170. Synthesis and Reactions of 2-(Alkylthio)-4,4-dimenthyl-1,3-thiazole-5(4*H*)-thiones

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Dedicated to Prof. Heinz G. Viehe on the occasion of his 65th birthday

(2.IX.94)

Six 2-(alkylthio)-substituted 4,4-dimethyl-1,3-thiazole-5(4H)-thiones were synthesized according to a new method. The reactions of these compounds with allyl- and benzyllithium reagents, 1,3-dipoles, and dimethyl acetylenedicarboxylate proceeded in a similar manner to 2-alkyl-substituted analogues, while methyllithium reacted in a different way yielding trithio-orthoester derivatives.

1. Introduction. – A few years ago, due to the lack of appropriate synthetic methods, 1,3-thiazole-5(4H)-thiones were only scarcely known five-membered heterocycles. In 1986, a convenient synthesis of 4,4-disubstituted 1,3-thiazole-5(4H)-thiones was developed by our group [1] [2]. It is based on a reaction involving reactive three-membered rings, the 3-amino-2H-azirines [3]: the addition reaction of thiocarboxylic acids and 3-amino-2H-azirines yielded thiodiamides. On heating with Lawesson reagent [4–6], cyclization of the thioamides afforded 2-substituted 1,3-thiazole-5(4H)-thiones in very good yields [2].

Another approach to 1,3-thiazole-5(4H)-thiones is the reaction of carboxylic acids with 3-amino-2H-azirines affording diamides; after thionation of the latter with *Heimgartner* reagent [7], 2-substituted 1,3-thiazole-5(4H)-thiones were obtained in fair-to-good yields [7].

However, 1,3-thiazole-5(4H)-thiones with substituents other than alkyl or aryl at C(2) are not accessible by these methods. Since 2-seleno- and 2-thio-substituted 4,5-dihydro-1,3-thiazoles could be useful intermediates in penam syntheses [8] [9], new approaches for the preparation of differently substituted 1,3-thiazole-5(4H)-thiones are still needed. In this paper, a new approach for the synthesis of 2-(alkylthio)-substituted 1,3-thiazole-5(4H)-thiones is described, and some reactions of these compounds with organolithium reagents, 1,3-dipoles, acetylenes, and reducing agents are reported and compared with the 2-alkyl-substituted analogues.

2. Synthesis of 2-(Alkylthio)-Substituted 1,3-Thiazole-5(4H)-thiones 1. – A synthesis was designed for 2-(alkylthio)-substituted 1,3-thiazole-5(4H)-thiones 1, based on the addition of trithiocarbonic acids 4 with 3-amino-2H-azirine 5, and subsequent cycliza-

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tion. The trithiocarbonic acids 4, prepared *in situ* from the addition of alkanethiolates 2 to CS_2 at 0°, followed by acidification with dry HCl gas, reacted with 5 to give dithiocarbamate 6. On treatment with HCl gas at room temperature, 6 afforded the 1,3-thiazole-5(4H)-thiones 1 (*Scheme 1*).

In most cases, the yields of **1a**-f were very good (*Table 1*), only 2-(isopropylthio)- and 2-(*tert*-butylthio)-1,3-thiazole-5(4*H*)-thiones, **1c** and **1d**, respectively, were formed in lower yields. The main by-product formed together with **1d** was 2,3,4,5-tetrahydro-4,4-dimethyl-1,3-thiazole-2,5-dithione (7). The structures of **1d** and 7 have been established by X-ray crystallography (*Fig. 1*).



Table 1. 2-(Alkylthio)-1,3-thiazole-5(4H)-thiones 1a-f Prepared According to Scheme 1

2	R	1	Yield [%]
2a	Me	1a	90
2b	Et	1b	92
2c	i-Pr	1c	43
2d ^a)	t-Bu	1d	33
2e ^a)	PhCH ₂	1e	86
2f ^a)	C ₁₂ H ₂₅	lf	81

^a) Prepared *in situ* from the corresponding thiol and NaH.



Fig. 1. ORTEP Diagram [10] of the molecular structures of a) 1d and b) 7

The five-membered ring of 1d is planar, and this planarity extends right through the side chain to the atom C(6) (*Fig. 1, a*). The mean deviation from the least-squares plane is 0.039 Å. The distribution of C-S bond lengths is quite large (1.73–1.86 Å), but can probably be attributed to electronic interactions within the five-membered ring.

In the crystal, 7 exists as the NH tautomer with two C=S bonds. Each molecule is involved in weak H-bonding between the N-H donor group and the S-atom acceptor of the C=S group neighboring the N-H group of an adjacent molecule (N···S distance 3.372(1) Å, H···S distance 2.55(1) Å; N-H···S angle 170(2)°). These molecules are related by a centre of inversion, so that the molecules are linked into dimeric units by pairs of H-bonds.

A likely mechanism for the formation of 7 via elimination of the t-Bu group in the cyclization step of 6d is shown in Scheme 2. In addition, the coupling products bis[(tert-butyl)trithiocarbonate] and di(tert-butyl) disulfide were isolated in small quantities, perhaps being formed via oxidation and radical coupling.



It is worth mentioning that the whole procedure can be conducted as a one-pot reaction. After removal of the solvent, 1,3-thiazole-5(4H)-thiones 1a-f were obtained by flash chromatography with hexane/CH₂Cl₂. Moreover, the intermediate dithiocarbamates 6 could also be isolated. *E.g.*, from the reaction of sodium methanethiolate (2a), CS_2 , and 5, 6a was obtained as a white crystalline material in 85% yield. As indicated by its NMR spectrum, 6a is in equilibrium with its imino tautomer. Under acidic conditions, 6a afforded 4,4-dimethyl-2-(methylthio)-1,3-thiazole-5(4H)-thione (1a) in 91% yield.

The mechanism for the formation of 2-(alkylthio)-substituted 1,3-thiazole-5(4H)thiones might be similar to that described for the thiocarboxylic acid/aminoazirine method [2]. The difference is that trithiocarbonic acids 4 replace the thiocarboxylic acids. The reaction with 5 affords the relatively stable dithiocarbamates 6 via ring enlargement of an intermediate aziridine, followed by ring opening (Scheme 3). Under acidic conditions, 6 cyclizes to 1 by elimination of the amine (cf. Scheme 2).

The attempt to synthesize the 2-(phenylthio) analogue failed, because sodium thiophenol did not react with CS_2 . After chromatography, only diphenyl disulfide was isolated, which had been formed *via* a radical pathway.



3. Addition Reactions of Organolithium Reagents and 1. – In the reactions of 2-alkylor 2-phenyl-substituted 1,3-thiazole-5(4H)-thiones with organometallic reagents, it has been shown that organolithium compounds undergo thiophilic addition exclusively [11]. In contrast, organocuprates only afford products of carbophilic addition [12] [13], while *Grignard* reagents react via carbophilic and/or thiophilic addition, depending on the nature of the *Grignard* reagent and the solvent used in the reaction [11]. Recently, we have found that allyl- and benzyllithium reagents unexpectedly react with various 2alkyl- and 2-phenyl-substituted 1,3-thiazole-5(4H)-thiones via carbophilic attack [14]. Here, we report on reactions of 2-(alkylthio)-substituted 1,3-thiazole-5(4H)-thiones 1 with methyl-, allyl-, and benzyllithium reagents.

3.1. Addition of MeLi. The addition reactions of 1a-c with MeLi were carried out at -78° in THF. After treatment with H₂O at $-78^{\circ} \rightarrow$ room temperature overnight, **8a**, **8c**, and **8e** were isolated in fair yields (*Table 2*).

The suprising result is that these products are not dithioacetals, as in the reaction of MeLi with 2-alkyl-substituted 1,3-thiazole-5(4H)-thiones [14], but trithio-orthoesters. Apparently, a MeS group at C(5) in 8 is formed by thiophilic addition of MeLi to the C=S S-atom of 1a-c, while the other alkylthio group at C(5) has been transferred from C(2) of a second molecule of 1. To confirm that an intermolecular transfer of an alkylthio or

$\frac{1) \text{ MeLi}'-78^{\circ}/10 \text{ min}}{2) \text{ H}_20/-78^{\circ} \rightarrow r.t/overnight} \xrightarrow{N}_{RS} \xrightarrow{N}_{S} \xrightarrow{R^1}_{SMe}$					
		1		8	
1	R	Disulfide	R ⁱ	8	Yield [%]
1a	Me	_	MeS	8a	36
la	Me	PhSSPh	PhS	8b	65
1b	Et	-	EtS	8c	41
1b	Et	MeSSMe	MeS	8d	35
1c	i-Pr		i-PrS	8e	34

Table 2. Reaction of 2-(Alkylthio)-1,3-thiazole-5(4H)-thiones 1a-c with MeLi

arylthio group to C(5) occurs, several sulfur compounds, including thiols, sulfides, and disulfides, were added to the reaction mixture. Thiols and sulfides had no effect on the reaction, *e.g.*, the reaction of **1b** and MeLi yielded **8c** in the presence and absence of *t*-BuSH or Me₂S. In contrast, disulfides do influence the reaction remarkably: in the presence of MeSSMe, **1b** and MeLi yielded **8d**, a MeS-transfer product from MeSSMe, instead of **8c**. Similarly, in the presence of PhSSPh, the reaction of **1a** and MeLi led to **8b** in 65% yield by a PhS-group transfer. These results suggest some similarity of the alkylthio or arylthio moieties in disulfides and in 2-(alkylthio)-substituted 1,3-thiazole-5(4H)-thiones **1**. Both of them can be transferred to C(5) of **1a**-**c** in the presence of an organolithium compound; however, the alkylthio or arylthio group in disulfides is more easily transferred. These results strongly suggest that the reaction proceeds *via* a radical mechanism. To confirm this, the radical-capturing agent Bu₃SnH was added to the solution of **1a** and MeLi to suppress the formation of **8a**. Indeed, **8a** was obtained in only 5% yield. However, this experiment is not conclusive, because it was shown in a control experiment that Bu₃SnH slowly destroyed the starting material **1a**.

3.2. Addition of Allyl- and Benzyllithium Reagents. Allyllithium was generated from allyl phenyl ether [15], while PhCH₂Li was prepared from (PhCH₂)₂O by cleavage with Li [16] [17]. At -78° in THF, 4,4-dimethyl-2-(methylthio)-1,3-thiazole-5(4H)-thione (1a) was treated with benzyl- and allyllithium reagents. After methylation with MeI, adducts 9a and 9b, respectively, were obtained in modest yields (Scheme 4).



These results are consistent with those of the reactions of allyl- and benzyllithium reagents with 2-alkyl-substituted 1,3-thiazole-5(4H)-thiones, in which the carbophilic additions were also observed exclusively [14].

4. 1,3-Dipolar Cycloaddition with 1. – According to the concept of 1,3-dipolar cycloaddition, discovered by *Huisgen* [18–21], thiocarbonyl compounds are dipolarophiles that smoothly react with 1,3-dipoles to give five-membered S-heterocycles. Recently, it has been shown that 4,4-disubstituted 1,3-thiazole-5(4H)-thiones are active dipolarophiles that undergo cycloadditions with the exocyclic C=S group [1] [22]. *E.g.*, the reaction of 4,4-dimethyl-2-phenyl-1,3-thiazole-5(4H)-thione and benzonitrilium betaines (benzonitrile oxide, -phenylimide, and -2-propanide) yielded stable spiro-heterocycles in high yield [23–25]. Therefore, it was of interest to study the reactivity of the new 2-(alkylthio)-substituted 1,3-thiazole-5(4H)-thiones 1a-f towards 1,3-dipoles.

4.1. With Benzonitrile Oxide. Benzonitrile oxide (11) was generated in situ from $N-(\alpha$ -chlorobenzylidene)hydroxylamine (10) in the presence of Et₃N [26]. The reaction with 1a-f in Et₂O at room temperature afforded, after chromatography, the expected cycloadducts 12 in very good yields (*Table 3*).

$\begin{array}{c} CI \\ Ph \end{array} = N \\ OH \end{array} \xrightarrow{Et_3N} Ph \xrightarrow{H} O^{-} \\ \hline H^{-} = N \\ \hline H^{-} O^{-} \\ \hline H^{-} = N \\ \hline H^{-} O^{-} \\ \hline H^{-} = N \\ \hline H^{-} \\$					
1 0	11		1 2		
1	R	12	Yield [%]		
1a	Me	12a	98		
16	Et	12b	98		
1c	i- P r	12c	98		
1d	t-Bu	12d	87		
le	PhCH ₂	12e	80		
1f	C ₁₂ H ₂₅	12f	94		

Table 3. 1,3-Dipolar Cycloaddition of Benzonitrile Oxide with 1a-f

In each reaction, only one isomer (as a racemate) was obtained, *i.e.*, the 1,3-dipolar cycloaddition proceeds in a regiospecific manner. The structures of **12a**-**f** were assigned according to their spectroscopic data, in particular the ¹³C-NMR chemical shifts.

4.2. With Benzonitrile 2-Propanide. In the presence of 1a, irradiation of 2,2-dimethyl-3-phenyl-2*H*-azirine (13) using a UV high-pressure Hg lamp with a *Pyrex*-filter afforded the two cycloaddition products 15 and 16 (Scheme 5).



Apparently, the reaction occurred through the intermediate benzonitrile 2-propanide (14), which was generated photolytically from 13. As a reactive 1,3-dipole, 14 underwent cycloaddition to 1a in a non-regiospecific manner to give 15 and 16 in a ratio of 15:1. This regioselectivity is quite similar to that of the analogous reaction with the 2-Ph-substituted 1,3-thiazole-5(4H)-thiones [24]. The structures of the two isomers 15 and 16 were confirmed by X-ray crystallography (*Fig. 2*). Since both 15 and 16 crystallize in centrosymmetric space groups, the crystals are racemic. In case of 15, there are two independent molecules in the asymmetric unit; however, there are no significant differences between the conformations of these molecules.

4.3. With Benzonitrile Phenylimide. It is well known that 2,5-diphenyl-2H-tetrazole (17) yields benzonitrile phenylimide (18) as a reactive intermediate either photochemically or thermally. Earlier experiments showed that 4,4-dimethyl-2-phenyl-1,3-thiazole-5(4H)-thione and 17 react under thermal conditions (reflux in mesitylene for 23 h) to afford the corresponding spiro-cycloadduct in fair yield; under photochemical conditions, no product was isolated [24] [27]. However, 1a and 17, under similar thermal conditions, led to a complex reaction mixture, from which only 16% of the expected



spiro-heterocycle 19 was isolated after chromatography. On the other hand, under photochemical conditions (irradiation in EtOH with a Hg high-pressure lamp behind Pyrex, 80 min), 1a and 17 reacted to give the cycloadduct 19 in 41% yield (*Scheme 6*).

The formation of only small amounts of 19 under thermal conditions is not due to the instability of the starting material 1a, because 1a was stable at 140° in mesitylene in the absence of 17. By monitoring the reaction by TLC, it was shown that 19 was already present in the reaction mixture after 1 h. As the reaction time was prolonged, several by-products appeared on TLC. After 24 h, no cycloadduct could be detected.



a) UV/EtOH/ 80 min (41%). b) 104°/3 h/mesitylene (16%).

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4.4. With Organoazides. Usually, organoazides react with thiocarbonyl compounds to give imines [28]. Formation of the corresponding imine was reported to occur also with azides and 2-phenyl- and 2-alkyl-1,3-thiazole-5(4H)-thiones [29]. In an analogous manner, heating of 2-(alkylthio)-4,4-dimethyl-1,3-thiazole-5(4H)-thiones of type 1 with alkyl azides 20 in toluene at 90° led to imines 21 in fair-to-good yields (*Table 4*).

$R_{\rm R} = \frac{1}{1000} + \frac{1}{1000} + \frac{1}{100000} + \frac{1}{100000000} + \frac{1}{10000000000000000000000000000000000$					
	H:	1	20	2 1	
1	R	20	R ¹	Time [d]	21 (Yield [%])
1a	Me	20a	C ₆ H ₁₃	4	21a (72)
1b	Et	20a	C_6H_{13}	3	21b (87)
1e	PhCH ₂	20a	$C_{6}H_{13}$	4	21c (65)
lf	$C_{12}H_{25}$	20a	$C_{6}H_{13}$	5	21d (93)
1a	Me	20ь	Cyclohexyl	5	21e (82)
le	i-Pr	20ь	Cyclohexyl	5	21f (68)
1a	Me	20c	EtOCOCH ₂	3	21g (90)
1b	Et	20d	1-Adamantyl	6	21h (83)
1c	i-Pr	20d	l-Adamantyl	8	21i (82)
1a	Me	20e	Ts	4	21j (11)

Usually, the reactions were run for 3-5 d in order to consume all of the starting material 1, but, with the bulky 1-azidoadamantane (20d), 6-8 d were required. Tosyl azide (20e) was less reactive towards 2-(methylthio)-1,3-thiazole-5(4H)-thione (1a). After heating in toluene at 90° for 4 d, imine 21j was obtained in only 11% yield. Apparently, the electron withdrawal of the Ts group has a retarding effect on the reaction.

Considering the steric hindrance caused by two Me groups in 1,3-thiazole-5(4H)-thiones 1, the formation of (Z)-imines should be favored in the reactions of organoazides 20 and 1. This was confirmed for imine 21g by X-ray crystallography (*Fig. 3*).



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The mechanism of the reaction of 1,3-thiazole-5(4*H*)-thiones **1** and azides involves the 1,3-cycloadduct **22** and/or **23** as an intermediate [29] (*Scheme 7*), which undergoes elimination of N_2 and S to afford the imine **21**, presumably *via* a spirocyclic thiaziridine **24** [30] [31].



This reaction mechanism is supported by the following facts: a) in the reaction of thioketene and alkyl azides, the 1,3-diplar cycloadducts were isolated as stable compounds [32] [33]; b) the reaction of 2,2,4,4-tetramethyl-3-(thioxo)cyclobutanone and phenyl azide yields a thiocarbonyl-imide intermediate which was trapped by a second thiocarbonyl group [34]; c) the elimination of S, similar to the proposed sequence $22/23 \rightarrow 24 \rightarrow 21$, was observed in several reactions [29] [35].

5. Cyclosubstitution Reactions with Dimethyl Acetylenedicarboxylate. – Five-membered heterocycles with an exocyclic double bond are known to react with electron-deficient acetylenes in a concerted, pericyclic reaction called cyclosubstitution [36]. It has been shown by our group that 2-aryl-substituted 1,3-thiazole-5(4H)-thiones 1 also react in this manner with various acetylenes to give 1,4-dithiafulvenes of type 25 and/or thiophene-2(3H)-thiones of type 26, depending on the ratio of acetylenedicarboxylate and 1, and the reaction conditions [37]. In an analogous reaction, 4,4-dimethyl-2-(methylthio)-1,3-thiazole-5(4H)-thione (1a) and dimethyl acetylenedicarboxylate in toluene was sealed in a glass tube and heated to 85° for 15 h. After chromatography, the two products 25 and 26 [37] were obtained in 43% yield as a 2:3 mixture (Scheme 8).



The reaction with **1a** favors the formation of 2-thioxothiophene-4,5-dicarboxylate **26**, a secondary cyclosubstitution product of **25** and dimethyl acetylenedicarboxylate [1] [36], whereas, with 2-aryl-substituted 1,3-thiazole-5(4H)-thiones at similar or even higher temperatures, the 1,4-dithiafulvene **25** is predominantly, if not exclusively, formed.

6. Reduction to Thiol Compounds. – Thiocarbonyl groups are easily reduced to thiol groups by many reducing reagents, including some organometallic compounds; NaBH₄ and LiAlH₄ are the most frequently used and very efficient reagents. In EtOH, reduction of 2-MeS-substituted 1,3-thiazole-5(4H)-thione 1a with NaBH₄ at room temperature afforded, after chromatography, the thiol 27 in a yield of 65% (Scheme 9).



7. Conclusion. – 2-(Alkylthio)-substituted 1,3-thiazole-5(4H)-thiones have been easily prepared by a concise synthesis in a one-pot reaction. Except for some bulky (alkylthio)-substituted derivatives, the yields are excellent. In this simple and general method, alkanethiolate, CS₂, and 3-amino-2*H*-azirines are starting materials.

The 2-(alkylthio)-substituted 1,3-thiazole-5(4*H*)-thiones 1 behave quite similarly to 2-alkyl-substituted analogues in 1,3-dipolar cycloadditions, cyclosubstitutions, reduction with NaBH₄, and oxidation to the corresponding sulfines [38]. The reactions of 1 with allyl- and benzyllithium reagents are also consistent with those of 2-alkyl-substituted analogues [14]; exclusive carbophilic addition is observed. In contrast, the reactions of 1 with MeLi yield unexpected products. After thiophilic attack of MeLi onto the C=S group, an alkylthio moiety is transferred to C(5) of the lithiodithioacetal intermediate leading to a trithio-orthoester instead of the dithioacetal structure. These results are not easily explained by ionic mechanisms, but might be explained by a radical pathway [39]. This proposal is supported by the fact that, in the presence of MeSSMe and PhSSPh, the MeS and PhS group, respectively, is attached to C(5) of the trithio-orthoester derivative.

Financial support of this work by the Swiss National Science Foundation and F. Hoffmann-La Roche AG, Basel, is gratefully acknowledged. Our thanks are also due to Mr. H. Frohofer for elemental analyses and for running IR spectra, Mr. T. Plüss for recording NMR spectra, Dr. A. Lorenzi-Riatsch for mass spectra, and Mr. M. Knöpfel for performing some experiments.

Experimental Part

General. See [40]. M.p.: *Mettler-FP5* apparatus; uncorrected. IR Spectra: *Perkin-Elmer 297* or *Perkin-Elmer 781* spectrophotometer in CHCl₃, unless stated otherwise; absorption in cm⁻¹. ¹H-NMR Spectra: unless indicated otherwise, *Bruker-AC-300* (300 MHz), *Varian EM-390* (90 MHz), and *Bruker AM-400* (400 MHz) spectrometer, in CDCl₃; chemical shifts in ppm; TMS (0 ppm) or CDCl₃ (7.27 ppm) as internal standard; coupling constants *J* in Hz. ¹³C-NMR Spectra: *Varian XL-200* (50.4 MHz) spectrometer in CDCl₃, unless stated otherwise; chemical shifts in ppm; CDCl₃ (77.0 ppm) as internal standard; multiplicity from DEPT spectra. MS: *Varian MAT-711, Varian MAT-112, Finnigan MAT-90, Finnigan SSQ-700*, and *Finnigan TSQ-700* mass spectrometers; E1 mode: direct injection, 70 eV; C1 mode: with 2-methylpropane or NH₃.

1. Synthesis of 1,3-Thiazole-5(4H)-thiones 1. – General Procedure. Into a suspension of sodium alkanethiolate 2 (12 mmol) in Et₂O (60 ml) at 0°, CS₂ (912 mg, 12 mmol) was added dropwise through a syringe and the reaction maintained at 0° for 2 h. Then, dry HCl gas was introduced into the suspension at 0° for 2 h. After removal of the solvent *i.v.*, the residue was dissolved in Et₂O (60 ml). At 0°, a soln. of 2,2-dimethyl-3-(N-methyl-N-phenylamino)-2H-azirine (5; 696 mg, 4 mmol) in Et₂O (4 ml) was added dropwise, the mixture stirred at 0° for 20 min and at r.t. overnight. After removal of the solvent *i.v.*, toluene (60 ml) was added and dry HCl gas introduced at r.t. during 2 h. The solvent was again removed, and chromatography with hexane/CH₂Cl₂ (8:1, then 4:1), yielded 1 as an orange product.

1.1. 4,4-Dimethyl-2-(methylthio)-1,3-thiazole-5(4H)-thione (1a). a) 690 mg (90%). Orange oil. B.p. 95–100°/ 0.05 Torr. IR: 2990m, 2940m, 2860w, 1575s, 1465m, 1455m, 1435m, 1420w, 1380w, 1360m, 1320w, 1240w, 1120s, 985s, 960s, 905s, 830s, 650m. ¹H-NMR: 2.64 (s, MeS); 1.54 (s, 2 Me). ¹³C-NMR: 249.8 (s, C(5)); 159.2 (s, C(2)); 96.0 (s, C(4)); 29.4 (q, 2 Me); 14.6 (q, MeS). C1-MS: 194 (15), 193 (9), 192 (100, [M + 1]⁺).

b) Into a suspension of **2a** (210 mg, 3 mmol) in Et₂O (10 ml) at 0°, CS₂ (228 mg, 3 mmol) was added and the reaction maintained at 0° for 2 h. Dry HCl gas was introduced into the suspension at 0°, the solvent removed *i.v.*, and Et₂O (10 ml) was added. A soln. of **5** (174 mg,1 mmol) in Et₂O (1 ml) was added dropwise, the mixture stirred at 0° for 20 min, and at r.t. overnight. After removal of the solvent *i.v.* and chromatography with hexane/AcOEt 8:1, 252 mg (85%) of S-methyl-N-[1-methyl-1-(N-methyl-N-phenylthiocarbamoyl)ethyl]dithiocarbamate (**6a**) were obtained. White crystals. M.p. 170–171°. IR: 3360m, 2980m, 2920w, 1595w, 1490s, 1465m, 1430m, 1385m, 1370s, 1355s, 1310w, 1250w, 1185w, 1170w, 1160w, 1105s, 1075w, 1030w, 1005m, 960w, 705m. ¹H-NMR: 7.45–7.25 (*m*, 5 arom. H); 6.92 (*s*, CONH); 3.69 (*s*, MeN); 2.51 (*s*, MeS); 1.89 (*s*, 2 MeN); 30.4, 28.6 (2q, 2 Me); 17.8 (q, MeS). CI-MS: 301 (5), 300 (7), 299 (43, [M + 1]⁺), 253 (10), 252 (14), 251 (100).

Into a soln. of **6a** (298 mg, 1 mmol) in toluene (10 ml) at r.t., dry HCl gas was introduced during 2 h. After removal of the solvent *i.v.* and chromatography with hexane/AcOEt 8:1, 173 mg (91%) of **1a** were obtained.

1.2. 2-(*Ethylthio*)-4,4-dimethyl-1,3-thiazole-5(4H)-thione (**1b**). 752 mg (92%). Orange oil. B.p. $100-110^{\circ}/$ 0.05. Torr. IR: 2990s, 2940m, 2880w, 1575s, 1465m, 1455m, 1440m, 1420w, 1380m, 1360m, 1270m, 1130s, 1120s, 1060m, 985s, 965s, 905s, 830s, 645m. ¹H-NMR: 3.22 (q, J = 7, MeCH₂S); 1.54 (s, 2 Me); 1.42 (t, J = 7, MeCH₂S). ¹³C-NMR: 249.7 (s, C(5)); 158.4 (s, C(2)); 96.0 (s, C(4)); 29.3 (q, 2 Me); 26.5 (t, MeCH₂S); 14.3 (q, MeCH₂S). CI-MS: 208 (21), 207 (14), 206 (100, [M + 1]⁺).

1.3. 2-(Isopropylthio)-4,4-dimethyl-1,3-thiazole-5(4H)-thione (1c). 376 mg (43%). Orange oil. B.p. $135-145^{\circ}/$ 0.06 Torr. IR: 2980m, 2940m, 2875m, 1575s, 1465m, 1455m, 1390w, 1370m, 1360m, 1245m, 1160m, 1120s, 1060m, 985s, 960s, 905s, 830s, 655m. ¹H-NMR: 3.99 (sept., J = 7, Me₂CH); 1.54 (s, Me₂C(4)); 1.46 (d, J = 7, Me₂CH). ¹³C-NMR: 249.9 (s, C(5)); 158.1 (s, C(2)); 96.1 (s, C(4)); 38.0 (d, Me₂CH); 29.3 (q, Me₂C(4)); 22.9 (q, Me₂CHS). CI-MS: 222 (13), 221 (11), 220 (100, [M + 1]⁺).

1.4. 2-[(tert-Butyl)thio]-4,4-dimethyl-1,3-thiazole-5(4 H)-thione (1d). Sodium 2-methylpropane-2-thiolate (2d) was prepared in situ from 2-methylpropane-2-thiol and NaH in Et₂O at 0°. According to the General Procedure, 314 mg (33%) of 1d and 192 mg (27%) of 2,3,4,5-tetrahydro-4,4-dimethyl-1,3-thiazole-2,5-dithione (7) were obtained.

Data of 1d: Orange crystals. M.p. 50–51°. IR: 2975*m*, 2950*m*, 2920*m*, 2860*w*, 1570*m*, 1470*w*, 1450*m*, 1390*w*, 1360*m*, 1350*w*, 1230*w*, 1160*m*, 1145*m*, 1115*s*, 1020*w*, 975*m*, 945*s*, 900*m*, 820*m*. ¹H-NMR: 1.62 (*s*, *t*-Bu); 1.55 (*s*, Me₂C). ¹³C-NMR: 250.1 (*s*, C(5)); 156.9 (*s*, C(2)); 51.3 (*s*, Me₃CS); 30.3 (*q*, Me₂C); 29.3 (*q*, Me₃CS). CI-MS: 236 (15), 235 (13), 234 (100, $[M + 1]^+$), 158 (6), 157 (13).

Data of 7: Orange crystals. M.p. 151.5–153.5°. IR (KBr): 3120*m*, 2975*m*, 2920*m*, 2850*w*, 2820*m*, 1510*s*, 1450*m*, 1375*m*, 1355*m*, 1335*m*, 1240*w*, 1190*w*, 1120*s*, 1020*s*, 975*m*, 935*m*, 835*m*, 715*m*, 650*m*. ¹H-NMR: 8.63 (br. *s*, NH); 1.67 (*s*, 2 Me). ¹³C-NMR ((D_6)DMSO): 242.4 (*s*, C(5)); 188.6 (*s*, C(2)); 84.7 (*s*, C(4)); 28.9 (*q*, 2 Me). EI-MS: 179 (8), 178 (10), 177 (68, M^+), 117 (11), 103 (9), 102 (8), 101 (44), 100 (100), 86 (13), 85 (17), 76 (26), 74 (51), 71 (20), 69 (11), 68 (11), 60 (11), 59 (52), 58 (18), 57 (11), 53 (9). Anal. calc. for C₅H₇NS₃ (177.31): C 33.87, H 3.98, N 7.90; found: C 34.26, H 4.38, N 7.87.

1.5. 2-(Benzylthio)-4,4-dimethyl-1,3-thiazole-5(4H)-thione (1e). Sodium phenylmethanethiolate (2e) was prepared in situ from benzenethiol and NaH in Et₂O. According to the General Procedure, 917 mg (86%) of 1e were obtained. Orange oil. B.p. 180°/0.06 Torr. IR: 3065w, 2990m, 2940m, 2865w, 1605w, 1575s, 1500m, 1455m, 1435w, 1415w, 1380w, 1360w, 1245w, 1125s, 1075w, 1035m, 985m, 965s, 905s, 865w, 830m, 700m, 650m. ¹H-NMR: 7.45-7.25 (m, 5 arom. H); 4.45 (s, PhCH₂S); 1.55 (s, 2 Me). ¹³C-NMR: 249.6 (s, C(5)); 158.1 (s, C(2)); 136.0 (s, 1 arom. C); 129.1, 128.6, 127.7 (3d, 5 arom. C); 95.9 (s, C(4)); 36.1 (t, PhCH₂S); 29.4 (q, 2 Me). CI-MS: 270 (14), 269 (14), 268 (100, $[M + 1]^+$).

1.6. 2-(Dodecylthio)-4,4-dimethyl-1,3-thiazole-5(4H)-thione (1f). Sodium dodecane-1-thiolate (2f) was prepared in situ from dodecane-1-thiol and NaH in Et₂O. According to the General Procedure, 558 mg (81%) of 1f were obtained. Orange oil. IR: 2975s, 2920s, 2915s, 2850s, 1570s, 1460m, 1430m, 1410w, 1375m, 1350m, 1120s, 980s, 960s, 900s, 825s, 640m. ¹H-NMR: 3.20 (t, J = 7.3, CH₂S); 1.8–1.7 (m, 1 CH₂); 1.53 (s, Me₂C); 1.45–1.25 (m, 9 CH₂); 0.89 (t, J = 7, Me). ¹³C-NMR: 249.9 (s, C(5)); 158.7 (s, C(2)); 96.0 (s, C(4)); 32.1, 31.9, 29.6, 29.5, 29.4, 29.34, 29.30, 29.02, 28.99, 28.6, 22.6 (11t, 11 CH₂); 29.3 (q, Me_2 C); 14.1 (q, Me). CI-MS: 349 (3), 348 (15), 347 (20), 346 (100, [M + 1]⁺).

2. Reaction of 1 with Organolithium Reagents. 2.1. Reactions with MeLi. General Procedure. Into a soln. of 1 (0.5 mmol) in THF (3 ml) at -78° , the organometallic reagent was added dropwise. After 10 min, t-BuCl (0.25 mmol) was added and the mxiture stirred 5 min at -78° . Then, the soln. was poured into a mixture of sat. aq. NH₄Cl (20 ml) and Et₂O (50 ml). The org. layer was separated, dried, and the solvent evaporated *i.v.* Chromatography with hexane/Et₂O 25:1 yielded the addition product.

2.1.1. 4,5-Dihydro-4,4-dimethyl-2,5,5-tris(methylthio)-1,3-thiazole (**8a**). From **1a** (86 mg, 0.45 mmol) and MeLi (0.38 ml, 0.6 mmol), 41 mg (36%) of **8a** were obtained. Colorless oil. IR: 2985s, 2925m, 2860w, 1565s, 1555s, 1455m, 1435m, 1420m, 1385m, 1365m, 1315w, 1240w, 1160m, 1010m, 990s, 965m, 950s, 910w, 865m, 650w. ¹H-NMR: 2.50 (*s*, MeS-C(2)); 2.23 (*s*, 2 MeS-C(5)); 1.50 (*s*, 2 Me). ¹³C-NMR: 160.7 (*s*, C(2)); 89.2 (*s*, C(4)); 83.8 (*s*, C(5)); 24.7 (*g*, 2 Me); 16.8 (*g*, 2 MeS-C(5)); 14.8 (*g*, MeS-C(2)). CI-MS: 256 (16), 255 (10), 254 (100, $[M + 1]^+$), 208 (12), 206 (7). Anal. calc. for C₈H₁₅NS₄ (253.47): C 37.91, H 5.97, N 5.53, S 50.60; found: C 38.12, H 6.08, N 5.34, S 50.10.

2.1.2. 4,5-Dihydro-4,4-dimethyl-2,5-bis(methylthio)-5-(phenylthio)-1,3-thiazole (**8b**). Reaction of **1a** (96 mg, 0.5 mmol) with MeLi (0.94 ml, 1.5 mmol) in the presence of PhSSPh (218 mg, 1 mmol) afforded 102 mg (65%) of **8b**. Colorless oil. IR: 2975*m*, 2920*m*, 1560*s*, 1550*s*, 1470*w*, 1450*w*, 1435*m*, 1410*w*, 1380*w*, 1360*w*, 1310*w*, 1155*m*, 1065*w*, 1020*w*, 1000*w*, 980*s*, 940*m*, 910*w*, 860*w*, 845*w*, 700*w*, 685*m*. ¹H-NMR: 7.65–7.6 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 2.45 (*s*, MeS–C(2)); 2.27 (*s*, MeS–C(5)); 1.60, 1.53 (2*s*, 2 Me). ¹³C-NMR: 161.3 (*s*, C(2)); 132.2 (*s*, 1 arom. C); 136.7, 129.5, 128.4 (3*d*, 5 arom. C); 90.5 (*s*, C(4)); 84.0 (*s*, C(5)); 24.8, 24.3 (2*q*, 2 Me); 17.5, 14.8 (2*q*, 2 MeS). CI-MS: 318 (18), 317 (17), 316 (100, [*M* + 1]⁺).

2.1.3. 2,5-Bis(ethylthio)-4,5-dihydro-4,4-dimethyl-5-(methylthio)-1,3-thiazole (8c). From 1b (103 mg, 0.5 mmol) and MeLi (0.38 ml, 0.6 mmol), 60 mg (41%) of 8c were obtained. Pale-yellow oil. IR: 2980s, 2935m, 2880m, 1565s, 1555s, 1455m, 1440m, 1420m, 1380m, 1365m, 1270m, 1160m, 1060w, 1010w, 980s, 955s, 910w, 870m, 700w. ¹H-NMR: 3.05–2.95 (m, MeCH₂S–C(2)); 2.75–2.6 (m, MeCH₂S–C(5)); 2.16 (s, MeS); 1.44, 1.39 (2s, 2 Me); 1.27, 1.20 (2t, $J = 7.37, 7.43, 2 MeCH_2S$). ¹³C-NMR: 160.4 (s, C(2)); 88.3 (s, C(4)); 83.9 (s, C(5)); 28.1, 26.6 (2t, 2 MeCH₂S); 24.7, 24.3 (2q, 2 Me); 17.1 (q, MeS); 14.6, 13.7 (2q, 2 MeCH₂S). CI-MS: 284 (19), 283 (15), 282 (100, [M + 1]⁺), 268 (4), 234 (8), 222 (16), 220 (7). Anal. calc. for C₁₀H₁₉NS₄ (281.53): C 42.66, H 6.80, N 4.98, S 45.56; found: C 42.83, H 6.91, N 4.98, S 45.27.

2.1.4. 2-(*Ethylthio*)-4,5-*dihydro*-4,4-*dimethyl*-5,5-*bis*(*methylthio*)-1,3-*thiazole* (**8d**). Reaction of **1b** (103 mg, 0.5 mmol) with MeLi (0.38 ml, 0.6 mmol) in the presence of MeSSMe (94 mg, 1 mmol) afforded 47 mg (35%) of **8d**. Colorless oil. IR: 2970*m*, 2920*m*, 1560*s*, 1550*s*, 1450*w*, 1430*w*, 1410*w*, 1380*w*, 1360*w*, 1260*w*, 1155*m*, 975*m*, 965*s*, 945*s*, 860*w*, 720*s*, 665*m*. ¹H-NMR: 3.07 (q, J = 7.4, MeCH₂S); 2.24 (s, 2 MeS); 1.51 (s, 2 Me); 1.35 (t, J = 7.4, MeCH₂S). ¹³C-NMR: 160.2 (s, C(2)); 88.7 (s, C(4)); 83.8 (s, C(5)); 26.7 (t, MeCH₂S); 24.6 (q, 2 Me); 16.8 (q, 2 MeS); 14.5 (q, MeCH₂S). CI-MS: 271 (2), 270 (19), 269 (14), 268 (100, [M + 1]⁺), 221 (5), 220 (11), 219 (3).

2.1.5. 2,5-Bis(isopropylthio)-4,5-dihydro-4,4-dimethyl-5-(methylthio)-1,3-thiazole (8e). From 1c (118 mg, 0.54 mmol) and MeLi (0.4 ml, 0.65 mmol), 56 mg (34%) of 8e were obtained. Pale-yellow oil. IR : 2970s, 2920m, 2860m, 1560m, 1550m, 1460m, 1450m, 1440m, 1415w, 1380m, 1360m, 1240m, 1155m, 1050m, 1005w, 975s, 950s, 860m, 660w. ¹H-NMR: 3.74 (sept., J = 6.8, Me₂CHS-C(2)); 3.16 (sept., J = 6.9, Me₂CHS-C(5)); 2.13 (s, MeS); 1.50, 1.33 (2s, 2 Me); 1.30, 1.29 (2d, J = 6.8, 6.9, 2 Me_2 CHS). ¹³C-NMR: 160.6 (s, C(2)); 87.3 (s, C(4)); 84.6 (s, C(5)); 38.4, 37.7 (2d, 2 Me₂CHS); 24.9, 24.44, 24.38, 23.9, 23.2, 22.9 (6g, 2 Me, 2 Me_2 CHS); 17.4 (g, MeS). CI-MS: 312 (19), 311 (20), 310 (100, [M + 1]⁺), 262 (7). Anal. calc. for C₁₂H₂₃NS₄ (309.58): C 46.56, H 7.49, N 4.52, S 41.43; found: C 46.64, H 7.41, N 4.52, S 41.40.

2.2. Reactions with Allyl- and Benzyllithium Reagents. The allyllithium soln. was prepared from allyl phenyl ether (670 mg, 5 mmol) and Li in Et_2O according to [15]; the PhCH₂Li soln. was prepared from (PhCH₂)₂O (396 mg, 2 mmol) and Li according to [16].

General Procedure. Into a soln. of **1a** (0.5 mmol) in THF (3 ml) at -78° , the organometallic reagent was added dropwise. After stirring for 10 min, the alkyl halide (1 mmol) was added and the reaction maintained at $-78^\circ \rightarrow r.t.$ overnight. Workup and purification proceeded as in *Exper. 2.1*.

2.2.1. 5-Benzyl-4,5-dihydro-4,4-dimethyl-2,5-bis(methylthio)-1,3-thiazole (9a). From 1a (100 mg, 0.52 mmol), PhCH₂Li, and MeI (74 mg, 0.52 mmol), 63 mg (41%) of 9a were obtained. Yellow powder. M.p. 68–69°. IR;

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3000*m*, 2980*m*, 2930*m*, 1565*s*, 1555*s*, 1500*m*, 1455*m*, 1435*m*, 1420*w*, 1385*w*, 1365*w*, 1315*w*, 1170*m*, 1080*w*, 1030*w*, 1010*m*, 990*s*, 950*m*, 940*m*, 915*w*, 700*s*. ¹H-NMR: 7.3–7.15 (*m*, 5 arom. H); 3.46, 2.92 (*AB*, *J* = 13.8, PhCH₂); 2.42 (*s*, MeS-C(2)); 1.78 (*s*, MeS-C(5)); 1.55, 1.29 (2*s*, 2 Me). ¹³C-NMR: 161.3 (*s*, C(2)); 137.7 (*s*, 1 arom. C); 130.0, 128.0, 127.1 (3*d*, 5 arom. C); 83.4, 82.5 (2*s*, C(4), C(5)); 42.2 (*t*, PhCH₂); 23.7, 23.2 (2*q*, 2 Me); 15.2, 14.8 (2*q*, 2 MeS). CI-MS: 300 (15), 299 (18), 298 (100, $[M + 1]^+$), 284 (14), 250 (10), 193 (3), 115 (8). Anal. calc. for C₁₄H₁₉NS₃ (297.51): C 56.52, H 6.44, N 4.71, S 32.33; found: C 56.29, H 6.27, N 4.54, S 32.00.

2.2.2. 5-Allyl-4,5-dihydro-4,4-dimethyl-2,5-bis(methylthio)-1,3-thiazole (9b). From 1a (96 mg, 0.5 mmol), allyllithium, and MeI (142 mg, 1 mmol), 82 mg (66%) of 9b were obtained. Yellow oil. IR: 2980m, 2935m, 1640w, 1565s, 1555s, 1460w, 1435m, 1420m, 1385w, 1360w, 1315w, 1240w, 1170m, 1125w, 990s, 955m, 925m. ¹H-NMR: 5.95-5.8 (m, CH₂=CH); 5.15-5.05 (m, CH₂=CH); 2.85-2.55 (m, CH₂); 2.41 (s, MeS-C(2)); 2.06 (s, MeS-C(5)); 1.47, 1.20 (2s, 2 Me). ¹³C-NMR: 161.1 (s, C(2)); 134.6 (d, CH₂=CH); 118.1 (t, CH₂=CH); 82.2, 81.5 (2s, C(4), C(5)); 39.6 (t, CH₂); 24.1, 23.3 (2q, 2 Me); 14.8, 14.7 (2q, 2 MeS). CI-MS: 250 (14), 249 (13), 248 (100, $[M + 1]^+$), 200 (19). Anal. calc. for C₁₀H₁₇NS₃ (247.45); C 48.54, H 6.92, N 5.66, S. 38.87; found: C 48.33, H 7.20, N 5.71, S 38.50.

3. Cycloadditions of 1 with 1,3-Dipoles. – 3.1. With Benzonitrile Oxide. General Procedure. Into a soln. of N- $(\alpha$ -chlorobenzylidene)hydroxylamine (10; 78 mg, 0.5 mmol) and 1 (0.5 mmol) in Et₂O (5 ml) at r.t., Et₃N (2 ml) was added dropwise and the reaction maintained at r.t. for 30 min. Then, the mixture was filtered, the filtrate concentrated *i.v.* and chromatographed with hexane/Et₂O 25:1.

3.1.1. 9,9-Dimethyl-7-(methylthio)-3-phenyl-1-oxa-4,6-dithia-2,8-diazaspiro[4.4]nona-2,7-diene (12a). From 1a (96 mg, 0.5 mmol), 152 mg (98%) of 12a were obtained. White crystals. M.p. 87.8–88.0°. IR: 2970w, 2920m, 1560m, 1550m, 1490w, 1455m, 1440m, 1425w, 1380w, 1360m, 1310w, 1270m, 1230w, 1170m, 1010m, 1000m, 980s, 945m, 920m, 880s, 685m, 640m. ¹H-NMR: 7.6–7.55 (m, 2 arom. H); 7.45–7.35 (m, 3 arom. H); 2.46 (s, MeS); 1.60, 1.43 (2s, 2 Me). ¹³C-NMR: 161.3 (s, C(7)); 156.3 (s, C(3)); 128.5 (s, 1 arom. C); 131.4, 128.9, 127.7 (3d, 5 arom. C); 127.1 (s, C(5)); 81.7 (s, C(9)); 27.2, 21.3 (2q, 2 Me); 14.4 (q, MeS). CI-MS: 313 (14), 312 (13), 311 (100, [M + 1]⁺). Anal. calc. for C₁₃H₁₄N₂S₃ (310.46); C 50.29, H 4.55, N 9.02, S 30.98; found: C 50.03, H 4.30, N 8.78, S 30.82.

3.1.2. 7-(*Ethylthio*)-9,9-dimethyl-3-phenyl-1-oxa-4,6-dithia-2,8-diazaspiro[4.4]nona-2,7-diene (**12b**). From **1b** (96 mg, 0.5 mmol), 158 mg (98%) of **12b** were obtained. White crystals. M.p. 59.0–59.3°. IR : 3060w, 2970m, 2925m, 2870w, 1550m, 1450m, 1445m, 1380m, 1360m, 1310w, 1275m, 1235w, 1170m, 1055w, 1045w, 1010m, 1000m, 970s, 925m, 880s, 685m, 655w, 640m. ¹H-NMR: 7.6–7.55 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 3.15–2.9 (*m*, MeCH₂S); 1.59, 1.43 (2s, 2 Me); 1.30 (t, J = 7.4, MeCH₂S). ¹³C-NMR: 160.5 (s, C(7)); 156.2 (s, C(3)); 128.1 (s, 1 arom. C); 131.4, 128.8, 127.8 (3d, 5 arom. C); 127.1 (s, C(5)); 81.7 (s, C(9)); 27.2, 21.3 (2q, 2 Me); 26.4 (t, MeCH₂S); 1.4.4 (q, MeCH₂S). CI-MS: 327 (13), 326 (15), 325 (100, [M + 1]⁺), 190 (45). Anal. calc. for C₁₄H₁₆N₂OS₃ (324.49): C 51.82, H 4.97, N 8.63, S 29.64; found: C 52.10, H 5.07, N 8.63, S 29.41.

3.1.3. 7-(*Isopropylthio*)-9,9-dimethyl-3-phenyl-1-oxa-4,6-dithia-2,8-diazaspiro[4.4]nona-2,7-diene (**12c**). From **1c** (110 mg, 0.5 mmol), 166 mg (98%) of **12c** were obtained. Pale-yellow crystals. M.p. 64–65°. IR: 2970m, 2920m, 2860w, 1580w, 1560m, 1550m, 1490w, 1460m, 1445m, 1380m, 1360m, 1310w, 1275m, 1240w, 1170m, 1155w, 1055m, 1010m, 1000m, 970s, 925m, 880m, 685m, 650m. ¹H-NMR: 7.6–7.55 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 3.77 (*sept.*, *J* = 6.8, Me₂CHS); 1.59, 1.44 (2s, 2 Me); 1.33, 1.32 (2d, *J* = 6.8, Me₂CHS). ¹³C-NMR: 160.2 (*s*, C(7)); 156.2 (*s*, C(3)); 131.4, 128.8, 127.7 (3d, 5 arom. C); 127.9, 127.2 (2s, 1 arom. C, C(5)); 81.8 (*s*, C(9)); 37.6 (*d*, Me₂CHS); 27.1, 21.3 (2q, 2 Me); 23.3, 22.7 (2q, Me₂CHS). CI-MS: 341 (14), 340 (22), 339 (100, [*M* + 1]⁺), 204 (14). Anal. calc. for C₁₅H₁₈N₂OS₃ (338.51): C 53.22, H 5.36, N 8.28, S 28.42; found: C 53.48, H 5.45, N 8.52, S 28.17.

3.1.4. 7-[(tert-Butyl)thio]-9,9-dimethyl-3-phenyl-1-oxa-4,6-dithia-2,8-diazaspiro[4.4]nona-2,7-diene (12d). According to the General Procedure, reaction of 1d (116 mg, 0.5 mmol) and 10 (78 mg, 0.5 mmol) in the presence of Et₃N (2 ml) at 0° for 1.5 h afforded 152 mg (87%) of 12d. White crystals. M.p. 82.0–82.5°. IR: 2960m, 2920m, 2900m, 2860w, 1580w, 1560s, 1490w, 1475w, 1450m, 1445m, 1390w, 1380w, 1360m, 1310w, 1275s, 1165m, 1000m, 965s, 945s, 880s, 685m, 640m. ¹H-NMR: 7.6–7.55 (m, 2 arom. H); 7.4–7.35 (m, 3 arom. H); 1.60, 1.44 (2s, 2 Me); 1.49 (s, t-Bu). ¹³C-NMR: 158.7, 156.3 (2s, C(7), C(3)); 131.3, 128.8, 127.8 (3d, 5 arom. C); 127.2, 127.1 (2s, 1 arom. C, C(5)); 82.5 (s, C(9)); 50.3 (s, Me₃C); 30.4 (q, Me₃C); 27.2, 21.3 (2q, 2 Me). CI-MS: 355 (17), 354 (21), 353 (100, [M + 1]⁺), 297 (6). Anal. calc. for C₁₆H₂₀N₂OS₃ (352.54): C 54.51, H 5.72, N 7.95, S 27.29; found: C 54.71, H 5.99, N 7.90, S 27.15.

3.1.5. 7-(*Benzylthio*)-9,9-dimethyl-3-phenyl-1-oxa-4,6-dithia-2,8-diazaspiro[4.4]nona-2,7-diene (12e). From 1e (147 mg, 0.55 mmol), 170 mg (80%) of 12e were obtained. White crystals. M.p. 101.4–101.6°. IR: 3050w, 3030w, 2995w, 2970w, 2930w, 1600w, 1565m, 1555m, 1490w, 1450w, 1445w, 1380w, 1360w, 1275m, 1225m, 1200m, 1170w, 1010w, 1000w, 970s, 925w, 880m, 780s, 730s, 720s, 685m, 665m, 645w. ¹H-NMR: 7.7–7.65 (m, 2 arom. H); 7.5–7.3 (m, 8 arom. H); 4.42, 4.30 (*AB*, *J* = 13.2, PhCH₂S); 1.70, 1.50 (2s, 2 Me). ¹³C-NMR: 160.2 (s, C(7)); 156.3 (s, C(3)); 136.4, 128.6 (2s, 2 arom. C); 131.4, 129.0, 128.8, 128.4, 127.8, 127.4 (6d, 10 arom. C); 127.1 (s, C(5)); 36.0 (t,

PhCH₂S); 27.2, 21.3 (2q, 2 Me). CI-MS: 389 (15), 388 (22), 387 (95, $[M + 1]^+$), 254 (9), 253 (15), 252 (100). Anal. calc. for C₁₉H₁₈N₂OS₃ (386.56): C 59.04, H 4.69, N 7.25, S 24.88; found: C 58.90, H 4.85, N 7.05, S 24.81.

3.1.6. 7-(*Dodecylthio*)-9,9-dimethyl-3-phenyl-1-oxa-4,6-dithia-2,8-diazaspiro[4.4]nona-2,7-diene (12f). In analogy to *Exper. 3.1.4*, from 1f (172 mg, 0.5 mmol), 219 mg (94%), of 12f were obtained. White crystals. M.p. 40.5°. IR: 2920s, 2840m, 1560m, 1550m, 1450m, 1440m, 1380w, 1360w, 1270m, 1195w, 1170w, 1010w, 970s, 920w, 880m, 710m, 685m, 660m. ¹H-NMR: 7.6-7.55 (m, 2 arom. H); 7.45-7.35 (m, 3 arom. H); 3.1-2.9 (m, CH₂S); 1.65-1.6 (m, CH₂); 1.59, 1.43 (2s, 2 Me); 1.3-1.2 (m, 9 CH₂); 0.81 (t, J = 6, Me). ¹³C-NMR: 160.7 (s, C(7)); 156.1 (s, C(3)); 131.3, 129.8, 127.7 (3d, 5 arom. C); 128.1 (s, 1 arom. C); 127.2 (s, C(5)); 81.7 (s, C(9)); 31.9, 31.8, 29.54, 29.53, 29.47, 29.3, 29.2, 29.1, 29.0, 28.6, 22.6 (11t, 11 CH₂); 27.2, 21.3 (2q, Me_2 C); 14.0 (2q, Me). CI-MS: 465 (16, [M + 1]⁺), 332 (11), 331 (21), 330 (100). Anal. calc. for C₂₄H₃₆N₂OS₃ (464.76): C 62.03, H 7.81, N 6.03, S 20.70; found: C 62.00, H 7.73, N 5.75, S 20.49.

3.2. With Benzonitrile 2-Propanide. In a Pyrex vessel, 1a (191 mg, 1 mmol) and 2,2-dimethyl-3-phenyl-2Hazirine (13; 363 mg, 2.5 mmol) were dissolved in pentane (130 ml). At r.t., the soln. was irradiated with a UV high-pressure Hg lamp for 2 h. After removal of the solvent *i.v.* and chromatography with hexane/Et₂O 20:1, 156 mg (46%) of 4,4,7,7-tetramethyl-2-(methylthio)-9-phenyl-1,6-dithia-3,8-diazaspiro[4.4]nona-2,8-diene (15) and 10 mg (3%) of 4,4,9,9-tetramethyl-2-(methylthio)-7-phenyl-1,6-dithia-3,8-diazaspiro[4.4]nona-2,7-diene (16) were obtained.

Data of **15**: Pale-yellow crystals. M.p. 84–86°. IR: 2980*s*, 2930*m*, 1625*m*, 1565*m*, 1555*m*, 1490*w*, 1460*m*, 1445*m*, 1380*m*, 1365*m*, 1315*w*, 1270*m*, 1200*m*, 1165*m*, 1140*s*, 1080*w*, 1045*w*, 1025*m*, 985*m*, 970*m*, 950*s*, 880*m*, 860*m*, 700*m*. ¹H-NMR: 7.75–7.7 (*m*, 2 arom. H); 7.4 -7.3 (*m*, 3 arom. H); 2.35 (*s*, MeS); 1.77, 1.73, 1.45, 1.42 (4*s*, 4 Me). ¹³C-NMR: 167.3, 163.2 (2*s*, C(2), C(9)); 135.1 (*s*, 1 arom. C); 129.3, 127.7, 127.6 (3*d*, 5 arom. C); 96.6 (*s*, C(5)); 82.6, 80.9 (2*s*, C(4), C(7)); 32.1, 32.0, 27.4, 21.7 (4*q*, 4 Me); 14.4 (*q*, MeS). CI-MS: 339 (18), 338 (20), 337 (100, [*M* + 1]⁺), 252 (27), 189 (7).

Data of **16**: Yellow crystals. M.p. 128–129°. IR: 2975*m*, 2930*m*, 2860*w*, 1590*m*, 1560*m*, 1550*m*, 1490*w*, 1465*m*, 1445*m*, 1385*m*, 1380*m*, 1360*m*, 1295*w*, 1255*m*, 1175*m*, 1150*m*, 1070*w*, 980*m*, 950*s*, 920*w*, 840*w*, 685*m*, 660*w*, 610*m*. ¹H-NMR: 7.8–7.75 (*m*, 2 arom. H); 7.5–7.35 (*m*, 3 arom. H); 2.52 (*s*, MeS); 1.87, 1.84, 1.40, 1.37 (4*s*, 4 Me). CI-MS: 339 (18), 338 (19), 337 (100, [*M* + 1]⁺).

3.3. With Benzonitrile Phenylimide. a). In a Pyrex vessel, **1a** (96 mg, 0.5 mmol) and 2,5-diphenyl-2H-tetrazole (**17**; 133 mg, 0.6 mmol) were dissolved in EtOH (130 ml). The soln. was irradiated with a UV high-pressure Hg lamp at r.t. for 80 min. After removal of the solvent *i.v.* and chromatography with hexane/CH₂Cl₂ 3:1, 79 mg (41%) of 9,9-dimethyl-7-(methylthio)-1,3-diphenyl-4,6-dithia-1,2,8-triazaspiro[4.4]nona-2,7-diene (**19**) were obtained. Brown oil. IR: 3040w, 2980m, 2960m, 2920w, 1590m, 1545m, 1485m, 1440m, 1375w, 1355w, 1305m, 1290m, 1235m, 1160m, 1080m, 1060m, 1020w, 970s, 950s, 920w, 900w, 860w, 685m. ¹H-NMR: 7.6-7.55 (*m*, 2 arom. H); 7.4-7.3 (*m*, 5 arom. H); 7.25-7.1 (*m*, 3 arom. H); 2.23 (*s*, MeS); 1.80, 1.51 (2s, 2 Me). ¹³C-NMR: 177.4, 163.5 (2s, C(3), C(7)); 143.6, 130.5 (2s, 2 arom. C): 129.7, 128.6, 127.8, 126.3, 125.7, 124.3 (6d, 10 arom. C); 90.2 (*s*, C(5)); 83.2 (*s*, C(9)); 28.5, 22.0 (2q, 2 Me); 14.5 (q, MeS). CI-MS: 388 (16), 387 (27), 386 (100, [M + 1]⁺), 338 (6), 281 (16).

b) A soln. of **1a** (109 mg, 0.57 mmol) and **17** (152 mg, 0.69 mmol) in mesitylene (3 ml) was heated to 140° for 3 h. After removal of the solvent *i.v.* and chromatography with hexane/CH₂Cl₂ 6:1, 2:1, 36 mg (16%) of **19** were obtained.

3.4. With Organoazides. General Procedure. Into a soln. of 1 (0.5 mmol) in toluene (2 ml), the organoazide 20 (1.5 mmol) was added in one portion. Avoiding any light, the soln. was heated to 90° until 1 disappeared (see Table 4). If necessary, an additional amount of 20 was added. Removal of the solvent *i.v.* and chromatography with hexane/CH₂Cl₂ 2:1 yielded 21.

3.4.1. N-Hexyl-4,4-dimethyl-2-(methylthio)-1,3-thiazole-5(4H)-imine (**21a**). Reaction of **1a** (130 mg, 0.68 mmol) with hexyl azide (**20a**; 347 mg, 2.7 mmol) afforded 126 mg (72%) of **21a**. Yellow oil. IR: 2965*s*, 2940*s*, 2860*m*, 1675*s*, 1660*s*, 1575*s*, 1465*m*, 1435*m*, 1380*m*, 1360*m*, 1320*w*, 1240*m*, 1190*m*, 1170*w*, 1120*w*, 990*s*, 960*m*, 920*s*, 835*m*, 640*m*. ¹H-NMR: 3.21 (*t*, *J* = 7.0, CH₂N); 2.57 (*s*, MeS); 1.7-1.65 (*m*, CH₂); 1.45 (*s*, Me₂C); 1.35–1.3 (*m*, 3 CH₂); 0.89 (*t*, *J* = 6.8, Me). ¹³C-NMR: 172.8 (*s*, C(5')); 157.4 (*s*, C(2')); 81.3 (*s*, C(4')); 62.0 (*t*, C(1)); 31.5, 29.8, 26.8, 22.5 (4*t*, 4 CH₂); 27.3 (*q*, Me₂C); 1.3.9 (*q*, MeS, Me). CI-MS: 261 (9), 260 (14), 259 (100, $[M + 1]^+$). Anal. calc. for C₁₂H₂₂N₂S₂ (258.45): C 55.77, H 8.58, N 10.84, S 24.81; found: C 55.90, H 8.82, N 10.66, S 24.55.

3.4.2. 2-(*Ethylthio*)-N-*hexyl-4,4-dimethyl-1,3-thiazole-5(4* H)-*imine* (**21b**). Reaction of **1b** (103 mg, 0.5 mmol) with **20a** (255 mg, 2 mmol) afforded 118 mg (87%) of **21b**. Yellow oil. IR: 2970s, 2940s, 2860m, 1665s, 1575s, 1460m, 1440m, 1420w, 1380m, 1360m, 1270m, 1240m, 1190m, 1170w, 1060w, 1020w, 980s, 925s, 840m, 665w, 640w, 630. ¹H-NMR: 3.20 (t, J = 7.0, CH₂N); 3.15 (q, J = 7.4, $MeCH_2S$); 1.7–1.6 (m, CH₂); 1.44 (s, Me₂C); 1.38 (t, J = 7.4, $MeCH_2S$); 1.35–1.3 (m, 3 CH₂); 0.89 (t, J = 6.7, Me). ¹³C-NMR: 172.8 (s, C(5')); 156.5 (s, C(2')); 81.3 (s, C(4')); 62.1 (t, C(1)); 31.5, 29.8, 26.8, 22.5 (4t, 4 CH₂); 27.2 (q, Me_2C); 25.7 (t, MeCH₂S); 1.4.4 (q, $MeCH_2S$); 1.39

(q, Me). CI-MS: 275 (10), 274 (16), 273 (100, [*M* + 1]⁺). Anal. calc. for C₁₃H₂₄N₂S₂ (272.48): C 57.31, H 8.88, N 10.28, S 23.54; found: C 57.38, H 8.93, N 10.08, S 23.65.

3.4.3. 2-(*Benzylthio*)-N-*hexyl*-4,4-dimethyl-1,3-thiazole-5(4H)-imine (**21c**). Reaction of **1e** (100 mg, 0.37 mmol) with **20a** (191 mg, 1.5 mmol) afforded 109 mg (65%) of **21c**. Yellow oil. IR: 2960*m*, 2920*m*, 2855*m*, 1665*m*, 1575*m*, 1495*w*, 1450*m*, 1430*w*, 1375*w*, 1365*w*, 1235*w*, 1185*m*, 1070*w*, 970*s*, 920*m*, 830*m*, 700*m*. ¹H-NMR: 7.4–7.25 (*m*, 5 arom. H); 4.40 (*s*, PhCH₂S); 3.20 (*t*, J = 7.0, CH₂N); 1.7–1.6 (*m*, CH₂); 1.46 (*s*, Me₂C); 1.35–1.25 (*m*, 4 CH₂); 0.89 (*t*, J = 6.7, Me). ¹³C-NMR: 172.7 (*s*, C(5')); 156.3 (*s*, C(2')); 136.6 (*s*, 1 arom. C); 129.1, 128.4, 127.4 (3*d*, 5 arom. C); 81.2 (*s*, C(4')); 62.1 (*t*, C(1)); 35.3 (*t*, PhCH₂S); 31.5, 29.8, 26.8, 22.5 (4*t*, 4 CH₂); 27.3 (*q*, *Me*₂C); 14.0 (*q*, Me). CI-MS: 337 (11), 336 (23), 335 (100, [*M* + 1]⁺), 261 (11), 245 (12), 122 (11). Anal. calc. for C₁₈H₂₆N₂S₂ (334.55): C 64.62, H 7.83, N 8.37, S 19.17; found: C 64.57, H 7.78, N 8.07, S 19.24.

3.4.4. 2-(*Dodecylthio*)-N-*hexyl-4,4-dimethyl-1,3-thiazole-5(4*H)-*imine* (**21d**). Reaction of **1f** (173 mg, 0.5 mmol) with **20a** (318 mg, 2.5 mmol) afforded 193 mg (93%) of **21d**. Yellow oil. IR: 3050s, 3020s, 2950s, 1705*m*, 1620*m*, 1510*m*, 1480*w*, 1420*w*, 1400*w*, 1285*w*, 1235*w*, 1210*w*, 1020s, 965*m*, 880*m*, 685*w*. ¹H-NMR: 3.20, 3.14 (2*t*, $J = 7.0, 7.3, CH_2S, CH_2N$); 1.75–1.6 (*m*, 2 CH₂); 1.43 (*s*, Me₂C); 1.4–1.25 (*m*, 12 CH₂); 0.9–0.85 (*m*, 2 Me). ¹³C-NMR: 172.9 (*s*, C(5')); 156.7 (*s*, C(2')); 81.3 (*s*, C(4')); 62.0 (*t*, C(1)); 38.5, 31.8, 31.5, 31.2, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.0, 28.6, 26.8, 22.6, 22.5 (15*t*, 15 CH₂); 27.2 (*q*, *Me*₂C); 14.0, 13.9 (2*q*, 2 Me). CI-MS: 415 (7), 414 (25), 413 (100, [*M* + 1]⁺). Anal. calc. for C₂₃H₄₄N₂S₂ (412.75): C 66.93, H 10.75, N 6.79, S 15.54; found: C 67.20, H 10.51, N 6.96, S 15.52.

3.4.5. N-*Cyclohexyl-4,4-dimethyl-2-(methylthio)-1,3-thiazole-5(4*H)-*imine* (**21e**). Reaction of **1a** (86 mg, 0.45 mmol) with *cyclohexyl azide* (**20b**; 251 mg, 2 mmol) afforded 94 mg (82%) of **21e**. Pale-yellow crystals. M.p. 55.0–55.5°. IR: 2980s, 2940s, 2860s, 1675s, 1660s, 1575s, 1570s, 1465m, 1455m, 1435m, 1420w, 1375m, 1360m, 1355m, 1330w, 1320m, 1245m, 1190m, 1170m, 1150w, 1140w, 1070m, 990s, 965s, 925s, 890m, 840s, 665w, 650m. ¹H-NMR: 2.6–2.55 (*m*, CHN); 2.56 (*s*, MeS); 1.8–1.25 (*m*, 5 CH₂); 1.43 (*s*, 2 Me). ¹³C-NMR: 170.2 (*s*, C(5')); 157.6 (*s*, C(2')); 81.0 (*s*, C(4')); 71.6 (*d*, CH); 32.5, 25.5, 24.4 (3t, 5 CH₂); 27.4 (*q*, 2 Me); 13.9 (*q*, MeS). CI-MS: 259 (10), 258 (16), 257 (100, [*M* + 1]⁺). Anal. calc. for C₁₂H₂₀N₂S₂ (256.43): C 56.21, H 7.86, N 10.92, S 25.01; found: C 56.22, H 7.93, N 10.70, S 24.77.

3.4.6. N-*Cyclohexyl-2-(isopropylthio)-4,4-dimethyl-1,3-thiazole-5(4H)-imine* (**21f**). Reaction of **1c** (110 mg, 0.5 mmol) with **20b** (251 mg, 2 mmol) afforded 96 mg (68%) of **21f**. Pale-yellow oil. IR: 2980*m*, 2940*s*, 2860*m*, 1665*m*, 1570*m*, 1515*w*, 1465*m*, 1455*m*, 1370*m*, 1360*w*, 1310*w*, 1245*m*, 1195*m*, 1160*w*, 1070*w*, 1060*m*, 980*s*, 965*m*, 925*s*, 890*w*, 840*m*, 660*m*. ¹H-NMR: 3.96 (*sept., J* = 6.8, Me₂CHS); 2.6–2.55 (*m*, CHN); 1.8–1.2 (*m*, 5 CH₂); 1.43 (*s*, Me₂C); 1.41 (*d*, *J* = 6.8, Me₂CHS). ¹³C-NMR: 170.3 (*s*, C(5')); 156.4 (*s*, C(2')); 81.1 (*s*, C(4')); 71.7 (*d*, CH); 36.8 (*d*, Me₂CHS); 32.5, 25.5, 24.5 (3*t*, 5 CH₂); 27.3 (*q*, Me₂C); 22.9 (*q*, Me₂CHS). CI-MS: 287 (10), 286 (17), 285 (100, [*M* + 1]⁺), 273 (4). Anal. calc. for C₁₄H₂₄N₂S₂ (284.49): C 59.11, H 8.50, N 9.85, S 22.54; found: C 59.40, H 8.53, N 9.61, S 22.33.

3.4.7. Ethyl 2-{ $\{4,4-Dimethyl-2-(methylthio)-1,3-thiazole-5(4H)-ylidene]amino\}acetate (21g). Reaction of 1a (86 mg, 0.45 mmol) with ethyl 2-azidoacetate (20c; 189 mg, 1.5 mmol) afforded 105 mg (90%) of 21g. Colorless crystals. M.p. 28–30°. IR: 2980m, 2925w, 1740s, 1655m, 1570m, 1460w, 1430w, 1395w, 1370m, 1355w, 1340w, 1310w, 1270m, 1240m, 1185s, 1095w, 1060w, 1030m, 985s, 960m, 935m, 915m, 835m, 635w. ¹H-NMR: 4.23 (q, <math>J = 7.1$, MeCH₂); 4.02 (s, CH₂N); 2.58 (s, MeS); 1.50 (s, 2 Me); 1.30 (t, J = 7.1, MeCH₂). ¹³C-NMR: 179.2 (s, C(5')); 168.6 (s, C=O); 156.3 (s, C(2')); 82.4 (s, C(4')); 61.4 (t, CH₂); 61.0 (t, MeCH₂O); 27.1 (q, Me₂C); 14.0 (q, MeS, MeCH₂). CI-MS: 263 (10), 262 (13), 261 (100, $[M + 1]^+$), 115 (2). Anal. calc. for C₁₀H₁₆N₂O₂S₂ (260.38): C 46.13, H 6.19, N 10.76, S 24.63; found: C 46.31, H 5.95, N 10.58, S 24.48.

3.4.8. N-Adamantyl-2-(ethylthio)-4,4-dimethyl-1,3-thiazole-5(4H)-imine (**21h**). Reaction of **1b** (103 mg, 0.5 mmol) with *I-azidoadamantane* (**20d**; 443 mg, 2.5 mmol) afforded 134 mg (83%) of **21h**. White crystals. M.p. 59°. IR: 2970m, 2920s, 2910s, 2850m, 1670m, 1660m, 1565m, 1450m, 1370w, 1350m, 1310m, 1265w, 1190m, 1110w, 1085w, 980m, 970s, 935w, 910m, 830m, 635m. ¹H-NMR: 3.15 (*q*, *J* = 7.4, MeCH₂); 2.15–2.1 (*m*, 3 CH); 1.85–1.8, 1.75–1.65 (2*m*, je 3 CH₂); 1.38 (*t*, *J* = 7.4, MeCH₂); 1.38 (*s*, Me₂C). ¹³C-NMR: 162.0 (*s*, C(5')); 157.9 (*s*, C(2')); 83.5 (*s*, C(4')); 56.6 (*s*, C(1)); 40.4, 36.5 (2*t*, je 3 CH₂); 29.5 (*d*, 3 CH); 27.7 (*q*, Me₂C); 25.4 (*t*, MeCH₂); 14.5 (*q*, MeCH₂). CI-MS: 325 (10), 324 (21), 323 (100, [*M* + 1]⁺). Anal. calc. for C₁₇H₂₆N₂S₂ (322.54): C 63.31, H 8.13, N 8.69, S 19.88; found: C 63.50, H 8.23, N 8.57, S 19.61.

3.4.9. N-Adamantyl-2-(isopropylthio)-4,4-dimethyl-1,3-thiazole-5(4H)-imine (21i). Reaction of 1c (110 mg, 0.5 mmol) with 20d (356 mg, 2 mmol) afforded 138 mg (82%) of 21i. Yellow oil. IR: 2960m, 2900s, 2840m, 1665m, 1650m, 1565m, 1450m, 1365w, 1350w, 1305w, 1235w, 1190m, 1110w, 1080w, 1050w, 975m, 965s, 930w, 905m, 825m. ¹H-NMR: 3.97 (sept., *J* = 6.8, Me₂CH); 2.11 (s, 3 CH); 1.85–1.8, 1.7–1.65 (2m, je 3 CH₂); 1.41 (d, *J* = 6.8, Me₂CH); 1.38 (s, Me₂C). ¹³C-NMR: 162.1 (s, C(5')); 157.6 (s, C(2')); 83.6 (s, C(4')); 56.6 (s, C(1)); 40.4 (t, 3 CH₂); 38.4 (d, Me₂CH); 36.4 (t, 3 CH₂); 29.5 (d, 3 CH); 27.7 (q, Me₂C); 23.0 (q, Me₂CH). CI-MS: 339 (11), 338 (22), 337

	Table 5. Crystallo,	graphic Data for Compoun	ids 1d, 7, 15, 16, and 21g		
	1d	7	15	16	21g
Crystallized from	hexane/CH ₂ Cl ₂	hexane/AcOEt	hexane/Et ₂ O	hexane/Et ₂ O	hexane/CH ₂ Cl ₂
Empirical formula	C ₉ H ₁₅ NS ₃	C ₅ H ₇ NS ₃	$C_{16}H_{20}N_2S_3$	$C_{16}H_{20}N_2S_3$	$C_{10}H_{16}N_2O_2S_2$
Formula weight	233.40	177.30	336.53	336.53	260.37
Crystal color, habit	orange, prism	orange, prism	colorless, prism	colorless, prism	colorless, prism
Crystal temp. [K]	173(1)	173(1)	173(1)	173(1)	173(1)
Crystal dimensions [mm]	$0.25 \times 0.27 \times 0.44$	0.28 imes 0.31 imes 0.40	$0.20 \times 0.22 \times 0.45$	$0.33 \times 0.35 \times 0.45$	$0.17 \times 0.20 \times 0.50$
Crystal system	monoclinic	monoclinic	triclinic	triclinic	triclinic
Lattice parameters					
Reflections for cell determination	23	20	25	19	24
2θ range [°]	$37 < 2\theta < 40$	$39 < 2\theta < 40$	$36 < 2\theta < 40$	$39 < 2\theta < 40$	$38 < 2\theta < 40$
a [Å]	10.241(3)	5.676(2)	11.422(2)	10.907(3)	7.607(2)
b [Å]	9.946(4)	12.896(1)	16.468(3)	11.138(2)	12.111(3)
c [Å]	11.887(2)	11.029(2)	9.615(1)	7.324(1)	7.340(1)
a [º]	06	90	90.71(1)	92.89(2)	98.60(2)
ß [0]	97.26(1)	98.92(3)	106.45(1)	95.28(2)	92.48(2)
y [9]	06	90	83.89(2)	107.88(2)	75.78(2)
$V[\mathbf{A}^3]$	1201.1(5)	797.5(4)	1724.4(5)	840.3(3)	648.1(3)
Space group	$P2_{1/n}$	$P2_{1/c}$	$P\overline{1}$	$P\overline{1}$	$P\overline{1}$
Ζ	4	4	4	2	2
$D_{\rm x}$ [g cm ⁻³]	1.291	1.476	1.296	1.330	1.334
Absorption coefficient μ (Mo K_x) [cm ⁻¹]	5.530	8.091	4.080	4.180	3.820
Absorption correction min, max	1	Ι	1	0.893, 1.041	0.751, 1.471
$2\theta(\max) [^{\circ}]$	60	09	55	55	09
Total reflections measured	3872	2634	8309	4071	4040
Symmetry independent reflections	3501	2317	7913	3867	3775
Reflections observed $(I > 3\sigma(I))$	2841	1900	6062	3277	3274
Variables	179	110	539	270	209
Final R	0.0284	0.0299	0.0346	0.0285	0.0268
$R_{\rm h}{}^{\rm a})$	0.0293	0.0314	0.0336	0.0309	0.0298
Goodness of fit s	1.748	2.500	1.573	2.293	2.009
Final Δ_{\max}/σ	0.0007	0.0006	0.001	0.0006	0.0003
$\Delta \rho$ (max, min) [e Å ⁻³]	0.27, -0.24	0.52, -0.56	0.49, -0.37	0.31, -0.27	0.32, -0.25
^a) Function minimized $\Sigma w(F_o - F_c)^2$;	$\frac{1}{w} = \sigma^2 (F_o) + (0.005F_o)^2.$				

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(100, $[M + 1]^+$), 295 (3), 238 (6). Anal. calc. for C₁₈H₂₈N₂S₂ (336.57): C 64.24, H 8.39, N 8.32, S 19.05; found: C 64.26, H 8.17, N 8.14, S 19.26.

3.4.10. N-[4,4-Dimethyl-2-(methylthio)-1,3-thiazole-5(4H)-ylidene]-p-toluenesulfonamide (21j). Reaction of 1a (96 mg, 0.5 mmol) with p-toluenesulfonyl azide (20e; 395 mg, 2 mmol) afforded 18 mg (11%) of 21j. White crystals. M.p. 85-86°. IR: 3040w, 2990w, 2940w, 2870w, 1585s, 1575s, 1515w, 1500w, 1455w, 1435w, 1380w, 1360w, 1330m, 1310m, 1295m, 1240w, 1190m, 1160s, 1120w, 1090m, 1020w, 990m, 970w, 925m, 850w, 830m, 810m, 670m, 630m. ¹H-NMR: 7.83, 7.33 (AA'BB', J = 8.4, 4 arom. H); 2.61 (s, MeS); 2.45 (s, Me); 1.44 (s, Me₂C). CI-MS: 347 (6), 346 (27, $[M + 1 + NH_3]^+$, 331 (14), 330 (19), 329 (100, $[M + 1]^+$), 279 (30).

4. Cyclosubstitution of 1a with Dimethyl Acetylenedicarboxylate. – A soln. of 96 mg (0.5 mmol) of 1a and dimethyl acetylenedicarboxylate (85 mg, 0.6 mmol) in toluene (2 ml) was heated in a sealed glass tube to 85° for 15 h (cf. [37]). After removal of the solvent *i.v.* and chromatography with hexane/Et₂O 4:1, 57 mg of a mixture (ratio 1:1.2 (¹H-NMR)) of dimethyl 2-isopropylidene-1,3-dithiol-4,5-dicarboxylate (25) and dimethyl 2,3-dihydro-3,3-dimethyl-2-thioxothiophene-4,5-dicarboxylate (26) were obtained.

Data of 25 [37]: ¹H-NMR (from mixture): 3.83 (s, 2 MeO); 1.69 (s, 2 Me).

Data of 26 [37]: ¹H-NMR (from mixture): 3.90, 3.89 (2s, 2 MeO); 1.48 (s, 2 Me).

5. Reduction of 1a. – Into a soln. of 1a (72 mg, 0.377 mmol) in EtOH (5 ml) at r.t., NaBH₄ (21 mg, 0.46 mmol) was added and the mixture stirred at r.t. for 20 min. After removal of the solvent and chromatography with hexane/Et₂O 25:1, 47 mg (65%) of 4.5-dihydro-4.4-dimethyl-2-(methylthio)-1.3-thiazole-5-thiol (27) were obtained. Colorless oil. 1R: 3070w, 2985m, 2980m, 2970m, 2930m, 2860w, 1565m, 1555m, 1465m, 1440w, 1435w, 1385w, 1365m, 1315w, 1270w, 1250w, 1170m, 1140w, 990s, 950m, 930w, 910w, 850w. ¹H-NMR: 4.67 (d, J = 9.4, H–C(5)); 2.43 (s, MeS); 2.00 (d, J = 9.4, SH); 1.35, 1.32 (2s, 2 Me). ¹³C-NMR: 162.1 (s, C(2)); 79.7 (s, C(4)); 59.5 (d, C(5)); 26.2, 22.2 (2q, 2 Me); 14.9 (q, MeS). C1-MS: 196 (22), 195 (6), 194 (100, $[M + 1]^+$), 115 (47), 100 (8).

6. Crystal-Structure Determination of 1d, 7, 15, 16, and 21g (see Table 5 and Figs. 1-3). – The intensities were collected on a Rigaku AFC5R rotating-anode diffractometer using graphite-monochromated MoK_x radiation $(\lambda = 0.71069 \text{ Å})$ and $\omega/2\theta$ scans. The intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction was applied for 16 and 21g using DIFABS [41]. Data collection and refinement parameters are listed in Table 5. Views of the molecules are shown in Figs. 1-3. The structures were solved by direct methods using SHELXS86 [42] which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were located in difference-electron-density maps, and their positions were allowed to refine together with individual isotropic temp. factors. All refinements were carried out on F using full-matrix least-squares procedures [43]. A correction for secondary extinction was applied in the case of 1d (coefficient 3.10 × 10⁻⁷). Neutral-atom scattering factors for non-H-atoms were taken from [44a] and the scattering factors for H-atoms form [45]. Anomalous dispersion effects were included in F_{cak} [46]; the values for $\Delta f'$ and $\Delta f''$ were those of [44b]. All calculations were performed using the TEXSAN [47] crystallographic software package.

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