Cycloadditions of Adamantanethione *S*-Methylide to CC Multiple Bonds [1]

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Received February 4, 1999

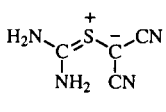
Dedicated to Reiner Sustmann, University of Essen, on the occasion of his 60th birthday.

Adamantanethione *S*-methylide (**12**) is a nucleophilic 1,3-dipole which easily combines with electrophilic acetylenic and ethylenic bonds affording dihydrothiophene and thiolane derivatives, usually in high yields. The *S*-methylide **12**, generated by extrusion of nitrogen from the 2,5-dihydro-1,3,4-thiadiazole **11**, can not be isolated, but is intercepted *in situ* by dipolarophiles; otherwise, **12** furnishes irreversibly the spirothiirane **13**. The ^{1}H nmr spectra and mass spectra establish the regiochemistry for the adducts of methyl propiolate, acrylonitrile, methyl acrylate, benzylidenemalononitrile and methyl α-cyanocinnamate. The 1,3-dipole does not react with common alkenes; the highly strained *trans*-cyclooctene gives rise to a cycloadduct.

J. Heterocyclic Chem., **36**, 959 (1999).

Introduction.

Thiocarbonyl ylides are not hypothetical intermediates. Many of the push-pull stabilized representatives like **1** [3] or **2** [4] are crystalline and stable; too stable in fact, because they do not show 1,3-dipolar activity.



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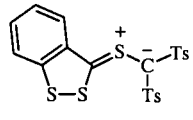

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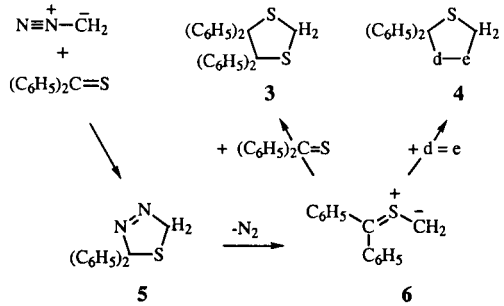
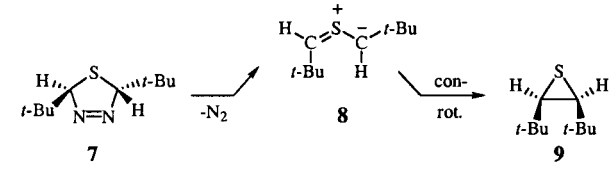
The first 1,3-cycloadditions of thiocarbonyl ylides were inadvertently carried out, when thiobenzophenone was reacted with diazomethane at 0°; tetraphenyl-1,3-dithiolane (**3**) was isolated by Bergmann *et al.* [5] and Schönberg *et al.* [6] in 1930/31. Fifty years later, the mechanism was elucidated in the Munich laboratory; it consists of two 1,3-dipolar cycloadditions, separated by a 1,3-dipolar cycloreversion [7]. At -78°, diazomethane still adds rapidly to thiobenzophenone, but the unimolecular nitrogen extrusion, **5** → **6**, is suppressed; the 2,5-dihydro-1,3,4-thiadiazole **5** becomes isolable at low temperature. The cycloreversion, **5** → **6** + nitrogen, proceeds at -45° with a half-reaction time of 34 minutes (deuteriochloroform). Thiobenzophenone *S*-methylide (**6**) is of fleeting existence; it can be captured *in situ* either by a second molecule of thiobenzophenone (→ **3**) or by a great variety of other multiple bond systems *d*=*e* affording cycloadducts **4** [7,8].



3 **4** **5** **6**

The transition state of the 1,3-dipolar cycloreversion, **5** → **6** + nitrogen, profits from the incipient conjugation energy of the phenyl groups. 2,5-Dihydro-1,3,4-thiadiazoles with aliphatic substituents should be more thermostable and, in fact, they are isolable as analytically pure compounds [9]. In 1970, Kellogg *et al.* prepared *trans*-2,5-di-*tert*-butyl-1,3,4-thiadiazoline (**7**), which on thermolysis furnished the *cis*-2,3-di-*tert*-butylthiirane (**9**); thus, the irreversible electrocyclic ring closure of the *endo,exo*-thiocarbonyl ylide **8** takes a *conrotatory* course [10].

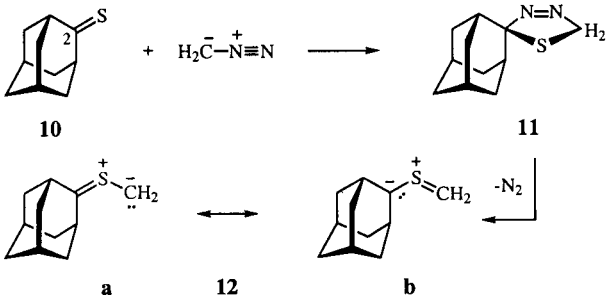


7 **8** **9**

The first-order cycloreversion, **7** → **8**, shows $t_{1/2}$ = 107 minutes at 80° in perdeuteriobenzene [11]. The 2',5'-dihydrospiro[adamantane-2,2'-(1,3,4)-thiadiazole] (**11**), described in a previous paper [12], expels nitrogen 120 times faster ($t_{1/2}$ = 55 s at 80° in xylene). The adamantanethione *S*-methylide (**12**) is an active 1,3-dipole which combines *in situ* with many types of multiple bonds as dipolarophiles: C≡C, C=C, C=O, C=S, C=N, N=N [13]. If not intercepted, **12** undergoes the irreversible electrocyclic ring closure to give thiirane **13**.

The conversion of the commercial adamantanone to the thione **10** [14] proceeds with 75-80% yield. Addition of diazomethane in pentane at -30° makes **11** easily available [12]; **11** can be stored in the deep-freeze. Therefore, **12** was chosen as one of the test systems for exploring the reactivity spectrum of thiocarbonyl ylides as 1,3-dipoles. We report here on the cycloadditions of **12** to CC multiple bonds.

Adducts to C≡C Triple Bonds.



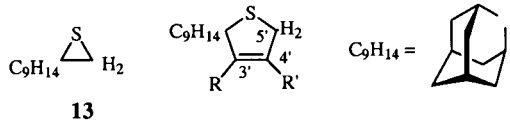
10 11

a 12 b

Aryl- and alkyl-substituted thiocarbonyl ylides are expected to be nucleophilic 1,3-dipoles, because their MO energies should approach those of allyl anions. Nucleophilic 1,3-dipoles will easily combine with electron-deficient dipolarophiles, according to Sustmann's MO perturbation-theoretical treatment of concerted cycloadditions [15]. This is the reason for the preponderance of electrophilic derivatives of acetylene and ethylene in Table 1. No cycloadducts of **12** were obtained with common alkenes and enol ethers, not even with norbornene and norbornadiene. *trans*-Cyclooctene, a potent dipolarophile, furnished the cycloadduct **50** in 40% yield.

The reaction enthalpy should favor cycloadditions to *nonconjugated* olefins, because no conjugation energy has to be sacrificed, in contrast to α,β-unsaturated carboxylic esters or nitriles. The lack of reactivity of common alkenes must have *kinetic* reasons: activation energies are too high.

The cycloadditions were carried out by heating 2 mmoles of **11** with 1.1 equivalents of dipolarophile at 40° in tetrahydrofuran for 8 hours (procedure A) or simply by using an excess of dipolarophile as solvent (procedure B). The crude product was subjected to a quantitative ^1H nmr analysis in deuteriochloroform by comparing the integral of an undisturbed adduct signal with that of a weighed standard. Comparison with the spectrum of the purified cycloadduct reveals whether or not regioisomers were formed.



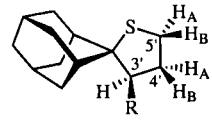
13

	R	R'
14	H	CO_2CH_3
15	CO_2CH_3	H
16	CO_2CH_3	CO_2CH_3

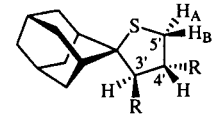
The triple bond of *propiolic ester* accepted **12** in both directions, in contrast to the double bond of acrylic ester or acrylonitrile (see below). The lower regioselectivity of the triple-bonded ester, compared with that of the double-bonded type, appears to be general [16] and may be connected with the higher polarizability of the acetylenic bond. Competition experiments of pairs of dipolarophiles for thiobenzophenone *S*-methylide (**6**) revealed a rather low reactivity of acetylenic carboxylic esters [8].

The assignment of structures **14** and **15** is based on the higher deshielding of 5'-H_2 by 4'-CO_2CH_3, compared with that by 3'-CO_2CH_3; the chemical shifts δ(5'-H_2) are 3.80 for **14** and 3.53 for **15**. The vinyl-H resonates at δ 7.25 in **14** and at 6.05 in **15**; the twisting of the 3'-ester group by the adamantyl residue in **15** diminishes the conjugation and the down-field shift of 4'-H. The allylic coupling of 5'-H_2 in **15** (2.0 Hz) is somewhat smaller than J_{vic} = 2.8 Hz for **15**. In the mass spectra of **14-16**, $M^{+\cdot}$ is the base peak for **15** and **16**, whereas [$M^{+\cdot}$ - CO_2CH_3] plays that role for **14**. Interestingly, the cycloreversion, $M^{+\cdot} \rightarrow$ **12**$^{+\cdot}$ + dipolarophile, is not noticeable. The m/z 91, probably the tropylium ion, appears in the mass spectra of all the adducts of Table 1.

Adducts to C=C Double Bonds.



17 R = CN
18 R = CO_2CH_3



19 R = CN
20 R = CO_2CH_3

The problem of regiochemistry arises in the case of *acrylonitrile* and *methyl acrylate* as dipolarophiles. They combined with **12** furnishing exclusively the 3'-substituted spirothiolanes **17** and **18**. That indicates a superior nucleophilicity of the CH_2 terminus in the thiocarbonyl ylide, symbolized by resonance structure **12a**. The 400 MHz ^1H nmr spectra reveal ABCDE patterns for the five protons of the heteroring. These spectra of higher order were elegantly solved by the iterative computer program DavinX [17]. The result is exemplified in Figure 1 for the 3'-carboxylic ester **18** by comparison of calculated and experimental spectra.

The five δ and eight J values of **18**, presented in Scheme 1, are chosen to demonstrate the structural conclusions. Of the two *gem*-coupling constants, -13.4 Hz is normal for a cyclopentane derivative and is assigned to 4'-H_2; J = -10.0 Hz for 5'-H_2 is lowered by interaction with the *vic*-heteroatom [18]. The deshielding of 5'-H_2 by the ring sulfur is stronger than the influence of the β-located ester function on δ(4'-H_2) [19]. Expectedly, the 3'-H appears at highest frequency (δ 3.48); its doublet of doublets identifies 4'-H_A and 4'-H_B as coupling partners. The regioisomer with the ester group in 4'-position is ruled out. The assignments were confirmed by a DQF-COSY experiment [20].

Table 1

Cycloadditions of Adamantanethione *S*-Methylide (**12**) to Acetylenic and Ethylenic Dipolarophiles at 40° (Data on yields refer to ^{1}H nmr analyses, those in brackets to isolation)

Procedure	Dipolarophile	% Yield	mp °C	Formula
	a. *Acetylenic dipolarophiles*			
B	Methyl propiolate	38 (28)	123-124	**14**
		+ 27 (24)	oil	**15**
B	Dimethyl acetylenedicarboxylate	(87)	119-120	**16**
	b. *Ethylenic dipolarophiles*			
B	Acrylonitrile	82 (73)	71-72	**17**
B	Methyl acrylate	89 (60)	101-102	**18**
A	Fumaronitrile	87 (75)	159-160	**19**
A	Dimethyl fumarate	90 (54)	76-78	**20**
A	Dimethyl maleate	92 (76)	131-132	**24**
A	Maleic anhydride	95 (54)	144-145	**25**
A	*N*-Methylmaleimide	97 (81)	151-152	**26**
A	*N*-Phenylmaleimide	92 (75)	167-168	**27**
A	Tetracyanoethylene	94 (75)	181-182	**28**
A	Dimethyl 2,3-dicyanofumarate	95 (51)	178-179	**29**
	Dimethyl 2,3-dicyanomaleate	+ (3)	125-128	**30**
A	Tetramethyl ethylenetetracarboxylate	84 (60)	122-123	**31**
A	Benzylidenemalononitrile	88 (76)	183-185	**44B**
A	(4-Nitrobenzylidene)malononitrile	91 (90)	238-240	**45B**
A	Methyl α-cyanocinnamate	93 (44)	131-132	**46B**
A	Methyl α-cyano-4-nitrocinnamate	93 (91)	216-218	**47B**
B	*trans*-Cyclooctene	(40)	83-85	**50**

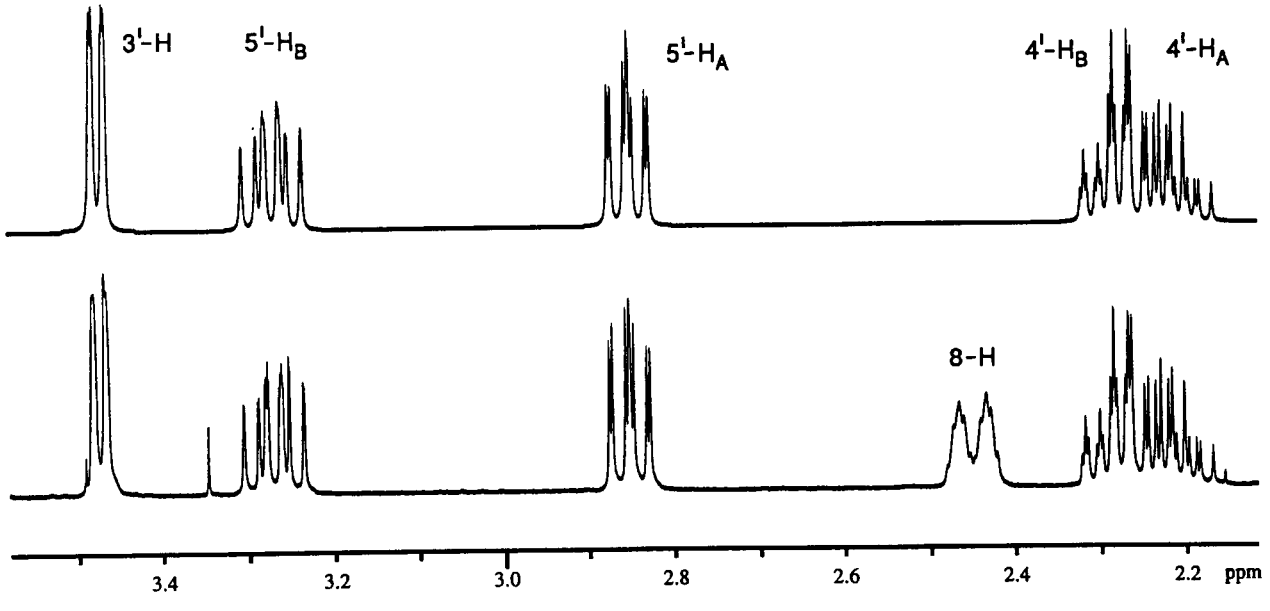
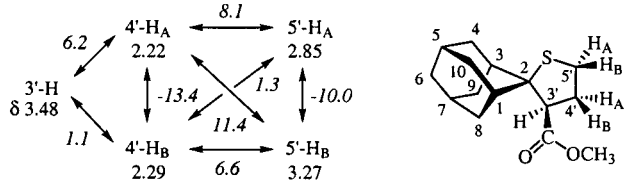


Figure 1. Section of the ^{1}H nmr spectrum (400 MHz, deuteriochloroform) of methyl ester **18** (below) and the DavinX-calculated spectrum of the five thiolane protons (above).

Scheme 1. The ^1H nmr parameters of the heteroring protons of **18**; in italics coupling constants in Hz.

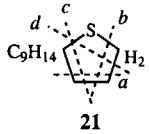
Scheme 1



The space-filling molecular model suggests steric hindrance to rotation for the methyl ester group of **18**, caused by the adamantane system. Even with the plane of the ester function nearly orthogonal to the 5-membered ring, the carbonyl oxygen comes close to one of the 8-H_2 which is downfield shifted to δ 2.45 and appears among the heteroring protons (Figure 1). Dihedral angles were estimated using the Dreiding molecular models: 20° for H-3' — 4'-H_A and 100° for H-3' — 4'-H_B fit J_{cis} = 6.2 Hz and J_{trans} = 1.1 Hz. In the framework of the Karplus-Conroy curve [19], the four J values, which result from coupling between 4'-H_2 and 5'-H_2 (Scheme 1), are likewise reconcilable with crude estimates of twist angles (H_A-4' — 5'-H_A and H_B-4' — 5'-H_B 30°, H_A-4' — 5'-H_B 150°, and H_B-4' — 5'-H_A 90°). In the preferred conformation of the thiolane ring, 3'-CO_2CH_3 and 5'-H_B are in *pseudo-axial* positions; the interaction shifts δ(5'-H_B) to 3.27 which is by 0.4 ppm higher than δ(5'-H_A).

Ten different chemical shifts for the adamantane skeleton in the ^{13}C nmr spectrum establish the chirality of **18**. DEPT differentiated the CH_2 and CH groups, and the two-dimensional HETCOR experiment [21] identified the signals. The range of the five δ(CH_2), 34.7-38.2 ppm, comes close to the value of adamantane itself (δ 37.8); the δ(C-5') and δ(C-4'), 30.4 and 33.1, are even slightly lower. Of the four adamantane-CH of **18**, C-5 and C-7 (δ 26.5, 26.9) resemble the parent (δ 28.4), whereas C-1 and C-3 (δ 36.7, 38.9) are adjacent to the quaternary C-2 (δ 68.9).

The cycloadducts of *fumaronitrile* (**19**) and *dimethyl fumarate* (**20**) show ABCD signals for the four heteroring protons in their ^1H nmr spectra. The multiplicity of the signals makes the assignments unequivocal. The four coupling constants of the 4H system of **20** (see Experimental) correlate well with those of **18** if a stronger buckling of the thiolane with *pseudo-diaxial* positions of the *trans*-CO_2CH_3 groups is assumed.



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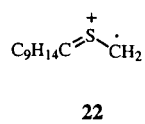

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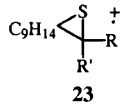


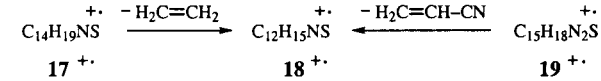
23

	R	R'
a	H	CN
b	H	CO_2CH_3
c	CN	CN
d	CN	CO_2CH_3

In the mass spectra of **17-20**, the molecular peak is the base peak for **17** and **20**; its intensity reaches 90% for **18** and 85% for **19**. The formal fragmentation pathways are shown in **21**. Very often, molecular formulae of splitting products were confirmed by the intensities of isotope peaks, *i.e.*, ^{13}C and (^{34}S+$^{13}C_2$), in some cases also by high resolution. However, the structures proposed for the radical ions are only kind of bookkeeping on the basis of smallest structural changes of the starting material.

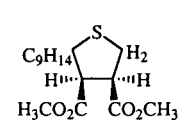
The major fragmentation (path *a* in **21**) is the cycloreversion: $M^{+\cdot} \rightarrow$ **12**$^{+\cdot}$ + dipolarophile; m/z 180 appeared as base peak for **19** and is represented with 16-56% in the other mass spectra. The open-chain structure **12**$^{+\cdot}$ and the cyclic form **13**$^{+\cdot}$ are worth discussing; we prefer the *distonic* ion **22**, *i.e.*, a species in which charge and spin density have different centers [22]. Sulfur loss would be expected for a thiirane radical cation, but $C_{11}H_{16}^{+\cdot}$ is missing in the spectra of **17-20**. On the other hand, CH_2 loss from **22** is prominent; m/z 166 for **10**$^{+\cdot}$ was found with 25-38% in the four ms.

In a second fragmentation pathway of $M^{+\cdot}$ (*b* in **21**), C-4' and C-5' are eliminated, formally olefinic. The mass spectrum of the fumaronitrile adduct **19** shows m/z 205 (20%) for $C_{12}H_{15}NS^{+\cdot}$, [$M^{+\cdot}$- acrylonitrile], established by the intensities of isotope peaks. The same m/z 205 (28%) in the mass spectrum of the acrylonitrile adduct **17** corresponds to the loss of ethylene and offers welcome validation for the regiochemistry of the original cycloaddition. The thiirane radical cation **23a** (or its distonic open-chain variant) is a conceivable candidate for $C_{12}H_{15}NS^+$ (m/z 205). The relations are summarized:



17 $^{+\cdot}$ **18** $^{+\cdot}$ **19** $^{+\cdot}$

Correspondingly, m/z 238 for $C_{13}H_{18}O_2S^{+\cdot}$ (**23b**) was observed as common radical cation in the mass spectra of **18** as [$M^{+\cdot}$- ethylene] and of **20** as [$M^{+\cdot}$- methyl acrylate], although in lower populations. A third fragmentation (*c* in **21**) is suggested by the appearance of m/z 207 for $C_{13}H_{19}O_2^+$ (formally 2-(methoxycarbonylmethylene)-adamantane$^+$, corroborated by isotope peaks and high resolution) in the spectra of **18** (100%) and **20** (29%). The peak m/z 212 (17%, sulfur-free) in the mass spectrum of **19** intimates a fourth fragmentation (*d* in **21**) with [$M^{+\cdot}$- CH_2S].



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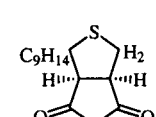
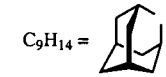


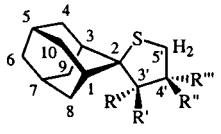


25 X = O
26 X = NCH_3
27 X = NC_6H_5

Dimethyl fumarate and *dimethyl maleate* afforded different cycloadducts, as expected for concerted additions; no mutual admixture of **20** and **24** was observed within the resolution of the ^1H nmr spectrum.

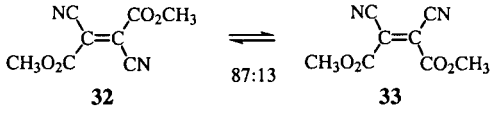
In the cycloadducts of maleic anhydride (**25**), *N*-methylmaleimide (**26**), and *N*-phenylmaleimide (**27**), the fused anhydride or dicarboximide ring stiffens the thiolane conformation. In their ^1H nmr spectra, values of $J_{3',4'}$ (7.2-8.0 Hz) are somewhat higher than those of **17** and **18** (5.5, 6.2 Hz), indicating smaller dihedral angles H-3' — 4'-H. In the mass spectrum of the *maleic anhydride* adduct **25**, the molecular peak (100%) was accompanied by those which show the loss of CO (46%), C_2O_3 (11%), and maleic anhydride (40%).

The adduct **28** of *tetracyanoethylene* (TCNE) has a plane of symmetry. In the ^1H nmr spectrum, the 5'-H_2 appears as a singlet (δ 3.66), and the ^{13}C nmr spectrum shows the reduced set of adamantane signals: one C_q, three CH, and three CH_2. The radical cation of **28** undergoes the cleavages *a-c*, characterized in **21**; the base peak is [M^+- TCNE].



	R	R'	R"	R'"
28	CN	CN	CN	CN
29	CN	E	CN	E
30	CN	E	E	CN
31	E	E	E	E

E = CO_2CH_3

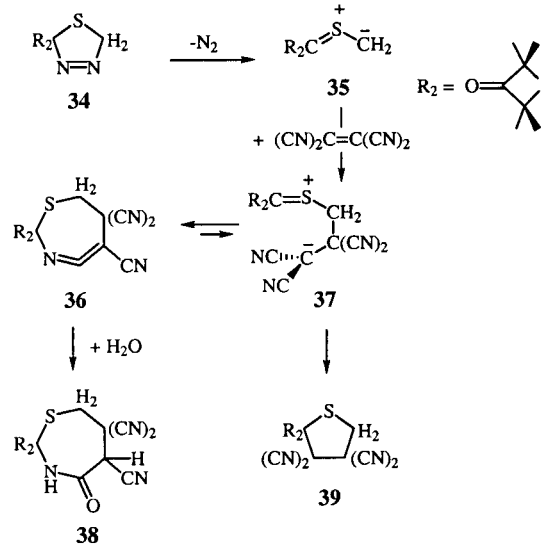


32 87:13 **33**

The *in situ* cycloaddition of **12** to *dimethyl 2,3-dicyanofumarate* (**32**) in tetrahydrofuran provided the *trans*- and *cis*-adducts, **29** and **30**, in 95% yield and in a 3:1 ratio; they were separated and isolated. We regarded the nonstereospecificity of this cycloaddition (and the analogous one of **35**) as an argument for the occurrence of a two-step mechanism [23]. A change from the concerted to the stepwise pathway *via* a zwitterionic intermediate was anticipated for the interaction of a highly nucleophilic 1,3-dipole (high π-MO energies) and a very electrophilic dipolarophile (low π-MO's); a second prerequisite should be steric hindrance on the part of one or both reactants [24].

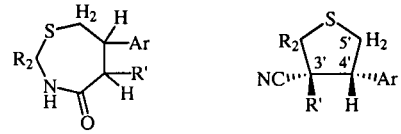
It turned out that the 1,3,4-thiadiazolines **11** and **34** catalyzed the *cis,trans* equilibration of dimethyl dicyanofumarate (**32**) and dicyanomaleate (**33**). A small amount of concentrated sulfuric acid suppressed the catalysis by **34** in deuteriochloroform as solvent; the cycloadditions of thiocarbonyl ylide **35** to **32** and **33** remained nonstereospecific [25]. This was good evidence, that rotation in a zwitterionic intermediate competes with the cyclization affording thiolanes.

The thiadiazoline **11** is a more efficient catalyst than **34** for the equilibration of **32** and **33**, and its suppression by sulfuric acid in deuteriochloroform was incomplete. Probably, it is only a small percentage of the two cycloadditions, **12** + **32** and **12** + **33**, which takes the nonstereospecific pathway [26].

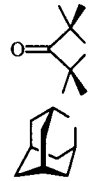


There was a second criterion for the occurrence of a two-step pathway. Reaction of 2,2,4,4-tetramethyl-3-thioxocyclobutanone *S*-methylide (**35**) with tetracyanoethylene furnished thiolane **39**. However, when the solvent tetrahydrofuran contained 1% of water, **39** was accompanied by 45% of the 7-membered lactam **38** [27]. The zwitterion **37** is in equilibrium with the cyclic ketene imine **36**, and the latter was trapped by water forming **38**. An analogous ketene imine, obtained by reaction of **35** with the highly electrophilic 2,3-bis(trifluoromethyl)-fumaronitrile, was even isolated and crystallized [28]; it easily reacted with water affording a 7-membered lactam, analogous to **38**.

When **11** was reacted with tetracyanoethylene in tetrahydrofuran in the presence of 2 vol% of water or methanol, only thiolane **28** was formed in 78% and 89% yield, respectively. Thus, no intermediate ketene imine appears to be involved here. Probably, the steric screening of **12** by the adamantane system is inferior to that which occurs in **35** by the tetramethylcyclobutanone ring.



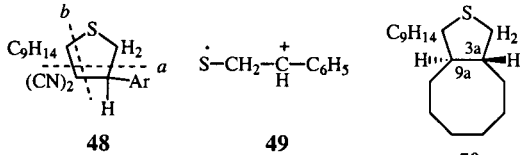
	R'	Ar		
40	CN	C_6H_5	**44**	
41	CN	4-$NO_2C_6H_4$	**45**	
42	CO_2CH_3	C_6H_5	**46**	
43	CO_2CH_3	4-$NO_2C_6H_4$	**47**	



The zwitterionic intermediate **37** requires an excellent stabilization of the anionic charge. We checked the dipolarophilic character of benzylidenemalononitrile and methyl α-cyanocinnamate as well as their *p*-nitro derivatives. Cinnamic ester is a poor dipolarophile, but a second electron-attracting group raises the activity. When thiocarbonyl ylide **35** was reacted with these dipolarophiles in tetrahydrofuran/water (vol. 97:3), in analogy to the reaction with tetracyanoethylene, 35-43% of the 7-membered lactams **40A-43A** were found besides the thiolanes **44A-47A** (30-55%), suggesting again the intermediacy of cyclic ketene imines [29].

On reacting the same benzylidene type dipolarophiles with **12**, the adducts **44B-47B** were formed in 88-93% yield (Table 1). The regiochemistry was established by the ABX pattern of 5'-H_2 and 4'-H in the ^1H nmr spectra; the X part (dd, 4'-H) is the most deshielded at δ 3.97-4.62. There was no evidence for a second regioisomer in the crude reaction solutions. The higher nucleophilicity of the CH_2 group of **12** again dictates the addition direction.

We repeated the reaction of **11** with methyl α-cyano-*p*-nitrocinnamate in tetrahydrofuran which contained 3% of water. The ^1H nmr analysis indicated 93% of **47B**, *i.e.*, the same yield as for the interaction in absolute tetrahydrofuran; no lactam signals appeared. This test, too, teaches that the reactivity of thiocarbonyl ylide **12** is not as easily diverted from the orthodox *concerted* pathway as that of **35**.



48 **49** **50**

In the mass spectra of **44B** and **45B**, the base peak is m/z 180 ($C_{11}H_{16}S^{+\cdot}$, **22**), indicating the cycloreversion. In the second major splitting (*b* in **48**), m/z 136 in the case of **44B** appears with an intensity of 67% and corresponds to $C_8H_8S^{+\cdot}$; the distonic ion **49** is conceivable. The left moiety of fragmentation path b, m/z 198 was found in the ms: of **44B** (4%) and **45B** (1.5%); $C_{13}H_{14}N_2^{+\cdot}$ was confirmed by high resolution and would fit 2-(dicyanomethylene)-adamantane. Further peaks in the mass spectra of **44B** and **45B** point to the radical cations of styrene and nitrostyrene.

In contrast to common alkenes, the highly strained *trans*-cyclooctene combined with thiocarbonyl ylide **12** furnishing **50** in 48% yield. Retention of structure at the double bond is assumed. In the mass spectrum, $\mathbf{10}^{+\cdot}$ features as base peak.

EXPERIMENTAL

Instruments and Techniques.

The ir spectra (potassium bromide discs) were recorded with a Perkin-Elmer 125 or a Beckmann FT IFS 45 instrument. Many of the early nmr spectra, recorded on Bruker WP80 CW (^1H 80 MHz) and Bruker WP80 DS (^{13}C 20 MHz), were repeated using a Varian XR 400S instrument (400 MHz for ^1H, 100 MHz for ^{13}C); these are marked. All nmr spectra were taken in acid-free deuteriochloroform, if not otherwise stated. In the iterative program DavinX [17], the data fed in from the nmr computer are specified with respect to number and rough δ values of the protons and their coupling relations. The program automatically varies the parameters until optimal agreement with the experimental spectrum is achieved. The ms: (EI spectra at 70 eV) were recorded on a AET 902 or a MAT 90 instrument; the latter printed peak intensities with high precision. Intensities of isotope peaks are given in the form, *e.g.*, ^{13}C % Calcd./% Found. High resolutions were obtained with the program CMASS on a MAT 95Q instrument (R >5000); small distortions of m/z can result when isotope peaks of preceding m/z values are not fully separated. tlc is thick-layer (2 mm of silica gel) chromatography. Melting points are uncorrected.

Dipolarophiles.

Dimethyl 2,3-Dicyanofumarate [30], Methyl α-Cyanocinnamate [31], 4-Nitrobenzylidene-malononitrile [32], Methyl α-Cyano-4-nitrocinnamate [33].

General Procedures for Cycloadditions.

A. 2',5'-Dihydrospiro[adamantane-2,2'-(1,3,4)-thiadiazole] (**11**) [12] (416 mg, 2.00 mmoles) and 2.20 mmoles of the dipolarophile in 4 ml of absolute tetrahydrofuran, magnetically stirred, were heated in an oil bath at 40°. Within 8 hours the expected volume of nitrogen was liberated, as controlled by a nitrometer; the final volume was established after cooling to room temperature. After removal of the solvent at the rotary evaporator, the weighed standard was added to the residue, usually *as*-tetrachloroethane (δ_H 4.28), if not stated otherwise. An aliquot of the solution in deuteriochloroform was subjected to quantitative ^1H nmr analysis by comparison of the standard signal with an undisturbed s or d of the product; the machine integrals were evaluated. Separation and purification of the adducts was achieved by recrystallization (mostly from methanol) or tlc.

In procedure B, 2.00 mmoles of **11** and 5 ml of the (less active) dipolarophile were heated without solvent at 40° for 8 hours; the excess of dipolarophile was distilled in vacuum, and the workup followed the description above. Table 1 lists the procedure and the mp, and compares the ^1H nmr-analytical yields and the isolated yields.

Methyl 2',5'-Dihydrospiro[adamantane-2,2'-thiophene]-4'-carboxylate (**14**) and -3'-carboxylate (**15**).

The ^1H nmr analysis, based on the two d of 5'-H_2, indicated 38% of **14** and 27% of **15**. After removal of the deuteriochloroform, the methanolic solution deposited 150 mg (28%) of **14**, which after recrystallization showed mp 123-124°; ir: ν 1228, 1235 st (C-O), 1646 m sharp (conj. C=C), 1723 vst (C=O), 2860, 2885, 2900, 2935 st (sat. C-H), 3050 cm^{-1} w (=C-H); ^1H nmr: δ 1.5-2.3 (m, 14 H), 3.75 (s, OCH_3), 3.80 (d, $^4J_{3',5'} = 2.0$ Hz, 5'-H_2), 7.25 (t, $^4J = 2.0$ Hz, 3'-H); ms: (50°) m/z (%) 264 (61) [M^+], 249 (18) [M^+- CH_3], 233 (9) [M^+- OCH_3], 205 (100) [M^+- CO_2CH_3], 204 (22), 170 (10), 169 (13), 143 (15), 121 (19), 97 (40), 91 (30) [$C_7H_7^+$], 79 (42), 59 (25) [$CH_3OC{\equiv}O^+$].

Anal. Calcd. for $C_{15}H_{20}O_2S$ (264.4): C, 68.14; H, 7.63; S, 12.13. Found: C, 68.38; H, 7.47; S, 12.31.

The residue of the mother liquor was subjected to tlc (petroleum ether/2-propanol 85:15); 125 mg (24%) of the isomer **15**

was isolated as a colorless oil; ir (film): ν 1222, 1258 st (C-O), 1640 w (C=C), 1729 cm^{-1} vst br (C=O); ^1H nmr δ 1.4-2.5 (m, 14 H), 3.53 (d, $J_{4',5'}$ = 2.8 Hz, 5'-H_2), 3.73 (s, OCH_3), 6.05 (t, J = 2.8 Hz, 4'-H); ms: (40°) m/z (%) 264 (100) [M^+], 232 (58) [M^+- CH_3OH; (^{34}S+$^{13}C_2$) 3.2/3.6], 217 (14), 205 (30) [M^+- CO_2CH_3], 204 (11), 156 (14), 150 (27), 129 (20), 93 (30), 91 (57) [$C_7H_7^+$], 79 (66) [$C_6H_7^+$], 59 (21) [$CH_3OC{\equiv}O^+$].

Anal. Calcd. for $C_{15}H_{20}O_2S$ (264.4): C, 68.14; H, 7.63; S, 12.13. Found: C, 67.80; H, 7.47; N, 12.38.

Dimethyl 2',5'-Dihydrospiro[adamantane-2,2'-thiophene]-3',4'-dicarboxylate (**16**).

This compound had ir: ν 1157, 1162, 1220, 1230, 1255, 1300, 1308 st (C-O), 1642 m (C=C), 1728, 1749 cm^{-1} vst (C=O); ^1H nmr: δ 1.5-2.5 (14 H), 3.73 (s, 5 H, OCH_3 and 5'-H_2), 3.83 (s, OCH_3); the coincidence at δ 3.73 is unraveled in [D_5]nitrobenzene: 3.64 (s, 5'-H_2), 3.65, 3.83 (2 s, 2 OCH_3); ms: (80°) m/z (%) 322 (100) [M^+], 290 (77) [M^+- CH_3OH; ^{34}S peak excludes M^+-S], 263 (31) [M^+- CO_2CH_3], 262 (22), 259 (16), 231 (18) [262-OCH_3], 204 (10) [M^+- 2 CO_2CH_3], 203 (11), 170 (26), 131 (22), 91 (20) [$C_7H_7^+$], 79 (30), 59 (19) [$CO_2CH_3^+$].

Anal. Calcd. for $C_{17}H_{22}O_4S$ (322.4): C, 63.33; H, 6.88; S, 9.95. Found: C, 63.62; H, 6.85; S, 9.95.

(±)-Spiro[adamantane-2,2'-thiolane]-3'-carbonitrile (**17**).

The ^1H nmr analysis showed no evidence for a second regioisomer; the colorless crystals of **17** were obtained from methanol; ir: ν 1443, 1453 st; 2230, 2240 m (C≡N), 2855, 2910 cm^{-1} st (C-H); ^1H nmr (400 MHz): δ 1.68-1.94 (m, 12 H), 2.27-2.34 (m, 2 H of adamantyl, superimposed by m of 4'-H_A); the five-proton system in the heteroring was simulated by DavinX [17]: 2.26 (4'-H_A), 2.50 (4'-H_B), 2.93 (5'-H_A), 3.18 (5'-H_B), 3.63 (3'-H), $J_{3',4'A}$ = 5.5 Hz, $J_{3',4'B}$ = 1.3 Hz, $J_{4'A,4'B}$ = -13.1 Hz, $J_{4'A,5'A}$ = 7.4 Hz, $J_{4'A,5'B}$ = 12.0 Hz, $J_{4'B,5'A}$ = 1.1 Hz, $J_{4'B,5'B}$ = 6.2 Hz, $J_{5'A,5'B}$ = -10.7 Hz; ms: (30°) m/z (%) 233 (100) [M^+; ^{13}C 15.6/15.3, (^{34}S+$^{13}C_2$) 5.6/5.1], 205 (28) [M^+- C_2H_4, **23a**; ^{13}C 3.8/4.7; (^{34}S+$^{13}C_2$) 1.5/1.6], 180 (56) [M^+- acrylonitrile, **22**; ^{13}C 6.9/6.9; ($^{13}C_2$+^{34}S) 2.9/2.7], 166 (30) [$C_{10}H_{14}S^+$, **10**$^+$; (^{34}S+$^{13}C_2$) 1.5/1.6], 91 (20) [$C_7H_7^+$].

Anal. Calcd. for $C_{14}H_{19}NS$ (233.4): C, 72.05; H, 8.21; N, 6.00; S, 13.74. Found: C, 72.04; H, 8.15; N, 5.98; S, 13.68.

Methyl Spiro[adamantane-2,2'-thiolane]-3'-carboxylate (**18**).

This compound had ir: ν 1162, 1180, 1219 st (C-O); 1370, 1455 st; 1734 cm^{-1} vst (C=O); ^1H nmr (400 MHz, DavinX, DQF-COSY): δ 1.52-2.08 (m, 13 H), 2.46 (d of quint, J_{gem} = 12.7 Hz, 8-H ?), 3.68 (s, OCH_3); H parameters of thiolane ring see Scheme 1 and Figure 1; ^{13}C nmr (100 MHz, DEPT, HETCOR): δ of CH 26.5, 26.9, 36.7, 38.9 (4 adamantyl-C), 52.8 (C-3'); CH_2 30.4 (C-5'), 33.1 (C-3'), 34.7, 35.0, 35.4, 37.9, 38.2 (5 adamantyl-C); 51.4 (OCH_3), 68.9 (C-2), 173.4 (C=O); ms: (MAT 95Q, 30°, high resolution Calcd./Found) m/z (%) 266.1335/.1332 (90) [M^+; ^{13}C 15.1/15.5], 238.1023/.1018 (6) [$C_{13}H_{18}O_2S^+$, M^+- C_2H_4. **23b**], 234.1074/.1070 (22) [$C_{14}H_{18}OS^+$, M^+- CH_3OH], 219.1380/.1379 (18) [$C_{14}H_{19}O_2^+$, M^+- CH_3S], 207.1380/.1337 (100) [$C_{13}H_{19}O_2^+$, M^+- S-CH=CH_2; ^{13}C 14.5/14.7; the deviation of the experimental high resolution is caused by the ^{13}C peak of m/z 206], 206.1125/.1103 (24) [$C_{13}H_{18}S^+$, M^+- HCO_2CH_3], 205.1224/.1188 (20) [$C_{13}H_{17}O_2^+$], 180.0969/.0955 (26) [$C_{11}H_{16}S^+$, **22**], 174.1041/.1053 (12) [$C_{12}H_{14}O^+$, 205 - OCH_3], 166.0813/.0810 (40) [$C_{10}H_{14}S^+$, **10**$^+$], 159.1170/.1159 (8) [$C_{12}H_{15}^+$], 145.0321/.0327 (8) [$C_6H_9O_2S^+$], 133.1014/.1007 (7) [$C_{10}H_{13}^+$, **10**-SH], 131.0858/.0829 (8) [$C_{10}H_{11}^+$], 117.0702/.0694 (8) [$C_{10}H_{11}^+$].

Anal. Calcd. for $C_{15}H_{22}O_2S$ (266.4): C, 67.63; H, 8.32; S, 12.04. Found: C, 67.44; H, 8.41; S, 12.21.

Spiro[adamantane-2,2'-thiolane]-3',4'-*trans*-dicarbonitrile (**19**).

This compound had ir: ν 2242 cm^{-1} st (C≡N); ^1H nmr: δ 1.4-2.5 (m, 14 H), 3.22, 3.44 (AB of ABCD, 2 dd, J_{gem} = 11.8 Hz, J_{vic} = 6.9, 3.4 Hz, 5'-H_2), 3.79 (C of ABCD, 8 lines visible, 4'-H), 3.95 (d, $J_{3',4'}$ = 1.3 Hz, 3'-H); ms: (110°) m/z (%) 258 (85) [M^+], 212 (17) [M^+- CH_2S; ^{13}C 2.6/2.7, no ^{34}S peak], 205 (20) [M^+- acrylonitrile, $C_{12}H_{15}NS^+$, **23a**; ^{13}C 2.6/2.8; (^{34}S+$^{13}C_2$) 1.0/1.2], 180 (100) [M^+- fumaronitrile, **22**; ^{13}C 12/13; (^{34}S+$^{13}C_2$) 5.1/5.3], 172 (12), 166 (25) [**10**$^+$], 133 (8) [**10**$^+$- SH], 91 (13) [$C_7H_7^+$].

Anal. Calcd. for $C_{15}H_{18}N_2S$ (258.4): C, 69.72; H, 7.02; N, 10.84; S, 12.41. Found: C, 70.05; H, 7.15; N, 10.81; S, 12.47.

Dimethyl Spiro[adamantane-2,2'-thiolane]-*trans*-3',4'-dicarboxylate (**20**).

The ^1H nmr analysis of the d at δ 3.89 with *sym*-tetrachloroethane (weight standard, δ 5.29) showed 90% of **20**; crystals were obtained from methanol, mp 76-78°; ir: ν 1169, 1194, 1213 st (C-O), 1733 cm^{-1} st br (C=O); ^1H nmr (400 MHz): δ 1.56-1.99 (m, 12 H), 2.08 (apparent t, br, 2 H), 2.48 (d of quintet, J_{gem} = 12.9 Hz, 1 H), 3.71, 3.72 (2 s, 2 OCH_3); the 4 H of the heteroring form an ABCD pattern which was solved by DavinX [17]: 3.30 (5'-H_B), 3.34 (5'-H_A), 3.51 (4'-H), 3.96 (3'-H), $J_{3',4'}$ = 3.0 Hz, $J_{4',5'A}$ = 4.7 Hz, $J_{4',5'B}$ = 8.1 Hz, $J_{5'A,5'B}$ = -11.3 Hz; ^{13}C nmr (100 MHz, DEPT): δ CH 26.6, 26.8, 36.6, 38.3; CH_2 31.3 (C-5'), 34.3, 34.7, 35.2, 37.5, 38.1 (5 adamantane-C); 51.9, 52.4 (2 OCH_3), 52.3 (C-4'), 56.2 (C-3'), 69.1 (C-2'), 172.9, 173.2 (2 C=O); ms: (105°) m/z (%) 324 (100) [M^+], 293 (10) [M^+- OCH_3; ^{13}C 1.7/1.9], 265 (12) [M^+- CO_2CH_3, (^{34}S+$^{13}C_2$) 0.67/0.68], 264 (15), 238 (4) [M^+-methyl acrylate, $C_{13}H_{18}O_2S^+$, **23b**; ^{13}C 0.61/0.67, (^{34}S+$^{13}C_2$) 0.23/0.23], 233 (9) [265-CH_3OH, (^{34}S+$^{13}C_2$) 0.49/0.59], 207 (29), $C_{13}H_{19}O_2^+$; ^{13}C 4.1/4.1; no ^{34}S peak], 205 (31), $C_{13}H_{17}O_2^+$], 180 (23) [M^+- dimethyl fumarate, **22**; ^{13}C 2.8/3.1; (^{34}S+$^{13}C_2$) 1.2/1.2], 174 (11), 166 (38) [**10**$^+$, (^{34}S+$^{13}C_2$) 2.1/2.0], 91 (10) [$C_7H_7^+$].

Anal. Calcd. for $C_{17}H_{24}O_4S$ (324.4): C, 62.93; H, 7.46; S, 9.88. Found: C, 62.90; H, 7.39; S, 9.91.

Dimethyl Spiro[adamantane-2,2'-thiolane]-*cis*-3',4'-dicarboxylate (**24**).

Freshly recrystallized **11** was used, because basic impurities catalyze the *cis,trans* isomerization of maleic ester; ir: ν 1174, 1195, 1216, 1239, 1275 st (C-O), 1724, 1744 cm^{-1} st br (C=O); ^1H nmr: δ 1.19-2.69 (m, 14 H), 2.90-3.83 (m, 4 H, 3'-H, 4'-H, 5'-H_2), superimposed by 3.69 (s, broadened, 2 OCH_3); the d at 3.74 due to 3'-H is not fully resolved.

Anal. Calcd. for $C_{17}H_{24}O_4S$ (324.4): C, 62.93; H, 7.46; S, 9.88. Found: C, 63.04; H, 7.28; S, 9.88.

Spiro[adamantane-2,2'-thiolane]-*cis*-3',4'-dicarboxylic Anhydride (**25**) [34].

Freshly sublimed *maleic anhydride* was reacted by procedure A; crystallization of **25** from dichloromethane/cyclohexane; ^1H nmr (400 MHz, ABCD system in the heterocycle simulated by DavinX): δ 1.63-2.0 (m, 11 H), 2.3-2.4 (m, 2 H), 2.59 (dd, 8-H ?), 3.22 (5'-H_A), 3.25 (5'-H_B), 3.76 (4'-H), 3.98 (3'-H), $J_{3',4'}$ = 8.0 Hz, $J_{4',5'A}$ = 1.3 Hz, $J_{4',5'B}$ = 8.4 Hz, $J_{5'A,5'B}$ = -13.0 Hz; ^{13}C nmr (20 MHz, H-decoupled and off-resonance, [D_6]acetone): δ 50.6, 55.2 (2 d, C-3', C-4'), 70.8 (s, C-2), 170.9, 174.6 (2 s, 2 C=O); ms: (80°) m/z (%) 278 (100) [M^+], 250 (46) [M^+- CO; ^{13}C 7.3/7.6;

($^{34}S+^{13}C_2$) 2.6/2.7], 232 (60), 206 (11) [M^+- C_2O_3; ($^{34}S+^{13}C_2$) 0.60/0.88], 205 (24), 204 (14), 180 (40) [**22**, ^{13}C 5.0/5.2; ($^{34}S+^{13}C_2$) 2.1/2.2], 166 (48) [**11**$^+$; ^{13}C 5.4/5.2; ($^{34}S+^{13}C_2$) 2.4/2.6], 121 (9) [$C_9H_{13}^+$], 91 (14) [$C_7H_7^+$].

Anal. Calcd. for $C_{15}H_{18}O_3S$ (278.4): C, 64.72; H, 6.52; S, 11.52. Found: C, 64.52; H, 6.62; S, 11.69.

N-Methylspiro[adamantane-2,2'-thiolane]-3',4'-dicarboximide (**26**).

sym-Tetrachloroethane was the weight standard; the d at δ 3.71 indicated 97% of **26**; ir: ν 1437, 1452 st; 1700 vst, 1772 cm^{-1} m (C=O); ^1H nmr (400 MHz): δ 1.63-2.03 (m, 11 H), 2.34 (m, 1 H), 2.53, 2.62 (2 d br, J_{gem} = 12 Hz, 2 H), 2.99 (s, NCH_3); the ABCD system was simulated by DavinX: 3.10 (5'-H_A), 3.18 (5'-H_B), 3.49 (4'-H), 3.71 (3'-H), $J_{3',4'}$ = 7.2 Hz, $J_{4',5'A}$ = 1.2 Hz, $J_{4',5'B}$ = 8.6 Hz, $J_{5'A,5'B}$ = -12.8 Hz; ms: (60°) m/z (%) 291 (90) [M^+], 180 (22) [**22**; ^{13}C 2.7/2.7], 166 (100) [**10**$^+$], 133 (9) [**10**$^+$- SH], 91 (17) [$C_7H_7^+$].

Anal. Calcd. for $C_{16}H_{21}NO_2S$ (291.4): C, 65.94; H, 7.26; N, 4.81; S, 11.00. Found: C, 65.87; H, 7.22; N, 4.59; S, 11.03.

N-Phenylspiro[adamantane-2,2'-thiolane]-3',4'-dicarboximide (**27**) [34].

This compound had ^1H nmr (400 MHz): δ 1.68-2.08 (m, 11 H), 2.41 (m, 1 H), 2.55, 2.68 (2 d br, J = 13 Hz, 2 H), 3.24, 3.26 (AB of ABCD, 2 dd, $J_{5'A,5'B}$ = 12.8 Hz, $J_{4',5'A}$ = 2.4 Hz, $J_{4',5'B}$ = 7.1 Hz, 5'-H_A, 5'-H_B), 3.65 (appar. dt, 4'-H), 3.88 (d, $J_{3',4'}$ = 7.3 Hz, 3'-H), 7.26-7.49 (m, C_6H_5); ms: (165°) m/z (%) 353 (100) [M^+], 307 (11), 180 (13) [**22**, ^{13}C 1.6/1.7, ($^{34}S+^{13}C_2$) 0.65/0.72], 166 (17) [**10**$^+$, ($^{34}S+^{13}C_2$) 0.84/0.98], 93 (17), 91 (7) [$C_7H_7^+$].

Anal. Calcd. for $C_{21}H_{23}NO_2S$ (353.5): C, 71.35; H, 6.56; N, 3.96; S, 9.07. Found: C, 71.10; H, 6.51; N, 3.95; S, 8.98.

Spiro[adamantane-2,2'-thiolane]-3',3',4',4'-tetracarbonitrile (**28**) [34].

This compound had ^1H nmr (400 MHz): Because of the σ plane, only five discrete, but still broadened signal groups appeared for the adamantane system at δ 1.80 (s, 2 H), 1.93 + 1.96 (2 d, 5 H), 2.05 (s, 1-H), 2.18 (d, J = 12.2, 2 H), 2.57 + 2.61 (d + s, 4 H); 3.68 (s, 5'-H_2); ^{13}C nmr (100 MHz, DEPT): δ CH 25.1, 25.6 (C-5, C-7), 39.0 (C-1/3), CH_2 33.9, 37.3 (C-8/C-9, C-4/C-10), 36.5, 37.1 (C-6, C-5'), C_q 50.5 (C-4'), 54.8 (C-3'), 70.7 (C-2), 110.3 (2 CN), 110.4 (2 CN); ms: (125°) m/z (%) 308 (58) [M^+], 230 (44) [M^+-$H_2C=C(CN)_2$, $C_{13}H_{14}N_2S^+$, **23c**; ^{13}C 6.3/6.8, ($^{34}S+^{13}C_2$) 2.4/2.4], 198 (51) [230-S, $C_{13}H_{14}N_2^+$; ^{13}C 7.3/8.1, no ^{34}S peak], 197 (30), 183 (11), 180 (100) [M^+- tetracyanoethylene, **22**; ^{13}C 12/14], 166 (3) [**10**$^+$], 142 (27), 133 (8) [**10**$^+$- SH], 95 (14), 93 (20), 91 (16) [$C_7H_7^+$], 79 (23), 78 (23), 77 (18).

Anal. Calcd. for $C_{17}H_{16}N_4S$ (308.4): C, 66.20; H, 5.23; N, 18.17; S, 10.40. Found: C, 66.33; H, 5.11; N, 18.20; S, 10.45.

Dimethyl *trans*-3',4'-Dicyanospiro[adamantane-2,2'-thiolane]-3',4'-dicarboxylate (**29**) and *cis*-Isomer **30**.

After the reaction of **11** with **32**, the ^1H nmr spectrum in perdeuteriobenzene established a 3:1 mixture of *trans*- and *cis*-isomer. The *trans*-compound **29** was pure after two recrystallizations from ethanol: 385 mg (51%), mp 178-179°; ir: ν 1250 vst (half-height width 90 cm^{-1}, C-O); 1435, 1458 st; 1762 vst, br (C=O), 2249 cm^{-1} w (C≡N); ^1H nmr: δ 1.5-2.8 (m, 14 H), 3.37, 3.53 (AB, J = 11.9 Hz, 5'-H_2), 3.87, 3.92 (2 s, 2 OCH_3); ms: (100°) m/z (%) 374 (100) [M^+], 343 (4) [M^+- OCH_3], 315 (78) [M^+- CO_2CH_3], 263 (17) [M^+- $H_2C=C(CN)CO_2CH_3$, **23d**; ^{13}C 2.65/2.63], 232 (33) [$C_{14}H_{18}NO_2^+$], 231 (18) [263 - S], 180 (49) [$C_{11}H_{16}S^+$, **22**; ^{13}C 6.0/6.8; ($^{34}S+^{13}C_2$) 2.5/3.0], 166 (8) [**10**$^+$], 133 (6) [**10**$^+$- SH], 91 (18) [$C_7H_7^+$].

Anal. Calcd. for $C_{19}H_{22}N_2O_4S$ (374.5): C, 60.94; H, 5.92; N, 7.48; S, 8.56. Found: C, 60.59; H, 5.90; N, 7.28, S, 8.60.

Isolation of the *cis*-Isomer **30** [35]. The oily residue of the mother liquors of several experiments was subjected to column chromatography on silica gel with cyclohexane/dichloromethane 1:1. On elution, impurities were followed by **29** and then by a crystal fraction which contained about 70% of **30** and 30% of **29**. The solubility of **30** was higher than that of **29** in all the solvents checked. A kinetic crystallization from hexane/dichloromethane was accomplished providing **30** (3%) in colorless platelets, mp 125-128°; ir: ν 1244, 1258 st br (C-O); 1748, 1757 st br (C=O), 2250 cm^{-1} (C≡N); ^1H nmr: δ 3.40, 4.00 (AB, J_{gem} = 11 Hz, 5'-H_2), 3.83, 3.85 (2 s, 2 OCH_3).

Anal. Calcd. for $C_{19}H_{22}N_2O_4S$ (374.5): C, 60.94; H, 5.92; N, 7.48; S, 8.56. Found: C, 60.93; H, 5.92; N, 7.26; S, 8.56.

Tetramethyl Spiro[adamantane-2,2'-thiolane]-3',3',4',4'-tetracarboxlate (**31**).

Upon tlc (dichloromethane/acetone 97:3) 60% of a colorless oil which solidified was obtained, mp 122-123°; ir: ν 1224-1289 vst br (C-O); 1434, 1465 st; 1733, 1750, 1763 cm^{-1} vst (C=O); ^1H nmr: δ 1.5-2.6 (m, 14 H), 3.47 (s, 5'-H_2), 3.71 (s, 2 OCH_3), 3.75 (s, 2 OCH_3); ms: (90°) m/z (%) 440 (91) [M^+], 409 (18), 381 (100) [M^+- CO_2CH_3; ^{13}C 21/23], 349 (10), 321 (13) [381-HCO_2CH_3; ^{13}C 2.5/2.6], 265 (17), 264 (25) [$C_{15}H_{20}O_4^+$, probably M^+- HS-CH=$C(CO_2CH_3)_2$], 243 (31), 233 (56) [264-OCH_3], 180 (44) [**22**], 166 (60) [**10**$^+$], 133 (15) [**10**$^+$- SH], 113 (20), 91 (36) [$C_7H_7^+$].

Anal. Calcd. for $C_{21}H_{28}O_8S$ (440.5): C, 57.26; H, 6.41; S, 7.28. Found: C, 57.27; H, 6.41; S, 7.29.

(±)-4'-Phenylspiro[adamantane-2,2'-thiolane]-3',3'-dicarbonitrile (**44B**).

The protocol was changed for **44B-47B**; 1.00 mmole of **13** and 1.10 mmoles of dipolarophile in 3 ml of absolute tetrahydrofuran were magnetically stirred and heated to 65° for 3 hours. After removal of the THF, the ^1H nmr analysis used *sym*-tetrachloroethane as a weight standard. Besides 88% of **44B**, no second regioisomer was nmr-visible; ir: ν 702 st, 774 m (aromatic CH out-of-plane deformation), 1456 st, 1477, 1501 w (C_6H_5 ring vibration), 2242 cm^{-1} st (C≡N); ^1H nmr: δ 1.5-2.8 (m, 14 H), ABX spectrum at 3.10 (dd, 5'-H_A), 3.45 (t, 5'-H_B), and 3.97 (dd, 4'-H) with J_{AB} = J_{BX} = 11.0 Hz, J_{AX} = 7.1 Hz), 7.12-7.78 (m, C_6H_5); ms: (120°) m/z (%) 334 (61) [M^+; ^{13}C 14.3/14.6, ($^{34}S+^{13}C_2$) 4.3/4.1], 198 (4.1) [$C_{13}H_{14}N_2^+$; ^{13}C 0.59/0.69, no ^{34}S peak], 180 (100) [$C_{11}H_{16}S^+$, **22**; ^{13}C 12.2/12.9); ($^{34}S+^{13}C_2$) 5.1/5.2], 166 (5) [$C_{10}H_{14}S^+$, **10**$^+$], 165 (6), 136 (67) [$C_8H_8S^+$, **49**], 135 (35), 104 (17) [$C_8H_8^+$, styrene$^+$], 91 (21) [$C_7H_7^+$].

Anal. Calcd. for $C_{21}H_{22}N_2S$ (334.5): C, 75.41; H, 6.63; N, 8.38; S, 9.59. Found: C, 75.57; H, 6.81; N, 8.43; S, 9.60.

4'-*p*-Nitrophenylspiro[adamantane-2,2'-thiolane]-3',3'-dicarbonitrile (**45B**).

Light-yellow crystals were obtained from ethyl acetate; ir: ν 1351, 1521 st (NO_2), 2245 cm^{-1} w (C≡N); ^1H nmr ([D_6]acetone): δ 1.6-3.2 (m, 14 H), ABX: 3.38, 3.52 (2 overlapping dd, 5'-H_A and 5'-H_B), 4.62 (dd, 4'-H) with J_{AB} = 10.5 Hz, J_{AX} = 8.5 Hz, J_{BX} = 11 Hz; 7.80-8.08 (AA'BB', C_6H_4); ms: (MAT 95Q, 80 °, high resolution, Calcd./Found) m/z (%) 379.1350/.1347 (79) [M^+; ^{13}C 18/20; ($^{34}S+^{13}C_2$) 5.6/6.1], 198.1154/.1140 (3.0)

[$C_{13}H_{14}N_2^+$, probably 2-(dicyanomethylene)adamantane], 197.1076/.1066 (1.5) [$C_{13}H_{13}N_2^+$], 180.0969/.0970 (100) [$C_{11}H_{16}S^+$, **22**; ^{13}C 12/13; (^{34}S+$^{13}C_2$) 5.1/5.3], 166.0813/.0799 (5.4) [$C_{10}H_{14}S^+$, **10**$^+$], 149.0475/.0431 (1.4) [$C_8H_7NO_2^+$, nitrostyrene$^+$], 147.1170/.1158 (2.4) [$C_{11}H_{15}^+$], 134.0189/.0186 (9) [$C_8H_6S^+$], 133.1014/.1008 (3.7) [$C_{10}H_{13}^+$, **10**$^+$- SH].

Anal. Calcd. for $C_{21}H_{21}N_3O_2S$ (379.5): C, 66.46; H, 5.58; N, 11.07; S, 8.45. Found: C, 66.49; H, 5.68; N, 10.82; S, 8.49.

Methyl 3'-Cyano-4'-phenylspiro[adamantane-2,2'-thiolane]-3'-carboxylate (**46B**).

This compound had ir: ν 702 st, 780 m (aromatic out-of-plane deformation); 1221 m, 1243 st br (C-O); 1456 m, 1496 w (C_6H_5 vibration), 1740 st (C=O), 2245 cm^{-1} w (C≡N); ^1H nmr: δ 1.4-2.7 (m, 14 H), ABX at 2.90 (dd, 5'-H_A), 3.37 (dd, 5'-H_B), 4.23 (dd, 4'-H) with J_{AB} = 10.5 Hz, J_{AX} = 5.5 Hz, J_{BX} = 12.5 Hz; 3.59 (s, OCH_3), 7.15-8.05 (m, C_6H_5); ms: (100°) m/z (%) 367 (66) [M$^+$], 308 (4.4) [M$^+$- CO_2CH_3; ^{13}C 0.99/1.13], 231 (5) [$C_{14}H_{17}NO_2^+$], 180 (100) [**22**; ^{13}C 12.2/12.5; (^{34}S+$^{13}C_2$) 5.1/5.0], 166 (11) [**10**$^+$, $C_{10}H_{14}S^+$], 136 (27) [$C_8H_8S^+$], 135 (17), 104 (9). 91 (14) [$C_7H_7^+$].

Anal. Calcd. for $C_{22}H_{25}NO_2S$ (367.5): C, 71.90; H, 6.86; N, 3.81; S, 8.73. Found: C, 72.00; H, 6.78; N, 3.79; S, 8.70.

Methyl 3'-Cyano-4'-*p*-nitrophenylspiro[adamantane-2,2'-thiolane]-3'-carboxylate (**47B**).

The s at δ 3.69 indicated 93% of **47B**; the same yield was observed in a second experiment which was carried out in moist tetrahydrofuran (3% of water). 91% of **47B** was isolated as pale-yellow crystals from methanol; after recrystallization from ethyl acetate mp 216-218° was observed; ir: ν 1221, 1251 st (C-O); 1348 vst, 1521 st (NO_2), 1598, 1606 w (aromatic ring vibration), 1740 st (C=O), 2245 w (C≡N); ^1H nmr: δ 1.3-2.8 (m, 14 H); 2.94 (dd, 5'-H_A), 3.38 (pseudo-t, 5'-H_B), and 4.36 (dd, 4'-H) with $J_{5'A,5'B}$ = 11.0 Hz, $J_{4',5'A}$ = 6.0 Hz, $J_{4',5'B}$ = 12.5 Hz; 3.63 (s, OCH_3), 7.57, 8.12 (AA'BB', C_6H_4); ms: (145°) m/z (%) 412 (19) [M$^+$], 353 (5) [M$^+$- CO_2CH_3], 180 (100) [**22**; may also contain $O_2NC_6H_4$-CH_2-C≡S$^+$], 166 (19) [**10**$^+$], 151 (9), 133 (11) [**10**$^+$-SH], 91 (30) [$C_7H_7^+$].

Anal. Calcd. for $C_{22}H_{24}N_2O_4S$ (412.5): C, 64.05; H, 5.86; N, 6.79; S, 7.77. Found: C, 64.41; H, 5.93; N, 6.62; S, 7.79.

Decahydrospiro[adamantane-2,1'-cycloocta[*c*]thiophene] (**50**).

Upon tlc (pentane/diethyl ether 9:1) 48% of a colorless oil as the first fraction was obtained which solidified and was recrystallized from ethanol; ^1H nmr: δ 1.1-2.2 (m, 26 H), 2.3-2.9 (m, 4 H); ms: (40°) m/z (%) 290 (53) [M$^+$], 243 (12) [M$^+$- CH_2S - H, no ^{34}S peak; ^{13}C 2.4/2.3], 180 (36) [**22**; (^{34}S+$^{13}C_2$) 1.9/1.9], 166 (100) [**10**$^+$], 91 (10) [$C_7H_7^+$].

Anal. Calcd. for $C_{19}H_{30}S$ (290.5): C, 78.55; H, 10.41; S, 11.04. Found: C, 78.61; H, 10.42; S, 11.08.

Acknowledgements.

We express our thanks to the *Fonds der Chemischen Industrie*, Frankfurt, for supporting our research. G.M. thanks the Alexander von Humboldt-Stiftung for a stipend. We thank *Reinhard Seidl* and Dr. *Werner Spahl* for the MS, *Helmut Schulz* and *Magdalena Schwarz* for the numerous elemental analyses. Furthermore, our thanks are going to Dipl. Chem. *Claudia Fulka* and Dr. *Elke Langhals* for some of their experiments included in this paper.

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