'Thiobenzophenone *S*-Methylide' (= (Diphenylmethylidenesulfonio)methanide), and C,C Multiple Bonds: Cycloadditions and Dipolarophilic Reactivities[1])

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Dedicated to *Siegfried Hünig* on the occasion of his 80th birthday

Thiobenzophenone and diazomethane afford thiadiazoline **1** at $-78°$. By elimination of N_2 from **1** at $-45°$ ($t_{1/2}$ *ca.* 1 h), (diphenylmethylidenesulfonio)methanide (**2**), which cannot be isolated but is interceptible by dipolarophiles, is set free. The nucleophilic 1,3-dipole **2** undergoes cycloadditions with electrophilic C,C multiple bonds; the structures of 16 cycloadducts were elucidated. One-step and two-step cycloaddition pathways are discussed in the light of the steric course observed for (*E*)/(*Z*)-isomeric ethylene derivatives. Competition experiments with pairs of dipolarophiles at $-45°$ and HPLC analysis of the adducts provided relative rate constants of 26 dipolarophiles, involving 2 C≡C, 13 C=C, 9 C=S, and 2 N=N bonds. In accordance with *Sustmann*'s reactivity model of concerted cycloadditions, **2** shows the highest selectivity of all known 1,3-dipoles, *i.e.*, the largest spread of rate constants ($k_{rel} = 1$ for methyl propiolate and 33×10^6 for TCNE). As a consequence of low LU energies, thiones are very active dipolarophiles, and fluorene-9-thione ($k_{rel} = 79 \times 10^6$) stands at the top.

1. Introduction. – Thiobenzophenone (**3**) and diazomethane furnish 4,4,5,5-tetraphenyl-1,3-dithiolane (**4**) as a 2:1 product at 0°, as observed by two groups in 1930 and 1931 [2][3]. *Schönberg* and his school extended the reaction to many pairs of thiones and diazoalkanes, but the mechanistic pathway remained unclear [4]. The key to the mechanism was offered by the observation that **3** and CH_2N_2 react by a 1:1 stoichiometry at $-78°$ to produce 2,5-dihydro-2,2-diphenyl-1,3,4-thiadiazole (**1**) [5][6]. The latter loses N_2 at $-45°$ with a half-life of 56 min in THF and affords (diphenylmethylidenesulfonio)methanide (**2**) in a 1,3-dipolar cycloreversion. The methanide **2** is not isolable, but is easily intercepted *in situ* by suitable dipolarophiles; with a second equiv. of **3** in that role, the 1,3-dithiolane **4** is formed in 95% yield (*Scheme 1*).

The first-order rate constant k_1 for the conversion **1** → **2** increases faster with rising temperature than k_2, which refers to the cycloaddition of CH_2N_2 with **3**. At $-78°$, $k_2 > k_1$ is found, but the ratio switches to $k_2 \ll k_1$ at 0°, *i.e.*, the initial cycloaddition becomes rate-determining, and thiadiazoline **1** assumes the role of a transient intermediate. Thus, the '*Schönberg* reaction' consists of two 1,3-dipolar cycloadditions linked by a 1,3-dipolar cycloreversion (*Scheme 1*) [6].

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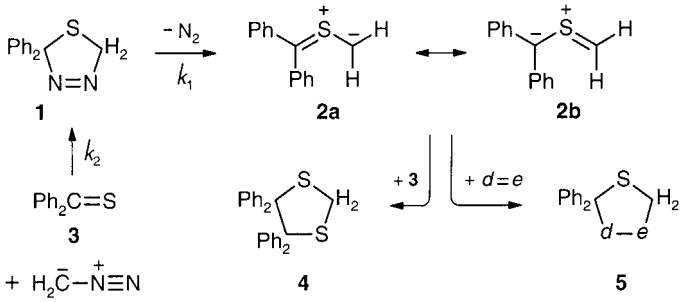
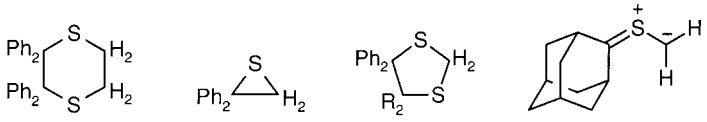
[1]) 1,3-Dipolar Cycloadditions: Part 121; Part 120: [1].

Scheme 1



The mechanistic insight opens the path to fruitful synthetic application. After the 1:1 reaction of CH_2N_2 with **3** at $-78°$, the solution of thiadiazoline **1** is allowed to warm up to $-45°$ in the presence of a second dipolarophile $d=e$, giving rise to a variety of cycloadducts of type **5**. In the absence of a suitable acceptor, **2** either dimerizes, furnishing the 1,4-dithiane **6**, or forms 2,2-diphenylthiirane (**7**) by electrocyclization.

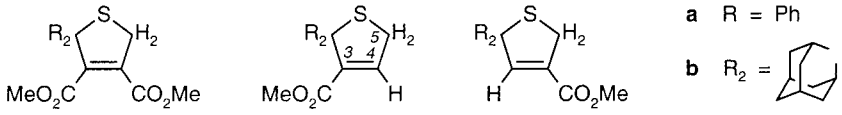


We recently published results of cycloadditions of **2** with aromatic and aliphatic thioketones, dithiocarboxylic esters, and trithiocarbonates [7]. Interestingly, only the 4,4,5,5-tetrasubstituted 1,3-dithiolanes **8** are formed, even though voluminous R groups would generate less hindrance in the second possible regioisomer. The cycloadditions of **2** with C=C and C≡C bonds and the phenomena of regiochemistry and steric course will be the subject of this report [5][8].

Diazomethane cycloadditions to aliphatic and alicyclic thioketones lead to 1,3,4-thiadiazolines that are stable at room temperature and eliminate N_2 at 40–80°. Among the thiocarbonyl ylides (for reviews, see [9]) formed, we singled out (adamantan-2-ylidenesulfonio)methanide (**9**) as a further model system; recent reports dealt with the scope of the additions of **9** to C=O, C=S [10], C≡C, and C=C bonds [11] as well as with structures and properties of the adducts.

The scope and limitations of a reagent are explored by rate measurements with a variety of partner molecules. The *in situ* generation of thiocarbonyl ylides prohibits direct kinetic studies of their cycloadditions. In the case of **2**, pairwise competition was used to establish the specific reactivity sequence of dipolarophiles *vs.* **2**, as described in this paper.

2. Results and Discussion. – 2.1. *C≡C Bonds as Dipolarophiles.* The addition of **2** to dimethyl acetylenedicarboxylate (DMAD) at $-45°$ furnished **10a** (71%). It was shown that DMAD does not enter the rate equation of N_2 evolution; the step preceding the cycloaddition, *i.e.*, the N_2 elimination **1** → **2** (k_1) is rate-determining [6].



10 **11** **12**

When **2** was liberated from **1** at $-45°$ in the presence of 7.5 equiv. of methyl propiolate in THF, only 19% of a crystalline cycloadduct was isolated along with 63% of 1,4-dithiane **6**. Thus, methyl propiolate is a weak dipolarophile, and the cycloaddition can hardly compete with the dimerization of the 1,3-dipole **2**.

The chemical shifts of the cycloadduct were compared with those of the thiolanes described in *Sect. 2.2* and those of the two regioisomers **11b** and **12b** obtained from **9** and methyl propiolate [11]. Whereas the ^{13}C chemical shifts slightly favored **12a**, $J = 2.9$ fits the vicinal 4,5-coupling in **11a** better than an allylic one in **12a**. The two-dimensional NMR analysis established the structure of the 3-carboxylate **11a**. NOESY showed the proximity of the MeO to both the vinylic H–C(4) and the *ortho*-H-atoms of Ph. A 2D-INADEQUATE experiment [12a] provided a $J(C(4), C(5)) = 38$, which agrees well with $J(C(2), C(3)) = 41$ observed for propylene [12b].

2.2. *C=C Bonds as Dipolarophiles.* In the standard procedure, the THF solution of **1** was prepared at $-78°$; after the addition of the dipolarophile, the solution was kept for 5 h (5.4 half-lives) in a $-45°$ bath and then allowed to reach room temperature. The small stationary concentration of **2** diminishes the chance of dimerization. The yields of isolated cycloadducts, given in *Table 1*, are not optimized; most experiments were performed only once.

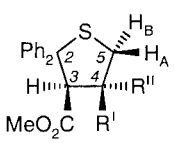
The cycloadduct, obtained with methyl acrylate, is the thiolane-3-carboxylate **13**. In the ^1H-NMR spectrum, H–C(3) appears as *dd* with $J = 7.2$ and 8.6 for *trans*- and *cis*-

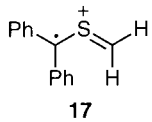
Table 1. *Cycloadditions of* **2** *with Acetylenic and Olefinic Dipolarophiles* (THF, $-45°$)

Dipolarophile	No.	Cycloadduct		Dimer **6**
		Yield [%]	M.p.	Yield [%]
Methyl propiolate	**11a**	19	101.5–102.5°	63
Dimethyl acetylenedicarboxylate	**10a**	71	140–142°	
Methyl acrylate	**13**	79	78.5–79.5°	
Dimethyl fumarate	**14**	80	146.5–148°	
Dimethyl maleate	**15**	65	120–122°	5
Tetramethyl ethylenetetracarboxylate	**16**	28	129–131°	33
Acrylonitrile	**23**	76	141–143°	
Fumaronitrile	**24**	91	198–200°	
Tetracyanoethylene	**25**	93	177–178.5°	
Maleic anhydride	**28**	96	126–128°	
N-Methylmaleimide	**29**	80	174–176°	
N-Phenylmaleimide	**30**	79	208–209°	
Dimethyl 2,3-dicyanofumarate	**38**	97	196–197°	
Dimethyl 2,3-dicyanomaleate	**39**	70[a)]	160.5–161.5°	
Diisopropyl 2,3-dicyanofumarate	**42**	62	147–149°	
2,3-Bis(trifluoromethyl)fumaronitrile	**43**	42	87–88°	

[a)] Equilibrium concentration

coupling, respectively; this feature is not compatible with the regioisomeric 4-carboxylate. Thus, the CH_2 group is the nucleophilic center in the 1,3-dipole **2**, as it was established for **9**.





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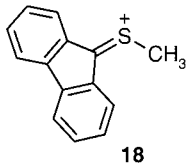

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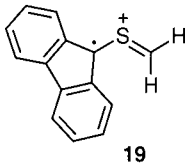

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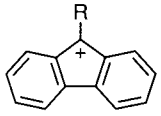
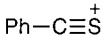
	R	R'	R''
13	H	H	H
14	H	H	CO_2Me
15	H	CO_2Me	H
16	CO_2Me	CO_2Me	CO_2Me



20 R = CH_3
21 R = H



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The reaction of **1** with 1.2 equiv. of dimethyl fumarate afforded 80% of **14**. The four ^1H signal groups of the saturated protons are resolved in the 400-MHz spectrum and allow the assignments with all coupling constants. The ^{13}C-NMR parameters of **13** and **14** reveal two different Ph groups as a consequence of chirality.

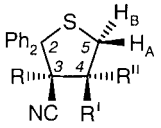
The mass spectrum of **14** (and the other thiolanes described here) disclose that the cycloaddition is reversed in the radical cation. The distonic radical ion **17** is an attractive structure for $\mathbf{2}^+$ (*m*/*z* 212, 27%), but also a thiirane formula is worth considering. The base peak is at *m*/*z* 210, probably the fluorenyl analogue **19**. The peak at *m*/*z* 211 occurs with 74% and might be the sulfonium ion **18**. The cyclization tendency of the benzhydryl cation is long known: *Schumann et al.* recognized the base peak in the MS of thiobenzophenone as 9-fluorenyl cation, with *m*/*z* 165 [13]. The radical cation $\mathbf{3}^+$ (*m*/*z* 198), the fluorenyl cation (**21**), and its 9-methyl derivative **20** (*m*/*z* 179) occur in the MS of **14** with 15, 17, and 26%, respectively. The peak at *m*/*z* 121 (11%) is a steady companion, probably **22**. The molecular formulae of the fragments were confirmed by high resolution (HR) and the intensities of ^{13}C and ^{34}S peaks; however, the structures are speculative.

The cycloaddition of **2** with dimethyl maleate furnished the *cis*-dicarboxylate **15** (65% isolated); ^1H-NMR analysis of the mother liquor did not show the *trans*-isomer **14**. As will be shown in *Sect. 2.4*, dimethyl maleate is 65 times less reactive than dimethyl fumarate *vs.* **2**. The lower dipolarophilic activity is revealed by the occurrence of 5% of dimer **6**.

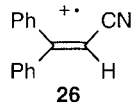
Even lower ranks tetramethyl ethylenetetracarboxylate, which in the reaction with **2** yielded 28% of thiolane **16** and 33% of dimer **6**. Here, the activating effect of the ester group is overcome by steric encumbrance: hindrance of coplanarity in the ground state of the tetraester reduces reactivity, and the twisted ester groups screen the approach of the 1,3-dipole.

This interpretation is confirmed by the rise of reactivity in the sequence acrylonitrile, fumaronitrile, and tetracyanoethylene (TCNE). Although yields are a fallacious criterion of reactivity, they increase in the above sequence (*Table 1*) and

reach 93% for the TCNE adduct **25**. Both of the hindrance effects discussed above are virtually absent in the nitrile series.



	R	R'	R''
23	H	H	H
24	H	H	CN
25	CN	CN	CN



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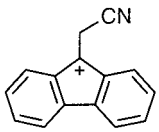

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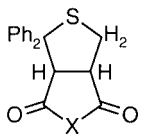


28 X = O
29 X = NMe
30 X = NPh

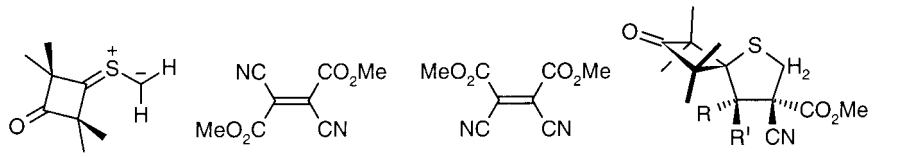
Structure **23** for the acrylonitrile adduct was established by NMR analysis of the ring protons with double resonance. The mass spectrum of **23** indicates that the cycloreversion gives rise to radical cation **17** (41%), and *m/z* 211 (**18**) is the base peak. According to HR-MS, two small peaks, *m/z* 205 (4%) and 204 (7%), are $C_{15}H_{11}N^+$ and $C_{15}H_{10}N^+$, corresponding to $[M - SCH_2CH_2]^+$ and $[M - SEt]^+$. These fragments, with the conceivable structures **26** and **27**, confirm the regiochemistry of **23**.

The fumaronitrile adduct **24** shows an *ABCX* spectrum of the four ring protons with a rather complex *X* part. This 400-MHz spectrum of higher order was elegantly solved by the iterative computer program DavinX [14], and the *Figure* (*Exper. Part*) displays a stunning agreement of observed and calculated absorptions. The comparison of the chemical shifts with those of **23** as well as the set of coupling constants allows an unequivocal assignment.

Maleic anhydride and maleimides are top dipolarophiles that produce good yields of cycloadducts **28**–**30** (*Table 1*). The reactions with dimethyl 2,3-dicyanofumarate and 2,3-dicyanomaleate demand special attention.

2.3. *Stereospecificity of Cycloadditions to* cis/trans-*Isomeric Dipolarophiles.* In concerted cycloadditions, the configuration of *cis*/*trans*-isomeric alkenes is retained. [(2,2,4,4-Tetramethyl-3-oxocyclobutan-1-ylidene)sulfonio]methanide (**31**) is a thiocarbonyl ylide with one highly hindered terminus. Its cycloaddition with dimethyl fumarate at 45° proceeds with > 99.97% retention, whereas dimethyl maleate provided the *cis*- and *trans*-cycloadducts in the ratio of 98.9/1.1 [15]. A greater loss of stereochemical integrity was observed for the reactions of **31** with dimethyl 2,3-dicyanofumarate (**32**) and dimethyl 2,3-dicyanomaleate (**33**): the *trans*- and *cis*-adducts, **34** and **35**, respectively, were obtained in the ratio 60 : 40 from **32** and 25 : 75 from **33** [16]. A two-step cycloaddition was assumed, and the zwitterionic nature of intermediate was deduced from interception experiments. When the reaction of **31** with TCNE was run in THF, which contained 2% (*v*/*v*) MeOH, a cyclic seven-membered lactim methyl ether was obtained [17]. In contrast, MeOH or H_2O did not interfere in the cycloaddition of **2** with TCNE.

Dimethyl 2,3-dicyanomaleate (**33**) was prepared from the easily available *trans*-isomer **32** [18] by irradiation in the presence of 1 equiv. of benzene-1,4-dicarbonitrile for 3 days [19]. This procedure, described by *Gotoh et al.*, requires the inconvenient separation of the photosensitizer. In our hands, the direct photoisomerization of **32** by



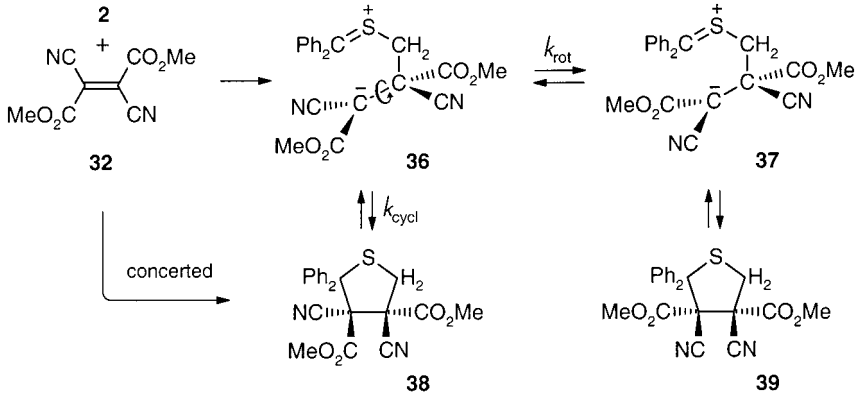
31 **32** **33** **34** R = CN, R' = CO_2Me; **35** R = CO_2Me, R' = CN

a high-pressure Hg arc in CH_2Cl_2 was efficient and furnished **32**/**33** in a ratio of 9:91 (for a preliminary report, see [20]).

The acceptor olefins **32** and **33** are base-sensitive. Even heterogeneous catalysis by KF suspended in $CDCl_3$ at room temperature promoted equilibration: **32**/**33** in a ratio of 88:12 was reached from either side in 3 days; the blank showed only 3% conversion of **33** to **32** under these conditions. In MeCN, however, the *cis*/*trans*-isomerization was much faster. The 1,3,4-thiadiazolines, the precursors of the thiocarbonyl ylides, also catalyze the *cis*/*trans*-isomerization **32** ⇌ **33**. The suppression of this catalysis was a prerequisite for studying the steric course of the above-mentioned cycloadditions of **31** with **32** and **33**; addition of acid minimized the isomerization, and 10 min at 80° were optimal [16].

Which of the two pathways (*Scheme 2*) will be used by the reaction of (diphenylmethylidenesulfonio)methanide (**2**) with the tetra-acceptor-substituted ethylene **32**? The steric encumbrance at the terminus of **2** is minor compared with that of **31**, but the diphenylmethylidene group offers excellent stabilization for the positive charge of zwitterion **36**/**37**. Since the cycloaddition of **2** with **32** was performed at −49° and that of **31** with **32** at +45–80°, the chance of a **1**-catalyzed isomerization of **32** to **33** occurring before the cycloaddition was strongly diminished.

Scheme 2



On stirring the solution of **1** with 1.1 equiv. of **32** in THF at −49° for 15 h, N_2 was evolved, and the suspended **32** slowly dissolved. The Et_2O-insoluble part of the reaction product contained the *trans*-thiolane **38** (97%) and the excess **32**. ^{1}H-NMR Analysis of

the mother liquor indicated 0.34% of *cis*-thiolane **39**, which would correspond to a stereospecificity of 99.7%.

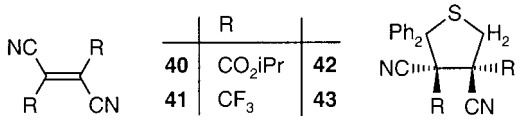
It is even doubted that **39** (0.34%) was formed *during* the cycloaddition. *cis* ⇌ *trans* Equilibration of the adducts **38** and **39** took place in refluxing MeCN, and **38**/**39** in a ratio of *ca.* 30:70 was reached from both sides, *i.e.*, a free-energy preference for the *cis*-adduct **39** by 1.4 kcal mol^{-1}. When the solution of pure *trans*-adduct **38** in THF was kept at 30° for 3 h, it contained 0.6% of **39**. Conceivably, the 0.34% of *cis*-thiolane **39** in the cycloaddition experiment described above is the product of subsequent isomerization during workup.

The zwitterions **36** and **37** are the intermediates of choice for the equilibration of cycloadducts **38**/**39**. Interestingly, **34** and **35**, *i.e.*, the adducts of **31**, are stable in refluxing MeCN. After heating **34** to 139° in PhCN for 7 d, some decomposition took place, but no isomerization was observed [15]. The *quasi*-benzhydryl cation in **36**/**37** is superior to the *quasi*-cyclobutyl cation that would be formed by subsequent ring opening of **34**/**35**.

As for the mechanism of the cycloaddition of **2** with **32**, there is no reason to postulate a two-step process *via* **36**/**37**. The assumption of a concerted pathway furnishing **38** and an isomerization of the cycloadduct *via* the zwitterion is not in conflict with the principle of microscopic reversibility. A two-step cycloaddition with a high ratio of k_{cycl}/k_{rot} for **36**/**37** is less probable, because a longer lifetime for the zwitterions **36**/**37** is expected than for those from **31** and **32** (for a discussion, see [21]).

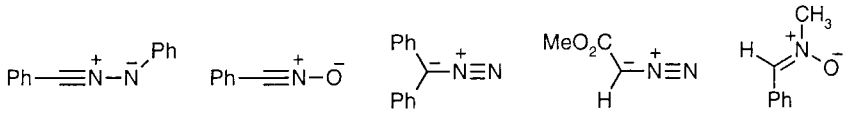
Reasons for the energetic preference ($\Delta\Delta G = 2.7$ kcal mol^{-1}) for the (*E*)-olefin **32** in the equilibrium **32** ⇌ **33** (88:12) are the dipole moment and steric hindrance of resonance in the (*Z*)-isomer **33**. Less obvious is the advantage of the *cis*-configuration in the corresponding cycloadducts **38**/**39** with a ratio of 30:70. According to the X-ray crystal-structure analysis [20], **39** assumes an envelope conformation with C(2) as the flap.

Diisopropyl 2,3-dicyanofumarate (**40**) and the corresponding maleate are less sensitive to base-catalyzed equilibration than the dimethyl esters **32**/**33** and were useful in elucidating the mechanism of the cycloadditions of **31** [16]. 2,3-Bis(trifluoromethyl)fumaronitrile (**41**) as dipolarophile reacts with **31** and other thiocarbonyl ylides by the two-step pathway and allows – uniquely – the isolation of intermediate cyclic seven-membered ketene imines [22]. However, **40** and **41** combined with **2** furnishing the thiolanes **42** and **43**, respectively. Both **40** and **41** were included in the measurements of k_{rel} (see *Sect. 2.4*).



2.4. *The Reactivity Scale of Dipolarophiles* vs. **2**. 2.4.1. *The Competition Method*. How does a reagent respond to structural variations of its reaction partner? Usually, a series of kinetic measurements with model substrates provides this information. However, when an unstable reagent is reacted *in situ*, conventional kinetic methods fail. The rapid-rate methodology is of help only in exceptional cases, *e.g.*, flash generation of a reagent. Generally applicable is the competition method for unveiling *relative*

reactivities. This approach has been utilized in our laboratory previously, *e.g.*, for the elaboration of dipolarophile activities *vs.* diphenylnitrilimine (**44**) [23] and benzonitrile *N*-oxide (**45**) [24].



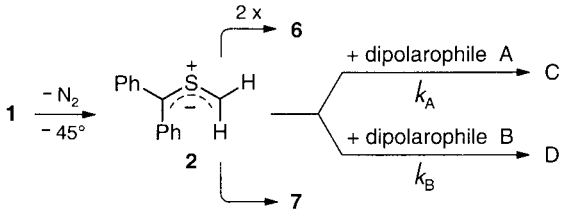
44 **45** **46** **47** **48**

Thiocarbonyl ylide **2** has a fleeting existence. As shown above, sufficiently reactive dipolarophiles intercept **2** and allow cycloadditions to be carried out on a preparative scale. A low stationary concentration of **2** at $-45°$, which is set free with $t_{1/2}$ of *ca.* 1 h, restricts the dimerization.

When two dipolarophiles in initial concentrations $[A]_0$ and $[B]_0$ compete for **2** (*Scheme 3*), the ratio of cycloadducts formed, $[C]_e$ and $[D]_e$, respectively, allows the evaluation of a competition constant κ by *Eqn. 1* [25]:

$$\kappa = \frac{k_A}{k_B} = \frac{\log [A]_0 - \log [A]_e}{\log [B]_0 - \log [B]_e} = \frac{\log [A]_0 - \log [[A]_0 - [C]_e]}{\log [B]_0 - \log [[B]_0 - [D]_e]} \quad (1)$$

Scheme 3



Since the concentrations of the cycloadducts are more conveniently determined than those of the unconsumed dipolarophiles, $[A]_e$ and $[B]_e$, the differences, $[A]_0 - [C]_e$ and $[B]_0 - [D]_e$, can be used instead. In contrast to conventional kinetic techniques, quantitative yields are not required, and a partial formation of **6** and **7** is of no harm, because the concentration of **2** does not appear in *Eqn. 1*. Prerequisites are irreversibility of the reaction and knowledge of the reaction order. Many rates of cycloadditions involving stable 1,3-dipoles were found to be of second order (for a review, see [26a]). It is not daring to assume the same for the additions of **2**.

The competition constant κ is the ratio of two second-order rate constants. A collection of κ values can be tied into a string of relative rate constants by the arbitrary assignment of the value 1 to a weak dipolarophile, methyl propiolate in our case. HPLC was used as analytical method, based on the calibration (and simulation) with artifical mixtures of pairs of pure cycloadducts. Competition constants $\geqslant 20$ are less reliable than smaller ones. We often searched for a third dipolarophile to fit in between two k_{rel} values that differed too much. After tentative tests with a pair of dipolarophiles, a higher concentration of the less reactive one made the analysis more dependable.

Cycloadditions of **2** in 30 competition experiments were performed with pairwise linking of 26 dipolarophiles (see *Table 5* in *Exper. Part.*) Multiplication of the κ values – upwards from below – furnishes the k_{rel} valued collected in *Table 2* (for a preliminary account, see [27]). Cycloadducts of thiones with **2**, which were recently described [6][7], were also included.

2.4.2. *Discussion of Dipolarophile Reactivity Spectrum*. 1,3-Dipoles (for definition, see [26b]) have the π-system of the allyl anion, but the nucleophilicity is complemented by the electrophilicity generated by the onium function in the middle. Nucleophilic and electrophilic character of 1,3-dipoles vary over a wide range.

Sustmann's reactivity model of concerted cycloadditions, generally accepted today, is based on the perturbation theoretical treatment of HO-LU interactions [28]. 1,3-Dipoles that are well-balanced in nucleophilic and electrophilic character (*Sustmann*'s type II) are described by U-shaped (more correct, parabolic) functions of dipolarophile reactivities; in these functions, $\log k_2$ is plotted *vs.* the electron density, *e.g.*, the ionization potential (*IP*) of the dipolarophilic π-bond. Common alkenes generate minimum rates.

1,3-Dipoles with nucleophilic predominance (*Sustmann*'s type I) command dipolarophilic activities depicted by deformed U functions, which – in the extreme – approach a straight line with the most electrophilic π-bond at the top. A kind of mirror image is observed for electrophilic predominance in the 1,3-dipole, and the most nucleophilic dipolarophiles display the highest cycloaddition rate (for a survey of examples, see [26a]).

In the mentioned deformation of the U function, one side becomes steeper, *i.e.*, large rate differences result from modest *IP* changes of dipolarophiles. The spread of $\log k_2$ defines the selectivity, which increases more as the 1,3-dipole approaches the nucleophilic or electrophilic extreme.

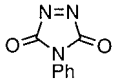
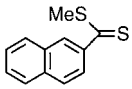
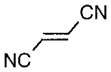
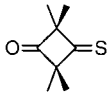
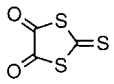
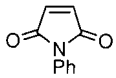
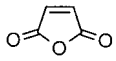
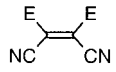
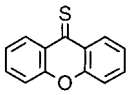
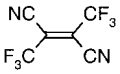
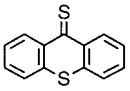
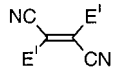
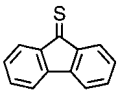
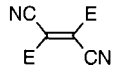
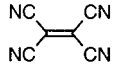
Thiocarbonyl ylides are allyl anions with a sulfonium center. Sulfur has nearly the same electronegativity as carbon (S 2.44, C 2.50 [29]), although $-S^+=$ has a higher value. With no N or O functions, thiocarbonyl ylides may well have the highest HO-LU energies among all known 1,3-dipoles.

The range of dipolarophilic reactivities (*Table 2*) confirms the pronounced nucleophilic character of **2**. Common and electron-rich alkenes are unreactive. The k_{rel} of acrylonitrile is increased 40-fold in fumaronitrile and by a factor of $1 \cdot 10^6$ in TCNE. The expectation for high selectivity of **2** is fulfilled: rate ratios for TCNE/acrylonitrile dramatically drop for the cycloadditions of diphenyldiazomethane (**46**) [30] and methyl diazoacetate (**47**) [31] (*Table 3*).

When comparing DMAD with methyl propiolate, a 340-fold increase of k_{rel} was observed *vs.* **2**, whereas **46** and *N*-benzylidenemethylamine *N*-oxide (**48**) – the latter a typical nucleophilic-electrophilic 1,3-dipole [32] – show smaller gains, 7.5 and 28-fold, respectively (*Table 3*). The fluctuations of the relative reactivities shown by C=C and C≡C bonds are puzzling, as exemplified by the rate ratios observed for dimethyl fumarate/DMAD: 16 for **2**, 3.6 for diphenylnitrilimine (**44**) [23], 2.0 for benzonitrile *N*-oxide (**45**) [24], 0.32 for **46** [30], 0.092 for **47** [31], and 0.013 for **48** [32].

Methyl acrylate reacts 9 times faster than acrylonitrile with **2**. This advantage of the MeOCO over the CN group as an activating substituent is also exhibited by dimethyl fumarate (k_{rel} 5400) and fumaronitrile (k_{rel} 1300). However, tetramethyl ethylene-

Table 2. *Cycloadditions of* **2** *in THF at* $-45°$: *Relative Rate Constants of Dipolarophiles, Established by Competition Experiments* ($E = CO_2Me$, $E' = CO_2{}^iPr$).

C≡C, C=C Bonds	k_{rel}	N=N Bonds	k_{rel}
	1[a])		$3.3 \cdot 10^5$
	32		$1.8 \cdot 10^7$
	40		
	82	C=S Bonds	
		$(PhS_2)C{=}S$	840
	280		$1.2 \cdot 10^3$
	337		
	$1.3 \cdot 10^3$		$1.3 \cdot 10^3$
	$5.4 \cdot 10^3$		$3.4 \cdot 10^4$
	$5.7 \cdot 10^4$	$(p\text{-}MeOC_6H_4)_2C{=}S$	$7.3 \cdot 10^4$
	$2.9 \cdot 10^5$	$Ph_2C{=}S$	$1.2 \cdot 10^6$
	$1.4 \cdot 10^6$		$1.8 \cdot 10^6$
	$1.7 \cdot 10^6$		$6.8 \cdot 10^6$
	$5.6 \cdot 10^6$		$7.9 \cdot 10^7$
	$7.7 \cdot 10^6$		
	$3.3 \cdot 10^7$		

[a]) Defined as 1.

Table 3. *Rate Comparison of Some 1,3-Dipolar Cycloaddition Reactions* (k_2 in $l \cdot mol^{-1} \cdot s^{-1}$, k_{rel} dimensionless)

	(Diphenyl methylidene-sulfonio)-methanide (**2**) (THF, −45°) k_{rel}	Diphenyl-diazomethane (**46**) (DMF, 40°) $10^4\ k_2$	Methyl diazo-acetate (**47**) (Toluene, 80°) $10^4\ k_2$	*N*-Benzylidene-methylamine *N*-oxide (**48**) (Toluene, 85°) $10^4\ k_2$
Tetracyanoethylene	$33 \cdot 10^6$	$19 \cdot 10^3$	97	
Fumaronitrile	1300	40		17
Acrylonitrile	32	47	7.2	3.1
TCNE/Acrylonitrile	*$1.03 \cdot 10^6$*	*400*	*14*	
Dimethyl fumarate	5300	247	12.3	7.3
Dimethyl maleate	82	6.9	3.1	2.5
Ratio	*65*	*36*	*4.0*	*2.9*
$MeO_2C-C\equiv C-CO_2Me$	340	764	134	570
$MeO_2C-C\equiv C-H$	1	102		20
Ratio	*340*	*7.5*		*28*

tetracarboxylate does not meet the expectation for a top-notch reaction partner of **2**. The low k_{rel} value of 40 reflects the compensation of electronic activation by steric hindrance; the twofold nature of the latter was discussed in *Sect. 2.1*.

Opposing electronic and steric effects are likewise the reason that dimethyl maleate (k_{rel} 82) lags behind dimethyl fumarate (k_{rel} 5400). The sinking rate ratio of dimethyl fumarate/maleate for the other 1,3-dipoles (*Table 3*) again underlines the superior selectivity of **2**. The planar bond system of *N*-phenylmaleimide (k_{rel} $5.7 \cdot 10^4$) and maleic anhydride (k_{rel} $2.9 \cdot 10^5$) give rise to unfettered electronic activation.

Table 2 presents some more tetra-acceptor-substituted ethylenes with k_{rel} above 1 million, but still below the $33 \cdot 10^6$ for TCNE. Dimethyl fumarate responds to the introduction of two CF_3 or CN groups with 320- and 1400-fold increases of k_{rel}. The values for dimethyl 2,3-dicyanofumarate and 2,3-dicyanomaleate differ only by a factor of 5.6.

The N=N bond exceeds the C=C bond in dipolarophilic activity: 4-phenyl-1,2,4-triazoline-3,5-dione reacts 320 times more rapidly with **2** than the C analogue, *N*-phenylmaleimide, and dimethyl azodicarboxylate is 60-fold faster than dimethyl fumarate (*Table 2*).

A great surprise was the high reactivity of the C=S bond, which was first brought to light by the elucidation of the *Schönberg* reaction (see *Sect. 1*) and led to the concept of thiones as 'superdipolarophiles' (for a review, see [33]). According to *ab initio* calculations, C=S π-bonds have lower LU energies than C=C bonds, and activation energies for cycloadditions to thiones (sometimes negative) profit from the reduced HO-LU distance [34]. Thiones are also 'superdienophiles' in *Diels-Alder* reactions [35].

With a k_{rel} value of $79 \cdot 10^6$, fluorene-9-thione tops the dipolarophilic reactivities shown in *Table 2*, and exceeds even TCNE by a factor of 2.4. Thiobenzophenone (**3**) (k_{rel} $1.2 \cdot 10^6$) ranks 68-fold lower than thiofluorenone, probably as a consequence of Ph twisting in **3** and strain in the five-membered ring of thiofluorenone. The k_{rel} values of thioxanthione ($6.8 \cdot 10^6$) and xanthione ($1.8 \cdot 10^6$) confirm the strain hypothesis.

Nevertheless, **3** reacts 3400 times more rapidly than DMAD with **2**; DMAD often figures as dipolarophile *par excellence*. Two electron-releasing 4-MeO groups diminish the rate of **3** 16-fold. It is noteworthy that a dithioester and two trithiocarbonates – despite resonance stabilization – undergo cycloadditions with **2**.

It appears that each 1,3-dipole commands its specific reactivity spectrum for dipolarophiles. Each 1,3-dipole has its place on the continuum between nucleophilic and electrophilic dominance. Superimposed are steric effects in the ground state and in the TS of cycloaddition. Various classes of 1,3-dipoles have different distances of the reacting termini; the bending energies of the linear 1,3-dipoles of the propargyl-allenyl type [26b] also enter the TS energies. Finally, the size of the cycloaddition enthalpy decides on earlier or later TS, altogether a colorful variety of phenomena that influence the rate of the cycloaddition.

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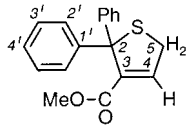
Experimental Part

1. *General*. Prep. layer chromatography (PLC): 20×20 cm glass plates, 2 mm *Merck* silica gel *60 PF_{254}* or *Merck* alumina *60 F_{254}, neutral type E*. M.p.: *Büchi SMP-20*; uncorrected. UV/VIS: *Zeiss RPQ*; λ_{max} (log ε), wavelength in nm. IR: *Perkin-Elmer 125*, *Beckman FT IFS 45*, KBr pellets. NMR: *Varian A60*, *Bruker WP80 CW* (^{1}H: 80 MHz), *Bruker WP80 DS* (^{13}C: 20.2 MHz, signal multiplicities by comparison of H-decoupled and off-resonance spectra), *Varian XR 400S* (^{1}H: 400 MHz; ^{13}C: 100 MHz and ^{1}H-couplings by DEPT); solvent was $CDCl_3$ (stored over dry K_2CO_3); chemical shifts δ relative to TMS, J in Hz. MS (EI spectra with 70 eV): *AEI MS902*, *Finnigan MAT 90*; *m/z* (%), intensities of isotope peaks reported as, *e.g.*, ^{13}C % calc./% found. For high-resolution (HR), the program CMASS on *MAT 95Q* ($R \leq 500$) was used; small distortions of HR values result from insufficient separation.

2. *Cycloadducts of (Diphenylmethylidenesulfonio)methanide* (**2**). 2.1. *Methyl 2,5-Dihydro-2,2-diphenylthiophene-3-carboxylate* (**11a**). The soln. of freshly distilled *thiobenzophenone* (**3**, 3.19 g, 16.1 mmol) in THF (30 ml) was magnetically stirred in a $-78°$ bath, and 1.0 equiv. of precooled CH_2N_2 soln. (20 ml, *ca.* 0.8M in THF) was slowly added until the blue color disappeared; the 'titration' became complete with a delay of 2–3 s, as described in [6]. After addition of methyl propiolate (10.1 g, 120 mmol, 7.5 equiv.), the bath temp. was increased to $-45°$. The N_2 elimination from dihydrothiadiazole **1** was finished in 6 h, during which the temp. was not allowed to rise above $-40°$. The solvent and the excess methyl propiolate were removed *i.v.*; trituration with MeOH/Et_2O 1:1 left 1.92 g of dimer **6** undissolved (m.p. 164–167° (dec., blue), [6] 166–169°). The mother liquor was concentrated to dryness and heated with MeOH; hot filtration gave a further 215 mg of **6** (together 63%). Adduct **11a** (664 mg, m.p. 95–98°) crystallized from the cooled MeOH soln. in two fractions, and another 240 mg was obtained after PLC (total yield 19%). M.p. 101.5–102.5° (2 × MeOH). ^{1}H-NMR (400 MHz): 3.56 (*s*, MeO); 4.00 (*d*, $J = 2.9$, $CH_2(5)$; 4.04 in diester **10**); 7.15 (*t*, $J = 2.9$, H–C(4)); arom. H: *Table 4*. ^{13}C-NMR (100 MHz): *Table 4*. The ^{1}H and ^{13}C shifts were correlated and identified by HETCOR. Among the proximity effects elucidated by gs-NOESY [36], small interactions of H–C(2′/6′) with $CH_2(5)$ and H–C(4), *i.e.*, across the ring, were noticed. The gs-HMBC [37] experiment indicated the $^3J(^{13}C,H)$ couplings in accordance with structure **11a**; the ^5J signal between C(1′) and $CH_2(5)$ is a homoallyl relation. ^3J(C,H) couplings of H–C(4) with C=O and C(2) are missing for reasons not understood. MS (60°): 296 (100, M^+; ^{13}C 20/19), 263 (16, $[M - HS]^+$), 250 (5, $[M - CH_2S]^+$), 237 (21, $[M - CO_2Me]^+$; $^{13}C_2 + ^{34}S$ 1.3/1.2), 231 (12), 219 (51, $[M - Ph]^+$; ^{13}C 7.6/8.6), 218 (15), 205 (12), 204 (17, $[219 - Me]^+$), 203 (21, $[218 - Me]^+$), 191 (15), 187 (21, $[218 - MeO]^+$), 175 (11), 165 (8, $C_{13}H_9^+$, **21**), 160 (8, $[219 - CO_2Me]^+$), 77 (4, Ph^+). Anal. calc. for $C_{18}H_{16}O_2S$ (296.37): C 72.94, H 5.44, S 10.82; found: C 73.03, H 5.33, S 10.94.

2.2. *Methyl 2,2-Diphenylthiolane-3-carboxylate* (**13**). Most of the cycloadditions of **2** were carried out with a stock soln. of **1**, which was prepared by passing diluted (N_2) gaseous CH_2N_2 [38] into the soln. of **3** (10 mmol) in

Table 4. *NMR Parameters of Methyl 2,5-Dihydro-2,2-diphenylthiophene-3-carboxylate* (**11a**) *in $CDCl_3$ and Data of Two-Dimensional Analysis*



Atom	δ(H) [ppm]	Multiplicity	gs-NOESY H-position	δ(C) [ppm]	gs-HMBC ^3J(CH) (^2J(CH)) H-position
MeO	3.56	*s*	C(4), C(2′/6′)	51.7	None
CH_2(5)	4.00	*d*	C(4) > C(2′/6′)	37.1	None
H–C(4)	7.15	*t*	C(5) > MeO > C(2′/6′)	142.4	(5)
H–C(4′)	7.22	*tt*	C(3′/5′) > C(2′/6′)	126.8	2′/6′
H–C(3′/5′)	7.29	*tm*	C(2′/6′), C(4′)	127.6	1′
H–C(2′/6′)	7.33	*dm*	C(3′/5′) > C(4′) > MeO > C(4), C(5)	128.8	4′
C(2)				72.9	2′/6′
C(3)				140.9	5
C(1′)				144.8	3′/5′, 5(^5J)
C=O				163.6	MeO

THF (30 ml) at −78° until the color changed from deep blue to light yellow; the soln. was divided into aliquots and stored at −78°. Methyl acrylate (1.21 g, 14.1 mmol) was added to 9.0 ml of the above soln. of **1** (3.0 mmol) at −78°. After 4 h at −40°, workup as described above afforded **13** (708 mg, 79%) in several fractions from Et_2O. M.p. 78.5–79.5° (Et_2O). ^{1}H-NMR (100 MHz): 2.2–3.3 (*m*, 4 H); 3.31 (*s*, MeO); 4.03 (*dd*, *J* = 7.2, 8.6, H–C(3)); 7.2–7.6 (*m*, 10 arom. H). ^{13}C-NMR (20.2 MHz): 30.4, 32.6 (2*t*, C(4), C(5)); 51.4 (*q*, MeO); 55.5 (*d*, C(3)); 69.4 (*s*, C(2)); 126.5, 126.9 (2*d*, 2 C(4′)); 127.2, 127.5, 127.9, 129.2 (4*d*, 2 C(2′/6′), 2 C(3′/5′)); 143.6, 146.1 (2*s*, 2 C(1′)); 171.4 (*s*, C=O). Anal. calc. for $C_{18}H_{18}O_2S$ (298.39): C 72.45, H 6.08, S 10.75; found: C 72.46, H 5.83, S 10.54.

2.3. *Dimethyl 2,2-Diphenylthiolane-3,4*-trans-*dicarboxylate* (**14**). **1** (3.27 mmol) and dimethyl fumarate (554 mg, 3.84 mmol) in THF (15 ml) were stirred at −45° for 5 h; clear soln. was obtained after 2 h. The usual workup gave crystalline **14** (863 mg, 74%) from $CHCl_3$/Et_2O. ^{1}H-NMR Analysis of the mother liquor with 1-methylnaphthalene as weight standard indicated a further 0.20 mmol of **14** (total yield, 80%). M.p. 146.5–148°. IR: 699*s*, 706*s*, 718*s*, 751*s* (arom. CH out-of-plane deform.); 1205*s*, 1262*vs* (C–O); 1435*s*, 1491*m*, 1596*w* (arom. ring vibration), 1736*vs* (C=O). ^{1}H-NMR (400 MHz): 3.11 (*t*, *J*(5A,5B) = *J*(4,5A) = 10.7, H_A–C(5)); 3.37 (*dd*, *J*(5A,5B) = 10.7, *J*(4,5B) = 8.5, H_B–C(5)); 3.76 (*ddd*, 6 lines by superimposition, *J*(3,4) = 11.4, *J*(4,5A) = 10.7, *J*(4,5B) = 8.5, H–C(4)); 3.36, 3.70 (2*s*, 2 MeO); 7.20–7.38 (*m*, 8 H of *cis*- and *trans*-Ph); 7.53 (*dm*, H–C(2′/6′) of *cis*-Ph). ^{13}C-NMR (20.2 MHz): 32.0 (*t*, C(5)); 49.6 (*d*, C(4)); 51.7, 52.2 (2*q*, 2 MeO), 57.6 (*d*, C(3)); 68.0 (*s*, C(2)); 126.9, 127.4 (2*d*, 2 C(4′)); 127.4, 127.7, 127.9, 129.3 (4*d*, 2 C(2′/6′), 2 C(3′/5′)); 143.2, 144.6 (2*s*, 2 C(1′)); 170.0, 172.3 (2*s*, 2 C=O). MS (80°): 356 (70, M^+, ^{13}C 15.6/15.2), 296 (14, $[M - HCO_2Me]^+$, HR: calc.: 296.0867; found: 296.0883), 279 (19, $[M - Ph]^+$; ^{13}C 3.0/3.3), 265 (12, $[296 - MeO]^+$, $C_{17}H_{13}OS^+$; ^{13}C 2.3/2.3), 263 (11), 238 (17, $[M - 2\ CO_2Me]^+$; $^{13}C_2 + {}^{34}$S 0.99/0.93), 237 (21), 212 (27, **17**; HR: calc.: 212.0657; found 212.0640), 211 (74, **18**), 210 (100, **19**; HR: calc.: 210.0501; found: 210.0535), 207 (18), 198 (15, **3**$^+$), 179 (17, **20**; HR: calc.: 179.0858; found: 179.0851), 178 (24), 165 (26, $C_{13}H_9^+$, **21**; HR.: calc.: 165.0702; found 165.0713), 121 (11, **22**; HR: calc.: 121.0111; found: 121.0109), 77 (5, Ph^+). Anal. calc. for $C_{20}H_{20}O_4S$ (356.43): C 67.39, H 5.66, S 9.00; found: C 67.43, H 5.63, S 9.00.

2.4. *Dimethyl 2,2-Diphenylthiolane-3,4*-cis-*dicarboxylate* (**15**). Dimethyl maleate (7.38 mmol) and **1** (3.16 mmol) were reacted in THF (10 ml). After removal of the solvent, dimer **6** (32 mg, 5%) remained undissolved in boiling MeOH (15 ml). Compound **15** (734 mg, 65%) was obtained in 3 fractions from MeOH/Et_2O. M.p. 120–122° (MeOH). ^{1}H-NMR (100 MHz): 3.16, 3.56 (2*s*, 2 MeO); 2.95–4.05 (*m*, H–C(4), CH_2(5)); 4.40 (*d*, *J* = 6.3, H–C(3)); 7.1–7.6 (*m*, 10 arom. H). ^{13}C-NMR (20.2 MHz): 32.3 (*t*, C(5)); 50.7 (*d*, C(4)); 51.3,

52.2 (2*q*, 2 MeO); 57.5 (*d*, C(3)); 69.2 (*s*, C(2)); 126.70, 127.0 (2*d*, 2 C(4′)); 126.79, 127.6, 128.4, 128.5 (4*d*, 2 C(2′/6′), 2 C(3′/5′)); 142.4, 147.7 (2*s*, 2 C(1′)); 170.8, 171.3 (2*s*, 2 C=O). Anal. calc. for $C_{20}H_{20}O_4S$ (356.43): C 67.39, H 5.66, S 9.00; found: C 67.66, H 5.53, S 9.17.

2.5. *Tetramethyl 2,2-Diphenylthiolane-3,3,4,4-tetracarboxylate* (**16**). The reaction of tetramethyl ethylenetetracarboxylate (7.70 mmol) and **1** (5.23 mmol) in THF (14 ml), and CH_2Cl_2 (15 ml) furnished dimer **6** (362 mg, 33%) and **16** (695 mg, 28%); **16** was separated from the excess of dipolarophile by fractional crystallization from MeOH. M.p. 129–131° (MeOH). IR: 1245v*s*, 1261v*s*, 1287*s* (C–O); 1730v*s*, 1743v*s*, 1755v*s*, 1760v*s* (C=O). ^{1}H-NMR (60 MHz): 3.48 (*s*, 2 MeO); 3.58 (*s*, 2 MeO), 3.87 (*s*, CH_2(5)); 7.08–7.75 (*m*, 10 arom. H). ^{13}C-NMR (20.2 MHz): 35.8 (*t*, C(5)); 52.5, 53.2 (2*q*, 2 MeO); 71.1, 73.8, 76.8 (3*s*, C(2), C(3), C(4)); 126.8, 130.6 (2 br. *d*, 10 arom. C); 144.4 (*s*, 2 C(1′)); 167.6, 168.6 (2*s*, 4 C=O). MS (80°): 472 (19, M^+), 413 (16, [M – CO_2Me]$^+$), 243 (69), 212 (52, **17**), 211 (47, **18**), 198 (97, **3**$^+$), 165 (100, **21**), 121 (82, **22**), 113 (19), 105 (17), 77 (27, Ph^+), 59 (39, MeOC≡O$^+$). Anal. calc. for $C_{24}H_{24}O_8S$ (472.50): C 61.00, H 5.12, S 6.79; found: C 61.33, H 5.05, S 6.78.

2.6. *2,2-Diphenylthiolane-3-carbonitrile* (**23**). Acrylonitrile (34 mmol) and **1** (3.75 mmol) in THF (10 ml) afforded **23** (753 mg, 76%). M.p. 141–143° ($CHCl_3$/MeOH). ^{1}H-NMR (360 Hz): 2.34, 2.48 (*C* and *D* of *ABCDX*, visible 14 and 12 lines, resp.; clarified by double resonance experiments, J(4A,4B) = 13.0, CH_2(4)); 3.16, 3.23 (*AB* of *ABCDX*, 14 lines, J(5A,5B) = 10.8, CH_2(5)); 3.95 (*X* of *ABCDX*, *dd*, J = 5.6, 9.0, H–C(3)); 7.23–7.42 (*m*, 8 arom. H); 7.50–7.55 (*m*, 2 arom. H). ^{13}C-NMR (20.2 MHz): 29.7, 32.3 (2*t*, C(4), C(5)); 43.2 (*d*, C(3)); 68.0 (*s*, C(2)); 118.6 (*s*, CN); 127.4, 127.7 (2*d*, 2 C(4′)); 126.6, 127.9, 128.5, 128.8 (4*d*, 2 C(2′/6′), 2 C(3′/5′)); 141.8, 143.6 (2*s*, 2 C(1′)). MS (70°): 265 (91, M^+), 232 (4.2, [M – SH]$^+$; HR: calc.: 232.1123; found: 232.1103; ^{13}C 0.78/0.86), 212 (41, $C_{14}H_{12}S^+$, **17**), 211 (100, $C_{14}H_{11}S^+$, **18**; HR: calc.: 211.0579; found: 211.0579), 205 (4, [M – SCH_2CH_2]$^+$, **26**; HR: calc.: 205.0889; found: 205.0905), 204 (7, $C_{15}H_{10}N^+$, **27**; HR: calc.: 204.0811; found: 204.0807), 203(6), 198 (8, **3**$^+$), 188 (11, [M – Ph]$^+$), 179 (12, $C_{14}H_{11}^+$, **20**), 178 (17), 165 (23, **21**), 121 (11, **22**), 115 (5), 77 (5, Ph^+). Anal. calc. for $C_{17}H_{15}NS$ (265.36): C 76.94, H 5.70, N 5.28, S 12.08; found: C 77.07, H 5.70, N 5.19, S 11.80.

2.7. *2,2-Diphenylthiolane-3,4*-trans-*dicarbonitrile* (**24**). Dihydrothiadiazole **1** (2.92 mmol) was reacted with fumaronitrile (3.19 mmol) in THF (10 ml) at −40°. The low solubility of **24** (771 mg, 91%) facilitated the isolation. M.p. 198–200° (acetone/Et_2O). IR: 1444*s*, 1490*s*, 1581*m*, 1592*m* (arom. ring vibration), 2247*m* (C≡N). ^{1}H-NMR (400 MHz): simulation of the exper. *ABCX* spectrum of the ring protons by DavinX [14] (*Fig.*); criteria of assignment: H–C(3) at highest frequency shows only one vicinal coupling, and H–C(4) three vicinal couplings; the negative sign is expected for J(5A,5B); substituent increments on ^{1}H chemical shifts for geminal CN (+1.13), *cis*-vicinal CN (+0.39), *trans*-vicinal CN (+0.58), evaluated from pyrazolidine derivatives [39], allow us to distinguish H_A–C(5) and H_B–C(5) of **24** on the basis of the $\delta_{(H)}$ of **23**; $J_{cis} > J_{trans}$ is unreliable in saturated five-membered rings and is violated by J(4,5A) < J(4,5B). ^{13}C-NMR: 32.5 (*t*, C(5)); 34.4 (*d*, C(4)); 46.8 (*d*, C(3)); 67.0 (*s*, C(2)); 115.4, 116.9 (2*s*, 2 CN); 126.4, 2 × 128.4, 128.7, 2 × 129.0 (6*d*, 10 arom. C); 139.8, 141.1 (2*s*, 2 C(1′). Anal. calc. for $C_{18}H_{14}N_2S$ (290.37): C 74.75, H 4.86, N 9.65, S 11.04; found: C 74.67, H 4.71, N 9.65, S 11.11.

2.8. *2,2-Diphenylthiolane-3,3,4,4-tetracarbonitrile* (**25**). Compound **1** (4.60 mmol) and TCNE (5.35 mmol) in THF (14 ml) were stirred at −45° for 6 h to produce **25** (1.45 g, 93%). M.p. 177–178.5° ($CHCl_3$). IR: 698*s*, 744*s*, 752*s* (arom. CH out-of-plane deform.); 1447*s*, 1496*m*, 1584*w* (arom. ring vibration), 2245*w* (C≡N). ^{1}H-NMR (80 MHz): 3.93 (*s*, CH_2(5)); 7.15–7.53 (*m*, 10 arom. H); application of substituent increments for *cis*-vicinal- and *trans*-vicinal-CN, mentioned above, to the introduction of a second 4-CN into **24** leads to a prediction for CH_2(5) of **25** at 3.91 and 3.97, in good agreement with the exper. value. ^{13}C-NMR (20.2 MHz, (D6)acetone): 38.6 (*t*, C(5)); 48.7 (*s*, C(4)); 58.7 (*s*, C(3)); 73.8 (*s*, C(2)); 111.6, 111.9 (2*s*, 4 CN); 128.6, 130.0, 130.5 (3*d*, 10 arom. C); 140.0 (*s*, 2 C(1′)). MS (150°): 340 (4, M^+), 339 (14, [M – H]$^+$), 230 (12, [M – $SCH_2C(CN)_2$], 229 (12), 212 (52, **17**), 211 (100, **18**), 203 (11), 179 (15, **20**), 178 (14), 165 (46, **21**), 135 (14, [212 – Ph]$^+$), 121 (24, **22**), 78 (13, PhH^+), 77 (24, Ph^+). Anal. calc. for $C_{20}H_{12}N_4S$ (340.39): C 70.57, H 3.55, N 16.46, S 9.42; found: C 70.70, H 3.67, N 16.27, S 9.46.

Attempts of Interference with an Intermediate [40]. In parallel experiments, **2** was reacted with 1.1 equiv. of TCNE in dry THF, in THF + 2 vol-% of H_2O, and in THF + 2 vol-% of MeOH. ^{1}H-NMR Analysis with *sym*-$C_2H_2Cl_4$ as weight standard indicated **25** in 89, 92, and 94% yields, respectively.

2.9. *2,2-Diphenylthiolane-3,4*-cis-*dicarboxylic Anhydride* (**28**) [41]. Compound **1** (10.0 mmol) in THF (20 ml) and maleic anhydride (10.0 mmol) in acetone (10 ml) were reacted at −40° and gave **28** (2.98 g, 96%). M.p. 126–128° (Et_2O). ^{1}H-NMR (60 MHz): 2.64 (*dd*, J = 7.5, 12.8, H_A–C(5)); 3.23 (*d*, J = 12.8, H_B–C(5)); 3.78 (*t*, J(4,5A) = J(3,4) = 7.5, H–C(4)); 4.33 (*d*, J = 7.5, H–C(3)); 7.22 (br. *m*, 10 arom. H). Anal. calc. for $C_{18}H_{14}O_3S$ (310.36): C 69.66, H 4.55; found: C 69.38, H 4.41.

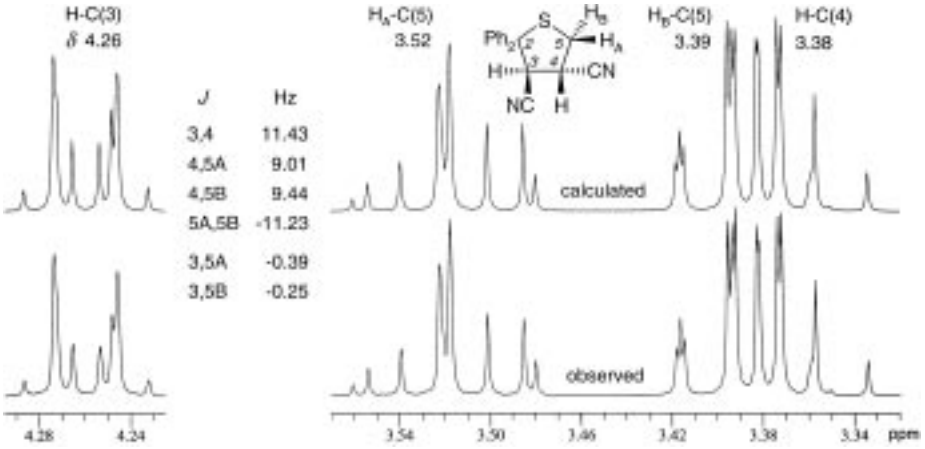


Figure. *Sections of the ^{1}H-NMR spectrum* (400 MHz, $CDCl_3$) *of 2,2-diphenylthiolane-3,4*-trans-*dicarbonitrile* (**24**). Below: *observed* ABCX *spectrum of ring protons*; above: *spectrum simulated by DavinX and calculated parameters.*

2.10. N-*Methyl-2,2-diphenylthiolane-3,4*-cis-*dicarboximide* (**29**) [41]. Compound **1** (10.0 mmol) in THF (20 ml) and *N*-methylmaleimide (10.0 mmol) in $CHCl_3$ (20 ml) were combined at $-78°$ and allowed to react at $-40°$. Adduct **29** (1.01 g) precipitated, and a further 1.59 g (total yield 80%) was obtained from the mother liquor. M.p. 174–176° (THF). ^{1}H-NMR (60 MHz): 2.84 (*s*, NMe); 2.70 (*dd*, H_A–C(5)); 3.29 (*dd*, H_B–C(5)); 3.62 (*td*, H–C(4)); 4.12 (*d*, H–C(3)) with J(5A,5B) = 12.8, J(4,5A) = J(3,4) = 7.6, J(4,5B) = 1.0 Hz; 7.28 ('d', 10 arom. H). MS (90°): 323 (100, M^+), 290 (24, $[M-HS]^+$, no ^{34}S peak), 246 (38, $[M-Ph]^+$; ^{13}C 5.5/5.5, $^{13}C_2$ + ^{34}S 5.4/6.2), 212 (25, **17**), 211 (57, **18**), 210 (17, **19**), 205 (9), 179 (10, **20**), 178 (17, $C_{14}H_{10}^+$), 165 (26, **21**), 161 (33), 135 (11, [**17** – Ph]$^+$), 121 (18, **22**), 77 (10, Ph^+). Anal. calc. for $C_{19}H_{17}NO_2S$ (323.40): C 70.56, H 5.30, N 4.33; found: C 70.66, H 5.30, N 4.04.

2.11. *2,2,*N-*Triphenylthiolane-3,4*-cis-*dicarboximide* (**30**) [41]. Prepared analogously to **29**, 79%. M.p. 208–209°. ^{1}H-NMR (60 MHz): 2.83 (*dd*, H_A–C(5)); 3.45 (*dd*, H_B–C(5)); 3.79 (*td*, H–C(4)); 4.26 (*d*, H–C(3)) with J(5A,5B) = 12.7, J(4,5A) = J(3,4) = 7.6, J(4,5B) = 1.6; 7.0–7.53 (*m*, 15 arom. H). MS (125°): 385 (100, M^+), 352 (10, $[M-SH]^+$), 308 (19, $[M-Ph]^+$), 256 (22), 212 (31, **17**), 211 (68, **18**); 210 (42, **19**), 179 (15, **20**), 178 (24, $C_{14}H_{10}^+$), 165 (22, **21**), 161 (23), 121 (18, **22**), 91 (6, $C_7H_7^+$), 77 (10, Ph^+). Anal. calc. for $C_{24}H_{19}O_2NS$ (385.41): C 74.79, H 4.97; found: C 74.99, H 4.85.

2.12. *Dimethyl 3,4*-trans- *and 3,4*-cis-*Dicyano-2,2-diphenylthiolane-3,4-dicarboxylate* (**38** and **39**). 2.12.1. *Data* of **38**. The reaction of **1** (2.98 mmol) with *dimethyl 2,3-dicyanofumarate* (**32**, 3.29 mmol) [18] in THF (23 ml) produced 78% of **38** ($CHCl_3$/Et_2O). M.p. 196–197°. ^{1}H-NMR (60 MHz): 3.71, 3.78 (2*s*, 2 MeO); 3.78, 4.03 (*AB*, J = 11.8, CH_2(5)); 7.2–7.8 (*m*, 10 arom. H). ^{13}C-NMR (20.2 MHz): 36.6 (*t*, C(5)); 54.2, 55.1 (2*q*, 2 MeO); 59.6, 65.7, 72.4 (3*s*, C(4), C(3), C(2)); 114.9, 115.2 (2*s*, CN); 127.64 (2×), 128.2, 130.0 (4*d*, 2 C(2′/6′), 2 C(3′/5′)); 128.00, 128.5 (2*d*, 2 C(4′)); 139.3, 143.0 (2*s* (2 C(1′)); 163.2, 163.7 (2*s*, 2 C=O). Anal. calc. for $C_{22}H_{18}N_2O_4S$ (406.45): C 65.01, H 4.46, N 6.89, S 7.89; found: C 65.06, H 4.41, N 6.84, S 7.90.

2.12.2. *Equilibration of* trans- *and* cis-*Dicarboxylate.* Compound **38** (149 mg, 0.367 mmol) was refluxed in abs. MeCN (10 ml, homogeneous soln.) for 48 h. After removal of the solvent, the ^{1}H-NMR analysis in $CDCl_3$ with *sym*-$C_2H_2Cl_4$ as weight standard indicated **38**/**39** = 29 : 71; the *s* of MeO at 3.31 was used for **39**, and the two *s* at 3.78 and 3.82 for **38** and **39**. No decomposition products were observed. A corresponding experiment, starting with pure **39** (see below), afforded **38**/**39** 32:68, *i.e.*, the equilibrium was reached from both sides within the analytical limits. After 4 h in refluxing MeCN, the isomerization **38** → **39** was 58%.

2.12.3. *Isolation of* **39**. Fractional crystallization of the equilibrium mixture from $CHCl_3$ provided the more soluble big prisms of **39**. M.p. 160.5–161.5°. IR: 1207v*s* (br.) (C–O); 1434*s*, 1448*s*, 1492*m*, 1597*w* (arom. ring vibration); 1745v*s*, 1722v*s* (C=O); 2242v*w*, 2248v*w* (C≡N; the low intensity contrasts with the normal intensity for **24**; the lit. reports a marked intensity decrease or even absence of C≡N in the proximity of O-functions [42]). ^{1}H-NMR (80 MHz): 3.33, 3.80 (2*s*, 2 MeO); 3.58, 4.17 (AB, J = 11.8, CH_2(5)); 7.1–7.8 (3*m*, 10 arom. H).

^{13}C-NMR (20.2 MHz): 37.2 (*t*, C(5)); 54.1, 54.9 (2*q*, 2 MeO); 60.0, 66.3, 74.7 (3*s*, C(4), C(3), C(2)); 115.2, 115.7 (2*s*, 2 CN); 127.9, 128.15, 128.36 (2×), 128.52, 129.5 (6*d*, 10 arom. C); 139.8, 140.9 (2*s*, 2 C(1′)); 164.3, 164.5 (2*s*, 2 C=O). MS (120°): 406 (69, M^+), 375 (9, $[M-\text{MeO}]^+$), 347 (85, $[M-\text{CO}_2\text{Me}]^+$), 212 (100, **17**), 211 (82, **18**), 198 (39, **3**$^+$), 165 (52, **21**), 121 (36, **22**), 77 (21, Ph^+), 59 (19, $[\text{CO}_2\text{Me}]^+$). Anal. calc. for $C_{22}H_{18}N_2O_4S$ (406.45): C 65.01, H 4.46, N 6.89, S 7.89; found: C 64.93, H 4.36, N 6.95, S 7.91.

2.12.4. *Stereospecificity of Cycloaddition*. Compound **1** (30.3 mmol), prepared from freshly purified **3** and CH_2N_2 in abs. THF (60 ml) at −78°, was added to the suspension of the powdered, little-soluble **32** (33.5 mmol) in THF (45 ml), which was stirred for 15 h in a bath at −49°. After evaporation of the solvent at r.t., ultrasonic trituration of the residue with Et_2O (100 ml) left 12.50 g of colorless crystals undissolved; ^{1}H-NMR analysis with *sym*-$C_2H_2Cl_4$ indicated **38** (MeO at 3.71) and **32** (MeO at 4.03) in a ratio of 96:4, corresponding to 97% yield of **38**. PLC (CH_2Cl_2) of the mother liquor, and ^{1}H-NMR analysis (MeO at 3.33) disclosed **39** (0.103 mmol, 0.34%). As a test for the configurational stability, pure **38** (30.3 mmol) was dissolved in THF (400 ml) at 30° and kept for 3 h at this temp.; workup and ^{1}H-NMR analysis as described above indicated **39** (0.62%) in the mother liquor.

2.13. *Dimethyl 2,3-Dicyanomaleate* (**33**). 2.13.1. *By Photoisomerization of* **32**. Pure and finely pulverized **32** (5.00 g, 25.8 mmol), suspended in abs. CH_2Cl_2 (250 ml), was irradiated with a high-pressure Hg lamp (*Mangels HPK 125*, duran glass filter) for 24 h at r.t.; the suspension was kept moving by a slow Ar stream, and a homogeneous soln. was slowly obtained. After removal of the solvent, ^{1}H-NMR analysis (3.94 for MeO of **33**, 4.03 for MeO of **32**) indicated **33**/**32** 91:9. The product was stirred with pure $CHCl_3$, and the undissolved **32** was filtered. The clear soln. was evaporated, and the residue was dissolved in 100 ml of abs. Et_2O by stirring. After filtration and addition of hexane (300 ml), and concentration *i.v.* to 2/3 of the volume, **33** crystallized at −23°; 3.7–4.3 g (76–86%) were obtained in 2–3 fractions. Colorless platelets showed a m.p. 37.5–38.5° ([19] 36–38°), but still contained 1–3% of **32**. Solvent purity and the absence of base are important for the success of the operation. Acid-washing of the glassware is recommended.

2.13.2. *Equilibration of* **32** *and* **33**. The small δ(H) differences of the MeO signals of **32** and **33** (see above) required calibration of ^{1}H-NMR-analytical data (80 MHz) with artificial mixtures of the *cis*/*trans* isomers. In $CDCl_3$ or C_6D_6 of high purity, the isomerization of **33** to **32** amounted to only 3% in 74 h at r.t.; in CD_3CN, however, the **33**/**32** ratio of 4:96 increased to 30:70 after 10 min, 49:51 (18 min), and 75:25 (42 min). Small quantities of NEt_3 or triethylenediamine generated violet to black colors of the $CDCl_3$ soln., probably resulting from electron transfer. Finely powdered KF catalyzed the isomerization in $CDCl_3$ or C_6D_6: starting with **33**, the conversion to **32** in $CDCl_3$ at r.t. was 15% after 9 min and 36% after 36 min, and after 3 d, **32**/**33** of 88:12 was reached from both sides. Dilute solns. (*ca.* 4 mg in 0.6 ml) are necessary for the isomerization experiments to avoid crystallization of **32**. Solubilities of **32** at r.t. in 1.0 ml of soln.: 8.50 mg in $CDCl_3$, 38.2 mg in MeCN.

2.14. *Diisopropyl 3,4*-trans-*Dicyano-2,2-diphenylthiolane-3,4-dicarboxylate* (**42**). 2.14.1. *Diisopropyl 2,3-Dicyanofumarate* (**40**) [40]. In analogy to the preparation of **32** [18], isopropyl cyanoacetate (253 g, 2.0 mol) and $SOCl_2$ (471 g, 3.8 mol) were refluxed for 3 h. The excess $SOCl_2$ was removed *i.v.*, and the product was triturated with warm i-PrOH (400 ml); after 5 h at +4°, **40** was filtered and recrystallized from i-PrOH with charcoal as decolorant: 52 g (21%), m.p. 122–123°. IR: 767*m*, 829*s*, 894*m*, 978*m*, 1100*s*, 1279v*s* (C−O), 1735v*s* (C=O), 2230v*w* (C≡N). ^{1}H-NMR (80 MHz): 1.41 (*d*, *J* = 6.0, 4 Me); 5.25 (*sept*, *J* = 6.0, 2 Me_2CH). ^{13}C-NMR (20.2 MHz): 21.4 (*q*, 4 Me); 74.1 (*d*, 2 Me_2CH); 111.3 (*s*, 2 CN), 126.0 (*s*, C(2/3)); 157.2 (*s*, 2 C=O). MS (60°): 209 (1, $[M-C_3H_5]^+$), 193 (4, $[M-OC_3H_5]^+$), 191 (6, $[M-\text{i-PrO}]^+$), 167 (3, $[193-\text{CN}]^+$), 150 (7, $[191-C_3H_5]^+$), 149 (7), 120 (2), 104 (2), 77 (4), 59 (13, $[\text{i-PrO}]^+$), 45 (18), 43 (100, $[C_3H_7]^+$), 41 (33, $[C_3H_5]^+$). Anal. calc. for $C_{12}H_{14}N_2O_4$ (250.25): C 57.59, H 5.64, N 11.20; found: C 57.65, H 5.48, N 11.24.

2.14.2. *Cycloaddition with* **2**. Dihydrothiadiazole **1** and **40** (3.00 mmol each) in THF (20 ml) were stirred at −45° for 5 h. Workup and crystallization from $(\text{i-Pr})_2O$ gave **42** (865 mg, 62%). M.p. 147–149°. IR: 1099v*s*, 1258v*s*, 1281*s* (C−O); 1447*s*, 1467*m*, 1492*m* (arom. ring vibration), 1748v*s* (C=O), 2250v*w* (C≡N). ^{1}H-NMR (80 MHz): 1.05, 1.26, 1.34 (3*d*, 1:2:1, *J* = 6.6, 4 Me); 3.74, 3.98 (*AB*, *J* = 11.5, CH_2(5)); 5.00 (*sept.*, *J* = 6.6, 2 Me_2CH); 7.06–7.35, 7.47–8.08 (2*m*, 10 arom. H). ^{13}C-NMR (20.2 MHz): 20.8, 20.9, 21.2, 21.3 (4*q*, 4 Me); 36.8 (*t*, C(5)); 59.7, 65.7 (2*s*, C(4), C(3)); 73.7, 73.8 (2*d*, 2 diastereotopic Me_2CH); 115.4 (*s*, 2 CN); 127.6, 127.8, 128.4, 130.4 (4*d*, 10 arom. C); 139.6, 143.3 (2*s*, 2 C(1′)); 162.2, 162.8 (2*s*, 2 C=O). MS (240°): 462 (35, M^+; ^{13}C 10.3/10.5), 375 (100, $[M-\text{CO}_2\text{iPr}]^+$; ^{13}C 25/24; $^{13}\text{C}_2+{}^{34}$S 7.3/7.6), 333 (24, $[375-C_3H_6]+$; ^{13}C 5.1/6.3; $^{13}\text{C}_2+{}^{34}$S 1.6/2.0), 212 (60, **17**), 211 (46, **18**), 198 (28, **3**$^+$), 179 (7, **20**), 178 (10, $C_{14}H_{10}{}^+$), 165 (28, **21**), 121 (14, **22**), 77 (5, Ph^+). Anal. calc. for $C_{26}H_{26}N_2O_4S$ (462.55): C 67.51, H 5.67, N 6.06, S 6.93; found: C 67.34, H 5.62, N 6.15, S 6.92.

2.15. *2,2-Diphenyl-3,4*-trans-*bis(trifluoromethyl)thiolane-3,4-dicarbonitrile* (**43**). Dihydrothiadiazole **1** (3.0 mmol) and **41** (3.3 mmol) [43] were reacted as usual and afforded **43** (540 mg, 42%). M.p. 87–88° (i-PrOH). IR: 1189v*s*, 1214v*s*, 1238v*s* (C−F); 1444*m*, 1496*m*, 1598*w* (arom. ring vibration), 2250v*w* (C≡N). ^{1}H-NMR: 3.68 (*s*, CH_2(5)); 7.23–7.55 (*m*, 10 arom. H). ^{13}C-NMR (20.2 MHz): 36.5 (*t*, C(5)); 59.8 (*q*,

^2J(C,F) = 29.9, C(4)); 62.8 (q, ^2J(C,F) = 26.4, C(3)); 74.5 (s, C(2)); 111.9 (q, ^3J(C,F) = 1.8, CN); 113.3 (br. s, CN); 121.8 (q, ^1J(C,F) = 289, CF_3); 122.0 (q, ^1J(C,F) = 287, CF_3); 127.9, 128.0, 128.2, 128.5, 129.6, 130.7 (6d, 10 arom. C); 137.3, 142.4 (2s, 2 C(1′)). ^{19}F-NMR (376 MHz): −58.2, −66.3 (2q, ^5J(F,F) = 5.7, 2 CF_3). MS (190°): 426 (22, M^+; ^{13}C 4.9/4.8), 357 (14, $[M - CF_3]^+$; ^{13}C 2.9/2.9), 234 (8), 212 (55, **17**), 210 (100, **19**), 198 (19, **3**$^+$), 179 (13, **20**), 178 (20, $C_{14}H_{10}^+$), 165 (47, **21**), 121 (19, **22**), 77 (10, Ph^+). Anal. calc. for $C_{20}H_{12}F_6N_2S$ (426.38): C 56.33, H 2.84, N 6.57; found: C 56.52, H 3.00, N 6.55.

3. *Measurements of Dipolarophile Activities* vs. **2**. 3.1. *HPLC Analysis.* An instrument *DuPont HPLC 830* was equipped with a steel column 4.6 mm × 25 cm filled with *Zorbax Sil* (neutral silica gel, *DuPont*), and a UV detector (270 nm). The mobile phase was adapted to each competition experiment and consisted of 97–65% (v/v) of hexane + 3–35% (v/v) of $CHCl_3$ + 0–0.2% (v/v) of MeOH (all solvents HPLC quality, *Merck*, *Aldrich*); the flow rate was usually 1.5 cm/min. A 50-µl *Syringe Loading Sample Injector* and a 50-µl sample loop were used for 30-µl injections. Sharp symmetrical peaks were observed for dipolarophiles and cycloadducts, and the reproducibility of the heights was better than ±1%. In a test with 4 concentrations of **10a**, the peak heights defined a straight line through the origin (r = 1.00). The pairs TCNE/**32**, TCNE/**40**, **32**/**33**, and TCNE/**41** were measured with a *Waters* model *440*, *Merck-Hitachi Intelligent Pump L-6200*, and *UV Detector 655A*; mobile phase for the *Zorbax Sil* column was here hexane/AcOEt 90 : 10.

3.2. *Choice of Dipolarophile Pairs and Procedure.* The first prerequisite is that the two dipolarophiles do not react with each other, at least not at −45°; therefore, combinations of thiones and electrophilic C,C multiple bonds are rare in *Scheme 3*. When reactivities widely differ, the analysis of the minor cycloadduct becomes problematic. Only for two pairs of *Scheme 4* values of $\kappa \geq 20$ could not be avoided. For instance., the initial concentration of methyl propiolate ($k_{rel} \equiv 1$) was chosen 5.5 times higher than that of acrylonitrile ($k_{rel} = 32$); a cycloadduct ratio of 5.4 : 1 was still analytically feasible; the total adduct yield dropped to 57% for this pair of low activity.

In preliminary experiments, the pairs were not only selected for moderate κ values. A composition of the mobile phase had to be found for undisturbed analysis of the two dipolarophiles and two cycloadducts. After the reaction with **2** and workup, the heights of the HPLC peaks were compared with those of an artificial mixture of the two cycloadducts. After linear extrapolation, the reaction mixture of adducts was simulated by the chromatogram of a second artificial mixture. Now, only small corrections were required to obtain the mmoles of cycloadducts.

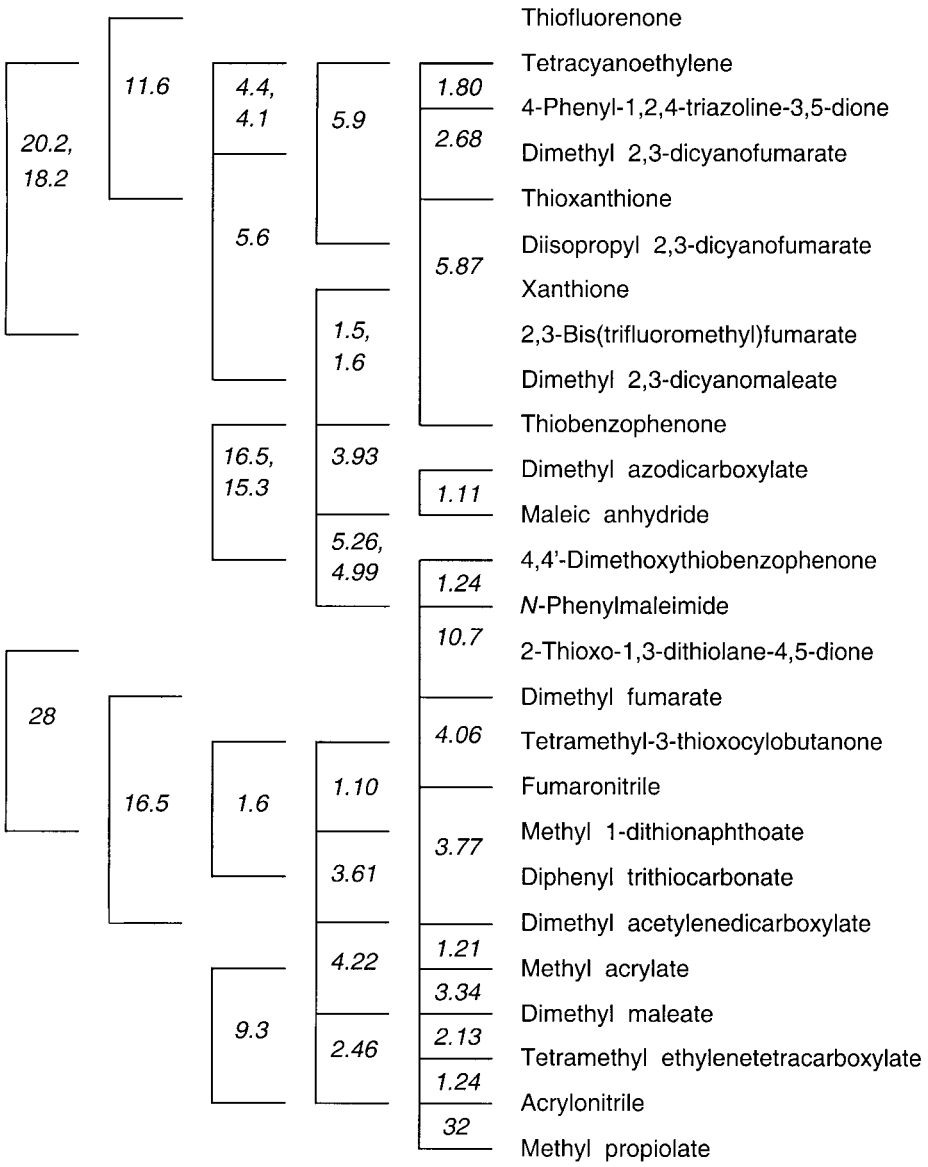
3.3. *Example: Competition Constant for Maleic Anhydride/*N*-Phenylmaleimide.* The soln. (2.00 ml) of **3** (0.493 mmol) in abs. THF was cooled to −78°, and 0.36M CH_2N_2 in THF (1.41 ml) was added portionwise, the last 0.1 ml dropwise until the blue color of **3** just faded; an excess of **3** would furnish **4** in the reaction with **2**, and excess CH_2N_2 would combine with all dipolarophiles of *Table 1*. Precooled solns. (5.00 ml each) of maleic anhydride (94.1 mg, 0.959 mmol) and *N*-phenylmaleimide (130.0 mg, 0.751 mmol) in THF were combined and added to the soln. of **1**; the total volume corresponded to 17.4 ml at 20°. The reaction mixture was kept at −45° for 5 h and then allowed to reach 20°. The THF of a 2.00 ml sample was removed *i.v.*, and the residue was dissolved in $CHCl_3$ (5.00 ml); 200 µl were diluted with 1.80 ml of the mobile phase (in 65% (v/v) hexane + 34.8% (v/v) $CHCl_3$ + 0.2% (v/v) MeOH), corresponding to a 25-fold dilution of the reaction soln. In the HPL chromatogram, the peaks of the dipolarophiles (4.2 and 8.1 min) were followed by those of **28** (12.8 min) and **30** (15.6 min).

Pure **28** (14.72 mg) and **30** (9.88 mg) were dissolved in $CHCl_3$ in 5-ml flasks. 100 µl of each were combined and diluted with the mobile phase to 2.00 ml. Comparison of their peak heights with those of the diluted reaction mixture indicated 0.257 mg/ml of **28** and 0.0562 mg/ml of **30**. A new artificial mixture of 180 µl of the above **28** soln., 57 µl of **30** soln., and 1.76 ml of mobile phase was prepared and analyzed; it allowed a correction of the above values to 0.252 mg/ml of **28** and 0.0556 mg/ml of **30**. Thus, the original reaction soln. contained (25 × 17.4) times (dilution factor) the following amounts: 0.354 mmol of **28** (72%) and 0.063 mmol of **30** (13%). *Eqn. 1* afforded $\kappa = k_A/k_B = 5.26$. A second independent competition experiment gave $\kappa = 4.99$.

3.4. *Survey. Table 5* is an overview of the κ values of 30 pairs on which the k_{rel} of 26 dipolarophiles in *Table 2* are based. A satisfactory separation of HPLC signals was not achieved for the pairs xanthione/**3** and tetramethyl-3-thioxocyclobutanone/diphenyl trithiocarbonate. Here, ^{1}H-NMR analysis employed the CH_2(5) signals of the cycloadducts and compared the integrals with those of 2-methylnaphthalene as weight standard.

Neither HPLC nor ^{1}H-NMR analysis provides values of k_{rel} with the same precision as conventional rate measurements. Starting in *Table 5* from below, analytical errors are propagated with each k_A/k_B upwards, although some double and triple links are restricting deviations.

Tabelle 5. *Cycloadditions of (Diphenylmethylidenesulfonio)methanide* (**2**) *in THF at* $-45°$: *Competition Experiments with Pairs of Dipolarophiles and HPLC Analysis* (in italics: competition constants $\kappa = k_A/k_B$)



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