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Synthesis of N-Unsubstituted 1,3-Thiazolidines by [2+3]-Cycloaddition of an Azomethine Ylide with Thiocarbonyl Compounds

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1,3-Dipolar cycloadditions of azomethine ylides with thiocarbonyl compounds have been used for the preparation of N-unsubstituted 1,3-thiazolidines. The reactive 1-phenyl-*N*-(trimethylsilyl)azomethine ylide (**1c**) was generated *in situ* by treatment of *N*-(benzylidene)[(trimethylsilyl)methyl]amine (**6**) with trimethylsilyl triflate and CsF in HMPA. All cycloadditions proceeded non-regioselectively, which led to mixtures of 4-phenyl- and 2-phenyl-substituted 1,3-thiazolidines.

Key words: azomethine ylides,1,3-dipolar cycloaddition, thiocarbonyl ylides, 1,3-thiazolidines, crystal structure

Azomethine ylides **1**, which can be generated by different methods, are well known 1,3-dipoles, which are convenient for the synthesis of five-membered nitrogen-heterocycles [1–8]. On the other hand, only a few examples of their [2+3]-cycloaddition with C=S groups have been known until recently [9–13]. Therefore, we decided to study this reaction systematically as a method for the preparation of differently substituted 1,3-thiazolidines. The suitability of this 1,3-dipolar cycloaddition for the synthesis of the penam skeleton has been demonstrated by Gallagher and coworkers [14,15].

The first method for generating reactive azomethine ylides that we chose was the thermal ring opening of aziridines [16–20]. As an example, the reaction of a dimethyl *cis*-aziridine-2,3-dicarboxylate **2** with thiobenzophenone leading to **3** is shown in Scheme 1. N-Unsubstituted 1,3-thiazolidine-2-carboxylates **5** could be prepared from *N*-arylidene α-amino esters **4** *via* the 1,3-dipolar cycloaddition of azomethine ylide **1b** [21] (Scheme 1).

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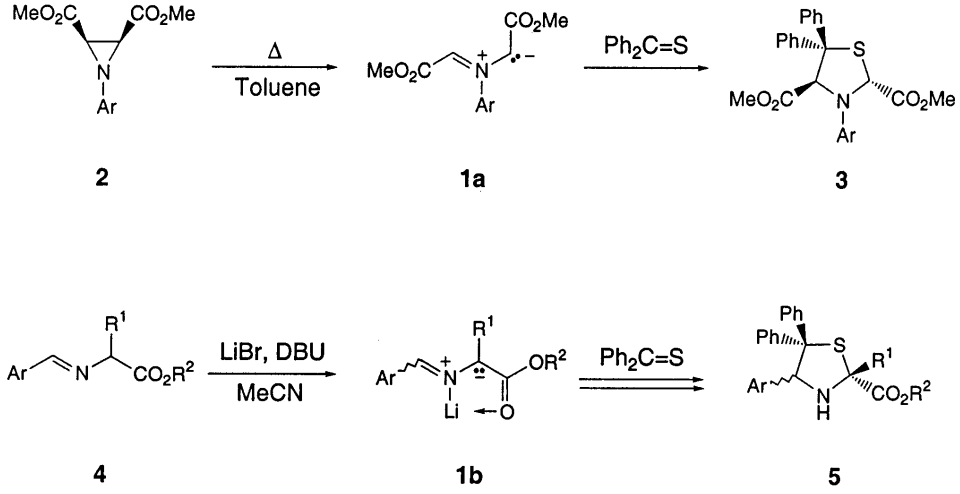
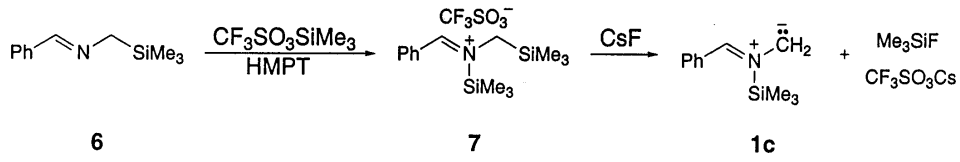
Scheme 1



Recently, we have described the reaction of a 1,3-thiazole-5(4*H*)-thione with azomethine ylide **1c** [22], generated from *N*-(benzylidene)[(trimethylsilyl)methyl]amine (**6**) *via* iminium salt **7** according to [23,24] (Scheme 2). Only catalytic amounts of trimethylsilyl triflate and CsF are needed as they are reformed in a catalytic cycle. During aqueous workup, the product was desilylated and N-unsubstituted spirocyclic 1,3-thiazolidines were obtained.

Scheme 2

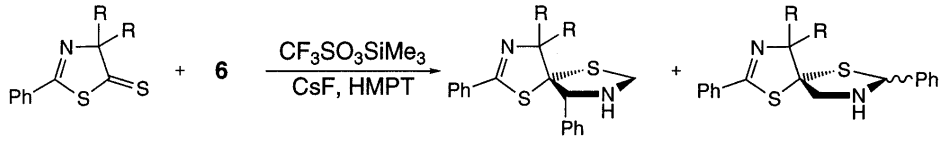


In the present paper, the results of the reaction of **1c** with two 1,3-thiazole-5(4*H*)-thiones **8a**,**b**, the cycloaliphatic thione **11**, and the aromatic thioketones **14a**,**b** are presented.

RESULTS AND DISCUSSION

The reaction of equimolar amounts of 4,4-dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione (**8a**) and **6** in hexamethylphosphoramide (HMPA) in the presence of 0.2 equivalents of trimethylsilyl trifluoromethylsulfonate (TMS-triflate) and CsF was carried out at room temperature. When **8a** had disappeared (TLC control, *ca.* 3 d), the mixture was poured into icewater and extracted with Et_2O. After evaporation of the solvent and column chromatography (SiO_2, hexane/AcOEt), a mixture of the l:l-adducts **9a** and **10a** was obtained (Scheme 3). Repeated preparative TLC yielded **9a** (16%) as a single compound, whereas **10a** (32%) was obtained as a l:l-mixture of two diastereoisomers (^{1}H-NMR evidence), which could not be separated. The structures of the products have been proposed on the basis of their spectroscopic data, especially ^{1}H- and ^{13}C-NMR (*cf.* [18,22]).

Scheme 3



8 **9** **10**

a: R = Ph, **b:** R-R = -$(CH_2)_4$-

Crystallization of **9a** from $CHCl_3$ yielded single crystals, and its structure has been established by X-ray crystallography (Figure 1). It is worth mentioning that only one stereoisomer of type **9** has been formed, in contrast to an experiment described earlier [22].

The analogous reaction of **6** with the spirocyclic 1,3-thiazole-5(4*H*)-thione **8b** led to similar results: **9b** was obtained in 21% yield as a single isomer, **10b** (31%) as a 1:1-mixture of two diastereoisomers* (Scheme 3).

Treatment of "monothione" **11** with **6** under the above-mentioned conditions for four days led to a mixture of the regioisomeric cycloadducts **12** and **13** as racemates in 62% yield (ratio 1.2:1, Scheme 4). In the ^{1}H-NMR spectrum ($CDCl_3$), **12** showed four Me signals at 1.48, 1.32, 1.29, and 0.83 ppm; the corresponding signals of **13** appe-

*All attempts to separate the diastereoisomers by prep. TLC or HPLC failed.

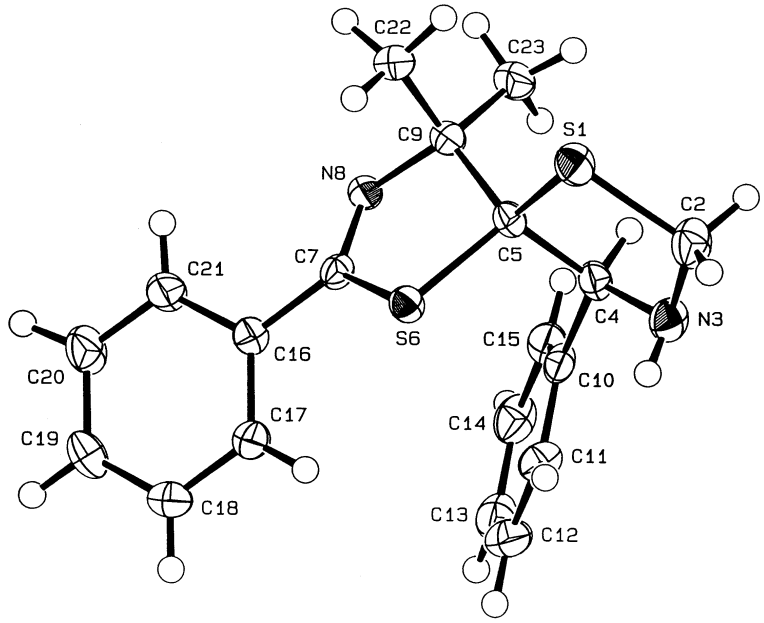
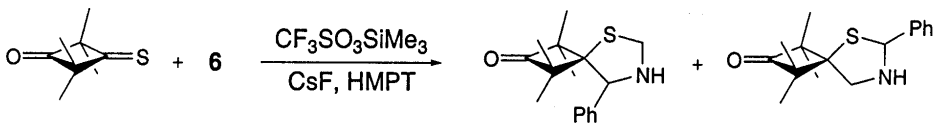


Figure l. ORTEP-plot [25] of the molecular structure of one of the two symmetry-independent molecules of **9a** (50% probability ellipsoids; arbitrary numbering of atoms).

ared at 1.33, 1.31, 1.17, and 1.13 ppm. The high- field shift of one Me signal in **12** is the result of the proximity of the Ph group. Furthermore, the absorptions of the CH_2 group (AB system at 4.22/4.12 ppm and 3.61/3.08 ppm of **12** and **13**, resp.) and the CH group (**12**: 4.90 ppm, **13**: 5.53 ppm) are indicative for the 4-phenyl- and 2-phenyl-substituted 1,3-thiazolidine ring. The corresponding ^{13}C-NMR signals are at 51.9 (*t*) and 69.6 (*d*) ppm for **12** and at 57.1 (*t*) and 72.5 (*d*) ppm for **13**. Reactions of azomethine ylides with carbonyl compounds are well documented [10]. The "monothione" **11** is an ideal model for comparison of the reactivities of C=S and C=O groups under identical steric and electronic conditions. In analogy to other 1,3-dipoles, azomethine ylide **lc** reacts chemoselectively with the C=S function, which reflects once more the "superdipolarophilic" properties of thiocarbonyl compounds [26].

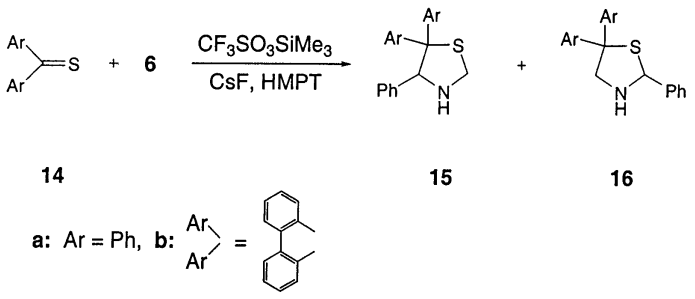
Scheme 4



11 **12** **13**

The analogous reactions of **6** with the aromatic thioketones **l4a,b** were much faster than those with **8a,b** and **11**. The starting materials disappeared within 12 h in the case of **14a** and within a few min in the case of **14b**. This corresponds with the general reactivity scale of thiocarbonyl compounds in 1,3-dipolar cycloadditions (*cf.* [26]). In both reactions, mixtures of the regioisomeric cycloadducts **15** and **16** were obtained in ratios of 1.6:1 (74% yield) and 3.2:1 (76% yield), respectively (Scheme 5). The regioisomers were separated by column chromatography; their structures were established on the basis of the NMR data in comparison with those of **9/10** and **12/13**. For example, the ^{13}C absorption of CH_2 (*t*) of **9**, **12**, and **15** (more polar fractions) appears at 51.8–52.2 ppm, whereas in the case of the isomers **10**, **13**, and **16** (less polar) CH_2 absorbs at 57.1–65.5 ppm. Furthermore, in the ^1H-NMR spectra, Ph*CH* of **9**, **12**, and **15** always absorbs at higher field (4.4–5.1 ppm) than in the isomers **10**, **13**, and **16** (4.8– 5.9 ppm). In addition, the structure of **15b** was confirmed by X-ray crystallography (Figure 2).

Scheme 5



14 **15** **16**

a: Ar = Ph, **b:** Ar, Ar =

In conclusion, we have shown that 1-phenyl *N*-(trimethylsilyl)azomethine ylide (**lc**) undergoes smooth [2+3]-cycloadditions with the C=S group of some thioketones and 1,3-thiazole-5(4*H*)-thiones to give N-unsubstituted 1,3-thiazolidines. In all cases, the regioselectivity of the cycloaddition is very low: the isomeric 4-phenyl- and 2-phenyl-substituted products were obtained in ratios of 1.2:1 to 3.2:1 in the case of thioketones **11** and **14**, and 1:1.5 to 1:2 in the case of 1,3-thiazole-5(4*H*)-thiones **8**. We propose that steric effects cause this change in the regioselectivity, *i.e.* the interaction of the C(4)-substituents of **8** with the Ph-group of the dipole **lc** in the transition state.

EXPERIMENTAL

General. See [18,21]. M.p.'s were determined on a Mettler-FP-5 apparatus and are not corrected. IR spectra were registered with a Perkin-Elmer FT-IR-1600 spectrophotometer (in KBr or as film). NMR-spectra were recorded in $CDCl_3$ on a Bruker-AC-300 (^1H, 300 MHz) or a Bruker-ARX-300 (^{13}C, 75.6 MHz) instrument. ESI-MS-spectra were registered with a Finnigan TSQ-700 spectrometer.

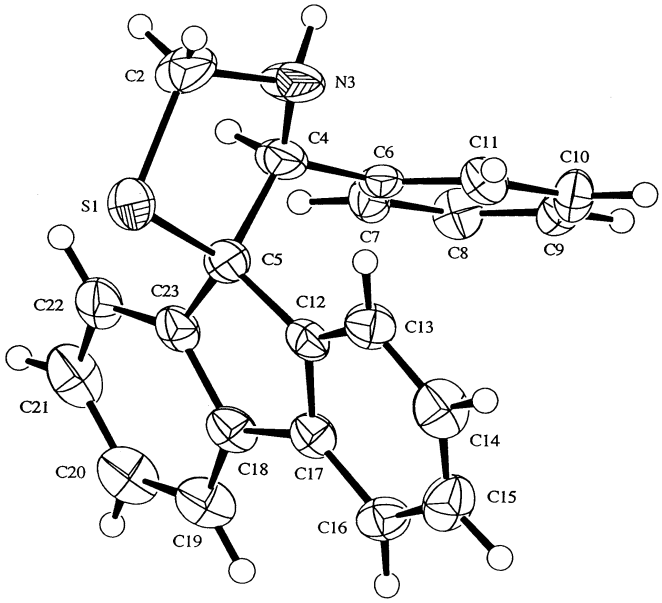


Figure 2. ORTEP-plot [25] of the molecular structure of one of the two symmetry-independent molecules of **15b** (50% probability ellipsoids; arbitrary numbering of atoms).

Starting materials. 4,4-Dimethyl-2-phenyl-1,3-thiazole-5(4*H*)-thione (**8a**) and 2-phenyl-3-thia-1-azaspiro[4.4]non-1-ene-4-thione (**8b**) were prepared according to [27] and [28], respectively. Thiobenzophenone (**14a**) was prepared by thionation of benzophenone with Lawesson reagent [29], 9*H*-fluorene-9-thione (**14b**) following the protocol in [30] and chromatographic purification, and 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**11**) by thionation of 2,2,4,4-tetramethylcyclobutane-1,3-dione with P_4S_{10} in pyridine as described in [31]. *N*-(Benzylidene)[(trimethylsilyl)methyl]amine (**6**) was synthesized from [(trimethylsilyl)methyl)azide [24] by reduction with $LiAlH_4$ and condensation of the resulting [(trimethylsilyl)methyl]amine with benzaldehyde in dry Et_2O in the presence of Na_2SO_4 and activated molecular sieves (4 Å) according to [32].

Reactions of *N*-(benzylidene)[(trimethylsilyl)methyl]amine (6) with thiocarbonyl compounds. *General procedure*. To a solution of trimethylsilyl triflate ($CF_3SO_3SiMe_3$; 45 mg, 0.2 mmol) and CsF (30 mg, 0.2 mmol) in hexamethylphosphoramide (HMPA; 5 ml), a solution of the thiocarbonyl compound (1 mmol) and **6** (191 mg, 1 mmol) in HMPA (5 ml) was slowly added at room temperature. The mixture was stirred until the thiocarbonyl compound disappeared (TLC), then poured into ice-water, and extracted with Et_2O (3x). The organic phases were dried over Na_2SO_4, the solvent was evaporated, and the residue was separated by column chromatography (SiO_2, hexane/AcOEt).

Reactions with 1,3-thiazole-5(4*H*)-thiones 8a,b. (*5*RS,*9*RS)-*4,4-Dimethyl-2,9-diphenyl-1,6-dithia-3,8-diazaspiro[4.4]non-2-ene* (**9a**). From **8a** (220 mg,1 mmol), after 3 d; more polar fraction: 55 mg (16%) as pale yellow solid. IR (KBr): 3292*m*, 3058*m*, 3030*m*, 2978*m*, 2929*m*, 2869*m*, 1591*s*, 1573*m*, 1489*m*, 1467*m*, 1446*s*, 1378*m*, 1359*m*, 1261*s*, 1203*m*, 1171*m*, 1123*m*, 1075*m*, 958*s*, 927*m*, 918*m*, 897*m*, 880*m*, 844*m*, 791*m*, 764*s*, 750*s*, 691*s*. ^{1}H-NMR: 7.45 (*d*,*J* = 7.0, 2 arom. H); 7.35–7.29 (*m*, 3 arom. H); 7.28–7.18 (*m*, 2 arom. H); 7.17– 6.98 (*m*, 3 arom. H); 4.43 (*s*, HC(9)); 4.34, 4.22 (*AB*, *J* = 9.3, H_2C(7)); 2.93 (br. *s*, NH);1.82, 1.60 (2*s*, 2 Me). ^{13}C-NMR:166.2 (*s*, C=N); 135.9, 132.9 (2*s*, 2 arom. C);130.7, 128.7, 127.8, 127.6, 127.4, 127.3 (6*d*, 10 arom. CH); 92.6, 79.1 (2*s*, C(4), C(5)); 72.4 (*d*, C(9)); 51.8 (*t*, C(7)); 27.8, 21.6 (2*q*, 2 Me). ESI-MS: 341 (100, $[M+1)^+$). Suitable crystals for the X-ray crystal-structure determination were obtained from $CHCl_3$.

(*5*RS, *7*RS)- *and* (*5*RS, *7*SR)-*4,4-Dimethyl-2,7-diphenyl-1,6-dithia-3,8-diazaspiro[4.4]non-2-ene* (**l0a**). From **8a** (220 mg,1 mmol), after 3 d; less polar fraction, 1:1-mixture of 2 diastereoisomers:109 mg (32%) as pale yellow oil. IR (film): 3299*m*, 3061*s*, 3027*s*, 2974*s*, 2931*s*, 1593*s*, 1575*s*, 1491*s*, 1447*s*, 1377*s*, 1358*s*, 1312*m*, 1260*s*, 1205*s*, 1173*s*, 1088*m*, 1028*m*, l001*m*, 986*m*, 954*s*, 908*m*, 863*m*, 840*m*, 764*s*, 732*s*, 691*s*, 673*s*. ^{1}H-NMR: 7.86–7.60 (*m*, 2 arom. H); 7.58–7.25 (*m*, 8 arom. H); 5.73, 4.84 (2*s*, HC(7)); 4.62, 4.53 (*AB*, *J* = 9.3, $H_2C(9)$); 3.56, 3.44 (*AB*, *J* = 12.4, $H_2C(9)$); 2.70 (br. *s*, NH);1.69, 1.64, 1.47, 1.33 (4*s*, 2 Me). ^{13}C-NMR: 165.1, 163.4 (2*s*, C=N); 138.9, 138.5, 133.6, 133.3 (4*s*, 2 arom. C); 131.3, 131.0, 130.5, 128.8, 128.7, 128.5, 128.4, 128.3, 128.2, 128.0, 127.9, 126.8 (12*d*,10 arom. CH); 94.8, 92.6, 79.1, 78.3 (4*s*, C(4), C(5)); 74.8, 73.6 (2*d*, C(7)); 64.2, 63.0 (2*t*, C(9))); 26.7, 25.8, 22.2, 21.0 (4*q*, 2 Me). ESI-MS: 341 (100, $[M+1]^+$).

(*4*RS,*5*RS)-*4,12-Diphenyl-1,13-dithia-3,11-diazadispiro[4.0.4.3]tridec-11-ene* (**9b**). From **8b** (246 mg,1 mmol), after 3 d; more polar fraction: 79 mg (21%) as pale yellow oil. IR (film): 3315*m*, 3062*m*, 3028*m*, 2961*s*, 2869*s*, 1593*s*, 1574*s*, 1491*s*, 1446*s*, 1382*m*, 1350*w*, 1323*m*, 1312*m*, 1255*s*, 1175*m*, 1156*m*, 1113*s*, 1076*m*, 1028*m*, l000*m*, 990*m*, 925*s*, 908*s*, 843*m*, 793*m*, 765*s*, 733*s*, 691*s*, 670*m*. ^{1}H-NMR: 7.34–7.27 (*m*, 2 arom. H); 7.26–7.17 (*m*, 3 arom. H); 7.16–7.04 (*m*, 2 arom. H); 6.99–6.84 (*m*, 3 arom. H); 4.24, 4.14 (*AB*, *J* = 9.2, $H_2C(7)$); 4.23 (*s*, HC(9)); 2.75 (br. *s*, NH); 2.48–2.43 (*m*,1 H); 2.41–2.26 (*m*, 1 H); 2.21–1.74 (*m*, 4 H); 1.73–1.58 (*m*, 2 H). ^{13}C-NMR: 165.7 (*s*, C=N); 135.4, 133.1 (2*s*, 2 arom. C); 130.5, 128.8, 127.9, 127.7, 127.5, 127.4 (6*d*,10 arom. CH); 91.6, 89.5 (2*s*, C(4), C(5)); 73.7 (*d*, C(9)); 51.8 (*t*, C(7)); 43.5, 31.4, 25.5, 23.9 (4*t*, 4 CH_2). ESI-MS: 367 (100, $[M+1)^+$).

(*2*RS,*5*RS)- and (*2*RS,*5*SR)-*4,12-Diphenyl-1,13-dithia-3,11-diazadispiro[4.0.4.3]tridec-11-ene* (**l0b**). From **8b** (246 mg, 1 mmol), after 3 d; less polar fraction; HPLC (hexane/AcOEt 4:1), 1:1-mixture of 2 diastereoisomers: 114 mg (31%) as pale yellow oil. IR (film): 3294*m*, 3062*m*, 3031*m*, 2972*s*, 2868*s*, 1592*s*, 1574*s*, 1490*m*, 1447*s*, 1381m, 1350*m*, 1325*m*, 1311*m*, 1298*m*, 1258*s*, 1174*m*, 1152*m*, 1117*s*, 1076*m*, 1028*m*, l001m, 948*s*, 929*m*, 896*m*, 845*m*, 804*m*, 765*s*, 752*s*, 691*s*. ^{1}H-NMR: 7.73–7.59 (*m*, 0.5 arom. H); 7.58–7.55 (*m*, 1 arom. H); 7.44–7.19 (*m*, 7 arom. H); 7.16–6.99 (*m*, 1.5 arom. H); 5.58, 4.49 (2*s*, HC(7)); 4.35, 4.29 (*AB*, *J* = 9.3, $H_2C(9)$); 3.38, 3.35 (*AB*, *J* =14.1, $H_2C(9)$); 2.75 (br. *s*, NH); 2.17–1.20 (*m*, 4 CH_2). ^{13}C-NMR: 165.0, 164.0 (2*s*, C=N); 140.2, 138.8, 136.8, 133.9 (4*s*, 2 arom. C); 133.7, 131.2, 130.8, 128.7, 128.4, 128.3, 128.0, 127.9, 127.8, 127.4, 126.7 (11*d*, 10 arom. CH); 91.2, 90.6, 90.1, 89.1 (4*s*, C(4), C(5)); 78.0, 75.2 (2*d*, C(7)); 65.4, 64.2 (2*t*, C(9)); 41.2, 40.3, 32.2, 31.6, 25.3, 25.1, 23.8, 23.3 (8*t*, 4 CH_2). ESI-MS: 367 (100, $[M+1]^+$).

Reaction with monothione 11. *8-Phenyl-5-thia-7-azaspiro[3.4]octan-2-one* (**12**). From **11** (158 mg, 1 mmol), after 4 d; more polar fraction: 53 mg (19%) as colorless oil. IR (film): 3030*m*, 2972*s*, 2930*m*, 1774*s*, 1702*m*, 1671*m*, 1600*m*, 1494*m*, 1464*s*, 1382*m*, 1367*m*, 1260*s*, 1225*m*, 1215*m*, 1207*m*, 1081*m*, 1026*s*. ^{1}H-NMR: 7.74 (*d*, *J* = 8. l, 2 arom. H); 7.38–7.26 (*m*, 3 arom. H); 4.90 (*s*, HC(8)); 4.22, 4.12 (*AB*, *J* = 9.1, $H_2C(6)$); 2.13 (br. *s*, NH); 1.48, 1.32, 1.29, 0.83 (4*s*, 4 Me). ^{13}C-NMR: 220.6 (*s*, C=O); 139.8 (*s*, 1 arom. C); 128.7, 128.6, 127.9 (3*d*, 5 arom. CH); 72.1 (*s*, C(4)); 69.6 (*d*, C(8)); 66.0, 60.7 (2*s*, Me_2C); 51.9 (*t*, C(6)); 24.4, 24.3, 23.9, 21.4 (4*q*, 4 Me). ESI-MS: 276 (100, $[M+1]^+$).

6-Phenyl-5-thia-7-azaspiro[3.4]octan-2-one (**13**). From **11** (158 mg, 1 mmol), after 4 d; less polar fraction; prep. TLC (hexane/AcOEt 10:1):114 mg (42%) as colorless oil. ^{1}H-NMR: 7.43–7.39 (*m*, 2 arom. H); 7.32–7.19 (*m*, 3 arom. H); 5.53 (*s*, HC(6)); 3.61, 3.08 (*AB*, *J* =12.9, $H_2C(8)$); 2.12 (br. *s*, NH); 1.33, 1.31, 1.17, 1.13 (4*s*, 4 Me). ^{13}C-NMR: 220.3 (*s*, C=O); 139.9 (*s*, 1 arom. C); 128.5, 128.3, 127.0 (3*d*, 5 arom. CH); 72.5 (*d*, C(6)); 70.3, 63.4, 61.9 (3*s*, C(4), 2 Me_2C); 57.1 (*t*, C(8)); 25.9, 19.3, 18.7 (3*q*, 4 Me). ESI-MS: 276 (100, $[M+1]^+$).

Reactions with thioketones l4a,b. *4,5,5-Triphenyl-1,3-thiazolidine* (**15a**). From **14a** (200 mg, 1 mmol), after 12 h; more polar fraction: 143 mg (45%) as yellowish oil. IR (film): 3314*m*, 3058*m*, 3031*m*, 2940*m*, 2877*m*, 1661*m*, 1599*m*, 1494*s*, 1445*s*, 1317*m*, 1262*m*, 1185*m*, 1157*w*, 1103*m*, 1080*m*, 1033*m*, 827*m*, 768*m*, 740*m*, 697*s*. ^{1}H-NMR: 7.52 (*d*, *J* = 7.7, 2 arom. H); 7.31–6.99 (*m*, 11 arom. H); 6.76 (*d*, *J* = 7.0, 2 arom. H); 5.13 (*s*, HC(4)); 4.47, 4.43 (*AB*, *J* = 9.2, $H_2C(2)$); 2.75 (br. *s*, NH). ^{13}C-NMR: 144.4, 141.4, 137.4 (3*s*, 3 arom. C); 130.6, 128.4, 128.1, 128.0, 127.6, 127.4, 127.1, 126.8, 126.6 (9*d*, 15 arom. CH); 73.6 (*d*, C(4)); 60.3 (*s*, C(5)); 52.2 (*t*, C(2)). ESI-MS: 318 (100, $[M+1]^+$), 289 (75), 255 (30), 210 (8).

2,5,5-Triphenyl-1,3-thiazolidine (**16a**). From **14a** (200 mg, 1 mmol), after 12 h; less polar fraction: 91 mg (29%) as yellowish oil. IR (film): 3314*s*, 3058*s*, 3028*s*, 2937*s*, 2829*m*, 1659*m*, 1598*s*, 1580*m*, 1492*s*, 1444*s*, 1390*m*, 1312*m*, 1280*m*, 1227*m*, 1183*m*, 1157*m*, 1081*s*, 1030*s*, 862*m*, 818*m*, 757*s*, 697*s*. ^{1}H-NMR: 7.49 (*dd*, *J* = 7.9, 0.8, 2 arom. H); 7.42 (*dd*-like, *J* = 7.3, 1.3, 3 arom. H); 7.39–7.17 (*m*, 10 arom. H); 5.92 (*s*, HC(2)); 4.11, 3.70 (*AB*, *J* = 12.6, $H_2C(4)$); 2.67 (br. *s*, NH). ^{13}C-NMR: 145.6, 145.1, 140.2 (3*s*, 3 arom. C); 128.5, 128.3, 128.2, 128.0, 127.9, 127.1, 126.7 (7*d*, 15 arom. CH); 74.6 (*d*, C(2)); 73.8 (*s*, C(5)); 65.5 (*t*, C(4)). ESI-MS: 318 (25, $[M+1]^+$), 317 (24, $M^{+\bullet}$), 316 (100), 307 (10).

4′-Phenylspiro[fluorene-9,5′-[1,3]thiazolidine] (**15b**). From **14b** (196 mg, 1 mmol), after *ca*. 10 min; more polar fraction: 183 mg (58%) as yellowish solid. IR (KBr): 3264*m*, 3062*m*, 3030m, 2930*m*, 2819*m*, 1446*s*, 1258*m*, 1193*m*, 1099*m*, 1074*m*, 1022*s*, 958*m*, 939*m*, 905*s*, 893*s*, 825*m*, 806*m*, 771*m*, 745*s*, 725*s*, 695*s*. ^{1}H-NMR: 7.78 (*dd*, *J* = 7.9, 0.6,1 arom. H); 7.44–7.26 (*m*, 5 arom. H); 7.25–7.05 (*m*, 2 arom. H); 6.88–6.74 (*m*, 3 arom. H); 6.38 (*d*, *J* = 7.4, 2 arom. H); 4.76, 4.73 (*AB*, *J* = 9.0, $H_2C(2')$); 4.60 (*s*, HC(4′)); 3.07 (br. *s*, NH). ^{13}C-NMR: 148.5, 146.9, 144.9, 140.7, 134.1 (5*s*, 5 arom. C); 128.1, 127.7, 127.6, 127.4, 127.1, 126.9, 125.9, 125.1, 124.0, 119.8, 199.5 (11d, 13 arom. CH); 78.9 (*d*, C(4′)); 69.7 (*s*, C(5′)); 54.0 (*t*, C(2′)). ESI-MS: 316 (100, $[M+1]^+$), 287 (60), 253 (45). Suitable crystals for the X-ray crystal-structure determination were obtained from MeOH/CH_2Cl_2.

2′-Phenylspiro[fluorene-9,5′-[1,3]thiazolidine] (**16b**). From **14b** (196 mg, 1 mmol), after *ca*. 10 min; less polar fraction: 58 mg (18%) as yellowish oil. IR (film): 3060*m*, 3028*m*, 2930*m*, 1447*s*, 1258*m*, 1190*m*, 1093*m*, 1061*m*, 1012*s*, 939*m*, 895*s*, 879*m*, 763*m*, 735*s*, 722*m*, 683*m*. ^{1}H-NMR: 7.88–7.59 (*m*, 3 arom. H); 7.58–7.03 (*m*, 10 arom. H); 6.23 (*s*, HC(2′)); 3.55, 3.50 (*AB*, *J* = 12.6, $H_2C(4')$); 2.90 (br. *s*, NH). ^{13}C-NMR: 151.4, 148.4, 139.4, 139.1, 138.8 (5*s*, 5 arom. C); 128.8, 128.7, 128.5, 128.1, 127.9, 127.8, 127.4, 127.2, 124.1, 123.7, 119.9 (11*d*, 13 arom. CH); 76.3 (*d*, C(2′)); 69.5 (*s*, C(5′)); 66.3 (*t*, C(4′)). ESI-MS: 316 (100, $[M+1]^+$).

Crystal-structure determination of 9a and 15b[*]. All measurements were made on a Rigaku AFC5R diffractometer using graphite-monochromated MoK_α radiation (λ = 0.71069 Å) and a 12 kW rotating anode generator. The intensities were corrected for Lorentz and polarization effects, but not for absorption. Data collection and refinement parameters are given in the Table, views of the molecules are shown in Figures 1 and 2. The structures were solved by direct methods using SHELXS86 [33] in the case of **9a** and SIR92 [34] in the case of **15b**, which, in each case, revealed the positions of all non-hydrogen atoms.

In the case of **9a**, there are two independent molecules with similar conformations in the asymmetric unit. The atomic coordinates were tested carefully for a relationship from a higher symmetry space group using the MISSYM routine [35] of the programm PLATON [36], but none could be found. The non-hydrogen atoms were refined anisotropically. All of the H-atoms were located in a difference electron density map and their positions were allowed to refine together with individual isotropic displacement parameters. In the case of **15b**, the asymmetric unit contains two symmetry-independent, but conformationally identical, molecules of **15a** plus one molecule MeOH. The non-hydrogen atoms were refined anisotropically. All of the H-atoms, except that of the OH group, were fixed in geometrically calculated positions (*d*(C–H) = 0.95 Å). The H-atom of the OH group was fixed in the position indicated by a difference electron density map. Each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent atom. The amine H-atoms could not be located in a difference electron density map, presumably because of slight disorder of the N-atoms, as shown by the elongated atomic displacement ellipsoids for these atoms. As two positions for each amine H-atom are possible because of the tetrahedral nature of the N-atom, the most likely position was chosen by considering which position would yield a hydrogen bonding interaction with appropriate geometry.

[*]Crystallographic data (excluding structure factors) for the structures of **9a** and **15b** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publications No. CCDC-194375 and 194376. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-((0)1223-336033: e-mail: deposit@ccdc.cam.ac.uk).

Refinement of each structure was carried out on F using full-matrix least-squares procedures, which minimised the function $\Sigma w(|F_o| - |F_c|)^2$. Corrections for secondary extinction were applied. Neutral atom scattering factors for the non-hydrogen atoms were taken from [37a], and the scattering factors for H-atoms were taken from [38]. Anomalous dispersion effects were included in F_{calc} [39]; the values for f' and f'' were those of [37b]. The values of the mass attenuation coefficients are those of [37c]. All calculations were performed using the TEXSAN [40] (for **9a**) or teXsan [41] (for **15b**) crystallographic software package.

Table. Crystallographic data for compounds **9a** and **15b**.

	9a	**15b**
Crystallized from	$CHCl_3$	$MeOH/CH_2Cl_2$
Empirical formula	$C_{19}H_{20}N_2S_2$	$C_{21}H_{17}NS \cdot 0.5CH_3OH$
Formula weight [g/mol]	340.50	331.45
Crystal color, habit	colorless, prism	colorless, prism
Crystal dimensions [nm]	0.27×0.32×0.43	0.20×0.43×0.50
Temperature [K]	173(1)	173(1)
Crystal system	orthorhombic	triclinic
Space group	*Pbca*	$P\bar{1}$
Z	16	4
Reflections for cell determination	25	25
2θ range for cell determination [°]	36–40	24–26
Unit cell parameters a [Å]	27.819(4)	13.856(3)
b [Å]	18.265(2)	13.903(4)
c [Å]	13.705(2)	9.493(3)
α [°]	90	104.47(3)
β [°]	90	99.80(3)
γ [°]	90	94.31(2)
V [Å^3]	6963(1)	1737.6(9)
D_x [g cm^{-3}]	1.299	1.267
$\mu(MoK_\alpha)$ [mm^{-1}]	0.306	0.190
Scan type	ω	$\omega/2\theta$
$2\theta_{(max)}$ [°]	55	50
Total reflections measured	9803	6395
Symmetry independent reflections	7973	6119
Reflections used [$I > 2\sigma(I)$]	5120	4213
Parameters refined	576	434
Final R	0.0417	0.0775
wR ($w = [\sigma^2(F_o) + (0.005F_o)^2]^{-1}$)	0.0330	0.0678
Goodness of fit	1.566	2.993
Secondary extinction coefficient	4.7(7)×10^{-8}	1(1)×10^{-7}
Final Δ_{max}/σ	0.0006	0.0001
$\Delta\rho$ (max; min) [e/Å^3]	0.34; –0.26	0.85; –0.51

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