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

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

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

However, 1,3-thiazole-5(4*H*)-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(4*H*)-thiones are still needed. In this paper, a new approach for the synthesis of 2-(alkylthio)-substituted 1,3-thiazole-5(4*H*)-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(4*H*)-thiones 1. – A synthesis was designed for 2-(alkylthio)-substituted 1,3-thiazole-5(4*H*)-thiones **1**, based on the addition of trithiocarbonic acids **4** with 3-amino-2*H*-azirine **5**, and subsequent cycliza-

[1] Taken in part from the Ph. D. thesis of *J. S.*, Universität Zürich, 1993.

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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(4*H*)-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*).

Scheme 1

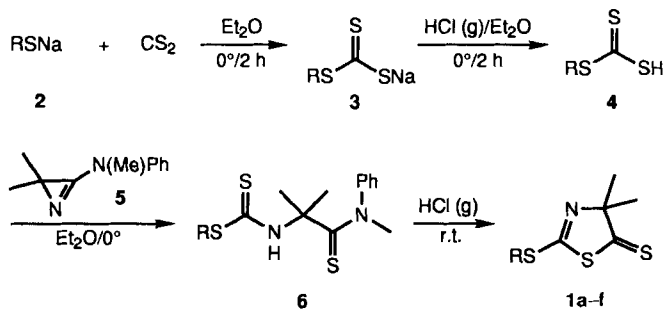


Table 1. *2-(Alkylthio)-1,3-thiazole-5(4*H*)-thiones* **1a–f** *Prepared According to* Scheme 1

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])	$C_{12}H_{25}$	**1f**	81

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

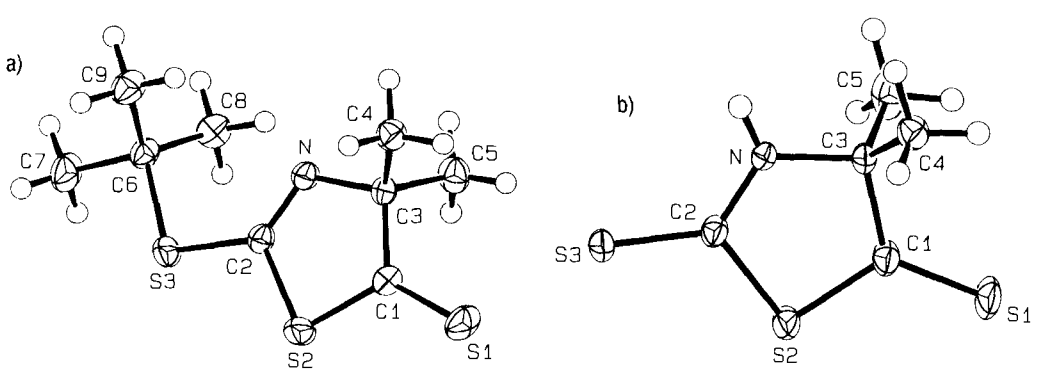


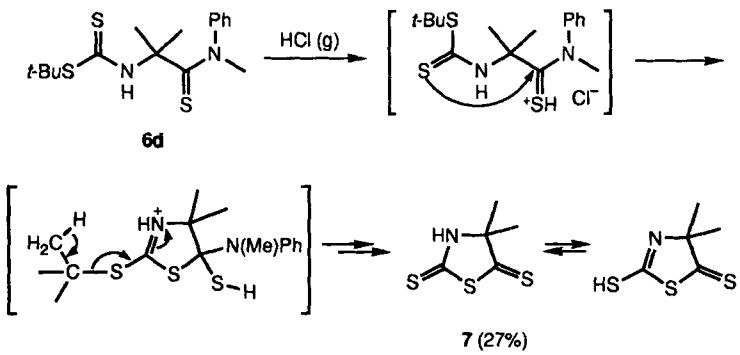
Fig. 1. *ORTEP Diagram* [10] *of the molecular structures of* a) **1d** *and* b) **7**

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.

Scheme 2

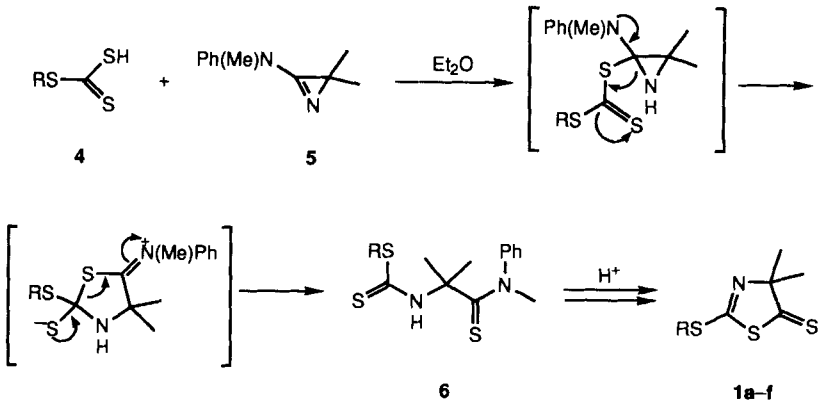


It is worth mentioning that the whole procedure can be conducted as a one-pot reaction. After removal of the solvent, 1,3-thiazole-5(4*H*)-thiones **1a–f** were obtained by flash chromatography with hexane/CH_2Cl_2. Moreover, the intermediate dithiocarbamates **6** could also be isolated. *E.g.*, from 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(4*H*)-thione (**1a**) in 91% yield.

The mechanism for the formation of 2-(alkylthio)-substituted 1,3-thiazole-5(4*H*)-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.

Scheme 3

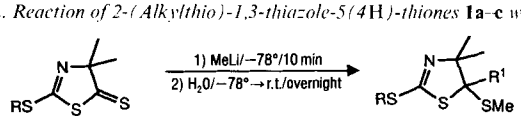


3. Addition Reactions of Organolithium Reagents and 1. – In the reactions of 2-alkyl- or 2-phenyl-substituted 1,3-thiazole-5(4*H*)-thiones with organometallic reagents, it has been shown that organolithium compounds undergo thiophilic addition exclusively [11]. In contrast, organocuprates only afford 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 2-alkyl- and 2-phenyl-substituted 1,3-thiazole-5(4*H*)-thiones *via* carbophilic attack [14]. Here, we report on reactions of 2-(alkylthio)-substituted 1,3-thiazole-5(4*H*)-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 H_2O at −78°→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(4*H*)-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

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

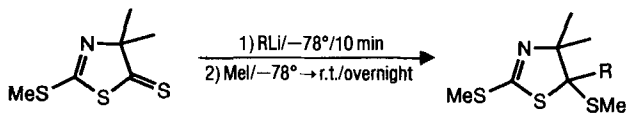


1	R	Disulfide	R^1	8	Yield [%]
1a	Me	–	MeS	**8a**	36
1a	Me	PhSSPh	PhS	**8b**	65
1b	Et	–	EtS	**8c**	41
1b	Et	MeSSMe	MeS	**8d**	35
1c	i-Pr	–	i-PrS	**8e**	34

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 Me_2S. 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(4*H*)-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 Bu_3SnH 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 Bu_3SnH slowly destroyed the starting material **1a**.

3.2. *Addition of Allyl- and Benzyllithium Reagents.* Allyllithium was generated from allyl phenyl ether [15], while $PhCH_2Li$ was prepared from $(PhCH_2)_2O$ by cleavage with Li [16] [17]. At −78° in THF, 4,4-dimethyl-2-(methylthio)-1,3-thiazole-5(4*H*)-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*).

Scheme 4



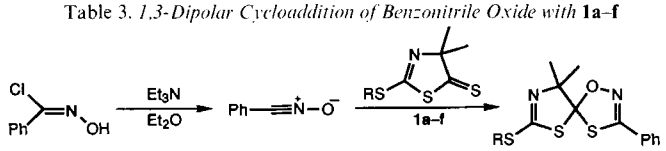
1a R = $PhCH_2$ **9a** (41%)
R = CH_2=$CHCH_2$ **9b** (66%)

These results are consistent with those of the reactions of allyl- and benzyllithium reagents with 2-alkyl-substituted 1,3-thiazole-5(4*H*)-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(4*H*)-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(4*H*)-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(4*H*)-thiones **1a–f** towards 1,3-dipoles.

4.1. *With Benzonitrile Oxide.* Benzonitrile oxide (**11**) was generated *in situ* from *N*-(α-chlorobenzylidene)hydroxylamine (**10**) in the presence of Et_3N [26]. The reaction with **1a–f** in Et_2O at room temperature afforded, after chromatography, the expected cycloadducts **12** in very good yields (*Table 3*).

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



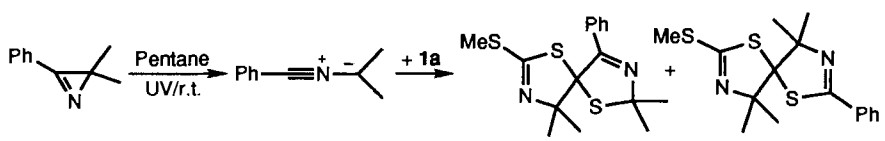
10 **11** **12**

1	R	12	Yield [%]
1a	Me	**12a**	98
1b	Et	**12b**	98
1c	i-Pr	**12c**	98
1d	*t*-Bu	**12d**	87
1e	$PhCH_2$	**12e**	80
1f	$C_{12}H_{25}$	**12f**	94

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 ^{13}C-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*).

Scheme 5



13 **14** **15** (46%) **16** (3%)

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(4*H*)-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 signifcant differences between the conformations of these molecules.

4.3. *With Benzonitrile Phenylimide.* It is well known that 2,5-diphenyl-2*H*-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(4*H*)-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

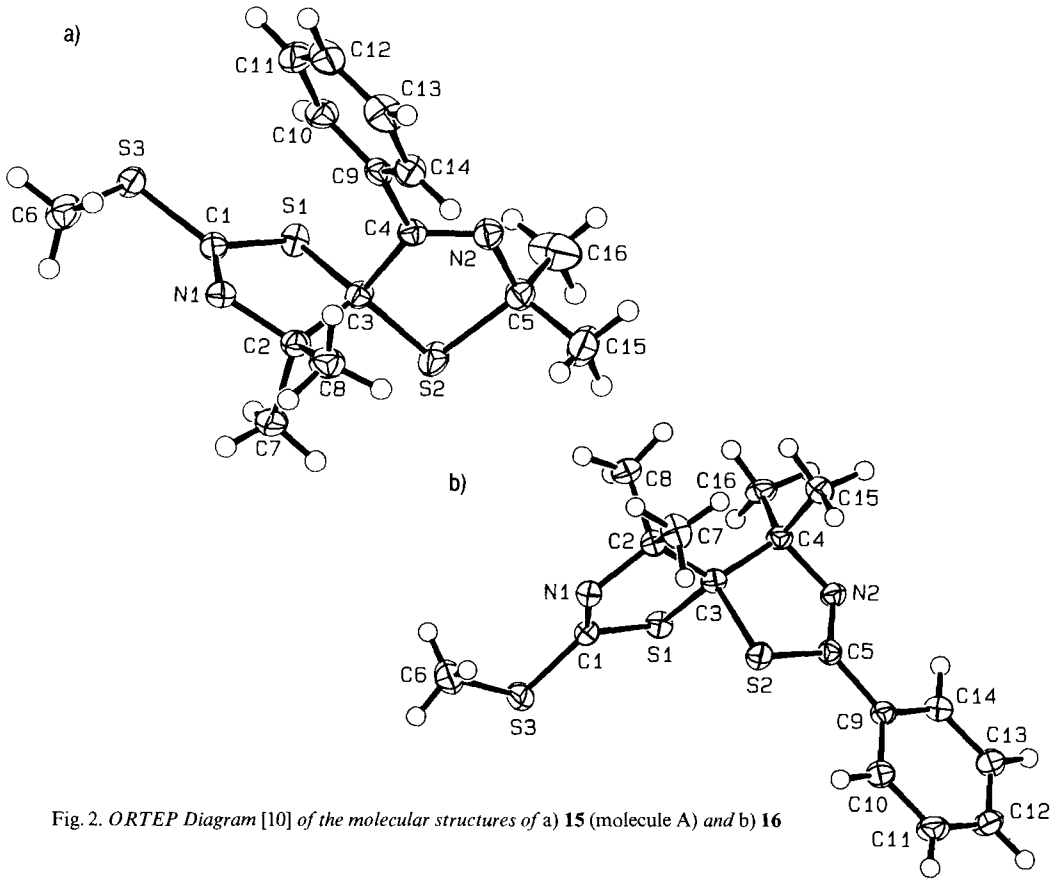
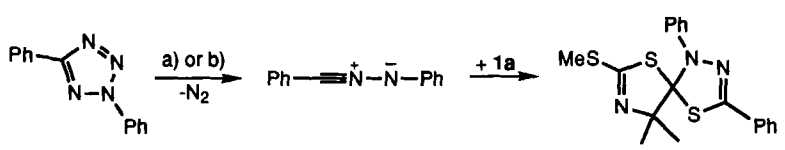


Fig. 2. *ORTEP Diagram* [10] *of the molecular structures of* a) **15** (molecule A) *and* b) **16**

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.

Scheme 6

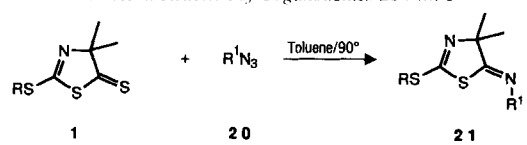


17 **18** **19**

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

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(4*H*)-thiones [29]. In an analogous manner, heating of 2-(alkylthio)-4,4-dimethyl-1,3-thiazole-5(4*H*)-thiones of type **1** with alkyl azides **20** in toluene at 90° led to imines **21** in fair-to-good yields (*Table 4*).

Table 4. *Reaction of Organoazides* **20** *with* **1**



1 **20** **21**

1	R	**20**	R^1	Time [d]	**21** (Yield [%])
1a	Me	**20a**	C_6H_{13}	4	**21a** (72)
1b	Et	**20a**	C_6H_{13}	3	**21b** (87)
1e	$PhCH_2$	**20a**	C_6H_{13}	4	**21c** (65)
1f	$C_{12}H_{25}$	**20a**	C_6H_{13}	5	**21d** (93)
1a	Me	**20b**	Cyclohexyl	5	**21e** (82)
1c	i-Pr	**20b**	Cyclohexyl	5	**21f** (68)
1a	Me	**20c**	$EtOCOCH_2$	3	**21g** (90)
1b	Et	**20d**	1-Adamantyl	6	**21h** (83)
1c	i-Pr	**20d**	1-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(4*H*)-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(4*H*)-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*).

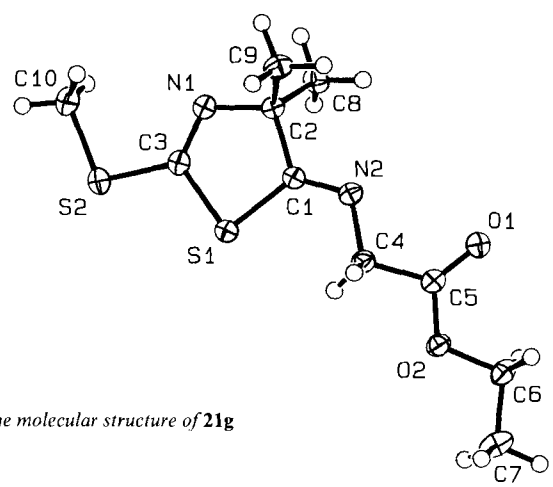
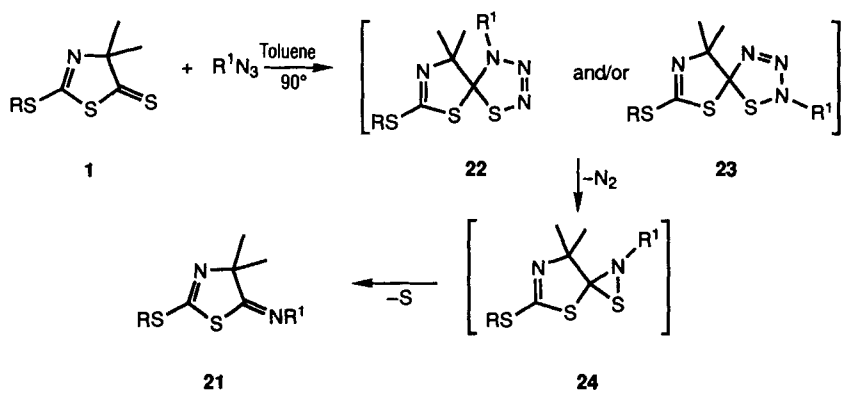


Fig. 3. *ORTEP Diagram* [10] *of the molecular structure of* **21g**

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].

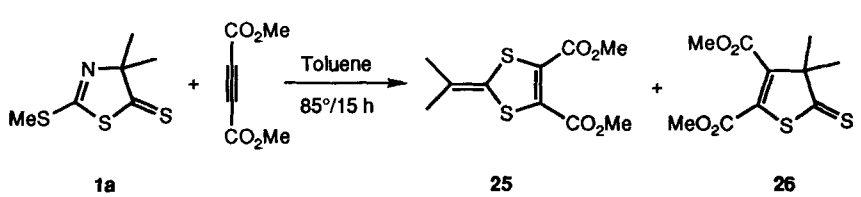
Scheme 7



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**→**24**→**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(4*H*)-thiones **1** also react in this manner with various acetylenes to give 1,4-dithiafulvenes of type **25** and/or thiophene-2(3*H*)-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(4*H*)-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*).

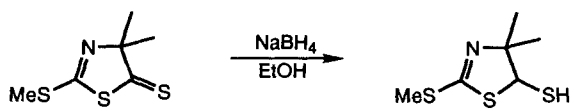
Scheme 8



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(4*H*)-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; $NaBH_4$ and $LiAlH_4$ are the most frequently used and very efficient reagents. In EtOH, reduction of 2-MeS-substituted 1,3-thiazole-5(4*H*)-thione **1a** with $NaBH_4$ at room temperature afforded, after chromatography, the thiol **27** in a yield of 65% (*Scheme 9*).

Scheme 9



1a **27** (65%)

7. Conclusion. – 2-(Alkylthio)-substituted 1,3-thiazole-5(4*H*)-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, CS_2, 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 $NaBH_4$, 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.

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Experimental Part

General. See [40]. M.p.: *Mettler-FP5* apparatus; uncorrected. IR Spectra: *Perkin-Elmer 297* or *Perkin-Elmer 781* spectrophotometer in $CHCl_3$, 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 $CDCl_3$; chemical shifts in ppm; TMS (0 ppm) or $CDCl_3$ (7.27 ppm) as internal standard; coupling constants *J* in Hz. ^{13}C-NMR Spectra: *Varian XL-200* (50.4 MHz) spectrometer in $CDCl_3$, unless stated otherwise; chemical shifts in ppm; $CDCl_3$ (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; EI mode: direct injection, 70 eV; CI mode: with 2-methylpropane or NH_3.

1. Synthesis of 1,3-Thiazole-5(4*H*)-thiones 1. – *General Procedure.* Into a suspension of sodium alkanethiolate **2** (12 mmol) in Et_2O (60 ml) at 0°, CS_2 (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 Et_2O (60 ml). At 0°, a soln. of *2,2-dimethyl-3-(*N*-methyl-*N*-phenylamino)-2*H*-azirine* (**5**; 696 mg, 4 mmol) in Et_2O (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/CH_2Cl_2 (8:1, then 4:1), yielded **1** as an orange product.

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

b) Into a suspension of **2a** (210 mg, 3 mmol) in Et_2O (10 ml) at 0°, CS_2 (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 Et_2O (10 ml) was added. A soln. of **5** (174 mg,1 mmol) in Et_2O (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: 3360*m*, 2980*m*, 2920*w*, 1595*w*, 1490*s*, 1465*m*, 1430*m*, 1385*m*, 1370*s*, 1355*s*, 1310*w*, 1250*w*, 1185*w*, 1170*w*, 1160*w*, 1105*s*, 1075*w*, 1030*w*, 1005*m*, 960*w*, 705*m*. ^{1}H-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 Me). ^{13}C-NMR: 206.0, 205.4 (2*s*, C=S); 196.1, 195.2 (2*s*, C=S); 129.2–124.4 (arom. C); 65.9 (*s*, Me_2C); 50.6, 44.2 (2*q*, MeN); 30.4, 28.6 (2*q*, 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(4*H*)-thione* (**1b**). 752 mg (92%). Orange oil. B.p. 100–110°/0.05. Torr. IR: 2990*s*, 2940*m*, 2880*w*, 1575*s*, 1465*m*, 1455*m*, 1440*m*, 1420*w*, 1380*m*, 1360*m*, 1270*m*, 1130*s*, 1120*s*, 1060*m*, 985*s*, 965*s*, 905*s*, 830*s*, 645*m*. ^{1}H-NMR: 3.22 (*q*, $J = 7$, MeCH_2S); 1.54 (*s*, 2 Me); 1.42 (*t*, $J = 7$, *Me*CH_2S). ^{13}C-NMR: 249.7 (*s*, C(5)); 158.4 (*s*, C(2)); 96.0 (*s*, C(4)); 29.3 (*q*, 2 Me); 26.5 (*t*, MeCH_2S); 14.3 (*q*, *Me*CH_2S). CI-MS: 208 (21), 207 (14), 206 (100, $[M + 1]^+$).

1.3. *2-(Isopropylthio)-4,4-dimethyl-1,3-thiazole-5(4*H*)-thione* (**1c**). 376 mg (43%). Orange oil. B.p. 135–145°/0.06 Torr. IR: 2980*m*, 2940*m*, 2875*m*, 1575*s*, 1465*m*, 1455*m*, 1390*w*, 1370*m*, 1360*m*, 1245*m*, 1160*m*, 1120*s*, 1060*m*, 985*s*, 960*s*, 905*s*, 830*s*, 655*m*. ^{1}H-NMR: 3.99 (*sept.*, $J = 7$, Me_2CH); 1.54 (*s*, $Me_2C(4)$); 1.46 (*d*, $J = 7$, Me_2CH). ^{13}C-NMR: 249.9 (*s*, C(5)); 158.1 (*s*, C(2)); 96.1 (*s*, C(4)); 38.0 (*d*, Me_2CH); 29.3 (*q*, $Me_2C(4)$); 22.9 (*q*, Me_2CHS). 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 Et_2O 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*. ^{1}H-NMR: 1.62 (*s*, *t*-Bu); 1.55 (*s*, Me_2C). ^{13}C-NMR: 250.1 (*s*, C(5)); 156.9 (*s*, C(2)); 51.3 (*s*, Me_3CS); 30.3 (*q*, Me_2C); 29.3 (*q*, Me_3CS). 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*. ^{1}H-NMR: 8.63 (br. *s*, NH); 1.67 (*s*, 2 Me). ^{13}C-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, $M^{+\cdot}$), 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 $C_5H_7NS_3$ (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(4*H*)-thione* (**1e**). *Sodium phenylmethanethiolate* (**2e**) was prepared *in situ* from benzenethiol and NaH in Et_2O. According to the *General Procedure*, 917 mg (86%) of **1e** were obtained. Orange oil. B.p. 180°/0.06 Torr. IR: 3065*w*, 2990*m*, 2940*m*, 2865*w*, 1605*w*, 1575*s*, 1500*m*, 1455*m*, 1435*w*, 1415*w*, 1380*w*, 1360*w*, 1245*w*, 1125*s*, 1075*w*, 1035*m*, 985*m*, 965*s*, 905*s*, 865*w*, 830*m*, 700*m*, 650*m*. ^{1}H-NMR: 7.45–7.25 (*m*, 5 arom. H); 4.45 (*s*, PhCH_2S); 1.55 (*s*, 2 Me). ^{13}C-NMR: 249.6 (*s*, C(5)); 158.1 (*s*, C(2)); 136.0 (*s*, 1 arom. C); 129.1, 128.6, 127.7 (3*d*, 5 arom. C); 95.9 (*s*, C(4)); 36.1 (*t*, Ph*C*H_2S); 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 Et_2O. According to the *General Procedure*, 558 mg (81%) of **1f** were obtained. Orange oil. IR: 2975*s*, 2920*s*, 2915*s*, 2850*s*, 1570*s*, 1460*m*, 1430*m*, 1410*w*, 1375*m*, 1350*m*, 1120*s*, 980*s*, 960*s*, 900*s*, 825*s*, 640*m*. ^{1}H-NMR: 3.20 (*t*, J = 7.3, CH_2S); 1.8–1.7 (*m*, 1 CH_2); 1.53 (*s*, Me_2C); 1.45–1.25 (*m*, 9 CH_2); 0.89 (*t*, J = 7, Me). ^{13}C-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 (11*t*, 11 CH_2); 29.3 (*q*, Me_2C); 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. NH_4Cl (20 ml) and Et_2O (50 ml). The org. layer was separated, dried, and the solvent evaporated *i.v.* Chromatography with hexane/Et_2O 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: 2985*s*, 2925*m*, 2860*w*, 1565*s*, 1555*s*, 1455*m*, 1435*m*, 1420*m*, 1385*m*, 1365*m*, 1315*w*, 1240*w*, 1160*m*, 1010*m*, 990*s*, 965*m*, 950*s*, 910*w*, 865*m*, 650*w*. ^{1}H-NMR: 2.50 (*s*, MeS–C(2)); 2.23 (*s*, 2 MeS–C(5)); 1.50 (*s*, 2 Me). ^{13}C-NMR: 160.7 (*s*, C(2)); 89.2 (*s*, C(4)); 83.8 (*s*, C(5)); 24.7 (*q*, 2 Me); 16.8 (*q*, 2 *Me*S–C(5)); 14.8 (*q*, *Me*S–C(2)). CI-MS: 256 (16), 255 (10), 254 (100, $[M+1]^+$), 208 (12), 206 (7). Anal. calc. for $C_8H_{15}NS_4$ (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*. ^{1}H-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). ^{13}C-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 *Me*S). 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: 2980*s*, 2935*m*, 2880*m*, 1565*s*, 1555*s*, 1455*m*, 1440*m*, 1420*m*, 1380*m*, 1365*m*, 1270*m*, 1160*m*, 1060*w*, 1010*w*, 980*s*, 955*s*, 910*w*, 870*m*, 700*w*. ^{1}H-NMR: 3.05–2.95 (*m*, $MeCH_2S$–C(2)); 2.75–2.6 (*m*, $MeCH_2S$–C(5)); 2.16 (*s*, MeS); 1.44, 1.39 (2*s*, 2 Me); 1.27, 1.20 (2*t*, J = 7.37, 7.43, 2 $MeCH_2S$). ^{13}C-NMR: 160.4 (*s*, C(2)); 88.3 (*s*, C(4)); 83.9 (*s*, C(5)); 28.1, 26.6 (2*t*, 2 $MeCH_2S$); 24.7, 24.3 (2*q*, 2 Me); 17.1 (*q*, MeS); 14.6, 13.7 (2*q*, 2 $MeCH_2S$). CI-MS: 284 (19), 283 (15), 282 (100, $[M+1]^+$), 268 (4), 234 (8), 222 (16), 220 (7). Anal. calc. for $C_{10}H_{19}NS_4$ (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*. ^{1}H-NMR: 3.07 (*q*, J = 7.4, $MeCH_2S$); 2.24 (*s*, 2 MeS); 1.51 (*s*, 2 Me); 1.35 (*t*, J = 7.4, $MeCH_2S$). ^{13}C-NMR: 160.2 (*s*, C(2)); 88.7 (*s*, C(4)); 83.8 (*s*, C(5)); 26.7 (*t*, $MeCH_2S$); 24.6 (*q*, 2 Me); 16.8 (*q*, 2 MeS); 14.5 (*q*, $MeCH_2S$). 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: 2970*s*, 2920*m*, 2860*m*, 1560*m*, 1550*m*, 1460*m*, 1450*m*, 1440*m*, 1415*w*, 1380*m*, 1360*m*, 1240*m*, 1155*m*, 1050*m*, 1005*w*, 975*s*, 950*s*, 860*m*, 660*w*. ^{1}H-NMR: 3.74 (*sept.*, J = 6.8, Me_2CHS–C(2)); 3.16 (*sept.*, J = 6.9, Me_2CHS–C(5)); 2.13 (*s*, MeS); 1.50, 1.33 (2*s*, 2 Me); 1.30, 1.29 (2*d*, J = 6.8, 6.9, 2 Me_2CHS). ^{13}C-NMR: 160.6 (*s*, C(2)); 87.3 (*s*, C(4)); 84.6 (*s*, C(5)); 38.4, 37.7 (2*d*, 2 Me_2CHS); 24.9, 24.44, 24.38, 23.9, 23.2, 22.9 (6*q*, 2 Me, 2 Me_2CHS); 17.4 (*q*, MeS). CI-MS: 312 (19), 311 (20), 310 (100, $[M+1]^+$), 262 (7). Anal. calc. for $C_{12}H_{23}NS_4$ (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 $PhCH_2Li$ soln. was prepared from $(PhCH_2)_2O$ (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°→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), $PhCH_2Li$, and MeI (74 mg, 0.52 mmol), 63 mg (41%) of **9a** were obtained. Yellow powder. M.p. 68–69°. IR:

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*. ^{1}H-NMR: 7.3–7.15 (*m*, 5 arom. H); 3.46, 2.92 (*AB*, J = 13.8, PhCH_2); 2.42 (*s*, MeS–C(2)); 1.78 (*s*, MeS–C(5)); 1.55, 1.29 (2*s*, 2 Me). ^{13}C-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*, PhCH_2); 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 $C_{14}H_{19}NS_3$ (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: 2980*m*, 2935*m*, 1640*w*, 1565*s*, 1555*s*, 1460*w*, 1435*m*, 1420*m*, 1385*w*, 1360*w*, 1315*w*, 1240*w*, 1170*m*, 1125*w*, 990*s*, 955*m*, 925*m*. ^{1}H-NMR: 5.95–5.8 (*m*, CH_2=C*H*); 5.15–5.05 (*m*, CH_2=CH); 2.85–2.55 (*m*, CH_2); 2.41 (*s*, MeS–C(2)); 2.06 (*s*, MeS–C(5)); 1.47, 1.20 (2*s*, 2 Me). ^{13}C-NMR: 161.1 (*s*, C(2)); 134.6 (*d*, CH_2=*C*H); 118.1 (*t*, *C*H_2=CH); 82.2, 81.5 (2*s*, C(4), C(5)); 39.6 (*t*, CH_2); 24.1, 23.3 (2*q*, 2 Me); 14.8, 14.7 (2*q*, 2 MeS). CI-MS: 250 (14), 249 (13), 248 (100, $[M + 1]^+$), 200 (19). Anal. calc. for $C_{10}H_{17}NS_3$ (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-(α-chlorobenzylidene)hydroxylamine* (**10**; 78 mg, 0.5 mmol) and **1** (0.5 mmol) in Et_2O (5 ml) at r.t., Et_3N (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/Et_2O 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: 2970*w*, 2920*m*, 1560*m*, 1550*m*, 1490*w*, 1455*m*, 1440*m*, 1425*w*, 1380*w*, 1360*m*, 1310*w*, 1270*m*, 1230*w*, 1170*m*, 1010*m*, 1000*m*, 980*s*, 945*m*, 920*m*, 880*s*, 685*m*, 640*m*. ^{1}H-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 (2*s*, 2 Me). ^{13}C-NMR: 161.3 (*s*, C(7)); 156.3 (*s*, C(3)); 128.5 (*s*, 1 arom. C); 131.4, 128.9, 127.7 (3*d*, 5 arom. C); 127.1 (*s*, C(5)); 81.7 (*s*, C(9)); 27.2, 21.3 (2*q*, 2 Me); 14.4 (*q*, MeS). CI-MS: 313 (14), 312 (13), 311 (100, $[M + 1]^+$). Anal. calc. for $C_{13}H_{14}N_2S_3$ (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: 3060*w*, 2970*m*, 2925*m*, 2870*w*, 1560*m*, 1550*m*, 1490*w*, 1455*m*, 1445*m*, 1380*m*, 1360*m*, 1310*w*, 1275*m*, 1235*w*, 1170*m*, 1055*w*, 1045*w*, 1010*m*, 1000*m*, 970*s*, 925*m*, 880*s*, 685*m*, 655*w*, 640*m*. ^{1}H-NMR: 7.6–7.55 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 3.15–2.9 (*m*, MeCH_2S); 1.59, 1.43 (2*s*, 2 Me); 1.30 (*t*, J = 7.4, *Me*CH_2S). ^{13}C-NMR: 160.5 (*s*, C(7)); 156.2 (*s*, C(3)); 128.1 (*s*, 1 arom. C); 131.4, 128.8, 127.8 (3*d*, 5 arom. C); 127.1 (*s*, C(5)); 81.7 (*s*, C(9)); 27.2, 21.3 (2*q*, 2 Me); 26.4 (*t*, MeCH_2S); 14.4 (*q*, *Me*CH_2S). CI-MS: 327 (13), 326 (15), 325 (100, $[M + 1]^+$), 190 (45). Anal. calc. for $C_{14}H_{16}N_2OS_3$ (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: 2970*m*, 2920*m*, 2860*w*, 1580*w*, 1560*m*, 1550*m*, 1490*w*, 1460*m*, 1445*m*, 1380*m*, 1360*m*, 1310*w*, 1275*m*, 1240*w*, 1170*m*, 1155*w*, 1055*m*, 1010*m*, 1000*m*, 970*s*, 925*m*, 880*m*, 685*m*, 650*m*. ^{1}H-NMR: 7.6–7.55 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 3.77 (*sept.*, J = 6.8, Me_2CHS); 1.59, 1.44 (2*s*, 2 Me); 1.33, 1.32 (2*d*, J = 6.8, Me_2CHS). ^{13}C-NMR: 160.2 (*s*, C(7)); 156.2 (*s*, C(3)); 131.4, 128.8, 127.7 (3*d*, 5 arom. C); 127.9, 127.2 (2*s*, 1 arom. C, C(5)); 81.8 (*s*, C(9)); 37.6 (*d*, Me_2CHS); 27.1, 21.3 (2*q*, 2 Me); 23.3, 22.7 (2*q*, Me_2CHS). CI-MS: 341 (14), 340 (22), 339 (100, $[M + 1]^+$), 204 (14). Anal. calc. for $C_{15}H_{18}N_2OS_3$ (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 Et_3N (2 ml) at 0° for 1.5 h afforded 152 mg (87%) of **12d**. White crystals. M.p. 82.0–82.5°. IR: 2960*m*, 2920*m*, 2900*m*, 2860*w*, 1580*w*, 1560*s*, 1490*w*, 1475*w*, 1450*m*, 1445*m*, 1390*w*, 1380*w*, 1360*m*, 1310*w*, 1275*s*, 1165*m*, 1000*m*, 965*s*, 945*s*, 880*s*, 685*m*, 640*m*. ^{1}H-NMR: 7.6–7.55 (*m*, 2 arom. H); 7.4–7.35 (*m*, 3 arom. H); 1.60, 1.44 (2*s*, 2 Me); 1.49 (*s*, *t*-Bu). ^{13}C-NMR: 158.7, 156.3 (2*s*, C(7), C(3)); 131.3, 128.8, 127.8 (3*d*, 5 arom. C); 127.2, 127.1 (2*s*, 1 arom. C, C(5)); 82.5 (*s*, C(9)); 50.3 (*s*, Me_3C); 30.4 (*q*, Me_3C); 27.2, 21.3 (2*q*, 2 Me). CI-MS: 355 (17), 354 (21), 353 (100, $[M + 1]^+$), 297 (6). Anal. calc. for $C_{16}H_{20}N_2OS_3$ (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: 3050*w*, 3030*w*, 2995*w*, 2970*w*, 2930*w*, 1600*w*, 1565*m*, 1555*m*, 1490*w*, 1450*w*, 1445*w*, 1380*w*, 1360*w*, 1275*m*, 1225*m*, 1200*m*, 1170*w*, 1010*w*, 1000*w*, 970*s*, 925*w*, 880*m*, 780*s*, 730*s*, 720*s*, 685*m*, 665*m*, 645*w*. ^{1}H-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, PhCH_2S); 1.70, 1.50 (2*s*, 2 Me). ^{13}C-NMR: 160.2 (*s*, C(7)); 156.3 (*s*, C(3)); 136.4, 128.6 (2*s*, 2 arom. C); 131.4, 129.0, 128.8, 128.4, 127.8, 127.4 (6*d*, 10 arom. C); 127.1 (*s*, C(5)); 36.0 (*t*,

PhCH_2S); 27.2, 21.3 (2*q*, 2 Me). CI-MS: 389 (15), 388 (22), 387 (95, $[M + 1]^+$), 254 (9), 253 (15), 252 (100). Anal. calc. for $C_{19}H_{18}N_2OS_3$ (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: 2920*s*, 2840*m*, 1560*m*, 1550*m*, 1450*m*, 1440*m*, 1380*w*, 1360*w*, 1270*m*, 1195*w*, 1170*w*, 1010*w*, 970*s*, 920*w*, 880*m*, 710*m*, 685*m*, 660*m*. ^{1}H-NMR: 7.6–7.55 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 3.1–2.9 (*m*, CH_2S); 1.65–1.6 (*m*, CH_2); 1.59, 1.43 (2*s*, 2 Me); 1.3–1.2 (*m*, 9 CH_2); 0.81 (*t*, *J* = 6, Me). ^{13}C-NMR: 160.7 (*s*, C(7)); 156.1 (*s*, C(3)); 131.3, 129.8, 127.7 (3*d*, 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 (11*t*, 11 CH_2); 27.2, 21.3 (2*q*, Me_2C); 14.0 (2*q*, Me). CI-MS: 465 (16, $[M + 1]^+$), 332 (11), 331 (21), 330 (100). Anal. calc. for $C_{24}H_{36}N_2OS_3$ (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-2*H-*azirine* (**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/Et_2O 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*. ^{1}H-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). ^{13}C-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*. ^{1}H-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-2*H-*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/CH_2Cl_2 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: 3040*w*, 2980*m*, 2960*m*, 2920*w*, 1590*m*, 1545*m*, 1485*m*, 1440*m*, 1375*w*, 1355*w*, 1305*m*, 1290*m*, 1235*m*, 1160*m*, 1080*m*, 1060*m*, 1020*w*, 970*s*, 950*s*, 920*w*, 900*w*, 860*w*, 685*m*. ^{1}H-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 (2*s*, 2 Me). ^{13}C-NMR: 177.4, 163.5 (2*s*, C(3), C(7)); 143.6, 130.5 (2*s*, 2 arom. C): 129.7, 128.6, 127.8, 126.3, 125.7, 124.3 (6*d*, 10 arom. C); 90.2 (*s*, C(5)); 83.2 (*s*, C(9)); 28.5, 22.0 (2*q*, 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/CH_2Cl_2 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/CH_2Cl_2 2:1 yielded **21**.

3.4.1. N-*Hexyl-4,4-dimethyl-2-(methylthio)-1,3-thiazole-5(4*H*)-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*. ^{1}H-NMR: 3.21 (*t*, *J* = 7.0, CH_2N); 2.57 (*s*, MeS); 1.7–1.65 (*m*, CH_2); 1.45 (*s*, Me_2C); 1.35–1.3 (*m*, 3 CH_2); 0.89 (*t*, *J* = 6.8, Me). ^{13}C-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 CH_2); 27.3 (*q*, Me_2C); 13.9 (*q*, MeS, Me). CI-MS: 261 (9), 260 (14), 259 (100, $[M + 1]^+$). Anal. calc. for $C_{12}H_{22}N_2S_2$ (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: 2970*s*, 2940*s*, 2860*m*, 1665*s*, 1575*s*, 1460*m*, 1440*m*, 1420*w*, 1380*m*, 1360*m*, 1270*m*, 1240*m*, 1190*m*, 1170*w*, 1060*w*, 1020*w*, 980*s*, 925*s*, 840*m*, 665*w*, 640*w*, 630. ^{1}H-NMR: 3.20 (*t*, *J* = 7.0, CH_2N); 3.15 (*q*, *J* = 7.4, *Me*CH_2S); 1.7–1.6 (*m*, CH_2); 1.44 (*s*, Me_2C); 1.38 (*t*, *J* = 7.4, *Me*CH_2S); 1.35–1.3 (*m*, 3 CH_2); 0.89 (*t*, *J* = 6.7, Me). ^{13}C-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 (4*t*, 4 CH_2); 27.2 (*q*, Me_2C); 25.7 (*t*, MeCH_2S); 14.4 (*q*, *Me*CH_2S); 13.9

(*q*, Me). CI-MS: 275 (10), 274 (16), 273 (100, $[M+1]^+$). Anal. calc. for $C_{13}H_{24}N_2S_2$ (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(4*H*)-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*. ^{1}H-NMR: 7.4–7.25 (*m*, 5 arom. H); 4.40 (*s*, PhCH_2S); 3.20 (*t*, $J = 7.0$, CH_2N); 1.7–1.6 (*m*, CH_2); 1.46 (*s*, Me_2C); 1.35–1.25 (*m*, 4 CH_2); 0.89 (*t*, $J = 6.7$, Me). ^{13}C-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*, PhCH_2S); 31.5, 29.8, 26.8, 22.5 (4*t*, 4 CH_2); 27.3 (*q*, *Me*$_2$C); 14.0 (*q*, Me). CI-MS: 337 (11), 336 (23), 335 (100, $[M+1]^+$), 261 (11), 245 (12), 122 (11). Anal. calc. for $C_{18}H_{26}N_2S_2$ (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: 3050*s*, 3020*s*, 2950*s*, 1705*m*, 1620*m*, 1510*m*, 1480*w*, 1420*w*, 1400*w*, 1285*w*, 1235*w*, 1210*w*, 1020*s*, 965*m*, 880*m*, 685*w*. ^{1}H-NMR: 3.20, 3.14 (2*t*, $J = 7.0$, 7.3, CH_2S, CH_2N); 1.75–1.6 (*m*, 2 CH_2); 1.43 (*s*, Me_2C); 1.4–1.25 (*m*, 12 CH_2); 0.9–0.85 (*m*, 2 Me). ^{13}C-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 CH_2); 27.2 (*q*, *Me*$_2$C); 14.0, 13.9 (2*q*, 2 Me). CI-MS: 415 (7), 414 (25), 413 (100, $[M+1]^+$). Anal. calc. for $C_{23}H_{44}N_2S_2$ (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: 2980*s*, 2940*s*, 2860*s*, 1675*s*, 1660*s*, 1575*s*, 1570*s*, 1465*m*, 1455*m*, 1435*m*, 1420*w*, 1375*m*, 1360*m*, 1355*m*, 1330*w*, 1320*m*, 1245*m*, 1190*m*, 1170*m*, 1150*w*, 1140*w*, 1070*m*, 990*s*, 965*s*, 925*s*, 890*m*, 840*s*, 665*w*, 650*m*. ^{1}H-NMR: 2.6–2.55 (*m*, CHN); 2.56 (*s*, MeS); 1.8–1.25 (*m*, 5 CH_2); 1.43 (*s*, 2 Me). ^{13}C-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 (3*t*, 5 CH_2); 27.4 (*q*, 2 Me); 13.9 (*q*, MeS). CI-MS: 259 (10), 258 (16), 257 (100, $[M+1]^+$). Anal. calc. for $C_{12}H_{20}N_2S_2$ (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(4*H*)-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*. ^{1}H-NMR: 3.96 (*sept.*, $J = 6.8$, Me_2C*H*S); 2.6–2.55 (*m*, CHN); 1.8–1.2 (*m*, 5 CH_2); 1.43 (*s*, Me_2C); 1.41 (*d*, $J = 6.8$, *Me*$_2$CHS). ^{13}C-NMR: 170.3 (*s*, C(5′)); 156.4 (*s*, C(2′)); 81.1 (*s*, C(4′)); 71.7 (*d*, CH); 36.8 (*d*, Me_2*C*HS); 32.5, 25.5, 24.5 (3*t*, 5 CH_2); 27.3 (*q*, *Me*$_2$C); 22.9 (*q*, *Me*$_2$CHS). CI-MS: 287 (10), 286 (17), 285 (100, $[M+1]^+$), 273 (4). Anal. calc. for $C_{14}H_{24}N_2S_2$ (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(4*H*)-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: 2980*m*, 2925*w*, 1740*s*, 1655*m*, 1570*m*, 1460*w*, 1430*w*, 1395*w*, 1370*m*, 1355*w*, 1340*w*, 1310*w*, 1270*m*, 1240*m*, 1185*s*, 1095*w*, 1060*w*, 1030*m*, 985*s*, 960*m*, 935*m*, 915*m*, 835*m*, 635*w*. ^{1}H-NMR: 4.23 (*q*, $J = 7.1$, MeCH_2); 4.02 (*s*, CH_2N); 2.58 (*s*, MeS); 1.50 (*s*, 2 Me); 1.30 (*t*, $J = 7.1$, *Me*CH_2). ^{13}C-NMR: 179.2 (*s*, C(5′)); 168.6 (*s*, C=O); 156.3 (*s*, C(2′)); 82.4 (*s*, C(4′)); 61.4 (t, CH_2); 61.0 (*t*, Me*C*H_2O); 27.1 (*q*, *Me*$_2$C); 14.0 (*q*, MeS, *Me*CH_2). CI-MS: 263 (10), 262 (13), 261 (100, $[M+1]^+$), 115 (2). Anal. calc. for $C_{10}H_{16}N_2O_2S_2$ (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(4*H*)-imine* (**21h**). Reaction of **1b** (103 mg, 0.5 mmol) with *1-azidoadamantane* (**20d**; 443 mg, 2.5 mmol) afforded 134 mg (83%) of **21h**. White crystals. M.p. 59°. IR: 2970*m*, 2920*s*, 2910*s*, 2850*m*, 1670*m*, 1660*m*, 1565*m*, 1450*m*, 1370*w*, 1350*m*, 1310*m*, 1265*w*, 1190*m*, 1110*w*, 1085*w*, 980*m*, 970*s*, 935*w*, 910*m*, 830*m*, 635*m*. ^{1}H-NMR: 3.15 (*q*, $J = 7.4$, MeCH_2); 2.15–2.1 (*m*, 3 CH); 1.85–1.8, 1.75–1.65 (2*m*, je 3 CH_2); 1.38 (*t*, $J = 7.4$, *Me*CH_2); 1.38 (*s*, Me_2C). ^{13}C-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 CH_2); 29.5 (*d*, 3 CH); 27.7 (*q*, *Me*$_2$C); 25.4 (*t*, MeCH_2); 14.5 (*q*, *Me*CH_2). CI-MS: 325 (10), 324 (21), 323 (100, $[M+1]^+$). Anal. calc. for $C_{17}H_{26}N_2S_2$ (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(4*H*)-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: 2960*m*, 2900*s*, 2840*m*, 1665*m*, 1650*m*, 1565*m*, 1450*m*, 1365*w*, 1350*w*, 1305*w*, 1235*w*, 1190*m*, 1110*w*, 1080*w*, 1050*w*, 975*m*, 965*s*, 930*w*, 905*m*, 825*m*. ^{1}H-NMR: 3.97 (*sept.*, $J = 6.8$, Me_2C*H*); 2.11 (*s*, 3 CH); 1.85–1.8, 1.7–1.65 (2*m*, je 3 CH_2); 1.41 (*d*, $J = 6.8$, *Me*$_2$CH); 1.38 (*s*, Me_2C). ^{13}C-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 CH_2); 38.4 (*d*, Me_2*C*H); 36.4 (*t*, 3 CH_2); 29.5 (*d*, 3 CH); 27.7 (*q*, *Me*$_2$C); 23.0 (*q*, *Me*$_2$CH). CI-MS: 339 (11), 338 (22), 337

Table 5. *Crystallographic Data for Compounds* **1d**, **7**, **15**, **16**, *and* **21g**

	1d	**7**	**15**	**16**	**21g**
Crystallized from	hexane/CH_2Cl_2	hexane/AcOEt	hexane/Et_2O	hexane/Et_2O	hexane/CH_2Cl_2
Empirical formula	$C_9H_{15}NS_3$	$C_5H_7NS_3$	$C_{16}H_{20}N_2S_3$	$C_{16}H_{20}N_2S_3$	$C_{10}H_{16}N_2O_2S_2$
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 × 0.27 × 0.44	0.28 × 0.31 × 0.40	0.20 × 0.22 × 0.45	0.33 × 0.35 × 0.45	0.17 × 0.20 × 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)
α [°]	90	90	90.71(1)	92.89(2)	98.60(2)
β [°]	97.26(1)	98.92(3)	106.45(1)	95.28(2)	92.48(2)
γ [°]	90	90	83.89(2)	107.88(2)	75.78(2)
V [Å^3]	1201.1(5)	797.5(4)	1724.4(5)	840.3(3)	648.1(3)
Space group	$P2_1/n$	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	4	4	4	2	2
D_x [g cm^{-3}]	1.291	1.476	1.296	1.330	1.334
Absorption coefficient μ (MoK_α) [cm^{-1}]	5.530	8.091	4.080	4.180	3.820
Absorption correction min, max	–	–	–	0.893, 1.041	0.751, 1.471
2θ(max) [°]	60	60	55	55	60
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_w[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
$\Delta\varrho$ (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 $\Sigma w(|F_o| - |F_c|)^2$; $1/w = \sigma^2(F_o) + (0.005F_o)^2$.

(100, $[M+1]^+$), 295 (3), 238 (6). Anal. calc. for $C_{18}H_{28}N_2S_2$ (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: 3040*w*, 2990*w*, 2940*w*, 2870*w*, 1585*s*, 1575*s*, 1515*w*, 1500*w*, 1455*w*, 1435*w*, 1380*w*, 1360*w*, 1330*m*, 1310*m*, 1295*m*, 1240*w*, 1190*m*, 1160*s*, 1120*w*, 1090*m*, 1020*w*, 990*m*, 970*w*, 925*m*, 850*w*, 830*m*, 810*m*, 670*m*, 630*m*. ^{1}H-NMR: 7.83, 7.33 (*AA'BB'*, J = 8.4, 4 arom. H); 2.61 (*s*, MeS); 2.45 (*s*, Me); 1.44 (*s*, Me_2C). 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/Et_2O 4:1, 57 mg of a mixture (ratio 1:1.2 (^{1}H-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]: ^{1}H-NMR (from mixture): 3.83 (*s*, 2 MeO); 1.69 (*s*, 2 Me).

Data of **26** [37]: ^{1}H-NMR (from mixture): 3.90, 3.89 (2*s*, 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., $NaBH_4$ (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/Et_2O 25:1, 47 mg (65%) of *4,5-dihydro-4,4-dimethyl-2-(methylthio)-1,3-thiazole-5-thiol* (**27**) were obtained. Colorless oil. IR: 3070*w*, 2985*m*, 2980*m*, 2970*m*, 2930*m*, 2860*w*, 1565*m*, 1555*m*, 1465*m*, 1440*w*, 1435*w*, 1385*w*, 1365*m*, 1315*w*, 1270*w*, 1250*w*, 1170*m*, 1140*w*, 990*s*, 950*m*, 930*w*, 910*w*, 850*w*. ^{1}H-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 (2*s*, 2 Me). ^{13}C-NMR: 162.1 (*s*, C(2)); 79.7 (*s*, C(4)); 59.5 (*d*, C(5)); 26.2, 22.2 (2*q*, 2 Me); 14.9 (*q*, MeS). CI-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_α radiation (λ = 0.71069 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 from [45]. Anomalous dispersion effects were included in F_{calc} [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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