (270 MHz) with a weight standard revealed the formation of *cis*- and *trans*-thiolanes, **17A** and **18A**, respectively, in identical ratios, 91:9 (*Table 3*), indicating a full equilibration of intermediates **19A** and **20A** (*Scheme 3*). The analogous reactions of **8B** with **15** and **16** afforded the *cis*- and *trans*-cycloadducts, **17B** and **18B**, respectively, also in virtually the same ratio. The numerical agreement of **17**/**18** in the structurally different series **A** and **B** is coincidental. After the reactions with 1.1 equiv. of dimethyl 2,3-dicyanomaleate (**16**), the excess of dipolarophile showed only a modest isomerization to the more stable *trans*-isomer **15**. We conclude that the conversion of the reactants to the zwitterions **19** and **20** is virtually irreversible.

Table 3. *Steric Course of Cycloadditions of Thiocarbonyl Ylides* **5A** *and* **5B** *to Dimethyl 2,3-Dicyanofumarate* (**15**) *and Dimethyl 2,3-Dicyanomaleate* (**16**) *in 7.6 mM H_2SO_4 in $CDCl_3$ at 80°*

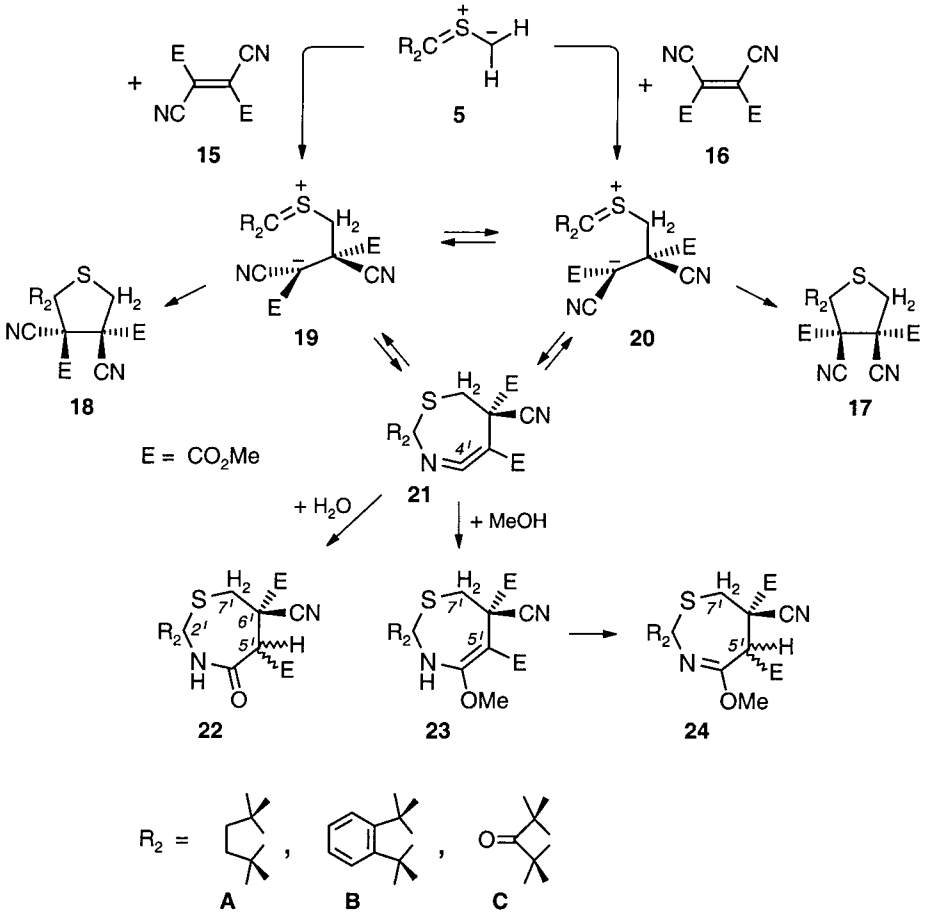
Product	**15**		**16**	
	cis/*trans*	Yield [%][a])	*cis*/*trans*	Yield [%][a])
Thiolanes **17**/**18**				
A	91:9	76	91:9	74
B	90:10	64	91:9	62
C	40:60	67	76:24	87
Cyclopropanes **28**/**27**				
A	*ca.* 30:70	8	*ca.* 40:60	10
B	44:56	16	47:53	17
C		0		0
Thione **7** and ketone **6**				
A		14		12
B		16		17

[a]) Yields calculated on the basis of the amounts of dihydrothiadiazoles **8A**–**8C** consumed.

These results contrast with the likewise nonstereospecific reactions of **8C** with **15** and **16** [10], in which retention still dominated over inversion (*Table 3*). In the case of the zwitterionic intermediates **19C** and **20C**, the rates of rotation (**19** $\rightleftharpoons$ **20**) and cyclization are of similar magnitude. For the pairs **19A** + **20A** and **19B** + **20B** – these are the first examples of its kind – full equilibrium is reached before the cyclization takes place. This is in agreement with greater steric hindrance to cyclization in the zwitterions **19** and **20** of the **A** and **B** series.

The combined yields of thiolanes **17** and **18**, **A** and **B**, are lower in the experiments performed at 80° (62–76%; *Table 3*) than in those carried out in refluxing CH_2Cl_2 (40°), which afforded 97 and 98%, respectively (*Sect. 2.3.1*). The ^{1}H-NMR spectra disclosed side-products: the *trans,cis*-isomers of dimethyl 1,2-dicyanocyclopropane-1,2-dicarboxylate (8–10% in series **A** and 16–17% in series **B**) as well as thiones **7** and ketones **6** (12–17%). It will be shown in *Sect. 2.3.6* that thiolanes **17** and **18** at higher temperature undergo cleavage to form cyclopropanes **27** and **28**, concomitant with stereoisomerization, **17** $\rightleftharpoons$ **18**. The ketones **6** are probably generated by an acid-catalyzed partial hydrolysis of **7** with traces of H_2O.

Scheme 3



We conclude from the experiments shown in *Table 3* that the complete loss of stereoretention in the formation of thiolanes **17**/**18**, **A** and **B**, has to be ascribed to the cycloaddition process itself and not to a preceding equilibration, **15** ⇌ **16**. As for the 'true' ratios of **17**/**18** under conditions of kinetic control, the experiments at 40° without acid (only *ca.* 1% of **27** + **28**) are more reliable: **17A**/**18A** 93 : 7 and **17B**/**18B** 94 : 6. The reason for the kinetic favor of the *cis*-thiolanes **17**, *i.e.*, the cyclization rate, **20** > **19**, is unknown.

2.3.5. *Reactions of Cyclic Ketene Imines with MeOH and H_2O.* The dead-end equilibrium of zwitterions **19** and **20** with the cyclic ketene imine **21** became product-determining, when the reaction of **8** with **15** was performed in the presence of H_2O or MeOH. *In situ* capture by 2 vol-% H_2O in THF furnished the lactams **22A** (74%) and **22B** (87%); in the latter case, the ^{1}H-NMR analysis revealed the continued presence of 4% of the *cis*-thiolane **17B**. Centers C(5′) and C(6′) are stereogenic. The observed diastereoisomer ratio of **22B**, **I**/**II** 85 : 15, was kinetically controlled, and the base-

catalyzed equilibration, *i.e.*, the epimerization at C(5′), led to a ratio of 38:62. The IR spectra of the crystalline lactams **22** showed amide I and NH absorptions, *e.g.*, at 1682 and 3325 cm^{-1} for **22B**.

The interception of **21** with MeOH in $CHCl_3$ (2:98 vol-%) offered a surprise: the primary products were the cyclic ketene *O*,*N*-acetals **23**, which slowly isomerized in solution to give the methyl imidates **24**. After attachment of MeOH at C(4′) of **21**, kinetic protonation is favored at the N-anion, and subsequent tautomerization gives rise to the more stable **24**. This is reminiscent of the protonation of enolate anions, which, under conditions of kinetic control, proceeds at the O-anion. In the trapping of **21C** with MeOH [10], however, the corresponding **23C** did not become NMR-visible, probably because the tautomerization to **24C** is too rapid. The slower process **23** → **24**, **A** and **B**, speaks again for greater steric hindrance in these spiro systems.

The IR spectra of the crystalline ketene *O*,*N*-acetals **23A** and **23B** show the NH band, and the strong absorption of the highly polarized C=C bond appears at 1594 and 1576 cm^{-1}, respectively. The C=O frequency of the conjugated 5′-CO_2Me is shifted under the influence of two electron-releasing β-substituents to 1666 (**23A**) and 1699 cm^{-1} (**23B**), whereas those of the 6′-CO_2Me (1753 and 1746 cm^{-1}) are normal. The C=N frequencies of the lactim methyl ethers were found at 1695 (**24A**) and 1700 cm^{-1} (**24B**), and both of their C=O absorptions were in the normal range.

The conversion **23** → **24**, **A** and **B**, in $CDCl_3$ required weeks at room temperature, but was catalyzed by *tert*-amines. As expected, **24** occurred in two diastereoisomers with respect to C(5′); for **24B** the equilibrium appears to be *ca.* 88:12.

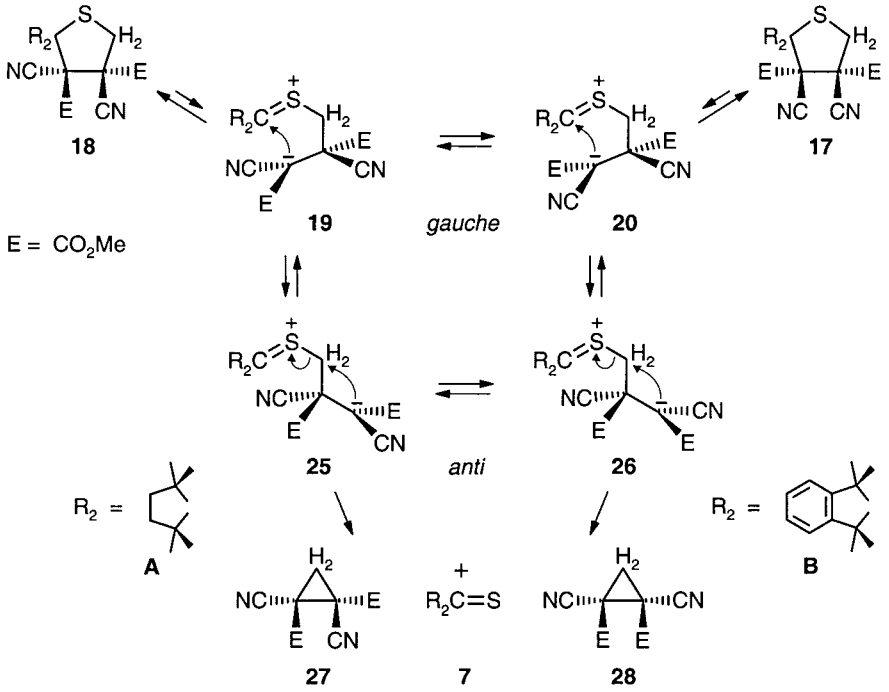
After the reaction of **8B** with **15** (in brackets: **16**) in $CDCl_3$ with 2 vol-% of MeOH, the ^{1}H-NMR analysis indicated 81% (70%) of **23B**, 12% (22%) of **24B**, as well as 3% (4%) of thiolane **17B**, corresponding to 93% (92%) of interception products. It may well be that the zwitterions **19B** and **20B** close the seven-membered ring to **21**, and the five-membered rings of **18** and **17**, respectively, with a rate ratio of 96:4.

In *Scheme 3*, the intermediate ketene imine **21** is in equilibrium with zwitterions **19** and **20**. Since the cumulative bond system constitutes a stereogenic center, we are dealing with two diastereoisomers of **21** that probably interconvert over a barrier and entertain equilibria with **19** and **20**, respectively. The structural differences between the diastereoisomers of **21** are wiped out in the H_2O and MeOH adducts **22**–**24**.

2.3.6. *Stereoisomerization of Thiolanes and Formation of Cyclopropanes.* Two more reactions of thiolanes contribute to the rich variety of reactivities. When *cis*-thiolane **17A** was heated in PhCN to 140° for 10 min, the ^{1}H-NMR analysis indicated quantitative yields of 2,2,5,5-tetramethylcyclopentanethione (**7A**), and of dimethyl *trans*- and *cis*-1,2-dicyanocyclopropane-1,2-dicarboxylate (**27** and **28**, resp.; *Scheme 4*). Identification of **27** and **28** was achieved by comparison with samples obtained in our laboratory from CH_2N_2 and **15** *via* thermolysis of the *trans*- and *cis*-pyrazolines [22]. In the thermolysis of **17A**, the cyclopropanes **27** (*trans*) and **28** (*cis*) were observed in a ratio of 49:51. Since isolated **27** was stable in PhCN at 140° for 5 h, the ratio must be the result of kinetic control.

When the thermolysis of **17A** was performed under milder conditions, at 87° in C_6D_6, a *cis* → *trans* isomerization of the thiolane, **17A** ⇌ **18A**, was observed besides the cleavage to **7A** and **27**, **28**. The ratio **17A**/**18A** 100:0 at the beginning decreased to

Scheme 4



59 : 41 after 15 h, and to 42 : 58 after 45 h at 87°. However, after 45 h, only 38% of thiolanes remained, as the irreversible cleavage became dominant. Thus, the equilibrium **17A** ⇌ **18A** cannot be established, and 35 : 65 is estimated from the time dependence of **17A**/**18A**.

In *Scheme 4*, the geometric isomerization of the thiolanes as well as the fragmentation to **7**, and **27** and **28** are ascribed to zwitterionic intermediates. We observed cyclopropane formation as a side reaction in the cycloadditions of a tetrasubstituted thiocarbonyl ylide (dimethyl derivative of **3**) to TCNE [8] and **15** [1]. Since S_N2 front-side attack is unfavorable, even in intramolecular cases, we assume that the rapidly equilibrating pool of zwitterions includes also the *anti*-conformations **25** and **26**. The latter should have higher dipole moments than the *gauche*-forms **19** and **20**, but may suffer less from *Van der Waals* strain. The *anti*-forms **25** and **26** offer the right stereoelectronic environment for cyclopropane formation by intramolecular nucleophilic displacement.

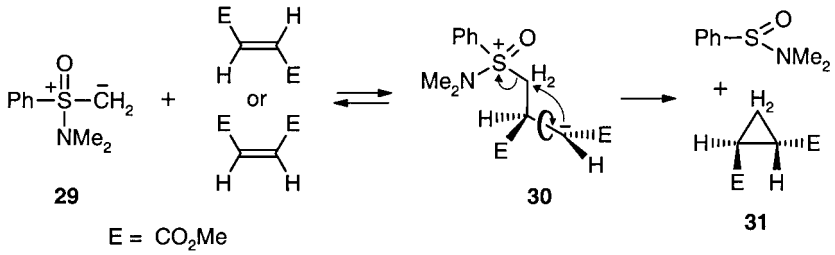
The thermolysis of the *cis*-thiolane **17B** of the spiro-tetramethylindan series reveals the same pair of parallel reactions, as observed for **17A**. On heating at 100° ($CDCl_3$), the ratio **17B**/**18B** reached 75 : 25 after 56 h and 55 : 45 after 216 h, but cyclopropane formation amounted to 40% (56 h) and 78% (216 h).

The thiolane equilibration and the cleavage reaction are competing; the evaluation of the complex rate equation is hampered by lack of data. The formation of the colored **7** invited spectrophotometric measurement. Some tentative kinetic runs dealt with the

solvent dependence. A thorough kinetic study would promise to shed more light on the reaction scheme.

The formation of **27** and **28** shows that thiocarbonyl ylides **5** share with other sulfonium ylides the ability to transfer methylene to electrophilic C=C bonds. The dimethyloxosulfonium methylide is a well-tested reagent [23]. The lack of stereospecificity is illustrated with the less aggressive (hence storable) methylide **29**, which converted both dimethyl fumarate and dimethyl maleate to the same *trans*-dicarboxylate **31** (*Scheme 5*), and excess of dimethyl maleate was transformed to dimethyl fumarate [24]. The reversible formation of a zwitterionic intermediate (here **30**), capable of undergoing rotation about the C–C bond, coresponds to the generally accepted mechanism.

Scheme 5



2.3.7. *Mass Spectra.* The assignments of molecular formulae of fragments were often supported by the intensities of isotope peaks (^{13}C, ^{34}S) and high-resolution data. The thiolanes with the spirocyclopentane system (**12A** and **17A**) show an early breakdown of the carbocyclic ring involving the cascade $[CH(CH_2)_n]^+$, $n = 5-2$, *i.e.*, from trimethylallyl to allyl cation. Many of the S-containing fragments suggest cations and radical cations of thiophene derivatives. The indanyl residue of the spirothiolanes **12B** and **17B** is more resistant. For example, $[M - Me - CH_2(CN)_2]^+$ and $[M - Me - SCH_2C(CN)_2]^+$ are strong fragments of **12B** and indicate the degradation of the thiolane ring, although a fragmentation reversing the thermal (3 + 2) cycloaddition was not observed. The cascade of methylated indenyl cations occurs to variable extents.

The products of interception with H_2O or MeOH, *i.e.*, the 1,3-thiazepine derivatives, show manifold S-retaining and S-losing fragmentations. Richly populated are the peaks $[M - S - CH_3]^+$ and $[M - S - CN]^+$, the latter sometimes as base peak. Obviously, M^+ opens the seven-membered rings at the S–C(2′) bond and invites the successive chopping up of the side chain. The cascades of the methylated allyl and indenyl cations in the mass spectra of the **A** and **B** series, respectively, are pronounced.

We express our sincere gratitude to the *Fonds der Chemischen Industrie*, Frankfurt, for the continued support of our research. *Helmut Huber* contributed many NMR spectra, and *Reinhard Seidl* was responsible for the mass spectra. *Helmut Schulz* and *Magdalena Schwarz* carried out the numerous elemental analyses.

Experimental Part

1. *General.* For instruments, see [8]. Column chromatography (CC): on silica gel. Prep. layer chromatography (PLC): 20 × 20 cm glass plates, 2-mm *Merck* silica gel *60PF*$_{254}$. IR: KBr pellets, if not stated

otherwise. ^{1}H- (80 MHz), ^{13}C-NMR (22.5 MHz; multiplicities from comparison with off-resonance spectra): acid-free $CDCl_3$, if not stated otherwise; most of the quant. ^{1}H-NMR analyses were carried out with *sym*-tetrachloroethane (5.93 ppm) or *as*-tetrachloroethane (4.28 ppm), henceforth *sym*-tet and *as*-tet. MS and high-resolution (HR) MS: intensities of isotope peaks reported as ^{13}C % calc./% found.

2. *6,6,9,9-Tetramethyl-4-thia-1,2-diazaspiro[4.4]non-1-ene* (**8A**). 2.1. *2,2,5,5-Tetramethylcyclopentanethione* (**7A**). *2,2,5,5-Tetramethylcyclopentanone* [25] (**6A**; 22.7 g, 162 mmol) and trimethyl orthoformate (28.4 g) in abs. MeOH (150 ml) was saturated with HCl and H_2S at 0°, kept in a closed flask for 4 weeks, and worked up with pentane (200 ml) and ice (400 g). The org. phase was concentrated to *ca.* 80 ml, and CC with pentane furnished **7A** (12.7 g, 50%) (unreacted ketone (10.6 g, 47%) eluted with Et_2O). Orange crystals. M.p. 64–66° ([26]: 72–74°). IR: 993*m*, 1100*m*, 1191*m*, 1275*m*, 1358*m*, 1459*m* (br.); 2888*m*, 2960*s* (C–H). ^{1}H-NMR: 1.17 (*s*, 4 Me); 1.92 (*s*, 2 CH_2). MS (25°): 156 (10, M^+), 142 (33, $[M-CH_2]^+$), 141 (15, $[M-Me]^+$), 140 (17, $[M-CH_4]^+$), 127 (80, $[141-CH_2]^+$, $C_7H_{11}S^+$ (dimethyl(methylthio)cyclopentenyl$^+$)), 125 (32), 123 (28, $[M-SH]^+$ (tetramethylcyclopentenyl$^+$)), 111 (31), 109 (43, $C_8H_{13}^+$ (trimethylcyclopentenyl$^+$)), 97 (48), 57 (100, *t*-Bu$^+$), 55 (73, $C_4H_7^+$ (methylallyl$^+$)).

2.2. *Reaction with CH_2N_2.* When **7A** (13.0 g, 83.2 mmol) in pentane (50 ml) was treated with ethereal CH_2N_2 (*ca.* 1.4 equiv.) at −10°, the orange color of **7A** disappeared within 4 h. Evaporation at −20°/15 mm left an off-white residue, which was twice recrystallized from pentane at −78° to give colorless **8A** (11.8 g, 72%). M.p. 60–61°. ^{1}H-NMR: 0.67 (*s*, 2 Me), 1.13 (*s*, 2 Me); 1.92 (*m*, 4 H); 5.62 (*s*, CH_2(3)). Anal. calc. for $C_{10}H_{18}N_2S$ (198.32): C 60.56, H 9.15, N 14.13, S 16.17; found: C 60.43, H 9.11, N 13.92, S 16.15.

2.3. *Kinetics of N_2 Extrusion from* **8A**. The volumetric technique was previously described in [27] and applied to *ca.* 0.25M **8A** in xylene at 40°. The first-order evaluation up to 78–88% reaction gave $k_1 \cdot 10^4$ [s^{-1}] = 1.04, 1.08, and 1.00 in three runs ($r = 0.9995$). An experiment in the presence of 1.1 equiv. of TCNE (red CT complex) in xylene at 40° furnished $k_1 \cdot 10^4$ [s^{-1}] = 1.22 ($r = 0.9998$). Runs in abs. THF at 40° produced $k_1 \cdot 10^4$ [s^{-1}]: 0.924, 0.910, 0.955, and, in the presence of 1.1 equiv. of TCNE, 1.01. Further rate constants $k_1 \cdot 10^4$ [s^{-1}]: 0.726, 0.694, and 0.686 in MeCN at 40°; 1.75, 1.71 in xylene at 45°; 3.03, 3.29 in xylene at 50°.

2.4. *4,4,7,7-Tetramethyl-1-thiaspiro[4.2]heptane* (**9A**). Compound **8A** (10.0 mmol) in benzene (10 ml) was heated at 40° for 15 h. Distillation at 83–85° (bath)/15 mm and recrystallization from MeOH furnished **9A** (1.02 g, 60%). An experiment in C_6D_6 with ^{1}H-NMR analysis (*as*-tet as standard) provided 81% of **9A**. M.p. 54–56°. IR: 1365*m*, 1380*m*, 1465*m* (br.), 1653*m*, 2868*m*, 2962*s* (C–H). ^{1}H-NMR: 0.88, 1.03 (2*s*, 2 × 2 Me); 1.70 (*m*, CH_2(5), CH_2(6)); 2.35 (*s*, CH_2(2)). ^{1}H-NMR (C_6D_6): 0.70, 1.04 (2*s*, 4 Me); 1.53 (*m*, 4 H); 2.14 (*s*, CH_2(2)). ^{13}C-NMR: 27.4 (*q* + *t*, 2 Me + C(2)); 31.3 (*q*, 2 Me); 39.0 (*t*, C(5), C(6)); 41.9 (*s*, C(4), C(7)); 69.3 (*s*, C(3)). MS (20°): 170 (28, M^+). 138 (17, $[M-S]^+$), 123 (100, $[M-Me-S]^+$), 109 (46, $C_8H_{11}^+$). Anal. calc. for $C_{10}H_{18}S$ (170.31): C 70.52, H 10.65, S 18.83; found: C 70.13, H 10.74, S 18.82.

2.5. *1-Methoxy-2,2,5,5-tetramethyl-1-(methylsulfanyl)cyclopentane* (**10A**). *a*) After heating **8A** (2.0 mmol) in MeOH (10 ml) at 65° for 1 h, distillation (110°/0.01 mm) afforded a colorless viscous oil that solidified (m.p. not sharp); **10A** was not obtained anal. pure. IR: 1079*s* (br., C–O), 1366*m*, 1383*m*, 1465*m* (br.); 2873*m*, 2945*s* (br., C–H). ^{1}H-NMR: 1.14, 1.20 (2*s*, 2 × 2 Me); 1.53 (*s*, CH_2(3), CH_2(4)); 1.95 (*s*, MeS); 3.45 (*s*, MeO). ^{13}C-NMR: 12.8 (*q*, MeS); 27.4, 29.4 (2*q*, 2 × 2 Me); 39.3 (*t*, C(3), C(4)); 50.2 (*s*, C(2), C(5)); 53.3 (*q*, MeO); 103.8 (*s*, C(1)). Anal. calc. for $C_{11}H_{22}OS$ (202.35): C 65.29, H 10.96; found: C 64.36, H 10.64. *b*) In an experiment without distillation, ^{1}H-NMR analysis (*sym*-tet) indicated 98% of **10A**.

3. *2,2′,3,5′-Tetrahydro-1,1,3,3-tetramethylspiro[1*H*-indene-2,2′-[1,3,4]thiadiazole]* (**8B**). 3.1. *Preparation.* The reaction of *2,3-dihydro-1,1,3,3-tetramethyl-2*H*-indene-2-thione* (**7B**) [28] with CH_2N_2 in Et_2O at −20° proceeded in some min, and crystallization from Et_2O/pentane at −78° afforded **8B** (82%). M.p. 94° (dec.). IR: 765*s* (arom. out-of-plane deform.), 991*s*, 1240*m*, 1377*m*, 1385*m*; 1467*m*, 1483*m*, 1579*m* (arom. ring vibr., N=N). ^{1}H-NMR: 0.97, 1.38 (2*s*, 2 × 2 Me); 5.73 (*s*, CH_2(5′)); 7.18 (br., *s*, 4 arom. H). ^{13}C-NMR: 22.4, 31.1 (2*q*, 2 × 2 Me); 50.6 (*s*, C(1), C(3)); 84.2 (*t*, C(5′)); 122.5, 127.4 (2*d*, 4 arom. C); 131.1 (*s*, C(2)); 148.4 (*s*, 2 arom. C_q). Anal. calc. for $C_{14}H_{18}N_2S$ (246.37): C 68.25, H 7.37, N 11.37, S 13.02; found: C 68.67, H 7.40, N 11.09, S 12.74.

3.2. *First-Order Rate Constants of N_2 Elimination.* $k_1 \cdot 10^4$ [s^{-1}]: 1.74, 1.63 in xylene at 50.1°; 0.798, 0.808 in MeCN at 50.1°, 161 in xylene at 100°.

3.3. *2,3-Dihydro-1,1,3,3-tetramethylspiro[1*H*-indene-2,2′-thiirane]* (**9B**). Workup of the above xylene soln. furnished colorless crystals from MeOH. For the NMR determination of yield (*as*-tet), **8B** (0.42 mmol) in C_6D_6 (0.5 ml) was heated to 50° for 17 h; the integral at 2.30 ppm showed 100%. M.p. 95–96°. IR: 755*s* (arom. out-of-plane deform.), 1358*m*, 1375*m*; 1452*m*, 1480*s*, 1585*w* (arom. ring vibr.). ^{1}H-NMR: 1.11, 1.34 (2*s*, 2 × 2 Me); 2.54 (*s*, CH_2(3′)); 6.8–7.2 (*m*, 4 arom. H). ^{13}C-NMR: 25.6, 32.9 (2*q*, 2 × 2 Me); 28.5 (*t*, CH_2(3′)); 45.6 (*s*, C(1), C(3)); 68.1 (*s*, C(2)); 122.5, 127.2 (2*d*, 2 × 2 arom. C); 148.8 (*s*, 2 arom. C_q). MS (30°): 218 (14, M^+), 203 (2, $[M-Me]^+$), 186 (21, $[M-S]^+$), 171 (100, $[M-S-Me]^+$, $C_{13}H_{15}^+$), 157 (40, $C_{12}H_{13}^+$ (trimethylindenyl$^+$)), 143 (8,

$C_{11}H_{11}^+$ (dimethylindenyl$^+$)), 141 (23), 129 (9, $C_{10}H_9^+$ (methylindenyl$^+$)), 128 (12, $C_{10}H_8^+$ (naphthalene$^+$)), 115 (11, (indenyl$^+$)), 91 (6, $C_7H_7^+$), 77 (13, Ph$^+$). Anal. calc. for $C_{14}H_{18}S$ (218.35): C 77.01, H 8.31, S 14.69; found: C 76.99, H 8.09, S 14.72.

3.4. *2,3-Dihydro-2-methoxy-1,1,3,3-tetramethyl-2-(methylsulfanyl)-1*H*-indene* (**10B**). The extrusion of N_2 (3 h, 60°) from **8B** (2.0 mmol) in MeOH (5 ml) and evaporation led to formation of a colorless oil. ^{1}H-NMR analysis (*sym*-tet) (2.04 (*s*) and 3.54 (*s*)) indicated 95 and 91% of **10B**, resp. Twice distilling at 100–110° (bath)/0.01 Torr provided **10B** (360 mg, 72%) as a highly viscous oil. IR (film): 754*s* (arom. out-of-plane deform.), 1080 + 1088v*s* (br., C–O), 1379*m*; 1465*m*, 1483*s*, 1592*w* (arom. ring vibr.). ^{1}H-NMR: 1.39, 1.45 (2*s*, 2 × 2 Me); 2.04 (*s*, MeS); 3.54 (*s*, MeO); 7.06 (center of *AA′BB*, 4 arom. H). ^{13}C-NMR: 12.8 (*q*, MeS); 27.4, 29.4 (2*q*, 2 × 2 Me); 53.4 (*q*, MeO); 53.5 (*s*, C(1), C(3)); 105.3 (*s*, C(2)); 121.8, 127.1 (2*d*, 4 arom. C); 148.4 (*s*, 2 arom. C_q). MS (30°): 203 (100, $[M-MeS]^+$, ^{13}C 15.7/14.8), 188 (6, $[203-Me]^+$), 173 (25, $[203-2\,Me]^+$, $C_{12}H_{13}O^+$; ^{13}C 3.35/3.31), 171 (61 $[203-MeOH]^+$, $C_{13}H_{15}^+$), 157 (11, $C_{11}H_{13}^+$), 156 (35 $[171-Me]^+$), 145 (13), 143 (12, $C_{11}H_{11}^+$), 141 (14), 129 (20, $C_{10}H_9^+$), 128 (17, naphthalene$^+$), 115 (13, $C_9H_7^+$). Anal. calc. for $C_{15}H_{22}OS$ (250.39): C 71.95, H 8.86, S 12.81; found: C 72.39, H 8.73, S 12.72.

4. *Reactions of Thiocarbonyl Ylides* **5** *with Ethenetetracarbonitrile*. 4.1. *2,2,5,5-Tetramethylspiro[cyclopentane-1,2′-thiolane]-3′,3′,4′,4′-tetracarbonitrile* (*=6,6,9,9-Tetramethyl-1-thiospiro[4.4]nonane-3,3,4,4-tetracarbonitrile;* **12A**). The reaction of **8A** with 1.1 equiv. of TCNE in abs. THF for 10 h at 40° provided colorless **12A** (Et_2O), m.p. 176° (dec.), which turned brown on storage. The ^{1}H-NMR analysis with *sym*-tet indicated 84% of **12A** (*s*, 2 H, at 3.76 ppm). IR: 1376*m*, 1468*s*; 2245v*w* (C≡N). ^{1}H-NMR: 1.49, 1.75 (2*s*, 2 × 2 Me); superimposed 1.65–1.80 (unresolved *AA′BB′*, $CH_2(3)$, $CH_2(4)$); 3.76 (*s*, $CH_2(5')$). ^{13}C-NMR: 27.6, 29.9 (2*q*, 2 × 2 Me); 39.1 (*t*, C(5′)); 40.9 (*t*, C(3), C(4)); 47.8, 54.9 (2*s*, C(3′), C(4′)); 50.4 (*s*, C(2), C(5)); 81.3 (*s*, C(1)); 111.5, 112.0 (2*s*, 2 × 2 CN). MS (75°): 298 (0.3, M^+), 283 (0.8, $[M-Me]^+$, ^{13}C 0.14/0.11), 246 (4), 245 (5), 228 (16, $[M-C_6H_{10}^+)$, 220 (6, $[M-CH_2(CN)_2]^+$, $C_{12}H_{16}N_2S^+$, ^{13}C 0.92/0.94), 187 (5, $[M-HSCH_2C(CN)_2]^+$), 176 (13), 173 (9), 150 (19, $[220-C_5H_{10}]^+$), 149 (11), 133 (13), 91 (9, $C_7H_7^+$), 83 (57, $C_6H_{11}^+$), 78 (33, $C_6H_6^+$), 77 (25), 69 (100, $C_5H_9^+$), 55 (27, $C_4H_7^+$), 52 (10), 51 (23), 41 (40, allyl$^+$). Anal. calc. for $C_{16}H_{18}N_4S$ (298.40): C 64.40, H 6.08, N 18.78, S 10.75; found: C 64.57, H 6.14, N 18.57, S 10.78.

4.2. *6′,7′-Dihydro-4′-methoxy-2,2,5,5-tetramethylspiro[cyclopentane-1,2′(5′*H*)-[1,3]thiazepine]-5′,6′,6′-tricarbonitrile* (*=10-Methoxy-1,1,4,4-tetramethyl-6-thia-11-azaspiro[4.6]undec-10-ene-8,8,9-tricarbonitrile*; **14A**). *a*) Compound **8A** and TCNE (2.00 mmol each) in $CDCl_3$/MeOH (98:2 vol-%, 25 ml) gave an orange-red soln. (CT complex), which was heated 30 min to 65°. After evaporation and trituration with Et_2O, colorless **14A** (250 mg, 385) was from MeOH. M.p. 118–119° (Et_2O). IR: 897*m*, 994*m*, 1248*s* (br., C–O), 1699v*s* (C=N), 2252v*w* (C=N). ^{1}H-NMR: 0.94, 1.08 (2*s*, 2 Me); 1.24 (*s*, 2 Me); 1.36–2.19 (*m*, $CH_2(3)$, $CH_2(4)$); 3.19, 3.52 (*AB*, *J* = 15.0, $CH_2(7')$); 3.80 (*s*, MeO); 5.50 (*s*, H–C(5′)). ^{13}C-NMR: 27.6, 27.8, 28.0, 28.4 (4*q*, 4 Me); 36.7, 38.0, 38.2 (3*t*, C(3), C(4), C(7′)); 37.1 (*s*, C(6′)); 39.7 (*d*, C(5′)); 49.5, 52.6 (2*s*, C(2), C(5)); 55.0 (*q*, MeO); 84.9 (*s*, C(1)); 111.5, 112.1, 112.4 (3*s*, 3 CN); 143.4 (*s*, C(4′)). MS (75°): 330 (9, M^+), 315 (16, $[M-Me]^+$), 303 (18, $[M-HCN]^+$), 288 (36, $[M-HCN-Me]^+$, $C_{15}H_{18}N_3OS^+$, ^{13}C 6.1/5.8; HR: calc. 288.117, found 288.110), 283 (41, $[M-S-Me]^+$, $C_{16}H_{19}N_4O^+$; HR: calc. 283.156, found 283.158), 272 (26, $[M-S-CN]^+$, $C_{16}H_{22}N_3^+$; HR: calc. 272.176, found 272.176), 269 (20), 261 (22, $[M-C_5H_9]^+$), 260 (32), 259 (62), 252 (72), 251 (85, $[283-MeOH]^+$), 246 (32, $[261-Me]^+$), 237 (93, $[252-Me]^+$), 234 (41, $[303-C_5H_9]^+$), 233 (52), 232 (100, $[288-C_4H_8]^+$, $C_{11}H_{10}N_3OS^+$; HR: calc. 232.054, found 232.051), 227 (11), 219 (14), 218 (21), 209 (38), 205 (43), 192 (33), 188 (40), 184 (67), 169 (21), 167 (12), 166 (23), 123 (74, $C_9H_{15}^+$), 111 (13), 82 (18), 69 (77, $C_5H_9^+$), 68 (13), 67 (13), 56 (13, $C_4H_8^+$), 55 (30, $C_4H_7^+$), 41 (55, allyl$^+$). Anal. calc. for $C_{17}H_{22}N_4OS$ (330.44): C 61.79, H 6.71, N 16.96, S 9.70; found: C 61.79, H 6.74, N 16.77, S 9.74.

b) Compound **8A** (227 μmol) and TCNE (235 μmol) in $CDCl_3$ (1 ml, with 2 vol-% of MeOH) reacted 5 min at 80°. ^{1}H-NMR Analysis (*sym*-tet) indicated 76% of **14A** (3.81 and 5.50 ppm).

4.3. *2,3-Dihydro-1,1,3,3-tetramethylspiro[1*H*-indene-2,2′-thiolane]-3′,3′,4′,4′-tetracarbonitrile* (**12B**). Compound **8B** (370 mg, 1.50 mmol) and TCNE (218 mg, 1.70 mmol) in abs. THF (15 ml) were stirred at 65° for 4 h. **12B** (350 mg, 67%) came from MeOH at –20° as yellow-brown crystals, which were pale-yellow after recrystallization from MeOH. M.p. *ca.* 177° (dec.). IR: 783*s* (arom. out-of-plane deform.), 1390*s*, 1396*s*; 1450*s*, 1472*s*, 1489*s*, 1494*w* (arom. ring. vibr.), 2247*w* (C≡N). ^{1}H-NMR: 1.89 (*s*, 4 Me); 3.86 (*s*, $CH_2(5')$); 7.01–7.33 (*m*, 4 arom. H). ^{13}C-NMR: 27.9, 30.7 (2*q*, 2 × 2 Me); 39.1 (*t*, C(5′)); 48.6, 54.4 (2*s*, C(3′), C(4′)); 53.5 (*s*, C(1), C(3)); 82.4 (*s*, C(2)); 111.4, 111.9 (2*s*, 2 × 2 CN); 122.1, 128.7 (2*d*, 4 arom. C); 145.7 (*s*, 2 arom. C_q). MS (80°): 346 (26, M^+, ^{13}C 5.8/5.6), 253 (35, $[M-Me-CH_2C(CN)_2]^+$, $C_{15}H_{13}N_2S^+$, ^{13}C 5.9/5.9, $^{13}C_2 + {}^{34}S$ 2.0/1.7), 236 [21, $[M-SCH_2C(CN)_2]^+$, $C_{16}H_{16}N_2^+$, ^{13}C 3.8/4.1), 221 (84, $[M-Me-SCH_2C(CN)_2]^+$, $C_{15}H_{13}N_2^+$, ^{13}C 14.1/14.6, $^{13}C_2$ 1.1/1.5, (dicyanomethylene)trimethylindanyl$^+$), 206 (23, $[221-Me]^+$, $C_{14}H_{10}N_2^+$, HR: calc. 206.0842, found 206.0854), 205 (20), 177 (14), 159 (100, $C_{12}H_{15}^+$, ^{13}C 13.3/12.5, free of S), 157 (16, $C_{12}H_{13}^+$ (trimethylindenyl$^+$), ^{13}C

2.1/2.7), 141 (13), 117 (30, $C_9H_7^+$ (indenyl$^+$), ^{13}C 3.0/3.4), 78 (10). Anal. calc. for $C_{20}H_{18}N_4S$ (346.44): C 69.33, H 5.24, N 16.17, S 9.26; found: C 69.46, H 5.23, N 16.21, S 9.27.

4.4. *2,3,6′,7′-Tetrahydro-4′-methoxy-1,1,3,3-tetramethylspiro[1*H*-indene-2,2′(5′*H*)-[1,3]thiazepine]-5′,6′,6′-tricarbonitrile* (**14B**). *a*) Compound **8B** (493 mg, 2.00 mmol) and TCNE (282 mg, 2.20 mmol) in $CDCl_3$ (25 ml, MeOH content 2 vol-%) were heated 4 h at 65°. After evaporation of the solvent, the light-brown oil crystallized from MeOH: **14B** (450 mg, 59%). M.p. 140–141° (MeOH). IR: 759*m*, 902*m*, 1240*s* (br., C–O); 1451*m*, 1483*m*, 1580*w* (arom. ring vibr.), 1695*s* (C=N), 2252*w* (C≡N). ^{1}H-NMR: 1.28, 1.41 (2*s*, 2 Me); 1.46 (*s*, 2 Me); 3.42, 3.64 (*AB*, *J* = 16.0, CH_2(7′)); 3.55 (*s*, MeO); 5.70 (*s*, H–C(5′)); 6.95–7.25 (*m*, 4 arom. H). ^{13}C-NMR: 25.1, 26.9, 28.6, 31.2 (4*q*, 4 Me); 36.4 (*t*, C(7′)); 37.3 (*s*, C(6′)); 40.0 (*d*, C(5′)); 53.1, 55.7 (2*s*, C(1), C(3)); 55.1 (*q*, MeO); 86.4 (*s*, C(2)); 111.5, 112.0, 112.4 (3*s*, 3 CN); 122.0, 122.3, 127.37, 127.55 (4*d*, 4 arom. C); 144.1, 146.4, 148.1 (3*s*, C(4′), 2 arom. C_q). MS (115°): 378 (4, M^+), 351 (25, [M – HCN, $C_{20}H_{21}N_3OS^+$, ^{13}C 5.6/5.9), 336 (25, [351 – Me]$^+$, ^{13}C 5.3/5.3), 331 (16, [M – S – Me]$^+$), 320 (35, [M – S – CN]$^+$, $C_{20}H_{22}N_3O^+$, ^{13}C 7.8/7.4), 317 (19, $C_{19}H_{17}N_4O)^+$, ^{13}C 4.1/4.3; HR: calc. 317.140, found 317.136), 308 (26, $C_{18}H_{16}N_2OS^+$, ^{13}C 5.1/4.8; HR: calc. 308.098, found 308.082), 306 (14, $C_{19}H_{20}N_3O^+$, ^{13}C 2.9/2.9), 299 (100, $C_{19}H_{15}N_4^+$; HR: calc. 299.129, found 299.129), 290 (36, $C_{18}H_{16}N_3O^+$, ^{13}C 7.2/7.8; HR: calc. 290.129, found 290.121), 285 (17, $C_{18}H_{13}N_4^+$, ^{13}C 2.0/2.4), 260 (11), 205 (15), 171 (59, $C_{13}H_{15}^+$), 157 (12, $C_{12}H_{13}^+$), 156 (23, $C_{12}H_{12}^+$), 155 (11), 143 (10, $C_{11}H_{11}^+$), 141 (16), 129 (21, $C_{10}H_9^+$), 128 (21, naphthalene$^+$), 119 (18), 115 (15, $C_9H_7^+$), 91 (12, tropylium$^+$). Anal. calc. for $C_{21}H_{22}N_4OS$ (378.48): C 66.64, H 5.86, N 14.80, S 8.47; found: C 66.81, H 5.87, N 14.67, S 8.45.

b) Compound **8B** (155 μmol) and TCNE (164 μmol) in $CDCl_3$ (1 ml + 2 vol-% MeOH) were reacted in a sealed NMR tube at 80° for 10 min. With dibenzyl as weight standard, the ^{1}H-NMR (270 MHz, JEOL) showed unconsumed **8B** (14 μmol; 0.97, 5.75 ppm); **14B** (115 μmol; 1.27, 3.42 + 3.64, 5.70 ppm); **12B** (4 μmol; 1.88, 3.86 ppm); a further product (16 μmol, with *s* at 4.68 (br., NH) and *s* at 3.98 (OMe) is probably the ketene *N,O*-acetal structure corresponding to **23**.

5. *Reactions with Dimethyl 2,3-Dicyanofumarate* (**15**) *and 2,3-Dicyanomaleate* (**16**). 5.1. *Dimethyl* cis-*3′,4′-Dicyano-2,2,5,5-tetramethylspiro[cyclopentane-1,2′-thiolane]-3′,4′-dicarboxylate* (= cis-*3,4-Dicyano-6,6,9,9-tetramethyl-1-thiaspiro[4.4]nonane-3,4-dicarboxylate*; **17A**) *and* trans-*Isomer* **18A**. 5.1.1. *Preparation*. *a*) Compound **8A** (4.80 g, 24.2 mmol) and **15** (5.09 g, 26.2 mmol) [29] in CH_2Cl_2 (100 ml) were refluxed for 12 h. At 41°, the generation of **5A** from **8A** is slow, and the little soluble **15** has time to dissolve. Evaporation left a pale-orange oil, which was triturated with Et_2O (50 m), and the excess **15** was filtered. Removal of Et_2O and recrystallization from MeOH furnished colorless **15A** (6.27 g, 71%; m.p. 114–117°). The oily residue of the mother liquor was separated by CC with pentane/Et_2O 80:20. Compound **18A** moves faster than **17A** and was crystallized from pentane/Et_2O (m.p. 106–108°; 80 mg, 0.9%).

b) The ^{1}H-NMR analysis (C_6D_6, *sym*-tet) of the crude product was based on the *d* at 3.73 (1 H) for **17A** and the *s* at 3.31 (3 H) for **18A**; the integrals indicated 90% of **17A** and 7% of **18A**.

c) A more productive path to the *trans*-isomer **18A** was based on the isomerization **17A** → **18A** on heating, concomitant with fragmentation (see *Sect. 5.6*). **8A** (5.00 mmol) and **15** (5.5 mmol, finely powdered) in toluene (10 ml) were stirred at 90° for 12 h. Separation by PLC gave **18A** (275 mg, 15%; m.p. 106–108°), and **17A** (393 mg, 22%; m.p. 114–117°).

5.1.2. *Data of* **17A**. IR: 915*m*, 1035*m*; 1216*m* + 1257v*s* (br. C–O); 1430*s* (br.); 1745v*s* (br., C=O); 2256v*w* (C≡N). ^{1}H-NMR (300 MHz): 1.17, 1.47, 1.75, 1.83 (4*s*, 4 Me); 1.58–1.82 (*m*, CH_2(3), CH_2(4)); 3.50, 3.91 (*AM*, *J* = 12.5, H_a–C(5′), H_b–C(5′) 3.85, 3.88 (2*s*, 2 MeO); (C_6D_6): 1.09, 1.31, 1.78, 1.85 (4*s*, 4 Me); 1.18–1.60 (*m*, CH_2(3), CH_2(4)); 3.08, 3.73 (*AM*, *J* = 12.6, CH_2(5′)); 3.09, 3.16 (2*s*, 2 MeO). ^{13}C-NMR: 26.9, 27.9, 30.8, 31.3 (4*q*, 4 Me); 37.0, 41.1, 42.6 (3*t*, C(3), C(4), C(5′)); 49.6, 51.3 (2*s*, C(2), C(5)); 54.2, 54.8 (2*q*, 2 MeO); 61.2, 63.0 (2*s*, C(3′), C(4′)); 83.1 (*s*, C(1)); 116.4, 117.1 (2*s*, 2 CN); 164.9, 165.8 (2*s*, 2 C=O). MS (60°): 364 (1.9, M^+), 305 (4.8, [M – CO_2Me]$^+$, $C_{16}H_{21}N_2O_2S^+$, ^{13}C 0.85/0.88), 294 (13, [M – C_5H_{10}]$^+$, $C_{13}H_{14}N_2O_4S^+$, $^{13}C_2$ + ^{34}S 0.70/0.86), 253 (3.2, [294 – Me – CN]$^+$; ^{13}C 0.40/0.48), 251 (9.3, $C_{11}H_9NO_4S^+$ (dimethyl cyanovinylthiophenedicarboxylate); ^{13}C 1.14/1.24), 209 (6, [294 – CO_2Me – CN]$^+$), 191 (9, [251 – HCO_2Me]$^+$), 183 (6, [209 – CN]$^+$), 177 (31), 176 (62, [209 – MeOH – H]$^+$, $C_9H_6NOS^+$), 156 (64, $C_9H_{16}S^+$, **7A**$^+$, ^{13}C 6.5/6.9; $^{13}C_2$ + ^{34}S 3.2/3.7), 148 (35), 147 (28), 123 (100, [**7A** – SH]$^+$, $C_9H_{15}^+$; ^{13}C 10.0/10.2, no S), 113 (22), 107 (48), 100 (18), 99 (16), 91 (18), 85 (36), 69 (46, $C_5H_9^+$), 59 (69, MeOC≡O$^+$), 41 (45). Anal. calc. for $C_{18}H_{24}N_2O_4S$ (364.45): C 59.32, H 6.64, N 7.69, S 8.80; found: C 59.44, H 6.78, N 7.56, S 8.83.

5.1.3. *Data of* **18A**. IR: 911*m*, 929*m*, 1025*m*; 1208v*s* + 1260v*s* (br. C–O); 1431*s*, 1447*m*; 1758v*s* + 1769v*s* (C=O); 2245v*w* (C≡N). ^{1}H-NMR (300 MHz): 1.15, 1.62, 1.68, 1.74 (4*s*, 4 Me); 1.35–1.88 (*m*, CH_2(3), CH_2(4)); 3.47, 3.61 (*AM*, *J* = 12.8, H_a–C(5′), H_b–C(5′)); 3.91, 3.97 (2*s*, 2 MeO). (C_6D_6): 0.94 (*s*, Me); 1.1–1.6 (*m*, CH_2(3), CH_2(4)); 1.69 (*s*, 2 Me); 1.79 (*s*, Me); 2.96, 3.19 (*AB*, *J* = 13.2, CH_2(5′)); 3.13, 3.31 (2*s*, 2 MeO). ^{13}C-NMR (100 MHz, DEPT): 25.8, 28.6, 31.5, 31.7 (4 Me); 37.2 (C(5′)); 40.5, 41.3 (C(3), C(4)); 49.87, 49.90

(C(2), C(5)); 54.4, 55.0 (2 MeO); 61.7, 64.5 (C(3′), C(4′)); 81.6 (C(1)); 116.3, 116.7 (2 CN), 163.99, 164.05 (2 C=O). MS (90°): similar to MS of **17A**. Anal. calc. for $C_{18}H_{24}N_2O_4S$ (364.45): C 59.32, H 6.64, N 7.69, S 8.80; found: C 59.55, H 6.67, N 7.85, S 8.82.

5.2. *Dimethyl* cis-*3′,4′-Dicyano-2,3-dihydro-1,1,3,3-tetramethylspiro[1*H*-indene-2,2′-thiolane]-3′,4′-dicarboxylate* (**17B**) *and* trans-*Isomer* **18B**. 5.2.1. *Isolation of the Cycloadducts. a*) Compound **8B** (500 mg, 2.03 mmol) and **15** (400 mg, 2.06 mmol) in CH_2Cl_2 (13 ml) were refluxed for 48 h. **17B** (415 mg, 50%) crystallized from MeOH. The residue of the mother liquor was partially separated by CC with CH_2Cl_2/cyclohexane 1:1. The isolation of **18B** (25 mg, 3%) was troublesome.

b) The product (refl. CH_2Cl_2, 40 h) was analyzed by ^{1}H-NMR (*sym*-tet) to show 92% of **17B** (2*s*, 1.98, 2.08), 6% of **18B** (*d*, 3.40), and *ca*. 1% each of cyclopropanes **28** (*d*, 2.34) and **27** (*s*, 2.58).

c) The isolation of *trans*-isomer **18B** is more convenient after controlled thermal isomerization: **8B** (1.89 mmol) and **15** (2.20 mol) in $CHCl_3$ (10 ml) reacted 4 h at 100° in a closed tube, PLC (pentane/Et_2O, 70:30) furnished **18B** (60 mg, 8%) and **17B** (71 mg, 9%) after recrystallization from MeOH.

5.2.2. *Data of* **17B**. M.p. 152°. IR: 757*m*, 765*m* (arom. out-of-plane deform.), 1252*s* (br. C–O); 1433*m*, 1451*m*, 1487*w*, 1596*w* (arom. ring vibration), 1759*s* + 1766*s* (C=O), 2245v*w* (C≡N). ^{1}H-NMR (400 MHz): 1.49, 1.66, 1.98, 2.08 (4*s*, 4 Me); 3.51, 3.96 (*AX*, *J* = 12.7, CH_2(5′)); 3.917, 3.924 (2*s*, 2 MeO); 7.06–7.30 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz, DEPT): 25.3, 28.1, 29.5, 31.3 (4 Me); 37.0 (C(5′)); 52.0, 54.7 (C(1), C(3)); 54.4, 55.0 (2 MeO); 61.3, 63.0 (C(3′), C(4′)); 84.4 (C(2)); 116.2, 117.2 (2 CN); 121.1, 122.2, 127.7, 127.9 (4 arom. CH); 147.8, 148.7 (2 arom. C_q); 165.0, 165.9 (2 C=O). MS (120°): 412 (12, M^+), 397 (2, $[M-Me]^+$), 353 (13, $[M-CO_2Me]^+$), 210 (18), 204 (40, **7B**$^+$), 189 (100, $[\mathbf{7B}-Me]^+$, $C_{12}H_{13}S^+$), 177 (10, $[\mathbf{7B}-SH]^+$), 176 (34), 171 (21, $C_{13}H_{15}^+$), 159 (34, $C_{12}H_{15}^+$), 156 (35, $C_{12}H_{12}^+$ (dimethylnaphthalene$^+$)), 146 (22, $C_{11}H_{14}^+$), 141 (16, $C_{11}H_{19}^+$), 129 (10, $C_{10}H_9^+$ (methylindenyl$^+$)), 128 (10, naphthalene$^+$), 115 (12, $C_9H_7^+$ (indenyl$^+$)), 91 (7, $C_7H_7^+$), 59 (7, MeOC≡O$^+$). Anal. calc. for $C_{22}H_{24}N_2O_4S$ (412.49): C 64.05, H 5.87, N 6.79, S 7.77; found: C 63.92, H 6.16, N 6.50, S 7.75.

5.2.3. *Data of* **18B**. M.p. 106–108°. IR: 757*m*, 1268*s* (br., C–O); 1436*m*, 1482*w*, 1592v*w* (arom. ring vibration), 1756*s* (br., C=O); 2248v*w* (C≡N). ^{1}H-NMR: 1.35, 1.86, 1.96, 2.08 (4*s*, 4 Me); 3.40, 3.58 (*AB*, *J* = 12.9, CH_2(5′)); 3.91, 3.95 (2*s*, 2 MeO); 7.0–7.3 (*m*, 4 arom. H). MS: similar to **17B**. Anal. calc. for $C_{22}H_{24}N_2O_4S$ (412.49): C 64.05, H 5.87, N 6.79, S 7.77; found: C 64.14, H 5.87, N 6.60, S 7.76.

5.3. cis,trans *Assignment by X-Ray Analyses.* All crystals were sealed in glass capillaries and mounted on the goniometer head of a *Nonius MACH3* four-circle diffractometer operating with MoK_α radiation and a graphite monochromator. The unit-cell dimensions resulted from a least-squares fit of the setting angles of 15 centered reflections, followed by a check of axial and *Laue* symmetry. ω-Scans with intensity-dependent variable scan speed were used to scan a quadrant (**17B** and **18A**) or a half sphere (**18B**). *Lorentz* and polarization corrections were performed. The structures were solved by SHELXS-86 and refined with SHELXL-76 (**17B** and **18A**) and SHELXL-93 (**18B**) [30]. Non-H-atoms were refined anisotropically with inclusion of H-atoms in calculated positions and fixed isotropic *U*. Crystallographic data (excluding structure factors) for the reported structures have been deposited with the *Cambridge Crystallographic Data Centre* (fax: ++44(1223)336-033 or e-mail: deposit@ccdc.cam.ac.uk) as supplementary publication; deposition Nos. in *Table 4*. Selected structure parameters are given in *Table 2*; for ZORTEP [21] plots see *Figs. 1–3*, crystallographic data in *Table 4*.

5.4. *Stereochemistry of Cycloaddition.* 5.4.1. *Thiadiazoline Catalysis of Dipolarophile Isomerization and Its Suppression*. In the equilibrium **16**/**15** 12:88 ($CDCl_3$, 25°), *dimethyl 2,3-dicyanomaleate* (**16**) constitutes the minor component and is, therefore, suitable for control experiments. About 0.1 mmol each of dihydrothiadiazole **8** and **16** (containing 2% of **15**) [16] were dissolved in 7.6 mM H_2SO_4 in $CDCl_3$ (sat. soln.) [10] and filled up to 1 ml. The ^{1}H-NMR *singlets* of MeO at 3.94 for **16** and 4.03 ppm for **15** showed a moderate decrease of **16**/**15** at r.t. (*Table 5*).

5.4.2. *Steric Course of Cycloadditions.* The reactions of dihydrothiadiazoles **8** with **15** and **16** were carried out in 7.6 mM H_2SO_4 in $CDCl_3$ (sat. soln.) by heating at 80° for 5 min (**8A**) or 10 min (**8B**). The high temp. favors the first-order N_2 elimination from **8** over the second-order catalysis of dipolarophile isomerization. Despite the incompleteness of N_2 extrusion, 8–17% of the products **17** and **18** thermolyzed and gave the cyclopropane derivatives **27** and **28** plus thione **7** (*Table 6*). Part of **7** hydrolyzed to ketone **6**.

The procedure is described for the reaction of **8A** with **15**: freshly recrystallized **8A** (39.5 mg, 199 μmol) and finely pulverized **15** (43.0 mg, 221 μmol) in $CDCl_3$ (H_2SO_4) (1 ml) were heated in a closed NMR tube under Ar for 5 min at 80° (immersion in bath). After releasing the N_2 pressure at −78°, 100 μl of a soln., which contained dibenzyl (96.7 mg, 531 μmol, in 1 ml of $CDCl_3$) as a weight standard, was added with a syringe. The well-resolved ^{1}H-NMR spectrum, recorded with a *JEOL* 270-MHz instrument, was section-wise amplified and expanded for integration.

Table 4. *X-Ray Crystallographic Data of Compounds* **17B**, **18A,** *and* **18B**

Compound	**17B**	**18A**	**18B**
Molecular formula	$C_{22}H_{24}N_2O_4S \cdot 0.5$ MeOH	$C_{18}H_{24}N_2O_4S$	$C_{22}H_{24}N_2O_4S$
Molecular mass	428.51	364.45	412.49
Crystal size [mm]	$0.23 \times 0.27 \times 0.53$	$0.23 \times 0.33 \times 0.53$	$0.17 \times 0.40 \times 0.57$
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$
Unit-cell parameters			
a [Å]	8.476(2)	14.373(3)	8.387(2)
b [Å]	17.550(5)	7.473(2)	9.755(2)
c [Å]	14.125(4)	17.780(4)	13.401(3)
α [°]	90	90	97.559(15)
β [°]	91.857(15)	105.187(15)	93.460(15)
γ [°]	90	90	109.31(2)
Volume [Å]	2100.0(10)	1842.9(8)	1019.5(4)
Z	4	4	2
D calc. [mg/mm^3]	1.349	1.314	1.344
$F(000)$	900	776	436
Index range	$\pm h, +k, +l$	$\pm h, +k, +l$	$\pm h, \pm k, +l$
2θ [°]	50	50	48
Temp. [K]	293(2)	293(2)	293(2)
Reflections collected	3977	3350	3352
Reflections unique	3212	2874	2963
Reflections observ. [$>2\sigma(I)$]	2771	2458	2768
R_{int}	0.0213	0.0217	0.0162
No. Variables	280	232	262
Final R ($2\sigma I$)	0.0434	0.0338	0.0430
Final wR	0.0399	0.0893($wR2$)	0.0383
Largest residual Peak [e/Å^3]	0.605	0.184	0.286
CCDC Deposition No.	177310	177311	177312

Table 5. *Suppression by Acid of Catalysis by* **8A** *and* **8B** *of the Isomerization* **16** → **15** *at Room Temperature*: *Decrease in the Ratio* **16**/**15** *as a Function of Time*

Catalyst	Time [min]					
	0	10	60	120	180	240
8A	98 : 2	97 : 3	96 : 4	93 : 7	89 : 11	88 : 12
8B	98 : 2	98 : 2	97 : 3	93 : 7	91 : 9	87 : 13

The following NMR signals (ppm) were suitable for the analysis of products from **8A** : **15**: 4.00 (*s*, 2 MeO); **16**: 3.94 (*s*, 2 MeO); **17A**: 1.46, 1.83 (2*s*, 2 Me), 3.49 (*d*, H_a–C(5′)); 3.84 (*s*, MeO); **18A**: 3.60 (*d*, H_b–C(5′)); **27**: 2.58 (*s*, CH_2(3)); **28**: 2.34 (*d*, *A* of *AB*); **8A**: 0.67, 1.13 (2*s*, 2 × 2 Me); **7A**: 1.92 (*s*, 2 CH_2); **6A**: 1.04 (*s*, 4 Me); dibenzyl: 2.92 (*s*, 2 CH_2). Signals for reactions of **8B**: **17B**: 1.65, 1.98, 2.07 (3*s*, 3 Me), 3.50 (*d*, *A* of *AX*, H_a–C(5′)); **18B**: 1.86 (*s*, Me); 3.43, 3.60 (*AB*, CH_2(5′)); **8B**: 0.97, 1.37 (2*s*, 2 × 2 Me); **7B**: 1.47 (*s*, 4 Me, disturbed), **6B**: 1.34 (*s*, 4 Me).

The analytical data of *Table 6* were supported by the analysis of an artificial mixture of pure **17A**, **18A** (or **17B** and **18B**, resp.), **15**, **16**, and dibenzyl in similar proportions. Nevertheless, the numerical results are not highly precise. Whenever feasible, several signals were evaluated for each of the 10 analyzed components of each mixture. The 12 H *s* of thione **7B** was not free-standing; a partial overlap required estimation.

The data of *Table 6* refer to μmol amount of analyzed products obtained from the reactants listed in the *Lines 1* and *2*. Under the reaction conditions, 7–15% of the thiadiazolines **8A** and **8B** remained undecomposed. Yields (*Table 3*) are based on the consumed **8A** and **8B**. NMR-Pure dimethyl 2,3-dicyanomaleate (**16**) [16] was used for the data in *Columns 3* and *5* of *Table 6*.

Table 6. *Reactions of Thiocarbonyl Ylides* **5A** *and* **5B** *with Dimethyl 2,3-Dicyanofumarate* (**15**) *or Dimethyl 2,3-Dicyanomaleate* (**16**) *in 7.6 mM H_2SO_4 in $CDCl_3$* (1 ml): *^{1}H-NMR Analysis of Steric Course*

Reaction	**8A** + **15**	**8A** + **16**	**8B** + **15**	**8B** + **16**
Reactants in μmol				
Dihydrothiadiazole **8**	199	203	198	194
Dipolarophile (**15**, **16**)	221	219	220	228
Products in μmol				
cis-Thiolane **17**	128	119	98	97
trans-Thiolane **18**	12	12	11	9
cis-Cyclopropane **28**	4	7	12	14
trans-Cyclopropane **27**	10	11	15	16
Thione **7**	13	10	22	25
Ketone **6**	12	11	5	4
Dihydrothiadiazole **8**	14	25	29	22
8, consumed	185	178	169	172
15 + **16**, unconsumed	67	70	84	92

The entry '**15** + **16**, unconsumed' in *Table 6* is the difference in the amount of dipolarophile at the beginning of the experiment and the amounts of thiolanes + cyclopropanes formed. The analysis of **16** by its *s* at 3.94 (2 MeO) is flawed by partial overlap, whereas the MeO signal of **15** (4.00 ppm) is isolated and allows reliable analysis. In the experiment of **8A** with the dicyanomaleate **16**, the 70 μmol of excess dipolarophile contain only 9 μmol of dicyanofumarate **15**, while in the reaction of **8B** + **16** the unconsumed dipolarophile consists of **15**/**16** 4 : 96. Thus, the isomerization catalysis leading to an equilibrium **15**/**16** 88 : 12, was suppressed for the reaction with **8B**, and even more so for **8A**.

5.5. *Interception of Ketene Imine Intermediates with H_2O and MeOH*. 5.5.1. *Dimethyl 6′-Cyano-2,2,5,5-tetramethyl-4′-oxospiro[cyclopentane-1,2′-[1,3]thiazepane]-5′,6′-dicarboxylate* (= *Dimethyl 8-Cyano-1,1,4,4-tetramethyl-10-oxo-6-thio-11-azaspiro[4.6]undecane-8,9-dicarboxylate*; **22A**). *a*) Compound **8A** (403 mg, 2.03 mmol) and **15** (388 mg, 2.00 mmol) in THF/H_2O (98 : 2 vol-%, 12.5 ml) were refluxed for 35 min. The colorless oil crystallized slowly from MeOH at −20°, and **22A**, **I** (310 mg, 41%) was obtained. M.p. 142–143°. IR: 1249*m*, 1326*m*, 1389*m* (C−O), 1664*s* (C=O, amide I), 1755*s* (C=O, ester), 2245v*w* (C≡N), 3221*m* (N−H, assoc.). ^{1}H-NMR: 1.13, 1.22, 1.26, 1.29 (4*s*, 4 Me); 1.66 (*s*, CH_2(3) + CH_2(4)); 3.25, 3.33 (*AB*, *J* = 15.2, CH_2(7′)); 3.76, 3.84 (2*s*, 2 MeO); 4.98 (*s*, H−C(5′)); 6.03 (br., *s*, NH); signals of minor isomer **II**: 5.13 (*s*, H−C(5′)); 6.35 (br., *s*, NH). ^{13}C-NMR: 25.9, 28.6 (2*q*, 2 Me); 29.0 (*q*, 2 Me); 35.8, 36.5, 38.3 (3*t*, C(3), C(4), C(7′)); 49.0, 50.2, 50.6 (3*s*, C(2), C(5), C(6′)); 53.1, 54.0 (2*q*, 2 MeO); 55.6 (*d*, C(5′)); 80.5 (*s*, C(1)); 117.6 (*s*, CN); 166.3, 166.7, 166.9 (3*s*, 3 C=O). MS (90°): 382 (3, M^+), 351 (6, $[M - MeO]^+$), 324 (28, $[M - CN - S]^+$, ^{13}C 5.3/4.6), 271 (20), 212 (45), 200 (12), 184 (43), 170 (16), 152 (26), 140 (23), 138 (15), 124 (100, $C_9H_{16}^+$ (tetramethylcyclopentene$^+$), ^{13}C 10/9, no S), 123 (31, $C_9H_{15}^+$), 107 (10), 101 (11), 83 (14, $C_6H_{11}^+$ (trimethylallyl$^+$)), 71 (28), 69 (33, $C_5H_9^+$ (dimethylallyl$^+$)), 59 (19, MeOC≡O$^+$), 56 (33, $C_4H_8^+$ (isobutene$^+$)). Anal. calc. for $C_{18}H_{26}N_2O_5S$ (382.47): C 56.52, H 6.85, N 7.33, S 8.38; found: C 56.45, H 6.88, N 7.10, S 8.39.

b) The product of reaction (25 min 60°) in THF/H_2O (97 : 3 vol-%) was analyzed by ^{1}H-NMR with trichloroethylene as standard: 65% of lactams **22A**, **I** and **22A**, **II** in a ratio of 76 : 24.

5.5.2. *Dimethyl 6′-Cyano-2′,3′,6′,7′-tetrahydro-4′-methoxy-2,2,5,5-tetramethylspiro[cyclopentane-1,2′-[1,3]thiazepine]-5′,6′-dicarboxylate* (= *Dimethyl 8-Cyano-10-methoxy-1,1,4,4-tetramethyl-6-thia-11-azaspiro[4.6]undec-9-ene-8,9-dicarboxylate*; **23A**). *a*) Compound **8A** (2.03 mmol) and **15** (1.99 mmol) in $CHCl_3$/MeOH (98 : 2 vol-%, 12.5 ml) were reacted 35 min in a 65° bath. After repeated evaporation with Et_2O, colorless crystals of **23A** (165 mg, 21%) were obtained from Et_2O. M.p. 136–137°. IR (nujol): 1125*m*, 1143*m*, 1229*s*, 1316*s* (C−O), 1467*s* (br.), 1508*m*; 1594*s* (C=C), 1666*s* (C=O of 5′-CO_2Me), 1753*s* (C=O of 6′-CO_2Me), 2252v*w* (C≡N), 3338*m* (N−H). ^{1}H-NMR: 1.14, 1.23 (2*s*, 2 Me); 1.21 (*s*, 2 Me); 1.36 (*s*, CH_2(3) + CH_2(4)); 3.08, 3.27 (*AB*, *J* = 14.2, CH_2(7′)); 3.70, 3.80 (2*s*, 2 MeO); 4.41 (br., *s*, NH). ^{13}C-NMR: 26.2, 27.7, 28.5, 29.8 (4*q*, 4 Me); 34.5, 36.8, 37.7 (3*t*, C(3), C(4), C(7′)); 49.7, 50.2, 55.0 (3*s*, C(2), C(5), C(6′)); 51.2, 53.7, 61.1 (3*q*, 3 MeO); 80.8, 84.1 (2*s*, C(1), C(5′)); 119.4 (*s*, CN); 167.3, 169.0, 169.8 (3*s*, C(4′), 2 C=O). MS (90°): 396 (23, M^+, ^{13}C 4.9/4.8), 381 (16, $[M - Me]^+$), 365 (19, $[M - MeO]^+$), 349 (61, $[M - S - Me]^+$, ^{13}C 12/13), 338 (60, $[M - S - CN]^+$, ^{13}C 11.9/11.8), 337 (28, $[M - CO_2Me]^+$), 305 (72, $[M - S - CO_2Me]^+$), 291 (18), 285 (21), 270 (27), 258 (73,

$C_{10}H_{12}NO_5S^+$, ^{13}C 8.1/8.5), 253 (27), 226 (100, $C_9H_8NO_4S^+$; HR: calc. 226.017, found 226.022), 213 (30), 198 (60), 163 (16), 123 (81, $C_9H_{15}^+$ (tetramethylcyclopentenyl$^+$)), 109 (14, $C_8H_{13}^+$), 91 (13, $C_7H_7^+$), 81 (15, $C_6H_9^+$), 69 (24, dimethylallyl$^+$), 59 (31, $MeOC{\equiv}O^+$), 55 (16, $C_4H_7^+$). Anal. calc. for $C_{19}H_{28}N_2O_5S$ (396.50): C 57.55, H 7.12, N 7.07, S 8.09; found: C 57.34, H 6.90, N 7.27, S 8.08.

b) The soln. of **23A** in $CDCl_3$ turned dark on addition of a trace of triethylenediamine; after 24 h the signals of **23A** disappear, and those of **24A** show a diastereoisomer ratio **I/II** 60/40.

5.5.3. *Dimethyl 6′-Cyano-6′,7′-dihydro-4′-methoxy-2,2,5,5-tetramethylspiro[cyclopentane-1,2′(5′*H*)-[1,3]thiazepine]-5′,6′-dicarboxylate* (= *Dimethyl 8-Cyano-10-methoxy-1,1,4,4-tetramethyl-6-thia-11-azaspiro-4.6]undec-10-ene-8,9-dicarboxylate*; **24A**). *a*) The product from **8A** and **15** contains the more of **24A** the longer the reaction time. The isolation of pure **23A** (*Sect. 5.5.2*) rests on the solubility in Et_2O, which is lower for **23A** than for **24A**. When **8A** and 1.1 equiv. of **15** in $CHCl_3$/MeOH (98 : 2 vol-%) were reacted for 1 h at 65°, excess **15** crystallized from CH_2Cl_2 at −20°, and methyl imidate **24A** (16%) was obtained from MeOH. Despite a sharp m.p. 146–147°, the sample contained diastereoisomers **I** and **II**, which we could not separate. A simpler access to **24A** consists of adding triethylenediamine to the reaction mixture before workup. IR: 1249*s* (br.), 1324*s* (C−O), 1695*s* (C=N), 1755*s* (C=O), 2245v*w* (C≡N); (nujol): no N−H. ^{1}H-NMR: 1.01, 1.10, 1.21, 1.23 (4*s*, 4 Me); 1.40–1.93 (*m*, CH_2(3), CH_2(4)); 3.20 (*s*, CH_2(7′)); 3.64, 3.73, 3.84 (3*s*, 3 MeO); 5.15 (*s*, H−C(5′) of isomer **I**); 5.38 (*s*, H−C(5′) of isomer **II**). ^{13}C-NMR: 27.9, 28.0, 28.1, 28.4 (4*q*, 4 Me); 35.6, 38.4, 38.5 (3*t*, C(3), C(4), C(7′)); 49.0, 49.6 (2*s*, C(2), C(5)); 52.2 (*s*, C(6′)); 52.7 (*d*, C(5′)); 52.9, 53.6, 53.9 (3*q*, 3 MeO); 84.7 (*s*, C(1)); 118.0 (*s*, CN); 148.0 (*s*, C(4′)); 167.9 (*s*, 2 C=O). MS (70°): Similar to MS of **23A**, only selected peaks: 381 (10, $[M-Me]^+$, ^{13}C 1.8/1.9, $^{13}C_2+^{34}$S 0.60/0.53), 365 (11, $[M-MeO]^+$, ^{13}C 2.1/1.9; $^{13}C_2+^{34}$S 0.67/0.53), 305 (100, $C_{17}H_{25}N_2O_3^+$), 291 (86), 270 (18, $C_{10}H_{10}N_2O_5S^+$, ^{13}C 2.0/2.3, $^{13}C_2+^{34}$S 1.78/1.74), 226 (89, $C_9H_8NO_4S^+$, ^{13}C 8.9/11.6; $^{13}C_2+^{34}$S 4.7/5.1 (protonated dimethyl cyanothiophenedicarboxylate)), 123 (53). Anal. calc. for $C_{19}H_{28}N_2O_5S$ (396.50): C 57.55, H 7.12, N 7.07, S 8.09; found: C 57.84, H 7.25, N 6.84, S 7.95.

b) ^{1}H-NMR analysis (*sym*-tet) indicated the presence of **23A** (38%, 4.41 ppm, NH), **24A**, **I** (15%, 5.15 ppm), **24A**, **II** (6%, 5.38 ppm). Thiolane **17A** was present, but signal overlap thwarted evaluation.

5.5.4. *Dimethyl 6′-Cyano-2,3-dihydro-1,1,3,3-tetramethyl-4′-oxospiro[1*H*-indene-2,2′-[1,3]thiazepane]-5′,6′-dicarboxylate* (**22B**). *a*) Compound **8B** (1.70 mmol) and **15** (1.70 mmol) in THF + 2 vol-% of H_2O (12.5 ml) were heated at 65° for 4.5 h. After repeated evaporation with Et_2O, **22B**, **I** (320 mg, 44%) crystallized from MeOH at −20°. M.p. 187–188° (dec., black). IR (nujol): 758*m*; 1172*s*, 1204*s*, 1220*s*, 1250*s* (br.), 1324*s* (C−O); 1377*s*, 1386*s*; 1455*s* (br.), 1585*w* (arom. ring vibr.), 1682*s* (br., amide-I), 1742*s*, 1758*s*, 1773*s* (C=O, ester), 2240v*w* (C≡N), 3325*m* (sharp, NH, assoc.). ^{1}H-NMR: 1.45 (*s*, 2 Me); 1.49, 1.54 (2*s*, 2 Me); 3.38, 3.59 (*AB*, *J* = 14.8, CH_2(7′)); 3.78, 3.88 (2*s*, 2 MeO); 5.13 (*s*, H−C(5′)); 5.60 (br., *s*, NH); 6.98–7.28 (*m*, 4 arom. H). ^{13}C-NMR: 25.0 (*q*, 2 Me); 28.4, 31.9 (2*s*, 2 Me); 35.4 (*t*, C(7′)); 48.9, 54.2, 54.3 (3*s*, C(1), C(3), C(6′)); 53.2, 54.3 (2*q*, 2 MeO); 55.9 (*d*, C(5′)); 81.7 (*s*, C(2)); 117.5 (*s*, CN); 122.7, 123.2, 128.1, 128.4 (4*d*, 4 arom. C); 145.8, 146.0 (2*s*, C(3A), C(7A)); 166.1, 166.7, 167.0 (3*s*, 3 C=O). MS (130°): 430 (< 0.2, M^+), 399 (4.5, $[M-MeO]^+$, ^{13}C 1.05/0.93, $^{13}C_2+^{34}$S 0.32/0.26), 372 (100, $[M-CN-S]^+$, $C_{21}H_{26}NO_3^+$, ^{13}C/23/23, $^{13}C_2$ 2.6/3.1, no S), 340 (11, $[372-MeOH]^+$, ^{13}C 2.5/2.3), 312 (19, $[372-HCO_2Me]^+$, $C_{19}H_{22}NO_3^+$, ^{13}C 4.1/3.8), 188 (18), 172 (99, $C_{13}H_{16}^+$, ^{13}C 14/14), 171 (88, tetramethylindenyl$^+$), 157 (23, $C_{12}H_{13}^+$ (trimethylindenyl$^+$)), 156 (19, $C_{12}H_{14}^+$ (dimethylnaphthalene$^+$)), 155 (17), 145 (14), 143 (8, $C_{11}H_{11}^+$), 131 (13), 129 (16, $C_{10}H_9^+$ (methylindenyl$^+$)), 128 (12, naphthalene$^+$), 115 (9, indenyl$^+$). Anal. calc. for $C_{22}H_{26}N_2O_5S$ (430.51): C 61.37, H 6.09, N 6.51, S 7.45; found: C 61.40, H 6.03, N 6.24, S 7.45.

b) A soln. of **22B**, **I** in $CDCl_3$ was treated with a trace of triethylenediamine. After 24 h, a 38 : 62 equilibrium of diastereoisomers was established: **I**, *s* at 5.13 (H−C(5′)) and *s* at 5.60 (NH); **II**, *s* at 5.40 (H−C(5′)) and *s* at 5.60 (NH).

c) Compound **8B** (156 μmol) and **16** (171 μmol) in THF + 2 vol-% of H_2O (1 ml) were heated at 80° for 15 min. ^{1}H-NMR analysis (270 MHz) with dibenzyl as standard showed **22B**, **I** (74%), **22B**, **II** (13%), and *cis*-thiolane **17B** (4%).

5.5.5. *Dimethyl 6-Cyano-2,2′,3,3′,6′,7′-hexahydro-4′-methoxy-1,1,3,3-tetramethylspiro[1*H*-indene-2,2′-[1,3]thiazepine]-5′,6′-dicarboxylate* (**23B**). *a*) Reaction of **8B** (4.06 mmol) and **15** (4.00 mmol) in $CHCl_3$/MeOH (98 : 2 vol-%, 12.5 ml) at 60°, 3.5 h. From much Et_2O, **23B** (995 mg, 56%) crystallized. M.p. 168–170°. IR (nujol): 756*s*, 795*m*; 1116*s*, 1131*s*, 1240*s* (br.), 1279*s* (C−O); 1378*m*, 1385*m*; 1458*s* (br.), 1499*s*; 1576*s* (C=C), 1699*s* (C=O of 5′-CO_2Me), 1746*s* (C=O of 6′-CO_2Me), 2250*w* (C≡N), 3400*m* (sharp, N−H). ^{1}H-NMR (400 MHz): 1.39, 1.43, 1.45, 1.52 (4*s*, 4 Me); 3.28, 3.47 (*AB*, *J* = 14.7, CH_2(7′)); 3.73, 3.75, 3.86 (3*s*, 3 MeO); 4.44 (br, *s*, NH); 7.15–7.31 (*m*, C_6H_4). ^{13}C-NMR (100 MHz, DEPT): 24.5, 24.8, 29.4, 31.2 (4 Me); 34.0 (C(7′)); 51.4, 53.8, 61.3 (3 MeO); 53.3, 54.3, 55.3 (C(1), C(2), C(6′)); 81.3, 85.2 (C(2), C(5′)); 119.5 (CN); 122.9, 123.4, 127.8, 128.2 (4 arom. CH); 146.4, 146.7 (C(3A), C(7A)); 167.4, 169.1, 169.7 (C(4′), 2 C=O). MS (120°): 444 (15, M^+,

^{13}C 3.5/3.6), 413 (12, [M – MeO]$^+$), 397 (26, [M – S – Me]$^+$, ^{13}C 6.4/7.7), 386 (100, [M – S – CN]$^+$, ^{13}C 25/23, no S), 371 (31, [386 – Me]$^+$, $C_{21}H_{25}NO_5^{\ddagger}$, ^{13}C 7.2/6.5, $^{13}C_2$ 0.8/1.0, no S), 353 (30, [M – S – CO_2Me]$^+$), 339 (36), 333 (13), 312 (15), 292 (52), 258 (92, $C_{10}H_{12}NO_5S^+$, ^{13}C 10.3/11.4, $^{13}C_2 + {}^{34}$S 4.6/5.8; HR: calc. 258.049, found 258.051), 226 (37), 203 (16), 172 (36, $C_{13}H_{16}^+$), 171 (60, $C_{13}H_{15}^+$ (tetramethylindenyl$^+$)), 157 (29, $C_{12}H_{13}^+$), 156 (50), 143 (22, $C_{11}H_{11}^+$), 142 (23, $C_{11}H_{10}^+$ (methylnaphthalene$^+$)), 141 (40), 129 (47, $C_{10}H_9^+$), 128 (42, $C_{10}H_8^+$), 117 (19), 1115 (32, indenyl$^+$), 91 (19, $C_7H_7^+$), 59 (35, MeOC≡O$^+$), 45 (25). Anal. calc. for $C_{23}H_{28}N_2O_5S$ (444.54): C 62.14, H 6.35, N 6.30, S 7.21; found: C 62.35, H 6.54, N 6.29, S 7.20.

b) On storing the $CDCl_3$ soln. of **23B** at r.t., a slow isomerization to the imidate **24B** was observed. Within 20 d, the signals of **23B** vanished, and the *s* of H–C(5′) at 5.31 and 5.59 showed **24B** with an isomer ratio of **I/II** 85 : 15 (*Sect. 5.5.6*). Base catalysis: in the presence of a small amount of triethylenediamine, the isomerization was complete after 1 h, **24B**, **I/II** 88 : 12.

5.5.6. *Dimethyl 6-Cyano-2,3,6′,7′-tetrahydro-4′-methoxy-1,1,3,3-tetramethylspiro[1*H*-indene-2,2′(5′*H*)-[1,3]thiazepine]-5′,6′-dicarboxylate* (**24B**). *a*) Two mmol each of **8B** and **15** in $CDCl_3$/MeOH (98 : 2 vol-%, 12.5 ml) were reacted at 70° for 4 h. After cooling, triethylenediamine (20 mg) was added, and the soln. kept for 16 h at 20°. On crystallization from MeOH at 20°, the top fractions gave **24B**, **I** (186 mg, 21%). M.p. 155–156°. IR: 756*m*, 792*w*, 115*s*, 1142*m*, 1182*m*, 1243*s*, 1276*s*, 1312*s* (C–O), 1499*s* (br.), 1585*s* (br., arom. ring vibr.), 1700*m* (C=N), 1748*s* (C=O), 2245*vw* (C≡N). ^{1}H-NMR (400 MHz): 1.34, 1.40 (2*s*, 2 Me); 1.46 (*s*, 2 Me); 3.34, 3.47 (*AB*, J = 15.1, CH_2(7′)); 3.41, 3.78, 3.90 (3*s*, 3 MeO); 5.36 (*s*, H–C(5′)); 7.06–7.28 (*m*, 4 arom. H). ^{13}C-NMR (100 MHz, DEPT): 24.8, 26.9, 28.8, 31.3 (4 Me); 35.4 (C(7′)); 49.1, 55.5, 61.9 (C(1), C(3), C(6′)); 52.9 (C(5′)); 53.0, 53.7, 54.0 (3 MeO); 86.3 (C(2)); 118.0 (CN); 122.0, 122.3, 126.9, 127.0 (4 arom. CH); 147.7, 148.9, 149.4 (C(3A), C(7A), C(4′)); 167.87, 167.96 (2 C=O). MS (90°): similar to **23B**. Anal. calc. for $C_{23}H_{28}N_2O_5S$ (444.54): C 62.14, H 6.35, N 6.30, S 7.21; found: C 62.18, H 6.37, N 6.14, S 7.22.

b) In experiments on a 100-μmol scale, **8B** was reacted with 1.1 equiv. of **15** and **16** in $CDCl_3$/MeOH (98 : 2, 1 ml) for 10 min at 80°. ^{1}H-NMR analyses (270 MHz) in $CDCl_3$ were carried out immediately after the addition of dibenzyl (*s* at 2.96, 2 CH_2) and, in the experiment with **16**, after 4 d again. Yields are given in *Table 7*. The excess of **16** was isomerized to **16**/**15** 91 : 9. Signals of *trans*-thiolane, cyclopropanes **27** and **28** were very small due to the efficient trapping by MeOH. Interception products amount to 92–93%. After 4 d, the tautomerization **23B** → **24B** had progressed.

Table 7. *Reaction of* **8B** (100 μmol) *with* **15** *or* **16** (1.1 equiv., in 1 ml of $CDCl_3$/MeOH 98 : 2 at 80° for 10 min – 4 d)

Product[a])	Yield [%][b])		
	15 (10 min)	**16** (10 min)	**16** (4 d)
23B[c])	81	70	26
24B, **I**[d])	9	19	58
24B, **II**[e])	3	3	9
17B[f])	3	4	4

[a]) Based on ^{1}H-NMR analysis (270 MHz) in $CDCl_3$. [b]) Yield calculated on the basis of the amount of **8B** consumed. [c]) δ 4.41 (*s*, NH). [d]) δ 5.36 (*s*, H–C(5′)). [e]) δ 5.64 (*s*, H–C(5′)). [f]) δ 1.98 (*s*, Me).

5.6. *Thermolysis of Thiolanes* **17**. 5.6.1. *Cleavage of* **17A** *at 140°*; *Dimethyl* trans- *and* cis-*1,2-Dicyanocyclopropane-1,2-dicarboxylate* (**27** and **28**, resp.). *cis*-Thiolane **17A** (80.5 mg, 0.221 mmol) in PhCN (0.50 ml) was heated in an NMR tube in the presence of octamethyltetrasiloxane (OMCTS) as weight standard to 140° for 10 min. The integrals of the ^{1}H-NMR spectrum (80 MHz) indicated quant. yields of thione **7A** (*s* at 1.92, 4 H) and the cyclopropanes **27** + **28** (*s* at 3.96, MeO of **27** + *s* at 3.85, MeO of **28**). After distilling the solvent and **7A** at 50° (bath)/1 mm, the NMR spectra of the residue showed **27**/**28** 49 : 51, identical with the spectra of authentic samples of **27** and **28** [22]. ^{13}C-NMR of **27**: 25.6 (*t*, C(3)); 28.17 (*s*, C(1), C(2)); 55.2 (*q*, 2 MeO); 112.1 (*s*, CN); 161.3 (*s*, 2 C=O). **28**: 25.6 (*t*, C(3)); 28.23 (*s*, C(1), C(2)); 54.9 (*q*, 2 MeO); 113.1 (*s*, CN); 162.0 (*s*, 2 C=O). A sample of **27** in PhCN was heated to 140° for 5 h and revealed no change in the ^{1}H-NMR spectrum.

Table 8. *Competing Reactions of* **17A** (270 μmol in C_6D_6): *Isomerization to* **18A** *and Cleavage to* **7A** *at 87°*

	Time [min]							
	155	325	495	905	1390	1660	2080	2670
17A[a]) + **18A**[b]) [μmol]	245	220	211	144	126	113	106	94
17A/**18A**	89 : 11	81 : 19	73 : 27	59 : 41	50 : 50	46 : 54	44 : 56	42 : 58
7A[c]) [%]	10	19	26	37	49	54	57	68

[a]) Determined by ^{1}H-NMR analysis: **17A**: δ 1.09 (*s*, Me); 3.73 (*d*, *AB* (left branch), $CH_2(5')$). [b]) **18A**: δ 0.94 (*s*, Me); 3.31 (*s*, MeO). [c]) **7A**: δ 1.09 (*s*, 4 Me).

5.6.2. *Competing* cis → trans *Isomerization and Cleavage of* **17A**. The soln. of **17A** (270 μmol) and OMCTS as standard in C_6D_6 (0.4 ml) was sealed in an NMR tube. Time-dependent spectra showed isomerization **17A** → **18A** and formation of **7A** as parallel reactions at 87° (*Table 8*).

Thus, in the equilibrium **17A** → **18A** (estimated 35 : 65, but not reached) the *trans*-thiolane **18A** is favored. The precision is insufficient for a kinetic evaluation. An analogous experiment in 1,2-dichlorobenzene at 87° gave rise to **7A** (44%), **17A**/**18A** 66 : 34, and **27**/**28** 44 : 56 after 660 min.

5.6.3. *Photometric Measurement of Thione Formation from* **17A**. The generation of thione **7A** from 0.1M **17A** at 87° was measured in a 1-cm cuvette at λ_{max} 498 nm ($\varepsilon = 13.4$) for PhCN, 499 nm ($\varepsilon = 13.3$) for 1,2-dichlorobenzene, and 500 nm ($\varepsilon = 11.3$) for mesitylene as functions of time. Remarkably, the experimental E_∞ agreed with the values calculated for 100% reaction. Plots of ln *E vs.* time gave curves with convex bending to the abscissa. The initial rate constants ($k_{exp} \cdot 10^5$ [s^{-1}] for the first 6% reaction) were measured in several solvents: mesitylene, 0.41; 1,2-dichlorobenzene, 1.6; PhCN, 3.1.

5.6.4. *Parallel Reactions in the Thermolysis of* **17B**. An experiment in $CDCl_3$ at 100° (sealed NMR tube) furnished the ^{1}H-NMR analytical data shown in *Table 9*.

Table 9. *Parallel Reactions of* **17B** (270 μmol in $CDCl_3$): *Isomerization to* **18B** *and Cleavage to* **27** *and* **28**

Time [h]	18	34	56	80	150	216
	Yield [rel. %][a])					
17B	69	58	45	36	17	12
18B	8	11	15	15	16	10
27[a]) + **28**	23	31	40	49	67	78

[a]) Determined by ^{1}H-NMR analysis: 1.98, 2.08 (2 Me, **17B**); 2.36 (*A* of *AB*, **28**); 2.57 (*B* of *AB*, **28**) + 2.56 (A_2, **27**); 3.40 (*A* of *AB*, **18B**); 3.51 (*A* of *AB*, **17B**).

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