34. New Addition Reactions of Organometal Compounds with 4,4-Dimethyl-1,3-thiazole-5(4*H*)-thiones

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Dedicated to Professor *H. Suschitzky* on the occasion of his 80th birthday

(I.XII.95)

Addition reactions of organometallic reagents with 4,4-disubstituted 1,3-thiazole-5(4*H*)-thiones were studied. Whereas the reactions with alkyllithium and alkyl *Grignard* reagents occurred in the thiophilic manner, the carbophilic addition was observed with allyllithium and allyl *Grignard* reagents. A radical reaction mechanism is proposed for rationalizing these observations (*Scheme 5*). A radical cyclization of the prepared 5-allyl-4,5-dihydro-1,3-thiazole-5-thiol derivatives yielded 1,6-dithia-3-azaspiro[4.4]non-2-enes (*Table 4*).

1. Introduction. – The chemical properties of 1,3-thiazole-5(4*H*)-thiones **1** have been studied recently [1–3]. With the exocyclic C=S group, **1** is highly reactive in many reactions typical for thiocarbonyl compounds [4–9], such as addition reactions with organometallics [10–12], cycloaddition reactions with 1,3-dipoles [13–19], 1,3-dienes [20] [21], oxiranes [21] [22] and ynamines [23], as well as cyclosubstitutions with acetylenes [24], previously observed with S-heterocycles containing an adjacent C=S group (*i.e.*, the fragment S–C=S).

In the reactions of **1** with organometallics, it was shown that organolithium reagents undergo thiophilic addition exclusively [10]. In contrast, organocuprates only afforded products of carbophilic addition [11] [12]. Products of carbophilic and/or thiophilic attack were obtained from the reaction of **1** with *Grignard* reagents, depending on the nature of the *Grignard* reagent and the solvent used in the reaction [10].

In this paper, we report on further results from addition reactions of organometallics with a variety of 2-alkyl-substituted 1,3-thiazole-5(4*H*)-thiones, in which some exceptions of the previously formulated rules were observed, and possible reaction mechanisms are discussed. Furthermore, the radical cyclization of some of the prepared 5-alkenyl-4,5-dihydro-1,3-thiazole-5(4*H*)-thioles was studied.

2. Addition Reactions with Organolithium Reagents. – 2.1. *With Methyllithium.* Differently substituted 1,3-thiazole-5(4*H*)-thiones **1** were treated with MeLi at −78° for 10 min. After protonation or alkylation, exclusively products **2**, formed *via* a thiophilic addition of the organolithium reagent, were obtained. The results are summarized in *Table 1*. In case of 2-methyl-substituted **1c**, the reaction at −78° gave **2c** only in very low yield, probably because of the instability of **1c** under the reaction conditions. The yield was improved when the reaction was performed at −94°, while for the 2-benzyl-substituted **1d**, a longer reaction time was needed to consume the starting material completely.

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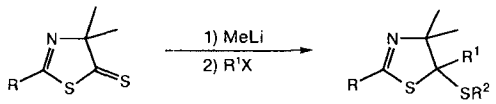


1 2 R^2 = Me

Table 1. *Thiophilic Addition of MeLi to* **1a–d**

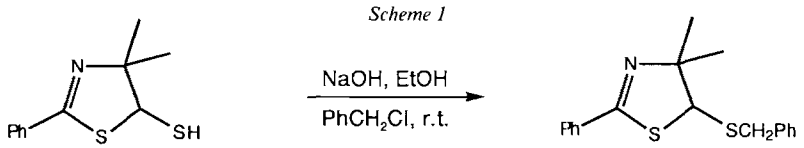
	R	Condition (1st step)	R^1X	Product	Yield [%]
1a	Ph	−78°, 10 min	$PhCH_2Br$	**2a**	78
1b	*t*-Bu	−78°, 10 min	H_2O	**2b**	87
1c	Me	−94°, 10 min	H_2O	**2c**	63
1d	$PhCH_2$	−78°, 30 min	H_2O	**2d**	54

2.2. *With Allyl- and Benzyllithium Reagents.* In constrast to the reactions with alkyllithium, the reaction of **1** with allyl- and benzyllithium compounds proceeded *via* carbophilic attack. At −78° in THF, **1** was treated with benzyllithium[3]). After alkylation with alkylhalides, adducts **2** were obtained as the sole products. Similarly, the reaction of **1** with allyllithium and (2-methylallyl)lithium[4]) occurred also *via* carbophilic addition (*Table 2*).

The structures of the adducts **2e–s** were confirmed by chemical and spectroscopic means and by comparison with adduct **2a**. *E.g.*, product **2a**, obtained *via* thiophilic addition of MeLi to **1a** followed by benzylation with benzyl bromide (*Table 1*), was also formed *via* carbophilic addition of benzyl lithium to **1a** followed by alkylation with MeI (*Table 2*). Similarly, adduct **2k**, prepared by carbophilic addition of allyllithium to **1a** and alkylation with MeI, was identical with the compound generated *via* thiophilic addition of MeLi to **1a** and subsequent allylation of the intermediate [10]. These results confirm that different types of intermediates are involved in the addition reactions with alkyl-(aryl)- and allyl(benzyl)-derived organolithium reagents.

The NMR data also provided evidence for the structures **2**. For comparison, 5-(benzylthio)-4,5-dihydro-4,4-dimethyl-2-phenyl-1,3-thiazole (**4**) was prepared by benzylation of 4,5-dihydro-1,3-thiazole-5-thiol **3** under basic conditions (*Scheme 1*).

Scheme 1



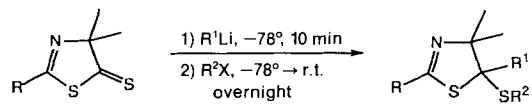
3 **4** (97%)

In the ^{1}H-NMR spectrum of **4**, $PhCH_2S$ gave rise to a narrow *AB* system at 3.78 and 3.75 ppm. Similar signals were found in compounds **2j**, **2m**, and **2s**. In contrast, $PhCH_2$ of **2a** showed a wide *AB* system at 3.63 and 3.07 ppm. In the ^{1}H-NMR spectra of **2e–g**, **2o**, **2r**, and **2u**, $PhCH_2$ also appeared as a wide *AB* system in this region. The differences in the chemical shifts reflect the different linkages of the $PhCH_2$ moieties in the two types of compounds. Moreover, the 2D ^{1}H,^{13}C-NMR coupling spectra gave direct evidence for the benzyl linkage: the ^{1}H,^{13}C long-range COSY of **2g** showed clearly that $PhCH_2$ was attached to C(5), and not to the S-atom at C(5).

[3]) Benzyllithium was generated either from dibenzyl ether by cleavage with Li [25] or from dibenzylmercury [26] by metal exchange with BuLi [27].

[4]) Allyllithium and (2-methylallyl)lithium were prepared from the corresponding phenyl ethers [28]. In comparison with other procedures [29–34], this method is most convenient.

Table 2. *Carbophilic Additions of Benzyl- and Allyllithium Compounds to* **1**



1 **2**

	R	R^1	R^2X	Product (yield [%])
1a	Ph	$PhCH_2$[a])	CH_2=$CHCH_2Br$	**2e** (93)
1a	Ph	$PhCH_2$[a])	CH_2=$CH(CH_2)_2Br$	**2f** (61[b]))
1a	Ph	$PhCH_2$	CH_2=$CH(CH_2)_3Br$	**2g** (67[a])[b]), 84[c]))
1a	Ph	$PhCH_2$[c])	MeI	**2a** (89)
1a	Ph	CH_2=$CHCH_2$	CH_2=$CH(CH_2)_2Br$	**2h** (92)
1a	Ph	CH_2=$CHCH_2$	CH_2=$CH(CH_2)_3Br$	**2i** (91)
1a	Ph	CH_2=$CHCH_2$	$PhCH_2Br$	**2j** (96)
1a	Ph	CH_2=$CHCH_2$	MeI	**2k** (99)
1a	Ph	CH_2=$C(Me)CH_2$	CH_2=$CHCH_2Br$	**2l** (95)
1a	Ph	CH_2=$C(Me)CH_2$	$PhCH_2Br$	**2m** (94)
1a	Ph	CH_2=$C(Me)CH_2$	MeI	**2n** (98)
1b	*t*-Bu	$PhCH_2$[c])	CH_2=$CHCH_2Br$	**2o** (98)
1b	*t*-Bu	CH_2=$CHCH_2$	$PhCH_2Br$	**2p**[d]) (74)
1b	*t*-Bu	CH_2=$CHCH_2$	MeI	**2q**[e]) (13)
1d	$PhCH_2$	$PhCH_2$[c])	CH_2=$CHCH_2Br$	**2r** (49)
1d	$PhCH_2$	CH_2=$CHCH_2$	$PhCH_2Br$	**2s**[f]) (17)

[a]) Benzyllithium prepared from dibenzylmercury.
[b]) By-product **2t** (R = Ph, R^1 = $PhCH_2$, R^2 = H) obtained in 4% yield.
[c]) Benzyllithium prepared from dibenzyl ether.
[d]) Structure of **2p**: R = *t*-Bu, R^1 = CH_2=$CHCH_2$, R^2 = H.
[e]) By-product **2p** obtained in 33% yield.
[f]) By-product **2u** (R = $PhCH_2$, R^1 = CH_2=$CHCH_2$, R^2 = H) obtained in 16% yield.

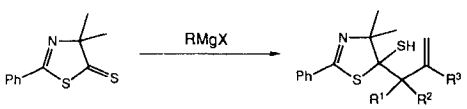
It was surprising that 2-(*tert*-butyl)-4,4-dimethyl-1,3-thiazole-5(4*H*)-thione (**1b**), in the reaction with allyllithium followed by treatment with benzyl bromide, gave thiol **2p** instead of the expected benzylation product. On replacing benzyl bromide in this reaction by MeI, the methylated **2q**, together with **2p**, was obtained in low yield. Similarly, in the reaction of 2-benzyl-4,4-dimethyl-1,3-thiazole-5(4*H*)-thione (**1d**) with allyllithium followed by treatment with benzyl bromide, a 1:1 mixture of **2s** and **2u** was obtained. In contrast, addition of benzyllithium to **1b**, followed by alkylation with allyl bromide, afforded **2o** in excellent yield.

It is worth mentioning that the two methods used for the preparation of benzyllithium led to different results in the reaction with **1**. *E.g.*, in the reactions with **1a**, benzyllithium derived from dibenzylmercury gave, after alkylation with 4-bromobut-1-ene and 5-bromopent-1-ene, **2f** and **2g** in only moderate yields. The thiol **2t** was isolated as a by-product in both cases. On the other hand, pure **2g** was obtained in much better yield using benzyllithium generated from dibenzyl ether.

Whereas most of the reactions of **1** and organolithium reagents led to the addition products in good-to-excellent yields, in case of 2-benzyl-4,4-dimethyl-1,3-thiazole-5(4*H*)-thione (**1d**), the adducts **2r** and **2s** were formed only in low yields (*Table 2*). It is possible

that the benzyl group, which under the reaction conditions might be deprotonated by the organolithium compound, is responsible for side reactions.

3. Addition Reactions with *Grignard* Reagents. – The 1,3-thiazole-5(4*H*)-thiones **1** readily undergo addition reactions with *Grignard* reagents. The allyl *Grignard* reagents used were prepared from the corresponding halides and Mg. Usually, the reactions were carried out at room temperature in THF or Et_2O, while the reaction of (3,3-dimethylallyl)magnesium bromide and **1a** was performed at 0°, due to the instability of the *Grignard* reagent. All addition reactions occurred *via* carbophilic attack yielding adducts **5**. The results are summarized in *Table 3*.



1a **5**

Table 3. *Reaction of Allyl* Grignard *Reagents with* **1a**

RX	R^1	R^2	R^3	Product (yield [%])	Ratio of diastereoisomers
CH_2=CHCH(Me)Cl	Me	H	H	**5a** (91)	3:2
MeCH=$CHCH_2$Br	Me	H	H	**5a** (85)	3:2
CH_2=C(Me)CH_2Cl	H	H	Me	**5b** (97)	–
Me_2C=$CHCH_2$Br	Me	Me	H	**5c** (70)	–

It is worth noting that the reaction of **1a** with the two *Grignard* reagents derived from 3-chlorobut-1-ene and 1-bromobut-2-ene (crotyl bromide) afforded the same product **5a**, in both cases in good yield. This result indicates that the same *Grignard* compound was formed from the two different halides and confirms an allylic rearrangement of *Grignard* reagents of type **A** and/or **B** (*cf.* [35] [36]; *Scheme 2*). From the equilibrium **A** ⇌ **B**, the

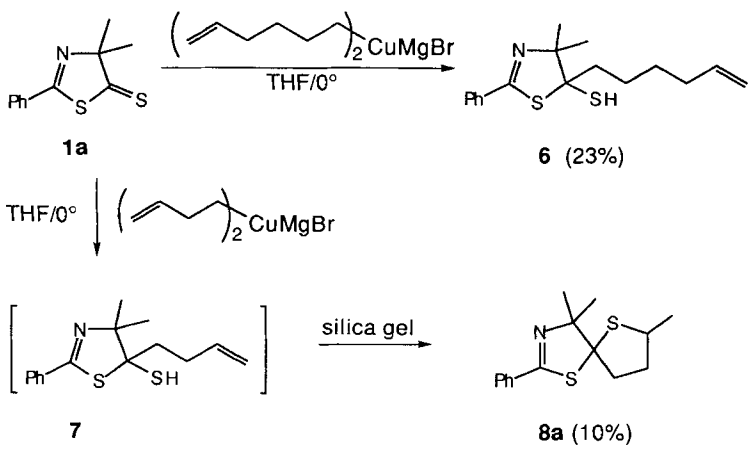
Scheme 2

A **B**

formation of two regioisomeric adducts could be expected in the reaction with **1**. However, all four *Grignard* reagents gave only one regioisomer, namely the product of the addition of the branched *Grignard* reagent of type **B**. This suggests that either the branched isomer **B** of the *Grignard* reagent is more reactive than the linear form **A**, or the linear form **A** reacts exclusively *via* inversion of the allyl moiety. A third possibility is a thiophilic addition of **A** followed by a sigmatropic [2,3]-rearrangement (for a discussion, see [36]).

4. Addition Reactions with Organocuprate Reagents. – Organocuprates are easily prepared from organolithium or *Grignard* reagents [37] by treatment with $CuBr \cdot SMe_2$ in THF at 0°, *e.g.*, but-3-enyl- and hex-5-enylcuprate were obtained from but-3-enylmagnesium bromide and hex-5-enylmagnesium bromide, respectively. The reaction of 1,3-thiazole-5(4*H*)-thione **1a** and hex-5-enylcuprate in THF yielded **6**, the product of the car-

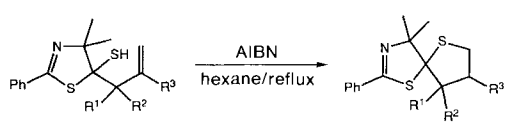
Scheme 3



bophilic addition, in only poor yield, while but-3-enylcuprate under analogous conditions afforded, after chromatography, the spiroheterocycle **8a** again in low yield (*Scheme 3*). The expected intermediate **7** of the latter reaction was detected in the crude reaction mixture by ^{1}H-NMR spectroscopy (δ 5.95–5.8 (*m*, 1 olef. H); 5.15–5.0 (*m*, 2 olef. H); 2.37 (*s*, SH)). Apparently, the cyclization to **8a** occurred during the chromatographic separation.

The major products in both reactions were 4,5-dihydro-4,4-dimethyl-2-phenyl-1,3-thiazole-5-thiol (**3**) [11] and the corresponding disulfide. The latter was formed during chromatography. Analogous reductions were reported as a result of the reactions of organocuprate [11] and *Grignard* reagents [6], respectively, to thiocarbonyl groups. A concerted mechanism was proposed to be responsible [11], in analogy to the reduction of carbonyl compounds with *Grignard* reagents [38].

5. Radical Cyclizations of 5-Alkenyl-4,5-dihydro-1,3-thiazole-5-thiols to Spiro Heterocycles. – By refluxing 5-allyl-4,5-dihydro-1,3-thiazole-5-thiols **5a–c** in hexane in the presence of the radical initiator α,α'-azoisobutyronitrile (AIBN), a radical cyclization into 1,6-dithia-3-azaspiro[4.4]non-2-enes **8b–d** occurred (*Table 4*). In the case of **8c**, the two diastereoisomers (**8c** and **8c'**) were separated by chromatography.



5 **8b-d**

Table 4. *Radical Cyclization of* **5** *to Spiroheterocycles* **8**

	R^1	R^2	R^3	Product (yield [%])	Ratio of diastereoisomers
5a	Me	H	H	**8b** (73)	2:1
5b	H	H	Me	**8c** (82)	4:1
5c	Me	Me	H	**8d** (56)	–

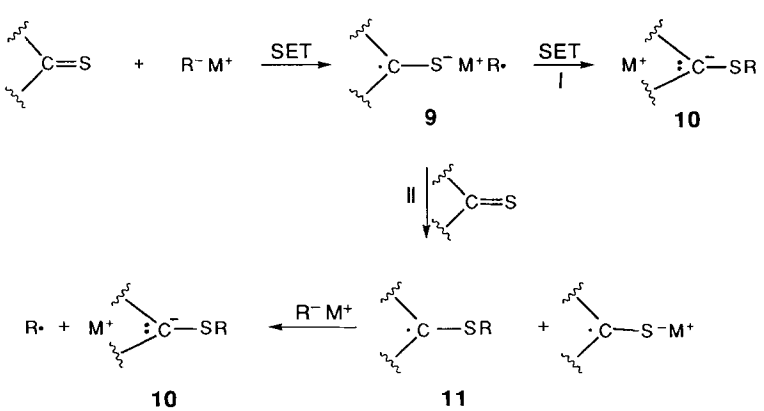
The formation of a five-membered ring seems to be strongly preferred (see also [12]), as the reaction of **1a** with but-3-enylcuprate yielded the spiro[4.4] heterocycle **8a** but none of the spiro[4.5] compound, while the formation of a six-membered ring was shown to be preferred over the corresponding seven-membered ring [12]. Futhermore, 5-(hex-5-enylthio)-4,5-dihydro-4,4-dimethyl-2-phenyl-1,3-thiazole-5-thiol (**6**) failed to form a spiro compound in the presence of various radical initiators, both thermally (AIBN, CuCl, $CuBr \cdot SMe_2$, CuI, dibenzoyl peroxide) and photochemically (irradiation with mercury high- and low-pressure lamps). Obviously, as an approach to the synthesis of spiro heterocycles, this radical cyclization is rather limited.

6. Discussion. – Allyl *Grignard* compounds were reported to react as carbophilic reagents with thiocarbonyl compounds [36] [39], and with substituted allyl *Grignards*, inversion of the allylic chain during the carbophilic addition was observed.

In contrast to the carbophilic addition of organometallics towards carbonyl compounds, thiophilic additions were reported for the reactions of alkyl- and aryllithium and *Grignard* reagents with thiocarbonyl compounds [10] [40–46]. Reactions of allyllithium compounds with thiocarbonyl groups were reported very rarely. To the best of our knowledge, only two such reactions are described so far. In 1974, *Rautenstrauch* [47] reacted (3-methylbut-2-enyl)lithium with adamantanethione and obtained the product resulting from carbophilic attack. One year later, *Beak et al.* [43] reported that the reactions of (benzhydryl)lithium with thiobenzophenone and 4,4′-dimethoxythiobenzophenone, respectively, also proceeded *via* carbophilic addition.

Numerous mechanistic investigations were carried out with the aim to find a rationale for the thiophilic additions. The mechanism of direct nucleophilic addition to the thiocarbonyl S-atom was proposed by considering the inverse polarization of the C=S bond [48], or by the HSAB principle [42] [49], as well as by the molecular-orbital theory [50]. This is supported by the reaction of thiocarbonyl compounds with (*Z*)- or (*E*)-substituted prop-2-enyl *Grignard* reagents, in which retention of the configuration was observed [43]. For the carbophilic addition of allylic organometallics, even more mechanistic hypotheses were presented, such as reaction through a six-center cyclic intermediate [51–54], *via* an ate complex [55] [56], a thiophilic addition followed by a [2,3]-sigmatropic shift [47], and

Scheme 4

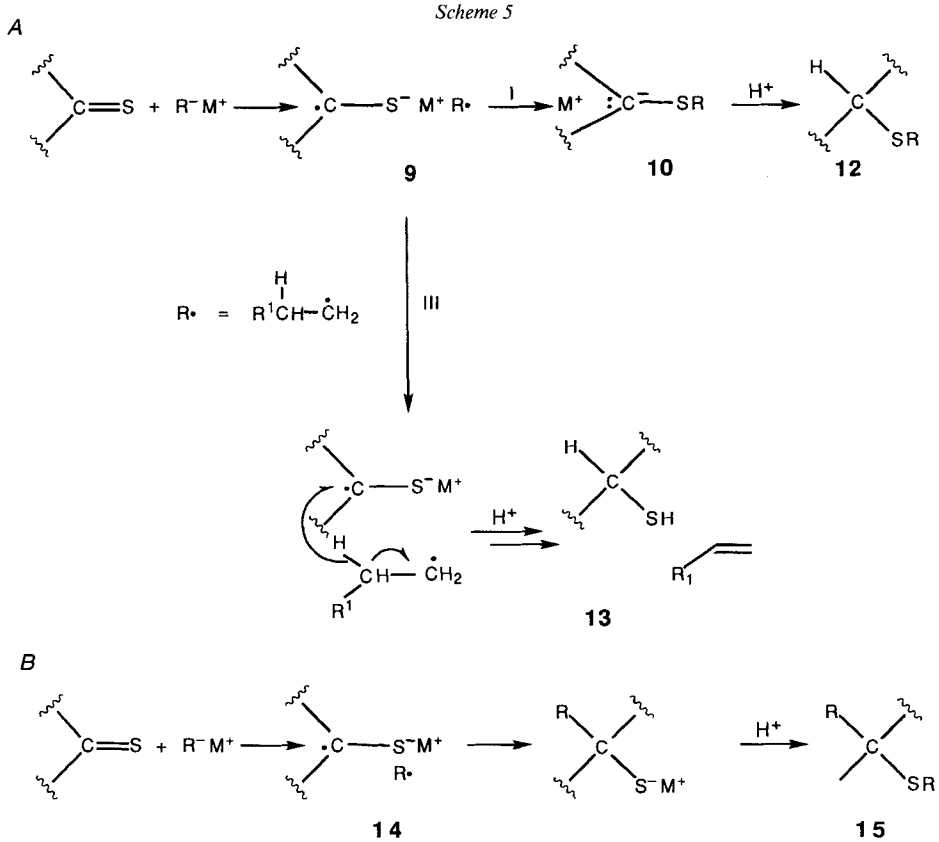


bimolecular electrophilic substitution (S_E2' mechanism) [57] [58]. *Thuillier* and coworkers [59] showed that the sigmatropic rearrangement does not occur in the reactions of allyl *Grignard* reagents and thiocarbonyl compounds. Therefore, the direct carbophilic addition was proposed by these authors and others [10] [36] [59]. In our experiments with allyllithium compounds, it seems that the thiophilic addition/sigmatropic shift mechanism again is not involved, and that the reaction proceeds in analogous manner to the reaction with benzyllithium *via* carbophilic attack. For the same reason, the mechanism *via* a six-center cyclic intermediate [51–54] could be ruled out.

In some reactions of alkyl- and aryllithium reagents with thiocarbonyl compounds, thioketyl radicals were detected by ESR spectroscopy [44] [49] [60–62]. *Beak* and coworkers [43] [44] proposed a radical mechanism for the thiophilic addition involving a single-electron transfer (SET) from the organometallic reagent to the thiocarbonyl group to form the caged radical pair **9**. Through a further SET (I) or a radical chain reaction (II), the ion pair **10** could be formed (*Scheme 4*), which then is protonated or alkylated.

Ohno et al. [46] [63] suggested another caged radical pair as the reaction intermediate. Instead of the thioketyl radical pair **9**, the SET from organolithium to the thiocarbonyl C-atom leads to a radical anion with the radical center on the S-atom and the negative

Scheme 5



charge on the C-atom. Through a radical-coupling procedure the products of the thiophilic attack are obtained.

In addition to the ESR evidence for the thioketyl radicals, the proposed mechanisms were also supported by the results of an isotope experiment: the reaction of di(*tert*-butyl) thioketone and (β,β-D_2)butyllithium afforded the reduction product 2,2,4,4-tetramethyl(3-D)pentane-3-thiol, which was generated by a β-D transfer onto the thiocarbonyl C-atom. By using butyllithium instead of the deuterated reagent, and by treatment of the reaction mixture with D_2O, the reduction product with a deuteriated thiol group was formed [46]. This result is consistent with mechanism *A* in *Scheme 5*. By the two radical mechanisms formulated in *Schemes 4* and *5*, most of the results reported in the literature can be explained.

Our results also suggest that in the reaction of **1** and organolithium and -magnesium compounds, a radical intermediate is involved. This is obvious for the formation of trithioorthoesters from 2-(alkylthio)-4,4-dimethyl-1,3-thiazole-5(4*H*)-thiones and MeLi [64]. On the basis of our experiments and the results reported in the literature, we propose the radical mechanisms formulated in *Scheme 5* for the reaction of the thiocarbonyl group of **1** with alkyl(aryl)metals (*A*) and allylmetals (*B*), respectively. Both mechanisms involve a single-electron transfer (SET) from the organometallic compound to the thiocarbonyl group. The difference between the two mechanisms is that different radical intermediates are formed. With alkyl- and arylmetals, the intermediate may be the caged radical pair **9**, which reacts either through a SET mechanism (I) to give the ion pair **10**, as in *Beak*'s mechanism, ultimately producing the addition products of type **12**, or *via* a shift of β-H of the organometallics (III) to give the reduction product **13**. In the case of allylmetals, considering the stability of allyl radicals, the resulting intermediate **14** in the reaction with thiocarbonyl compounds is more likely to be a free radical. It undergoes radical coupling to give the *C*-addition product **15**.

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Experimental Part

General. See [64].

1. *Reaction of* **1** *with Organolithium Reagents.* 1.1. *General Procedures. Method A:* To 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 mixture was stirred 5 min at −78°. Then, the soln. was poured into sat. aq. NH_4Cl soln./Et_2O 2:5 (70 ml). The org. layer was dried and evaporated. Chromatography with hexane/Et_2O 25:1 yielded the addition product.

Method B: To a soln. of **1** (0.5 mmol) in THF (3 ml) at −78°, the organometallic reagent was added dropwise. After stirring for 10 min, an alkyl halide (1 mmol) was added and the mixture maintained at −78° → r.t. overnight. Workup and purification as in *Method A*.

1.2. *With Methyllithium.* 1.2.1. *5-Benzyl-4,5-dihydro-4,4-dimethyl-5-(methylthio)-2-phenyl-1,3-thiazole* (**2a**). According to *Method B*, from 4,4-dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione (**1a**; 111 mg, 0.5 mmol), MeLi (0.37 ml, 0.6 mmol), and benzyl bromide (171 mg, 1 mmol): 128 mg (78%) of **2a**. Pale yellow powder. M.p. 68–69°. IR: 1590*m*, 1580*m*, 1495*m*, 1455*m*, 1450*m*, 1430*w*, 1385*w*, 1360*w*, 1260*m*, 1175*m*, 1080*w*, 960*s*, 940*m*, 700*s*, 690*s*. ^{1}H-NMR: 7.85–7.8 (*m*, 2 arom. H); 7.45–7.3 (*m*, 8 arom. H); 3.63, 3.07 (*AB*, J = 13.8, PhCH_2); 1.83 (*s*, MeS); 1.74, 1.44 (2*s*, Me_2C). ^{13}C-NMR: 162.9 (*s*, C(2)); 138.0, 133.2 (2*s*, 2 arom. C); 131.1, 130.2, 128.4, 128.0, 127.9, 127.1 (6*d*, 10 arom. CH); 82.7, 81.7 (2*s*, C(4), C(5)); 42.2 (*t*, PhCH_2); 23.4, 23.1 (2*q*, Me_2C); 15.4 (*q*, MeS). CI-MS: 330 (11), 329 (23), 328 (100, $[M+1]^+$), 280 (14), 145 (11). Anal. calc. for $C_{19}H_{21}NS_2$ (327.51): C 69.68, H 6.46, N 4.28, S 19.58; found: C 69.70, H 6.38, N 4.39, S 19.45.

1.2.2. *2-(*tert*-Butyl)-4,5-dihydro-4,4-dimethyl-5-(methylthio)-1,3-thiazole* (**2b**). According to *Method B*, from 2-(*tert*-butyl)-4,4-dimethyl-1,3-thiazole-5(4*H*)-thione (**1b**; 1.0 g, 5 mmol) and MeLi (6.25 ml, 10 mmol): 938 mg (87%) of **2b**. Colorless oil. IR: 1610*s*, 1475*m*, 1460*s*, 1435*m*, 1380*m*, 1365*s*, 1260*m*, 1180*m*, 1045*s*, 1010*m*, 1000*s*, 950*m*, 890*m*, 840*m*, 660*m*. ^{1}H-NMR: 4.43 (*s*, H–C(5)); 2.05 (*s*, MeS); 1.40, 1.26 (2*s*, Me_2C); 1.15 (*s*, Me_3C). ^{13}C-NMR: 174.7 (*s*, C(2)); 79.7 (*s*, C(4)); 66.8 (*d*, C(5)); 37.7 (*s*, Me_3C); 29.0 (*q*, Me_3C); 27.1, 23.2 (2*q*, Me_2C); 15.3 (*q*, MeS). CI-MS: 219 (5), 218 (56, $[M + 1]^+$), 191 (5), 172 (5), 171 (10), 170 (100), 135 (12), 126 (6), 125 (59). Anal. calc. for $C_{10}H_{19}NS_2$ (217.40): C 55.25, H 8.81, N 6.44, S 29.50; found: C 55.23, H 8.77, N 6.61, S 29.67.

1.2.3. *4,5-Dihydro-2,4,4-trimethyl-5-(methylthio)-1,3-thiazole* (**2c**). According to *Method A*, from 2,4,4-trimethyl-1,3-thiazole-5(4*H*)-thione (**1c**; 236 mg, 1.48 mmol) and MeLi (1.1 ml, 1.51 mmol) at –94° for 10 min: 163 mg (63%) of **2c**. Colorless oil. IR: 1670*w*, 1630*s*, 1505*w*, 1460*m*, 1435*m*, 1385*m*, 1370*m*, 1365*m*, 1240*m*, 1190*m*, 1155*m*, 1140*m*, 1120*m*, 880*m*, 830*m*, 630*m*. ^{1}H-NMR: 4.62 (*s*, H–C(5)); 2.21 (*s*, Me–C(2)); 2.15 (*s*, MeS); 1.50, 1.37 (2*s*, Me_2C). ^{13}C-NMR: 162.0 (*s*, C(2)); 80.1 (*s*, C(4)); 68.9 (*d*, C(5)); 27.3 (*q*, *Me*–C(2)); 23.4, 20.5 (2*q*, Me_2C); 15.8 (*q*, MeS). CI-MS: 177 (9), 176 (100, $[M + 1]^+$), 165 (12), 160 (29), 146 (21), 128 (30). Anal. calc. for $C_7H_{13}NS_2$ (175.32): C 47.96, H 7.47, N 7.99, S 36.58; found: C 47.90, H 7.31, N 7.92, S 36.42.

1.2.4. *2-Benzyl-4,5-dihydro-4,4-dimethyl-5-(methylthio)-1,3-thiazole* (**2d**). According to *Method A*, from 2-benzyl-4,4-dimethyl-1,3-thiazole-5(4*H*)-thione (**1d**; 940 mg, 4 mmol) and MeLi (7.5 ml, 12 mmol) at –78° for 30 min: 540 mg (54%) **2d**. Colorless oil. IR: 1615*s*, 1600*m*, 1495*m*, 1455*m*, 1430*w*, 1420*w*, 1360*w*, 1240*w*, 1105*m*, 700*s*. ^{1}H-NMR: 7.35–7.25 (*m*, 5 arom. H); 4.56 (*s*, H–C(5)); 3.80 (*s*, PhCH_2); 2.04 (*s*, MeS); 1.51, 1.39 (2*s*, Me_2C). ^{13}C-NMR: 165.5 (*s*, C(2)); 135.6 (*s*, 1 arom. C); 128.8, 128.5, 127.0 (3*d*, 5 arom. CH); 79.7 (*s*, C(4)); 67.9 (*d*, C(5)); 40.9 (*t*, PhCH_2); 27.0, 23.1 (2*q*, Me_2C); 15.4 (*q*, MeS). CI-MS: 254 (6), 253 (11), 252 (72, $[M + 1]^+$), 206 (8), 205 (14), 204 (100), 191 (9). Anal. calc. for $C_{13}H_{17}NS_2$ (251.42); C 62.11, H 6.82, N 5.57, S 25.51; found: C 62.34, H 7.02, N 5.81, S 25.22.

1.3. *With Allyl- and Benzyllithium Reagents.* 1.3.1. *5-(Allylthio)-5-benzyl-4,5-dihydro-4,4-dimethyl-2-phenyl-1,3-thiazole* (**2e**). The benzyllithium soln. was prepared from dibenzyl mercury [26] (574 mg, 1.5 mmol) and 1.6M BuLi in hexane (2.1 ml, 3.3 mmol) in THF (6 ml) [27]. According to *Method B*, **1a** (100 mg, 0.45 mmol), benzyllithium, and allyl bromide (206 mg, 1.7 mmol) gave 148 mg (93%) of **3a**. Pale yellow oil. IR: 1595*m*, 1575*m*, 1495*m*, 1450*m*, 1385*m*, 1310*m*, 1260*s*, 1200*m*, 1175*m*, 1080*m*, 990*m*, 955*s*, 925*m*, 700*s*, 695*s*, 620*m*. ^{1}H-NMR: 7.75–7.65 (*m*, 2 arom. H); 7.35–7.1 (*m*, 8 arom. H); 5.55–5.4 (*m*, CH_2=C*H*); 4.9–4.8 (*m*, CH_2=CH); 3.47, 2.96 (*AB*, J = 13.7, PhCH_2); 2.9–2.45 (*m*, CH_2S); 1.63, 1.32 (2*s*, Me_2C). ^{13}C-NMR: 163.1 (*s*, C(2)); 138.0, 133.3 (2*s*, 2 arom. C); 132.8, 131.2, 130.4, 128.5, 128.1, 128.0 (6*d*, 10 arom. CH); 127.2 (*d*, CH_2=*C*H); 118.1 (*t*, *C*H_2=CH); 82.8, 82.2 (2*s*, C(4), C(5)); 42.9 (*t*, Ph*C*H_2); 35.5 (*t*, CH_2S); 23.3, 23.2 (2*q*, Me_2C). CI-MS: 356 (6), 355 (14), 354 (62, $[M + 1]^+$), 320 (8), 287 (14), 281 (13), 280 (69), 264 (10), 237 (32), 230 (15), 198 (14), 197 (100), 190 (7), 163 (28), 145 (19), 133 (6), 105 (10), 89 (17). Anal. calc. for $C_{21}H_{23}NS_2$ (253.55): C 71.34, H 6.56, N 3.96; found: C 71.42, H 6.47, N 3.89.

1.3.2. *5-Benzyl-5-(but-3-enylthio)-4,5-dihydro-4,4-dimethyl-2-phenyl-1,3-thiazole* (**2f**). As described in *1.3.1*, from **1a** (111 mg, 0.5 mmol) benzyllithium, and 4-bromobut-1-ene (135 mg, 1 mmol): 82 mg (61%) of **2f** and 6 mg (4%) of *5-benzyl-4,5-dihydro-4,4-dimethyl-2-phenyl-1,3-thiazole-5-thiol* (**2t**).

2f: Colorless oil. IR: 1640*w*, 1595*m*, 1575*m*, 1495*m*, 1450*m*, 1385*w*, 1360*w*, 1260*s*, 1175*m*, 1080*w*, 1000*w*, 955*s*, 920*m*, 700*s*, 690*s*. ^{1}H-NMR: 7.85–7.8 (*m*, 2 arom. H); 7.5–7.25 (*m*, 8 arom. H); 5.7–5.55 (*m*, CH_2=C*H*); 4.9–4.85 (*m*, CH_2=CH); 3.60, 3.08 (*AB*, J = 13.7, PhCH_2); 2.45–2.35, 2.15–2.0 (2*m*, 1:3, 2 CH_2); 1.73, 1.44 (2*s*, Me_2C). ^{13}C-NMR: 163.0 (*s*, C(2)); 136.4 (*d*, CH_2=*C*H); 138.0, 133.3 (2*s*, 2 arom. C); 131.1, 130.3, 128.4, 128.0, 127.9, 127.0 (6*d*, 10 arom. CH); 115.5 (*t*, *C*H_2=CH); 82.7, 82.1 (2*s*, C(4), C(5)); 42.8 (*t*, PhCH_2); 32.7, 31.4 (2*t*, 2 CH_2); 23.2, 23.1 (2*q*, Me_2C). CI-MS: 370 (12), 369 (26), 368 (100, $[M + 1]^+$), 280 (17), 145 (5). Anal. calc. for $C_{22}H_{25}NS_2$ (367.58): C 71.89, H 6.83, N 3.81, S 17.45; found: C 71.94, H 6.72, N 3.72, S 17.54.

2t: White powder. M.p. 83.5–84.0°. IR: 1595*m*, 1575*m*, 1495*m*, 1465*w*, 1450*m*, 1385*w*, 1360*w*, 1310*w*, 1260*s*, 1200*w*, 1175*m*, 1080*w*, 955*s*, 720*w*, 700*s*, 690*s*, 620*w*. ^{1}H-NMR: 7.85–7.8 (*m*, 2 arom. H); 7.5–7.3 (*m*, 8 arom. H); 3.51, 3.05 (*AB*, J = 13.4, PhCH_2); 2.23 (*s*, SH); 1.71, 1.53 (2s, Me_2C). ^{13}C-NMR: 164.2 (*s*, C(2)); 137.6, 135.5 (2*s*, 2 arom. C); 131.3, 130.9, 128.4, 128.1, 128.0, 127.3 (6*d*, 10 arom. CH); 81.6, 78.5 (2*s*, C(4), C(5)); 44.5 (*t*, Ph*C*H_2); 23.7, 21.6 (2*q*, Me_2C). CI-MS: 315 (5), 314 (28, $[M + 1]^+$), 282 (10), 281 (18), 280 (100), 228 (8). Anal. calc. for $C_{18}H_{19}NS_2$ (313.49): C 68.97, H 6.11, N 4.47, S 20.46; found: C 68.94, H 6.13, N 4.58, S 20.75.

1.3.3. *5-Benzyl-4,5-dihydro-4,4-dimethyl-5-(pent-4-enylthio)-2-phenyl-1,3-thiazole* (**2g**). 1.3.3.1. As described in *1.3.1*, from **1a** (111 mg, 0.5 mmol), benzyllithium, and 5-bromopent-1-ene (149 mg, 1 mmol): 127 mg (67%) of **2g** and 7 mg (4%) of **2t**.

2g: Pale yellow oil. IR: 1640*w*, 1595*m*, 1575*m*, 1495*m*, 1455*m*, 1450*m*, 1385*w*, 1360*w*, 1260*m*, 1180*m*, 1080*w*, 1000*w*, 960*s*, 950*s*, 920*m*, 700*s*, 690*s*. ^{1}H-NMR: 7.85–7.8 (*m*, 2 arom. H); 7.5–7.3 (*m*, 8 arom. H); 5.65–5.55 (*m*, CH_2=C*H*); 4.85–4.8 (*m*, CH_2=CH); 3.59, 3.07 (*AB*, J = 13.7, PhCH_2); 2.4–2.3, 2.1–1.85 (2*m*, 1:3, 2 CH_2); 1.73,

1.44 (2*s*, Me_2C); 1.55–1.4 (*m*, CH_2S). ^{13}C-NMR: 163.0 (*s*, C(2)); 138.0, 133.4 (2*s*, 2 arom. C); 137.4 (*d*, CH_2=*C*H); 131.0, 130.3, 128.4, 128.0, 127.9, 127.0 (6*d*, 10 arom. CH); 114.9 (*t*, *C*H_2=CH); 82.7, 82.2 (2*s*, C(4), C(5)); 42.7 (*t*, Ph*C*H_2); 33.0, 31.5, 27.7 (3*t*, 3 CH_2); 23.3, 23.1 (2*q*, *Me*$_2$C). CI-MS: 384 (12), 382 (100, $[M + 1]^+$), 370 (6), 292 (12), 281 (6), 280 (31), 238 (5), 231 (5), 197 (5), 145 (11). Anal. calc. for $C_{23}H_{27}NS_2$ (381.61): C 72.39, H 7.13, N 3.67, S 16.80; found: C 72.42, H 7.36, N 3.54, S 16.52.

1.3.3.2. The benzyllithium soln. was prepared from dibenzyl ether (396 mg, 2 mmol) and Li [24]. According to *Method B*, **1a** (135 mg, 0.61 mmol), benzyllithium, and 5-bromopent-1-ene (182 mg, 1.22 mmol) gave 195 mg (84%) of **2g**.

1.3.4. *5-Benzyl-4,5-dihydro-4,4-dimethyl-5-(methylthio)-2-phenyl-1,3-thiazole* (**2a**). In analogy to *1.3.3.1*, from **1a** (111 mg, 0.5 mmol), benzyllithium, and MeI (142 mg, 1 mmol): 146 mg (89%) of **2a**.

1.3.5. *5-Allyl-5-(but-3-enylthio)-4,5-dihydro-4,4-dimethyl-2-phenyl-1,3-thiazole* (**2h**). The allyllithium soln. was prepared from allyl phenyl ether (670 mg, 5 mmol) and Li in Et_2O [28]. According to *Method B*, **1a** (111 mg, 0.5 mmol), allyllithium, and 4-bromobut-1-ene (135 mg, 1 mmol) gave 145 mg (92%) of **2h**. Pale yellow oil. IR: 1640*m*, 1595*m*, 1575*m*, 1490*w*, 1460*w*, 1450*m*, 1430*w*, 1380*w*, 1360*w*, 1260*m*, 1175*m*, 990*m*, 955*s*, 920*s*, 690*m*. ^{1}H-NMR: 7.75–7.7 (*m*, 2 arom. H); 7.4–7.3 (*m*, 3 arom. H); 6.05–5.9, 5.75–5.6 (2*m*, 2 CH_2=C*H*); 5.2–5.1, 5.1–4.85 (2*m*, 2 CH_2=CH); 2.95–2.85 (*m*, 1 H); 2.7–2.5 (*m*, 3 H); 2.25–2.2 (*m*, 2 H); 1.57, 1.28 (2*s*, Me_2C). ^{13}C-NMR: 163.0 (*s*, C(2)); 136.4, 135.0 (2*d*, 2 CH_2=*C*H); 133.3 (*s*, 1 arom. C); 131.0, 128.4, 127.8 (3*d*, 5 arom. CH): 118.0, 115.8 (2*t*, 2 *C*H_2=CH); 81.8, 80.7 (2*s*, C(4), C(5)); 40.4 (*t*, CH_2=CH*C*H_2); 32.7 (*t*, CH_2=CH*C*H_2CH_2S); 31.0 (*t*, CH_2S); 24.2, 22.8 (2*q*, *Me*$_2$C). CI-MS: 320 (11), 319 (20), 318 (100, $[M + 1]^+$), 264 (5), 230 (28), 189 (9), 175 (9), 145 (10). Anal. calc. for $C_{18}H_{23}NS_2$ (317.52): C 68.09, H 7.30, N 4.44, S 20.20; found: C 67.89, H 7.50, N 4.26, S 19.90.

1.3.6. *5-Allyl-4,5-dihydro-4,4-dimethyl-5-(pent-4-enylthio)-2-phenyl-1,3-thiazole* (**2i**). As described in *1.3.5*, from **1a** (111 mg, 0.5 mmol), allyllithium, and 5-bromopent-1-ene (149 mg, 1 mmol): 150 mg (91%) of **2i**. Pale yellow oil. IR: 1640*m*, 1595*m*, 1580*m*, 1490*w*, 1450*m*, 1385*w*, 1360*w*, 1260*m*, 1175*m*, 1000*m*, 990*m*, 955*s*, 920*s*, 690*m*. ^{1}H-NMR: 7.75–7.7 (*m*, 2 arom. H); 7.4–7.25 (*m*, 3 arom. H); 6.05–5.9, 5.7–5.55 (2*m*, 2 CH_2=C*H*); 5.2–5.05, 4.9–4.8 (2*m*, 2 CH_2=CH); 2.95–2.85, 2.7–2.65 (2*m*, 2 H); 2.6–2.45, 2.1–2.0, 1.6–1.5 (3*m*, 2 H each); 1.57, 1.28 (2*s*, Me_2C). ^{13}C-NMR: 163.1 (*s*, C(2)); 137.4, 135.0 (2*d*, 2 CH_2=*C*H); 133.3 (*s*, 1 arom. C); 131.0, 128.3, 127.8 (3*d*, 5 arom. CH); 118.0, 115.2 (2*t*, 2 *C*H_2=CH); 81.8, 80.7 (2*s*, C(4), C(5)); 40.4 (*t*, CH_2=CH*C*H_2–C(5)); 32.9, 31.0, 27.8 (3*t*, 3 CH_2); 24.2, 22.8 (2*q*, *Me*$_2$C). CI-MS: 334 (11), 333 (18), 332 (100, $[M + 1]^+$). Anal. calc. for $C_{19}H_{25}NS_2$ (331.55): C 68.83, H 7.60, N 4.22, S 19.34; found: C 69.00, H 7.66, N 3.98, S 19.09.

1.3.7. *5-Allyl-5-(benzylthio)-4,5-dihydro-4,4-dimethyl-2-phenyl-1,3-thiazole* (**2j**). As described in *1.3.5*, from **1a** (111 mg, 0.5 mmol), allyllithium, and benzyl bromide (171 mg, 1 mmol): 170 mg (96%) of **2j**. Colorless oil. IR: 1595*m*, 1580*m*, 1495*m*, 1450*m*, 1385*w*, 1360*w*, 1260*m*, 1245*m*, 1175*m*, 1000*w*, 955*s*, 920*m*, 710*m*, 690*s*. ^{1}H-NMR: 7.9–7.85 (*m*, 2 arom. H); 7.5–7.4 (*m*, 3 arom. H); 7.35–7.2 (*m*, 5 arom. H); 6.15–6.05 (*m*, CH_2=C*H*); 5.3–5.2 (*m*, CH_2=CH); 3.88, 3.78 (*AB*, J = 11.2, Ph*C*H_2); 3.1–2.8 (*m*, CH_2=CHCH_2); 1.78, 1.41 (2*s*, Me_2C). ^{13}C-NMR: 163.1 (*s*, C(2)); 134.8 (*d*, CH_2=*C*H); 136.5, 133.2 (2*s*, 2 arom. C); 131.1, 129.2, 128.41, 127.37, 127.9, 127.1 (6*d*, 10 arom. CH); 118.2 (*t*, *C*H_2=CH); 81.9, 81.1 (2*s*, C(4), C(5)); 40.3 (*t*, CH_2=CHCH_2); 36.6 (*t*, Ph*C*H_2); 24.2, 22.9 (2*q*, *Me*$_2$C). CI-MS: 356 (10), 355 (23), 354 (100, $[M + 1]^+$), 264 (7), 230 (25), 207 (17), 157 (24), 122 (16). Anal. calc. for $C_{21}H_{23}NS_2$ (353.55): C 71.34, H 6.56, N 3.96, S 18.14; found: C 71.51, H 6.78, N 3.83, S 18.00.

1.3.8. *5-Allyl-4,5-dihydro-4,4-dimethyl-5-(methylthio)-2-phenyl-1,3-thiazole* (**2k**). As described in *1.3.5*, from **1a** (111 mg, 0.5 mmol), allyllithium, and MeI (142 mg, 1 mmol): 135 mg (99%) of **2k**. Pale brown powder. M.p. 51.5–52.5°. IR: 1640*w*, 1595*m*, 1575*m*, 1490*w*, 1460*w*, 1450*m*, 1430*w*, 1420*w*, 1380*w*, 1360*w*, 1260*m*, 1175*m*, 955*s*, 920*m*, 690*m*. ^{1}H-NMR: 7.85–7.8 (*m*, 2 arom. H); 7.5–7.35 (*m*, 3 arom. H); 6.1–6.0 (*m*, CH_2=C*H*); 5.25–5.15 (*m*, CH_2=CH); 3.05–3.0, 2.8–2.7 (2*m*, CH_2=CHCH_2); 2.11 (*s*, MeS); 1.66, 1.35 (2*s*, Me_2C). ^{13}C-NMR: 162.8 (*s*, C(2)); 135.0 (*d*, CH_2=*C*H); 133.2 (*s*, 1 arom. C); 131.1, 128.4, 127.8 (3*d*, 5 arom. CH); 118.0 (*t*, *C*H_2=CH); 81.8, 80.5 (2*s*, C(4), C(5)); 39.8 (*t*, CH_2=CHCH_2); 24.0, 23.0 (2*q*, *Me*$_2$C); 15.0 (*q*, MeS). CI-MS: 280 (11), 279 (19), 278 (100, $[M + 1]^+$), 230 (13), 157 (14), 145 (15).

1.3.9. *5-(Allylthio)-4,5-dihydro-4,4-dimethyl-5-(2-methylallyl)-2-phenyl-1,3-thiazole* (**2l**). The (2-methylallyl)lithium was prepared from (2-methylprop-2-enyl) phenyl ether (740 mg, 5 mmol) and Li in Et_2O [28]. According to *Method B*, **1a** (111 mg, 0.5 mmol), (2-methylallyl)lithium, and allyl bromide (121 mg, 1 mmol) gave 151 mg (95%) of **2l**. Pale yellow crystals. M.p. 66–67°. IR: 1635*w*, 1595*m*, 1575*m*, 1490*w*, 1460*m*, 1450*m*, 1385*w*, 1375*w*, 1360*w*, 1260*m*, 1175*m*, 990*w*, 960*s*, 920*m*, 905*s*, 690*m*. ^{1}H-NMR: 7.85–7.8 (*m*, 2 arom. H); 7.5–7.4 (*m*, 3 arom. H); 5.85–5.7 (*m*, CH_2=C*H*); 5.15–5.0 (*m*, CH_2=CH); 5.0–4.95 (*m*, CH_2=C); 3.25–3.05 (*m*, CH_2=CHCH_2); 2.97, 2.67 (*AB*, J = 14.2, CH_2–C(5)); 1.96 (*s*, CH_2=C*M*e); 1.73, 1.27 (2*s*, Me_2C). ^{13}C-NMR: 163.6 (*s*, C(2)); 141.5 (*s*, CH_2=*C*); 133.1 (*s*, 1 arom. C); 132.5 (*d*, CH_2=*C*H); 131.1, 128.4, 127.9 (3*d*, 5 arom. CH); 118.3 (*t*, *C*H_2=C); 116.3 (*t*, *C*H_2=CH); 83.7, 79.4 (2*s*, C(4), C(5)); 44.7 (*t*, *C*H_2C(5)); 35.1 (*t*, CH_2S); 23.24, 23.21, 22.9 (3*q*, *Me*$_2$C, CH_2=C*Me*). CI-MS: 320 (10), 319 (19), 318 (100, $[M + 1]^+$). Anal. calc. for $C_{18}H_{23}NS_2$ (317.52): C 68.09, H 7.30, N 4.41; found: C 68.41, H 7.47, N 4.53.

1.3.10. *5-(Benzylthio)-4,5-dihydro-4,4-dimethyl-5-(2-methylallyl)-2-phenyl-1,3-thiazole* (**2m**). As described in *1.3.9*, from **1a** (111 mg, 0.5 mmol), (2-methylallyl)lithium, and benzyl bromide (171 mg, 1 mmol): 172 mg (94%) of **2m**. Pale yellow crystals. M.p. 74–75°. IR: 1640*w*, 1595*m*, 1575*w*, 1490*w*, 1460*w*, 1450*m*, 1380*w*, 1375*w*, 1360*w*, 1310*m*, 1175*w*, 960*s*, 925*m*, 905*s*, 690*m*. ^{1}H-NMR: 7.9–7.85 (*m*, 2 arom. H); 7.5–7.4 (*m*, 3 arom. H); 7.25–7.15 (*m*, 5 arom. H); 5.0–4.95 (*m*, CH_2=C); 3.78, 3.57 (*AB*, *J* = 10.9, PhCH_2); 3.01, 2.70 (*AB*, *J* = 14.2, CH_2–C(5)); 1.97 (*s*, CH_2=C*Me*); 1.81, 1.32 (2*s*, Me_2C). ^{13}C-NMR: 163.7 (*s*, C(2)); 141.4 (*s*, CH_2=*C*); 136.5, 133.1 (2*s*, 2 arom. C); 131.1, 129.3, 128.5, 128.3, 127.9, 127.0 (6*d*, 10 arom. CH); 116.4 (*t*, *C*H_2=CH); 83.8, 79.7 (2*s*, C(4), C(5)); 44.6 (*t*, *C*H_2–C(5)); 36.6 (*t*, PhCH_2); 23.3, 23.2, 22.8 (3*q*, *Me*$_2$C, CH_2=C*Me*). CI-MS: 370 (10), 369 (20), 368 (100, $[M + 1]^+$). Anal. calc. for $C_{22}H_{25}NS_2$ (367.58): C 71.89, H 6.86, N 3.81, S 17.45; found: C 71.92, H 6.96, N 3.80, S 17.41.

1.3.11. *4,5-Dihydro-4,4-dimethyl-5-(2-methylallyl)-5-(methylthio)-2-phenyl-1,3-thiazole* (**2n**). As described in *1.3.9*, from **1a** (111 mg, 0.5 mmol), (2-methylallyl)lithium, and MeI (142 mg, 1 mmol): 142 mg (98%) of **2n**. Pale yellow crystals. M.p. 82.0–82.5°. IR: 1645*m*, 1595*s*, 1575*m*, 1490*m*, 1460*m*, 1450*s*, 1435*m*, 1420*m*, 1385*m*, 1375*m*, 1360*m*, 1310*m*, 1260*s*, 1200*m*, 1175*m*, 1075*w*, 1030*m*, 1000*w*, 960*s*, 940*s*, 900*s*, 690*s*, 620*m*. ^{1}H-NMR: 7.85–7.8 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 5.0–4.95 (*m*, CH_2=C); 2.99, 2.66 (*AB*, *J* = 14, CH_2–C(5)); 2.00 (*s*, MeS); 1.95 (*s*, CH_2=C*Me*); 1.69, 1.28 (2*s*, Me_2C). ^{13}C-NMR: 163.7 (*s*, C(2)); 141.7 (*s*, CH_2=*C*); 133.1 (*s*, 1 arom. C); 131.1, 128.4, 127.8 (3*d*, 5 arom. CH); 116.1 (*t*, *C*H_2=C); 83.6, 78.9 (2*s*, C(4), C(5)); 44.4 (*t*, *C*H_2–C(5)); 23.4, 22.84, 22.80 (3*q*, *Me*$_2$C, CH_2=C*Me*). CI-MS: 294 (10), 293 (17), 292 (100, $[M + 1]^+$), 244 (5). Anal. calc. for $C_{16}H_{21}NS_2$ (291.48): C 65.93, H 7.26, N 4.81, S 22.00; found: C 66.17, H 7.22, N 4.79, S 21.84.

1.3.12. *5-(Allylthio)-5-benzyl-2-(*tert*-butyl)-4,5-dihydro-4,4-dimethyl-1,3-thiazole* (**2o**). As described in *1.3.3.2*, from **1b** (101 mg, 0.5 mmol), benzyllithium, and allyl bromide (121 mg, 1 mmol): 164 mg (98%) of **2o**. Colorless oil. IR: 1630*w*, 1605*m*, 1490*m*, 1470*m*, 1460*m*, 1450*m*, 1380*m*, 1360*m*, 1260*w*, 1170*m*, 1075*m*, 1040*m*, 1010*m*, 990*s*, 950*w*, 920*m*, 890*w*, 695*s*, 655*m*. ^{1}H-NMR: 7.35–7.15 (*m*, 5 arom. H); 5.6–5.45 (*m*, CH_2=C*H*); 4.95–4.85 (*m*, CH_2=CH); 3.41, 2.93 (*AB*, *J* = 13.6, PhCH_2); 2.85–2.8, 2.4–2.35 (2*m*, CH_2=CHCH_2); 1.55, 1.23 (2*s*, Me_2C); 1.15 (*s*, Me_3C). ^{13}C-NMR: 173.9 (*s*, C(2)); 138.0 (*s*, 1 arom. C); 133.0 (*d*, CH_2=*C*H); 130.3, 127.9, 126.9 (3*d*, 5 arom. CH); 117.6 (*t*, *C*H_2=CH); 81.9, 81.4 (2*s*, C(4), C(5)); 43.3 (*t*, PhCH_2); 37.9 (*s*, Me_3*C*); 35.6 (*t*, CH_2=CH*C*H_2); 28.9 (*q*, *Me*$_3$C); 23.0, 22.9 (2*q*, *Me*$_2$C). CI-MS: 336 (11), 335 (23), 334 (100, $[M + 1]^+$), 260 (8), 244 (7), 224 (7), 217 (5), 216 (32), 180 (21).

1.3.13. *5-Allyl-2-(*tert*-butyl)-4,5-dihydro-4,4-dimethyl-1,3-thiazole-5-thiol* (**2p**). As described in *1.3.5*, from **1b** (101 mg, 0.5 mmol), allyllithium, and benzyl bromide (171 mg, 1 mmol): 90 mg (74%) of **2p**. Colorless oil. IR: 1635*w*, 1600*s*, 1470*m*, 1460*m*, 1425*w*, 1380*m*, 1360*s*, 1260*m*, 1240*w*, 1170*m*, 1120*w*, 1040*m*, 990*s*, 970*m*, 920*m*, 655*w*, 640*w*. ^{1}H-NMR: 6.0–5.85 (*m*, CH_2=C*H*); 5.2–5.1 (*m*, CH_2=CH); 2.75–2.65, 2.45–2.4 (2*m*, CH_2=CHCH_2); 2.28 (*s*, SH); 1.40, 1.25 (2*s*, Me_2C); 1.12 (*s*, Me_3C). ^{13}C-NMR: 175.9 (*s*, C(2)); 134.9 (*d*, CH_2=*C*H); 119.5 (*t*, *C*H_2=CH); 80.1 (*s*, C(4)); 75.6 (*s*, C(5)); 43.8 (*t*, CH_2=CH*C*H_2); 37.7 (*s*, Me_3*C*); 28.6 (*q*, *Me*$_3$C); 23.8, 21.2 (2*q*, *Me*$_2$C). CI-MS: 246 (11), 245 (16), 244 (100, $[M + 1]^+$), 210 (10).

1.3.14. *5-Allyl-2-(*tert*-butyl)-4,5-dihydro-4,4-dimethyl-5-(methylthio)-1,3-thiazole* (**2q**). As described in *1.3.5*, from **1b** (101 mg, 0.5 mmol), allyllithium, and MeI (142 mg, 1 mmol): 59 mg of **2q**/**2p** 2:5.

2q: Colorless oil. ^{1}H-NMR (from mixture): 6.05–5.9 (*m*, CH_2=C*H*); 5.25–5.1 (*m*, CH_2=CH); 2.9–2.85, 2.7–2.6 (2*m*, CH_2=CHCH_2); 2.11 (*s*, MeS); 1.54, 1.23 (2*s*, Me_2C); 1.22 (*s*, Me_3C). ^{13}C-NMR (from mixture): 177.0 (*s*, C(2)); 135.2 (*d*, CH_2=*C*H); 117.7 (*t*, *C*H_2=CH); 81.0, 79.2 (2*s*, C(4), C(5)); 39.8 (*t*, CH_2=CH*C*H_2); 37.8 (*s*, Me_3*C*); 28.9 (*q*, *Me*$_3$C); 23.9, 23.1 (2*q*, *Me*$_2$C); 14.9 (*q*, MeS). CI-MS (mixture): 260 (8), 259 (14), 258 (82, $[M + 1]^+$ of **2q**), 246 (12, $[M + 1]^+$ of **2p**), 245 (17), 244 (100), 210 (7), 126 (5), 125 (48).

1.3.15. *5-(Allylthio)-2,5-dibenzyl-4,5-dihydro-4,4-dimethyl-1,3-thiazole* (**2r**). As described in *1.3.3.2*, from **1d** (118 mg, 0.5 mmol), benzyllithium, and allyl bromide (121 mg, 1 mmol): 91 mg (49%) of **2r**. Pale yellow crystals. M.p. 72–73°. IR: 1630*w*, 1610*m*, 1600*m*, 1580*w*, 1490*m*, 1460*w*, 1450*m*, 1425*w*, 1380*m*, 1360*m*, 1230*w*, 1165*m*, 1090*m*, 1075*m*, 1025*w*, 1000*w*, 985*w*, 950*w*, 920*m*, 830*w*, 700*s*. ^{1}H-NMR: 7.3–7.1 (*m*, 10 arom. H); 5.45–5.3 (*m*, CH_2=C*H*); 4.85–4.8 (*m*, CH_2=CH); 3.73, 3.70 (*AB*, *J* = 14.5, PhCH_2–C(2)); 3.37, 2.89 (*AB*, *J* = 13.6, PhCH_2–C(5)); 2.7–2.65, 2.2–2.1 (2*m*, CH_2=CHCH_2); 1.57, 1.28 (2*s*, Me_2C). ^{13}C-NMR: 165.3 (*s*, C(2)); 137.6, 135.6 (2*s*, 2 arom. C); 132.7 (*d*, CH_2=*C*H); 130.2, 128.9, 128.5, 127.9, 127.0, 126.9 (6*d*, 10 arom. CH); 117.7 (*t*, *C*H_2=CH); 82.7, 81.9 (2*s*, C(4), C(5)); 43.1, 41.4 (2*t*, 2 PhCH_2); 35.4 (*t*, CH_2S); 23.0, 22.8 (2*q*, *Me*$_2$C). CI-MS: 370 (13), 369 (26), 368 (100, $[M + 1]^+$), 294 (8). Anal. calc. for $C_{22}H_{25}NS_2$ (367.58): C 71.89, H 6.86, N 3.81, S 17.45; found: C 71.68, H 6.63, H 3.59, S 17.21.

1.3.16. *5-Allyl-2-benzyl-5-(benzylthio)-4,5-dihydro-4,4-dimethyl-1,3-thiazole* (**2s**). As described in *1.3.5*, from **1d** (118 mg, 0.5 mmol), allyllithium, and benzyl bromide (171 mg, 1 mmol): 60 mg of 1:1 mixture of **2s** and *5-allyl-2-benzyl-4,5-dihydro-4,4-dimethyl-1,3-thiazole-5-thiol* (**2u**) were obtained.

2s: Colorless oil. ^{1}H-NMR (from mixture): 7.25–7.05 (*m*, 10 arom. H): 5.85–5.65 (*m*, CH_2=C*H*); 5.1–4.95 (*m*, CH_2=CH); 3.99, 3.96 (*AB*, *J* = 7.1, PhCH_2S); 3.4–3.1 (*m*, PhCH_2); 2.55–2.25 (*m*, CH_2=CHCH_2); 1.32, 1.21 (2*s*, Me_2C). ^{13}C-NMR (from mixture): 169.5 (*s*, C(2)); 138.9–126.1 (12 arom. C); 134.7 (*d*, CH_2=*C*H); 119.6 (*t*, CH_2=CH); 80.2, 76.4 (2*s*, C(4), C(5)); 43.7, 43.4 (2*t*, 2 PhCH_2); 39.7 (*t*, CH_2=CHCH_2); 23.7, 21.2 (2*q*, *Me*$_2$C). CI-MS (mixture): 370 (14), 369 (24), 368 (100, $[M + 1]^+$), 336 (6).

2u: Colorless oil. ^{1}H-NMR (from mixture): 7.25–7.05 (*m*, 5 arom. H); 5.85–5.65 (*m*, CH_2=C*H*); 5.1–4.95 (*m*, CH_2=CH); 3.4–3.1 (*m*, PhCH_2); 2.55–2.25 (*m*, CH_2=CHCH_2); 1.36, 1.17 (2*s*, Me_2C). ^{13}C-NMR (from mixture): 172.3 (*s*, C(2)); 139.5–127.2 (6 arom. C); 134.5 (*d*, CH_2=*C*H); 119.6 (*t*, CH_2=CH); 80.3, 76.2 (2*s*, C(4), C(5)); 43.7 (*t*, PhCH_2); 39.8 (*t*, CH_2=CHCH_2); 23.7, 21.2 (2*q*, *Me*$_2$C).

2. *Reactions of* **1** *with* Grignard *Reagents*. 2.1. *4,5-Dihydro-4,4-dimethyl-5-(1-methylallyl)-2-phenyl-1,3-thiazole-5-thiol* (**5a**). 2.1.1. To a mixture of Mg (240 mg, 10 mmol) in Et_2O (3 ml) at r.t. 3-chlorobut-1-ene (181 mg, 2 mmol) was added slowly to maintain the mixture gently boiling. Then, the mixture was stirred for 20 min and the resulting *Grignard* reagent transferred into a soln. of **1a** (100 mg, 0.45 mmol) in Et_2O (2 ml) by means of a syringe. After stirring for 5 min at r.t., the soln. was poured into a mixture of sat. aq. NH_4Cl soln. (20 ml) and Et_2O (40 ml). The org. phase was separated, dried, and evaporated. Chromatography with hexane/Et_2O 20:1 gave 114 mg (91%) of **5a**. Colorless oil. ^{1}H-NMR (2 diastereoisomers, 2:3): 7.75–7.65 (*m*, 2 arom. H); 7.4–7.3 (*m*, 3 arom. H); 6.1–5.8 (*m*, CH_2=C*H*); 5.2–5.05 (*m*, CH_2=CH); 3.1–3.0 (*m*, CH); 2.30, 2.24 (2*s*, SH); 1.71, 1.60, 1.33 (3*s*, Me_2C); 1.30, 1.16 (2*d*, *J* = 6.7, 6.6, *Me*CH). ^{13}C-NMR (2 diastereoisomers, 2:3): 162.7, 162.4 (2*s*, C(2)); 142.1, 139.0 (2*d*, CH_2=*C*H); 133.3 (*s*, 1 arom. C); 128.3, 127.8 (2*d*, 5 arom. CH); 116.5, 115.9 (2*t*, CH_2=CH); 82.8, 82.6 (2*s*, C(4)); 81.2, 80.4 (2*s*, C(5)); 45.4, 44.8 (2*d*, CH); 25.8, 24.8, 22.8, 20.8, 20.6, 16.2 (6*q*, 3 Me). EI-MS: 277 (9, M^+), 222 (5), 190 (8), 145 (100), 121 (11), 104 (25), 77 (7), 55 (20), 43 (25).

2.1.2. To a mixture of Mg (240 mg, 10 mmol) in Et_2O (3 ml) at r.t., 1-bromobut-2-ene (270 mg, 2 mmol) was added so that the mixture boiled gently. The mixture was stirred at r.t. for 20 min and the resulting *Grignard* reagent transferred into a soln. of **1a** (100 mg, 0.45 mmol) in Et_2O (2 ml) by means of a syringe. After stirring at r.t. for 5 min and workup as in *2.1.1*, 107 mg (85%) of **5a** (diastereoisomers, 2:3) were obtained.

2.2. *4,5-Dihydro-4,4-dimethyl-5-(2-methylallyl)-2-phenyl-1,3-thiazole-5-thiol* (**5b**). As described in *2.1.1*, from 2-methylallyl chloride (181 mg, 2 mmol), Mg (240 mg, 10 mmol), and **1a** (100 mg, 0.45 mmol): 122 mg (97%) of **5b**. Colorless oil. ^{1}H-NMR: 7.75–7.65 (*m*, 2 arom. H); 7.4–7.25 (*m*, 3 arom. H); 5.00–4.92 (*m*, CH_2=C); 2.81, 2.50 (*AB*, *J* = 13.8, CH_2–C(5)); 2.45 (*s*, SH); 1.88 (*s*, Me); 1.62, 1.25 (2s, Me_2C). CI-MS: 278 (100, $[M + 1]^+$), 244 (12), 175 (33), 145 (76), 104 (21).

2.3. *4,5-Dihydro-4,4-dimethyl-5-(1,1-dimethylallyl)-2-phenyl-1,3-thiazole-5-thiol* (**5c**). The *Grignard* reagent was prepared from 3,3-dimethylallyl bromide (447 mg, 3 mmol) and Mg (360 mg, 15 mmol) in Et_2O (4 ml) at 0° and then added to a soln. of **1a** (100 mg, 0.45 mmol) in Et_2O (2 ml). After stirring at 0° for 10 min and workup as in *2.1.1*, 93 mg (70%) of **5c** were obtained. Colorless oil. ^{1}H-NMR: 7.75–7.7 (*m*, 2 arom. H); 7.4–7.3 (*m*, 3 arom. H); 6.45–6.35 (*m*, CH_2=C*H*); 5.05–4.9 (*m*, CH_2=CH); 2.55 (*s*, SH); 1.68, 1.38, 1.33 (3*s*, 2 Me_2C). CI-MS: 292 (72, $[M + 1]^+$), 258 (8), 222 (12), 190 (46), 145 (100), 104 (17), 69 (15).

3. *Reactions of* **1** *with Organocuprates*. 3.1. *5-(Hex-5-enyl)-4,5-dihydro-4,4-dimethyl-2-phenyl-1,3-thiazole-5-thiol* (**6**). To a suspension of CuBr·SMe_2 (410 mg, 2 mmol) in THF (5 ml) at –5 to –2°, 1.3M hex-5-enylmagnesium bromide in Et_2O (3 ml) was added. After 5 min, a soln. of **1a** (400 mg, 1.81 mmol) in THF (2 ml) was added dropwise and the mixture maintained at 0° for 2 h. Then, 1,4-dithio-DL-threitol (DTT; 308 mg, 2 mmol) was added, the mixture stirred at r.t. for 30 min and filtered through a short silica-gel column, the filtrate evaporated, and the residue chromatographed (CC with hexane/Et_2O 20:1, then prep. TLC with hexane/Et_2O 4:1, 4 × developing): 129 mg (23%) of **6**. Colorless oil. IR: 1590*m*, 1575*m*, 1450*m*, 1380*m*, 1310*m*, 1260*s*, 1240*m*, 1175*m*, 1140*m*, 960*s*, 690*s*. ^{1}H-NMR: 7.8–7.75 (*m*, 2 arom. H); 7.5–7.35 (*m*, 3 arom. H); 5.9–5.75 (*m*, CH_2=C*H*); 5.05–4.95 (*m*, CH_2=CH); 2.37 (*s*, SH); 2.15–1.45 (*m*, 4 CH_2); 1.64, 1.39 (2*s*, Me_2C). ^{13}C-NMR: 164.3 (*s*, C(2)); 138.4 (*d*, CH_2=*C*H); 133.5 (*s*, 1 arom. C); 131.2, 128.4, 128.0 (3*d*, 5 arom. CH); 114.7 (*t*, CH_2=CH); 81.7, 78.5 (2*s*, C(4), C(5)); 38.7, 33.5, 29.0, 28.2 (4*t*, 4 CH_2); 24.1, 21.5 (2*q*, *Me*$_2$C). CI-MS: 306 (100, $[M + 1]^+$), 274 (29), 272 (36), 224 (95), 190 (22), 145 (16), 121 (6).

3.2. *4,4,7-Trimethyl-2-phenyl-1,6-dithia-3-azaspiro[4.4]non-2-ene* (**8a**). As described in *3.1*, from **1a** (400 mg, 1.81 mmol), CuBr·SMe_2 (410 mg, 2 mmol), and 1M but-3-enylmagnesium bromide in Et_2O (4 ml): 51 mg (10%) of **8a**. Pale yellow oil. IR (film): 3060*w*, 3030*w*, 2970*s*, 2925*s*, 2880*m*, 1590*s*, 1575*s*, 1490*m*, 1450*s*, 1435*m*, 1380*m*, 1360*m*, 1260*s*, 1210*m*, 1175*m*, 950*s*, 770*s*, 690*s*, 675*s*, 620*s*. ^{1}H-NMR (2 diastereoisomers, 1:4): 8.0–7.75 (*m*, 2 arom. H); 7.5–7.35 (*m*, 3 arom. H); 3.7–3.5 (*m*, 1 H); 2.45–2.1 (*m*, 3 H); 1.95–1.8 (*m*, 1 H); 1.54, 1.50, 1.64, 1.57 (4*s*, Me_2C); 1.40, 1.32 (2*d*, *J* = 6.4, 6.7, *Me*CH). ^{13}C-NMR (2 diastereoisomers, 1:4): 165.8 (*s*, C(2)); 133.5 (*s*, 1 arom. C); 131.0, 128.4, 128.3, 128.2, 127.9, 127.8 (6*d*, 5 arom. CH); 88.7, 88.3 (2*s*, C(4)); 79.2, 79.0 (2*s*, C(5)); 44.2, 43.0

(2*d*, C(7)); 43.3, 40.1, 39.1, 37.5 (4*t*, C(8), C(9)); 24.9, 24.8, 23.6, 22.4, 22.2, 22.0 (6*q*, 3 Me). EI-MS: 277 (5, $M^{+\cdot}$), 145 (100), 104 (64). Anal. calc. for $C_{15}H_{19}NS_2$ (277.45): C 64.94, H 6.90, N 5.05; found: C 65.15, H 6.75, N 4.87.

4. *Radical Cyclization of* **5**. 4.1. *4,4,9-Trimethyl-2-phenyl-1,6-dithia-3-azaspiro[4.4]non-2-ene* (**8b**). A soln. of **5a** (90 mg, 0.32 mmol) and AIBN (5 mg) in hexane (3 ml) was heated under reflux for 4 h. After evaporation and chromatography (hexane/Et_2O 10:1), 63 mg (70%) of **8b** were obtained. Colorless oil. IR (film): 3060*w*, 3015*w*, 2980*s*, 2940*s*, 2870*w*, 1595*s*, 1575*m*, 1450*s*, 1375*m*, 1360*m*, 1260*s*, 1210*m*, 1180*m*, 960*s*, 870*m*, 780*s*, 690*s*, 620*s*. ^{1}H-NMR (2 diastereoisomers, 1:2): 7.8–7.75 (*m*, 2 arom. H); 7.5–7.35 (*m*, 3 arom. H); 3.15–1.9 (*m*, CH, 2 CH_2); 1.72, 1.57, 1.49, 1.46 (4*s*, Me_2C); 1.18, 1.09 (2*d*, J = 6.7, 6.4, *Me*CH). ^{13}C-NMR (2 diastereoisomers, 1:2): 166.4 (*s*, C(2)); 133.4 (*s*, 1 arom. C); 131.0, 130.9, 128.4, 128.3, 127.9, 127.7 (6*d*, 5 arom. CH); 95.9, 88.4 (2*s*, C(4)); 79.2, 78.5 (2*s*, C(5)); 46.5, 45.9 (2*d*, CH); 38.8, 36.7, 28.9, 28.6 (4*t*, 2 CH_2); 26.5, 26.4, 21.4 (3*q*, *Me*$_2$C); 16.4, 13.6 (2*q*, *Me*CH). CI-MS: 278 (62, $[M + 1]^+$), 277 (7), 175 (9), 145 (100), 104 (10). Anal. calc. for $C_{15}H_{19}NS_2$ (277.45): C 64.94, H 6.90, N 5.05; found: C 64.99, H 6.67, N 4.83.

4.2. *4,4,8-Trimethyl-2-phenyl-1,6-dithia-3-azaspiro[4.4]non-2-ene* (**8c**). As described in *4.1*, with **5b** (122 mg, 0.44 mmol) and AIBN (30 mg) in hexane (5 ml; 6 h): 21 mg (17%) of **8c** and 79 mg (65%) of **8c′**.

8c: Colorless oil. IR (film): 3060*w*, 3030*w*, 2970*s*, 2935*s*, 1595*s*, 1575*s*, 1450*s*, 1380*m*, 1360*m*, 1265*s*, 1230*m*, 1210*m*, 1175*m*, 1130*m*, 955*s*, 770*s*, 690*s*, 675*s*, 620*s*. ^{1}H-NMR: 7.8–7.75 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 3.1–1.9 (*m*, CH, 2 CH_2); 1.54, 1.51 (2*s*, Me_2C); 1.20 (*d*, J = 6.1, *Me*CH). ^{13}C-NMR: 165.9 (*s*, C(2)); 134.0 (*s*, 1 arom. C); 131.2, 128.5, 128.0 (3*d*, 5 arom. CH); 87.7 (*s*, C(4)); 79.4 (*s*, C(5)); 50.7, 39.2 (2*t*, 2 CH_2); 39.4 (*d*, CH); 24.7, 22.8 (2*q*, *Me*$_2$C); 18.4 (*q*, *Me*CH). CI-MS: 278 (100, $[M + 1]^+$), 175 (46), 145 (12), 104 (6). Anal. calc. for $C_{15}H_{19}NS_2$ (277.45): C 64.94, H 6.90, N 5.05; found: C 65.16, H 7.18, N 4.89.

8c′: Colorless oil. IR (film): 3060*w*, 3030*w*, 2975*s*, 2935*s*, 2880*w*, 1595*s*, 1575*s*, 1490*w*, 1460*m*, 1450*s*, 1380*m*, 1360*m*, 1265*s*, 1210*m*, 1180*m*, 1140*m*, 960*s*, 880*m*, 770*s*, 690*s*, 680*s*, 615*s*. ^{1}H-NMR: 7.75–7.7 (*m*, 2 arom. H); 7.4–7.3 (*m*, 3 arom. H); 3.0–2.0 (*m*, CH, 2 CH_2); 1.48, 1.40 (2*s*, Me_2C); 1.09 (*d*, J = 6.6, *Me*CH). ^{13}C-NMR: 165.6 (*s*, C(2)); 133.6 (*s*, 1 arom. C); 130.9, 128.2, 127.8 (3*d*, 5 arom. CH); 86.0 (*s*, C(4)); 80.9 (*s*, C(5)); 49.3, 40.8 (2*t*, 2 CH_2); 38.5 (*d*, CH); 24.1, 21.9 (2*q*, *Me*$_2$C); 18.8 (*q*, *Me*CH). CI-MS: 278 (28, $[M + 1]^+$), 175 (18), 145 (100), 104 (20). Anal. calc. for $C_{15}H_{19}NS_2$ (277.45): C 64.94, H 6.90, N 5.05; found: C 64.80, H 6.98, N 4.90.

4.3. *4,4,9,9-Tretramethyl-2-phenyl-1,6-dithia-3-azaspiro[4.4]non-2-ene* (**8d**). As described in *4.1*, with **5c** (89 mg, 0.31 mmol) and AIBN (5 mg) in hexane (5 ml; 6 h): 50 mg (56%) of **8d**. White powder. M.p. 64–66°. IR (KBr): 3055*w*, 2980*m*, 2930*m*, 1590*m*, 1465*m*, 1440*m*, 1375*m*, 1355*m*, 1260*m*, 960*s*, 780*m*, 760*s*, 690*s*. ^{1}H-NMR: 7.8–7.75 (*m*, 2 arom. H); 7.45–7.35 (*m*, 3 arom. H); 3.05–2.95 (*m*, CH_2S); 2.3–2.0 (*m*, CH_2); 1.81, 1.51, 1.44, 1.34 (4*s*, 2 Me_2C). ^{13}C-NMR: 163.3 (*s*, C(2)); 133.9 (*s*, 1 arom. C); 130.9, 128.3, 127.9 (3*d*, 5 arom. CH); 97.4 (*s*, C(4)); 79.8 (*s*, C(5)); 48.6 (*s*, C(9)); 48.5, 26.0 (2*t*, 2 CH_2); 27.1, 25.5, 23.5, 22.5 (4*q*, 2 *Me*$_2$C). CI-MS: 292 (100, $[M + 1]^+$), 189 (5), 156 (24), 145 (70). Anal. calc. for $C_{16}H_{21}NS_2$ (291.48): C 65.93, H 7.26, N 4.81; found: C 65.96, H 7.28, N 4.62.

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