Cyclic Seven-Membered Ketene Imines from Hindered 'Thiocarbonyl Ylides' and 2,3-Bis(trifluoromethyl)fumaronitrile: Properties and Surprising Reactions[1])

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Dedicated to *Meinhart H. Zenk* on the occasion of his 70th birthday

'Thiocarbonyl ylide' **2B** is accessible from 1,1,3,3-tetramethylindanthione and CH_2N_2, and subsequent N_2 extrusion at 40–50°. *In situ* cycloaddition of the sterically hindered **2B** with 2,3-bis(trifluoromethyl)fumaronitrile ((*E*)-**3**) affords the isolable spirocyclic ketene imine **4B** in high yield. X-Ray analysis discloses angle deformation, with ring strain being responsible for the high reactivity of **4B**. In $CDCl_3$ at 40°, **4B** isomerizes to the *trans*-spirothiolane **6B** and fragments to 1,2-bis(trifluoromethyl)cyclopropane-1,2-dicarbonitrile (**12**) (+ thioketone **11B**) in parallel reactions with a ratio of *ca.* 4:1. *Van der Waals* strain limits the thermal stability of **6B,** which, at 60° in $CDCl_3$, is slowly converted to **11B** and **12**. Kinetics studies are in accordance with the zwitterionic intermediate **5B** in *gauche* and *anti* conformations. In CD_3CN, **4B** enters into a third parallel reaction, which leads to a formal adduct with CD_3CN. X-Ray analysis reveals the amidine **13**; this deep-seated, unexpected structural change is rationalized with the assumption of a nine-membered cyclic intermediate. In CD_3CN at 80°, **13** and **12** (+ **11B**) are stable and occur in a ratio of *ca.* 1:1. Hindered 'thiocarbonyl ylides' **2C** and **2D** produce, in reactions with (*E*)-**3** or (*Z*)-**3,** the cyclic ketene imines **4C** and **4D**, respectively, which likewise isomerize to *trans*-thiolanes **6C** and **6D**. In contrast to **6B** and **6C**, the less-hindered thiolane **6D** is thermostable and does not fragment; it undergoes *trans* ⇌ *cis* equilibration in PhCN at 139°. Structural assignments of thiolanes are based on ^{19}F-NMR spectroscopy.

1. Introduction. – A switch from the concerted mechanism of 'normal' 1,3-dipolar cycloadditions to a two-step pathway was observed whenever two conditions were fulfilled: first, 1,3-dipole and dipolarophile differ strongly in electrophilicity and nucleophilicity, and, second, one terminus of the 1,3-dipole is sterically hindered (for a review, see [2]). The efforts in the Munich laboratory concentrated on the cycloadditions of the highly nucleophilic (alkylidenesulfonio)methanides ('thiocarbonyl ylides', for a review, see [3]) with tetra-acceptor-substituted ethenes.

The alicyclic thiocarbonyl ylides **2A**–**2D** are easily available by 1,3-dipolar cycloreversion from the 2,5-dihydro-1,3,4-thiadiazoles **1A**–**1D**, which, in turn, are prepared by addition of CH_2N_2 to the sterically hindered thioketones (*Scheme 1*). The 1,3-dipoles **2A**–**2D** are not isolable, but undergo irreversible electrocyclization to give thiiranes. However, **2A**–**2D** are interceptible by 1,3-dipolar cycloaddition with dipolarophilic multiple-bond systems.

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[1]) 1,3-Dipolar Cycloadditions, Part 128; Part 127: [1].

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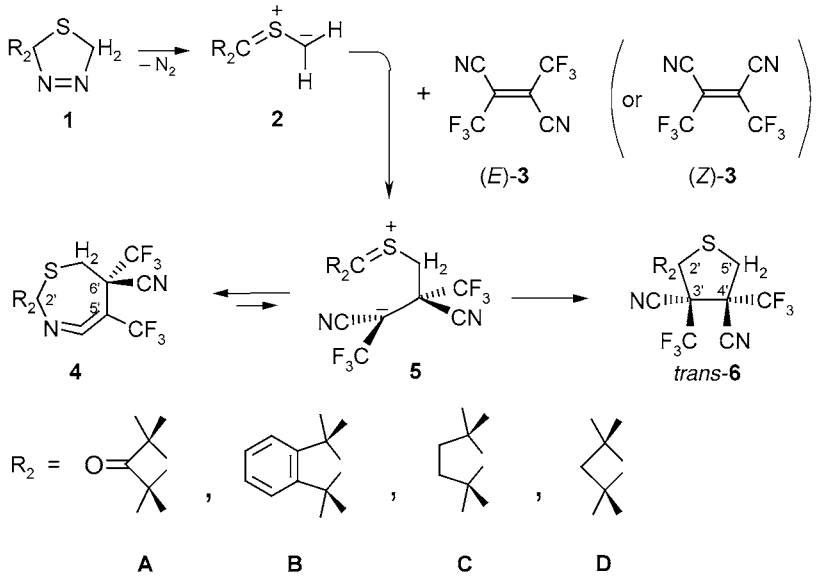
Scheme 1



In *concerted* cycloadditions to (*E*)/(*Z*)-isomeric dipolarophiles, configurational retention is mandatory. In 1986, experiments carried out by *Mloston* and *Langhals* established non-stereospecificity for the cycloadditions of **2A** to dimethyl 2,3-dicyanofumarate and dimethyl 2,3-dicyanomaleate; the loss of stereochemical integrity was ascribed to rotation in a zwitterionic intermediate [4–6].

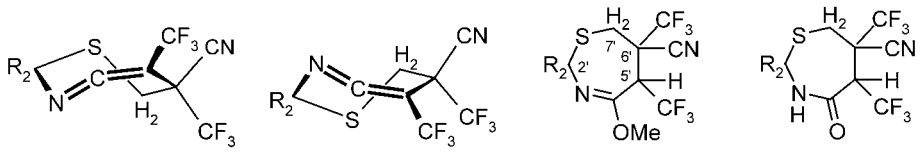
Further evidence for the two-step pathway was provided by the reaction of **2A** with ethenetetracarbonitrile (TCNE). On the way to the thiolane, a short-lived intermediate was intercepted by MeOH or H_2O, and the structure of a cyclic seven-membered ketene imine was proposed [7][8]. The highly strained spirocyclic ketene imine **4A** was isolated when dihydrothiadiazole **1A** was thermolyzed ($CDCl_3$, 40°) in presence of 2,3-bis(trifluoromethyl)fumaronitrile ((*E*)-**3**) [9][10] (*Scheme 1*). The zwitterion **5A** was considered as a plausible intermediate.

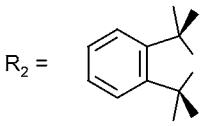
The S-methanides of 1,1,3,3-tetramethylindanthione and 2,2,5,5-tetramethylcyclopentanethione, **2B** and **2C**, have a more strongly screened terminus than **2A**. In their 1,3-cycloadditions with dimethyl 2,3-dicyanofumarate and dicyanomaleate, full rotational equilibrium of the intermediate zwitterions was attained before the thiolane ring closure [11]. Study of the reactions of **2B**–**2D** with the 'magic' tetra-acceptor-ethylene **3** turned out to be rewarding.

2. Results and Discussion. – 2.1. *Preparation of the Cyclic Ketene Imine* **4B**. When the N_2 extrusion from **1B** in cyclohexane/benzene at 50° took place in the presence of 1.1 equiv. of (*E*)-**3** for 6 h, ^{19}F-NMR analysis with weight standard indicated three products: ketene imine **4B** (83%), *trans*-thiolane **6B** (4%), and the tetra-substituted cyclopropane *trans*-**12** (4%; *cf. Scheme 2*). Since **4B** is slowly converted to **6B** and **12** at 50° (*Sect. 2.4*), the kinetically controlled preponderance of **4B** was expected to be even

higher; probably, **4B** is the sole 'primary product'. For the reaction of **2A** with (*E*)-**3** at 40°, we have already reported 'primary ratios' of **4A**/**6A** 81:19 in $CDCl_3$ and 85:15 in benzene [10]. When the intermediate zwitterion **5B** undergoes ring closure *via* the carbanion, the pairs of geminal dimethyl groups act as a barricade against thiolane formation. The terminal N-atom of the linear CN group meets less resistance in the closure of the ketene imine ring. The 'barricade effect' is smaller in zwitterion **5A** than in **5B**, due to the back-bending of the geminal dimethyl groups in the four-membered ring.

2.2. *Structure of the Spirocyclic Ketene Imine* **4B**. The lemon-yellow crystals of **4B** are sensitive to moisture, but they can be stored in the deep-freeze. The X-ray analysis was published in a short communication in 1990 [12]. Whereas the bond lengths of the cumulated system C=C=N (1.33 and 1.20 Å) are rather 'normal' and correspond to those of diphenylketene *N*-*p*-tolylimine [13], the strain shows up in angle deformations. The linear array C=C=N of open-chain ketene imines is bent to 163.8°, and the dihedral angle of the allene-type system (in allene 90°) has shrunk to 58°. The seven-membered ring is conceivable in a *transoid* or *cisoid* diastereoisomer with respect to the CF_3 groups. The *transoid* arrangement, as shown in **7**, was found in the crystal of **4B**. It is significant that the reaction of **2B** with 2,3-bis(trifluoromethyl)maleonitrile ((*Z*)-**3**) furnished the same products as that with (*E*)-**3**: 85% of the *transoid* **4B,** 2% of *trans*-thiolane **6B**, and 2% of *trans*-**12**.





The *as*-stretching frequency of the ketene imine group leads to strong IR absorption of **4B** at 2022 + 2030 cm^{-1}. The ^1H- and ^{13}C-NMR spectra of **4B** are related to those of ketene imine **4A** [10]. The ^{13}C signals at δ 185.6 for C (4′) and at 61.7 for C(5) are in line with those of open-chain ketene imines [14] and can be explained by a nitrilium-ylide formula as resonance contributor. The ^{19}F-NMR *quadruplet* at δ −55.7 with $^5J(F,F) =$ 4.6 Hz remains sharp from +50° to −60°. The signal at −73.8 is a *singlet* with a half-width of 26 Hz at 25° and reflects a dynamic phenomenon [15]. The signal height of the *singlet* is, at +50°, only 10% of that of the sharp *quadruplet* at δ −55.7 and increases on lowering the temperature to −70° (77% height); it becomes a well-defined *quadruplet* at −60°. At higher temperature (100° in toluene), the still broad signal at −73.8 assumes a *quadruplet* shape and is accompanied by signals of thermolysis products. No separation of the signal was observed at low temperature. We infer an equilibration of

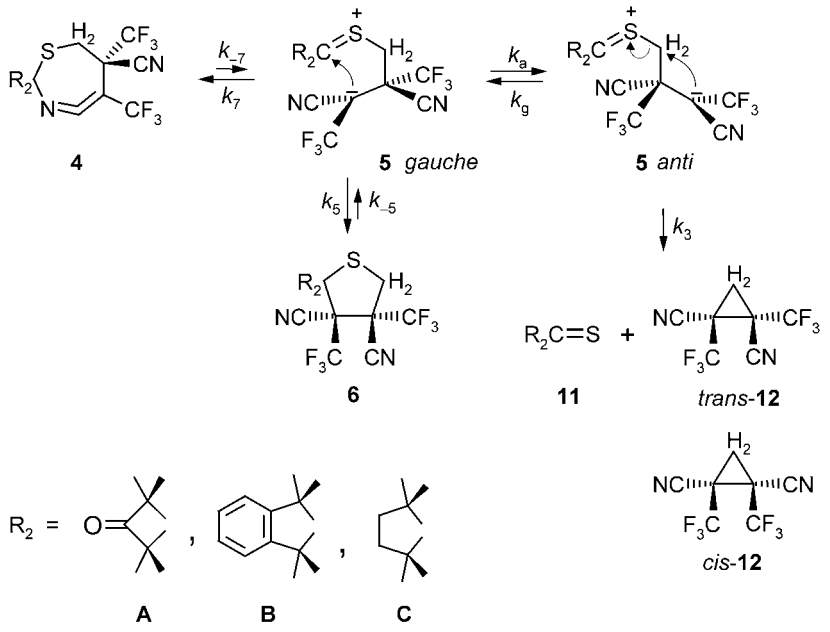
the *transoid* structure **7** with a small amount of the *cisoid* diastereoisomer **8**, so small that it cannot be 'seen' directly.

2.3. *Reactions of* **4B** *with MeOH and* H_2O. As in the example of **4A** [10], the rapid reaction with MeOH afforded two diastereoisomeric lactim methyl ethers **9**, one of which was obtained in pure form. The addition of H_2O led to a homogenous lactam **10**, but after several days in solution, a second diastereoisomer (acidic H–C(5′)) was detected in the ^{19}F-NMR spectrum. The larger couplings ^5J(F,F) of **9a** (8.4 Hz) and **10a** (8.3 Hz) – compared with **4B** (4.6 Hz) – indicate closer proximity of the CF_3 groups.

2.4. *Competing Reactions in the Thermolysis of* **4B**. In solution at 60°, the ketene imine **4A** quantitatively isomerized to the thermodynamically more-stable thiolane **6A** [10]. With increasing solvent polarity, the first-order rate constant was increased by a factor of 10^3. As shown in *Scheme 1*, it is the same zwitterion **5A** that was considered responsible for formation and ring contraction of the ketene imine **4A**.

The ketene imine **4B** in $CDCl_3$ at 40–60° furnished not only thiolane **6B**, but also 1,2-bis(trifluoromethyl)cyclopropane-1,2-dicarbonitriles, *trans*-**12** and *cis*-**12**, and 1,1,3,3-tetramethylindanthione (**11B**). This was a novel feature, and the question arose whether these fragmentation products are formed from **4B** or **6B**. Both can be regarded as precursors as depicted in *Scheme 2*, which is based on the well-examined and successful hypothesis of zwitterionic intermediates **5**. The complex system involves consecutive and parallel reactions, some of them reversible. Consequently, the rate equation with seven rate constants is somewhat unwieldy. Rapid equilibration of the *gauche* and *anti* conformations of zwitterion **5B** (see below) is a simplifying assumption.

Scheme 2



The rate constants k_7, k_5, and k_3 stand for the ring closures leading to seven-, five-, and three-membered rings, respectively, starting from **5B**.

The stability of **6B** in $CDCl_3$ *at 40°* (*i.e.*, $k_{-5} \approx 0$ in *Scheme 2*) facilitated mechanistic elucidation. Specifically, ^{19}F-NMR monitoring of the solution of **4B** revealed that the products **6B** and **12** were formed in the constant ratio of *ca.* 3.7:1 (*Table 1*). This must be the 'primary rate ratio' (kinetic control) of the two competing reactions under the given conditions. Any conversion of **6B** to **12** should have shifted the product ratio towards **12** with increasing reaction time. The concentration of **4B** decreased in a first-order reaction with a half-life of 34 h.

Table 1. *Competing Thermal Reactions of Ketene Imine* **4B** *in $CDCl_3$ at 40°; Time-Dependent Percentage Ratios of* **4B**, **6B**, *and* **12** (^{19}F-NMR Analysis)

Time [h]	**4B**	**6B**	**12**	**6B/12**
13	76	19	5	3.8
37	50	39	11	3.5
59	36	51	14	3.6
129	6	71	19	3.7
199	2	79	19	4.2
295		78	22	3.5

Steady-state treatment for the pool of **5B** leads to the rate law in *Eqn. 1*, which describes a first-order decrease of the concentration of **4B**. The rate constants k_5 and k_3 in the numerator of the fraction refer to the partitioning of the material into pathways that furnish **6B**, and **11B** and **12**, respectively.

$$-\frac{d[\mathbf{4B}]}{dt} = k_{-7}\left(\frac{k_5 + k_3}{k_7 + k_5 + k_3}\right)[\mathbf{4B}] = k_{exp}[\mathbf{4B}] \quad (1)$$

In the thermolysis of **4B** in $CDCl_3$ *at 60°*, thiolane **6B** was likewise converted to **11B** and **12**. ^{1}H-NMR Monitoring presented time-dependent concentrations of **6B**, which are typical for an intermediate in consecutive reactions: **6B** passed through a broad maximum of 66% after 13 h. The first-order decrease of **4B** proceeded with $t_{1/2} = 3.6$ h. After 6 $t_{1/2}$, the signal of **4B** had disappeared, and the slow, further reaction **6B** → **12** followed now the first-order kinetics with $t_{1/2} = 607$ h, *i.e.*, the conversion **4B** → **6B** is 170 times faster than **6B** → **11B** + **12.** The equilibrium of **6B** with a small concentration of the energetically disfavored **4B** remains established, *i.e.*, $[\mathbf{4B}] = K[\mathbf{6B}]$, while **6B** is transformed to **11B** + **12**. For this second phase of the reaction, *Eqn. 2* reveals the first order in **6B** and the composite nature of k_{exp} in the framework of *Scheme 2*.

$$+\frac{d[\mathbf{12}]}{dt} = (k_{-5} + k_{-7}K)\frac{k_3}{k_7 + k_5 + k_3}[\mathbf{6B}] = k_{exp}[\mathbf{6B}] \quad (2)$$

The k_{exp} value for **4B** → **6B** in $CDCl_3$ at 60° allows comparison with **4A** → **6A** [10]: ketene imine **4A** disappears 66 times faster than **4B**. One of the reasons lies in the ratio k_7/k_5, which is reflected by the 'primary ratios' [**4**][**6**] in the reaction of **2** with (*E*)-**3**: it amounts to 4.3 in the example of **2A** [10] and perhaps to 100 or more for **2B**. The high steric requirements of the tetramethylindanyl residue ('barricade effect' in ring closure) seem to be responsible.

In the overall conversion **4B** → **11B** + **12**, thiolane **6B** in *Scheme 2* was formed as a result of a 'nonproductive side-equilibrium'. The formation of a tetrasubstituted cyclopropane (+ thione **11B**) was also observed in the reaction of thiocarbonyl ylide **2B** with dimethyl 2,3-dicyanofumarate in $CDCl_3$ at 80°, where it amounted to 10% of the thiolane yield; heating the cycloadduct in PhCN at 140° for 10 min completed the fragmentation [11]. S_N2 Reactions with front-side attack are not favored, not even in intramolecular examples [16]. Therefore, a nucleophilic substitution providing **11B** + **12** requires the *anti* conformation of zwitterion **5B**. In the propensity for intramolecular substitution, **5B** exceeds **5A**, the higher steric hindrance to ring closure once again offering an explanation.

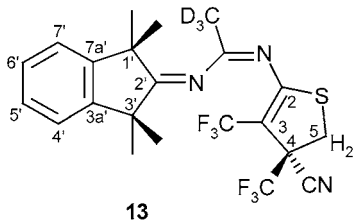
For the isolation of thiolane **6B**, the ketene imine **4B** was heated in $CDCl_3$ at 40°, *i.e.*, conditions under which **6B** still does not undergo fragmentation. Among the NMR-spectroscopic properties of the colorless **6B**, the 'through-space' C,F-coupling between Me and CF_3 group is noteworthy: three of the four Me groups show $^5J(C,F) = 1.8–6.6$ Hz. In cyclopropane *trans*-**12**, the ^{19}F-NMR signal is a *triplet* with $^4J(F,H) = 0.1$ Hz. Evidence for the not isolated *cis*-**12** came from the ^{19}F-NMR spectrum of reaction mixtures, where the sharp signal accompanies that of *trans*-**12** in the ratio of *trans*/*cis ca.* 95:5. Interestingly, the CF_3 groups of *cis*-**12** couple with only one of the $CH_2(3)$ H-atoms (*d*, $J(F,H) = 1.4$ Hz). The origin of *cis*-**12** is the intramolecular displacement in an *anti,cisoid* conformation of zwitterion **5**, not shown in *Scheme 2*.

The thermal fragmentation of the hexasubstituted thiolane **6B** (→ **11B** + **12**) attains completion, and its thermodynamics merit a rough estimate. The ring strain of cyclopropane exceeds that of cyclopentane by 21 kcal · mol^{-1} [17]. Another endothermic contribution, with *ca.* +14 kcal · mol^{-1} [18], stems from the conversion of two C–S bonds into a C=S bond. The increase of translational entropy (two molecules out of one) enters the free energy balance with *ca.* −9 kcal · mol^{-1}. What is it that overcompensates the remaining +26 kcal · mol^{-1} to drive fragmentation?

The *Van der Waals* strain of the substituents in the tightly packed spirothiolane requires relief: on one hand, back-bending of the substituents in the cyclopropane **12** reduces the non-bonding interaction, and the generation of an sp^2-hybridized center on the part of the thione **11B** likewise reduces strain. On the other hand, the loss of spiro-annulation is highly beneficial to the fragmentation process in the case of **6B**. The role played by the 'perfluoroalkyl effect' [19] might be minor since CF_3-free spirothiolanes likewise undergo fragmentation.

2.5. *Thermolysis of* **4B** *in* CD_3CN*: Formation of an Unexpected Product*. CD_3CN was used as a highly polar solvent to observe the decay of ketene imine **4B**. During the reaction (15 h at 40° and 21 h at 80°), the ^{19}F-NMR spectrum displayed appearance and disappearance of thiolane **6B**. Two major products persisted at 80°: the cyclopropanes **12** (*trans/cis ca.* 95:5) reached 41%, and a new product was present in 39% yield. Elementary analyses of the crystals isolated indicated a formal adduct of **4B** with one molecule of CD_3CN; an X-ray analysis revealed the unexpected structure **13**.

^{19}F-NMR Monitoring indicated that compounds **6B**, **13** and **12** were formed in parallel reactions from **4B** with a constant rate ratio of 4.2:2.0:1 during 15 h *at 40°* (*Table 4* in *Exper. Part*); *i.e.*, formation of **13** was twice as fast as that of **12**. On subsequent heating to *80°* for 21 h, **6B** slowly disappeared, and the yield of cyclopropanes **12** caught up with that of **13**. In another experiment, the conversion



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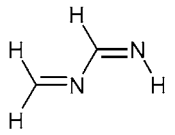

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of **4B** in CD_3CN was observed *at 21°* for 12 days, and a ratio of 8 : 1 for **13**/**12** showed an even higher preference for **13** at the same low temperature.

According to the X-ray diffraction (*Fig. 1* and *Table 2*), **13** is an imine, which is formally derived from 1,1,3,3,-tetramethylindan-2-one and acetamidine. The latter, in turn, is linked to a tetrasubstituted 4,5-dihydrothiophene ring. The five-membered heterocycle is envelope-shaped, $CH_2(5)$ serving as the flap, with a folding angle of 24°. The enamine plane (C(3)−C(2)−N(2)) cuts the amidine plane (N(2)−N(3)−C(10)) at an angle of 28.2°. Here, C(12) still lies in the amidine plane, but the indanylidenimine plane (C(11)−C(13)−N(3)) is orthogonally arranged to the amidine system (92.2°), *i.e.*, the two C=N bonds of **13** fail to be conjugated. These deviations from planarity are the result of steric constraints.

According to quantum-chemical calculations (MP2/6-31G*//6-31G*) of '1,3-diazabutadiene' (= *N*-(iminomethyl)methanimine; **14**), the (*Z*)-arrangement of N(1)−H at the (*E*)-heterodiene system is favored, compared with (*E*)-N−H (ΔE

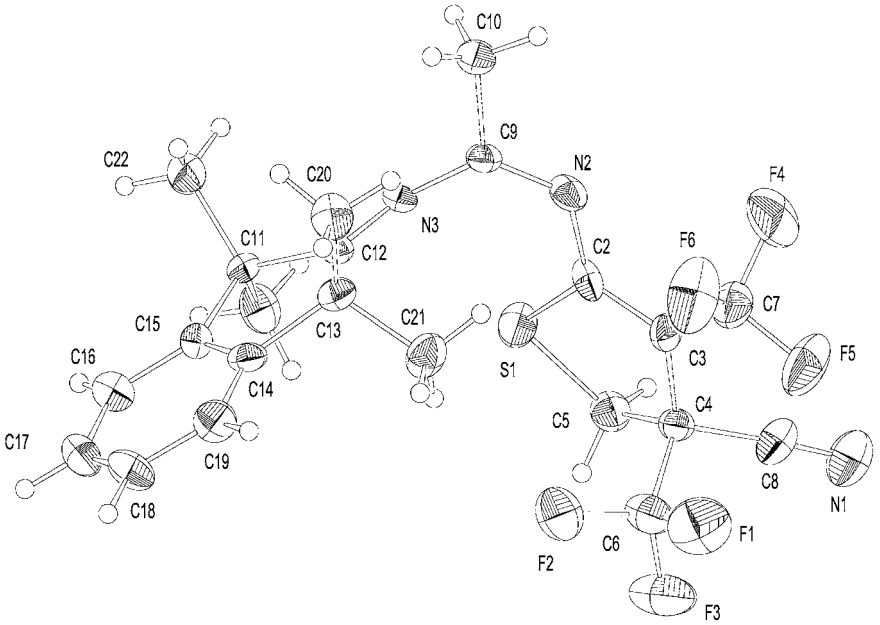


Fig. 1. *X-Ray structure of compound* **13** (ZORTEP plot; thermal ellipsoid represent 30% probability)

Table 2. *X-Ray Structure of Compound* **13**: *Selected Bond Lengths and Angles* (position numbering from *Fig. 1*; standard deviation in parentheses)

Bond lengths [Å]					
S–C(2)	1.750(9)	C(4)–C(5)	1.544(12)	N(2)–C(9)	1.286(10)
C(2)–C(3)	1.337(12)	C(5)–S	1.815(9)	C(9)–N(3)	1.366(11)
C(3)–C(4)	1.516(11)	C(2)–N(2)	1.385(11)	N(3)–C(12)	1.256(10)
Bond angles [°]					
C(5)–S–C(2)	90.9(5)	C(2)–C(3)–C(4)	114.8(8)	C(4)–C(5)–S	108.0(6)
S–C(2)–C(3)	115.0(7)	C(3)–C(4)–C(5)	105.6(7)	S–C(2)–N(2)	122.7(7)

2.8 kcal · mol^{-1}) [20][21]. The X-ray analysis of a 2,4-diaryl-1-(*tert*-butyl) derivative of **14**, carried out by *Würthwein* and co-workers [20], disclosed a torsion angle of 109.7° at the C(2)–N(3) bond, not far from the twisting observed at the N(3)–C(9) bond of **13**.

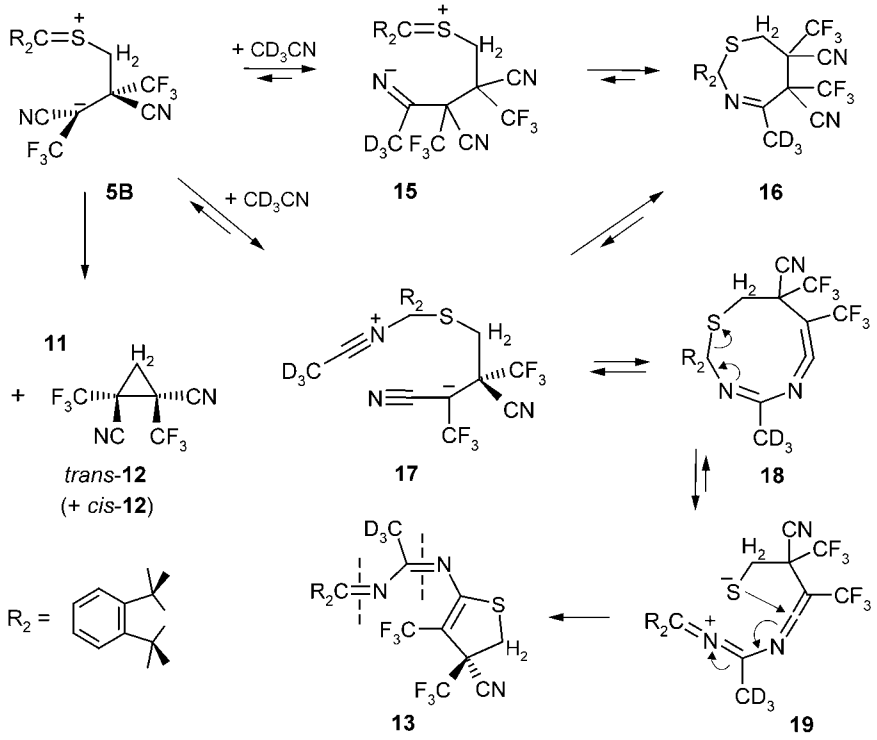
It was only *post festum* that we succeeded in interpreting the ^{13}C-NMR spectrum. Whereas the ^{13}C assignments for **4B** and **6B** were routine, those of **13** required additional 2D-NMR experiments with HMQC [22] and HMBC techniques [23]; the signal of C(3) was not even found in the F-decoupled spectrum.

Two signals for four Me groups appear in the ^{13}C-NMR spectrum of **13**, but C(1′) and C(3′) have identical chemical shifts, and the six aromatic C-atoms are pairwise isochronous. This scenario opens up two possibilities: a hindered N-inversion at the C(2′)=N axis would render the Me pair at C(1′) magnetically different from that at C(3′). On the other hand, an N-inversion that is rapid on the NMR time scale would eliminate the difference between 'above' and 'below', and pairwise diastereotopic Me groups could be the result of the rather distant stereogenic C(4)-atom; in that case, the two Me groups above the plane of formula **13** would be different from those behind the projection plane.

The ^{1}H-NMR spectrum (400 MHz) confirms the second interpretation. All four Me groups have the same chemical shift (δ 1.25), and the four aromatic H-atoms give rise to a perfect $AA'BB'$ spectrum. Apart from the tiny ^{13}C shift difference of the Me pairs (δ 25.36, 25.48), the indan system in **13**, thus, does not 'feel' the diastereotopicity. CH_2(5) is much closer to the stereogenic center C(4): an AB spectrum with $^2J = 12.8$ Hz was observed, the left branch of which reveals additional coupling with CF_3 at C(4), ^4J(F,H) = 0.88 Hz. A heteronuclear double-resonance experiment allowed the assignment of the positions of the two CF_3 groups.

Scheme 3 offers a mechanistic rationalization for the pathway to **13**. Since zwitterion **5B** is the logical intermediate, the formulae of **4B** and **6B** are not repeated. Our first guess was a nucleophilic attack on $CD_3C{\equiv}N$ by the carbanion of **5B**; it would produce the seven-membered ring of **16** *via* zwitterion **15**. The pathway *via* nitrilium ion **17** would constitute a second route to **16**. However, while **16** might well participate in the equilibrium at low temperature, a thermodynamic preference for such a heptasubstituted thiazepine derivative is rather doubtful. A ring closure of **17** *via* the nitrile N-atom instead of the carbanion seems improbable at first glance. On the other hand, an equilibration with the nine-membered cyclic ketene imine **18** may pave the way to energetically more-favorable products. The reversible ring opening of **18** to afford the iminium thiolate **19** might be followed by an exothermic step: the bonding of

Scheme 3



the thiolate function to the electrophilic center of the ketene imine then furnishes the stable **13**.

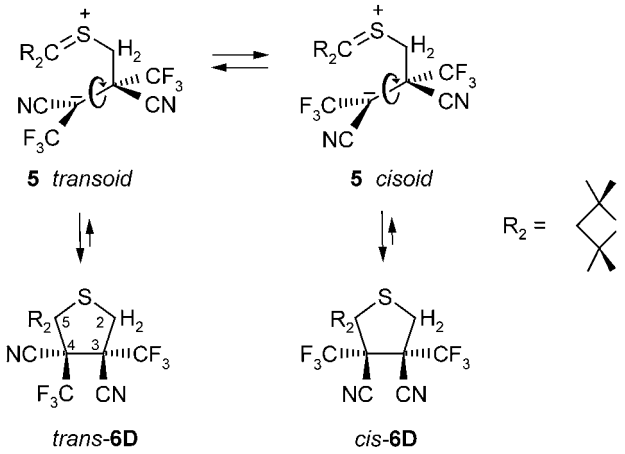
2.6. *Reactions of 'Thiocarbonyl Ylides'* **2C** *and* **2D** *with* **3**. The results of a cursory study indicate that the tetramethylcyclopentylidene group of **2C** (*Scheme 1*) causes higher steric hindrance than the tetramethylcyclobutylidene residue in the lower homolog **2D**; the back-bending of the Me groups in the four-membered ring may be responsible. In their reactions with **3**, the behavior of the 1,3-dipole **2C** is similar to that of **2B**, whereas **2D** shows notable differences. The formation of ketene imines **4C** and **4D** was spectroscopically established, but isolation was not attempted.

After incomplete thermolysis of thiadiazoline **1C** in CCl_4 (2.5 h at 40°) in the presence of (*E*)-**3**, the solution showed the strong IR absorption of the ketene imine group of **4C** at 2010 cm^{-1}. On the assumption of identical oscillator strengths of **4C** and pure **4A**, comparison of the integrals led to an estimate of the **4C** concentration that corresponded well with the result of ^{1}H-NMR analysis. The products **4C** and **6C** occurred in a ratio of 74 : 26 after 2.5 h, and 28 : 72 after 10 h at 40°. In contrast to **4B**, ketene imine **4C** did not form cyclopropanes **12** + thione **11C** *at 40°*. However, the reaction of **1C** with (*E*)-**3** *at 80°* (10 min) afforded **6C** (64%), *trans*-**12** (25%), *cis*-**12** (1%), while the amount of 4% of **4C** remained unchanged.

The thermolysis of **1C** in the presence of (*Z*)-**3** in C_6D_6 at 40° and 80° led to similar product ratios as the reactions with (*E*)-**3**. Although the isomerization (*Z*)-**3** ⇌ (*E*)-**3**, catalyzed by the dihydrothiadiazole **1C** [10], did not reach equilibrium, only *trans*-thiolane **6C** was found, and the ^{19}F-NMR spectrum offered no evidence for the presence of the *cis*-thiolane. The intermediacy of the *transoid* ketene imine (*Sect. 2.2*) eliminates the difference between the reactions with (*Z*)-**3** and (*E*)-**3**.

When the spiro-dihydrothiadiazole **1D** was heated with (*E*)-**3** at 40° in $CDCl_3$, the N_2 extrusion reached 51% after 90 min. ^{1}H-NMR Analysis indicated ketene imine **4D** and thiolane *trans*-**6D** in the ratio of 62:38. Evaluation of the IR absorption at 2007 cm^{-1} confirmed **4D** as major product. After 20 h at 40°, the conversion of **4D** to *trans*-**6D** was virtually complete (*Scheme 4*).

Scheme 4



The fragmentation of thiolane **6B** to give **11B** + **12** (PhCN, 80°) showed a half-reaction time of 14.1 h and the rate for **6C** → **11C** + **12** is probably similar. In contrast, the tetramethylcyclobutane-spiro-thiolane **6D** showed remarkable thermal stability. In PhCN at 139°, no fragmentation to **11D** + **12** was observed. Instead, ^{19}F-NMR monitoring revealed a *trans* ⇌ *cis* equilibration of **6D**. According to rate measurements, the system moves towards an equilibrium of *trans*-**6D**/*cis*-**6D** 43:57 with a half-reaction time of 18 h at 139°. Interestingly, the signals of **3** ((*E*)/(*Z*) 91:9) appeared, indicating 6% cycloreversion in 0.4M soln. in PhCN at 139°.

2.7. *Stereochemistry of Thiolanes.* How were the configurations of the spirothiolanes **6A**–**6D** determined? F,F Coupling is transmitted 'through space' (overlap of non-bonded orbitals) and not only by way of the bond system [24]. Higher ^5J(F,F) constants are expected for *cis*-located CF_3 groups than for the corresponding *trans*-isomers. Values of 15.0–15.7 Hz were observed for three *cis*-thiolanes, whereas five *trans*-thiolanes display the (uncomfortably) large range of 4.1–11.6 Hz (*Table 3*). The difference between the two chemical shifts, $\Delta\delta$(F), varies from one system to another. However, within each of the three *trans*/*cis* pairs, the *cis*-isomer shows the smaller $\Delta\delta$(F).

Table 3. *^{19}F-NMR Data of Ketene Imines and Thiolanes* (Cl_3CF as frequency standard). **6E** is defined in *Fig. 3*.

Formula	δ(F) of CF_3 [ppm]		Conditions (Solvent, T)	^5J(F,F) [Hz]	$\Delta\delta$(F) [ppm]
Seven-membered cyclic ketene imines					
	CF_3–C(5)	CF_3–C(6)			
4A[a])	−56.3	−73.6	$CDCl_3$, 50°	4.4	17.3
4B	−55.7	−73.8	$CDCl_3$, 50°	4.6	18.1
Spirothiolanes					
	CF_3–C(3)	CF_3–C(4)			
trans-**6A**[a])	−54.2	−65.0	$CDCl_3$, 25°	7.9	10.8
cis-**6A**[a])	−58.6	−65.1	$CDCl_3$, 25°	15.0	6.5
trans-**6B**	−58.2	−63.9	$CDCl_3$, 25°	11.6	5.7
	−57.2	−63.1	CD_3CN, 40°	11.4	5.9
trans-**6C**	−57.3	−65.8	$CDCl_3$, 25°	9.8	8.5
	−57.0	−65.5	C_6D_6, 25°	9.9	8.5
trans-**6D**	−57.1	−67.0	$CDCl_3$, 25°	7.2	9.9
	−56.8	−67.0	C_6D_6, 25°	7.3	10.2
cis-**6D**	−56.5	−66.5	CD_3CN, 25°	7.4	10.0
	−58.1	−66.0	CD_3CN, 25°	15.7	7.9
trans-**6E**[a])	−58.6	−66.6	CD_3CN, 100°	4.1	8.0
	flat	−66.3	CD_3CN, 21°	2.6	
cis-**6E**[a])	−57.9	−65.0	CD_3CN, 100°	15.4	7.9
	flat	−65.2	CD_3CN, 21°	15.2	

[a]) Ref. [10].

For the seven-membered cyclic ketene imines **4A** and **4B**, *Table 3* presents F,F-coupling constants of 4.4 and 4.6 Hz. The $\Delta\delta$(F) has grown to 17.3 and 18.1 ppm, respectively.

No matter whether (*E*)-**3** or (*Z*)-**3** was used as dipolarophile, strong kinetic control in favor of *trans*-thiolanes **6B**–**6D** resulted. The mentioned catalysis of (*E*)-**3** $\rightleftharpoons$ (*Z*)-**3** by the dihydrothiadiazole **1** – the latter is the precursor of **2** [10] – is only partially responsible. The major driving force is the nearly complete formation of the ketene imines **4B**–**4D** as 'primary products', combined with the preference for the *transoid* structure **7** in the mobile equilibrium **7** $\rightleftharpoons$ **8** (*Sect. 2.2*). On ring opening with k_{-7}, the ketene imines furnish *trans*-**6** *via* the *transoid* zwitterion **5**. It was only in the ring contraction of **4A** (C_6D_6, 80°, 10 min) that a small amount of *cis*-thiolane (*trans*-**6A**/*cis*-**6A** 98.4 : 1.6) was analyzed [10].

Distinct *quadruplets* result from F,F coupling for the upfield thiolane signals at −63 to −67 ppm in *Table 3*, whereas *broadened singlets* were observed for those at −54 to −58 ppm. What is the reason for the line-broadening, and how are the CF_3 groups assigned to C(3) and C(4)?

Thiolane *trans*-**6D** was chosen as model for the NMR study. The ^{1}H-NMR signals (400 MHz) of two Me groups showed ^6J(F,H) = 2.88 and 1.65 Hz, respectively. According to an HMBC experiment, one of these Me groups is bonded to C(6), the other to C(8). When the sparsely structured ^{19}F-*singlet* at −57.1 was subjected to line-narrowing (*Lorentz–Gauss* transformation [25]), a 25-line spectrum (*Fig. 2*, *a*) was obtained; the distances disclosed the above F,H-couplings in addition to ^5J(F,F) = 7.2 Hz. The computer simulation of the $A_3B_3X_3Y_3$ spectrum (no terms of higher order) by the program PERCH [26] afforded, after a few steps of iteration, a nearly perfect

match (*Fig. 2, b*). Only CF_3–C(4) is in suitable proximity to two of the four Me-groups to allow for the 'through space' F,H coupling. Analysis of the second ^{19}F signal (*qd* at −67.2) reveals a weak F,H coupling ($^4J = 0.7$ Hz) with one of the CH_2(2) H-atoms, as is appropriate for CF_3–C(3). The ^{13}C-NMR spectrum, supported by 2D techniques, confirmed these assignments.

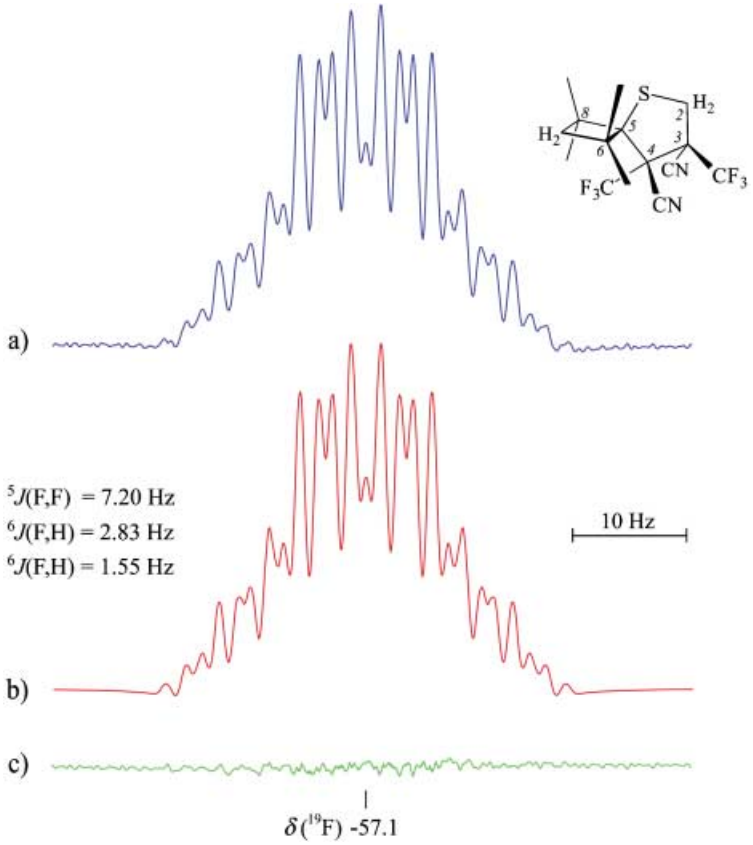


Fig. 2. *^{19}F-NMR Spectrum* (377 MHz) *of spirothiolane* trans-**6D** *in $CDCl_3$ at 25°. a*) Expanded and line-narrowed signal at −57.1 ppm; *b*) calculated signal and *J* values after iteration; *c*) difference of *a* and *b* (noise).

In the ^1H-decoupled ^{19}F-NMR spectrum of *trans*-**6D**, the signal height of CF_3–C(4) is only 55% of that of CF_3–C(3). A dynamic phenomenon appears to be responsible. Here, the adamantane-spiro-thiolane *trans*-**6E** [10] (*Fig. 3*) served as model. At 70°, the ^{19}F signal of CF_3–C(3′)[3]) is a broad *singlet* (half-width *ca.* 120 Hz) at −58.9, which disappears in the base-line at 20°. On cooling to −35°, three *triplets* emerged (*Fig. 3*), stretching over 6000 Hz and revealing hindered rotation at the C(3)–CF_3 bond. The *triplets* show ^2J(F,F) values of *ca.* 105 Hz, and the additional splitting into *quadruplets* by ^5J(F,F) is unresolved. The second CF_3 signal at −66.4 still looks sharp, but expansion

[3]) According to the numbering rules of spiro compounds, CF_3–C(4) of **6D** corresponds to CF_3–C(3′) of **6E**. In *Table 3*, the numbering of monocyclic thiolanes was used.

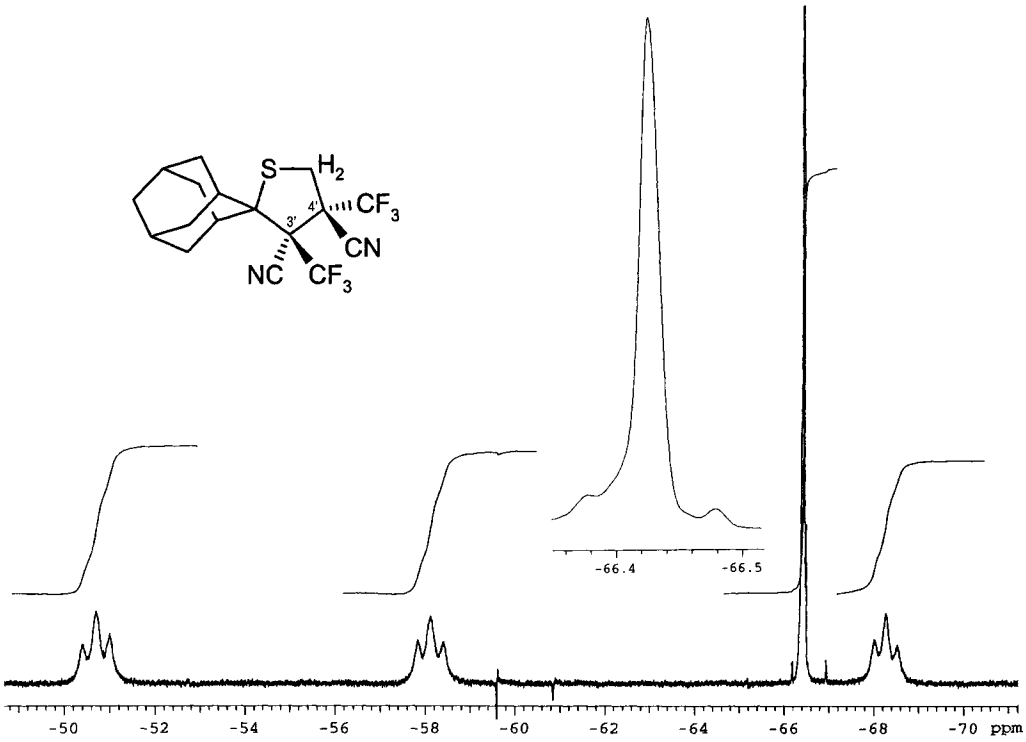


Fig. 3. *^{19}F-NMR Spectrum* (376 MHz) *of spirothiolane* trans-**6E** *in CD_3CN at 35°. Inset:* expanded signal at $-66.4°$ ppm.

(*Fig. 3*, *inset*) shows a blunt *singlet* because three different F,F and two F,H couplings are not resolved.

In *Sect. 2.4*, it was estimated that the pentasubstituted thiolanes **6B** and **6C** suffer from *Van der Waals* strain of $>26\ \text{kcal}\cdot\text{mol}^{-1}$. The hindered single-bond rotation of $C(3)-CF_3$, observed in *trans*-**6E**, illustrates this pressure.

Conclusions. – The reactions of thiocarbonyl ylides **2** with acceptor-substituted ethylenes are successful probes for the switch from the concerted to the two-step mechanism of 1,3-dipolar cycloadditions. Since the generation of the not isolable **2** from the dihydrothiadiazole **1** by cycloreversion is the slow step of the reaction sequence, no direct rate measurements are possible, but phenomena of kinetic competition provide insight. The assumption of a short-lived intermediate **5,** in which reactants **2** and **3** are linked by *one* σ bond, allows a consistent description of all observations (for a review; see [2]).

The reactivity of the 1,5-zwitterion **5** reflects the steric hindrance exerted by the spiro-attached tetramethylcycloalkylidene group R_2. The screening of the spiro-C-atom as terminus of the 1,3-dipole increases in the order: **5D** < **5A** < **5B**, **5C**. Distinguishing experimental criteria were: the extent of non-stereospecificity in the 1,5-cyclization giving thiolanes **6** [6], the ratio of 1,7- *vs.* 1,5-cyclization ('barricade

effect'), the competing reactions of *gauche*-**5** and the *anti*-**5** (ring closure *vs.* intramolecular substitution to give **11** + **12**), as well as reversibility of 1,7- and 1,5-cyclization and its temperature dependence (*Schemes 1* and *2*).

Coulombic forces favor *gauche*-**5** over the *anti*-conformation, but steric hindrance affects *anti*-**5** less than *gauche*-**5**. The amount of nonbonded interaction in **4** and **6** as isolable products (*Sect. 2.4*) signalizes a 'state of emergency'. The thermal lability of ketene imine **4B** and thiolane **6B** exceeds that of **4A** and **6A**, respectively. Whereas **4A** exclusively furnishes **6A** at 60°, the conversion **4B** → **6B** at 40° is already accompanied by some fragmentation (→ **11B** + **12**) *via anti*-**5B**, as confirmed by kinetic data. The reaction of **5B** with CD_3CN and the astonishing sequence affording **13** (*Scheme 3*) illustrate the striving for relief from *Van der Waals* strain.

Concerning the electronic nature of intermediate **5**, the possibilities of 1,5-biradical and 1,5-zwitterion can be considered. A criterion for the zwitterionic **5** is the high promotion by solvent polarity, which was observed for the rate of ring opening of **4A** in the conversion **4A** → **6A** (*Sect. 2.4* and [10]). On the other hand, a 1,5-biradical **5** would also be stabilized by thioether and CN functions.

1,3-Dithiolanes are formed by 1,3-cycloadditions of thiocarbonyl ylides **2** with thioketones [1]. Recently, quantum-chemical calculations (density functional B3LYP) of transition structures and intermediates, carried out by *Sustmann et al.* [27][28], revealed concerted and two-step processes. The participating 1,5-biradicals and 1,5-zwitterions appear to be not fundamentally different, but rather to be species located on a continuous scale, dependent on substitution. In our opinion, the tetrahedral CH_2 group in **5** does not prevent the delocalization of one electron between positions 1 and 5.

We express our gratitude to the *Fonds der Chemischen Industrie*, Frankfurt, for the support of our research program. Our thanks are due to *Helmut Huber* for his help in recording the NMR spectra, and to *Reinhard Seidl* for the mass spectra. The elemental analyses were carried out by *Helmut Schulz* and *Magdalena Schwarz*.

Experimental Part

1. *General*. For instruments, see [1]. Prep. layer chromatography (PLC): 2 mm, 20 × 20 cm glass plates. KBr pellets were used for IR spectroscopy, if not stated otherwise. It is known that IR absorptions of C≡N in the proximity of other acceptor substituents are weak or even absent [29]; this effect was also pronounced for neighboring CF_3 groups. NMR Spectra were recorded in acid-free $CDCl_3$, if not stated otherwise. As weight standards for quant. ^{1}H-NMR analysis (usually ± 5%, relative), *as*-tetrachloroethane (δ 4.28) or *sym*-tetrachloroethane (δ 5.98) were used. For ^{19}F-NMR analysis, Cl_3CF served as chemical-shift standard and (1,1-dichloro-2,2,2-trifluoroethyl)benzene (δ −78.2 in $CDCl_3$), abbreviated as DICHLO, as weight standard. In ^{13}C-NMR spectra, multiplicities were determined by comparison of H-decoupled and off-resonance spectra. EI-MS: 70 eV; intensities of isotope peaks are given as, *e.g.*, ^{13}C % calc./% found.

2. *Thiocarbonyl Ylide* **2B** (= [*(1,1,3,3-Tetramethylindanylidene)sulfonio]methanide*) *and* (*E*)-*2,3-Bis(trifluoromethyl)but-2-enedinitrile* ((*E*)-**3**). 2.1. *2,3,6′,7′-Tetrahydro-4′,5′-didehydro-1,1,3,3-tetramethyl-5′,6′-bis(trifluoromethyl)spiro[1*H*-indene-2,2′(2′*H*)-*[1,3]thiazepine]-6′-carbonitrile* (**4B**). The conditions of isolation are based on the NMR studies (*Sect. 4*, below) of formation and ring contraction of **4B**. *2,2′,3,5′-Tetrahydro-1,1,3,3-tetramethylspiro[1*H*-indene-2,2′-[1,3,4]thiadiazole]* [11] (**1B**; 1.08 g, 4.38 mmol) and (*E*)-**3** [10][30] (1.07 g, 5.00 mmol) in abs. cyclohexane (5 ml) and abs. benzene (2 ml) were heated to 50° for 6 h. After evaporation at r.t., the oily residue crystallized from pentane: **4B** (1.28 g, 68%). Lemon-yellow crystals. M.p. 88–90°. IR (nujol): 712*s*, 758*m*, 761*s* (arom. out-of-plane deform.); 1080, 1119, 1159, 1190, 1215, 1243, 1254, 1271, 1289 (all v*s* or *s*, C–F stretch.); 1383*s*, 1408*m*, 1453*s*, 1465*s* (arom. ring vibr.), 2022 and 2030v*s* (br., C=C=N *as*-stretch.), 2260v*w* (C≡N). IR (CCl_4): 2019v*s* (br., C=C=N). ^{1}H-NMR (80 MHz): 1.45, 1.50 (2×), 1.53 (4*s*, 4 Me); 3.15, 3.48 (*AB*, ^2J(H,H) = 14.8, CH_2(7′); 6.95–7.45 (*m*, 4 arom. H). ^{13}C-NMR (90.6 MHz): 25.1, 26.0, 28.2, 31.3 (4*q*, 4 Me); 36.0 (*t*, C(7′)); 43.9 (*q*, ^2J(C,F) = 34.9, C(6′)); 50.7, 54.8 (2*s*, C(1), C(3)); 61.7 (*q*, ^2J(C,F) = 39, C(5′)); 96.9

(*s*, C(2)); 112.8 (*s*, CN); 122.4 (*q*, ^1J(C,F) = 286.3, CF_3); 122.9 (*q*, ^1J(C,F) = 285.1, CF_3); 122.37, 122.51 (2*d*, 2 arom. CH); 128.26, 128.32 (2*s*, 2 arom. CH, coupl. not resolved); 145.6, 146.3 (2*s*, 2 arom. C_q); 185.7 (*q*, ^3J(C,F) = 2.8, C(4')). ^{19}F-NMR ($CDCl_3$, 376 MHz) [15]): −55.67 (*q*, ^5J(F,F) = 4.6, F_3C−C(6′) at 25°; sharp *q* from +50° to −60°, softens at −70°); −73.80 (br. *s*, F_3C−C(5′)); ratio of signal heights (δ −74/−56): 0.10 (50°), 0.17 (25°), 0.68 (−60°), 0.77 (−70°); continuous change of δ from −55.74 and −73.82° (+50°) to −55.29 and −73.25° (−60°). ^{19}F-NMR ((D_8)toluene, 100°): −55.29 (*q*), −73.80 (*q* recognizable, height ratio 0.25). Anal. calc. for $C_{20}H_{18}F_6N_2S$ (432.43): C 55.55, H 4.20, N 6.48; found: C 55.83, H 4.30, N 6.28.

2.2. *Product Analysis after Reaction at 50°.* Dihydrothiadiazole **1B** (0.375 mmol) and (*E*)-**3** (0.397 mmol) in (D_{12})cyclohexane (0.5 ml) and 3 drops of C_6D_6 were heated in a sealed NMR tube at 50°. After 6 h, the ^{13}F-NMR analysis with DICHLO indicated ketene imine **4B** (83%), thiolane **6B** (4.3%), and cyclopropane *trans*-**12** (3.5%); the excess of **3** showed (*E*)/(*Z*) 99:1. In a corresponding experiment, **1B** (0.286 mmol) and 2,3-bis(trifluoromethyl)maleonitrile [10] ((*Z*)-**3**; 0.321 mmol, 99% purity) were reacted at 50° for 6 h, and the analysis gave **4B** (85%), **6B** (*ca.* 2%), and **12** (*ca.* 2%); the ratio (*E*)-**3**/(*Z*)-**3** 26:74 (after 2 h) in the unconsumed dipolarophile revealed partial isomerization.

3. *Reactions of* **4B** *with MeOH and H_2O.* 3.1. *2,3,6′,7′-Tetrahydro-4′-methoxy-1,1,3,3-tetramethyl-5′,6′-bis(trifluoromethyl)spiro[1*H*-indene-2,2′(5′*H*)-[1,3]thiazepine]-6′-carbonitrile* (**9**). The yellow crystals of **4B** (0.339 mmol) were dissolved in abs. MeOH (2.5 ml), and soon colorless crystals precipitated. After removal of the solvent, ^{19}F-NMR analysis ($CDCl_3$) with DICHLO showed 70% of **9** (−61.3), and a diastereoisomer ratio of 59:41 for **9a** (−69.1) and **9b** (−70.1). Twice recrystallized from MeOH, **9a**/**9b** 91:9 had a melting range of 141–168°, but correct elemental analyses were obtained. Further separation was achieved with PLC on alumina (cyclohexane/AcOEt 95:5); one fraction, recrystallized from MeOH, was pure **9a** (13%), m.p. 167–169° [15].

Data of **9a**. IR (KBr): 721*m*, 761*s* (arom. out-of-plane deform.); 1031*m*, 1125*m*, 1195*s*, 1213*s*, 1248*s*, 1278*s*, 1287*s* (C−F), 1450*m*, 1484*m* (arom. ring vibr.), 1690*s* (C=N), 2250v*w* (C≡N). ^{1}H-NMR (360 MHz): 1.30, 1.43, 1.47, 1.48 (4*s*, 4 Me); 3.31, 3.66 (*AB*, ^2J(H,H) = 16.4, CH_2(7′)); 3.59 (s, MeO); 5.49 (*q*, ^3J(F,H) = 7.8, H−C(5′)); 7.05–7.35 (*m*, 4 arom. H). ^{13}C-NMR (20.2 MHz) [15]: 25.1, 26.6, 28.7, 31.2 (4*q*, 4 Me); 34.8 (*tq*, ^3J(C,F) = 1.8, C(7′)); 44.0 (*q*, ^2J(C,F) = 28.7, C(6′)); 48.0 (*dq*, ^2J(C,F) = 31.1, C(5′)); 52.5, 55.8 (2*s*, C(1), C(3)); 54.2 (*q*, MeO); 85.5 (*s*, C(2)); 113.6 (*q*, ^3J(C,F) = 2.4, CN); 122.6 (*q*, ^1J(C,F) = 285.7, CF_3); 123.1 (*q*, ^1J(C,F) = 280.8, CF_3); 122.0, 122.3, 127.1, 127.4 (4*d*, 4 arom. CH); 146.9, 149.0 (2*s*, 2 arom. C_q); 149.1 (br. *s*, C(4′)). ^{19}F-NMR: −61.3 (*sym.-quint.* results from ^3J(F,H) ≈ ^5J(F,F) = 8.4, CF_3−C(5′)); −69.1 (*q*, ^5J(F,F) = 8.4, CF_3−C(6′)). MS (170°): 464 (1.7, M^+; ^{13}C 0.39/0.39), 406 (22, $[M-S-CN]^+$, $C_{20}H_{22}F_6NO^+$; ^{13}C 4.9/4.9, $^{13}C_2$ 0.52/0.59, S-free), 278 (100, $C_8H_6F_6NOS^+$; ^{13}C 8.9/8.8, $^{13}C_2 + {}^{34}$S 4.8/4.4), 171 (19, $C_{13}H_{15}^+$), 156 (8, $[171-Me]^+$). Anal. calc. for $C_{21}H_{22}F_6N_2OS$ (464.47): C 54.30, H 4.77, N 6.03; found: C 54.46, H 4.70, N 5.90.

Data of **9b** (from mixture with **9a**). ^{1}H-NMR (360 MHz): 1.18, 1.36, 1.42, 1.50 (4*s*, 4 Me); 3.39 (*s*, MeO); 3.39, 3.42 (*AB*, ^2J(H,H) = 16, CH_2(7′)).

3.2. *2,3-Dihydro-1,1,3,3-tetramethyl-4′-oxo-5′,6′-bis(trifluoromethyl)-spiro[1*H*-indene-2,2′-[1,3]thiazepane]-6′-carbonitrile* (**10**). The stirred soln. of **4B** (0.694 mmol) in MeCN (3 ml) was dropwise treated with H_2O (1 ml). After 30 min, the solvent was evaporated, and the residue was recrystallized twice from cyclohexane and little CH_2Cl_2: the colorless needles of **10** (125 mg, 40%) showed a m.p. 207–208°. In a preceding experiment in the NMR-tube, ^{19}F-NMR analysis with DICHLO indicated 66% of a homogenous **10a**; further signals did not indicate a second diastereoisomer. IR: 706*m*, 755*s* (arom. out-of-plane deform.); 1128, 1163, 1189, 1211, 1242, 1271, 1288 (all *s*, C−F); 1452*m*, 1483*m* (arom. ring vibr.), 1642*m*, 1678v*s* (NH−CO), 1724*m* (not clarified), 3210 (br., NH). ^{1}H-NMR (80 MHz): 1.43, 1.45, 1.48, 1.50 (4*s*, 4 Me); 3.41, 3.53 (*AB*, ^2J(H,H) = 15.4, CH_2(7′)); 5.09 (*q*, ^3J(F,H)) = 7.8, H−C(5′)); 5.80 (br. *s*, NH), 7.0–7.4 (*m*, 4 arom. CH). ^{19}F-NMR (94.2 MHz): −62.1 (apparent *quint.*, ^3J(F,H) ≈ ^5J(F,F) = 8.3, F_3C−C(5′)); −69.1 (*q*, ^5J(F,F) = 8.3, F_3C−C(6′)). Anal. calc. for $C_{20}H_{20}F_6N_2OS$ (450.44): C 53.33, H 4.48, N 6.22; found: C 53.61, H 4.36, N 6.46.

A fraction, which was isolated from the mother liquor after several days, contained **10a**/**10b** 76:24. **10b** showed δ(F) −61.8 (*dq*, not fully resolved, F_3C−C(5′)); −68.8 (*q*, ^5J(F,F) = 9.5, F_3C−C(6′)).

4. *Kinetics of Ring Contraction of* **4B** *and Cleavage.* 4.1. *In PhCN at 80°.* The reaction of **4B** (0.144 mmol) in PhCN (0.5 ml) was monitored by ^{1}H-NMR; the NMR tube was heated in a 80° thermostat, and five machine integrals were evaluated for each concentration. The rapid isomerization of **4B** to **6B** was detected by the disappearance of the *d* at 3.05 of the *AB* for CH_2(7′) and the emergence of the *s* at 3.38 for CH_2(5′) of **6B** and of the *s* at 2.76 for CH_2(3) of *trans*-**12**. The concentration of **6B** passed a maximum of 64% after 20 min. Twelve concentration measurements within 1.7–22 h follow the first-order rate law for **6B** → **12** with $k_{\mathbf{6B}} \cdot 10^5 = 1.63$ [s^{-1}] and correlation coefficient $r = 0.994$. After 3 d, 98% of **12** was determined *vs.* octamethylcyclotetrasiloxane as weight standard.

4.2. *In $CDCl_3$ at 60°*. ^{1}H-NMR Monitoring (sealed NMR tube) of the signals: *d* at 3.15 (*B* of *AB*, **4B**), *s* at 3.49 (**6B**), and *s* at 2.46 (*trans*-**12**). The first-order decrease of **4B** (8 points) proceeded with $k_{4B} \cdot 10^5 = 5.4$ [s^{-1}], $r = 0.969$. The concentration of **6B** went through a broad maximum of 66% after 13 h. After **4B** had been consumed, the further formation of *trans*-**12** (12 points) obeyed the first-order law with $k_{6B} \cdot 10^7 = 3.2$ [s^{-1}], $r = 0.997$.

4.3. *In $CDCl_3$ at 40°*. For monitoring by ^{19}F-NMR, the following signals were used: −55.6 (*quint.*, **4B**), −58.2 and −63.9 (2*q*, **6B**), −66.2 (*s*, *trans*-**12**). Neglecting small amounts of side-products, the sum of **4B**, **6B**, and **12** was set to 100%, and the ratios are given in *Table 1*; the ratio **6B**/**12** remained virtually constant. The decrease of **4B** was a first-order reaction with $k_{4B} \cdot 10^6 = 5.6$ [s^{-1}] and $r = 0.997$. In another experiment, **4B** (0.26 mmol) in $CDCl_3$ (0.5 ml) was heated at 40° for 8 d, and ^{1}H-NMR analysis with 1,1,2,2-tetrachloroethane indicated 78% of **6B**.

5. trans-*2,3-Dihydro-1,1,3,3-tetramethyl-3′,4′-bis(trifluoromethyl)-spiro[1*H*-indene-2,2′-thiolane]-3′,4′-dicarbonitrile* (**6B**). Ketene imine **4B** (1.15 g, 2.66 mmol) in abs. $CHCl_3$ (5 ml) was heated to 40° for 10 d. After evaporation of the solvent, cyclopropane **12** and thione **11B** were removed by bulb-to-bulb distillation at 70°/0.1 Torr. The yellow oily residue crystallized at r. t.; pure colorless **6B** (36%) was obtained from MeOH. M.p. 113°. IR: 741*m*, 761*s* (arom. out-of-plane deform.), 1176v*s*, 1215v*s* (br., C−F); 1392*m*, 1468*m*, 1485*m*; 2260v*w* (C≡N). ^{1}H-NMR (80 MHz): 1.59 (*q*, ^6J(F,H) ~ 3, Me); 1.90, 2.00, 2.06 (3*s*, 3 Me); 3.49 (*s*, broadened, CH_2(5′)); 7.0–7.4 (*m*, 4 arom. CH). ^{13}C-NMR (20.2 MHz): 27.2 (*qq*, ^5J(C,F) = 1.8, Me); 27.4 (*s*, Me); 29.4 (*qq*, ^5J(C,F) = 1.8, Me); 32.3 (*qq*, ^5J(C,F) = 6.6, Me); 35.9 (*tq*, ^3J(C,F) = 1.8, CH_2(5′)); 54.7, 55.1 (2*s*, C(1), C(3)); 60.1 (*q*, ^2J(C,F) = 31.3, C(3′) or C(4′)); 62.9 (*q*, ^2J(C,F) = 28.7, C(4′) or C(3′)); 85.9 (*s*, C(2)); 112.1 (*q*, ^3J(C,F) = 3.1, CN); 113.3 (*s*, CN); 121.8 (*q*, ^1J(C,F) = 289.3, CF_3); 121.9 (*q*, ^1J(C,F) = 287.5, CF_3); 121.4, 122.3, 127.8, 127.9 (4*d*, 4 arom. CH); 148.4, 149.1 (2*s*, 2 arom. C_q). ^{19}F-NMR (94.2 MHz): −58.2 (br. *q*, ^5J(F,F) = 11.6, F_3C−C(3′)); −63.9 (*q*, ^5J(F,F) = 11.6, F_3C−C(4′)). MS (50°): 432 (0.9, $M^{+\bullet}$), 363 (0.7, $[M - CF_3]^+$), 279 (0.4, $[M - 2\ CF_3 - Me]^+$), 264 (0.7, $[M - 2\ CF_3 - 2\ Me]^+$), 228 (1.8, $[M - C_{13}H_{16}S]^+$, **12**$^+$), 204 (20, $C_{13}H_{16}S^+$, **11B**$^+$), 189 (67, $[204 - Me]^+$), 156 (23, $C_{12}H_{12}^+$), 141 (11), 115 (8), 69 (100, CF_3^+). Anal. calc. for $C_{20}H_{18}N_2F_6S$ (432.43): C 55.55, H 4.20, N 6.48; found: C 55.66, H 4.18, N 6.63.

6. trans-*1,2-Bis(trifluoromethyl)cyclopropane-1,2-dicarbonitrile* (*trans*-**12**). Ketene imine **4B** (0.786 mmol) was heated in a closed tube to 140° for 2 h. The 19F-NMR spectrum showed *trans*-**12** at −66.2. A second sharp signal at −62.0 (*d*, ^4J(H,F) = 1.4), *ca.* 8% of *trans*-**12**, is ascribed to *cis*-**12**, which was not isolated. After separation from thione **11B** by two sublimations at 40–50°, *trans*-**12** (130 mg, 72%) was obtained. M.p. 58–59°. IR (melt between NaCl plates): 709*m*, 782*m*, 898*m*, 1023*m*, 1089*s*, 1131v*s*, 1206v*s*, 1281v*s* (C−F), 2265m (C≡N), 3128*s* (C−H). ^{1}H-NMR (80 MHz): 2.46 (*s*, broadened, CH_2(3)). ^{13}C-NMR (20.2 MHz): 20.2 (*t*, further split with ^3J(C,F) = 1.8, C(3)); 25.1 (*qq*, ^2J(C,F) = 39.8, ^3J(C,F) = 1.2, C(1), C(2)); 108.7 (*s*, 2 CN); 120.0 (*q*, ^1J(C,F) = 278.9, 2 CF_3). ^{19}F-NMR (94.2 MHz): −66.2 (*t*, *s* on H decoupling, ^4J(F,H) ≈ 0.10, 2 CF_3). MS (100°): 228 (6, *M*+), 209 (1.5, $[M - F]^+$), 159 (0.9, $[M - CF_3]^+$), 120 (5, $C_4HF_3N^+$), 102 (5), 69 (100, CF_3^+). Anal. calc. for $C_7H_2F_6N_2$ (228.10): C 36.86, H 0.88, N 12.28; found: C 37.08, H 0.94, N 12.11.

7. *Reaction of* **4B** *with CD_3CN*. 7.1. *Experiments with ^{19}F-NMR Monitoring*. Ketene imine **4B** (0.547 mmol) in CD_3CN (0.5 ml) was sealed in an NMR tube and heated in a bath for 14.8 h at 40° and, subsequently, 21 h at 80°. ^{19}F-NMR Spectra (94.2 MHz) were recorded, and the following signals were integrated: *q* (−54.4) and *q* (−72.8) for **4B**, *q* (−57.2) and *q* (−63.1) for **6B**, *s* (−65.2) for *trans*-**12**, *d* (−61.1) for *cis*-**12**, and br. *s* (−54.0) and br. *s* (−73.4) for **13**. The machine integrals of each product were expressed as percentage of the total integral between −50 and −75 ppm. The five products mentioned above made up for 80–85% of the total integral, and their relative yields (sum set to 100) are given in *Table 4*. After 21 h at 80°, **6B** had disappeared, and 38% of **13**, 41% of *trans*-**12**, and 2.8% of *cis*-**12** were analyzed as final yields (sum 82.4%); various small signals of unidentified side-products made up the remainder. Finally, the tube was opened, and DICHLO was added; the integral obtained with the weight standard deviated only 2% from the total integral mentioned, which corresponded to the initial concentration of **4B**.

In a second experiment, **4B** (0.463 mmol) reacted in CD_3CN (0.5 ml) at 21°, and ^{19}F-NMR analysis indicated after 22 h (282 h) 52% (1.5%) of **4B**, 16.5% (41%) of **6B**, 1.7% (5.1%) of *trans*-**12**, and 14.6% (41%) of **13**. Subsequently, the tube was heated to 80° for 23 h. The final yields, determined with DICHLO as standard, were 32% of *trans*-**12**, 2.3% of *cis*-**12**, and 42% of **13**, *i.e.*, the amount of **13** has barely increased. Whether, at higher temp., **13** rolls back and is also converted to **12**, is an open question. For the preparation of **13** from **4B** and CD_3CN, long reaction times at r.t. are recommended.

7.2. N^1-*[2,3-Dihydro-1,1,3,3-tetramethyl-(1*H*-inden-2-ylidene)]*-N^2-*[4-cyano-4,5-dihydro-3,4-bis(trifluoromethyl)-2-thienyl][2,2,2-$^2H_3$]acetimidamide* (**13**). The reaction solns. of the two experiments (*Sect. 7.1*) were evaporated; **12** and **11B** were removed by bulb-to-bulb distillation at 50°/0.01 Torr. Crystallization of the residue

Table 4. *Reaction of* **4B** *with* (E)-**3** *in* CD_3CN*; Reaction-Time Profile by* ^{19}*F-NMR Monitoring.* Relative Yields of Five Products.

Temp.	Time [h]	**4B**	6B	**13**	*trans*-**12**	*cis*-**12**
40°	2.2	51	30	12	8	
40°	4.7	27	44	20	9	
40°	8.3	12	52	24	11	0.5
40°	11.0	8	53	26	12	0.5
40°	14.8 (= 0)	4	54	28	13	0.7
80°	3.3	–	25	41	32	1.4
80°	6.9	–	13	42	43	2.1
80°	13.4	–	4	46	47	2.4
80°	21.0	–	–	46	50	3.4

from hot cyclohexane gave colorless **13** (101 mg, 21%). M.p. 127–128°. IR: 725*m*, 755*m*, 759*s* (arom. out-of-plane deform.); 1122, 1170, 1186, 1204, 1336 (all v*s*., C–F); 1483*m* (arom. ring vibr.), 1579 + 1590v*s*, 1726*s* (C=N, N–C=C), 2240v*w* (C≡N), 2975*s* (C–H). ^{1}H-NMR (400 MHz, C_6D_6): 1.25 (*s*, 4 Me); 2.85, 2.96 (*AB*, ^2J(H,H) = 12.8, left branch split to *q*, ^4J(F,H) = 0.88, CH_2(5)); 6.87, 7.07 (*AA′BB′*, symmetrical, 2 × 8 lines, 4 arom. CH). ^{13}C-NMR (90.6 MHz, $CDCl_3$, 50° for sharper signals): 26.7 (low intens., *sept.*, 5 lines visible, CD_3 ?); 28.36, 28.48 (2*q*, 2 × 2 Me); 35.6 (*t*, C(5)); 49.3 (*s*, C(1′), C(3′)); 54.6 (*qq*, ^2J(C,F) = 32.0, ^3J(C,F) = 6.8, C(4)); 114.5 (*q*, ^3J(C,F) = 1.6, CN); 121.8 (*q*, ^1J(C,F) = 271.8, CF_3); 122.5 (*d*, 2 arom. CH); 123.5 (*q*, ^1J(C,F) = 286.6, CF_3); 128.1 (*d*, 2 arom. CH); 146.0 (*s*, C(3a′), C(7a′)); 163.7 (weak *s*, C_q); 165,8 (*m*, *s* on H decoupl., C_q); 187.6 (*s*, C_q). ^{13}C-NMR (100.6 MHz, C_6D_6, 50°; field gradient enhanced, assignments supported by HMQC [22], HMBC [23]; approximate values of J(C,H) from HMBC spectrum): 54.7 (^2J(C,H) ≈ 6–7 with both CH_2(5), C(4); on irradiation at δ(F) −55.3, the large coupling ^2J(C,F) remained, and the small ^3J(C,F) was suppressed; thus, δ(F) −55.3 belongs to C*F*$_3$ at C(3)); 122.3 (*q*, no long-range C,H coupl.; on irradiation at δ(F) −55.3, the ^1J(C,F) coupling disappears, *C*F$_3$–C(3)); 123.8 (^3J(C,H) ≈ 6 with CH_2(5); irradiation at δ(F) −55.3 leaves ^1J(C,F) untouched, *C*F$_3$ at C(4)); 122.4 (on F-decoupling, *d* with ^1J(C,H) = 161 and δ(H) 6.87 as coupling partner; C(4′) and C(7′)); 128.1 (*d*, ^1J(C,H) with δ(H) 7.07, C(5′), C(6′)); 146.0 (C(3a′) and C(7a′), coupled with δ(H) 6.87, ^2J(C,H) ≈ 15–18); 163.9 (^3J(C,H) ≈ 6, cross-peak with one of CH_2(5), C(2)); 165.8 (*s*, probably broadened by nuclear quadrupole relaxation by two N-atoms, imidamide C); 187.3 (*s*, long-range C,H coupl. with Me, C(2′)). ^{19}F-NMR (94.2 MHz, $CDCl_3$): −55.7 (*q*, ^5J(F,F) = 6.8); −74.1 (blunt *s* at 25°, *q* at 43°, sharper at 72°, ^5J(F,F) = 6.8). ^{19}F-NMR (376.5 MHz, C_6D_6, 65°): −55.3 (*q*, ^5J(F,F) = 6.7, F_3C–C(3)); −73.9 (br. *s*, F_3C–C(4)). MS (70–80°): 476 (64, M^+), 461 (5, $[M - Me]^+$), 449 (3, $[M - HCN]^+$), 407 (100, $[M - CF_3]^+$), 363 (5, $[407 - CD_3CN]^+$), 290 (27), 196 (28), 177 (31), 171 (44, $C_{13}H_{15}^+$), 156 (25, $C_{12}H_{12}^+$), 141 (13, $C_{11}H_9^+$), 69 (8, CF_3^+). Anal. calc. for $C_{22}H_{18}D_3F_6N_3S$ (476.50): C 55.45, H + D 5.08, N 8.82; found: C 55.69, H + D 5.20, N 8.52.

7.2. *X-Ray-Diffraction Analysis of* **13** (*Fig. 1*). Although the scan width is high (as a consequence of the imperfection of the single crystal), the bond lengths and angles (*Table 2*) unequivocally establish the structure. The crystal was a monoclinic plate (0.13 × 0.33 × 0.53 mm) of space group $P2_1/c$. The crystal was sealed in a glass capillary and mounted on the goniometer head of a *Nonius MACH3* four-circle diffractometer operating with MoK_α radiation (λ = 0.71073 Å) and graphite monochromator. Unit cell dimensions: a = 12.148(6), b = 12.249(4), c = 15.334(3) Å, β = 93.62(3)°, V = 2277.2(14) Å^3, Z = 4, $D_{calc.}$ 1.381 mg/mm^3, F(000) = 976, T = 293(2) K, μ = 0.205/mm. The unit-cell dimensions resulted from a least-square fit of the setting angles of 25 centered reflections; $\omega - 2\theta$ scan, scan width 2.47 + 0.71 tan θ, maximum measuring time 90 s, θ range 3.64–23.73° for all $\pm h$, $+ k$, $\pm l$ reflections, 3597 reflections collected, 3451 independent (R_{int} = 0.0691), and 1579 reflections with $I > 2\sigma(I)$. *Lorentz*, polarization, and absorption corrections (T_{max}/T_{min} 0.9999 and 0.9823) were performed. The structure was solved by SHELXS-86 and refined with SHELXL-93 [31]; final R_1 = 0.1243 and $wR2$ = 0.2372 for 1579 reflections with $I > 2\sigma(I)$, and $wR2$ = 0.2852 for all data. Maximum and minimum of the final difference *Fourier* synthesis were 0.271 and −0.291 eÅ^{-3}. Non-H-atoms were refined anisotropically with inclusion of H-atoms in calculated positions and fixed isotropic U; ZORTEP plot [32]. The deposition No. CCDC – 219 837 contains supplementary data, which can be obtained from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 IEZ, UK (fax: +44 (1223)336-003; e-mail (deposit@ccdc.cam.ac.uk).

8. *[(2,2,5,5-Tetramethylcyclopentylidene)sulfonio]methanide* ('Thiocarbonyl Ylide'; **2C**) *and* **3**. 8.1. *In CCl_4 at 40°*. Dihydrothiadiazole **1C** [11] (0.504 mmol) and (*E*)-**3** (0.654 mmol) in CCl_4 (3 ml, filtered over Al_2O_3) were heated at 40° for 2.5 h. The strong IR absorption at 2010 + 2023 cm^{-1} indicated ketene imine **4C**. The integral absorption, measured between NaCl plates, path length 0.2 mm, was compared with that of ketene imine **4A** in CCl_4. The assumption of identical oscillator strengths allows analysis of 0.230 mmol (46%) of **4C**. A ^{1}H-NMR analysis was based on the *s* at δ 5.55 for **1C**, *d* at 3.18 (left branch of *AB*) for ketene imine **4C**, and the *s* at 3.52 for thiolane **6C**; it provided relative yields of **1C**/**4C**/**6C** 43 : 42 : 15. Two further ^{1}H-NMR analyses after 5 (10) h furnished ratios 24 : 45 : 31 (6 : 26 : 68); after 40 h at 40°, the signals of **1C** and **4C** had disappeared.

8.2. *Steric Course in C_6D_6 at 80°*. The catalysis of (*E*)/(*Z*)-equilibration of **3** by the dihydrothiadiazoles **1** can be reduced by choosing short reaction times at high temp. [10]. **1C** (0.581 mmol) and (*E*)-**3** (0.743 mmol) in C_6D_6 (0.5 ml) were heated in an acid-rinsed, sealed NMR tube at 80° for 10 min. The ^{19}F-NMR analysis with DICHLO was based on the *q* at −55.1 and *s* at −73.6 for **4C** (4%), *q* at −57.0 and *q* at −65.5 for **6C** (64%), *s* at −66.2 for *trans*-**12** (25%), and *d* at −62.0 for *cis*-**12** (1.0%). The excess **3** showed (*E*)/(*Z*) 95 : 5 (*s* at −62.3 and *s* at −59.3). A corresponding experiment with (*Z*)-**3** afforded **4C** (4%), **6C** (61%), *trans*-**12** (23%), and *cis*-**12** (2.0%); the ratio (*E*)/(*Z*)-**3** 68 : 32 indicated much isomerization, but not equilibrium.

8.3. *Steric Course in C_6D_6 at 40°*. **1C** (0.233 mmol) and (*E*)-**3** (0.411 mmol) in C_6D_6 (0.5 ml) were heated at 40° for 12.5 h, and the ^{19}F-NMR analysis as described above furnished **4C** (4%), **6C** (60%), *trans*-**12** (4%); (*E*)/(*Z*)-**3** 95 : 5; **1C** was not fully consumed. Under the same conditions, an experiment with (*Z*)-**3** provided **4C** (4%), **6C** (61%), *trans*-**12** (4%), and (*E*)/(*Z*)-**3** 62 : 38. Thus, at 40° the conversion of **6C** to *trans*-**12** + **11C** was slow, but the (*E*)/(*Z*)-isomerization of **3** was not suppressed.

8.4. trans-*6,6,9,9-Tetramethyl-3,4-bis(trifluoromethyl)-1-thiaspiro[4.4]nonane-3,4-dicarbonitrile* (**6C**). Dihydrothiadiazole **1C** (0.980 g, 4.94 mmol) and (*E*)-**3** (1.08 g, 5.04 mmol) in abs. benzene (5 ml) were heated to 50° for 5 h; a preceding experiment in a NMR tube yielded 75% of **6C**. After evaporation, the oily residue crystallized on trituration with pentane, and recrystallization from the same solvent gave colorless **6C** (770 mg, 41%). M.p. 75°. IR: 1176, 1181, 1218, 1239 (all v*s*, C−F); 1470*m*; 2255v*w* (C≡N). ^{1}H-NMR (80 MHz): 1.42 (*q*, ^6J(F,H) = 2.4, Me); 1.51, 1.63 (2*s*, 2 Me); 1.73 (*q*, ^6J(F,H) = 2.0, Me); 1.7–2.3 (*m*, CH_2(7), CH_2(8)); 3.54, 3.56 (*AB*, ^2J(H,H) = 13.5, CH_2(2)). ^{13}C-NMR (20.2 MHz): 26.6 (*qq*, ^5J(C,F) = 5.5, Me); 28.3 (*qq*, ^5J(C,F) = 1.8 , Me); 31.8 (*qq*, ^5J(C,F) = 4.3, Me); 32.5 (*q*, Me); 36.8 (*tq*, ^3J(C,F) = 1.8, C(2)); 41.2, 41.3 (2*t*, C(7), C(8)); 50.4, 51.9 (2*s*, C(6), C(9)); 61.5 (*q*, ^2J(C,F) = 28.1, C(3) or C(4)); 62.3 (*q*, ^2J(C,F) = 29.9, C(4) or C(3)); 84.7 (*s*, C(5)); 112.3 (*q*, ^3J(C,F) = 2.4, CN); 113.6 (br. *s*, CN); 121.8 (*q*, ^1J(C,F) = 287.5, CF_3); 122.4 (*q*, ^1J(C,F) = 288.7, CF_3). ^{19}F-NMR (94.2 MHz, $CDCl_3$): −57.3 (*q*, broadened by F,H coupling, ^5J(F,F) = 9.8, CF_3−C(4)); −65.8 (*q*, sharp, ^5J(F,F) = 9.8, CF_3−C(3)); ^{19}F-NMR (94.2 MHz, C_6D_6): −57.0 (br. *q*), −65.5 (*q*), ^5J(F,F) = 9.9. MS (30°): 384 (2, M^+), 369 (0.3, $[M - Me]^+$), 314 (6, $[M - HCF_3]^+$), 228 (5, $C_7H_2F_6N_2^+$, **12**$^+$), 156 (22, $C_9H_{16}S^+$), 141 (9, $[156 - Me]^+$), 123 (35, $[156 - HS]^+$), 69 (100, CF_3^+), 56 (18, $C_4H_8^+$). Anal. calc. for $C_{16}H_{18}F_6N_2S$ (384.39): C 49.99, H 4.72, N 7.29; found: C 50.39, H 4.75, N 7.06.

9. *[(2,2,4,4-Tetramethylcyclobutylidene)sulfonio]methanide* ('Thiocarbonyl Ylide'; **2D**) *and* **3**. 9.1. *Reaction in CCl_4 at 40°*. Dihydrothiadiazole **1D** [6] (1.05 mmol) and (*E*)-**3** (1.37 mmol) in CCl_4 (3 ml, filtered over Al_2O_3) were heated to 40° for 90 min. The ^{1}H-NMR spectrum indicated a ratio **1D**/**4D**/**6D** of 49 : 33 : 18; anal. signals: 5.53 (*s*, **1D**), 2.68 and 3.25 (*AB*, ^2J(H,H) = 15.0, **4D**), 3.42 and 3.53 (*AB*, *trans*-**6D**). After 230 min at 40°, the ratio **1D**/**4D**/**6D** had changed to 16 : 25 : 59, and, after 20 h at 40°, only the signals of **6D** persisted. Furthermore, the CCl_4 soln. showed after 90 min reaction at 40° the IR band at 2007 (sh, 2028, C=C=N stretch.), and the integral absorption (see *Sect. 8.1*) confirmed the concentration of **4D**. The reaction of **1D** with (*E*)-**3** in C_6D_6, 19 h at 40°, produced a nearly quant. yield of *trans*-**6D** (^{1}H-NMR, 1,1,1,2-tetrachloroethane). The ^{19}F-NMR spectrum showed no impurities; the excess of **3** had a ratio (*E*)/(*Z*) of 91 : 9, but signals of *cis*-**6D** were not observed.

9.2. trans-*5,5,8,8-Tetramethyl-3,4-bis(trifluoromethyl)-1-thiaspiro[3.4]octane-3,4-dicarbonitrile* (*trans*-**6D**). After reaction of **1D** (2.15 mmol) and (*E*)-**3** (2.35 mmol) in abs. benzene (5 ml) at 40° for 18 h, the solvent was removed, and the residue was recrystallized from pentane: *trans*-**4D** (295 mg, 37%). M.p. 93–94°. IR: 1174, 1196, 1226 (v*s*, fused to br. band, C−F), 2260v*w* (C≡N). ^{1}H-NMR (400.2 MHz): 1.39, 1.41 (2*d*, ^4J(H,H) = 0.51, 0.44, 2 Me); 1.60 (*qt*, ^6J(F,H) = 2.88, ^4J(H,H) = 0.51, Me); 1.67 (*qt*, ^6J(F,H) = 1.65, ^4J(H,H) = 0.51, Me); 1.71, 1.79 (*AB*, ^2J(H,H) = 11.3, *B* part is broader, CH_2(7)); 3.42, 3.53 (*AB*, ^2J(H,H) = 12.6, CH_2(2); the *A* part is broader, due to H,F coupling, which is resolved by line narrowing, ^4J(F,H) ≈ 0.6). ^{13}C-NMR (100.6 MHz): 27.7 (*qq*, ^6J(C,F) = 3.8, Me; HMQC shows coupling with δ(H) 1.67); 28.3 (*qq*, ^6J(C,F) = 6.0, Me; 1 H coupling with δ(H) 1.61); 30.06 (*q*, Me; couples with H at 1.39); 30.46 (*q*, Me; bonded to H at 1.41); 35.2 (*tq*, ^3J(C,F) = 1.5, C(2)); 45.6 (s, C(6); HMBC shows long-range coupling with δ(H) 1.39, 1.67); 47.0 (*s*, C(8); couples with H at 1.41, 1.60); 49.4 (*t*, C(7); long-range coupling with H of all four Me); 58.9 (*tq*, couples with CH_2(2), ^2J(C,H) =

2.7; ^2J(C,F) = 29.5, collapses on irrad. at δ(F) −67.2, C(3)); 61.6 (*q*, ^2J(C,F) = 29.9, F coupling eliminated on irrad. at δ(F) −56.8, no C,H coupling, C(4)); 77.3 (*s* between $CDCl_3$ signals, ^{1}H-HMBC shows ^3J(C,H) ≈ 5–8 with four Me, spiro-C(5)); 111.6 (*q*, ^3J(C,F) = 2.4, sharp *s* on selective decoupling at δ(F) −56.8, *C*N−C(4)); 113.8 (*q*, ^3J(C,F) = 2.4 on H decoupling; F-decoupled, *dd* with ^3J(C,H) = 5.4, 7.3, couples with both CH_2(2), *C*N−C(3)); 121.8 (*q*, ^1J(C,F) = 288.4; becomes *s* on select. decoupling at δ(F) −56.8, *C*F_3−C(4)); 122.1 (*q* with ^1J(C,F) = 287.2, *d* with ^3J(C,H) = 3.8, couples with δ(H) 3.53 of CH_2(2), *C*F_3−C(3)). ^{19}F-NMR (*Jeol*; 376.6 MHz): −57.1 (on line narrowing 25 lines, the distances of which reveal ^5J(F,F) as well as ^6J(F,H) with two of four Me; computer simulation in *Fig. 2*, *CF*$_3$−C(4)); −67.2 (*qd* with ^5J(F,F) = 7.1, ^4J(F,H) = 0.70, coupled with δ(H) 3.42 of CH_2(2); C*F*$_3$−C(3)). ^{19}F-NMR (*Bruker*; 94.2 MHz, C_6D_6, H-decoupled): −56.8 (*q*, ^5J(F,F) = 7.4); −67.0 (*q*, ^5J(F,F) = 7.4); the first *q* of CF_3 at C(4) has 55% of the height, which the second *q* (CF_3 at C(3)) displays. MS (30°): 370 (0.1, M^+), 355 (0.3, $[M-Me]^+$), 314 (100, $[M-C_4H_8]^+$), 287 (5, $[314-HCN]^+$), 245 (4, $[314-CF_3]^+$), 218 (2, $[245-HCN]^+$), 178 (6), 86 (20), 69 (24, CF_3^+), 56 (14, $C_4H_8^+$). Anal. calc. for $C_{15}H_{16}F_6N_2S$ (370.36): C 48.64, H 4.36, N 7.57; found: C 48.43, H 4.33, N 7.40.

9.3. *Thermal* trans ⇌ cis *Equilibration of* **6D**. Thiolane *trans*-**6D** (0.19 mmol) in PhCN (0.5 ml) in a sealed NMR tube was heated at 139°, and the conversion to *cis*-**6D** was monitored by ^{19}F-NMR (94.1 MHz, C_6D_{12} lock); signals: −56.9 (*s*, *trans*-**6D**), −58.6 (*q*, *cis*-**6D**). The equilibrium *trans*/*cis* 43:57 was approximated after 123 h, and the rate followed the first-order law for reversible reactions. Evaluation of 12 readings from 0–49.9 h by linear regression provided $(k_{trans}+k_{cis})\cdot 10^4 = 6.41$ [s^{-1}] with $r = 0.997$. During the reaction, the *s* of **3** appeared and amounted to 6.1% after 123 h; (*E*)/(*Z*)-**3** 91:9, *i.e.*, equilibrium. Thiolane *cis*-**6D** was not isolated. ^{19}F-NMR (PhCN) of *cis*-**6D**: −58.7 (*qq*, ^5J(F,F) = 15.4, ^6J(F,H) = 2.4, CF_3−C(4)); −66.4 (*q*, ^5J(F,F) = 15.4, CF_3−C(3)). A second isomerization experiment was carried out in MeCN at 110°; decomposition prevented a kinetic evaluation.

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