1,3-Thiazolidine-dicarboxylates from Thioketones and Thermally Generated Azomethine Ylides

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Dedicated to Professor *Waldemar Adam* on the occasion of his 65th birthday

The reaction of 9*H*-fluorene-9-thione (**1**) with the *cis*- and *trans*-isomers of dimethyl 1-(4-methoxyphenyl)-aziridine-2,3-dicarboxylate (*cis*- and *trans*-**2**, resp.) in xylene at 110° yielded exclusively the spirocyclic cycloadduct with *trans*- and *cis*-configurations, respectively (*trans*- and *cis*-**3**, resp.; *Scheme 1*). Analogously, less-reactive thioketones, *e.g.*, thiobenzophenone (**5**), and *cis*-**2** reacted stereoselectively to give the corresponding *trans*-1,3-thiazolidine-2,4-dicarboxylate (*e.g.*, *trans*-**8**; *Scheme 2*). On the other hand, the reaction of **5** and *trans*-**2** proceeded in a nonstereoselective course to provide a mixture of *trans*- and *cis*-substituted cycloadducts. This result can be explained by an isomerization of the intermediate azomethine ylide. Dimethyl 1,3-thiazolidine-2,2-dicarboxylates **14** and **15** were formed in the thermal reaction of dimethyl aziridine-2,2-dicarboxylate **11** with aromatic thioketones (*Scheme 3*). On treatment of **14** and **15** with *Raney*-Ni in refluxing EtOH, a desulfurization and ring-contraction led to the formation of azetidine-2,2-dicarboxylates **17** and **18**, respectively (*Scheme 4*).

Introduction. – Saturated 1,3-thiazole carboxylates are compounds of considerable importance, as some representatives show interesting biological activities. Special attention is focused on 1,3-thiazolidine-4-carboxylates and -2,4-dicarboxylates [1–3]. This type of 1,3-thiazole derivatives can be used as building blocks in the synthesis of pharmaceuticals such as immunomodulating drugs (*cf.* [3] and refs. cit. therein) or antibiotics (*cf.* [4]). Some examples of dipeptides containing 1,3-thiazolidine-4-carboxylic acid have also been prepared [3][5].

The most frequently used method for the synthesis of 1,3-thiazolidine carboxylates is based on cyclocondensation reactions of cysteine with carbonyl compounds. For example, 1,3-thiazolidine-2,4-dicarboxylic acid was prepared starting from glyoxylic acid [1]. Retrosynthetic analysis leads to the conclusion that 1,3-dipolar cycloaddition of azomethine ylides substituted by ester groups with C=S dipolarophiles should offer convenient and stereocontrolled access to this class of compounds. This concept has already been explored by *Gallagher* and co-workers for the synthesis of penam and penem skeletons [6].

One method that can be used to generate appropriate azomethine ylides is the stereoselective thermal ring opening of aziridine-carboxylates. For example, aziridine-

[1]) Part of the planned Ph. D. thesis of *K.U.*, University of Łódź.

2,3-dicarboxylates were used by *Huisgen* and co-workers to demonstrate the scope of orbital symmetry rules [7][2]). Furthermore, 1,3-diarylaziridine-2,2-dicarboxylates are also well-known as convenient precursors of azomethine ylides [9]. Although azomethine ylides belong to the most extensively explored class of 1,3-dipoles [10], reactions with C=S dipolarophiles were rarely reported. One of the reasons seems to be the instability of many thioketones and thioaldehydes. In recent years, however, sterically crowded and relatively stable thioketones have been prepared and successfully applied in syntheses of S heterocycles [11]. Within the last decade, we have reported on 1,3-dipolar cycloadditions of differently generated azomethine ylides with thiocarbonyl compounds [12–15].

The topic of the present paper are reactions of aromatic thioketones with aziridine dicarboxylates leading to 1,3-thiazolidine-dicarboxylates. Furthermore, a novel ring contraction of the five-membered products to azetidine-dicarboxylates is presented.

Results and Discussion. – As 9*H*-fluorene-9-thione (**1**) easily undergoes dimerization in a hetero-*Diels-Alder* fashion [16], the reaction with aziridines required modified conditions compared with typical procedures for analogous reactions [12]: a solution of **1** was added in small portions to a heated solution of the respective aziridine. After each addition, the color of **1** disappeared immediately. As soon as 0.9 equiv. of **1** had been added to a solution of *cis*-**2** or *trans*-**2** (*Scheme 1*), the solvent was evaporated, and the crude residue was examined by ^{1}H-NMR spectroscopy. In each case, a single product was detected, showing two *singlets* at 6.08/5.00 and 5.67/4.95 ppm, respectively. The products were isolated after chromatographic workup in 50 and 23% yield[3]), and characterized as spiro-1,3-thiazolidines *trans*-**3** and *cis*-**3**, respectively. The relative configurations were assigned on the basis of the observation that conrotatory ring opening of *cis*-**2** leads stereoselectively to the azomethine ylide s-*trans*-**4**; *trans*-**2** is the precursor of s-*cis*-**4** [7][13], and the cycloaddition proceeds suprafacially.

The reactions of thiobenzophenone (**5**), 9*H*-xanthene-9-thione (xanthione, **6**), and 9*H*-thioxanthene-9-thione (thioxanthione, **7**) with aziridines *cis*-**2** or *trans*-**2** were carried out in toluene at 90° (*Scheme 2*). The mixtures were heated until the color of **5**–**7** disappeared. With *cis*-**2**, the formation of a single product was observed in all cases; therefore, the reactions occurred with complete stereoselectivity to give 1,3-thiazolidines *trans*-**8**, *trans*-**9**, and *trans*-**10** with the ester groups in a *trans* relationship. In contrast to this result, the reactions of **5** and **6** carried out with *trans*-**2** under the same condition led to mixtures of *trans*-**8** and *trans*-**9**, respectively, together with their diastereoisomers, *i.e.*, the expected *cis*-configured cycloadducts *cis*-**8** and *cis*-**9**. The *cis*/*trans* ratio determined in the crude mixture by ^{1}H-NMR spectroscopy was *ca.* 4:1 in both cases. The lower selectivity observed in the reactions of *trans*-**2** corresponds to similar results reported for reactions with several C,C dipolarophiles [17][4]) and 1,3-thiazole-5(4*H*)-thiones [13]. Apparently, the azomethine ylide s-*cis*-**4** undergoes an

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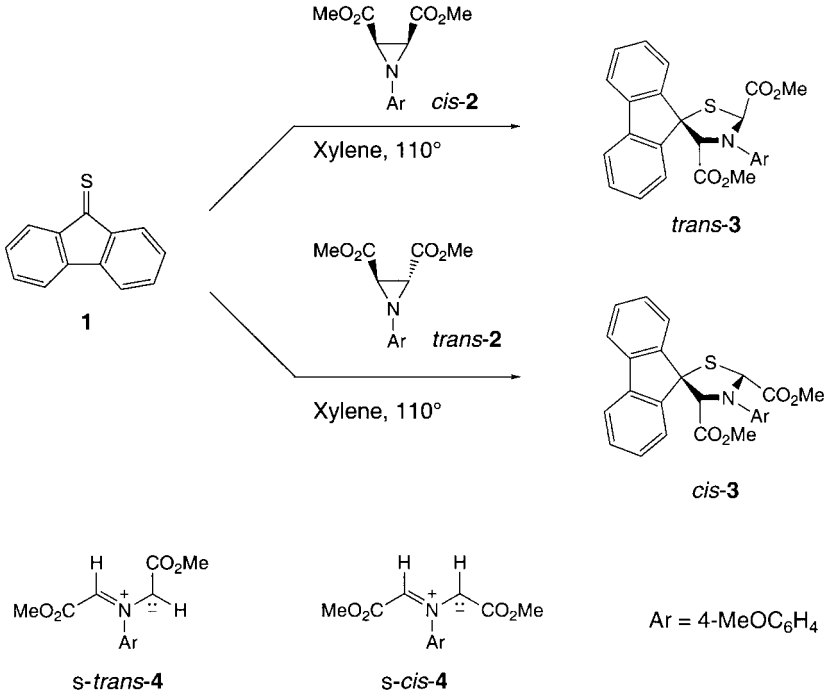
[2]) The *cis*- and *trans*-isomers of dimethyl 1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate were the preferred models in the investigation of the thermal and photochemical electrocyclic ring opening of aziridines to azomethine ylides [7] and the equilibration of the stereoselectively formed 1,3-dipoles [8].

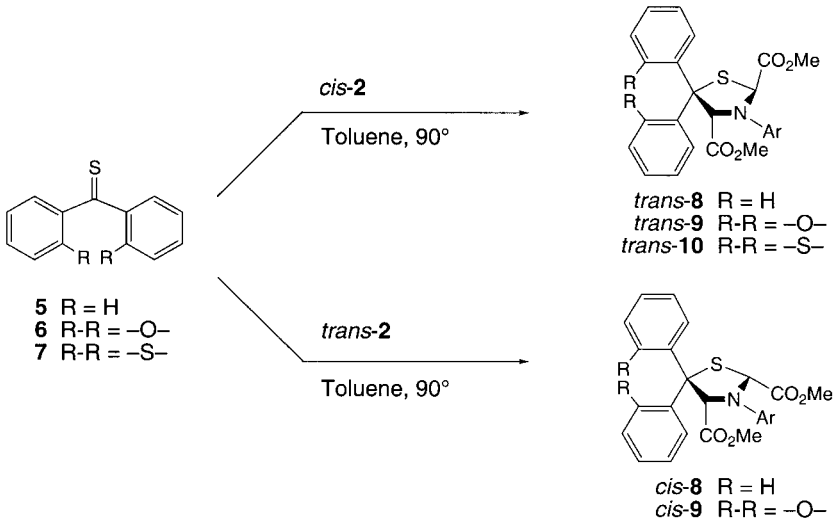
[3]) Small amounts of the yellow dimer of **1** were separated as a less-polar fraction.

[4]) For a kinetics study, see [18].

Scheme 1



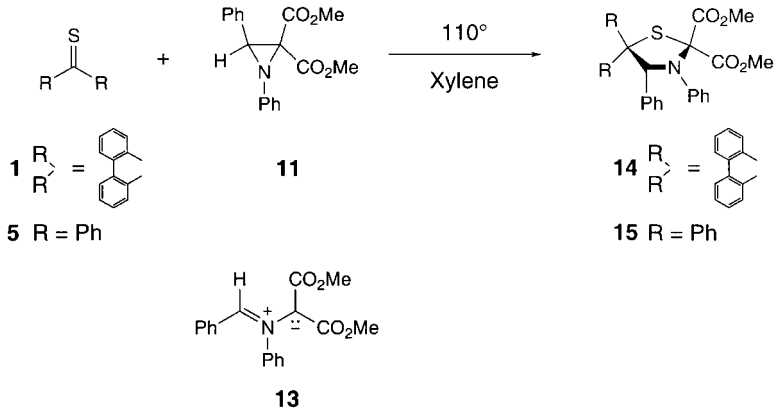
Scheme 2



isomerization (rotation around the N–C bond) to give s-*trans*-**4**, when less-reactive dipolarophiles are involved. In the case of the least reactive **7** with *trans*-**2**, no formation of a cycloadduct was observed.

For the preparation of 1,3-thiazolidine-2,2-dicarboxylates, thioketones **1** and **5** were reacted with dimethyl 1,3-diphenylaziridine-2,2-dicarboxylate (**11**) (*Scheme 3*). This aziridine was prepared *in situ* by thermolysis of dimethyl 4,5-dihydro-1,5-diphenyl-1*H*-1,2,3-triazole-4,4-dicarboxylate **12a** [9][5]). In both cases, with **1** and **5**, a regioselective formation of the corresponding 1,3-thiazolidine **14** and **15**, respectively, was observed. After chromatographic workup and crystallization, pure cycloadducts were obtained, and the structure of **14** has been established by X-ray crystallography [20]. The result shows that C(2) bears the two ester groups, and Ph is attached to C(4). By comparison of spectral data, the analogous regioisomer was assigned to cycloadduct **15**.

Scheme 3



To examine the earlier reported structure of adduct **16** of adamantanethione and the azomethine ylide generated from **11** [12] in the light of the present results, **16** was resynthesized under the conditions described above. Crystals of **16** suitable for X-ray

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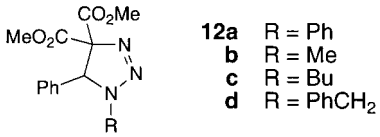
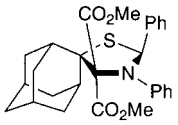
[5]) Whereas the generation of **11**/**13** from **12a** is well-documented [9], similar access to *N*-alkyl-substituted analogues is unknown. Recently, the *N*-methyl derivative **12b** has been prepared and used in thermal reactions as a potential precursor of the corresponding azomethine ylide, but in none of the experiments was any evidence for the intermediacy of this dipole found [19]. To examine other *N*-alkyl derivatives of type **12**, we pepared compounds **12c** and **d** with a Bu and $PhCH_2$ substituent, respectively, at N(1) by [3+2] cycloaddition of the corresponding azides with dimethyl benzylidenemalonate. On the basis of the ^{13}C-NMR data, the analogous structure to **12a** was ascribed to the new 4,5-dihydro-1,2,3-triazoles **12c** and **12d**. Both compounds were heated in xylene (130°), but no evolution of N_2 was observed. Furthermore, on heating in the presence of thiobenzophenone (**5**), the blue color of **5** did not disappear even after a few hours.



crystal-structure determination were obtained from MeOH, and the analysis showed that, in this case, the cycloaddition occurred with the opposite regioselectivity compared with those shown in *Scheme 3* [20]. Based on this observation, we conclude that cycloadditions of azomethine ylide **13** with aromatic and cycloaliphatic thioketones proceed with opposite regioselectivity. The same difference is well-documented for 1,3-dipolar cycloadditions of aromatic thioketones and adamantane-thione with thiocarbonyl ylides [21][22].



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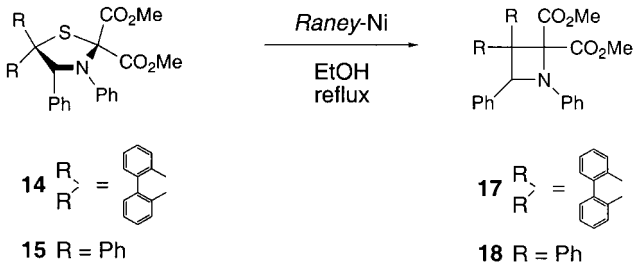
The 1,3-thiazolidines described above were used as models to study desulfurization processes of saturated five-membered S heterocycles. The reagent most frequently used for desulfurization is *Raney*-Ni, and its applications have been reviewed [23]. In a typical manner, a solution of **14** or **15** in $MeOH/CH_2Cl_2$ was stirred at room temperature with a portion of *Raney*-Ni, until TLC showed complete conversion of starting materials. In each case, only one product, **17** or **18**, respectively, was formed. The ^{1}H-NMR spectra showed a similar set of signals as observed for **14** or **15**. For example, the spectrum of **17** formed from **14** was characterized by a *singlet* at 6.97 ppm (1 H) and two *singlets* for MeO at 3.60 and 2.99 ppm. The $[M+1]^+$ peak (CI-MS) was registered at *m*/*z* 478, indicating that the product differs from **14** by one S-atom. All spectroscopic data are in accordance with the structure of azetidine derivatives **17** and **18**.

Scheme 4



14 R, R =

15 R = Ph

17 R, R =

18 R = Ph

To the best of our knowledge, conversions of 1,3-thiazolidines to azetidines *via* desulfurization have never been reported. Numerous 1,3-thiazole derivatives by treatment with *Raney*-Ni were desulfurized to give open-chain N-containing products [23]. The above-described formation of azetidines depends strongly on the structure of the starting material. Attempted desulfurization of **16** was unsuccessful, and the starting material was recovered. In the case of *trans*-**8**, a mixture of unidentified products was obtained. Our results show that the substitution pattern of the 1,3-thiazolidine ring is crucial for the conversion into azetidine derivatives.

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Experimental Part

1. *General.* See [24]. *9*H-*Fluorene-9-thione* (**1**) was prepared from 9*H*-fluorene-9-one and P_4S_{10} as reported by *Lawesson* and co-workers [16]. *Thiobenzophenone* (**5**), *9*H-*xanthene-9-thione* (xanthione, **6**), and *9*H-*thioxanthene-9-thione* (thioxanthione, **7**) were obtained by thionation of the corresponding ketones with *Lawesson*'s reagent [25]. *Dimethyl* cis- *and* trans-*1-(4-methoxyphenyl)aziridine-2,3-dicarboxylate* (*cis*- and *trans*-**2**) were obtained according to a modified procedure reported by *Szeimies* and *Huisgen* [26]. *Dimethyl 1,3-diphenylaziridine-2,2-dicarboxylate* (**11**) was prepared *in situ* by thermal extrusion of N_2 from *4,5-dihydro-1,5-diphenyl-1*H-*1,2,3-triazole-4,4-dicarboxylate* (**12a**) [9].

2. *Reactions of* **1** *with Aziridine Dicarboxylates* **2** *and* **11**. *a*) A soln. of **1** (196 mg, 1.0 mmol) and *cis*- or *trans*-**2** (258.5 mg, 1.1 mmol) in 2 ml of toluene were heated to 110° (oil bath). After 1 h, the olive-green color of **1** disappeared, the solvents were evaporated, the crude residues were analyzed by ^{1}H-NMR spectroscopy, and the products were separated by column chromatography (CC, SiO_2) with a mixture of petroleum ether and increasing amounts of CH_2Cl_2 as eluant. Anal. pure products were obtained by recrystallization from an appropriate solvent.

b) A soln. of **12a** (373 mg, 1.1 mmol) in 1 ml of xylene was heated under magnetic stirring to 130° (oil bath). After 30 min, the evolution of N_2 ceased and the soln. containing **11** was used directly for further experiments. The temp. of the oil bath was reduced to *ca.* 110°, and a soln. of **1** (196 mg, 1.0 mmol) in 1 ml of xylene was added in small portions within *ca.* 30 min. When the addition was complete, heating was continued for *ca.* 30 min.

Dimethyl trans-*3′-(4-Methoxyphenyl)spiro[9*H-*fluorene-9,5′-[1,5]thiazolidine]-2′,4′-dicarboxylate* (*trans*-**3**). Reaction with *cis*-**2**. Yield: 215 mg (50%). M.p. 179–180° (MeOH). IR (KBr): 750*s*, 1039*m*, 1173*s*, 1201*s*, 1248*m*, 1448*m*, 1512*s*, 1736v*s* (C=O), 1755v*s* (C=O). ^{1}H-NMR: 3.32, 3.70, 3.77 (3*s*, 3 MeO); 4.97, 6.06 (2*s*, H–C(2′), H–C(4′)); 6.79 (br. *s*, 4 arom. H); 7.17–7.83 (*m*, 8 arom. H). ^{13}C-NMR: 52.8, 53.3, 55.7 (3*q*, 3 MeO); 62.8 (*s*, C(5′)); 64.3, 74.7 (2*d*, C(2′), C(4′)); 114.7, 119.4, 119.6, 120.0, 125.3, 126.0, 127.4, 128.7, 128.9, 129.4 (10*d*, 12 arom. CH); 138.2, 140.6, 141.6, 150.8, 154.6 (5*d*, 6 arom. C); 169.6, 171.3 (2*s*, 2 C=O). CI-MS: 462 (85, $[M+1]^+$), 358 (38), 254 (51), 226 (100), 196 (22), 194 (36). Anal. calc. for $C_{26}H_{23}NO_5S$ (461.54): C 67.66, H 5.02, N 3.03, S 6.95; found: C 66.99, H 5.04, N 3.00, S 6.89.

Dimethyl cis-*3′-(4-Methoxyphenyl)spiro[9*H-*fluorene-9,5′-[1,3]thiazolidine]-2′,4′-dicarboxylate* (*cis*-**3**). Reaction with *trans*-**2**. Yield: 128 mg (28%). M.p. 166–167° (MeOH). IR (KBr): 764*s*, 817*m*, 1040*s*, 1170v*s*, 1249v*s*, 1288v*s*, 1406*s*, 1510*s*, 1762v*s* (br). ^{1}H-NMR: 3.23, 3.76, 3.83 (3*s*, 3 MeO); 4.94, 5.66 (2*s*, H–C(2′), H–C(4′)); 6.83–6.95 (*m*, 4 arom. H); 7.25–7.67 (*m*, 8 arom. H). ^{13}C-NMR: 51.6, 52.8, 55.5 (3*q*, 3 MeO); 63.5 (*s*, C(5′)); 65.8, 74.9 (2*d*, C(2′), C(4′)); 114.7, 119.3, 119.6, 119.9, 123.8, 126.8, 127.8, 128.3, 128.9, 129.0 (10*s*, 12 arom. CH); 139.3, 139.4, 139.7, 143.4, 146.9 (5*s*, 6 arom. C); 168.5, 170.3 (2*s*, 2 C=O). CI-MS: 462 (100, $[M+1]^+$), 358 (41), 335 (16), 256 (28), 254 (34), 226 (82). Anal. calc. for $C_{26}H_{23}NO_5S$ (461.54): C 67.66, H 5.02, N 3.03, S 6.95; found: C 67.60, H 5.07, N 3.22, S 6.78.

*Dimethyl 3′,4′-Diphenylspiro[9*H-*fluorene-9,5′-[1,3]thiazolidine]-2′,2′-dicarboxylate* (**14**). Reaction with **12a**. Yield (after CC): 210 mg (42%). M.p. 200–201° (MeOH). IR (KBr): 700*s*, 731*s*, 750*s*, 1124*m*, 1257v*s*, 1450*m*, 1493*m*, 1734v*s* (C=O), 1761*s* (C=O). ^{1}H-NMR: 3.42, 3.85 (2*s*, 2 MeO); 5.95 (*s*, H–C(4′)); 6.50–8.30 (*m*, 18 arom. H). ^{13}C-NMR: 52.8, 53.2 (2*q*, 2 MeO); 64.4 (*s*, C(5′)); 77.0 (*s*, C(2′)); 78.7 (*d*, C-(4′)); 119.0, 119.8, 125.3, 125.6, 126.4, 126.5, 126.9, 127.4, 127.6, 128.0, 128.3, 129.0 (12*d*, 18 arom. CH); 133.7, 139.0, 141.3, 143.4, 144.2, 147.7 (6*s*, 6 arom. C); 168.9, 169.6 (2*s*, 2 C=O). CI-MS: 508 (33, $[M+1]^+$), 476 (5, $[M-MeO]^+$), 346 (32), 312 (100), 224 (22), 197 (17), 182 (32). Anal. calc. for $C_{31}H_{25}NO_4S$ (506.60): C 73.49, H 4.77, N 2.76, S 6.33; found: C 73.52, H 4.80, N 2.87, S 5.98.

3. *Reaction of* **5** *with* **11**. The reaction was carried out as described in *2*, *b*). *Dimethyl 3,4,5,5-Tetraphenyl-1,3-thiazolidine-2,2-dicarboxylate* (**15**). Yield: 320 mg (63%). M.p. 152–154° (MeOH) ([12]: 153–155°). IR (KBr): 746*m*, 1254v*s*, 1313*s*, 1444*m*, 1504*s*, 1599*m*, 1738v*s* (C=O). ^{1}H-NMR: 3.18, 3.98 (2*s*, 2 MeO); 6.18 (*s*, H–C(4)); 6.60–7.85 (*m*, 20 arom. H). ^{13}C-NMR: 52.8, 53.7 (2*q*, 2 MeO); 69.7 (*s*, C(5)); 74.0 (*d*, C(4)); 77.3 (*s*, C(2)); 113.5, 117.8, 119.7, 127.0, 127.2, 127.4, 127.8, 128.2, 129.1, 129.2, 129.5, 130.1 (12*d*, 20 arom. CH); 138.2, 140.2, 143.6, 144.4 (4*s*, 4 arom. C); 168.6, 168.7 (2*s*, 2 C=O).

4. *Reactions of* **5**, **6**, *and* **7** *with Dimethyl Aziridine-2,3-dicarboxylates* **2**. *General Procedure.* A soln. of aziridine **2** (282 mg, 1.1 mmol) in 1 ml of toluene was heated (oil bath) under magnetic stirring to 90°. After 10 min, a soln. of 1 mmol of thioketone in 1 ml of toluene was added. The flask was equipped with a condenser,

and the heating was continued until complete consumption of the thioketone (TLC). The solvent was removed *i.v.*, and the crude mixtures were analyzed by ^{1}H-NMR spectroscopy. Pure products were isolated after crystallization or CC (SiO_2) with a mixture of petroleum ether and increasing amounts of CH_2Cl_2. Anal. pure products were obtained by recrystallization from an appropriate solvent.

4.1. *Reactions with* cis-**2**. *With Thiobenzophenone* (**5**). Reaction time 20 h; the ^{1}H-NMR spectrum revealed the presence of only one product showing 2 *s* for CH at 5.55 and 5.62 ppm. Crystallization from MeOH afforded 345 mg (71%) of *dimethyl* trans-*3-(4-methoxyphenyl)-5,5-diphenyl-1,3-thiazolidine-2,4-dicarboxylate* (*trans*-**8**). Colorless prisms. M.p. 126–127°. IR (KBr): 698*m*, 1041*m*, 1173*s*, 1196*s*, 1259*s*, 1444*w*, 1514*s*, 1734v*s* (C=O), 1751v*s* (C=O). ^{1}H-NMR: 3.08, 3.32, 3.70 (3*s*, 3 MeO); 5.55, 5.62 (2*s*, H–C(2), H–C(4)); 6.45–6.97 (*m*, 4 arom. H); 7.08–7.57 (*m*, 10 arom. H). ^{13}C-NMR: 51.7, 52.4, 55.7 (3*q*, 3 MeO); 63.9, 73.1 (2*d*, C(2), C(4)); 66.7 (*s*, C(5)); 115.4, 115.6, 127.1, 128.1, 128.2, 128.3, 129.2 (7*d*, 14 arom. CH); 139.1, 139.9, 146.7, 153.8 (4*s*, 4 arom. C); 170.7, 171.3 (2*s*, 2 C=O). CI-MS: 464 (100, $[M+1]^+$), 422 (17), 360 (30). Anal. calc. for $C_{26}H_{25}NO_5S$ (463.55): C 67.37, H 5.43, N 3.02, S 6.92; found: C 66.99, H 5.47, N 3.07, S 6.81.

*With 9*H-*Xanthene-9-thione* (**6**). Reaction time 30 h; the ^{1}H-NMR spectrum revealed the presence of only one product showing 2*s* for CH at 5.03 and 5.98 ppm. CC (SiO_2) led to 175 mg (34%) of *dimethyl* trans-*3′-(4-methoxyphenyl)spiro[9*H-*xanthene-9,5′-[1,3]thiazolidine]-2′,4′-dicarboxylate* (*trans*-**9**). Colorless crystals. M.p. 183–185°. IR (KBr): 756*m*, 1039*w*, 1171*s*, 1196*s*, 1246v*s*, 1319*m*, 1444*s*, 1477*s*, 1512*s*, 1736v*s* (C=O), 1759*s* (C=O). ^{1}H-NMR: 3.05, 3.67, 3.72 (3*s*, 3 MeO); 5.03, 5.98 (2*s*, H–C(2′), H–C(4′)); 6.65–6.85 (*m*, 4 arom. H); 6.92–7.42 (*m*, 8 arom. H). ^{13}C-NMR: 51.7, 52.5, 55.5 (3*q*, 3 MeO); 59.0 (*s*, C(5′)); 66.3, 80.7 (2*d*, C(2′), C(4′)); 114.8, 116.3, 121.7, 121.8, 123.1, 123.9, 129.6, 129.9, 130.9, 131.1 (10*d*, 12 arom. CH); 125.0, 138.8, 151.2, 151.3, 155.9 (5*s*, 6 arom. C); 168.8, 171.6 (2*s*, 2 C=O). CI-MS: 478 (100, $[M+1]^+$), 374 (35), 266 (16), 213 (66). Anal. calc. for $C_{26}H_{23}NO_6S$ (477.54): C 65.39, H 4.85, N 2.93, S 6.72; found: C 65.08, H 5.00, N 2.98, S 6.85.

*With 9*H-*Thioxanthene-9-thione* (**7**). Reaction time 24 h; the ^{1}H-NMR spectrum revealed the presence of only one product showing 2*s* for CH at 5.45 and 5.90 ppm. Crystallization from MeOH afforded 7 mg (14%) of *dimethyl* trans-*3′-(4-methoxyphenyl)spiro[9*H-*thioxanthene-9,5′-[1,3]thiazolidine]-2′,4′-dicarboxylate* (*trans*-**10**). Colorless crystals. M.p. 178–179°. IR (KBr): 750*m*, 1030*m*, 1170*s*, 1250*s*, 1430*m*, 1500*s*, 1745v*s* (C=O). ^{1}H-NMR: 3.00, 3.65, 3.80 (3*s*, 3 MeO); 5.45, 5.90 (2*s*, H–C(2′), H–C(4′)); 6.33-6.83 (*m*, 4 arom. H); 7.08–7.67 (*m*, 8 arom. H). ^{13}C-NMR: 51.4, 52.8, 55.6 (3*q*, 3 MeO); 63.7, 72.8 (2*d*, C(2′), C(4′)); 66.7 (*s*, C(5′)); 115.0, 119.1, 126.6, 126.7, 127.4, 128.1, 128.2, 128.5, 131.5, 132.2 (10*d*, 12 arom. CH); 134.5, 135.5, 137.7, 139.0, 154.9 (5*s*, 6 arom. C); 170.1, 170.7 (2*s*, 2 C=O). CI-MS: 494 (77, $[M+1]^+$), 462 (7), 390 (9), 266 (50), 229 (100), 196 (44). Anal. calc. for $C_{26}H_{23}NO_5S_2$ (493.60): C 63.26, H 4.69, N 2.84, S 12.99; found: C 62.64, H 4.73, N 2.85, S 13.05.

4.2. *Reactions with* trans-**2**. *With* **5**. Reaction time 10 h; the ^{1}H-NMR spectrum of the reaction mixture indicated the presence of *cis*-**8** and *trans*-**8** in a ratio of *ca.* 4:1. The main product was separated as the more polar fraction after CC (SiO_2, petroleum ether/CH_2Cl_2): *Dimethyl* cis-*3-(4-Methoxyphenyl)-5,5-diphenyl-1,3-thiazolidine-2,4-dicarboxylate* (*cis*-**8**). Yield: 60 mg (24%). Colorless crystals. M.p. 117–118° (MeOH). IR (KBr): 1740v*s* (C=O). ^{1}H-NMR: 3.25, 3.74, 3.76 (3*s*, 3 MeO); 5.22, 5.26 (2*s*, H–C(2), H–C(4)); 6.56–6.87 (*m*, 5 arom. H); 7.01–7.36 (*m*, 8 arom. H). ^{13}C-NMR: 51.8, 52.9, 55.6 (3*q*, 3 MeO); 62.7, 73.3 (2*d*, C(2), C(4)); 67.5 (*s*, C(5)); 114.0, 115.1, 126.8, 127.1, 128.0, 128.1, 128.3, 128.8 (8*d*, 14 arom. CH); 138.5, 138.6, 145.8, 152.9 (4*s*, 4 arom. C); 169.3, 170.6 (2*s*, 2 C=O). CI-MS: 464 (100, $[M+1]^+$), 360 (63), 266 (22), 256 (29), 239 (37). Anal. calc. for $C_{26}H_{25}NO_5S$ (463.55): C 67.37, H 5.43, N 3.02, S 6.92; found: C 67.03, H 5.43, N 3.01, S 6.88.

With **6.** Reaction time 37 h; the ^{1}H-NMR spectrum of the crude product indicated the presence of *cis*-**9** and *trans*-**9** in a ratio of *ca.* 4:1. CC gave the main product as the more polar fraction.

Dimethyl cis-*3′-(4-Methoxyphenyl)spiro[9*H-*xanthene-9,5′-[1,3]thiazolidine]-2′,4′-dicarboxylate* (*cis*-**9**). Yield: 105 mg (22%). Colorless prisms. M.p. 151–152° (MeOH). IR (KBr): 749*s*, 1039*s*, 1183v*s*, 1205v*s*, 1249v*s*, 1270*s*, 1445v*s*, 1475*s*, 1510v*s*, 1600*m*, 1749v*s* (C=O), 1757v*s* (C=O). ^{1}H-NMR: 3.10, 3.67, 3.80 (3*s*, 3 MeO); 4.62, 5.73 (2*s*, H–C(2′), H–C(4′)); 6.57–6.88 (*m*, 4 arom. H); 6.93–7.50 (*m*, 8 arom. H). ^{13}C-NMR: 51.7, 52.9, 55.6 (3*q*, 3 MeO); 59.5, 81.0 (2*d*, C(2′), C(4′)); 68.2 (*s*, C(5′)); 114.9, 116.2, 121.1, 121.8, 123.4, 123.8, 129.4, 129.5, 129.9, 131.2 (10*d*, 12 arom. CH); 125.6, 139.5, 151.4, 151.8, 156.1 (5*s*, 6 arom. C); 168.7, 170.2 (2*s*, 2 C=O). CI-MS: 478 (100, $[M+1]^+$), 266 (58), 213 (31). Anal. calc. for $C_{26}H_{23}NO_6S$ (477.54): C 65.39, H 4.85, N 2.93, S 6.71; found: C 65.18, H 4.93, N 2.88, S 6.82.

With **7**. After 24 h of heating, decomposition of starting materials was observed, and no [3 + 4] cycloadduct could be detected in the mixture.

5. *Reaction of Adamantanethione with Azomethine Ylide* **13**. To the preheated soln. of **12a** (373 mg, 1.1 mmol) in 2 ml of xylene (see *2,b*) was added freshly prepared adamantanethione (166 mg, 1 mmol). After heating for 4 h, no adamantanethione was detected by TLC; the solvent was evaporated *i.v.*, and the residue was

triturated with a small amount of MeOH. After storage in the refrigerator overnight, colorless crystals were filtered and recrystallized from MeOH.

Dimethyl 3′,4′-Diphenylspiro[adamantane-2,5′-[1,3]thiazolidine]-2′,2′-dicarboxylate (**16**): Yield: 308 mg (82%). Colorless crystals. M.p. 150–152° ([12]: 152–154°). IR (KBr): 700*m*, 748*m*, 1053*m*, 1207*s*, 1225v*s*, 1294*s*, 1498*s*, 1597*s*, 1747v*s* (C=O), 1765v*s* (C=O). ^{1}H-NMR: 1.43–2.51 (*m*, 10 H); 3.55, 3.80 (2*s*, 2 MeO); 5.93 (*s*, H–C(2)); 6.32–7.58 (*m*, 10 arom. H). ^{13}C-NMR: 26.4, 26.8, 35.9, 37.2 (4*d*, 4 CH); 32.6, 33.2, 37.1, 38.1, 38.5 (5*t*, 5 CH_2); 52.4, 53.2 (2*q*, 2 MeO); 67.3 (*d*, C(2)); 71.5 (*s*, C(5)); 83.5 (*s*, C(4)); 114.7, 118.6, 126.6, 127.2, 128.4, 128.6 (6*d*, 10 arom. CH); 143.0, 146.0 (2*s*, 2 arom. C); 168.3, 170.0 (2*s*, 2 C=O).

6. *Desulfurization of 1,3-Thiazolidines* **14**, **15** *with* Raney*-Ni*. To a soln. of 0.5 mmol of **14** or **15** in 3 ml of CH_2Cl_2 was added *Raney*-Ni (*ca.* three-fold weight amount) suspended in MeOH. The mixture was stirred magnetically at r.t. for 48 h. Then, the mixture was filtered to remove *Raney*-Ni, and the black residue was washed with 5 ml of CH_2Cl_2 (3×). The org. solns. were combined, the solvents were removed *i.v.*, and the solid residues were crystallized from MeOH.

*Dimethyl 1′,4′-Diphenylspiro[9*H*-fluorene-9,3′-azetidine]-2′,2′-dicarboxylate* (**17**). Yield: 185 mg (78%). Colorless prisms. M.p. 200–201° (MeOH). IR (KBr): 694*m*, 752*s*, 1053*m*, 1140*s*, 1232v*s*, 1271v*s*, 1317*s*, 1450v*s*, 1495v*s*, 1604*s*, 1736v*s* (C=O), 1753v*s* (C=O). ^{1}H-NMR: 3.14, 3.58 (2*s*, 2 MeO); 6.17 (*s*, H–C(4′)); 6.94–7.80 (*m*, 18 arom. H). ^{13}C-NMR: 51.7, 52.5 (2*q*, 2 MeO); 60.4 (*s*, C(2′)); 69.8 (*d*, C(4′)); 82.5 (*s*, C(3′)); 115.5, 119.2, 120.0, 120.6, 125.6, 125.7, 126.6, 127.1, 127.5, 127.8, 127.9, 128.8, 129.3 (13*d*, 18 arom. CH); 137.1, 140.5, 141.0, 142.6, 143.3, 148.2 (6*s*, 6 arom. C); 166.9, 168.7 (2*s*, 2 C=O). CI-MS: 476 (55, $[M+1]^+$), 255 (46), 224 (100), 222 (85). Anal. calc. for $C_{31}H_{25}NO_4$ (475.55): C 78.30, H 5.30, N 2.95; found: C 77.98, H 5.07, N 2.94.

Dimethyl 1,3,3,4-Tetraphenylazetidine-2,2-dicarboxylate (**18**). Yield: 198 mg (83%). Colorless crystals. M.p. 154–155° (MeOH/CH_2Cl_2). IR (KBr): 706*s*, 764*m*, 1057*m*, 1138*m*, 1267v*s*, 1448*m*, 1495v*s*, 1603*s*, 1738v*s* (C=O), 1751v*s* (C=O). ^{1}H-NMR: 2.99, 3.60 (2*s*, 2 MeO); 6.37 (*s*, H–C(4)); 6.84–7.44 (*m*, 20 arom. H). ^{13}C-NMR: 51.8, 52.3 (2*q*, 2 MeO); 62.7 (*s*, C(2)); 70.7 (*d*, C(4)); 86.0 (*s*, C(3)); 115.1, 120.5, 126.6, 127.2, 127.4, 127.6, 128.3, 128.5, 128.7, 129.1 (10*d*, 20 arom. CH); 137.9, 140.5, 142.0, 148.9 (4*s*, 4 arom. C); 168.1, 170.2 (2*s*, 2 C=O). CI-MS: 478 (100, $[M+1]^+$), 222 (18). Anal. calc. for $C_{31}H_{27}NO_4$ (477.56): C 77.97, H 5.70, N 2.93; found: C 77.69, H 5.52, N 2.96.

7. *Synthesis of* N*-Substituted 4,5-Dihydro-5-phenyl-1*H*-[1,2,3]triazole-4,4-dicarboxylates* **12c** *and* **12d**. *General Procedure.* Dimethyl benzylidenemalonate (2.20 g, 10 mmol) and 35 mmol of $PhCH_2N_3$ and BuN_3 azide, resp., without solvent were placed in a round-bottom flask, and the mixture was heated to 50° (oil bath). While heating during the day and keeping at r.t. at night, the reaction was continued for 30 d. Then, remaining azide was removed by bulb-to-bulb distillation at 40°/10^{-3} Torr. The residual, thick oil was purified by CC (SiO_2) with hexane and increasing amounts of CH_2Cl_2 as the eluant. Pure products were isolated as thick oils, which did not crystallize even after storage in the refrigerator for several days.

*Dimethyl 1-Butyl-4,5-dihydro-5-phenyl-1*H*-[1,2,3]triazole-4,4-dicarboxylate* (**12c**). Yield: 2.25 g (71%). Colorless oil. IR ($CHCl_3$): 1124*m*, 1171*m*, 1286v*s*, 1437*s*, 1456*m*, 1741v*s* (C=O), 2875*w*, 2958*s*, 3008*m* (br.). ^{1}H-NMR: 0.89 (*t*, Me); 1.10–1.85 (*m*, 2 CH_2); 3.20, 3.90 (2*s*, MeO); 3.70 (*t*, CH_2N); 5.35 (*s*, H–C(5)); 7.10–7.45 (*m*, 5 arom. H). ^{13}C-NMR: 13.6 (*q*, Me); 19.9, 29.9, 47.9 (3*t*, 3 CH_2); 52.4, 53.8 (2*q*, 2 MeO); 66.0 (*d*, C(5)); 94.9 (*s*, C(4)); 128.3, 129.0, 129.3 (3*d*, 5 arom. CH); 133.9 (*s*, 1 arom. C); 165.5, 167.0 (2*s*, 2 C=O). CI-MS: 320 (100, $[M+1]^+$), 262 (10), 162 (9). Anal. calc. for $C_{16}H_{21}N_3O_4$ (319.36): C 60.18, H 6.63, N 13.16; found: C 60.18, H 6.45, N 13.31.

*Dimethyl 1-Benzyl-4,5-dihydro-5-phenyl-1*H*-[1,2,3]triazole-4,4-dicarboxylate* (**12d**). Yield: 2.40 g (67%). Colorless oil. IR ($CHCl_3$): 1130*s*, 1285v*s*, 1440*s*, 1456*s*, 1741v*s* (C=O), 2956*m*, 3014*s*. ^{1}H-NMR: 3.16, 3.76 (2*s*, 2 MeO); 4.24, 5.32 (*AB*, $J = 15.0$, CH_2); 5.05 (*s*, H–C(5)); 6.95–7.80 (*m*, 10 arom. H). ^{13}C-NMR: 52.0 (*t*, CH_2); 52.5, 53.8 (2*q*, 2 MeO); 64.9 (*d*, C(5)); 95.0 (*q*, C(4)); 128.4, 128.5, 128.7, 129.0, 129.1, 129.3 (6*d*, 10 arom. CH); 133.2, 134.7 (2*s*, 2 arom. C); 165.2, 166.6 (2*s*, 2 C=O). CI-MS: 354 (100, $[M+1]^+$), 296 (8), 268 (7). Anal. calc. for $C_{19}H_{23}N_3O_4$ (357.41): C 63.85, H 6.49, N 11.76; found: C 63.15, H 5.42, N 11.76.

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