Reactions of Sterically Hindered 'Thiocarbonyl Ylides' with 1,2-Bis(trifluoromethyl)ethene-1,2-dicarbonitrile: Isolation of a Cyclic Seven-Membered Ketene Imine[1])

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Dedicated to *George A. Olah* on the occasion of his 75th birthday

When 'thiocarbonyl ylide' **1A** (=(2,2,4,4-tetramethyl-3-oxocyclobutylidenesulfonio)methanide) is generated from the dihydrothiadiazole **5A** by N_2 extrusion at 40° in the presence of 2,3-bis(trifluoromethyl)fumaronitrile ((*E*)-**10**), a cyclic seven-membered ketene imine **11** and *trans*-thiolane **12** are formed (81:19). The reaction of **1A** with (*Z*)-**10** furnishes **11**, **12**, and *cis*-thiolane **25** in the ratio of 82:12:6. The strained ketene imine **11** is crystalline and storable as a consequence of the stabilizing 'perfluoroalkyl effect'. The ketene imine group is stereogenic; **11** has a *transoid* structure with respect to the CF_3 groups, and there is no evidence for the *cisoid* diastereoisomer. Ketene imine **11** adds H_2O, MeOH, and $PhNH_2$. In solution at 60°, **11** undergoes an irreversible ring contraction, furnishing the thiolanes **12**/**25** 98:2. The rate constant of this first-order rearrangement increases 850-fold, as the solvent polarity rises from cyclohexane to CD_3CN, in accordance with a zwitterionic intermediate. It is the same intermediate that is initially formed from **1A** and **10**, and its intramolecular *N*- and *C*-alkylation give rise to **11** and **12** + **25**, respectively. In contrast to **1A**, thiocarbonyl ylide **27**, which harbors the sterically less-demanding adamantylidene group, reacts with (*E*)-**10** to give *trans*-thiolane **29**, but no ketene imine. The precursor **26** catalyzes the (*Z*)/(*E*) isomerization of **10** ((*E*)/(*Z*) *ca.* 95:5 at equilibrium), thus obviating conclusions on steric course and mechanism of this cycloaddition.

1. Introduction. – In 1963, the assumption that 1,3-dipolar cycloadditions take a *concerted*, although not necessarily *synchronous* pathway (equal strength of the two new σ-bonds in the transition state (TS)), was buttressed with rather limited experimental evidence [2]. This concertedness is undisputed today for 'normal' 1,3-dipolar cycloadditions (review on mechanism: [3]), and for the related *Diels-Alder* reactions as well [4]. However, all experimental evidence for one-step processes is indirect and based on the contrasting behavior of two-step reactions. The capture of intermediates in two-step processes provides the power of conviction.

'Thiocarbonyl ylides' (=(methylidenesulfonio)methanides) are very electron-rich 1,3-dipoles that differ from allyl anions in having the middle C-atom replaced by a sulfonium function. We studied their reactions with electron-deficient ethylene

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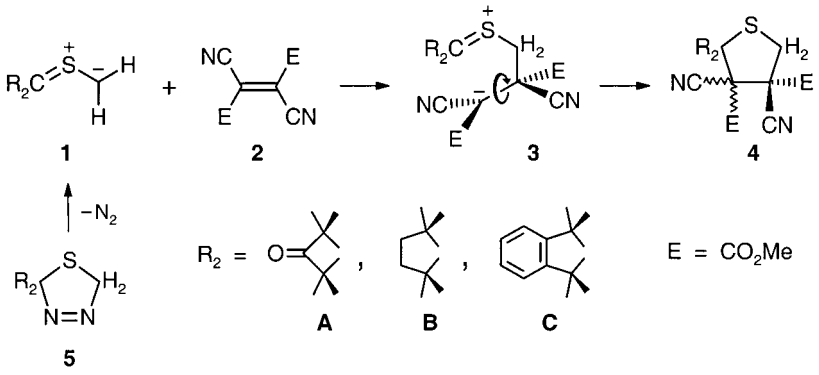
derivatives in the expectation of reaching the two-step mechanism *via* a zwitterionic intermediate. With the sterically hindered thiocarbonyl ylide **1A**, we probed the borderline region between concerted and two-step processes. For reactions of highly electrophilic 1,3-dipoles with very nucleophilic dipolarophiles, it was likewise shown that they pass the mechanistic borderline [5].

The cycloadditions of **1A** with dimethyl fumarate and dimethyl maleate proceeded with a stereospecificity of $> 99.9\%$, in accordance with concertedness. However, in the reactions of **1A** with dimethyl 2,3-dicyanofumarate (**2**) and dimethyl 2,3-dicyanomaleate, the loss of stereospecificity indicated the switch of mechanism (*Scheme 1*) [6][7]. Two electron-attracting substituents at the carbanionic center are required to stabilize zwitterion **3**, and rotation competes with ring closure ($\rightarrow$ **4**). Full rotational equilibrium of *trans*- and *cis*-zwitterions **3** was achieved, when more bulky thiocarbonyl ylides were employed. The *S*-methanides **1B** and **1C**, derived from 2,2,5,5-tetramethylcyclopentanethione and 1,1,3,3-tetramethylindan-2-thione, converted the mentioned *trans*/*cis*-isomeric acceptor-ethylenes to the spirothiolanes **4B** and **4C** in identical *trans*/*cis* ratios of 5:95 [1].

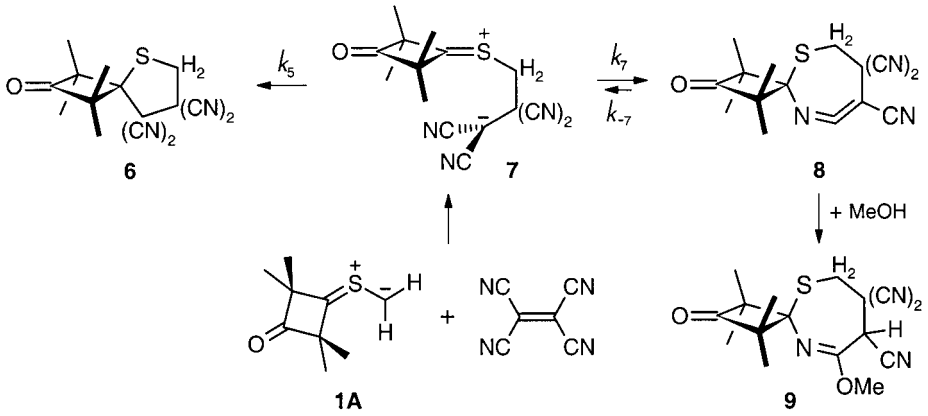
Scheme 1



The zwitterion is the turntable in the reaction system, and a surprising feature was demonstrated for the reaction of **1A** with ethenetetracarbonitrile (TCNE). Whereas in absolute THF at 45° the spirothiolane-tetracarbonitrile **6** was formed in high yield, the seven-membered lactim methyl ether **9** became the major product, when the medium contained MeOH (*Scheme 2*). Even with 1.2 equiv. of MeOH, a product ratio for **6**/**9** 35:65 was reached, which remained constant with higher concentration of MeOH [8][9]. According to our interpretation, zwitterion **7** undergoes *irreversible* 1,5 cyclization ($\rightarrow$ **6**) and *reversible* 1,7 ring closure to give a seven-membered cyclic ketene imine **8** with a rate ratio of 35:65. The ketene imine is intercepted by MeOH ($\rightarrow$ **9**), and, in the absence of MeOH, returns to the zwitterion **7**, which is partitioned on the two pathways again.

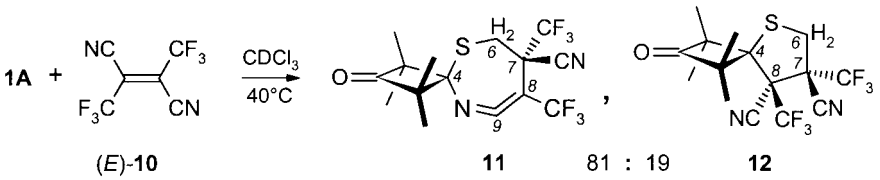
The rate-determining step is the N_2 elimination from the 2,5-dihydro-1,3,4-thiadiazole **5A**, the precursor of **1A**. The half-life ($t_{1/2}$) of **5A** in THF at 40° amounts to 88 min. Our endeavors to detect the ketene imine **8** by its IR frequency at *ca.* 2000 cm^{-1} were in vain. Obviously, the lifetime of this elusive intermediate is too short.

Scheme 2



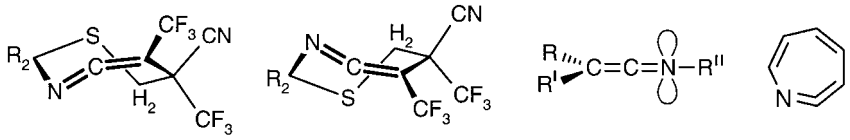
2. Results and Discussion. – 2.1. *Reaction of* **1A** *with 2,3-Bis(trifluoromethyl)fumaronitrile* ((*E*)-**10**). The remarkable tetra-acceptor-ethylenes **10**, (*E*) and (*Z*), were introduced by *Cairns* and co-workers [10]. Nucleophilic catalysts establish an (*E*)⇌(*Z*) equilibrium of *ca.* 95:5. The ketene imine intermediate became isolable, when **10** was employed as dipolarophile (for a preliminary communication, see [11]). The generation of **1A** from **5A** in the presence of 1.2 equiv. of (*E*)-**10** in $CDCl_3$ at 40° furnished ketene imine **11** and thiolane **12** in the ratio of 81:19 (^{1}H-NMR analysis; *Scheme 3*). The pale-yellow needles of **11** crystallized from CS_2 at low temperature, and the colorless *trans*-thiolane **12** was obtained from the mother liquor.

Scheme 3



2.2. *Properties of the Cyclic Ketene Imine* **11**. Compound **11** shows the strong IR absorption of cumulated bond systems at 2007 cm^{-1}, close to the range characteristic for open-chain ketene imines. In the ^{1}H-NMR spectra of **11** and **12**, the *AB* pattern of CH_2(6) is a consequence of chirality, and the geminal coupling constants, 15.2 Hz for **11** and 11.8 Hz for **12**, are characteristic for seven- and five-membered rings of this series. The four Me *singlets* of **12** are found at higher frequencies than those of **11**. The closer proximity of CF_3 and Me groups in **12** is supported by two of the Me signals of **12** (none in **11**) that reveal H,F coupling with F_3C–C(8). The ^{13}C-NMR signals of C(7) and C(8) in both **11** and **12** are split into *quadruplets* by ^2J(C,F) = 31–34 Hz. The ^{13}C shifts of the ketene imine group of **11**, 63.5 for C(8) and 188.9 for C(9) (*q*, ^3J(C,F) ≈ 3), correspond to parameters reported for open-chain ketene imines [12].

As an allene-type bond system, the ketene imine group is a stereogenic group, and the cyclic ketene imine **11** should occur in diastereoisomers of types **13** and **14**. Two X-ray analyses of related ketene imines, *i.e.*, those with spirocyclic 2,2,6,6-tetramethylcyclohexane [13] and 1,1,3,3-tetramethyl-2-indane rings [14], established the configuration of **13**, and the same *transoid* structure is assumed for **11**. Both geometrical isomers, (*E*)-**10** and (*Z*)-**10**, furnished the same ketene imine **11**.



13 *transoid* **14** *cisoid* **15** **16**

Dynamic NMR studies and MO calculations of acyclic ketene imines suggest enantiomerization by N-inversion, rather than rotation about the C=C=N axis [15][16], an outcome in accordance with topomerization studies of ketimines [17]. Barriers of 14–15 kcal mol^{-1} were measured for trialkylketene imines; they are substantially reduced by aryl or electron-attracting substituents at the C-atom. The introduction of the ketene imine group into a seven-membered ring generates strain and causes bending of and twisting about the C=C=N axis. Since the N-inversion process ideally passes a linear arrangement of four atoms, as shown in **15**, the barrier should go up in cyclic ketene imines. *Firl et al.* prepared an eight-membered ketene imine (unstable yellow oil, not analytically pure) and concluded an N-inversion mechanism from an observed barrier of 19 kcal mol^{-1} [18].

Whereas the N-inversion process of cyclic ketene imines becomes the more costly, energetically speaking, the smaller the ring size, the opposite is expected for the C=N rotation mechanism. Rotation is the only pathway for the enantiomerization of *allenes*. The π-MOs of allene-type bond systems are stretching in orthogonal planes. The fitting into a ring of common size reduces the dihedral angle to $< 90°$, *i.e.*, an approach to the TS of enantiomerization. High-caliber MO calculations confirm the decrease of barrier height on reduction of the ring size of cyclic allenes [19][20].

Considering substituent effects and steric hindrance, the barrier to diastereoisomerization, **13** $\rightleftharpoons$ **14**, is hard to predict. The ^{19}F-NMR spectrum of **11** at 50° shows a *quadruplet* at -56.3 ppm with $^5J(F,F) = 4.4$ Hz and at -73.6 ppm a coalesced signal of the second CF_3 group (probably $F_3C-C(8)$). Still an unstructured hump at 25°, the second signal becomes a *quadruplet* at –30° and sharpens at –60°, but no duplication of signals was observed. The ^{19}F shifts remain virtually the same from $+50°$ to $-60°$. The coalescence phenomenon requires further study, but seems to be unconnected with conversion to a diastereoisomer. The low-temperature spectrum is compatible with a frozen structure **13** or an equilibrium involving only little of the less favored **14** (nonbonded interaction of *cisoid* CF_3 groups).

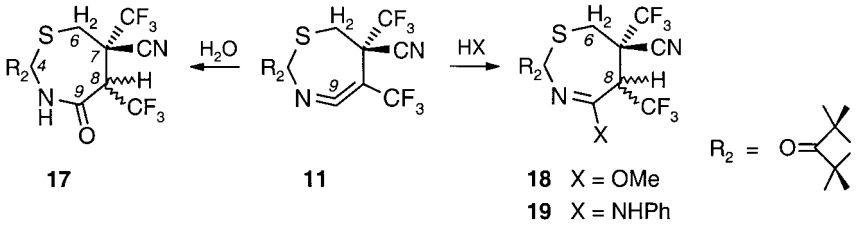
Numerous strained cyclic cumulenes are known as transient intermediates in dimerizations or rearrangements (for reviews, see [21]). When we described the cyclic ketene imine **11** in 1989 [11], it was the first stable and isolable cumulene in a seven-membered ring. The last decade has brought much progress; sila and phospha ring members allow even the preparation of six-membered cyclic allenes [22][23]. On the

side, the highly thermolabile, seven-membered ketene imine **16** was generated by flash photolysis of phenyl azide in the Ar matrix at 8 K by *Chapman* and *Le Roux* [24]; **16** plays a key role in the chemistry of phenylnitrene and pyridylcarbene [25].

We ascribe the stability of **11** to the 'perfluoroalkyl effect' [26]: CF_3 groups prefer saturated C-atoms as bonding partners, and stabilize strained ring systems (for reviews, see [27]) [28]. The interplay of thermodynamic and kinetic effects in our example will be discussed in *Sect. 2.4*.

2.3. *Reactions of Ketene Imine* **11** *with HX*. The rapid reaction of **11** in THF with H_2O provided the lactam **17** in two diastereoisomers **a**/**b** 4:1, which differ in configuration at C(8) (*Scheme 4*). The major product, **17a**, was obtained pure. The equilibrium (**a**/**b** *ca.* 17:83), established by base catalysis, shows a preponderance of **17b**.

Scheme 4



The addition of MeOH to **11** furnished the lactim methyl ether **18**, likewise in two diastereoisomers, **a**/**b** 55:45. In contrast to normal lactams, **17a** reacted with CH_2N_2 and afforded the methyl ether **18**, but now **a**/**b** 28:72. The mixture of stereoisomers, **18a** + **18b**, showed two sets of ^{1}H-NMR parameters. The H–C(8) of **17** is acidified by four electron-attracting groups, and appeared as *quadruplets* at 4.83 (**18a**) and 4.58 ppm (**18b**) with $^3J(H,F) = 8.0$ Hz. The reaction of **11** with $PhNH_2$ produced the cyclic amidine **19** (80%) in a 2:1 diastereoisomer ratio with respect to C(8).

Reactions of open-chain, arylated ketene imines with H_2O or ROH require acid or base catalysis, and the addition of $PhNH_2$ proceeds in refluxing toluene [29]. The high rate of nucleophilic HX additions to **11** is a consequence of ring strain and CF_3 substitution. *C*,*C*-Bis(trifluoromethyl)ketene imines react with HX likewise at room temperature [30].

2.4. *Isomerization of Ketene Imine* **11** *to Thiolane* **12**. In the reaction of **1A** with TCNE, the rapid isomerization to thiolane **6** made the ketene imine **8** (interceptible by H_2O or MeOH) appear as hypothetical intermediate [9]. In the case of **11**, this ring contraction proceeds as kind of slow-motion picture (for a preliminary communication, see [31]).

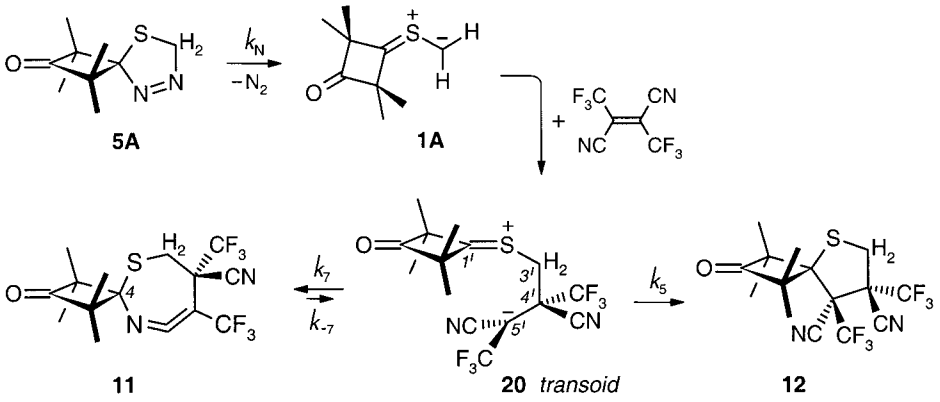
The isomerization in solutions of **11** is slow at room temperature, but becomes conveniently measurable at 60°. The reaction is strictly first-order, and the rate constants were measured by ^{1}H-NMR analysis in several solvents (*Table 1*). With rising solvent polarity, k_{exp} increases by three powers of ten. The half-lives of **11** at 60° stretch from 48 h in cyclohexane to 7.1 min in MeCN. The values of log k_{exp} show a fairly linear relation with E_T, a widely used parameter of solvent polarity [32].

Table 1. *First-Order Rate Constants for the Conversion of Ketene Imine* **11** *to Thiolane* **12** (k_{exp}, ^{1}H-NMR Analysis) *and the* N_2 *Elimination from* **5A** (k_N, Volumetry)

Solvent	$k_{exp} \cdot 10^6$ [s^{-1}]		$(\mathbf{11})_o/(\mathbf{12})_o$	$k_N \cdot 10^6$ [s^{-1}] at 40°	^{1}H-NMR Signals	
	at 60°	at 40°			**11**	**12**
(D_{12})Cyclohexane	1.94			206	2.78 (*d*)	3.50 (*d*)
CS_2	4.02		2.3		2.76 (*d*)	3.65 (*d*)
$CDCl_3$	21.1		4.3	114	4 Me	4 Me
C_6D_6	22.1		5.7	122	4 Me	4 Me
1,2-Dichlorobenzene	33.3				2.70 (*d*)	3.42 (d)
(D_8)THF	159	13.6	5.3	131	3.01 (*d*)	3.82 (*d*)
PhCN	497	80.4		120	3.08 (*d*)	3.61 (*s*)
CD_3CN	1640			97	3.07 (*d*)	3.70 (*s*)

The N_2 elimination from thiadiazoline **5A** is a 1,3-dipolar cycloreversion, and its rate constants k_N at 40° exhibit a small inverse relation on solvent polarity (*Table 1*). Two k_{exp} values at 40° for the ring contraction **11** → **12** are slower than the N_2 extrusion from **5A** (k_N) by factors of only 9.7 in THF and 1.5 in PhCN. Thus, during the generation of **1A** from **5A** (*Scheme 5*), substantial amounts of the ketene imine **11** will isomerize to **12** in polar solvents, whereas, in nonpolar media, this fraction is small. Measurement of the time dependence of the ratio **11**/**12** allowed an estimate of the initial $(\mathbf{11})_o/(\mathbf{12})_o$ in *Table 1*. The value **11**/**12** 81:19 for $CDCl_3$ (*Scheme 3*) is such an extrapolation.

Scheme 5



The mechanism for the conversion of ketene imine **8** to thiolane **6**, delineated in *Scheme 2*, is strongly confirmed by the study of the isolated ketene imine **11** (*Scheme 5*). The ring opening with k_{-7} must be the slow step, and the transient zwitterion **20** is rapidly distributed among the two cyclization pathways, k_7 and k_5, until, finally, all the material arrives at the thermodynamically favored thiolane **12**. The partition coefficient, $k_5/(k_5 + k_7)$ in *Eqn. 1*, defines the fraction of **20** going to **12**.

$$k_{exp} = k_{-7}\left(\frac{k_5}{k_5 + k_7}\right) \quad (1)$$

$$k_{-7} = k_{exp}\left(1 + \frac{k_7}{k_5}\right) = k_{exp}\left(1 + \frac{(\mathbf{11})_o}{(\mathbf{12})_o}\right) \quad (2)$$

The initial product ratio, $(\mathbf{11})_o/(\mathbf{12})_o$ in *Table 1*, reflects k_7/k_5 for the zwitterion **20**. When the latter would be formed in the same conformational manifold by the ring opening of **11** as in the cycloaddition, **1** + (*E*)-**10**, then *Eqn. 2* allows the evaluation of k_{-7}, *e.g.*, $8.6 \cdot 10^{-5}$ [s^{-1}] for the reaction in $CDCl_3$ at 40°.

The base-catalyzed alkylation of nitriles takes place at the carbanionic center. When this normal course is sterically hindered, *N*-alkylation furnishes ketene imines [33]. The two cyclizations of **20** in *Scheme 5* offer *intramolecular* analogues.

The high dependence of k_{exp} on solvent polarity indicates that the activation process of the rate-determining step is accompanied by an increase of charge separation. Since k_7/k_5, *i.e.*, $(\mathbf{11})_o/(\mathbf{12})_o$ in *Table 1*, is less solvent-dependent than k_{exp}, the step with k_{-7} in *Eqn. 1* must go along with a rise of polarity. This insight is most welcome since, for thiocarbonyl ylides, the solvent dependence of cycloaddition rates remains hidden behind the activation barrier of the precursor's initial N_2 elimination. Here, the solvent sensitivity of k_{-7} is evidence for the polarity of the ring-opened species **20**. Further, the rates of *concerted* 1,3-dipolar cycloadditions usually show a small negative response to solvent polarity [3].

How does the 'perfluoroalkyl effect' stabilize the strained ketene imine **11**, compared with the short-lived tricyano analogue **8**? The ring opening to restore the zwitterion is endothermic, and its TS should be product-like. A second CN group stabilizes the anionic charge in zwitterion **7** (*Scheme 2*) better than the CF_3 group does in **20**. The substituent constants σ_p^- (electron withdrawal 'diluted' by the benzene ring) are 1.00 for CN and 0.65 for CF_3, and the inductive electron attraction *F* also confirms the superiority of CN (0.51) over CF_3 (0.38) [34]. A competition experiment revealed that thiocarbonyl ylide **1A** reacts with TCNE 11 times faster than with (*E*)-**10**. Of course, such rate ratios mirror not only anion stabilities and ground-state energies, but also system-inherent factors. Probably, we still need the somewhat mysterious 'perfluoroalkyl effect' to explain the dramatic increase of barrier height, *i.e.*, the *kinetic stabilization*, for the ring opening of ketene imine **11** *vs.* that of **8**.

2.5. *Stereochemistry of Ring Contraction of Ketene Imine* **11**. Inspection of molecular models suggests that **11** in the *transoid* structure **13** should preferably furnish the *trans*-zwitterion **20** (*trans* with respect to the C(4′)–C(5′) bond and *gauche* for the C(3′)–C(4′) bond) on ring opening and *vice versa* for the *cisoid* structure **14**. The heterolysis of the C(4)–N(10) bond is accompanied by rehybridization to give rise to a quasi-planar C(1′) bond system in the four-membered ring. The amount of pyramidalization (low inversion barrier at C(5′)) at the carbanionic center of **20** is uncertain, and the designation *transoid* is chosen in *Scheme 5*.

The search for *cis*-thiolane **25** (*cf. Scheme 7*) in the rearrangement of **11** was successful, when an enriched sample became available (see *Sect. 2.6.2*). The thiolane formed by ring contraction of **11** in CD_3CN at 60° contained **12** (*trans*) and **25** (*cis*) in the ratio 98.2 : 1.8 (in C_6D_6 98.1 : 1.9), as established by ^{19}F-NMR analysis with the help

of ^{13}C-satellite technique. No thermal *trans* → *cis* isomerization of thiolane **12** was observed in CD_3CN at 160°. The uncertainty whether some *cisoid* conformation **14** occurs along with **13** in the ketene imine **11** limits mechanistic conclusions.

2.6. *Steric Course of Cycloaddition of* **1A** *to (*E*)-***10*** and (*Z*)-***10***.* The zwitterion **20** formed from the reactants is partitioned between **11** and **12**. Information on the configuration of the *initially formed* thiolane can be gained only under conditions of slow isomerization **11** → **12**, *i.e.*, in nonpolar solvents (*Sect. 2.4*). The pair (*Z*)-**10** and (*E*)-**10** equilibrates in the presence of nucleophilic reagents to give a ratio of *ca.* 5:95. In MeCN, a spontaneous isomerization takes place [35], but in C_6D_6 the purity of (*Z*)-**10** was not diminished at 60°.

2.6.1. *(*Z*)/(*E*) Isomerization of* **10** *under Conditions of Cycloaddition.* In preceding studies with dimethyl 2,3-dicyanomaleate and the (*E*)-isomer **2**, a catalysis of the (*Z*)/(*E*) isomerization by the dihydrothiadiazole **5A** was noticed and slowed with 0.0076M H_2SO_4 in $CDCl_3$ as reaction medium [7]. When **5A** was heated with 1.7 equiv. of (*Z*)-**10** in C_6D_6 at 40°, monitoring by ^{19}F-NMR revealed a slow isomerization of the acceptor ethylene, which approached a plateau of (*Z*)-**10**/(*E*)-**10** 93:7 (still a modest effect), after **5A** had virtually disappeared after 5.3 half-lives (*Fig.*). Not only catalysis by **5A**, but also by thiocarbonyl ylide **1A** could be responsible for the isomerization of (*Z*)-**10**; formation of zwitterion **20**, conformational rotation, and dissociation back to the reactants would offer an attractive mechanism. An experiment described in *Sect. 10.3*

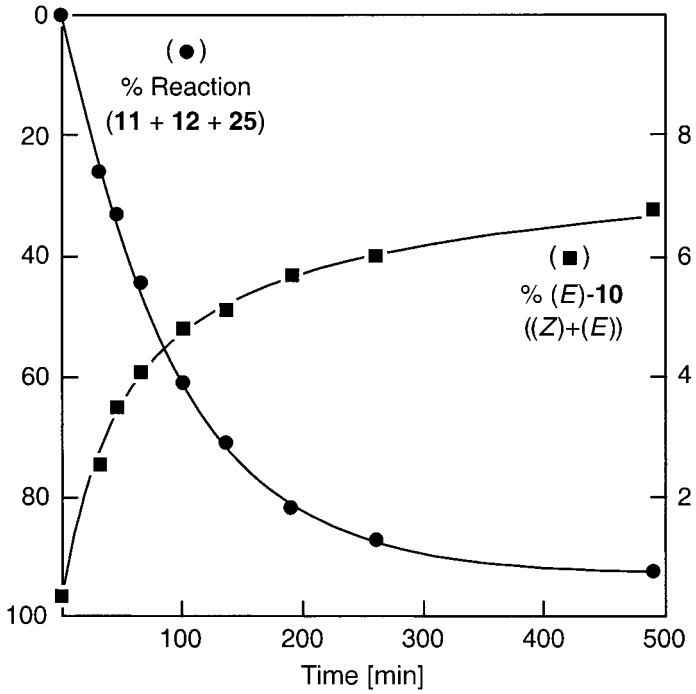
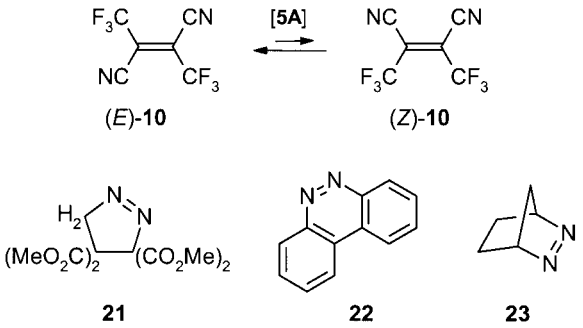


Figure. *Catalysis of isomerization of (*Z*)-***10*** to (*E*)-***10*** by dihydrothiadiazole* **5A** (^{19}F-NMR analysis). The decrease of **5A** is represented by the increase of the three products on the left ordinate.

of the *Exper. Part* favors catalysis by **5A**, all the more, as in the reaction of **1A** with **2** a dissociation of zwitterion **3A** was not observed [7].

Since (*Z*)-**10** was not isomerized by the reaction products, **11** and **12**, it is improbable that the thioether function of **5A** is responsible. The *cis*-azo group of **5A** turned out to be the 'culprit'. 1-Pyrazoline **21**, benzo[*c*]cinnoline (**22**), and 1,2-diazanorbornene (**23**) as model compounds displayed increasing catalytic activity for (*Z*)-**10** → (*E*)-**10** (*Scheme 6*). Linear plots of pseudo-first-order reactions were observed, *e.g.*, (*Z*)-**10**/(*E*)-**10** 50:50 was reached from (*Z*)-**10** after 15 h in 0.01M **23** in C_6D_6 at 24°.

Scheme 6



21 **22** **23**

2.6.2. *Nonstereospecificity of the Two-Step Cycloaddition*. Generation of **1A** from **5A** in C_6D_6 at 40° in the presence of 1.7 equiv. of (*Z*)-**10** afforded **11**, *trans*-thiolane **12**, and *cis*-thiolane **25** with the ratio 82:12:6 in 88% yield, while the excess of **10** had attained a (*E*)/(*Z*) ratio of 7:93 (*Table 2, Entry 1*). ^{19}F-NMR monitoring 'on the way' disclosed little change of the product ratio and raised doubts that the opulent share of *trans*-thiolane **12** could originate only from the small concentration of (*E*)-**10** formed by the **5A**-catalyzed isomerization. The major pathway from (*Z*)-**10** to *trans*-thiolane **12** appears to be the rotation of the *cisoid* zwitterion **24** to the more favored *transoid* conformer **20** and ring closure, in accordance with a two-step mechanism of cycloaddition (*Scheme 7*). Reactions of **5A** with (*Z*)-**10** at higher temperature (*Table 2*) support this conclusion.

After reaction of **5A** with (*Z*)-**10**, the ketene imine **11** was removed by hydration (→**17**) from the solution and the *cis*-thiolane **25** was characterized by elemental analyses and spectra in a 36:64 mixture with **12**.

The F,F coupling amounted to $^5J = 7.9$ for **12** (*trans*) and 15.0 Hz for **25** (*cis*); $J(cis) > J(trans)$ was also observed for other pairs of 1,3-dipolar cycloadducts obtained from (*Z*)-**10** and (*E*)-**10** in our laboratory [13]. This is in harmony with the distances of vicinal CF_3 groups in five-membered rings, *trans* > *cis*, since F,F coupling is transmitted through space.

The observation of a catalyzed isomerization (*E*)-**10** → (*Z*)-**10** has not much leeway, due to the 95:5 equilibrium. ^{19}F-NMR Analysis brought to light an (*E*)/(*Z*) ratio of 98.4:1.6 in the excess of **10**, after **5A** was reacted with 1.03 equiv. of (*E*)-**10** (C_6D_6, 80°, 10 min; *Entry 5*, *Table 2*); the product ratio revealed also a little bit of *cis*-thiolane **25**. Reactions of **5A** with (*Z*)-**10** and (*E*)-**10** in 0.0076M H_2SO_4 in $CDCl_3$ (80°, 6 min)

Scheme 7

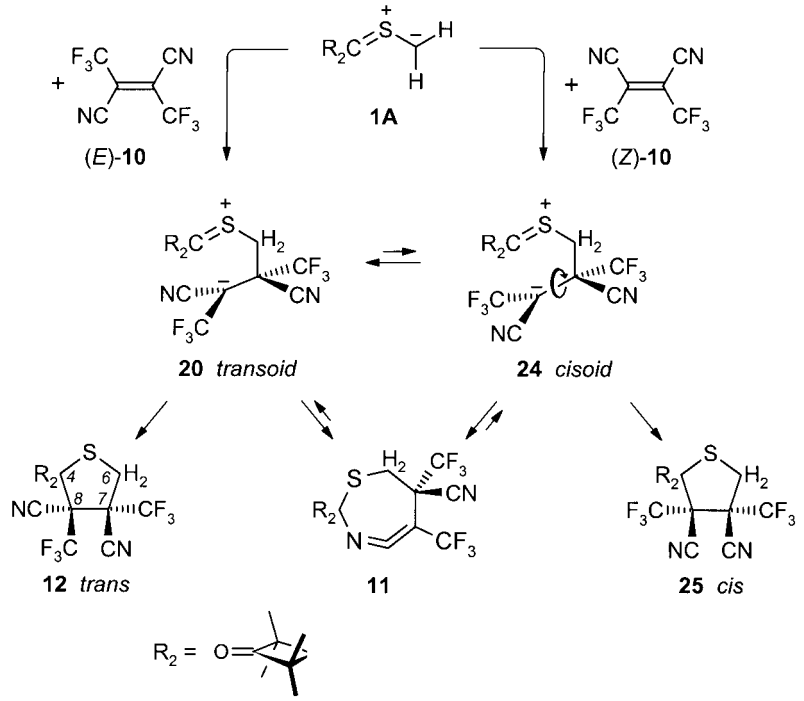


Table 2. *^{19}F-NMR Analysis of the Stereochemistry of the Reactions of Thiocarbonyl Ylide* **1A** *with 2,3-Bis(trifluoromethyl)maleonitrile* ((*Z*)-**10**) *and 2,3-Bis(trifluoromethyl)fumaronitrile* ((*E*)-**10**)

Entry	Equiv. of **10**	Reaction conditions (solvent, temp., time)	(*E*)/(*Z*) in excess **10**	Product ratio **11** / **12** / **25**	% **11**+**12**+**25**
1	1.7 (*Z*)	C_6D_6, 40°, 8.2 h	7:93	82 : 12 : 6	88
2	1.4 (*E*)	$CDCl_3$, 40°, 6 h	*ca.* 100:0	80 : 20[a])	97
3	1.5 (*Z*)	(D_{12})Cyclohexane, 80°, 10 min	5:95	73 : 17 : 10	
		3 h	11:89	47 : (Σ53)	97
4	1.4 (*E*)	(D_{12})Cyclohexane, 80°, 10 min	[a])	58 : 42[a])	
		3 h	[a])	43 : 57[a])	83
5	1.03 (*E*)	C_6D_6, 80°, 10 min	98.4:1.6	59 : 40 : 0.65	
6	1.2 (*Z*)	$CDCl_3$(H_2SO_4), 80°, 6 min	6:94	81 : 12 : 7	86
7	1.2 (*E*)	$CDCl_3$(H_2SO_4), 80°, 6 min	[a])	77 : 23[a])	93
8	1.1 (*Z*)	Heptane, 105°, 1.5 min	8:92	68 : 20 : 12	[a])

[a]) Not determined.

furnished similar product ratios (*Table 2*, *Entries 6* and *7*) as those without acid; the protective function of strong acid is missing in the case of acceptor ethylene **10**.

The rotational equilibrium of the *transoid* zwitterion **20** and the *cisoid* conformer **24** (both *gauche* at C(3′)–C(4′) bond) probably lies far on the side of the former. The nonbonded repulsion of the CF_3 groups destabilizes **24**. The *Van der Waals* radius

(1.20 Å for H, 1.47 Å for F [36]) of CF_3 not only exceeds that of C≡N, but the valence-shell of the F-atoms make the CF_3 group much harder to deform than the 'soft' π-cylinder of the CN group. *Taft*'s steric constant E_s is -0.51 for CN, -1.24 for Me, and -2.40 for CF_3 [36]. The 'conformational energies' ($e \rightarrow a$ at cyclohexane) likewise illustrate the increasing steric demand: C≡N 0.2, Me 1.74, CF_3 2.4–2.5, *t*-Bu 4.7–4.9 kcal mol^{-1} [37].

2.7. *Reactions of a Sterically Less Demanding Thiocarbonyl Ylide with* **10**. In the reaction of 'adamantanethione *S*-methylide' (**27**) (=(adamantylidenesulfonio)methanide) with TCNE, no ketene imine intermediate was interceptible with H_2O or MeOH. The stereospecificity test for the cycloadditions of **27**, applied to dimethyl 2,3-dicyanomaleate and 2,3-dicyanofumarate, did not give a reliable answer, because the catalysis of (*Z*)/(*E*) isomerization by thiadiazoline **26** could not be suppressed [38].

We face a similar situation in the reactions of **27** with (*E*)-**10** and (*Z*)-**10** (*Scheme 8*). The precursor **26** catalyzed the equilibration of (*Z*)-**10** and (*E*)-**10** stronger than **5A**. After the reaction with (*Z*)-**10** (1.7 equiv., $CDCl_3$, 40°, 10 h), the excess of **10** showed a (*E*)/(*Z*) ratio of 31:69, and a ratio of 80:20 was observed for *trans*/*cis*-thiolane, **29**/**31** (*Table 3*, *Entry 3*). According to previous experience, the disturbing thiadiazoline catalysis of (*Z*)/(*E*) isomerization of tetra-acceptor ethylenes can be diminished by reaction at higher temperature [7]. However, *Entry 4* with **26** and (*Z*)-**10** at 80° (C_6D_6, 9 min) provided similar results, as those observed at 40°. The corresponding reactions of **26** with (*E*)-**10** at 40° and 80° (*Table 3*, *Entries 1* and *5*) underlined the strong preference for the formation of *trans*-thiolane **29**, which is reminiscent of the reactions of **1A**.

The isolated thiolanes **29** and **31** revealed their *trans*- and *cis*-located CF_3 groups with $^5J(F,F) = 3.9$ and 15.0 Hz, respectively. The CF_3 group at C(4′) couples with C(5′):

Scheme 8

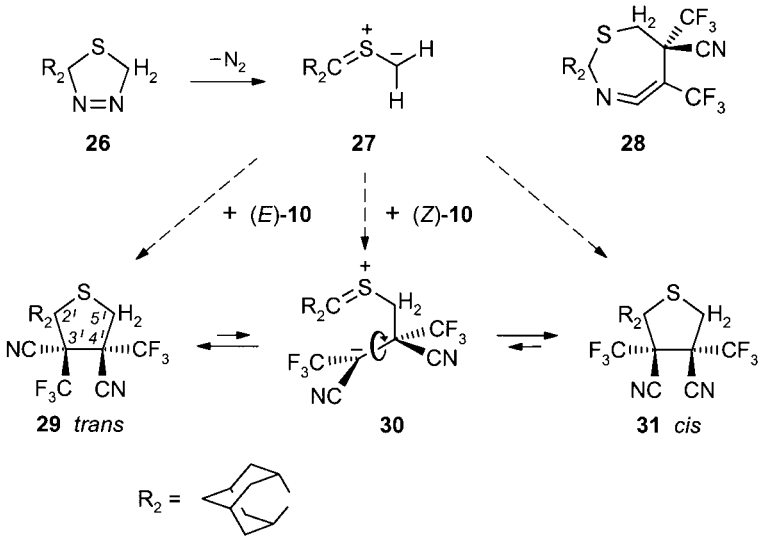


Table 3. *^{19}F-NMR Analysis of Reactions of Thiocarbonyl Ylide* **27** *with (*Z*)-***10*** and (*E*)-***10***

Entry	Equiv. of **10**	Reaction conditions (solvent, temp., time)	(*E*)/(*Z*) in excess **10**	Product ratio **29**/**31**	% **29** + **31**
1	1.1 (*E*)	THF, 40°, 8 h	[a])	*ca.* 100 : 0	94
2	1.1 (*Z*)	THF, 40°, 8 h	[a])	*ca.* 100 : 0	96
3	1.7 (*Z*)	$CDCl_3$, 42°, 10 h	31 : 69	80 : 20	[a])
4	1.8 (*Z*)	C_6D_6, 80°, 9 min	32 : 68	75 : 25	*ca.* 100
5	1.8 (*E*)	C_6D_6, 80°, 10 min	98 : 2	99 : 1	*ca.* 100

[a]) Not determined.

^3J(C,F) = 3.8 (**29**) and 3.6 Hz (**31**). As expected for chiral molecules, all ten C-atoms of the adamantane skeleton of **29** and **31** display different ^{13}C shifts.

The strong IR absorption of ketene imines near 2000 cm^{-1} should facilitate finding **28** in the reaction system. However, no such band was observed when the reaction of **26** with (*E*)-**10** in CCl_4 at 40° was interrupted after 1 h (*i.e.*, at less than $t_{1/2}$). We inferred from the size of the IR signal after admixing a small amount of **11** that a concentration of **28** $\geq$ 0.6% should have become IR-visible. In contrast to TCNE, **10** reacts rapidly with H_2O and MeOH, thus thwarting an interception experiment with **28**.

The failure to curb the catalyzed (*Z*)/(*E*) isomerization of **10** forbids drawing binding mechanistic conclusions from the nonstereospecificity of the cycloadditions of **27**. In one scenario, the cycloaddition step would proceed with retention of the configuration of **10**. Since zwitterion **30** is not passed, occurrence of ketene imine **28** is not required. Generally, (*E*)-ethylenic structures are more reactive dipolarophiles than their (*Z*)-isomers [3]. Competition experiments for (diphenylmethylidenesulfonio)-methanide confirmed this for a 'thiocarbonyl ylide' with a factor of 5.5 [39]. Therefore, it is no contradiction that the reactions of **26** with (*Z*)-**10** lead to more **29**(*trans*) in the thiolane product than would be expected from the (*E*) share observed in the excess of **10**.

A second series of events appears more likely to us. The cycloadditions of **27** take place *via transoid* and *cisoid* conformers of zwitterion **30**, as shown in *Scheme 7* for **1A**. Either $k_5 > k_7$ (definitions in *Scheme 5*) holds, *i.e.*, **29** and **31** are formed much faster than **28**, or k_{-7} is sufficiently high to prevent accumulation of ketene imine **28**. Both assumptions make sense because the steric screening of the reaction center in the adamantylidene compound **27** is lower than that in **1A**, and k_5 should profit from it.

A further feature of the adamantylidene series is the thermal equilibration of the thiolanes, **29**(*trans*) and **31**(*cis*). The conversion of **29** in CD_3CN at 110° reached a **29**/**31** ratio of 87 : 13 in 40 h and 71 : 29 in 100 h. ^{19}F-NMR Monitoring of the solution of **29** in PhCN at 139° allowed kinetic evaluation by the rate law of reversible first-order reactions. The equilibrium, **29**/**31** 68 : 32 is established with $(k_{29} + k_{31}) = 1.78 \cdot 10^{-4}$ [s^{-1}]. As illustrated in *Scheme 8*, the inversion probably takes place *via* zwitterion **30** by rotation. The temperature is much higher than for the cycloaddition process (40° and 80°) and, therefore, does not allow differentiation of the two scenarios designed above to explain the non-stereospecificity.

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Experimental Part

1. *General*. See [1]. All NMR spectra were recorded in $CDCl_3$, if not stated otherwise. ^{19}F-NMR Spectra, usually H-decoupled, with *Jeol FX90* (84 MHz) or *Varian XL100* (94 MHz); shifts are relative to Cl_3CF, *J* in Hz. The EI-MS spectra with 70 eV; intensities of isotope peaks are reported as, *e.g.*, ^{13}C % calc./% found.

2. *2,3-Bis(trifluoromethyl)fumaronitrile* ((*E*)-**10**) *and 2,3-Bis(trifluoromethyl)maleonitrile* ((*Z*)-**10**). Modifications of the original procedure [10]: ethyl trifluoroacetate (4 mol) was reduced with LAH to trifluoroacetaldehyde hydrate [40], which was converted to the trifluoroacetaldehyde cyanohydrin [41] (80%). The pyrolysis of the 1-cyano-2,2,2-trifluoroethyl chlorosulfite in the gas phase over refluxing S (salt bath 460°) [10] gave reproducible results; for details of apparatus, procedure, and separation of (*E*)-**10** and (*Z*)-**10** by prep. GC, see [35].

3. *Reaction of Thiocarbonyl Ylide* **1A** *with (*E*)-***10***.* 3.1. *Cycloaddition in CDCl$_3$. 1,1,3,3-Tetramethyl-8-thia-5,6-diazaspiro[3.4]oct-5-en-2-one* (**5A**) [42] (405 mg, 2.04 mmol) and (*E*)-**10** (526 mg, 2.46 mmol) in dry $CDCl_3$ (3 ml) were reacted under Ar at 40° for 11 h (6.5 half-lives of **5A**). ^{1}H-NMR analysis with *as*-tetrachloroethane (4.28 ppm) as weight standard indicated ketene imine **11** (68%), thiolane **12** (26%), and lactam **17** (4%). After removal of solvent and excess **10**, the residue was dissolved in CS_2 (4 ml, distilled from P_4O_{10}) under Ar (**17** was filtered), and **11** (343 mg, 43%, purity 97%) crystallized in 15 h at −18°. Recrystallization from CS_2 at −78° afforded the pale-yellow, anal. pure **11** (298 mg, 38%). The mother liquor furnished the thiolane **12** as colorless crystals from pentane at −78°.

3.2. *Initial Product Ratios in Various Solvents.* Some **11** isomerized to **12** during the thermolysis of **5A** at 40°. Even at 25°, the conversion **11** → **12** in $CDCl_3$ reached 11% after 4 d and 18% after 8 d. In NMR-tube experiments, the ratio **11**/**12** was determined after partial decomposition of **5A** and the initial ratio $(\mathbf{11})_o/(\mathbf{12})_o$ was approximated. The reaction of **5A** with (*E*)-**10** in $CDCl_3$ at 40° afforded **11**/**12** 79:21 (after 40 min), 76:24 (6 h), 74:26 (9 h), and 72:28 (11 h); an initial ratio of 81:19 was estimated. In C_6D_6 ratios of 84:16 (40 min), 81:19 (6 h), 78:22 (18 h) were measured, and 85:15 was extrapolated to zero time. Further initial ratios **11**/**12**: 70:30 in CS_2, 84:16 in (D_8)THF. For the signals of the ^{1}H-NMR analysis, see *Sect. 7* and *Table 1*.

3.3. *1,1,3,3-Tetramethyl-2-oxo-7,8-bis(trifluoromethyl)-5-thia-10-azaspiro[3.6]deca-8,9-diene-7-carbonitrile* (**11**). M.p. 87–88°. The pale-yellow needles are sensitive to moisture, but can be briefly handled in open air for weighing and the usual operations. The substance was stored under dry Ar in the deep-freeze. IR (between NaCl plates): 789*m*, 751*m* (CF_3 *sym*-deform. vibr. [43]), 1031*m*, 1081*s*; 1138*s*, 1161*s*, 1206*s*, 1255*s*, 1268*s*, 1290*s* (C−F), 1465*s*; 1784v*s*, 1795v*s* (C=O), 2007v*s*, 2031*s* (C=C=N), 2250v*w* (C≡N). IR (C_6H_6): 1136*s*, 1270v*s*, 1251*s* (C−F), 1791*s* (C=O), 2008*s* (sh), 2030*m* (C=C=N). ^{1}H-NMR ($CDCl_3$, 80 MHz): 1.27, 1.35, 1.41, 1.43 (4*s*, 4 Me); 2.83, 3.41 (*AB*, J_{gem} = 15.2, CH_2(6)). ^{1}H-NMR (C_6D_6, 80 MHz): 0.86, 0.96, 0.99, 1.05 (4*s*, 4 Me); 2.27, 2.67 (*AB*, J_{gem} = 15.0, *B* part broadened by H,F coupling, CH_2(6)). ^{13}C-NMR (20.2 MHz): 21.1 (*q*, 2 Me); 21.9, 23.9 (2*q*, 2 Me); 36.8 (*t*, C(6)); 43.9 (*q*, ^2J(C,F) = 32, C(7)); 63.5 (*q*, ^2J(C,F) = 34, C(8)); 66.1, 69.4 (2*s*, C(1), C(3)); 85.2 (*q*, ^5J(C,F) = 2, C(4)); 112.3 (br. *s*, C≡N); 122.0 (*q*, ^1J(C,F) = 270, CF_3); 122.8 (*q*, ^1J(C,F) = 285, CF_3); 188.9 (*q*, ^3J(C,F) = 3, C(9)); 214.3 (*s*, C=O). ^{19}F-NMR (84.3 MHz) at 50°: −56.3 (*q*, ^5J(F,F) = 4.4); −73.6 (br. *s*); ratio of signal heights (−73.6/−56.3) is 0.09 at 50° and rises, with lowering the temp., to 0.13 at 25°, 0.71 at −30° and −60°. ^{19}F-NMR (−60°): −55.9 (*q*, ^5J(F,F) = 4.2); −73.1 (*q*, ^5J(F,F) ≈ 4.0). MS (30°): 384 (3, $M^{+\bullet}$), 356 (3), 314 (27, $[M - C_4H_6O]^+$), 246 (16), 218 (7), 95 (8), 86 (14), 70 (100, $C_4H_6O^+$), 69 (19, CF_3^+). Anal. calc. for $C_{15}H_{14}F_6N_2OS$ (384.34): C 46.87, H 3.67, N 7.29; found: C 46.74, H 3.70, N 7.34.

3.4. *1,1,3,3-Tetramethyl-2-oxo-*trans*-7,8-bis(trifluoromethyl)-5-thiaspiro[3.4]octane-7,8-dicarbonitrile* (**12**). M.p. 78–80°. IR: 711*m*, 1013*w*; 1164*m*, 1196v*s*, 1225v*s*, 1266*m* (C−F); 1476*w*, 1790*s* (C=O), 2250 (C≡N, just visible). ^{1}H-NMR (80 MHz): 1.54, 1.57 (2*s*, 2 Me); 1.65 (*q*, ^6J(H,F) = 2.8, Me); 1.73 (br. *s*, Me); 3.48, 3.64 (*AB*, J_{gem} = 11.8, *A* part broadened by H,F coupling, CH_2(6)). ^{1}H-NMR (C_6D_6): 1.22, 1.33 (2*s*, 2 Me): 1.41 (*q*, *J*(H,F) = 2.8, Me); 1.48 (br. *s*, *q* not resolved, Me); 2.29, 2.79 (*AB*, J_{gem} = 12.1, *A* branch: 2 partially resolved *q*, CH_2(6)). ^{13}C-NMR (20.2 MHz): 23.02, 23.05 (on H-decoupling 2 *q*, ^5J(C,F) = 4.2, 2 Me); 26.4 (*q*, 2 Me); 34.5 (*t*, C(6)); 59.1, 61.5 (2*q*, ^2J(C,F) = 31 resp. 32, C(7), C(8)); 69.4, 69.5 (2*s*, C(1), C(3)); 72.7 (*s*, C(4)); 111.0 (*q*, ^3J(C,F) = 2.5, CN); 113.3 (br. *s*, CN); 121.4, 121.6 (2*q*, ^1J(C,F) = 287, 2 CF_3); 214.9 (*s*, C=O). ^{19}F-NMR

(84.3 MHz): −54.2 (*q*, outer lines unresolved, ^5J(F,F) = 7.9, CF_3); −65.0 (*q*, ^5J(F,F) = 7.9, CF_3). MS (20 eV, 30°): 384 (0.09, $M^{+\bullet}$), 314 (10, $[M-$dimethylketene$]^+$, $C_{11}H_8F_6N_2S^+$, ^{13}C 1.23/1.36, $^{13}C_2+{}^{34}$S 0.52/0.44), 287 (2.5, $[314-HCN]^+$), 218 (13, $[314-HCN-CF_3]^+$, $C_9H_7F_3NS$, ^{13}C 1.3/1.7, $^{13}C_2+{}^{34}$S 0.65/0.75, cyano-isopropyliotrifluoromethylthiophene), 178 (4), 161 (2), 86 (3), 70 (100, $C_4H_6O^+$, ^{13}C 4.5/4.8, dimethylketene$^+$), 69 (6). Anal. calc. for $C_{15}H_{14}F_6N_2OS$ (384.34): C 46.87, H 3.67, N 7.29; found: C 47.18, H 3.91, N 7.21.

4. *1,1,3,3-Tetramethyl-2,9-dioxo-7,8-bis(trifluoromethyl)-5-thia-10-azaspiro[3.6]decane-7-carbonitrile* (**17**). *a*) When ketene imine **11** (1.2 mmol) in THF (5 ml) was treated with H_2O (0.2 ml), an exothermic reaction set in. After evaporation of the solvent, the ^{1}H-NMR spectrum showed two br. NH bands at 6.6 and 6.9 ppm in a 4:1 ratio, corresponding to diastereoisomers **17a** and **17b**, resp. Fractional crystallization from MeOH afforded pure **17a** (67%). M.p. 213–214°. IR: 701*m*, 904*m*, 1064*m*; 1132*s*, 1190*s*, 1207*s*, 1248*s*, 1271*s* (C–F); 1339*m*, 1391*m*; 1695*vs* (amide I); 1786*s* (C=O), 3310 (br., N–H). ^{1}H-NMR (80 MHz): 1.33 (*s*, Me); 1.40 (*s*, 2 Me); 1.51 (*s*, Me); 3.27, 3.38 (*AB*, J_{gem} = 15.3, CH_2(6)); 3.98 (*q*, ^3J(H,F) = 7.0, H–C(8)); 6.55 (br. *s*, NH; disappears with D_2O). ^{19}F-NMR (85.2 MHz): −62.5 (*qq*, 6 lines recorded, F,F and H,F coupling, CF_3 at C(8)); −68.2 (*q*, J(F,F) = 9.2, CF_3 at C(7)). ^{19}F-NMR of isomer **17b**: −61.9 (*m*, CF_3); −67.3 (*q*, J(F,F) = 8.5, CF_3). MS (30°): 402 (0.3, $M^{+\bullet}$), 387 (0.8, $[M-Me]^+$, ^{13}C 0.12/0.13), 334 (13, $[M-C_4H_6N]^+$, $C_{11}H_{10}F_6NO_2S^+$; HR: calc. 334.0328; found 334.0353), 332 (28, $[M-C_4H_6O]^+$), 312 (1.3, $[332-HF]^+$), 224 (100), 174 (5), 127 (4), 70 (15, $C_4H_6O^+$), 69 (2 peaks, 37.0 + 4.8, $C_4H_7N^+$ and CF_3^+), 68 (5, $C_4H_6N^+$). Anal. calc. for $C_{15}H_{16}F_6N_2O_2S$ (402.36): C 44.77, H 4.01, N 6.96; found: C 45.07, H 4.11, N 6.76.

b) Attempts to separate the mixture of **11** and **12** (*Sect. 3.1*) by TLC on silica gel failed, but **11** was converted to lactam **17a**/**17b** 4:1, whereas **12** remained unchanged.

4.3. *Equilibration of Lactams* **17a** *and* **17b**. Triethylenediamine (8.9 mg) was added to a soln. of **17a** (22.2 mg) in $CDCl_3$ (0.6 ml) in an NMR tube, and the isomerization was monitored by ^{19}F-NMR at 25°: **17a**/**17b** 69:31 (after 3 h), 30:70 (22 h), 17:83 (78 h).

5. *9-Methoxy-1,1,3,3-tetramethyl-2-oxo-7,8-bis(trifluoromethyl)-5-thia-10-azaspiro[3.6]dec-9-ene-7-carbonitrile* (**18**). 5.1 *From* **11** *with MeOH*. Ketene imine **11** (1.50 mmol) in dry $CDCl_3$ (3 ml) at 0° was stirred under Ar, and MeOH (1 ml) was dropwise added. After 30 min, the solvent was removed, and the oily residue was subjected to ^{1}H-NMR analysis with *sym*-tetrachloroethane as weight standard. The two *q* at 4.55 and 4.79 for H–C(8) indicated 75% of the diastereoisomers **18a** and **18b** in a ratio of 55:45. The separation by PLC (SiO_2; Et_2O/pentane 2:8, 2 ×) failed. From MeOH, at −26° colorless crystals were obtained. M.p. 80–90° (**18a**/**18b** 45:55). IR: 700*m*, 718*m*, 920*m* (br.), 981*m*, 1014*m*, 1033*m*; 1137*s*, 1168*s*, 1184*s*, 1207*s*, 1255*s*, 1279*s*, 1297*s* (C–F); 1685*s* (C=N), 1784 (C=O). ^{1}H-NMR (80 MHz) of **18a**: 1.05, 1.29, 1.38, 1.43 (4*s*, 4 Me); 2.92, 3.35 (*AB*, J_{gem} = 15.0, CH_2(6)); 3.71 (s, MeO); 4.83 (*q*, ^3J(H,F) = 8.0, H–C(8)). ^{1}H-NMR of **18b**: 1.07, 1.30, 1.33, 1.40 (4s, 4 Me); 3.02, 3.49 (*AB*, J_{gem} = 16.0, signals broadened by H,F-coupling, CH_2(6)); 3.81 (*s*, MeO); 4.58 (*q*, ^3J(H,F) = 8.0, H–C(8)). MS (35°): 416 (0.3, $M^{+\bullet}$), 401 (2.1, $[M-Me]^+$; HR: calc. 401.0755, found 401.0796), 346 (100, $[M-C_4H_6O]^+$, ^{13}C 13.3/14.3, $^{13}C_2+{}^{34}$S 5.4/5.1), 331 (18, $[346-Me]^+$, ^{13}C 2.2/2.4), 278 (70, $C_{11}H_5SNF_5^+$; HR: calc. 278.0062, found 278.0054), 210 (11), 70 (3, $C_4H_6O^+$), 69 (8, CF_3^+ and/or $C_4H_5O^+$), 68 (18, $C_4H_6N^+$). Anal. calc. for $C_{16}H_{18}F_6N_2O_2S$ (416.39): C 46.15, H 4.36, N 6.73; found: C 46.50, H 4.47, N 6.75.

5.2. *From* **17a** *and* CH_2N_2. **17a** (0.50 mmol) was treated with CH_2N_2 (0.80M) in THF (2 ml) for 14 h at 20°. Evaporation and PLC (petroleum ether/Et_2O 4:1) provided a colorless oil (172 mg, 83%), which contained **18a**/**18b** 28:72. Crystals from pentane at −78°, m.p. 66–72°; the ^{1}H-NMR spectra showed the identity.

6. *1,1,3,3-Tetramethyl-2-oxo-9-(phenylamino)-7,8-bis(trifluoromethyl)-5-thia-10-azaspiro[3.6]dec-9-ene-7-carbonitrile* (**19**). The reaction of **11** (0.83 mmol) with $PhNH_2$ (1.0 mmol) in $CDCl_3$ (3 ml) under Ar was completed after 10 min (^{1}H-NMR). Colorless crystals (EtOH, −26°) contained **19a**/**19b** 2:1 (315 mg, 80%). M.p. 148–151°. IR ($CHCl_3$): 1130*s*, 1168*s* (br.), 1263*s*, 1340*m*, 1351*m* (C–F); 1598*s* (arom. ring vibr.); 1620–1660 (br.), tip at 1644 (C=N); 1784*s* (C=O); 3392*w*, 3487*m* (N–H). ^{1}H-NMR (80 MHz) of **19a**: 1.13, 1.17, 1.30, 1.52 (4s, 4 Me); 3.05, 3.29 (*AB*, J_{gem} = 14.6, CH_2(6)); 4.62 (*q*, J(H,F) = 9.0, H–C(8)); 6.52 (br., disappears with D_2O, NH); 6.55–7.42 (*m*, Ph). ^{1}H-NMR of **19b**: 0.75, 1.25, 1.30, 1.45 (4*s*, 4 Me); 3.36 (A_2, CH_2(6)); 4.03 (*q*, ^3J(H,F) = 7.0, H–C(8)). MS (30°): 477 (4.5, $M^{+\bullet}$, ^{13}C 1.0/1.1), 407 (100, $[M-C_4H_6O]^+$, ^{13}C 19/22, $^{13}C_2+{}^{34}$S 6.1/7.1), 392 (3, $[407-Me]^+$), 387 (3, $[407-HF]^+$), 339 (45), 321 (12), 320 (11), 299 (46), 286 (15), 217 (16), 84 (9), 77 (36, Ph^+), 70 (19, dimethylketene$^+$), 69 (20 + 5). Anal. calc. for $C_{21}H_{21}F_6N_3OS$ (477.47): C 52.82, H 4.43, N 8.80; found: C 52.45, H 4.60, N 8.95.

7. *Isomerization of Ketene Imine* **11** *to Thiolane* **12**. *Kinetics.* The ^{1}H-NMR monitoring of the ring contraction was based in $CDCl_3$ and C_6D_6 on the 4 Me signals of **12**, which appear at higher frequencies than those of **11**, without overlap. In the other solvents given in *Table 1*, the *AB* spectra of CH_2(6) were integrated, usually the right branch of **11** and the left branch of **12** being suitable. The ketene imine **11** (50–100 mg) was weighed into the NMR tube, and, after addition of the dry solvent (0.5 ml) and flushing with Ar, the tube was

sealed and immersed in a thermostat at $60.0 \pm 0.2°$. In regular intervals, the NMR tube was cooled to 25°, and the integral curve was recorded in the 80-MHz spectrometer. To be independent of field stability, percents of **12** in (**11** + **12**) were determined. The least-squares evaluation of the rate constants comprised 10–20 concentration measurements up to 73–88% reaction. The quality of the linear first-order plots was shown by correlation coefficients $r = 0.9944 - 0.9989$.

For the measurement of the more rapid reactions in CD_3CN and PhCN ($t_{1/2}$ 7.1 and 23.2 min, resp., at 60°), the NMR tube remained in the probe of the instrument, which was adjusted to 60° by the ethyleneglycol thermometer. A higher number of concentration measurements (> 50) helped to overcome the deviations of the single one. After 8–10 half-lives, the tubes were opened, and *as*-tetrachloroethane was added as weight standard; the yields of **12** were 87–97%.

8. *Competition of (*E*)-***10*** and TCNE for Thiocarbonyl Ylide* **1A**. Experiments with 'thiobenzophenone *S*-methylide' had shown that TCNE is 19 times more reactive than (*E*)-**10** [39]. Therefore, a higher concentration of (*E*)-**10** (409.5 mg, 1931 μmol) was competing with TCNE (28.34 mg, 221 μmol) in C_6D_6 (2 ml) for **1A**, which was generated from **5A** (45.9 mg, 231 μmol) in a sealed ampoule at 40° in 8 h. ^{1}H-NMR Analysis with standard indicated **6** (86.4 μmol) and **11** + **12** (83.0 μmol); **11**/**12** 77:23. Evaluation with *Eqn. 1* from [39] gave $\kappa = 11.2$.

9. *Stereochemistry of Ring Contraction of* **11**. The conversion of **11** took place in sealed NMR tubes in CD_3CN and C_6D_6 at 60°. The ^{19}F-NMR signals at −64.7 (**12**) and −65.6 (**25**) were suitable for analysis in CD_3CN (−67.0 and −66.6 in C_6D_6). One of the middle lines of the *q* of **25** in the H-decoupled and expanded spectrum was compared with the corresponding line in the ^{13}C-satellite of **12**. The integral ratio indicated 1.8% of **25** in the thiolane mixture of the experiment in CD_3CN (1.9% in C_6D_6). After isomerization of **11** in (D_{12})cyclohexane at 96°, one of the inner lines of the *q* at −60.0 (**25**) and one of the outer lines of the *q* at −67.3 (**12**) were integrated: **12**/**25** 92.5:7.5.

10. *Catalysis of (*Z*)/(*E*) Isomerization of* **10**. Since the equilibrium is on the side of (*E*)-**10** ((*E*)/(*Z*) *ca.* 95:5), (*Z*)-**10** is suitable for investigating the catalyzed isomerization (*Table 2*). To avoid adventitious base catalysis, the glassware (including NMR tubes) were carefully cleaned and acid-rinsed. Nevertheless, the reproducibility was moderate.

10.1. *Thermostability of (*Z*)-***10***.* A sample of (*Z*)-**10**, purified by GC, in C_6D_6, showed the ^{19}F-NMR *s* at 59.2 ppm. An admixture of 0.55% of (*E*)-**10** was analyzed by comparing the integral of its *s* at −62.3 with that of the ^{13}C-satellites ($A_3A'_3X$ spectrum at −60.7 ppm) of (*Z*)-**10**. After heating at 60° for 22 h, the (*Z*)/(*E*) ratio was virtually unchanged.

10.2. *Cyclic Azo Compounds as Catalysts.* The pseudo-first-order reactions were evaluated by *Eqn. 3* for reversible systems:

$$kt = \frac{A_o - A_e}{A_o} \ln \frac{A_o - A_e}{A_t - A_e} \qquad (3)$$

A_o is % (*Z*) in $((Z)+(E))_o$, A_e is % (*Z*) at equilibrium (4.0 in C_6D_6 [35]), A_t the time-dependent (*Z*)-content. Example: (*Z*)-**10** (60.8 mg, 284 μmol, 3.1% (*E*)-content) and dihydropyrazol **21** (37.4 mg, 124 μmol) [44] in C_6D_6 (0.5 ml) were heated in a sealed NMR tube at 40°. Six ratios $(Z)_t/(E)_t$ were determined by ^{19}F-NMR from 0–710 h. Least-squares evaluation gave a straight line with $r = 0.999$ and the pseudo-first-order rate constant $(k_{(Z)} + k_{(E)}) = 1.0 \cdot 10^{-7}$ [s^{-1}]. Analogous experiments were carried out with **22** [45] and **23** [46].

10.3. *Dihydrothiadiazole* **5A** *as Catalyst. a*) *Entry 1, Table 2:* The reaction of **5A** (170 μmol) and (*Z*)-**10** (284 μmol) in C_6D_6 (0.5 ml) at $40 \pm 1°$ was monitored by ^{19}F-NMR. Razor-sharp signals gave ((*Z*)-**10**)/((*E*)-**10**), and for '% Reaction' in the *Figure* the sum (**11** + **12** + **25**) was compared with ((*Z*)-**10** + (*E*)-**10**). After 8.2 h, the tube was cooled and opened (N_2 pressure). (1,1-Dichloro-2,2,2-trifluoroethyl)benzene was added as weight standard (*s*, −77.9), and the yields of **11** (72%), **12** (11%), and **25** (5%) were determined.

b) It was considered that not **5A**, but the 1,3-dipole **1A** was the isomerization catalyst. In that case, the presence of TCNE, which captures **1A** by a factor of 11 faster than **10** (*Sect. 8*), should diminish the share of isomerization (*Z*)-**10** → (*E*)-**10**. TCNE (354 μmol), (*Z*)-**10** (339 μmol, > 99.5% pure), and **5A** (154 μmol) in C_6D_6 (0.9 ml) were reacted at 40°. After 260 (470) min, ^{19}F-NMR analysis indicated (*Z*)-**10**/(*E*)-**10** 94:6 (91:9). The yield of **6** was 67% after 470 min, as analyzed by ^{1}H-NMR with *as*-tetrachloroethane as standard.

11. *Steric Course of Cycloadditions of* **1A** *with* **10**. ^{19}F-NMR Parameters for analysis in C_6D_6 ((D_{12})cyclohexane): −73.4 (−74.2) for **11**; −56.8, −67.0 (−67.3) for **12**; −60.0, −66.6 (−60.4, −67.1) for **25**; −59.2 (−59.9) for (*Z*)-**10**, −62.6 (−63.0) for (*E*)-**10**. All experiments of *Table 2* were carried out in sealed NMR tubes to avoid loss of **10**; both isomers have b.p. *ca.* 100°. Only *Entries 1* and *2* furnished initial product ratios, without isomerization **11** → **12**. The share of **25** (*cis*) in **12** + **25** appears to increase in the experiments at 80° and 105°

despite the now opulent ring contraction of **11**. Solvent in *Entries 6* and *7* is the 0.0076M H_2SO_4 in $CDCl_3$ previously applied [7].

12. *1,1,3,3-Tetramethyl-2-oxo*-cis-*7,8-bis(trifluoromethyl)-2-thiaspiro[3.4]octane-7,8-dicarbonitrile* (**25**, enriched). 12.1. *Entry 8* of *Table 2:* (*Z*)-**10** (4.37 mmol) in heptane (5 ml) was heated in a 95° bath; the soln. of **5A** (3.71 mmol) in heptane (4 ml) was added portionwise within 3 min. After 5 min at 95° and cooling, the soln. was reacted with H_2O (0.5 ml) in acetone (10 ml) for 30 min, concentrated, and **17** was filtered. Distillation of the mother liquor at 90°(bath)/0.4 Torr afforded a colorless oil (330 mg), which was filtered with CH_2Cl_2 over silica gel. ^{19}F-NMR indicated that the oily product consisted of **12** and **25** (64:36). GC (*Varian 3700* instrument) on *Carbowax* in a quartz capillary (25 m) separated **12** and **25** into discrete peaks.

12.2. *Data of* **25** (+**12**). The NMR parameters of **25** were obtained by subtraction. The ^{1}H-NMR *s* at 3.59 ppm belongs to CH_2(6) of **25** and rises within the *AB* spectrum of CH_2(6) of **12**. ^{19}F-NMR (94.2 MHz, $CDCl_3$): −65.14 (*q*, ^5J(F,F) = 14.9, CF_3−C(7)); −58.6 (*qq*, ^5J(F,F) = 15.0, ^6J(H,F) = 2.5, CF_3−C(8)). ^{19}F-NMR ((D_{12})cyclohexane): −67.1 (*q*, ^5J(F,F) = 14.9); −60.4 (*qq*, ^5J(F,F) = 14.9, ^6J(H,F) = 2.4). ^{19}F-NMR (CD_3CN): −65.6 (*q*, ^5J(F,F) = 15.2); −58.7 (*qq*, ^5J(F,F) = 15.3, ^6J(F,H) = 2.4). Anal. calc. for $C_{15}H_{14}F_6N_2OS$ (384.34): C 46.87, H 3.67, N 7.29; found: C 47.22, H 3.82, N 7.14.

13. *Reactions of (Adamantylidenesulfonio)methanide* (**27**) *with* **10**. 13.1. trans-*3′,4′-Bis(trifluoromethyl)-spiro[adamantane-2,2′-thiolane]-3′,4′-dicarbonitrile* (**29**; *Table 3*, *Entry 1*). 2′,5′-Dihydrospiro[adamantane-2,2′-[1,3,4]thiadiazole] (**26**, 2.0 mmol) [47] and (*E*)-**10** (2.2 mmol) in abs. THF (4 ml) were stirred at 40° for 8 h. After evaporation, ^{1}H-NMR analysis ($CDCl_3$) with *sym*-tetrachloroethane indicated 94% of **29**, which crystallized from EtOH. M.p. 120–121°. IR: 712*m*, 733*m* (*sym*. deform. vibr.), 1168*m*, 1194v*s*, 1208*s*, 1236*s* (C−F); 1454*m*, 2250v*w* (C≡N). ^{1}H-NMR (400 MHz): 1.72–2.57 (*m*, 12 H); 2.75 (*d* of *oct.*, J_{gem} = 13.4, 1 H); 2.88 (*d* of *oct.*, J_{gem} = 14.3, 1 H); 3.40, 3.51 (*AB*, *J* = 13.1, CH_2(5′)). ^{13}C-NMR (100.6 MHz, DEPT): CH of adamantane: 25.7, 26.1 (C(5), C(7)); 35.2 (br. by C,F coupling, C(1) or C(3)); 35.6 (*q*, *J*(C,F) = 1.5, C(3) or C(1)); CH_2 of adamantane: 32.9 (*q*, *J*(C,F) = 1.1), 35.6 (*q*, *J*(C,F) = 1.5), 37.2, 38.3, 38.4; 33.2 (*q*, ^3J(C,F) = 3.8, C(5′)); 61.9, 62.4 (2*q*, ^2J(C,F) = 29.4 resp. 27.5, C(3′), C(4′)); 73.8 (C(2)); 112.6, 113.9 (2*q*, ^3J(C,F) = 1.9, 2 CN); 121.8, 122.5 (2*q*, ^1J(C,F) = 287.3 resp. 290.0, 2 CF_3). ^{19}F-NMR ($CDCl_3$): −57.7 (br. *s*, CF_3); −65.6 (*q*, ^5J(F,F) = 4.3, CF_3). ^{19}F-NMR (C_6D_6): −59.4 (br. *s*); −67.2 (*q*, ^5J(F,F) = 3.9). ^{19}F-NMR (CD_3CN at 21°): −58 to −60 (flat); −67.0 (*q*, ^5J(F,F) = 2.9). ^{19}F-NMR (CD_3CN at 100°): −58.6 (slightly br. *s* without *q* structure); −66.6 (*q*, ^5J(F,F) = 4.1); the reason for the coalescence phenomenon will be studied further. MS (50°): 394 (100, $M^{+\bullet}$), 367 (4, $[M - HCN]^+$), 325 (33, $[M - CF_3]^+$), 273 (36, $[M - 2\,CN]^+$), 241 (18, $[M - CF_3(CN)CCH_2S]^+$, $C_{13}H_{14}F_3N^+$), 191 (17), 180 (88, $C_{10}H_{14}SCH_2^+$, **27**$^+$ or corresponding thiirane$^+$), 166 (19, $C_{10}H_{14}S^+$, adamantanethione$^+$), 133 (19, $C_{10}H_{13}^+$), 121 (87), 108 (29), 95 (76), 93 (50), 91 (37), 79 (71), 69 (57, CF_3^+), 67 (38), 55 (31), 41 (51). Anal. calc. for $C_{17}H_{16}F_6N_2S$ (394.38): C 51.77, H 4.09, N 7.10; found: C 51.89, H 4.15, N 7.16.

13.2. *Further Cycloadditions of* **27** *with (*Z*)-***10*** and (*E*)-***10***. In terms of efficiency, the catalysis of the isomerization (*Z*)-**10** ⇌ (*E*)-**10** by **26** exceeds that observed with **5A**.

a) *Table 3*, *Entry 3:* After the reaction of **26** with 1.7 equiv. of (*Z*)-**10** ($CDCl_3$, 40°, 10 h), ^{19}F-NMR analysis indicated (*E*)/(*Z*) 32:68 in the excess of **10** and a 80:20 ratio of **29**(*trans*) and **31**(*cis*). The analysis was based on the sharp *q* of **29** at −65.6 and the br. *q* at −63.9 for **31**, as well as the *s* of (*Z*)-**10** at −60.4 and that of (*E*)-**10** at −57.4.

b) The reaction of **26** with 1.4 equiv. of (*E*)-**10** in CCl_4 (0.8 ml) at 40° was interrupted after 1 h. The IR spectrum of the cooled sample (NaCl cuvette, 0.2 mm) did not exhibit a signal in the 2000-cm^{-1} range. Addition of 1 μmol of ketene imine **11** furnished a discernible peak. If ketene imine **28** would be present, it must be < 0.6%.

13.3. cis ⇌ trans *Equilibration of Thiolanes* **29** *and* **31**. *a*) *In CD_3CN at 110°*. *trans*-Thiolane **29** (0.19 mmol) in CD_3CN (0.6 ml) in a sealed NMR tube was immersed in a 110° bath. The ratio **29**/**31** was determined by integration of the ^{19}F-NMR signals at −67.0 (**29**) and −65.2 (**31**); **29**/**31** (time [h]): 87:13 (40), 71:29 (101), 70:30 (169). Comparison with (1,1-dichloro-2,2-difluoroethyl)benzene (−77.6 ppm) indicated 90% (**29** + **31**) after 169 h.

b) *In PhCN at 139°*. ^{19}F-NMR Monitoring of the *q* at −67.2 (**29**) and *q* at −65.4 (**31**) for 1438 min gave 7 ratios of **29**/**31**; the ratio 67.6:32.4 after 559 min was the optimal equilibrium value for the application of *Eqn. 3*, which led by linear regression to $k_{29} = 5.8 \cdot 10^{-5}$ [s^{-1}] and $k_{31} = 1.2 \cdot 10^{-4}$ [s^{-1}] with $r = 0.9993$.

13.4. cis-*3′,4′-Bis(trifluoromethyl)spiro[adamantane-2,2′-thiolane]-3′,4′-dicarbonitrile* (**31**). By heating of **29** (5.6 mmol) in abs. CH_3CN (10 ml) in a closed tube at 125° for 15 h, the equilibrium was approached. After workup with H_2O/Et_2O and filtration of the soln. in CH_2Cl_2 over silica gel, **29** (2.8 mmol) crystallized from MeOH, and the mother liquor was subjected to CC (silica gel; hexane/CH_2Cl_2 3:1). The last fraction (380 mg)

was pure **31**. M.p. 82–83.5° (MeOH). IR: 717*m*, 737*m* (sym. CF_3-deform.); 1153*s*, 1165*s*, 1188*s*, 1213*s*, 1238*s*, 1259*s* (C–F), 2250v*w* (C≡N). ^{1}H-NMR (80 MHz): 1.68–3.28 (*m*, 14 H); 3.45 (nearly A_2, CH_2(5′)). ^{13}C-NMR (90.6 MHz): CH and CH_2 of adamantane: 25.4, 25.6, 31.8 (br.), 33.2, 36.9, 37.0 (*q*, J(C,F) = 2.7), 37.7, 38.4, 38.8; 37.0 (*q*, ^3J(C,F) = 3.6, C(5′)); 60.8 (*q*, ^2J(C,F) = 28.0, (C(3′) or (C(4′)); 61.5 (*q*, ^2J(C,F) = 30.7, C(4′) or C(3′)); 113.7 (*q*, ^3J(C,F) = 1.7, CN); 114.6 (br. *s*, CN); 121.97, 122.02 (2*q*, ^1J(C,F) = 287.0 resp. 290.7, 2 CF_3). ^{19}F-NMR (94.1 MHz, C_6D_6): −58 to −59 (flat, CF_3); −65.7 (*q*, ^5J(F,F) = 15.0, CF_3). ^{19}F-NMR (CD_3CN, 21°): −58 to −59 (flat); −65.2 (*q*, ^5J(F,F) = 15.2). ^{19}F-NMR (CD_3CN, 100°): −57.9 (br. *q*) and −65.0 (*qd*; *q* on H-decoupl., ^5J(F,F) = 15.4). MS (80°): similar to **29**. Anal. calc. for $C_{17}H_{16}F_6N_2S$ (394.38): C 51.77, H 4.09, N 7.10; found: C 51.91, H 4.08, N 7.04.

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