Cycloadditions of 'Thiocarbonyl Ylides' with Tetracyanoethylene (= Ethenetetracarbonitrile): Interception of Intermediates[1])

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Dedicated to *Edgar Heilbronner* on the occasion of his 80th birthday

Thiocarbonyl ylides (= sulfonium ylides) belong to the most nucleophilic 1,3-dipoles (high HO energy). In their reactions with tetracyanoethylene (TCNE = ethenetetracarbonitrile; low LU energy), a borderline crossing from the concerted mechanism to a two-step pathway *via* a 1,5-zwitterion was observed. Steric hindrance at one or both termini of the 1,3-dipole is an additional requirement. The ylides **3** and **13**, set free by N_2 elimination of dihydro-1,3,4-thiadiazoles, underwent electrocyclization or 1,4-H shift. Ylides **3** and **13** are bases and afforded MeOH adducts of different regiochemistry. Whereas **3** and TCNE in abs. THF at 45° furnished the (3 + 2) cycloadduct **20**, a MeOH content of 0.5–5 vol-% in THF gave rise to a seven-membered lactim ether **22** and thiolane **20** in a 65:35 ratio (*Scheme 4*). Water (0.5–1 vol-%) in THF led to lactam **24** and adduct **20** in the same ratio. The zwitterion **26**, assumed to be the first intermediate, enters competing reactions: the irreversible ring closure to thiolane **20** and the reversible formation of a strained, cyclic seven-membered 'ketene imine' **28**, which is intercepted by MeOH or H_2O. The *gauche*-conformation **32** of an analogous zwitterion, produced from the tetrasubstituted 'thiocarbonyl ylide' **13** with TCNE (*Scheme 5*), led to the thiolane derivative **35**, while the *anti*-conformation **33** afforded the thioxo compound **5** and cyclopropane derivative **36** by intramolecular nucleophilic substitution.

1. Introduction. – The common π-electronic classification, $[{}_{\pi}4_s + {}_{\pi}2_s]$, stresses the mechanistic kinship of the *Diels-Alder* reaction with its younger brother, the 1,3-dipolar cycloaddition. These thermal cycloadditions are allowed to be concerted by orbital control [2]. However, two-step processes *via* diradical or zwitterionic intermediates are alternative pathways. Nearly 40 years ago, concerted processes were dubbed 'no mechanism reactions' by *Doering* and *Roth* [3]. Today, concertedness is no longer an enigma. The concerted nature of the usual (*i.e.*, those without special structural features) *Diels-Alder* reactions [4] and 1,3-dipolar cycloadditions [5] is in harmony with experimental criteria and calculations. A lively account of the conceptual history, which also reflects the development of quantum-chemical calculations of transition states (TS), was given by *Houk* and co-workers [6]. Becke3LYP/6-31G* and related methods are the present state of art in TS calculations of *Diels-Alder* [7] and 1,3-dipolar cycloaddition reactions [8].

Recently, *Schleyer* and co-workers found a new criterion of aromaticity in the 'nucleus-independent-chemical shift' (NICS) [9]. Negative NICS values for the TSs of

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[1]) 1,3-Dipolar Cycloadditions, Part 122; Part 121: [1]

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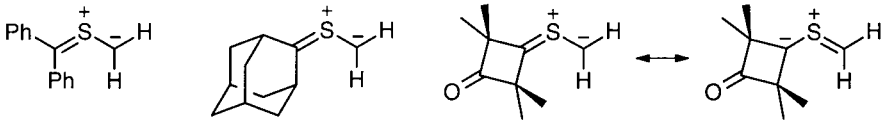
some 1,3-dipolar cycloadditions of fulminic acid and formaldimine *N*-oxide suggested strong aromatic character [10].

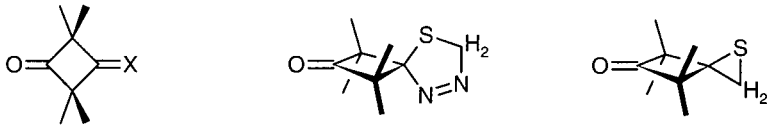
An important role in the theoretical development was played by *Sustmann*'s highly successful reactivity model of concerted cycloadditions (1971), which was based on the application of perturbation MO theory [11]. In the case of extremely different FMO energies of the cycloaddition partners, the concept allows one to foresee a borderline crossing to a mechanism *via* a zwitterionic intermediate. In 1986, we reported experimental evidence for the first two-step 1,3-dipolar cycloadditions; the evidence consisted of violation of stereospecificity [12] and interception of an intermediate [13].

Our model system is the reaction of 'thiocarbonyl ylides' (=sulfoniomethanides; for a recent review, see [14]; high π-MO energies) with tetra-acceptor-substituted ethenes (low π-LU energies). Massive steric encumbrance of at least one terminus of the 1,3-dipole is an additional requirement for the occurrence of an intermediate in which only *one* bond connects the reactants.

Steric hindrance in (diphenylmethylenesulfonio)methanide (**1**) and (adamantylidenesulfonio)methanide (**2**) is insufficient for initiating the two-step pathway in the reactions with tetracyanoethylene (TCNE = ethenetetracarbonitrile) [1][15]. However, two pairs of geminal dimethyl groups in [(2,2,4,4-tetramethyl-3-oxocyclobutylidene)sulfonio]methanide – formula **3** presents the allylic resonance structures – shield the pathway to C(3) of the cyclobutane moiety more efficiently.



1 **2** **3**



4 X = O; **5** X = S **6** **7**

In 1970, the easily available 3-thioxo derivative **5** [16] was reacted with diazomethane by *Diebert*, and an 'unstable intermediate' on the path to thiirane compound **7** was assigned the structure of the spiro-dihydro-1,3,4-thiadiazole derivative **6** [17]. Unsuspecting of the intermediacy of 'thiocarbonyl ylide' **3**, *Diebert* noticed the formation of a 1,3-dithiolane when **6** was decomposed in the presence of **5**. The dihydro thiadiazole **6** was later fully characterized [18], and the cycloadditions of **3** to various dipolarophiles (C≡C, C=C, C=S, C=O, N=N bonds) were the topic of a short account [19]. We report here on the reactions of **3** and its dimethyl derivative **13** with TCNE which were mentioned in two preliminary communications [13][20].

2. Results and Discussion. – 2.1. *Formation of 'Thiocarbonyl Ylide'* **3** *and Reactions with HX*. The thermal N_2 extrusion from **6** ($t_{1/2}$ 88 min in THF at 40°) is a 1,3-dipolar

cycloreversion, giving rise to 1,3-dipole **3** and N_2. Kinetic measurements reveal a moderate negative dependence of the rate constant on solvent polarity (*Table 1*). This effect was also observed for the N_2 elimination from the corresponding dihydrothiadiazoles, leading to **1** [21] and **2** [22]. It indicates diminishing charge separation in the activation process, *i.e.*, a reduction of polarity. A consideration of the partial dipole moments clarifies the phenomenon.

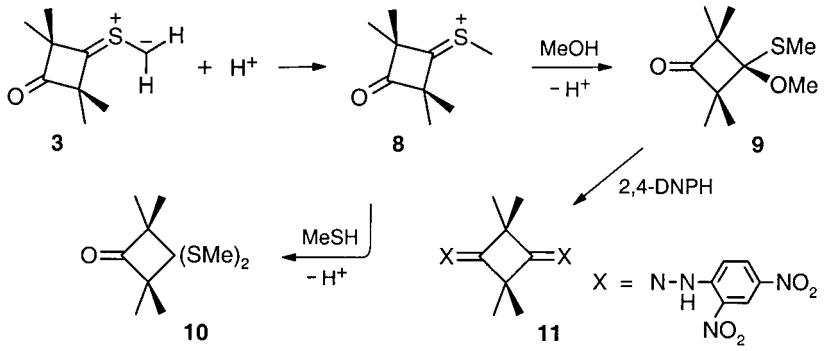
Table 1. *First-Order Rate Constants for the N_2 Evolution from 1,1,3,3-Tetramethyl-8-thia-5,6-diazaspiro[3.4]oct-5-en-2-one* (**6**); *Variation of Solvent and Temperature*

Temp.	Solvent	$k_1 \cdot 10^4$ [s^{-1}]	Temp.	Solvent	$k_1 \cdot 10^4$ [s^{-1}]
40°	Cyclohexene	2.1	40°	$CHCl_3$	1.14
40°	Xylene	1.67, 1.75	40°	Acetonitrile	0.96, 0.98
40°	Diethyl fumarate	1.60	40°	Sulfolane	0.80
40°	Dimethyl maleate	1.41	46°	Xylene	4.7
40°	THF	1.28, 1.35	49°	CCl_4 [17]	5.2
40°	Benzene	1.23, 1.24	50°	Xylene	6.2, 6.8
40°	Benzonitrile	1.20			

Dimethyl maleate and diethyl fumarate are active dipolarophiles that avidly capture **3**, but, when used as solvents for **6** show similar rate constants as inert solvents. These dipolarophiles do not intervene in the rate-determining step, $\mathbf{6} \rightarrow \mathbf{2} + N_2$.

In the absence of intercepting reagents, the ylide **3** undergoes electrocyclization furnishing thiirane **7** (74% in xylene, 40°, 8 h). When the N_2 elimination from **6** took place in MeOH with catalysis by CF_3CO_2H at 40°, the dimethyl monothioacetal **9** was formed in 80% yield, whereas passing of MeSH into the solution of **6** in benzene at 40° afforded the dithioacetal **10** (*Scheme 1*). In the ^{1}H-NMR spectrum of **9**, the *singlets* of MeS and MeO were found at 1.92 and 3.37 ppm, respectively, and the conversion to the bis(2,4-dinitrophenylhydrazone) **11** revealed the unchanged C-skeleton.

Scheme 1

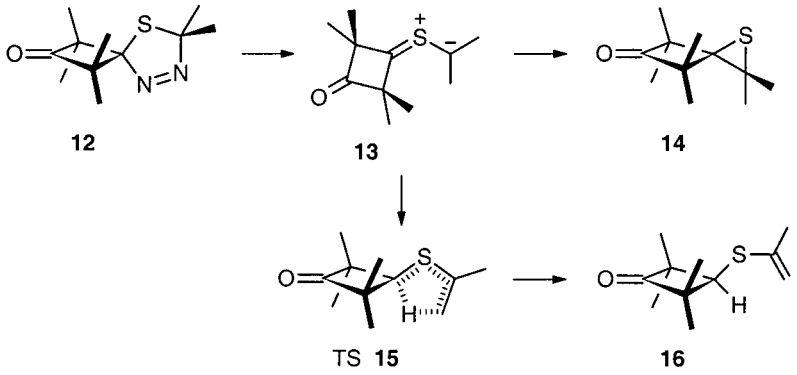


As observed for **1** and **2**, protonation takes place at the methanide C-atom of **3**, and the alkylidenesulfonium ion **8** combines with MeOH or MeSH. When **6** was decomposed in benzene in the presence of 5 mol-% of CF_3CO_2H at 40°, the formation of **10** (11%) and dione **4** (46%) besides thiirane derivative **7** (38%) suggests a more complex sequence of steps.

The MS of **9** and **10** show a strong peak for $[M-\text{dimethylketene}]^+$. This peak likewise appears in the MS of most cycloadducts of **3**, usually accompanied by *m/z* 70 for dimethylketene$^+$, which can also bear the positive charge in the fragmentation process.

2.2. *'Thiocarbonyl Ylide'* **13**: *1,4-H Shift and Reaction with MeOH.* The cycloaddition of 2-diazopropane to **5** furnished the spirocyclic tetrasubstituted dihydrothiadiazole derivative **12**, which lost N_2 at 51° in toluene with a half-life of 125 min, *ca.* 7 times slower than **6**, to give the intermediate **13** (*Scheme 2*). The N_2 extrusion from **12** at 70° is 2.1 times faster in toluene ($t_{1/2}$ 18 min) than in MeCN (33 min). The small decrease of polarity in the TS of N_2 elimination was mentioned above for **6**. Thiirane compound **14** and thioenol ether **16** were found as stabilization products of the 1,3-dipole **13**. According to the ^{1}H-NMR analysis with weight standard, the thermolysis of **12** at 51° (100°) gave 38% (90%) of **14** and 33% (8%) of **16**, both in toluene. In MeCN at 70°, 94% of **14** and only a trace of **16** were formed.

Scheme 2

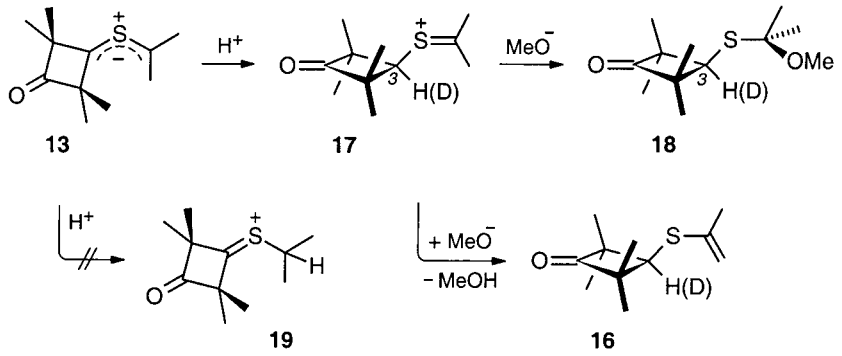


The ^{1}H-NMR spectrum of **14** shows three *singlets* for two Me groups each, and the IR absorption at 1782 cm^{-1} characterizes the cyclobutanone derivative. The signals of two vinylic protons at 4.68 and 4.96 ppm, and the *singlet* at 3.37 for H–C(3) are observed for **16**. The ^{13}C-NMR resonances of the vinylic C-atoms, *triplet* at 107.9 for $=CH_2$ and *singlet* at 141.3 for =C–S, likewise confirm structure **16**.

The conversion **13** → **16** is a 1,4-H shift *via* TS **15**, which competes here with the electrocyclization **13** → **14**; the latter dominates at 100°. The thermal suprafacial 1,4-H shift is a six-electron process in which orbital control allows concertedness. It is the counterpart of the sigmatropic 1,5-shift typical for alkylated 1,4-dienes. The chemistry of 1,3-dipoles offers various examples of 1,4-H shifts (*e.g.*, in 'carbonyl ylides' (=oxonium ylides) [23]) and has previously been observed for some 'thiocarbonyl ylides' [24].

When the cycloreversion **12** → **13** took place in MeOH at 60° (6 h), the thiocyclobutanone **16** (51%) and its formal MeOH adduct **18** (37%), but no thiirane compound **14**, were formed (*Scheme 3*); **16** and **18** were separated by prep. TLC. The structure of monothioacetal **18** was established by the ^{1}H-NMR (3*s* for 3 Me_2C and a *s* for H–C(3) at 3.05 ppm) and MS data (*m/z* 73 (100%) is probably the carboxonium

Scheme 3



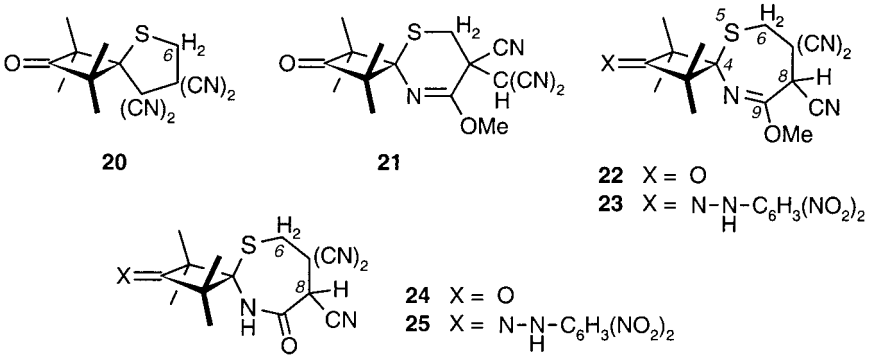
ion $[Me_2C{=}OMe]^+$, formed by β-elimination of the S-substituent). The data confirm for **18** a regiochemistry of MeOH addition, which is opposite to that observed for **9**.

In the thermolysis of **12**, electrocyclization and 1,4-H shift are competing for **13**. Why is thiirane derivative **14** missing in the MeOH reaction, whereas the thioenol ether **16** is present? Thiirane compound **14** is stable to MeOH at 60° and cannot be an intermediate here. The reaction of **13** with MeOD at 60° afforded **16** and **18** in the unchanged ratio 60:40, and the D label (80–85%) appeared at C(3) of *both* compounds. Since D-free **16** (from the MeOH reaction) was not deuterated by MeOD at 60°, **16** must be formed by another pathway in the MeOH(D) reaction. The lack of a H/D isotope effect on the product ratio **16**/**18** suggests the sulfonium ion **17** as a common intermediate. An initiating H- or D-transfer to **13** is in accordance with the basicity of 'thiocarbonyl ylides'. Subsequently, the MeO^- addition competes with deprotonation: **18** and **16** are irreversibly formed.

In the regioisomeric proton adducts **17** and **19**, the i-Pr group of **19** lies in the plane of the alkylidenesulfonium ion, and *Van der Waals* collision with a geminal dimethyl group of the ring is unavoidable. On the other hand, the ring protonation giving **17** relieves the *Van der Waals* strain of **13** by rotation about the C(3)–S bond. Thus, **17** may be the more favorable proton adduct, but the ring position 3 of **13** is more highly screened. Experience shows that proton transfers are processes that suffer the least from steric hindrance.

2.3. '*Thiocarbonyl Ylide*' **3** *and TCNE*. 2.3.1. *Interception of an Intermediate*. When dihydrothiadiazole derivative **6** was heated in the presence of 1.1 equiv. of TCNE in abs. THF at 45° for 8 h, the N_2 elimination was complete, and the ^{1}H-NMR analysis indicated cycloadduct **20** in 84% yield (*cf. Scheme 4*). The spectroscopic properties of **20** are as expected: in the ^{1}H-NMR spectrum, as a consequence of a σ-plane, $CH_2(6)$ appears as *singlet* at 3.83 ppm, whereas the $\Delta\delta$(H) of the two geminal-dimethyl groups' *singlets* at 1.48 and 1.96 reflects the deshielding by the CN groups on one side of the ring. In the mass spectrum, the low population of M^+ (0.03%) indicates a high fragmentation rate. The radical cation of dimethylketene (*m*/*z* 70) is the base peak, whereas $[M - C_4H_6O]^+$ (*m*/*z* 228) occurs only to 0.9%. No peak above *m*/*z* 70 reaches 5%.

On repeating the reaction in MeOH/THF 1:99 (*v*/*v*), a new product appeared besides **20**, which was separated by prep. TLC. The molecular formula indicated a



product of **3**/TCNE/MeOH 1:1:1. The new compound and **20** occurred in a 66:34 ratio in 97% yield. Cycloadduct **20** was resistant to refluxing MeOH, and TCNE remained unchanged when heated in MeOH/THF 2:98 (*v*/*v*) at 40° for 6 h. The latter observation is a kind of anomaly, considering the high electrophilicity of TCNE. This inertness to alcohols in the strict absence of base served us previously for the interception of zwitterionic intermediates in the reaction of TCNE with vinyl ethers [25]. It is obvious that also in the present case, an intermediate is captured by MeOH.

The new compound is the spirocyclic lactim ether **22** with a seven-membered ring, though most of the properties are likewise compatible with the six-membered-ring structure **21**. In the ^{1}H-NMR spectrum of **22**, the *AB* pattern of the CH_2(6) and four different shifts for the two Me_2C groups are evidence of chirality. The H–C(8) is easily exchanged with D_2O. The ^{13}C-NMR spectrum displays three *singlets* for the CN groups, and the imidate C-atom, C(9), resonates at 146.5 ppm. The C=O signal at 216.7 is typical for a four-membered ring ketone (cyclobutanone: 208.2 ppm [26]). With respect to the spiro atom, **22** is an S,N-acetal. It required (2,4-dinitrophenyl)hydrazine (2,4-DNPH) in strong acid to convert **22** into the bis-hydrazone **11**, whereas the monohydrazone **23** was formed under mild acidic conditions. The double set of ^{1}H-NMR signals of **23** is indicative of (*Z*)/(*E*) isomerism.

When the N_2 extrusion from **6** was carried out in THF containing 1 vol-% of H_2O, the ^{1}H-NMR analysis indicated the formation of 45% of the corresponding seven-membered spirolactam **24** and 24% of adduct **20**. The separation was achieved by fractional crystallization of the brown crude product; TCNE is less resistant to H_2O than the MeOH. Although the total yield (69%) was lower than in the MeOH experiment, the ratio **24**/**20** 65:35 was virtually the same as that of **22**/**20** above.

The IR NH absorption of **24** appears at 3277 and 3387 cm^{-1}, and that of amide I at 1698 cm^{-1}; the missing amide II band is indicative of a '*cis*-amide' group, which is enforced in aliphatic lactams up to the nine-membered one [27]. The lactam **24** is soluble in 1N NaOH and was converted by CH_2N_2 in THF to the lactim methyl ether **22** (72%). As described for **22**, 2,4-DNPH converted **24** to the monohydrazone **25** and, with stronger acid, to **11**.

2.3.2. *The Mechanistic Pathway with Two Intermediates.* In a series of experiments, the MeOH content of the THF was varied in the *in situ* reactions of **3** with 1.1 equiv. of TCNE (*Table 2*). In the experiments with 1–5 vol-% of MeOH, the ratio of **22**/**20**

amounted to 65 : 35 within the error of the ^{1}H-NMR analysis, and the yields fluctuated from 88-97% (*Table 2*). The run with 0.5 vol-% of MeOH furnished a yield of 85% and **22**/**20** 60 : 40, *i.e.*, 51% of **22** was formed with only 62 mol-% of MeOH present in the solution. That speaks for an intermediate that eagerly binds MeOH. On the other hand, an excess of MeOH cannot bring the yield of cycloadduct **20** below the 35% threshold. Obviously, the same limit is observed for the reaction in the presence of H_2O, in which lactam **24** is the interception product (*Table 2*).

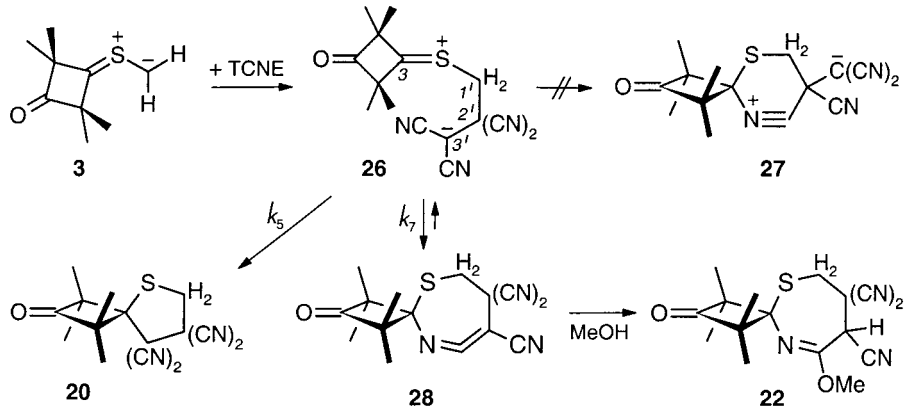
Table 2. *Reactions of Dihydrothiadiazole Derivative* **6** (0.20M) *and TCNE* (0.22M) *in THF* (45°, 5 h): *Influence of MeOH and H_2O Concentration in the Solvent*

ROH	vol-%	equiv.		Product ratio[a])	Yield [%][a])
	0	0	**22**/**20**	0 : 100	84
MeOH	0.50	0.62	**22**/**20**	60 : 40	85
MeOH	1.00	1.23	**22**/**20**	66 : 34	97
MeOH	2.00	2.47	**22**/**20**	68 : 32	88
MeOH	3.00	3.70	**22**/**20**	63 : 37	94
MeOH	5.00	6.17	**22**/**20**	64 : 36	95
H_2O	0.50	2.78	**24**/**20**	65 : 35	69
H_2O	1.00	5.55	**24**/**20**	65 : 35	68

[a]) By ^{1}H-NMR analysis in (D_6)acetone.

The pathway leading to the interceptible intermediate (65%) must be *reversible*, because in dry THF, it returns and forms cycloadduct **20** irreversibly. The conclusion, that *two* intermediates are involved, finds support in mechanistic considerations. We assume zwitterion **26** with its well-stabilized charges as the first intermediate (*Scheme 4*). The negative charge is distributed by resonance over C(3′) and the N-atoms of the malononitrile group. The steric hindrance that thwarts the concerted cycloaddition of TCNE also impedes the bond formation of the carbanionic C(3′) of **26** with the C(3) of the sulfonium ion. The linear nitrile group at C(3′) more easily penetrates the barricade of the geminal dimethyl groups, and the 'ketene imine' **28** is formed by fitting the anionic N-atom into the electron gap at C(3). With respect to the

Scheme 4



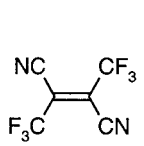
new σ-bond, C(1′)–C(2′), **26** is in a *gauche*-conformation, and the side chain of the four-membered ring, C(3)–C(3′), forms kind of helical coil.

In our preferred interpretation (several variants are conceivable), zwitterion **26** closes the five-membered thiolane ring of **20** (k_5) and the seven-membered ring of ketene imine **28** (k_7) with a rate ratio $k_5/k_7 = 35:65$. The two pathways of intramolecular alkylation of the nitrile anion in **26** are known from intermolecular analogues, too. When the electronically favored *C*-alkylation of the carbanion is sterically hindered, *N*-alkylation affords 'ketene imines' [28].

The inclusion of the cumulated bond system into the seven-membered ring of **28** creates strain; no stable allene-type system in a seven-membered ring has been described previously [29]. Open-chain 'ketene imines' accept alcohols and H_2O less rapidly than ketenes. We ascribe the high rate of addition in the case of **28** to the relief of ring strain. Because of angle strain and conformational strain, the 'ketene imine' **28** is at an energetic disadvantage, compared with thiolane **20**. Therefore, in the absence of MeOH or H_2O, **28** will return to zwitterion **26** and is again distributed on the two cyclization pathways until, finally, all the material reaches the 'harbor' of the five-membered ring in **20** (*Scheme 4*).

The evidence for the occurrence of the cyclic ketene imine **28** is indirect. Our effort of observing the IR absorption of the cumulated-bond system in the region of 2000 cm^{-1} during the reaction in dry solvent was not successful. The initial reaction **6** → **3** + N_2 is the slow step, and the stationary concentrations of intermediates on the path to **20** remain small.

Corroboration of the daring mechanistic scheme came from the reaction of **3** with 2,3-bis(trifluoromethyl)fumaronitrile (**29**), which afforded the cyclic ketene imine **30a** and the thiolane **31a** in a 78:22 ratio ($CDCl_3$, 40°) [30]. Both products were obtained crystalline, and the rapid reactions of **30a** with MeOH and H_2O provided lactim ether and lactam, respectively. An X-ray analysis of the related compound **30b** confirmed the structure of the seven-membered cyclic ketene imine [31]. The 'CF_3 effect' [32] stabilizes **30a**,**b**, compared with **28**.



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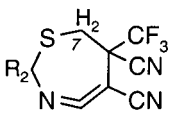

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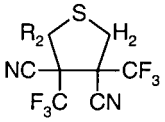

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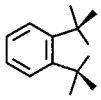
a R_2 =

b R_2 =



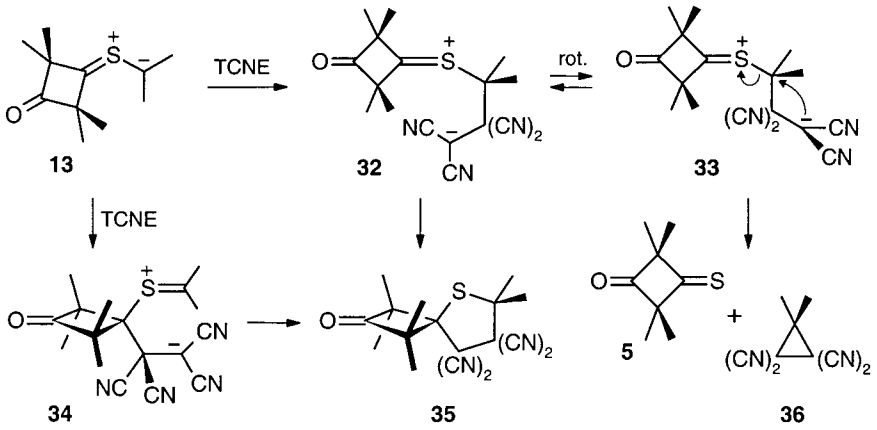
As mentioned above, the spectroscopic data of **22** and **24** are also compatible with **21** and the corresponding six-membered lactam. Mechanistic reasons were in favor of the seven-membered rings, since the *Ritter* reaction (for a review, see [33]) of the 'inner' CN group of **26** with the alkylidenesulfonium center would primarily give rise to nitrilioalkanide **27**. The latter is even more strained than **28**, because the linear nitrilium ion has to be forced into a six-membered ring.

The zwitterion **26** should be able to rotate about the C(2′)–C(3′) bond. That rotation is invisible in the TCNE experiment, but the exchange of TCNE by dimethyl 2,3-dicyanofumarate brings it to light by a decreasing stereospecificity of thiolane

formation [34]. It should be emphasized that the two-step mechanism *via* zwitterion is observed only for 'thiocarbonyl ylides' of strong steric demand like **3**. In the reactions of **1** and **2** with TCNE, no intermediate was interceptible with MeOH and H_2O, and the additions of **1** and **2** to dimethyl 2,3-dicyanofumarate proceeded without loss of stereochemical integrity [1][15].

2.4. *'Thiocarbonyl Ylide'* **13** *and TCNE*. 2.4.1. *Cycloaddition and Intramolecular Substitution*. Thermolysis of dihydrothiadiazole **12** (toluene 60°, 6 h) in the presence of TCNE furnished cycloadduct **35** (49%), 3,3-dimethylcyclopropane-1,1,2,2-tetracarbonitrile (**36**; 38%), and 3-thiono derivative **5** (25%). The splitting products **36** and **5** (*Scheme 5*) are expected in equivalent amounts; some of the volatile **5** was removed with the solvent.

Scheme 5



The structure of the thiolane derivative **35** with its plane of symmetry is in accord with its ^{1}H-NMR data (3*s* at 1.42, 1.92, and 1.97 ppm for 3 Me_2C, of which 2 were shifted downfield due to the proximity of the CN functions).

The formation of **36** + **5** corresponds to the transfer of the isopropylidene group from **13** to TCNE. The 1,5-zwitterion is again the intermediate of choice. Whereas the cyclization to **35** requires the *gauche*-zwitterion **32**, the *anti*-conformation **33** (*anti* with respect to the newly formed σ-bond) is the logical precursor for the intramolecular nucleophilic substitution leading to **5** + **36**. The prototype of the latter is the first synthesis of a cyclopropane ring, described by *W. H. Perkin Jr.* in 1884 [35]. The *quasi*-linear arrangement of nucleophilic reagent and C–X bond is mandatory for S_N2 reactions, also for the intramolecular variant [36]. Only the *anti*-conformer **33** fulfills this condition.

The ratio of the two pathways furnishing **35** and **36** was only slightly dependent on the temperature: 56 : 44 in toluene at 40° and 60°, 54 : 46 at 110° (toluene), and 49 : 51 at 130° (xylene). The cyclization was favored by increasing solvent polarity (50°): 60 : 40 in benzene and 87 : 13 in MeCN.

The reaction of 2-diazopropane with TCNE in THF at 0° afforded the cyclopropane **36** (63%), identical with the specimen obtained from **12** and TCNE. Could it be that a

cycloreversion **12** → **5** + 2-diazopropane competes with the N_2 elimination at 40–130°, and that the isolated **36** originates from 2-diazopropane and TCNE? However, such a *retro*-cycloaddition of dihydrothiadiazole derivative **12** was not observed in the thermolysis experiments described in *Sect. 2.2*. Further, cycloadduct **35** is thermostable: no change was noticed on heating its solution in CD_3CN at 200° (13 h).

2.4.2. gauche- *and* anti-*Conformation of the Zwitterion*. We discussed the reaction of **3** + TCNE (*Scheme 4*) by means of the *gauche*-zwitterion **26** and neglected the *anti*-conformation. Experience in the related world of 1,4-zwitterions, which occur as intermediates in the (2 + 2) cycloaddition of TCNE with vinyl ethers [25], may be pertinent for the 1,5-zwitterions discussed here. Calculations of butane-1,4-diyl diradical showed an energetic advantage of the *anti*-conformation (with respect to the 2,3-bond) over the *gauche*-form: 1.1 kcal mol^{-1} by SCF, STO-3G [37a], and 1.8 kcal mol^{-1} by SCDI/6-31G* [37b]. In the mentioned 1,4-zwitterions, the distance of the charge centers is in the *anti*-conformer double as large as in the *gauche*-form, *i.e.*, Coulombic attraction is expected to favor *gauche* over *anti*. There is manifold evidence for an initial formation of the *gauche*-zwitterion in the cyclobutane formation from donor and acceptor ethenes (for a discussion, see [38a]).

No cyclopropanetetracarbonitrile was found in the reaction of 'thiocarbonyl ylide' **3** with TCNE. When the *gauche*-zwitterions **26** and **32** are compared, the increase of the *Van der Waals* strain by the additional Me groups possibly diminishes the 'Coulombic advantage' of **32** (*gauche*) over **33** (*anti*). Now both conformations side by side might control the reaction. Excessive *Van der Waals* strain makes the regioisomeric 1,5-zwitterion **34** unlikely. Formally, **34** could cyclize to **35**, but would not lead to the fragmentation products **5** + **36**.

The reaction of **13** with TCNE in H_2O/THF 2:98 (*v*/*v*), at 50° provided **35** and **36** in an unchanged ratio 60:40, albeit in lower yield because of the instability of TCNE to H_2O at 50°. No interception product like **24** was isolated here. While the methanide **3** reacted with **29** to give 78% of the cyclic ketene imine **30a**, the reaction of the 2-propanide **13** afforded only 5% of the 7,7-dimethyl derivative of **30a** besides the thiolane and cyclopropane derivative [30]. Conceivably, the seven-membered ring suffers more from the additional *Van der Waals* strain by the geminal dimethyl groups than the thiolane.

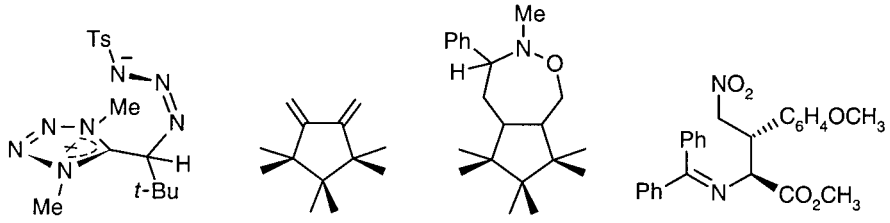
3. Conclusions. The experimental evidence for concertedness is indirect and results from comparison with established two-step processes. Diagnostic criteria of two-step cycloadditions were elaborated in the Munich laboratory for 1,4-dipolar cycloadditions [38b] and, especially, for the (2 + 2) cycloadditions of donor and acceptor ethenes [38a], mentioned above. The present study is part of a systematic search for the borderline crossing from the concerted 1,3-dipolar cycloaddition to the two-step pathway *via* a 1,5 zwitterion. A great difference of the HO-LU energies of the partners alone did not induce the switching of mechanism; steric hindrance at one or both termini of the 1,3-dipole turned out to be mandatory. For well-understood reasons, the concerted process is more sensitive to steric effects than the formation of the zwitterion.

In this paper, the occurrence of the 1,5-zwitterion from 'thiocarbonyl ylide' **3** and TCNE is deduced from the reversible formation of a strained cyclic ketene imine

intercepted by MeOH or H_2O. The ketene imine **28** is the result of a bifurcation on the pathway leading to the (3 + 2) cycloadduct. Similarly, the formation of a hexasubstituted cyclopropane **36** from **13** and TCNE is regarded as a side-stepping *via* the *anti*-conformation of the zwitterion, which cannot directly close the five-membered ring of the cycloadduct.

Both phenomena illustrate the reactivity potential of the zwitterionic intermediates. The preparative virtues of 1,3-dipolar cycloadditions are mild conditions, high yields, stereoretention at up to four terminal centers, and compatibility with a wide range of substituents. All these qualities appear to be connected with the concerted pathway and vanish when reactive intermediates emerge on the reaction profile.

A crossing of the mechanistic borderline is also expected when the FMO energies are exchanged, *i.e.*, in the reaction of a strongly electrophilic 1,3-dipole with a very nucleophilic dipolarophile. Indeed, *Quast et al.* reported the isolation of the 1,5-zwitterion **37** from tosyl azide and an alkylidenedihydro-1*H*-tetrazole; on warming it closes the five-membered ring, which, however, is transformed to secondary products [39]. An enlightening detail: the X-ray structure of **37** with its small distance of the charge centers resembles the *gauche*-zwitterions **26** and **32**.



37 **38** **39** **40**

Another borderline was transgressed when diene **38** was reacted with *N*-methyl-*C*-phenylnitrone. *Mayr et al.* isolated some (4 + 3) cycloadduct **39** besides diastereoisomeric (3 + 2) cycloadducts [40]. A 1,5-diradical was assumed on the pathway to **39**.

Recently, *Vivanco et al.* observed an intermediate **40** in the thermal (3 + 2) cycloaddition of methyl *N*-(diphenylmethylene)glycinate with 4-methoxy-β-nitrostyrene; **40** cyclized to a pyrrolidine derivative at room temperature [41]. Since the reaction medium contained Et_3N, the sequence of base-catalyzed *Michael* addition and nitroaldol reaction appears to be unrelated to the mechanism *via* zwitterion discussed here.

We express our sincere thanks to the *Fonds der Chemischen Industrie*, Frankfurt, for supporting our research program. *G. M.* is indebted to the *Alexander von Humboldt Foundation* for a stipend. Our thanks go to *Helmut Huber* for many NMR spectra and to *Reinhard Seidl* for the mass spectra. *Helmut Schulz* and *Magdalena Schwarz* provided the elemental analyses.

Experimental Part

1. *General.* See [1]; NMR spectra in dry $CDCl_3$, if not otherwise mentioned. The quant. ^{1}H-NMR analyses were run with 1,1,2,2-tetrachloroethane (5.92 ppm) as weight standard, if not otherwise stated.

2. *1,1,3,3-Tetramethyl-8-thia-5,6-diazaspiro[3.4]oct-5-en-2-one* (**6**). 2.1. *Preparation.* The conversion of *2,2,4,4-tetramethyl-3-thioxocyclobutanone* (**5**) [16] with CH_2N_2 to **6** was described in [17, 18]; 87% of **6**. Colorless

crystals, which can be stored at $-25°$ for several weeks. M.p. 40–42°. Whereas the regiochemistry of CH_2N_2 addition to adamantanethione depends on solvent polarity [22][42], from **5** only **6** was formed in Et_2O, THF, or MeOH. For ^{1}H-NMR and elemental analyses, see [18].

2.2. *Kinetics of N_2 Extrusion*. The nitrometric technique [21] was carried out with 2–3 mmol of **6** in 15 ml of solvent in a bath of $40 \pm 0.2°$. Graphic evaluation of 20–30 volume readings indicated the first order for 2–3 half-lives; linear regression showed correlations with $r = 0.999$. Results in *Table 1*.

2.3. *4,4,6,6-Tetramethyl-1-thiaspiro[2.3]hexan-5-one* (**7**). The above thermolysis solns. furnished **7** as colorless crystals. M.p. 79–81° ([17]: 80–82). ^{1}H-NMR analyses ($CDCl_3$) with weight standard: 84% of **7** for the reaction in THF, 88% of **7** for that in benzene. ^{1}H-NMR: 1.15 (*s*, 2 Me); 1.22 (*s*, 2 Me); 2.57 (*s*, CH_2(2)).

When **6** was heated in benzene (40°, 10 h) in the presence of 5 mol-% of CF_3CO_2H, the yield of **7** fell to 38%, and dithioacetal **10** (11%) as well as dione **4** (46%) were observed.

2.4. *Reaction with MeOH*. The soln. of **6** (396 mg, 2.00 mmol) in MeOH (5 ml) + 2 drops of CF_3CO_2H was heated at 40° for 8 h. Workup with aq. Na_2CO_3 soln. and CH_2Cl_2 afforded *3-methoxy-3-methylthio-2,2,4,4-tetramethylcyclobutanone* (**9**; ^{1}H-NMR indicated 80% of **9**, and 61% was isolated after prep. TLC (2 mm of silica gel; with CH_2Cl_2)). Colorless oil, which solidified below 20°. IR: 884*m*, 918*m*, 1033*s*, 1092*s*, 1117*s* (C–O); 1485*s*, 1780*s* (C=O). ^{1}H-NMR: 1.23 (br. *s*, 4 MeC); 1.92 (*s*, MeS); 3.37 (*s*, MeO). MS (20°): 202 (10, M^+), 187 (6, $[M - Me]^+$), 132 (100, $[M - Me_2C{=}C{=}O]^+$; $^{13}C_2 + {}^{34}S$ calc.: 5.0; found: 5.4), 117 (29, $[C_5H_9OS]^+$), 95 (7), 87 (11), 85 (9, $[Me_2C{=}C{=}OMe]^+$), 70 (25, $C_4H_6O^+$, dimethylketene$^+$), 55 (8, $C_3H_3O^+$). Anal. calc. for $C_{10}H_{18}O_2S$ (202.31): C 59.36, H 8.97, S 15.85; found: C 59.46, H 8.96, S 15.84.

The unchanged ^{1}H-NMR spectrum after 2 weeks in $CDCl_3$ shows that **9** has no tendency to disproportionate.

2.5. *Conversion of* **9** *to 2,2,4,4-Tetramethylcyclobutane-1,3-dione Bis(2,4-dinitrophenyl)hydrazone* (**11**). For 5 h, **9** and 2,4-DNPH (2.2 equiv.) were refluxed in H_2SO_4/EtOH: 64% of yellow **11**. M.p. 324–326 (dec., mixed m.p.) ([16a]: 320–322° (dec.)).

2.6. *Conversion of* **3** *to 2,2,4,4-Tetramethylcyclobutane-1,3-dione* (**4**). A soln. of **6** (1.00 mmol) in THF (5 ml), containing 3 vol-% of H_2O and 2 drops of CF_3CO_2H, was stirred at 40° for 8 h. After workup, ^{1}H-NMR analysis showed 72% of **4**.

2.7. *Reaction of* **3** *with MeSH*. A slow stream of MeSH was passed into the stirred soln. of **6** (270 mg, 1.36 mmol) in benzene (5 ml) at 40°. Workup after 8 h and ^{1}H-NMR analysis established 66% of *2,2,4,4-tetramethyl-3,3-bis(methylthio)cyclobutanone* (**10**). Prep. TLC (pentane/CH_2Cl_2 8:2, 3× developed) produced **10** (143 mg, 48%) as the first zone; the second afforded 60 mg of an unknown compound with 4 Me signals at 1.22, 1.27, 1.30, 1.35. Adduct **10** crystallized from MeOH at −78°. M.p. 88–90°. IR: 838*m*, 1026*m*, 1364*m*, 1379*m*, 1465*m*, 1782*s* (C=O). ^{1}H-NMR ($CDCl_3$): 1.40 (*s*, 4 MeC); 2.05 (*s*, 2 MeS). ^{1}H-NMR (C_6D_6): 1.31 (*s*, 4 MeC); 1.75 (*s*, 2 MeS). ^{13}C-NMR: 14.4 (*q*, 2 MeS); 22.2 (*q*, 4 *Me*C); 67.0 (*s*, C(2), C(4)); 70.2 (*s*, C(3)); 219.0 (*s*, C=O). MS (20°): 218 (0.5, M^+), 203 (65, $[M - Me]^+$), 148 (83, $[M - C_4H_6O]^+$), 133 (15, $C_5H_9S_2^+$), 101 (100, $C_5H_9S^+$, $[Me_2C{=}C{=}SMe]^+$), 95 (22), 85 (35, $C_4H_5S^+$), 81 (51), 67 (16), 61 (19). Anal. calc. for $C_{10}H_{18}OS_2$ (218.38): C 55.00, H 8.31, S 29.37; found: C 55.04, H 8.27, S 29.29.

3. *Reaction of* **3** *with TCNE*. 3.1. *Cycloaddition in Abs. THF*. A soln. of **6** (198 mg, 1.00 mmol) and freshly sublimed TCNE (141 mg, 1.10 mmol) in abs. THF (5 ml) was heated to 45° for 8 h. After evaporation, ^{1}H-NMR analysis in (D_6)acetone indicated *1,1,3,3-tetramethyl-2-oxo-5-thiaspiro[3.4]octane-7,7,8,8-tetracarbonitrile* (**20**; 84%; *s* at 4.26). Isolated was 57% of **20** as colorless crystals (EtOH). M.p. 213–215° (dec.). IR: 1373*m*, 1390*m*, 1450*m*, 1468*m*, 1795*s* (C=O), 2253*w* (C≡N). ^{1}H-NMR ($CDCl_3$): 1.48 (*s*, 2 Me); 1.96 (*s*, 2 Me); 3.83 (*s*, CH_2(6)). ^{1}H-NMR ((D_6)acetone): 1.46 (*s*, 2 Me); 1.94 (*s*, 2 Me); 4.26 (*s*, CH_2(6)). ^{13}C-NMR (100 MHz, DEPT): 22.7 (2 Me); 22.9 (2 Me); 37.6 (C(6)); 48.1 (*s*, C(7)); 52.7 (*s*, C(8)); 67.9 (*s*, C(1), C(3)); 70.1 (*s*, C(4)); 110.0, 110.4 (2*s*, 4 CN); 212.5 (C=O). MS (40°): 298 (0.03, M^+), 255 (0.21), 228 (0.91, $[M - C_4H_6O]^+$, ^{13}C 0.11/0.14), 220 (0.51, $[M - H_2C{=}C(CN)_2]^+$), 201 (1.2, $[228 - HCN]^+$), 160 (2.3), 150 (2.4), 145 (4), 86 (1, $[Me_2C{=}C{=}S]^+$), 85 (3, $C_4H_5S^+$), 70 (100, $[Me_2C{=}C{=}O]^+$, ^{13}C 4.5/4.5), 42 (14, $C_3H_6^+$), 41 (7, Allyl$^+$). Anal. calc. for $C_{15}H_{14}N_4OS$ (298.36): C 60.38, H 4.73, N 18.78, S 10.75; found: C 60.15, H 4.81, N 18.52, S 10.56.

3.2. *Reaction in THF with Variable MeOH Content*. In 4 volumetric flasks (10 ml), 0.10, 0.20, 0.30, and 0.50 ml of abs. MeOH, measured with a *Hamilton* syringe, were filled with abs. THF; analogously, 0.10 ml of MeOH was filled with THF to 20 ml. In 5 ml of each mixture, **6** (1.00 mmol) and TCNE (1.10 mmol) were reacted as described in *Sect. 3.1*. For the quant. ^{1}H-NMR analysis in (D_6)acetone, the machine integral of the right branch (*AB* spectrum of CH_2(6)) at 3.50 was suitable for **22**. The *s* at 4.26 for CH_2(6) of **20** was not sufficiently separated from the left-hand branch (4.09) of the above *AB* of **22**; therefore, the integral of the right-hand *d* was deducted from that of the sum to obtain a 2 H integral for **20**. The results are shown in *Table 2*.

3.3. *9-Methoxy-1,1,3,3-tetramethyl-2-oxo-5-thia-10-azaspiro[3.6]dec-9-ene-7,7,8-tricarbonitrile* (**22**). The separation of **20**/**22** succeeded with prep. TLC (silica gel; acetone/petroleum ether 3:7), and **22** was obtained from EtOH in colorless needles. M.p. 175–177° (dec.). IR: 1000*m*, 1032*m*, 1256*s* (C–O), 1456*m*, 1465*m*; 1700*s* (C=N); 1784*s* (C=O), 2250*w* (C≡N). ^{1}H-NMR (80 MHz): 1.11, 1.32, 1.40, 1.41 (4*s*, 4 MeC); 3.05, 3.58 (*AB*, *J* = 15.3, CH_2(6)); 3.82 (*s*, MeO); 5.22 (*s*, H–C(8), disappears with D_2O). ^{13}C-NMR (20.2 MHz): 20.7, 21.6, 22.1, 23.9 (4*q*, 4 *Me*C); 36.8 (*s*, C(7)); 37.0 (*t*, C(6)); 40.0 (*d*, C(8)); 55.8 (*q*, MeO); 67.2, 70.0 (2*s*, C(1), C(3)); 74.1 (*s*, C(4)); 111.0, 111.6, 111.9 (3*s*, 3 CN); 146.5 (*s*, C(9)); 216.7 (*s*, C(2)). MS (90°): 330 (0.3, M^+), 303 (14, [*M* – HCN]$^+$), 271 (2, [*M* – HCN – MeOH]$^+$), 260 (68, [*M* – dimethylketene]$^+$), 233 (45, [*M* – C_4H_6O – HCN]$^+$, 192 (21), 182 (7), 167 (14), 82 (15), 71 (100, $C_4H_7O^+$). Anal. calc. for $C_{16}H_{18}N_4O_2S$ (330.40): C 58.16, H 5.49, N 16.96, S 9.71; found: C 58.15, H 5.57, N 16.73, S 9.72.

3.4. *2-[(2,4-Dinitrophenyl)hydrazono]-9-methoxy-1,1,3,3-tetramethyl-5-thia-10-azaspiro[3.6]dec-9-ene-7,7,8-tricarbonitrile* (**23**). A soln. of **22** (0.76 mmol) and 2,4-DNPH (1.00 mmol) in EtOH (6 ml) and a drop of conc. H_2SO_4 soln. was refluxed for 10 h. After cooling, the orange-yellow **23** (259 mg, 67%) was filtered. (*Z*)/(*E*) Isomer ratio *ca.* 3:1 (by ^{1}H-NMR; double signal set). M.p. (dec.) 202–203° ($CHCl_3$/hexane). IR: 1260*m*, 1282*m* (C–O); 1339*s*, 1517*s*, (NO_2); 1592*m*, 1619*s* (C=N); 2255v*w* (C≡N). ^{1}H-NMR: 1.22, 1.42, 1.45, 1.52, 1.57, 1.62, 1.70 (7*s*, 4 MeC of 2 stereoisomers); 3.04, 3.56 (*AB*, J_{gem} = 16.0, CH_2(6)); 3.80, 3.87 (2*s*, MeO); 5.15, 5.30 (2*s*, H–C(8), disappears with D_2O); 7.80 (*d*, *J* = 9.5, H–C(6′)); 8.25 (*dd*, *J* = 9.5, 2.2, H–C(5′)); 9.5 (*d*, *J* = 2.2, H–C(3′)); 11.0 (br. *s*, NH). Anal. calc. for $C_{22}H_{22}N_8O_5S$ (510.53): C 51.75, H 4.34, N 21.95, S 6.28; found: C 51.66, H 4.45, N 21.99, S 6.30.

3.5. *Conversion of* **22** *to* **11**. After refluxing of **22** (0.30 mmol) in EtOH (4 ml) and conc. H_2SO_4 soln. (2 ml) for 10 h, 2,4-DNPH (0.70 mmol) was added, and the mixture was heated for further 4 h. On cooling, **12** (49 mg, 33%) crystallized. M.p. 323–325° (dec.), no depression of m.p. in the mixture with authentic **11**. IR: 743*m*, 833*m*, 1079*s*; 1312*s*, 1337*s*, 1505*s*, 1518*s* (NO_2); 1592*s*, 1617*s* (C=N); 3328*m* (NH). Anal. calc. for $C_{20}H_{20}N_8O_8$ (500.42): C 48.00, H 4.03, N 22.39; found: C 47.78, H 4.35, N 22.13.

3.6. *Reaction of* **3** *with TCNE in THF with Variable H_2O Content*. A soln. of freshly recrystallized **6** (396 mg, 2.00 mmol) and sublimed TCNE (282 mg, 2.20 mmol) in pure THF (4.95 ml) and H_2O (50 µl) was stirred in a 45° bath for 5 h. After removal of the solvent *i.v.*, the ^{1}H-NMR analysis in (D_6)acetone was based on the integrals at 4.26 (*s*, CH_2(6)) for **20** (0.48 mmol, 24%) and 5.17 (*s*, H–C(8)) for **24** (0.90 mmol, 45%). An analogous experiment with 0.5 vol-% of H_2O furnished **20**/**24** 35:65 with 68% yield.

3.7. *1,1,3,3-Tetramethyl-2,9-dioxo-5-thia-10-azaspiro[3.6]decane-7,7,8-tricarbonitrile* (**24**). The brown residue of the above experiment was triturated with EtOH (3 ml) to give colorless crystals, m.p. 155–170°, which still contained 8% of **20**. Pure prisms of **24** (202 mg, 31%) were obtained from acetone/EtOH. M.p. 171–173°. Crystals soluble in 1N NaOH. IR (nujol): 1698*s* (amide I), 1785 (C=O); no amide II; 2260v*w* (C≡N); 3277*m*, 3387*m* (NH). ^{1}H-NMR ((D_6)acetone): 1.38, 1.40, 1.50, 1.53 (4*s*, 4 Me); 3.77, 4.18 (*AB*, *J* = 15.8, CH_2(6)); 5.17 (*s*, H–C(8); disappears with D_2O); 7.15 (br. *s*, NH; disappears with D_2O). ^{13}C-NMR ((D_6)acetone): 19.1, 21.0, 22.2, 24.6 (4*q*, 4 Me); 36.5 (*t*, C(6)); 38.6 (*s*, C(7)); 44.6 (*d*, C(8)); 68.1, 69.1, 70.6 (3*s*, C(1), C(3), C(4)); 112.0, 113.2, 113.3 (3*s*, 3 CN); 161.7 (*s*, O=C(9)); 216.1 (*s*, O=C(2)); the following J(^{13}C,^{1}H) were observed in the fully coupled spectrum: C(6), ^1J = 150.7; C(8), ^1J = 142; C(4), ^3J = 4.3; N*C*–C(8), ^2J = 9.8; C(9), ^2J = 6.1; C(2), ^3J = 3.7, 4.9. MS (120°): 316 (0.3, M^+), 289 (3, [*M* – HCN]$^+$), 246 (5, [*M* – dimethylketene]$^+$), 219 (4, [246 – HCN]$^+$), 176 (6), 151 (32, $C_6H_3N_2OS^+$), 139 (5, $C_8H_{13}NO^+$), 96 (48), 70 (19, dimethylketene$^+$), 69 (98, $C_4H_5O^+$), 54 (24, $C_3H_2O^+$), 41 (39, allyl$^+$), 27 (100, HCN$^+$). Anal. calc. for $C_{15}H_{16}N_4O_2S$ (316.38): C 56.94, H 5.10, N 17.71, S 10.14; found: C 56.62, H 5.13, N 17.89, S 10.11.

3.8. *Stability Tests. a*) Cycloadduct **20** (1 mmol) in THF (5 ml) + 2 vol-% H_2O or MeOH was refluxed for 6 h. ^{1}H-NMR: only **20**. Mixed m.p. without depression.

b) TCNE (1.00 mmol) in THF (5 ml) and MeOH (0.1 ml) was heated to 40° for 6 h. Evaporation left TCNE (96%). M.p. 193–196°; mixed m.p. without depression.

c) The soln. of TCNE in THF + H_2O (2 vol-%) became dark at 40°, and no starting material was isolated after 6 h.

3.9. *2-[(2,4-Dinitrophenyl)hydrazono]-1,1,3,3-tetramethyl-9-oxo-5-thia-10-azaspiro[3.6]decane-7,7,8-tricarbonitrile* (**25**). As described for **23** with **24**: yellow **25** (74%), which crystallized on cooling and was triturated with refluxing $CHCl_3$. M.p. 199–200°. IR: 1086*m*, 1142*m*; 1313*s*, 1339v*s*, 1507*s*, 1533*s* (NO_2); 1594*s*, 1619v*s* (C=N); 1700*s* (br. amide I), 2255v*w* (CN); 3333*m*, 3390*m* (NH). ^{1}H-NMR ((D_6)acetone): 1.50, 1.57, 1.65 (2×), 1.70, 1.72, 1.82, 1.85 (8*s*, 4 Me of each of (*Z*)- and (*E*)-isomers); 3.77, 4.15 (*AB*, *J* = 15.8, CH_2(6)); 5.30, 5.45 (2*s*, H–C(8)); 7.1 (br. *s*, NH (amide)); 7.80 (*d*, *J* = 9.6, H–C(6′)); 8.27 (*dd*, *J* = 9.6, 2.4, H–C(5′)); 8.85 (*d*, *J* = 2.4, H–C(3′)); 10.9 (br. *s*, NH (hydrazone)). MS (170°, 20 eV): 452 (0.1, [*M* – NO_2]$^+$), 427 (0.04, [*M* – C_4H_5O]$^+$), 319 (19), 304 (5), 151 (7, $C_6H_3N_2OS^+$), 150 (13), 122 (7), 96 (13), 95 (10), 81 (7), 70 (13, dimethylketene$^+$), 69

(20), 68 (37), 43 (15), 41 (11), 27 (100, HCN^+). Anal. calc. for $C_{21}H_{20}N_8O_5S$ (496.50): C 50.80, H 4.06, N 22.57, S 6.46; found: C 50.70, H 4.29, N 22.30, S 6.55.

Lactam **24** was converted to **11** (45%) as described for **22** → **11**. M.p. 318–321° (dec.).

3.10. *Methylation of* **24** *with* CH_2N_2. Lactam **24** (0.50 mmol) in THF (5 ml) was treated with CH_2N_2 (2 equiv.) in THF (*ca.* 2 ml). After 2 min, the N_2 evolution had ceased; the soln. was evaporated, and the residue was triturated with EtOH (2 ml). The colorless **22** (118 mg, 72%) was recrystallized from EtOH. M.p. 172–174°. Mixed m.p., IR and ^{1}H-NMR: identical with those of the specimen of *Sect. 3.3.*

4. *1,1,3,3,7,7-Hexamethyl-8-thia-5,6-diazaspiro[3.4]oct-5-en-2-one* (**12**). 4.1. *Preparation*. A soln. of **5** (4.70 mg, 3.01 mmol) in pentane (10 ml) at 0° was treated dropwise with the red 2-diazopropane [43] in Et_2O just until the red color of **5** disappeared. After evaporation, the colorless residue crystallized from pentane (5 ml) at −78°: **12** (569 mg, 84%). Long needles. M.p. 54–55° (gas). IR: 1023*s*, 1039*s*, 1379*m*, 1463*m* (br.); 1576*m* (N=N); 1786*s* (C=O). ^{1}H-NMR: 1.22, 1.27 (2*s*, 2 Me–C(1), 2 Me–C(3)); 1.72 (*s*, 2 Me–C(7)). MS (30°): 226 (0.7, M^+), 211 (38, $[M-Me]^+$), 198 (74, $[M-N_2]^+$), 166 (27 $[M-N_2-S]^+$), 128 (100, [198 – dimethylketene]$^+$), 123 (30), 113 (37, $[128-Me]^+$), 96 (34, $C_7H_{12}^+$), 81 (48, $C_6H_9^+$), 70 (13, dimethylketene$^+$), 69 (14, $C_4H_5O^+$), 41 (49, allyl$^+$). Anal. calc. for $C_{11}H_{18}N_2OS$ (226.34): C 58.37, H 8.02, N 12.38, S 14.17; found: C 58.60, H 8.14, N 12.59, S 14.21.

4.2. *Kinetics of* N_2 *Extrusion*. Nitrometry, as described in *Sect. 2.2*, provided $k_1 \cdot 10^4$ [s^{-1}]: 0.920 in toluene at 51°, 6.43 in toluene at 70°, and 3.01 in MeCN at 70°. Linearization with $r = 0.999$.

4.3. *Thermolysis of* **12**. The toluene of the 51° (10 h) experiment above (*Sect. 4.2*) was evaporated. The ^{1}H-NMR analysis showed 38% of **14** (*s* at 1.15, 2 Me) and 33% of **16** (*s* at 2.00, =C–Me). Attempts at separation by prep. TLC or fractional crystallization failed. In an experiment at 100°, the N_2 evolution from **12** (2.00 mmol) in toluene (10 ml) was finished after 5 min. ^{1}H-NMR Analysis showed 90% of **14** and 8% of **16** (see *Sect. 4.4*). The soln. of the residue in MeOH (3 ml) gave after 3 d at −78° *2,2,4,4,6,6-hexamethyl-1-thiaspiro[2.3]hexan-5-one* (**14**, 126 mg, 32%). Colorless crystals. M.p. 61–62.5°. IR: 1030*m*, 1087*m*, 1366*m*, 1379*m*, 1458*m*; 1782v*s* (C=O). ^{1}H-NMR: 1.15, 1.47, 1.67 (3*s*, 6 Me). Anal. calc. for $C_{11}H_{18}OS$ (198.32): C 66.61, H 9.15, S 16.17; found: C 66.30, H 9.07, S 16.08.

The product of thermolysis of **12** in MeCN at 70° (*Sect. 4.2*) was analyzed by ^{1}H-NMR ($CDCl_3$) with trichloroethene as standard: **14** (94%) and only a trace of **16**.

4.4. *Reaction of* **13** *with MeOH*. A soln. of **13** (678 mg, 3.00 mmol) in MeOH (10 ml) was heated in a 60° bath for 6 h. Evaporation and ^{1}H-NMR analysis indicated 51% of **16** (*s* at 4.68, $=CH_2$) and 37% of **18** (*s* at 3.25, MeO). Prep. TLC (silica gel; CH_2Cl_2/pentane) afforded **16** (280 mg, 47%) from the first zone. The second zone provided, after renewed prep. TLC, **18** (110 mg, 16%). Both products, colorless oils, were distilled at 40°/0.5 mm.

Data of 2,2,4,4-Tetramethyl-3-[(1-methylethenyl)sulfanyl]cyclobutanone (**16**). IR (film): 845*s*, 898*s* (CH out-of-plane); 1026*s*, 1094*s*, 1366*s*, 1446*s*; 1612*s* (S–C=C), 1777v*s* (br., C=O). ^{1}H-NMR: 1.22, 1.32 (2*s*, 4 Me); 1.97 (*dd*, allylic coupling, =CMe), 3.37 (*s*, H–C(3)); 4.68 (br. *s*, 1 H, CH_2=); 4.96 (*q*, *J*(allyl) = 2.2, 1 H, CH_2=). ^{13}C-NMR (20.2 MHz): 19.6 (*q*, 2 Me); 23.7 (*q*, Me); 24.8 (*q*, 2 Me); 53.7 (*d*, C(3)); 60.4 (*s*, C(2),C(4)); 107.9 (*s*, $=CH_2$); 141.3 (*s*, =CS); 219.9 (*s*, C=O). MS (100°): 198 (7, M^+), 128 (100, $[M-$dimethylketene$]^+$), 113 (80, $[128-Me]^+$), 97 (40, $C_7H_{13}^+$), 95 (14, $C_7H_{11}^+$),70 (6, dimethylketene$^+$), 69 (19, $C_4H_5O^+$), 59 (51), 55 (49), 41 (52, allyl$^+$). Anal. calc. for $C_{11}H_{18}OS$: C 66.61, H 9.15, S 16.17; found: C 66.94, H 9.21, S 16.12.

Data of 3-[(1-Methoxy-1-methylethyl)sulfanyl]-2,2,4,4-tetramethylcyclobutanone (**18**). IR (film): 788*s*, 912*m*, 1026*s*; 1072v*s*, 1125*s*, 1185*s* (C–O); 1365*s*, 1380*s*, 1460*s*; 1773v*s*; (br., C=O). ^{1}H-NMR: 1.20, 1.25, 1.52 (3*s*, 6 MeC); 3.05 (*s*, H–C(3)); 3.25 (*s*, MeO). MS (100°): 230 (0.8, M^+), 199 (1, $[M-MeO]^+$), 198 (1.3), 160 (0.4, $[M-$dimethylketene$]^+$), 128 (5, [160 – MeOH]), 113 (2, [128 – Me]), 97 (10, $C_7H_{13}^+$), 88 (9), 73 (100, probably $[Me_2C=OMe]^+$), 72 (9), 70 [5, dimethylketene$^+$], 55 (10, $C_4H_7^+$), 42 (14), 41 (16, allyl$^+$). Anal. calc. for $C_{12}H_{22}O_2S$ (230.36): C 62.56, H 9.63, S 13.92; found: C 62.82, H 9.36, S 13.72.

The decomposition of **6** in MeOH was repeated at 90° in the sealed tube. Workup and ^{1}H-NMR-analysis showed **16**/**18** 57:43, nearly unchanged when compared with the 60° experiment.

4.5. *Reaction of* **13** *with MeOD*. A soln. of **12** (2.00 mmol) in MeOD (1 ml) was heated at 60° for 6 h. After evaporation, ^{1}H-NMR analysis indicated **16**/**18** 60:40. In both compounds, H–C(3) was replaced by D to the extent of 80–85%. In two test experiments, **14** and **16** were heated in MeOD at 60° for 6 h; no incorporation of D was noticed.

5. *Reaction of* **13** *with TCNE*. 5.1. *Cycloaddition and Intramolecular Substitution in Toluene*. A soln. of **12** (452 mg, 2.00 mmol) and TCNE (282 mg, 2.20 mmol) in toluene (4 ml) heated to 60° for 6 h (N_2 evolution). After evaporation *i.v.*, the soln. of the residue in (D_6)acetone was analyzed by ^{1}H-NMR with 1,1,1,2-tetrachloroethane as standard; the machine integrals indicated **35** (*s* at 1.42; 49%), **36** (*s* at 1.80; 38%), and *ca.* 25% of **5** (*s* at 1.30). Trituration of the residue with $CHCl_3$ (3 ml, 1 h, 0°) gave crude **36** (134 mg) with m.p. 192–

196°. Recrystallization from $CHCl_3$/pentane furnished colorless needles of **36** (98 mg, 29%). The mother liquor gave **35** (196 mg, 30%).

Data of 1,1,3,3,6,6-Hexamethyl-2-oxo-5-thiaspiro[3.4]octane-7,7,8,8-tetracarbonitrile (**35**). Colorless prisms from MeOH. M.p. 174–176°. IR: 1392*m*, 1396*m*, 1467*m*, 1474*m*, 1705*m*; 1790*s* (C=O), 2252*w* (C≡N). ^{1}H-NMR: 1.42, 1.92, 1.97 (3*s*, 6 Me). Anal. calc. for $C_{17}H_{18}N_4OS$ (326.41): C 62.55, H 5.56; found: C 62.36, H 5.68.

Data of 3,3-Dimethylcyclopropane-1,1,2,2-tetracarbonitrile (**36**). M.p. 207–209° (dec.) ([44]: 209.5–210°). IR (nujol): 1109*m*, 2259*m* (C≡N). ^{1}H-NMR ((D_6)acetone): 1.80 (*s*, 2 Me). MS (50°): 170 (12, M^+), 169 (10), 155 (26, $[M-Me]^+$), 143 (42, $[M-HCN]^+$), 130 (100, $[M-CH_2CN]^+$?), 118 (17), 116 (29), 206 (19, $[Me_2C{=}C(CN)_2]^+$), 105 (12), 79 (24, $[105-CN]^+$), 53 (59, $C_4H_5^+$). Anal. calc. for $C_9H_6N_4$ (170.17): C 63.52, H 3.55, N 32.93; found: C 63.46, H 3.68, N 32.72.

5.2. *Independent Synthesis of* **36** [45]. TCNE (206 mg, 1.61 mmol) in abs. THF (15 ml) at 0° was treated dropwise with 2-diazopropane in Et_2O, until the light-yellow soln. turned colorless (N_2 evolution). Recrystallization of the residue from $CHCl_3$ gave **36** (172 mg, 63%). Colorless needles. M.p. 207–208° (dec.). Mixed m.p. showed identity.

5.3. *Compound* **13** *and TCNE: Variation of Solvent.* By ^{1}H-NMR analysis ($CDCl_3$), the following ratios of **35**/**36** (% yield) were determined: benzene (5 h reflux), 59:11 (98%), +27% of **5**; benzene (50°, 18 h), 60:40 (84%); THF (50°, 18 h), 61:39 (88%); THF + 2 vol-% of H_2O (60°, 6 h), 60:40 (reduced yield, due to reaction of TCNE with H_2O); toluene (110°, 15 min), 54:46 (85%); xylene (130°, 3 min), 49:51 (98%); CD_3CN (50°, 30 h), 87:13 (92%).

Thermal stability of **35**: no reaction in closed tube experiments in benzene (140°, 68 h), benzonitrile (140°, 68 h), and CD_3CN (195–200°, 13 h).

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Received April 5, 2001