1,3-Oxathiole and Thiirane Derivatives from the Reactions of Azibenzil and α-Diazo Amides with Thiocarbonyl Compounds

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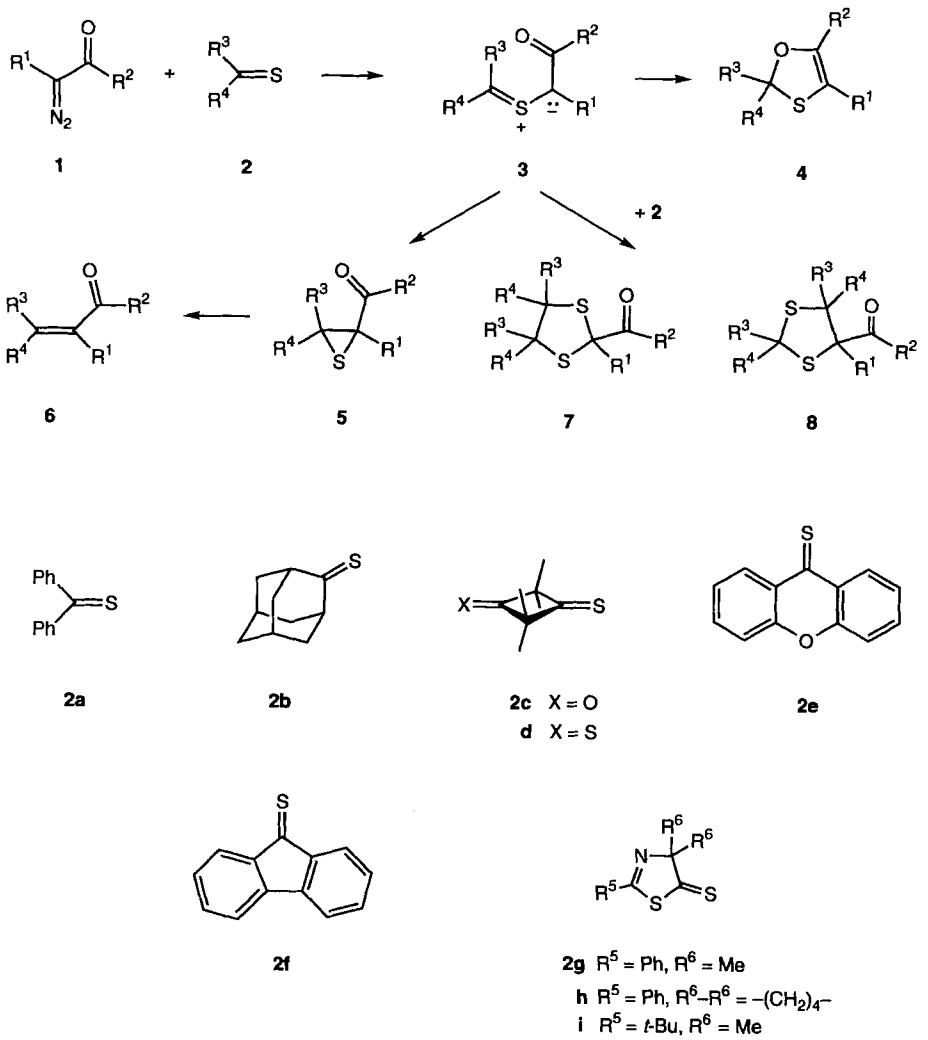
The reactions of α-diazo ketones **1a,b** with 9*H*-fluorene-9-thione (**2f**) in THF at room temperature yielded the symmetrical 1,3-dithiolanes **7a,b**, whereas **1b** and 2,2,4,4-tetramethylcyclobutane-1,3-dithione (**2d**) in THF at 60° led to a mixture of two stereoisomeric 1,3-oxathiole derivatives *cis*- and *trans*-**9a** (*Scheme 2*). With 2-diazo-1,2-diphenylethanone (**1c**), thio ketones **2a–d** as well as 1,3-thiazole-5(4*H*)-thione **2g** reacted to give 1,3-oxathiole derivatives exclusively (*Schemes 3* and *4*). As the reactions with **1c** were more sluggish than those with **1a,b**, they were catalyzed either by the addition of $LiClO_4$ or by $Rh_2(OAc)_4$. In the case of **2d** in THF/$LiClO_4$ at room temperature, a mixture of the monoadduct **4d** and the stereoisomeric bis-adducts *cis*- and *trans*-**9b** was formed. Monoadduct **4d** could be transformed to *cis*- and *trans*-**9b** by treatment with **1c** in the presence of $Rh_2(OAc)_4$ (*Scheme 4*). Xanthione (**2e**) and **1c** in THF at room temperature reacted only when catalyzed with $Rh_2(OAc)_4$, and, in contrast to the previous reactions, the benzoyl-substituted thiirane derivative **5a** was the sole product (*Scheme 4*). Both types of reaction were observed with α-diazo amides **1d,e** (*Schemes 5–7*). It is worth mentioning that formation of 1,3-oxathiole or thiirane is not only dependent on the type of the carbonyl compound **2** but also on the α-diazo amide. In the case of **1d** and thioxocyclobutanone **2c** in THF at room temperature, the primary cycloadduct **12** was the main product. Heating the mixture to 60°, 1,3-oxathiole **10d** as well as the spirocyclic thiirane-carboxamide **11b** were formed. Thiirane-carboxamides **11d–g** were desulfurized with $(Me_2N)_3P$ in THF at 60°, yielding the corresponding acrylamide derivatives (*Scheme 7*). All reactions are rationalized by a mechanism *via* initial formation of acyl-substituted thiocarbonyl ylides which undergo either a 1,5-dipolar electrocyclization to give 1,3-oxathiole derivatives or a 1,3-dipolar electrocyclization to yield thiiranes. Only in the case of the most reactive 9*H*-fluorene-9-thione (**2f**) is the thiocarbonyl ylide trapped by a second molecule of **2f** to give 1,3-dithiolane derivatives by a 1,3-dipolar cycloaddition.

1. Introduction. – Recently, we have reported on reactions of some α-diazo carbonyl compounds with thiocarbonyl compounds [1][2]. Whereas α-diazo ketones **1** (R^1 = H, R^2 = Ph, *t*-Bu) reacted with thio ketones **2a–d** and with 1,3-thiazole-5(4*H*)-thiones **2g–i** to give 1,3-oxathioles of type **4** (*Scheme 1*), we isolated only a thiirane of type **5** and an α,β-unsaturated ketone of type **6** in the case of 9*H*-xanthene-9-thione (**2e**) [1].

On the other hand, in reactions with ethyl diazoacetate (**1**, R^1 = H, R^2 = EtO), we have never observed the formation of a corresponding 1,3-oxathiole [2]. The reactions with the more reactive thio ketones **2a**, **2b**, and **2f** lead to 1,3-dithiolanes **7** and/or **8**, the so-called '*Schönberg* products' [3] which were isolated as the sole products. With the sterically crowded **2c** and **2d** as well as with **2e**, thiirane formation took place; in the latter case, the thiirane desulfurized spontaneously, and only the α,β-unsaturated ester of type **6** could be isolated. The key intermediates for all isolated products are thiocarbonyl ylides of type **3**. These intermediates undergo a 1,5- or 1,3-dipolar electrocyclization to give **4** and **5**, respectively, or can be trapped by the thiocarbonyl compound to yield **7**/**8**.

[1]) Part of the Ph.D. thesis of *M.K.*, University of Zürich, 1997.

Scheme 1

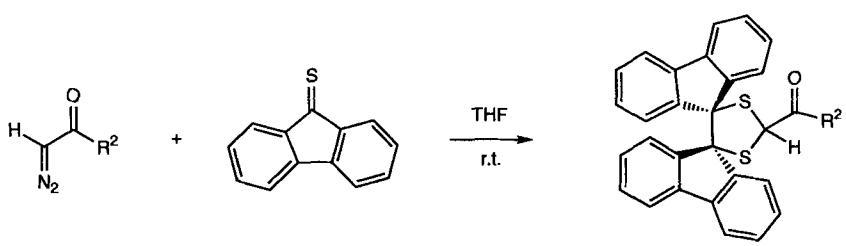


These results clearly demonstrate that the reaction pathway depends on the 1,3-dipolar reactivity of **2** as well as on the substituent R^2 of **3**. Obviously, thiocarbonyl ylides **3** with an ester group (R^2 = RO) do not undergo a 1,5-dipolar electrocyclization but are preferentially trapped by the 'superdipolarophiles' [4][5] **2a**, **2b**, and **2f** *via* a 1,3-dipolar cycloaddition to give 1,3-dithiolanes (*cf.* also [6]). If the C=S compound **2** is less reactive, *e.g.*, **2c–e**, ring closure to thiirane predominates.

The aim of the present work was to further investigate the scope and limitation of the 1,5-dipolar electrocyclization of thiocarbonyl ylides **3** and, in particular, the influence of the substituent R^2 in diazo compounds **1** on the course of the reaction with thio ketones.

2. Results. – 2.1. *Reactions with α-Diazo Ketones.* As 9*H*-fluorene-9-thione (**2f**) is the most powerful C=S dipolarophile [4][5], it should be the best candidate for trapping thiocarbonyl ylides of type **3** (R^1 = H), which have been shown to undergo mainly a 1,5-dipolar electrocyclization [1]. Therefore, we examined the reactions with α-diazo ketones **1a**, **b** using **2f** as the thiocarbonyl compound. When portions of **2f** were added to THF solutions of **1a** or **1b** at room temperature, the green color disappeared immediately and only the '*Schönberg* products' **7a** and **7b**, respectively, were isolated in high yield after precipitation with hexane (*Scheme 2*). On the other hand, the analogous reaction of **1b** with dithione **2d** required more vigorous conditions and was performed at 60° in the presence of $LiClO_4$ [2]). In this case, the 1,3-oxathioles *cis*- and *trans*-**9a** were formed exclusively in a ratio of *ca.* 1:2. As in similar 2:1 adducts, the assignment of the *cis*- and *trans*-structures is easy, as *cis*-**9a** shows two Me signals in the NMR spectra, but *trans*-**9a** only one, since all four Me groups of *trans*-**9a** are homotopic.

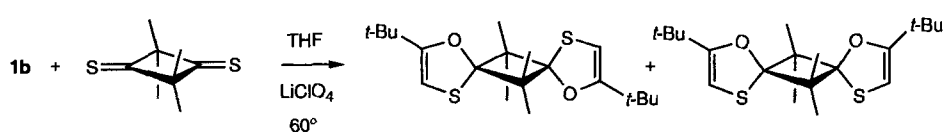
Scheme 2



1a R^2 = Ph
b R^2 = *t*-Bu

2f

7a R^2 = Ph
b R^2 = *t*-Bu



1b

2d

trans - **9a**

cis - **9a**

The reactions of 2-diazo-1,2-diphenylethanone (= azibenzil; **1c**) with thiones **2a–c** were more sluggish and required slightly different reaction conditions, because **1c** slowly decomposed in solution even at room temperature. Therefore, **1c** and **2a** were reacted in THF at room temperature in the presence of $LiClO_4$. After 15 h, the reaction was complete and chromatographic workup gave 1,3-oxathiole **4a** [9] in 51% yield (*Scheme 3*). The structure of this product was established by X-ray crystallography (*Fig. 1*).

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[2]) It has been shown that some reactions of diazo compounds and thiocarbonyl compounds proceed faster in the presence of $LiClO_4$ [7] (*cf.* [8]).

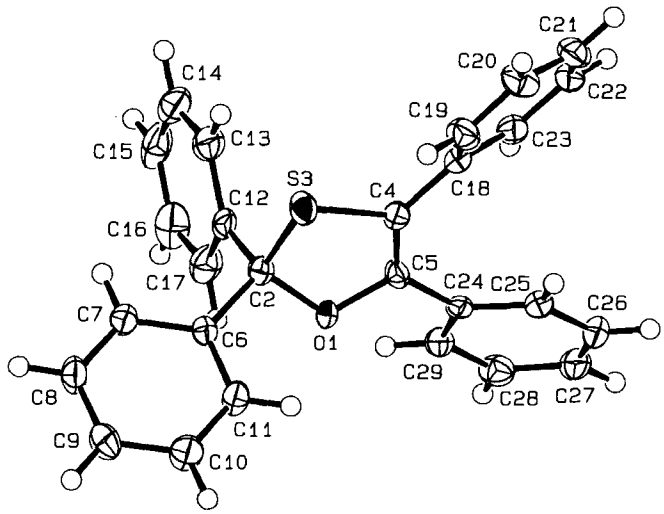
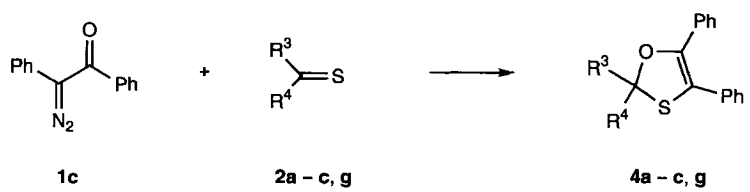


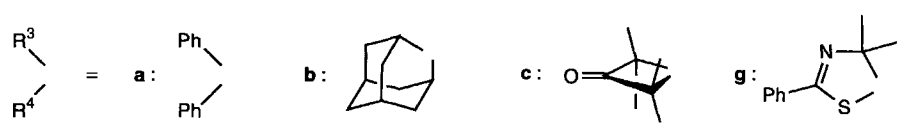
Fig. 1. *ORTEP Plot* [10] *of the molecular structure of 1,3-oxathiole* **4a** (ellipsoids with 50% probability)

The reaction of 2 equiv. of **1c**[3]) with the sterically crowded thione **2c** was performed under analogous conditions and yielded the spirocyclic **4c** (*Scheme 3*). Unexpectedly, **1c** did not react with adamantane-2-thione (**2b**), neither in the presence of $LiClO_4$ nor at higher temperature; only decomposition of **1c** was observed. Therefore, the reaction in THF at room temperature was catalyzed by addition of $Rh_2(OAc)_4$ (*cf.* [11][12]). A vigorous N_2 evolution took place, and, after chromatographic workup, 1,3-oxathiole **4b** was obtained in 72% yield.

Scheme 3



1c **2a – c, g** **4a – c, g**

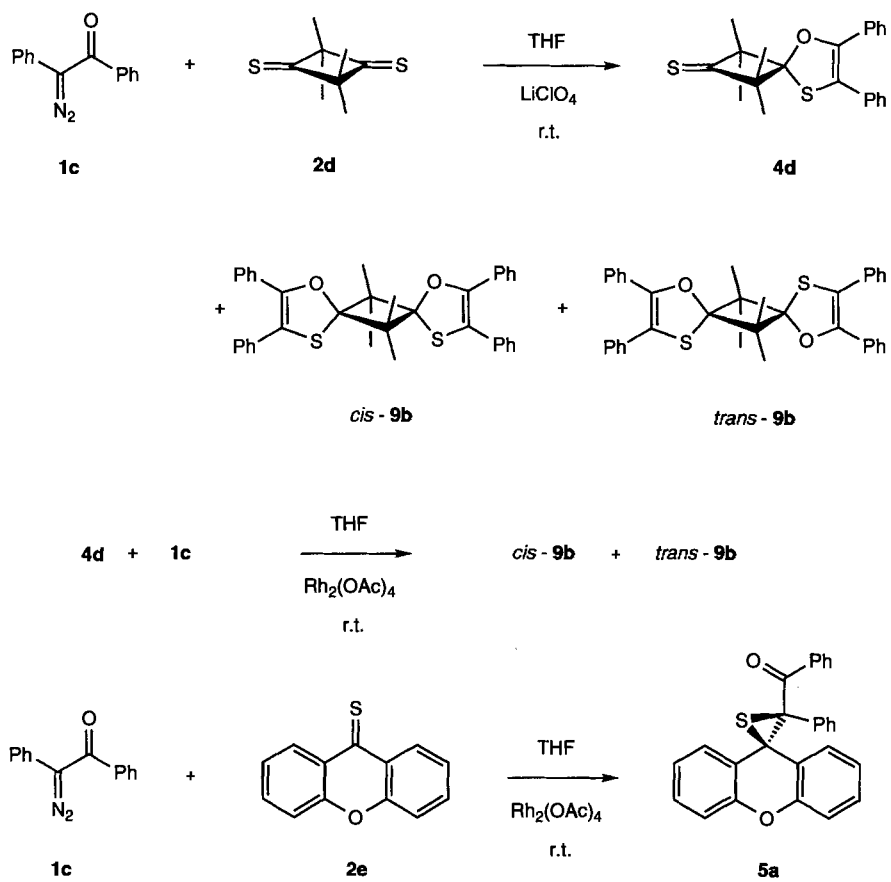


Similarly, the less reactive 1,3-thiazole-5(4*H*)-thione **2g** reacted with **1c** only in the presence of $Rh_2(OAc)_4$ to give **4g** exclusively in 61% yield. In all these reactions, no product other than the 1,3-oxathiole derivative **4** could be isolated.

[3]) An excess of **1c** was used because of its slow decomposition under the reaction conditions.

A solution of dithione **2d** in THF/$LiClO_4$ at room temperature was treated with an excess of **1c**. After stirring for 3 days, **2d** was completely consumed (TLC), and chromatographic workup yielded the 1:1 adduct **4d** (50%) and a mixture of the stereoisomeric 1:2 adducts *cis*-**9b** and *trans*-**9b** (*ca.* 1:2, 10% yield; *Scheme 4*). Treatment of **4d** in THF at room temperature with an excess of **1c** in the presence of $Rh_2(OAc)_4$ yielded again a 1:2 mixture of *cis*-**9b** and *trans*-**9b**. As in the case of *cis*-**9a** and *trans*-**9a**, the determination of the structures was based on the NMR spectra of the mixture of the isomers.

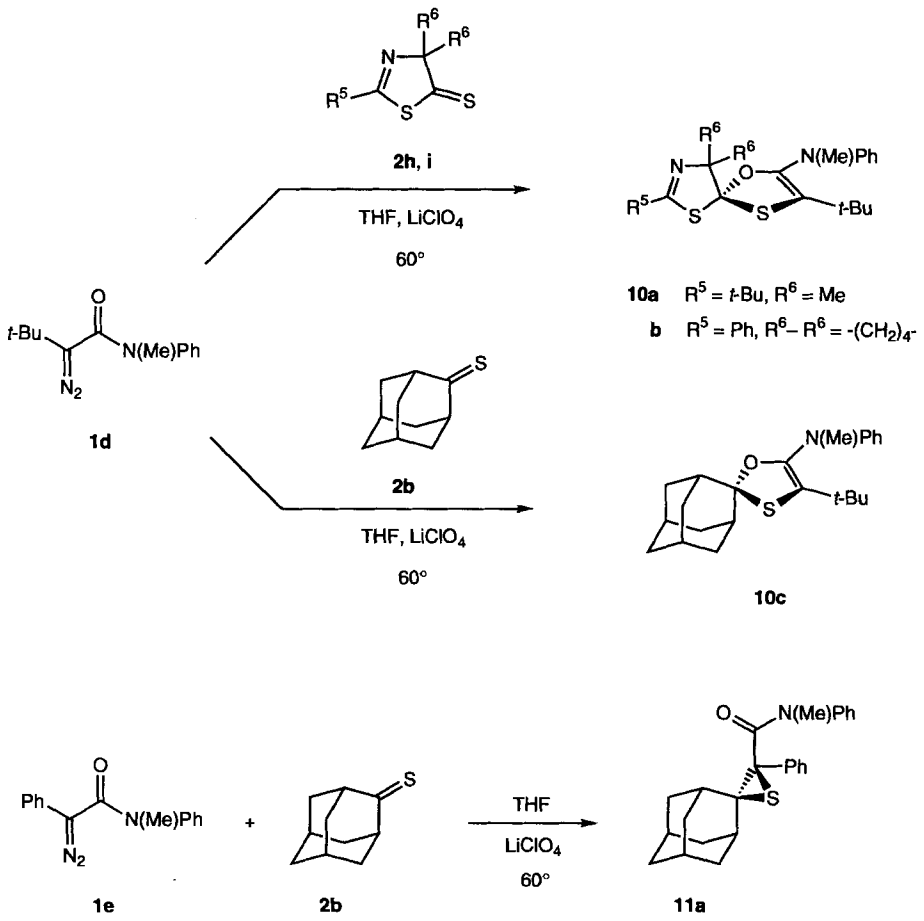
Scheme 4



Again, another result was obtained with 9*H*-xanthene-9-thione (**2e**). The reaction with **1c** proceeded only when catalyzed with $Rh_2(OAc)_4$. The sole product, isolated in low yield, was thiirane **5a** (*Scheme 4*).

2.2. *Reactions with α-Diazo Amides.* The reactions of α-diazo amide **1d** with 1,3-thiazole-5(4*H*)-thiones **2h**, **i** in THF/$LiClO_4$ at 60° was complete after 20 h. The sole product obtained in 64 and 69% yield after chromatography was the spirocyclic 1,3-oxathiole **10a** and **10b**, respectively (*Scheme 5*). The corresponding reaction of **1d** and

Scheme 5



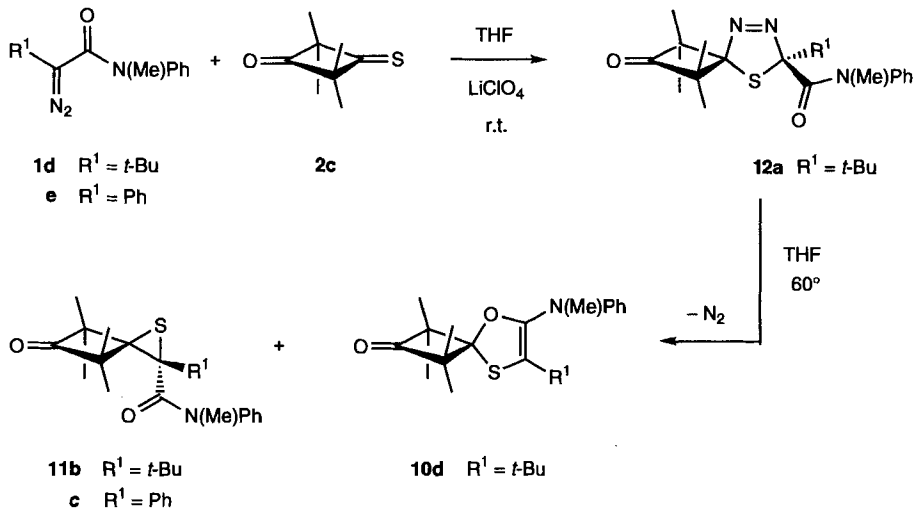
2b proceeded more quickly and was terminated after only 1 h, yielding 1,3-oxathiole **10c** (80%). Under the same conditions, the less reactive **1e** was only consumed after 5 h, and thiirane **11a** was obtained in 13% yield (*Scheme 5*). No other product could be isolated.

The red color of a solution of equimolar amounts of **1d** and **2c** in THF in the presence of $LiClO_4$ disappeared at room temperature within 30 min, but only *ca.* 12% of the calculated amount of N_2 evolved[4]). After chromatographic workup, the spirocyclic 2,5-dihydro-1,3,4-thiadiazole-2-carboxamide **12a**, *e.g.*, the initial [3 + 2] cycloadduct, was obtained in 79% yield (*Scheme 6*). Recrystallization from $MeOH/CH_2Cl_2$ gave suitable crystals for an X-ray crystal-structure determination (*Fig. 2*).

Heating a THF solution of **12a** to 60° led to the decomposition of the adduct and evolution of N_2 with a half-life of 20 min. The two products were separated chromatographically, and the 1,3-oxathiole derivative **10d** and the thiirane-carboxamide **11b** were

[4]) The amount of N_2 was determined volumetrically with a gas burette attached to the reaction vessel.

Scheme 6



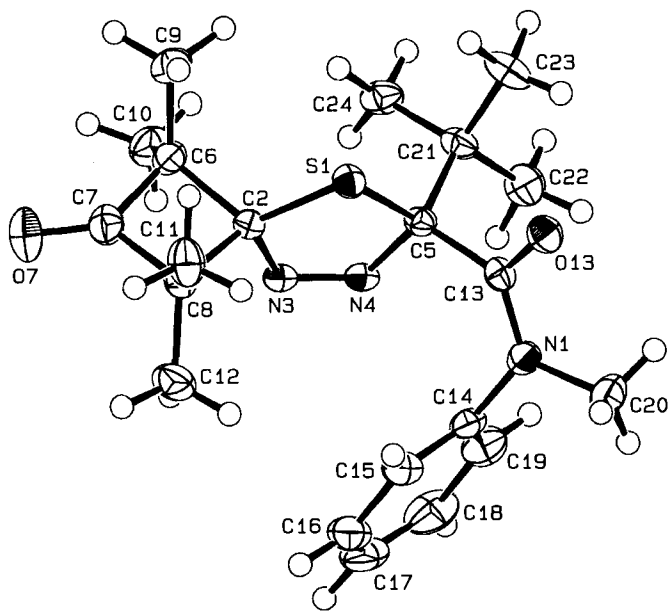


Fig. 2. *ORTEP Plot* [10] *of the molecular structure of* **12a** (ellipsoids with 50% probability)

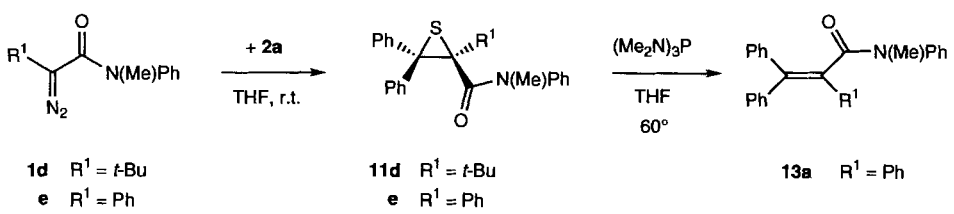
isolated in 21% and 70% yield, respectively. All attempts to trap the intermediate thiocarbonyl ylide with the 'superdipolarophiles' [4] **2a**, **2b**, **2f**, or with fumarodinitrile failed. Apparently, the intermolecular trapping cannot compete with the intramolecular electrocyclizations.

It is worth mentioning that the ^{1}H- and ^{13}C-NMR spectra of **11b** in $CDCl_3$ at *ca.* 30° show two sets of signals for most of the H- and C-atoms. In (D_6)DMSO at 115°, all C-atoms absorb as a single signal, and in the ^{1}H-NMR spectrum only MeN appears as two broad *singlets*, whereas all other doubled signals collapsed to *singlets*. This observation can be explained by the presence of two hardly interconvertible rotamers. Examination of a *Dreiding* model of **11b** showed that the rotation of the amide group is seriously hindered by the *t*-Bu group.

Surprisingly, the analogous reaction of **1e** and **2c** yielded only one product, the thiirane-carboxamide **11c**. Neither the corresponding primary adduct of type **12** nor a 1,3-oxathiole derivative of type **10d** could be detected. These results support our earlier observation that steric hindrance is essential for the enhanced stability of cycloadducts of type **12** [13].

α-Diazo amides **1d,e** reacted with **2a** in THF at room temperature spontaneously. The evolution of N_2 ceased after 15 and 30 min, respectively. In both cases, only a single product was obtained which was characterized as thiirane-carboxamide **11d** and **11e**, respectively (*Scheme 7*). The doubling of most of the signals in the ^{1}H- and ^{13}C-NMR spectra of **11d** ($CDCl_3$, *ca.* 30°) showed that again two rotamers were present. Treatment of **11e** with $(Me_2N)_3P$ in THF at 60° led to the desulfurized α,β-unsaturated amide **13a** which also showed two sets of signals in the NMR spectra.

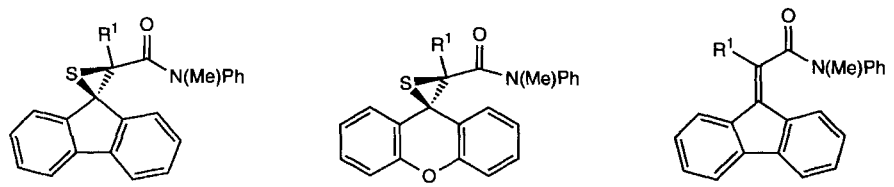
Scheme 7



1d R^1 = *t*-Bu
e R^1 = Ph

11d R^1 = *t*-Bu
e R^1 = Ph

13a R^1 = Ph



11f R^1 = *t*-Bu
g R^1 = Ph

11h R^1 = *t*-Bu
i R^1 = Ph

13b R^1 = *t*-Bu
c R^1 = Ph

The reaction of **1d,e** with **2f** proceeded even more quickly. A vigorous N_2 evolution was observed after each addition of **2f** to a THF solution of the diazo amides, and the green color of **2f** disappeared immediately. Chromatographic workup gave thiirane-carboxamides **11f** and **11g** in 49 and 90% yield, respectively (*Scheme 7*). Again, two con-

formers were detected in the case of the *t*-Bu derivative **11f** (NMR), whereas the Ph derivative **11g** showed only one set of signals. Desulfurization of **11f,g** with $(Me_2N)_3P$ yielded fluorenylidene-carboxamides **13b,c**. Very unexpectedly, prep. TLC (SiO_2; hexane/AcOEt 4:1) of crude **13b** gave two slightly different compounds (R_f *ca.* 0.25 and 0.3) as colorless oils. In $CDCl_3$ at room temperature, each of them yielded a *ca.* 1.5:1 mixture of both compounds (NMR); apparently, the two isolated compounds are two rotamers of **13b**.

The reactions of **1d,e** with the less reactive 9*H*-xanthene-9-thione (**2e**) were performed in the presence of $LiClO_4$ at 60°. The evolution of N_2 was terminated after 7 and 40 h, respectively, again showing that 2-diazo-3,3-dimethylbutanamide **1d** is significantly more reactive than 2-diazo-2-phenylacetamide **1e**. The only products isolated from the reaction mixtures were thiirane-carboxamides **11h** and **11i**, respectively (*Scheme 7*). The structure of **11h** was established by X-ray crystallography (*Fig. 3*). It is worth mentioning that crystallization of **11h** from $MeOH/CH_2Cl_2$ gave single crystals with only one well-defined structure of the molecule, although two conformers were present in solution (NMR). Furthermore, the crystals were enantiomerically pure; *i.e.*, crystallization proceeded with spontaneous resolution of the racemic material. The attempts to desulfurize **11h,i** with $(Me_2N)_3P$ failed; the starting materials were recovered unchanged.

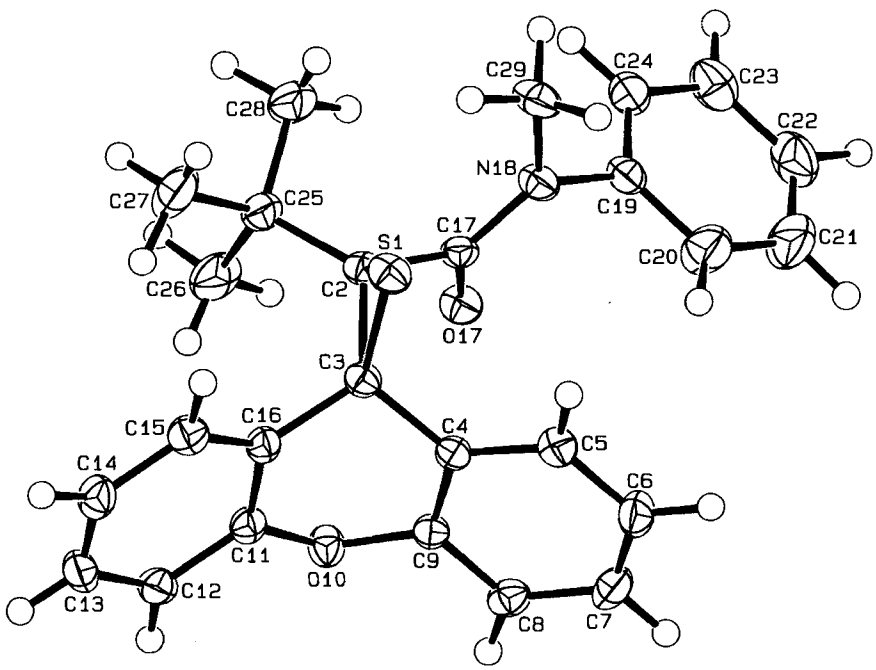
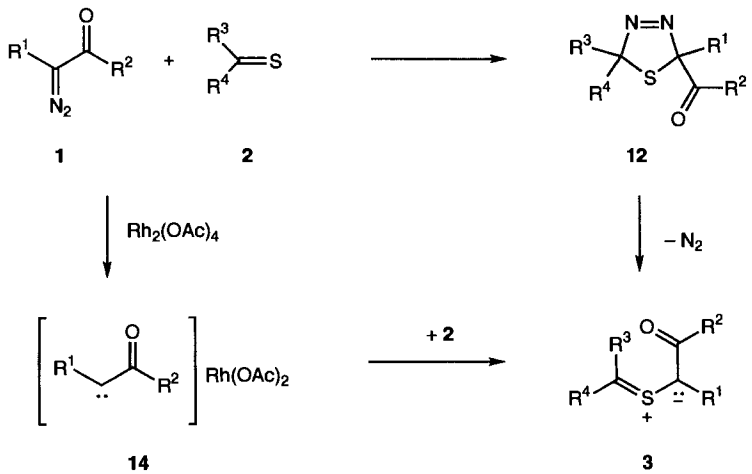


Fig. 3. *ORTEP Plot* [10] *of the molecular structure of* **11h** (ellipsoids with 50% probability)

3. Discussion. – The results of the described experiments can be rationalized by the following reaction mechanism (*Scheme 8*): a regioselective 1,3-dipolar cycloaddition of diazo compound **1** with the C=S group of **2** leads to a 2,5-dihydro-1,3,4-thiadiazole **12**.

This initially formed cycloadduct was stable enough to be isolated only in the case of the reaction of α-diazo amide **1d** with the sterically crowded thione **2c** (*Scheme 6*). In all other reactions, **12** decomposed immediately under the reaction conditions by elimination of N_2, yielding an acyl-substituted thiocarbonyl ylide of type **3** as a reactive intermediate. In the Rh-catalyzed reactions of **1c** (*cf.* [11][12]) with thiones **2b** and **2e**, as well as with 1,3-thiazole-5(4*H*)-thione **2g**, decomposition of **1c** by elimination of N_2 leads to a Rh-carbenoid of type **14**, which subsequently reacts with the thiocarbonyl compound to give the corresponding thiocarbonyl ylide **3**.

Scheme 8



In the reaction of **1a,b** with 9*H*-fluorene-9-thione (**2f**), which, according to *Huisgen* and coworkers, is the most reactive C=S dipolarophile [4][5], the dipolar intermediate **3** is trapped by a 1,3-dipolar cycloaddition yielding the '*Schönberg* product' of type **7** (*Scheme 2*). In all other cases, **3** undergoes a cyclization to give either a 1,3-oxathiole or a thiirane (*cf. Scheme 1*). The 1,5-dipolar electrocyclization to 1,3-oxathioles **9** is the preferred stabilization in the reactions with α-diazo ketones (*Schemes 2–4*). Only azibenzil (**1c**) and 9*H*-xanthene-9-thione (**2e**) yielded the thiirane derivative **5a** *via* a 1,3-dipolar electrocyclization. In this case, as in the reaction of **1c** with 9*H*-fluorene-9-thione (**2f**) [9] and the reactions of **1a** and **1b** with **2e** [1], a reasonable explanation of why the 1,5-ring closure does not occur is the steric hindrance by the *peri*-H-atoms in the transition state (*cf.* [1]).

The reactions of α-diazo amides **1d** and **1e** with **2e** and **2f** again give exclusively thiirane-carboxamides as products (*Scheme 7*), and with 1,3-thiazole-5(4*H*)-thiones **2g–i** only 1,3-oxathiol-5-amines of type **10a,b** are formed (*Scheme 5* and [14]). On the other hand, the unexpected formation of thiirane-carboxamides **11d,e** in the reaction of **1d,e** with **2a** (*Scheme 7*) indicates that the type of the dipolar electrocyclization (1,3 *vs.* 1,5) depends not only on the thiocarbonyl compound **2** but also on the diazo compound **1**. In the reaction of **1d** and **2c**, thiirane-carboxamide **11b** as well as 1,3-oxathiol-5-amine **10d** are formed (*Scheme 6*). It should be emphasized that, in some cases, the reaction type

is different even between the two α-diazo amides **1d** and **1e**, *e.g.*, **1e** and **2c** give only thiirane-carboxamide **11c**. An analogous difference is observed in the reaction with adamantane-2-thione (**2b**): whereas **1d** reacted to yield 1,3-oxathiol-5-amine **10c**, the only product isolated from the reaction with **1e**, albeit in low yield, was thiirane-carboxamide **11a** (*Scheme 5*).

In conclusion, it is evident that the ratio of 1,5- *vs.* 1,3-dipolar electrocyclization of acyl-substituted thiocarbonyl ylides **3** depends on the substitutents R^3, R^4 as well as R^1 and R^2. Although there are still some unexplained effects, our recent experiments show that a keto group (R^2 = Ph, *t*-Bu) favors the 1,5-ring closure, whereas with an ester group (R^2 = EtO) thiirane formation *via* a 1,3-dipolar electrocyclization is the exclusive reaction. With an amide group (R^2 = Ph(Me)N, both reaction, types are observed, and, in this case, the type of substituent R^1 clearly influences the course of the reaction.

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Experimental Part

General. See [15][16]. If not otherwise stated, IR spectra in $CHCl_3$ (cm^{-1}), NMR spectra in $CDCl_3$ (^1H, 300 MHz; ^{13}C, 75.5 MHz; ppm), and CI-MS with NH_3 (*m/z*, rel. %).

1. *Starting Materials.* All thiocarbonyl derivatives and diazo compounds were prepared following known protocols: *Thiobenzophenone* (**2a**) [17], *tricyclo[3.3.1.1^{3,7}]decane-2-thione* (= *adamantanethione*; **2b**) [18], *2,2,4,4-tetramethyl-3-thioxocyclobutanone* (**2c**) [19], *2,2,4,4-tetramethylcyclobutane-1,3-dithion* (**2d**) [19], *9H-xanthene-9-thione* (**2e**) [17], *9H-fluorene-9-thione* (**2f**) [20], *4,4-dimethyl-2-phenyl-1,3-thiazole-5(4H)-thione* (**2g**) [21], *2-phenyl-3-thia-1-azaspiro[4.4]non-1-ene-4-thione* (**2h**) [22], *2-(*tert*-butyl)-4,4-dimethyl-1,3-thiazole-5(4H)-thione* (**2i**) [22], *α-diazoacetophenone* (**1a**) [23], *1-diazo-3,3-dimethylbutan-2-one* (**1b**) [1], *2-diazo-1,2-diphenylethanone* (= azibenzil; **1c**) [24], *2-diazo-*N*,3,3-trimethyl-*N*-phenylacetamide* (**1d**) [14], and *2-diazo-*N*-methyl-*N*,2-diphenylacetamide* (**1e**) [14].

2. *Reactions of α-Diazo Ketones* **1a** *and* **1b**. 2.1. *General Procedure.* To a soln. of thiocarbonyl compound **2** (1 mmol) in THF (2 ml), **1a** or **1b** (1–2 mmol) was added and the mixture stirred at 20–60°. The evolution of N_2 was followed volumetrically using a gas burette attached to the reaction vessel. The solvent was evaporated, and the products were isolated by chromatography (SiO_2; CC or prep. TLC).

2.2. *Reactions with* **2f**. *{Dispiro[[9H]fluorene-9,4′-[1,3]dithiolane-5′,9″-[9H]fluorene]-2-yl}(phenyl)-methanone* (**7a**). To a soln. of **1a** (146 mg, 1 mmol) in THF (1 ml), **2f** (196 mg, 1 mmol) was added at r.t. After the green color of the soln. disappeared, **7a** was precipitated by addition of hexane, filtered, washed with Et_2O, and dried: 209 mg (82%). Colorless crystals. M.p. 216–217°. IR: 3059*m*, 1687*s*, 1446*s*, 1277*m*, 1202*m*, 1184*m*, 1001*m*, 675*s*, 652*m*, 633*m*. ^{1}H-NMR: 8.15–8.1 (*m*, 2 arom. H); 7.65–7.1 (*m*, 19 arom. H); 6.70 (*s*, SCHS). ^{13}C-NMR: 192.4 (*s*, C=O); 140.5, 135.9, 127.9, 126.8 (4*s*, 9 arom. C); 134.5, 129.3, 127.3, 120.0, 119.6 (5*d*, 21 arom. CH); 75.8 (*s*, C(4′), C(5′)); 55.3 (*d*, C(2′)). CI-MS: 529 (30), 528 (100, $[M + NH_4]^+$), 511 (14, $[M + 1]^+$), 329 (49), 328 (20), 315 (21), 314 (32), 297 (22), 283 (35). Anal. calc. for $C_{34}H_{22}OS_2$ (510.68): C 79.97, H 4.34; found: C 79.53, H 4.41.

1-{Dispiro[[9H]fluorene-9,4′-[1,3]dithiolane-5′,9″-[9H]fluorene]-2′-yl}-2,2-dimethylpropan-1-one (**7b**). With **1b** (126 mg, 1 mmol) and **2f** (196 mg, 1 mmol), analogous to the previous protocol: 187 mg (88%) of **7b**. Colorless crystals. M.p. 214.1–215.6°. IR: 3055*m*, 2964*m*, 1704*s*, 1476*m*, 1446*s*, 1366*m*, 1282*m*, 1157*m*, 1058*m*, 1034*m*, 998*m*, 737*s*, 652*m*. ^{1}H-NMR: 7.4–7.1 (*m*, 16 arom. H); 6.20 (*s*, SCHS); 1.40 (*s*, *t*-Bu). ^{13}C-NMR: 208.7 (*s*, C=O); 140.3, 140.0 (2*s*, 8 arom. C); 128.7, 126.9, 126.6, 126.2, 119.6, 119.0 (6*d*, 16 arom. CH); 75.8 (*s*, C(4′), C(5′)); 52.4 (*d*, C(2′)); 44.8 (*s*, Me_3C); 27.0 (*q*, Me_3C). CI-MS: 508 (100, $[M + NH_4]^+$), 197 (25). Anal. calc. for $C_{32}H_{26}OS_2$ (490.69): C 78.33, H 5.34; found: C 77.80, H 5.36.

2.3. *Reaction of* **1b** *with* **2d**. cis- *and* trans-*2,9-Di(*tert*-butyl)-6,6,12,12-tetramethyl-1,8-dioxa-4,11-dithiadispiro[4.1.4.1]dodeca-2,9-diene* (*cis*- and *trans*-**9a**). According to *2.1*, in the presence of $LiClO_4$; **2d** (86 mg, 0.5 mmol), **1b** (184 mg, 1.46 mmol), 60°, 8 h. CC (hexane/Et_2O 60:1): 116 mg (63%) of a *ca.* 1:2 mixture *cis*-**9a**/*trans*-**9a**. Colorless solid. IR: 2965*s*, 2930*s*, 2905*m*, 2870*m*, 1630*m*, 1480*m*, 1465*s*, 1390*m*, 1380*m*, 1365*m*, 1290*m*,

1185*m*, 1082*s*, 1030*m*, 1000*s*, 970*m*, 948*m*, 705*s*, 680*m*. ^{1}H-NMR: 4.85, 4.80 (2*s*, 2:1, 2 × 2 =CHS); 1.22, 1.16, 1.13 (3*s*, 2 × 2 Me_2C); 1.12 (*s*, 2 × 2 Me_3C). ^{13}C-NMR: 158.5, 158.1 (2*s*, 1:2, 2 × 2 =*C*(*t*-Bu)O); 107.3, 106.5 (2*s*, 1:3, 2 × 2 COS); 86.4, 85.5 (2*d*, 3:1, 2 × 2 =CHS); 57.8 (*s*, 2 × 2 Me_2*C*); 33.6 (*s*, 2 × 2 Me_3*C*); 28.2 (*q*, 2 × 2 *Me*$_3$C); 25.9, 22.6, 17.5 (3*q*, 1:4:1, 2 × 2 *Me*$_2$C). CI-MS: 370 (25), 369 (100, $[M + 1]^+$), 184 (25).

3. *Reactions of α-Diazo Ketone* **1c**. 3.1. *Reaction with* **2a**. According to *2.1*, in the presence of $LiClO_4$; **2a** (200 mg, 1 mmol), **1c** (444 mg, 2 mmol [5]), r.t., 15 h. CC (hexane/Et_2O 20:1): 201 mg (51%) *2,2,4,5-tetraphenyl-1,3-oxathiole* (**4a**). Pale-green crystals. M.p. 140.0–142.0°. IR: 3060*m*, 3010*m*, 1625*m*, 1600*m*, 1495*m*, 1450*s*, 1175*m*, 1065*s*, 1030*m*, 1000*m*, 960*m*, 700*s*, 665*m*, 628*m*. ^{1}H-NMR: 7.65–7.6 (*m*, 4 arom. H); 7.45–7.1 (*m*, 16 arom. H). ^{13}C-NMR: 143.8 (*s*, =*C*PhO); 141.5, 132.3, 130.8 (3*s*, 4 arom. C); 129.1, 128.5, 128.11, 128.08, 127.7, 127.5, 126.5 (7*d*, 20 arom. CH); 111.7, 99.6 (2*s*, Ph_2*C*OS, =*C*PhS). CI-MS: 394 (30), 393 (100, $[M + 1]^+$), 199 (25). Anal. calc. for $C_{27}H_{20}OS$ (392.52); C 82.62, H 5.14, S 8.17; found: C 82.71, H 5.33, S 7.90.

Suitable crystals for the X-ray crystal-structure determination were grown from hexane/Et_2O.

3.2. *Reaction with* **2b**. To a soln. of **2b** (83 mg, 0.5 mmol) and $Rh_2(OAc)_4$ (5 mg) in toluene (1 ml) at r.t., **1c** (282 mg, 1.27 mmol) was added in 3 portions (within 30 min). After each addition, vigorous N_2 evolution was observed. Prep. TLC (hexane/CH_2Cl_2 5:1): 129 mg (72%) of *4,5-diphenylspiro[1,3-oxathiole-2,2'-tricyclo-[3.3.1.1^{3,7}]decane]* (**4b**). Colorless crystals. M.p. 86.1–86.5°. IR: 3060*m*, 3000*s*, 2930*s*, 2910*s*, 2860*s*, 1715*m*, 1700*m*, 1680*m*, 1625*m*, 1600*s*, 1495*s*, 1470*m*, 1450*s*, 1350*m*, 1320*m*, 1310*m*, 1280*m*, 1178*m*, 1115*m*, 1100*s*, 1065*s*, 1050*m*, 1030*m*, 1000*s*, 970*m*, 955*m*, 910*m*, 690*s*, 640*m*. ^{1}H-NMR: 7.4–7.2 (*m*, 10 arom. H); 2.58, 2.37, 2.33 (3 br. *s*, 4 H); 1.95–1.7 (*m*, 10 H). ^{13}C-NMR: 142.0 (*s*, =*C*PhO); 133.5, 131.5 (2*s*, 2 arom. C); 128.9, 128.6, 128.0, 127.8, 127.5, 127.4 (6*d*, 10 arom. CH); 110.7, 103.2 (2*s*, =*C*PhS, C_q); 39.5, 26.8, 26.5 (3*d*, 4 CH); 37.4, 35.8, 33.8 (3*t*, 5 CH_2). CI-MS: 362 (27), 361 (100, $[M + 1]^+$), 167 (23). Anal. calc. for $C_{24}H_{24}OS$ (360.52): C 79.96, H 6.71; found: C 80.31, H 6.83.

3.3. *Reaction with* **2c**. According to *2.1*, in the presence of $LiClO_4$; **2c** (78 mg, 0.5 mmol), **1c** (213 mg, 0.96 mmol), r.t., 24 h. CC (hexane/AcOEt 8:1): 81 mg (46%) of *1,1,3,3-tetramethyl-6,7-diphenyl-5-oxa-8-thia-spiro[3.4]oct-6-en-2-one* (**4c**). Colorless solid. M.p. 175.7–179.5°. IR: 3015*m*, 2975*m*, 1790*m*, 1772*s*, 1498*m*, 1462*m*, 1445*m*, 1380*m*, 1210*s*, 1090*m*, 1075*s*, 1060*m*, 1030*m*, 958*m*, 698*s*, 665*s*. ^{1}H-NMR: 7.4–7.2 (*m*, 10 arom. H); 1.385, 1.382 (2*s*, 2 Me_2C). ^{13}C-NMR: 219.6 (*s*, C=O); 142.3 (*s*, =*C*PhO); 132.1, 130.2 (2*s*, 2 arom. C); 129.0, 128.6, 128.2, 128.1, 127.9, 127.0 (6*d*, 10 arom. CH); 110.0, 101.0 (2*s*, *C*OS, =*C*PhS); 66.3 (*s*, 2 Me_2*C*); 22.8, 18.7 (2*q*, 2 *Me*$_2$C). CI-MS: 352 (25), 351 (100, $[M + 1]^+$). Anal. calc. for $C_{22}H_{22}O_2S$ (350.48): C 75.39, H 6.33, S 9.15; found: C 75.50, H 6.40, S 8.78.

3.4. *Reaction with* **2g**. To a soln. of **2g** (221 mg, 1 mmol) and $Rh_2(OAc)_4$ (5 mg) in THF (1 ml) at r.t., 222 mg (1 mmol) of **1c** were added in 2 portions (within 10 min). A vigorous N_2 evolution occurred. At −20°, a colorless solid precipitated which was purified by CC (hexane/CH_2Cl_2 1:1): 127 mg (61%) of *4,4-dimethyl-2,7,8-triphenyl-6-oxa-1,9-dithia-3-azaspiro[4.4]nona-2,7-diene* (**4g**). Colorless crystals. M.p. 174.5–176.8°. IR: 3060*m*, 2975*m*, 1632*m*, 1598*s*, 1575*m*, 1495*m*, 1445*s*, 1360*m*, 1260*s*, 1240*m*, 1178*m*, 1088*m*, 1065*s*, 1028*s*, 1000*m*, 950*s*, 870*s*, 615*m*. ^{1}H-NMR: 7.85–7.8 (*m*, 2 arom. H); 7.5–7.15 (*m*, 13 arom. H); 1.85, 1.54 (2*s*, Me_2C). ^{13}C-NMR: 163.7 (*s*, C=N); 141.5 (*s*, =*C*PhO); 133.6, 131.5, 130.0 (3*s*, 3 arom. C); 131.4, 129.1, 128.8, 128.5, 128.18, 128.15, 127.6 (7*d*, 15 arom. CH); 121.7, 112.4 (2*s*, =*C*PhS, *C*OS$_2$); 82.0 (*s*, Me_2*C*); 24.9, 21.5 (2*s*, *Me*$_2$C). CI-MS: 417 (27), 416 (100, $[M + 1]^+$).

3.5. *Reaction with* **2d**. To a soln. of **2d** (86 mg, 0.5 mmol) in THF (1 ml) in the presence of $LiClO_4$ at r.t., 445 mg (2 mmol) of **1c** were added in small portions within 3 d. CC (hexane) yielded **4d** and a mixture *cis*-**9b**/*trans*-**9b**. The latter was purified by prep. TLC (hexane/CH_2Cl_2 10:1).

1,1,3,3-Tetramethyl-6,7-diphenyl-5-oxa-8-thiaspiro[3.4]oct-6-ene-2-thione (**4d**). Yield: 92 mg (50%). Orange solid. R_f 0.4. M.p. 120.0–123.0°. IR: 2960*s*, 2920*m*, 1612*s*, 1600*s*, 1575*m*, 1495*s*, 1460*s*, 1445*s*, 1388*m*, 1360*s*, 1305*s*, 1225*s*, 1090*s*, 1070*s*, 1030*s*, 1000*s*, 955*s*, 915*m*, 890*m*, 760*s*, 695*s*, 680*s*, 650*m*, 635*m*. ^{1}H-NMR: 7.4–7.2 (*m*, 10 arom. H); 1.46, 1.44 (2*s*, 2 Me_2C). ^{13}C-NMR: 142.4 (*s*, =*C*PhO); 132.3, 130.4 (2*s*, 2 arom. C); 129.1, 128.7, 128.2, 127.9, 127.1 (5*d*, 10 arom. CH); 110.2, 104.8 (2*s*, =*C*PhS, *C*SO); 69.7 (*s*, 2 Me_2*C*); 26.8, 22.7 (2*s*, 2 *Me*$_2$C). CI-MS: 368 (24), 367 (100, $[M + 1]^+$). Anal. calc. for $C_{22}H_{22}OS_2$ (366.55): C 72.09, H 6.05, S 17.50; found: C 72.12, H 6.08, S 17.82.

cis- *and* trans-*6,6,12,12-Tetramethyl-2,3,9,10-tetraphenyl-1,8-dioxa-4,11-dithiadispiro[4.1.4.1]dodeca-2,9-diene* (*cis*- and *trans*-**9b**; ratio *ca.* 1:2). Yield: 27 mg (10%). Colorless solid. R_f 0.1 and 0.15. IR: 3060*m*, 3000*m*, 2985*m*, 2930*m*, 1630*m*, 1600*m*, 1500*s*, 1468*s*, 1445*s*, 1380*m*, 1370*m*, 1240*s*, 1090*m*, 1070*s*, 1030*s*, 1000*s*, 970*m*, 960*m*, 910*m*, 690*s*. ^{1}H-NMR: 7.45–7.2 (*m*, 2 × 20 arom. H); 1.50, 1.46, 1.44 (3*s*, 3.4:1:1, 2 × 2 Me_2C). ^{13}C-NMR: 142.4,

[5]) Excess of **1c** because of slow decomposition in soln.

142.0 (2*s*, 1:2, 2 × 2 =*C*PhO); 132.7, 130.7, 130.5 (3*s*, 2 × 4 arom. C); 129.1, 128.6, 128.1, 128.0, 167.72, 127.67, 127.2, 127.1 (8*d*, 2 × 20 arom. CH); 110.2, 109.4, 104.9, 104.2 (4*s*, 2:1:1:2, 2 × 2 =*C*PhS, 2 × 2 *C*SO); 56.5 (*s*, 2 × 2 Me_2C); 26.5, 23.0, 18.4 (3*q*, 1:4:1, 2 × 2 Me_2C). CI-MS: 562 (39), 561 (100, $[M + 1]^+$), 367 (48), 351 (43).

To a soln. of **4d** (65 mg, 0.18 mmol) and $Rh_2(OAc)_4$ (*ca.* 5 mg) in THF (1 ml) at r.t., **1c** (180 mg, 0.8 mmol) was added in 4 portions within 20 min. After each addition, N_2 evolved. Prep. TLC (hexane/CH_2Cl_2 10:1) yielded 25 mg (25%) of a 1:2 mixture *cis*-**9b**/*trans*-**9b**.

3.6. *Reaction with* **2e**. To a soln. of **2e** (53 mg, 0.25 mmol) and $Rh_2(OAc)_4$ (*ca.* 5 mg) in toluene (1 ml) at r.t., **1c** (245 mg, 1.1 mmol) was added in 3 portions within 15 min. After each addition, N_2 evolved vigorously. Prep. TLC (hexane/CH_2Cl_2 1:1, 2 × developed) yielded crude **5a**, which was purified by prep. TLC (hexane/AcOEt 20:1, 2 × developed): 25 mg (27%) *of (phenyl){3-phenylspiro[thiirane-2,9'-[9H]xanthene]-3-yl}methanone* (**5a**). Colorless crystals. M.p. 183.9–184.8°. IR: 3060*m*, 3020*m*, 3000*m*, 1670*s*, 1600*s*, 1575*m*, 1490*s*, 1475*s*, 1450*s*, 1315*s*, 1290*m*, 1248*s*, 1185*s*, 1160*m*, 1120*s*, 1100*s*, 1075*m*, 1040*m*, 1025*m*, 1010*m*, 1000*m*, 940*m*, 930*m*, 880*m*, 815*m*, 695*s*, 630*s*. ^{1}H-NMR: 8.29 (*dd*, *J* = 7.9, 1.8, 1 arom. H); 7.96 (*dd*, *J* = 7.4, 1.9, 1 arom. H); 7.45–7.05 (*m*, 14 arom. H); 6.76 (*dd*, *J* = 8.0, 1.3, 1 arom. H); 6.7–6.65 (*m*, 1 arom. H). ^{13}C-NMR: 189.6 (*s*, C=O); 151.6, 149.6, 137.5, 136.9, 136.2, 133.2 (6*s*, 6 arom. C); 131.4, 130.6, 129.6, 129.0, 128.6, 128.5, 128.1, 127.9, 127.7, 127.2, 122.4, 122.3, 115.1, 114.4 (14*d*, 18 arom. CH); 63.3 (*s*, C_q). The second C_q could not be localized. CI-MS: 407 (16, $[M + 1]^+$), 376 (30), 375 (100).

4. *Reactions of α-Diazo Amides* **1d,e**. 4.1. *General Procedure*. To a soln. of **1d** or **1e** (1 mmol) in THF (2 ml), 0.5–1.5 mmol of thiocarbonyl compound **2** were added, and the mixture was stirred at r.t. or 60° for 5 min to 40 h. The evolution of N_2 was followed volumetrically using a gas burette attached to the reaction vessel.

4.2. *Reactions of* **1d** *with* **2h,i**. *2,8-Di(*tert*-butyl)-*N*,4,4-trimethyl-*N*-phenyl-6-oxa-1,8-dithia-3-azaspiro[4.4]nona-2,7-dien-7-amine* (**10a**). According to *4.1*, in the presence of $LiClO_4$; **2h** (101 mg, 0.5 mmol), **1d** (139 mg, 0.6 mmol), 60°, 20 h. CC (hexane/AcOEt 20:1): 130 mg (64%) of **10a**. Colorless crystals. M.p. 107.5–107.9°. IR: 3000*m*, 2965*s*, 2900*m*, 2860*m*, 1660*m*, 1600*s*, 1500*s*, 1478*s*, 1460*m*, 1365*s*, 1350*m*, 1325*m*, 1300*m*, 1270*m*, 1120*m*, 1040*s*, 1030*s*, 995*s*, 965*m*, 880*s*, 820*m*, 710*m*, 690*m*, 655*m*. ^{1}H-NMR: 7.25–7.2 (*m*, 2 arom. H); 6.85–6.8 (*m*, 3 arom. H); 3.03 (*s*, MeN); 1.59, 1.33 (2*s*, Me_2C); 1.17, 1.16 (2*s*, 2 *t*-Bu). ^{13}C-NMR: 175.2 (*s*, C=N); 128.9, 118.9, 113.7 (3*d*, 5 arom. CH); 80.5 (*s*, Me_2C); 38.2, 33.2 (2*s*, 2 Me_3C); 30.1, 28.8 (2*q*, 2 Me_3C); 24.0, 21.2 (2*q*, Me_2C). The signals for 1 arom. C, 1 spiro C, =CO, and =CS could not be localized (*cf.* **10b**). CI-MS: 406 (21), 405 (82, $[M + 1]^+$), 404 (23), 220 (100), 203 (29). Anal. calc. for $C_{22}H_{32}N_2OS_2$ (404.64): C 65.30, H 7.97, N 6.92; found: C 65.47, H 7.97, N 6.57.

*3-(*tert*-Butyl)-*N*-methyl-*N*,12-diphenyl-1-oxa-4,13-dithia-11-azadispiro[4.0.4.3]trideca-2,11-dien-2-amine* (**10b**). According to *4.1*, in the presence of $LiClO_4$; **2i** (124 mg, 0.5 mmol), **1d** (139 mg, 0.6 mmol), 60°, 20 h. CC (hexane/AcOEt 20:1): 155 mg (69%) of **10b**. Colorless solid. M.p. 88–93°. IR: 3000*m*, 2960*s*, 2900*m*, 2870*m*, 1600*s*, 1575*m*, 1500*s*, 1475*m*, 1448*m*, 1363*m*, 1348*s*, 1325*m*, 1300*m*, 1270*m*, 1255*m*, 1120*m*, 1038*s*, 1008*m*, 975*s*, 968*s*, 940*m*, 710*m*, 690*s*, 615*m*. ^{1}H-NMR: 7.75–7.7 (*m*, 2 arom. H); 7.4–7.2 (*m*, 5 arom. H); 6.8–6.75 (*m*, 3 arom. H); 3.02 (*s*, MeN); 2.35–1.6 (*m*, 4 CH_2); 1.19 (*s*, *t*-Bu). ^{13}C-NMR: ((D$_6$)DMSO, 80° [6]): 162.8 (*s*, C=N); 146.4 (*s*, =CON); 139.3, 134.0 (2*s*, 2 arom. C); 131.0, 128.9, 128.4, 128.1, 118.8, 113.6 (6*d*, 10 arom. CH); 119.1, 115.3 (2*s*, =*C*SR, *C*S$_2$O); 91.7 (*s*, *C*(CH$_2$)$_2$); 38.3 (*t*, CH_2); 33.2 (*s*, Me_3C); 32.6 (*t*, CH_2); 30.1 (*q*, Me_3C); 25.5, 25.4, (2*t*, 2 CH_2). CI-MS: 451 (40, $[M + 1]^+$), 450 (59), 220 (100), 219 (26), 203 (31). Anal. calc. for $C_{26}H_{30}N_2OS_2$ (450.67): C 69.30, H 6.71, N 6.22; found: C 69.45, H 6.78, N 6.14.

4.3. *Reactions with* **2b**. *4-(*tert*-Butyl)-*N*-methyl-*N*-phenylspiro[1,3-oxathiole-2,2'-tricyclo[3.3.1.1^{3,7}]decan]-5-amine* (**10c**). According to *4.1*, in the presence of $LiClO_4$; **2b** (83 mg, 0.5 mmol), **1d** (135 mg, 0.58 mmol), 60°, 1 h. CC (hexane/AcOEt 60:1): 147 mg (80%) of **10c**. Colorless crystals. M.p. 116.8–117.4°. IR: 3000*m*, 2960*s*, 2910*s*, 2860*s*, 1660*m*, 1600*s*, 1500*s*, 1463*m*, 1453*m*, 1360*m*, 1350*m*, 1330*m*, 1275*m*, 1128*m*, 1100*s*, 1060*s*, 1045*s*, 1038*s*, 1003*s*, 995*m*, 928*m*, 692*m*, 670*m*. ^{1}H-NMR: 7.25–7.2 (*m*, 2 arom. H); 6.85–6.8 (*m*, 3 arom. H); 3.05 (*s*, MeN); 2.4–1.5 (*m*, 14 H); 1.13 (*s*, *t*-Bu). ^{13}C-NMR: 148.0 (*s*, =CON); 139.4 (*s*, 1 arom. C); 128.9, 118.2, 113.3 (3*d*, 5 arom. CH); 116.5, 96.4 (2*s*, R_2*C*OS, =*C*SR); 38.2 (*q*, MeN); 37.4, 35.0, 33.1 (3*t*, 5 CH_2); 32.8 (*s*, Me_3C); 30.1 (*q*, Me_3C); 27.1, 26.3, 22.7 (3*d*, 4 CH). CI-MS: 371 (24), 370 (100, $[M + 1]$, 238 (23). Anal. calc. for $C_{23}H_{31}NOS$ (369.57): C 74.75, H 8.46, N 3.79, S 8.68; found: C 74.30, H 8.50, N 3.69, S 8.99

N-Methyl-N,3-diphenylspiro[thiirane-2,2'-tricyclo[3.3.1.1^{3,7}]decane]-3-carboxamide (**11a**). According to *4.1*, in the presence of $LiClO_4$; **2b** (83 mg, 0.5 mmol), **1e** (163 mg, 0.65 mmol), 60°, 5 h. CC (hexane/AcOEt 40:1): 25 mg (13%) of **11a**. Colorless oil. No other product could be isolated. IR: 3060*m*, 3000*m*, 2929*s*, 2850*s*, 1645*s*, 1595*s*, 1495*s*, 1470*m*, 1450*s*, 1420*m*, 1370*s*, 1295*m*, 1280*m*, 1130*m*, 1110*m*, 1100*m*, 1075*m*, 960*m*, 910*m*. ^{1}H-NMR:

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[6]) In $CDCl_3$ at *ca.* 28°, the signals for 2 spiro C-atoms, =CO, and =CS could not be detected.

7.45–6.65 (*m*, 10 arom. H); 3.21 (*s*, MeN); 2.9–8.85 (*m*, 14 H). ^{13}C-NMR: 168.8 (*s*, C=O); 143.2, 135.7 (2*s*, 2 arom. C); 129.7, 128.7, 128.5, 127.4 (4*d*, 10 arom. CH); 67.4, 62.1 (2*s*, 2 C_q); 39.5 (*q*, MeN); 39.1 (*d*, CH); 38.9, 38.5, 37.5, 37.1 (4*t*, 4 CH_2); 35.6 (*d*, CH); 35.2 (*t*, CH_2); 27.5, 26.6 (2*d*, 2 CH). CI-MS: 391 (24), 390 (98, $[M + 1]^+$), 301 (30), 167 (100).

4.4. *Reactions with* **2c**. 4.4.1. *With* **1d**. According to *4.1*, in the presence of $LiClO_4$; **2c** (78 mg, 0.5 mmol), **1d** (116 mg, 0.5 mmol), 60°, 30 min. CC (hexane/AcOEt 6:1): 153 mg (79%) of *7-(*tert*-butyl)-*N,*1,1,3,3-pentamethyl-2-oxo-*N*-phenyl-8-thia-5,6-diazaspiro[3.4]oct-5-ene-7-carboxamide* (**12a**). Colorless crystals. M.p. 103.4–105.5°. IR: 3005*s*, 2970*s*, 2930*m*, 1785*s*, 1640*s*, 1595*s*, 1570*m*, 1495*s*, 1480*m*, 1460*s*, 1440*m*, 1395*m*, 1380*m*, 1368*s*, 1275*m*, 1135*m*, 1025*s*, 910*m*, 700*s*, 685*m*, 660*m*. ^{1}H-NMR: 7.35–7.25 (*m*, 3 arom. H); 7.1–7.0 (*m*, 2 arom. H); 3.35 (*s*, MeN); 1.30, 1.29, 1.24, 1.19 (4*s*, 2 Me_2C); 1.14 (*s*, *t*-Bu). ^{13}C-NMR: 218.4 (*s*, C=O); 169.0 (*s*, NC=O); 143.8 (*s*, 1 arom. C); 129.3, 128.3, 128.0, (3*d*, 5 arom. CH); 125.1, 109.7 (2*s*, C(4), C(7)); 67.6, 67.3 (2*s*, 2 Me_2C); 41.8 (*s*, Me_3C); 41.2 (*q*, MeN); 27.3 (*q*, Me_3C); 24.4, 23.4, 19.5, 19.0 (4*q*, 2 Me_2C). CI-MS: 360 (17, $[M + 1]^+$), 204 (100). Anal. calc. for $C_{21}H_{29}N_3O_2S$ (387.53): C 65.09, H 7.54, N 10.84; found: C 65.19, H 7.55, N 10.71.

Suitable crystals for the X-ray crystal-structure determination were grown from $MeOH/CH_2Cl_2$.

4.4.2. *Thermal Decomposition of* **12a**. A soln. of **12a** (132 mg, 0.34 mmol) in THF (2 ml) was stirred at 60° (5 h). CC (hexane/AcOEt 10:1): *7-(*tert*-butyl)-1,1,3,3-tetramethyl-6-(*N*-methyl-*N*-phenylamino)-5-oxa-8-thiaspiro[3.4]oct-6-en-2-one* (**10d**) and *2-(*tert*-butyl)-*N,*4,4,6,6-pentamethyl-5-oxo-*N*-phenyl-1-thiaspiro[2.3]hexane-2-carboxamide* (**11b**).

Data of **10d**: Yield: 26 mg (21%). Colorless oil. R_f 0.45. IR (film): 2960*s*, 2925*s*, 2900*m*, 2860*m*, 1785*s*, 1770*s*, 1750*m*, 1660*s*, 1600*s*, 1500*s*, 1478*m*, 1460*s*, 1390*m*, 1380*s*, 1365*s*, 1345*m*, 1320*m*, 1295*m*, 1270*m*, 1235*m*, 1118*m*, 1090*m*, 1053*s*, 1042*s*, 1030*s*, 750*s*, 692*s*, 665*m*. ^{1}H-NMR: 7.25–7.2 (*m*, 2 arom. H); 6.8–6.75 (*m*, 3 arom. H); 3.06 (*s*, MeN); 1.31, 1.23 (2*s*, 2 Me_2C); 1.16 (*s*, *t*-Bu). ^{13}C-NMR: 220.5 (*s*, C=O); 147.6 (=CON); 139.4 (*s*, 1 arom. C); 129.0, 118.7, 113.5 (3*d*, 5 arom. CH); 116.0, 94.4 (2*s*, C(7), C(4)); 53.4 (*s*, 2 Me_2C); 38.1 (*q*, MeN); 33.0 (*s*, Me_3C); 30.0 (*q*, Me_3C); 22.6, 18.4 (2*q*, 2 Me_2C). CI-MS: 360 (34, $[M + 1]^+$), 238 (100).

Data of **11b**: Yield: 86 mg (70%). Colorless oil. R_f 0.1. IR: 3020*m*, 3000*s*, 2970*s*, 2930*s*, 2870*m*, 1778*s*, 1750*m*, 1632*s*, 1605*m*, 1595*s*, 1495*s*, 1470*s*, 1455*s*, 1398*m*, 1382*s*, 1365*s*, 1150*m*, 1105*m*, 1025*s*, 968*m*, 700*s*, 660*m*. ^{1}H-NMR (2 rotamers): 7.45–7.1 (*m*, 5 arom. H); 3.54, 3.24 (2*s*, MeN); 1.65, 1.61, 1.49, 1.43 (4*s*, 2 Me); 1.30, 1.26 (2*s*, *t*-Bu); 1.25, 1.16, 1.15, 1.08 (4*s*, 2 Me). ^{1}H-NMR ((D_6)DMSO, 115°): 7.4–7.15 (*m*, 5 arom. H); 3.37, 2.80 (2 br. *s*, MeN); 1.57, 1.38 (2*s*, 2 Me); 1.26 (*s*, *t*-Bu); 1.13, 1.10 (2*s*, 2 Me). ^{13}C-NMR (2 rotamers): 220.8, 220.4 (2*s*, C=O); 168.6, 167.8 (2*s*, NC=O); 145.4, 145.3 (2*s*, 1 arom. C); 129.5, 128.5, 127.4, 127.1, 126.5 (5*d*, 5 arom. CH); 68.3, 68.0, 64.9, 64.4, 64.1, 64.0 (6*s*, 2 C_q, 2 Me_3C); 42.3, 42.1 (2*q*, MeN); 38.2, 37.5 (2*s*, Me_3C); 30.6, 29.5 (2*q*, Me_3C); 25.3, 25.1, 24.6, 24.52, 24.47, 24.4, 24.3, 23.7 (8*q*, 2 Me_2C). ^{13}C-NMR ((D_6)DMSO, 115°): 218.4 (*s*, C=O); 167.5 (*s*, NC=O); 145.6 (*s*, 1 arom. C); 128.9, 126.8, 126.7 (3*d*, 5 arom. CH); 68.4, 64.5, 64.4, 63.6 (4*s*, 2 Me_2C, 2 C_q); 41.8 (*s*, MeN); 37.7 (*s*, Me_3C); 29.8 (*q*, Me_3C); 24.8, 24.3, 24.2, 23.5 (4*q*, 2 Me_2C). CI-MS: 361 (25), 360 (100, $[M + 1]^+$), 198 (20). Anal. calc. for $C_{21}H_{29}NO_2S$ (359.54): C 70.16, H 8.13, N 3.90, S 8.92; found: C 69.80, H 8.15, N 3.98, S 8.97.

4.4.3. *With* **1e**. According to *4.1*, in the presence of $LiClO_4$; **2c** (78 mg, 0.5 mmol), **1e** (163 mg, 0.65 mmol), r.t., 5 h. CC (hexane/Et_2O 5:1) and recrystallization from MeOH: 104 mg (55%) of *N,4,4,6,6-pentamethyl-5-oxo-*N*,2-diphenyl-1-thiaspiro[2.3]hexane-2-carboxamide* (**11c**). Colorless solid. M.p. 127.2–133.0°. IR: 3000*m*, 2970*m*, 2920*m*, 1778*s*, 1650*s*, 1595*s*, 1495*s*, 1452*m*, 1445*m*, 1420*m*, 1365*s*, 1292*m*, 1278*m*, 1155*m*, 1030*m*. ^{1}H-NMR: 7.7–6.7 (*m*, 10 arom. H); 3.23 (*s*, MeN); 1.82, 1.20, 0.78, 0.54 (4*s*, 2 Me_2C). ^{13}C-NMR: 220.8 (*s*, C=O); 168.9 (*s*, NC=O); 143.3, 135.8 (2*s*, 2 arom. C); 128.7, 128.4, 128.0, 127.7, 127.2 (5*d*, 10 arom. CH); 71.6, 64.5, 63.4, 56.1 (4*s*, 2 Me_2C, 2 C_q); 39.4 (*q*, MeN); 24.8, 24.7, 24.1, 21.9 (4*q*, 2 Me_2C). CI-MS: 381 (25), 380 (100, $[M + 1]^+$).

4.5. *Reactions with* **2a**. *2-(*tert*-Butyl)-*N*-methyl-*N*,3,3-triphenylthiirane-2-carboxamide* (**11d**). According to *4.1*; **2a** (139 mg, 0.7 mmol), **1d** (119 mg, 0.5 mmol), r.t., 15 min. CC (hexane/AcOEt 20:1): 132 mg (64%) of **11d**. Colorless crystals. M.p. 141.1–141.5°. IR: 3060*m*, 3000*s*, 2965*m*, 2930*m*, 1630*s*, 1595*s*, 1495*s*, 1470*m*, 1445*s*, 1435*m*, 1395*m*, 1365*s*, 1223*m*, 1110*m*, 710*s*, 700*s*, 660*m*. ^{1}H-NMR (2 rotamers): 7.8–7.55 (*m*, 4 arom. H); 7.25–7.1 (*m*, 9 arom. H); 6.75–6.7 (*m*, 1 arom. H); 6.3–6.25 (*m*, 1 arom. H); 3.45, 2.77 (2*s*, MeN); 1.09 (*s*, *t*-Bu). ^{13}C-NMR (2 rotamers): 168.4 (*s*, C=O); 145.5, 143.5, 142.9, 142.5, 140.7, 140.6 (6*s*, 3 arom. C); 130.8, 130.4, 130.3, 128.9, 128.5, 127.7, 127.6, 127.24, 127.18, 127.1, 127.0, 126.9, 126.8, 126.7, 126.5, 126.2 (16*d*, 15 arom. CH); 67.5, 66.2, 64.8, 63.8 (4*s*, 2 C_q); 41.4, 41.0 (2*q*, MeN); 38.7, 38.2 (2*s*, Me_3C); 30.4, 29.6 (2*q*, Me_3C). ESI-MS: 423 (75, $[M + Na]^+$), 402 (100, $[M + 1]^+$), 234 (55), 219 (65). Anal. calc. for $C_{26}H_{27}NOS$ (401.58): C 77.77, H 6.78, N 3.49; found: C 77.59, H 6.79, N 3.35.

*N-Methyl-*N*,2,3,3-tetraphenylthiirane-2-carboxamide* (**11e**). According to *4.1*; **2a** (99 mg, 0.5 mmol), **1e** (188 mg, 0.75 mmol), r.t., 30 min. CC (hexane/CH_2Cl_2 1:1): 151 mg (72%) of **11e**. Colorless solid. M.p. 146.2–149.8°. IR: 3060*m*, 3000*m*, 1643*s*, 1595*s*, 1493*s*, 1445*s*, 1420*m*, 1373*s*, 1298*m*, 1280*m*, 968*w*. ^{1}H-NMR: 7.5–6.8

(*m*, 20 arom. H); 3.12 (*s*, MeN). ^{13}C-NMR: 167.1 (*s*, C=O); 143.6, 141.0, 139.7, 136.4 (4*s*, 4 arom. C); 131.0, 129.1, 128.8, 127.7, 127.5, 127.3, 127.0, 126.5 (8*d*, 20 arom. CH); 65.4, 61.4 (2*s*, 2 C_q); 38.6 (*q*, MeN). CI-MS: 423 (28), 422 (100, $[M + 1]^+$), 390 (31). Anal. calc. for $C_{28}H_{23}NOS$ (421.57): C 79.78, H 5.50, N 3.32; found: C 79.94, H 5.50, N 3.42.

Desulfurization of **11e**. To a soln. of **11e** (101 mg, 0.24 mmol) in THF (2 mmol), $(Me_2N)_3P$ (80 mg, 0.5 mmol) was added and the mixture stirred at 60° (2 h). CC (hexane/AcOEt 4:1): 58 mg (62%) of N-*methyl*-N,*2,3,3-tetraphenylprop-2-enamide* (**13a**). Colorless solid. M.p. 120.4–123.2°. IR: 2976*m*, 1628*m*, 1595*m*, 1522*m*, 1495*m*, 1475*m*, 1420*m*, 1372*m*, 1125*s*, 1046*m*, 928*m*, 879*s*, 849*m*. ^{1}H-NMR (2 rotamers): 7.45–6.7 (*m*, 20 arom. H); 3.31, 3.23 (2*s*, MeN). ^{13}C-NMR (2 rotamers): 171.5 (*s*, C=O); 143.3, 141.8, 141.7, 141.6, 138.5, 134.8 (6*s*, 4 arom. C, 2 =C); 130.4, 130.3, 130.0, 129.0, 128.4, 128.3, 128.2, 128.1, 128.0, 127.9, 127.7, 127.5, 127.2, 127.0, 126.3, 125.3 (16*d*, 20 arom. CH); 39.3, 37.0 (2*q*, MeN). CI-MS: 391 (29), 390 (100, $[M + 1]^+$).

4.6. *Reactions with* **2f**. *3′(*tert*-Butyl)-*N*-methyl-*N*-phenylspiro[[9*H*]fluorene-9,2′-thiirane]-3′-carboxamide* (**11f**). To a soln. of **1d** (116 mg, 0.5 mmol) in THF (2 ml) at r.t., 128 mg (0.65 mmol) of **2f** were added in portions within 5 min. After each addition, vigorous N_2 evolution was observed. CC (CH_2Cl_2/hexane 2:2): 98 mg (49%) of **11f**. Colorless crystals. M.p. 72.4–73.3°. IR: 3059*m*, 3023*m*, 2964*m*, 2925*m*, 1643*s*, 1594*s*, 1493*s*, 1477*s*, 1447*s*, 1395*m*, 1361*s*, 1325*m*, 1292*m*, 1270*m*, 1218*m*, 1197*m*, 1177*m*, 1142*m*, 1105*m*, 1065*m*, 1031*m*, 965*w*, 799*m*, 779*m*, 770*m*, 758*s*, 737*s*, 696*m*, 673*m*. ^{1}H-NMR (2 rotamers): 7.7–7.1 (*m*, 13 arom. H); 3.75, 3.30 (2*s*, MeN); 1.35, 1.30 (2*s*, *t*-Bu). ^{13}C-NMR (2 rotamers): 168.4, 168.0 (2*s*, C=O); 147.2, 145.4, 144.11, 144.08, 142.6, 139.7, 125.6, 125.5 (8*s*, 4 arom. C); 129.03, 128.96, 128.4, 128.2, 128.1, 127.1, 126.8, 126.7, 126.6, 126.1, 126.04, 125.99, 123.5, 120.3, 119.6 (15*d*, 13 arom. C); 64.7, 64.2, 55.8, 55.6 (4*s*, C(2′), C(3′)); 41.5, 39.8 (2*q*, MeN); 37.8, 37.2 (2*s*, Me_3C); 31.7, 31.0 (2*q*, Me_3C). CI-MS: 417 (14, $[M + NH_4]^+$), 400 (13, $[M + 1]^+$), 385 (69), 370 (20), 268 (100).

Desulfurization of **11f**. To a soln. of **11f** (98 mg, 0.25 mmol) in THF (2 ml), $(Me_2N)_3P$ (120 mg, 0.74 mmol) was added and the mixture stirred at 60° (22 h). Prep. TLC (hexane/AcOEt 4:1, 3× developed): 2 rotamers of *2-(9*H*-fluoren-9-ylidene)-*N*,3,3-trimethyl-*N*-phenylbutanamide* (**13b**).

Rotamer 1: Yield: 36 mg (40%). Colorless oil. R_f 0.25. ^{1}H-NMR: 7.9–7.85, 7.75–7.7, 7.45–7.0 (3*m*, 13 arom. H); 3.54 (*s*, MeN); 1.25 (*s*, *t*-Bu). ^{13}C-NMR: 171.1 (*s*, C=O); 148.8, 142.8, 141.3, 139.6, 138.3, 135.2, 134.7 (3*s*, 5 arom. C, 2 =C); 129.3, 129.2, 128.1, 128.0, 127.7, 127.1, 126.3, 126.1, 124.9, 119.3, 119.1 (11*d*, 13 arom. CH); 36.7 (*q*, MeN); 34.7 (*s*, Me_3C); 29.7 (*q*, Me_3C). CI-MS: 369 (26), 368 (100, $[M + 1]^+$).

Rotamer 2: Yield: 28 mg (31%). Colorless oil. R_f 0.3. ^{1}H-NMR: 8.15–8,1, 7.85–7.7, 7.5–7.25 (3*m*, 13 arom. H); 3.19 (*s*, MeN); 1.74 (*s*, *t*-Bu). ^{13}C-NMR: 170.9 (*s*, C=O); 147.4, 142.4, 141.6, 139.5, 138.1, 135.5, 130.3 (7*s*, 5 arom. C, 2 =C); 129.2, 128.1, 128.0, 127.6, 127.1, 126.31, 126.25, 125.3, 124.1, 119.4, 119.1 (11*d*, 13 arom. CH); 38.8 (*q*, MeN); 35.6 (*s*, Me_3C); 30.5 (*q*, Me_3C).

A soln. of *Rotamer 1* in $CDCl_3$ was kept for 3 d at r.t. After this time, a 1.5:1 mixture of *Rotamer 1* and *Rotamer 2* was detected by ^{1}H-NMR.

N-*Methyl*-N,*3′-diphenylspiro[[9*H*]fluorene-9,2′-thiirane]-3′-carboxamide* (**11g**). To a soln. of **1e** (163 mg, 0.65 mmol) in THF (2 ml) at r.t., 98 mg (0.65 mmol) of **2f** were added in portions within 5 min. After each addition, vigorous N_2-evolution was observed. CC (CH_2Cl_2/hexane 1:1): 188 mg (90%) of **11g**. Colorless crystals. M.p. 181.5–182.7°. IR (KBr): 1642*s*, 1592*s*, 1495*m*, 1480*m*, 1448*m*, 1418*m*, 1375*s*, 1295*m*, 1280*m*, 1178*w*, 1140*w*, 1110*w*, 1075*w*, 1020*w*, 965*w*, 795*m*, 768*m*, 785*s*, 700*s*, 660*m*, 650*m*. ^{1}H-NMR: 7.70 (*d*, *J* = 7.3, 1 arom. H); 7.62 (*d*, *J* = 7.5, 1 arom. H); 7.4–7.15 (*m*, 14 arom. H); 6.69 (*t*, *J* = 7.5, 1 arom. H); 5.81 (*d*, *J* = 7.8, 1 arom. H); 3.29 (*s*, MeN). ^{13}C-NMR: 167.7 (*s*, C=O); 144.2, 143.1, 141.9, 141.4, 140.4, 137.0 (6*s*, 6 arom. C); 131.1, 129.1, 128.4, 128.3, 128.1, 128.0, 127.6, 127.0, 126.1, 124.5, 123.3, 119.9, 119.6 (13*d*, 18 arom. CH); 59.3, 56.9 (2*s*, 2 C_q); 39.0 (*q*, MeN). CI-MS: 420 (4, $[M + 1]^+$), 344 (100).

Desulfurization of **11g**. To a soln. of **11g** (106 mg, 0.25 mmol) in THF (2 ml), $(Me_2N)_3P$ (82 mg, 0.5 mmol) was added and the mixture stirred at 60° (30 min). CC (CH_2Cl_2/hexane 3:1): 89 mg (92%) of *2-(9*H*-fluoren-9-ylidene)-*N*-methyl-*N*,2-diphenylethanamide* (**13c**). Yellow crystals. M.p. 165.5–166.7°. IR: 3060*m*, 3000*m*, 2400*w*, 1630*s*, 1595*s*, 1495*s*, 1422*m*, 1448*s*, 1420*m*, 1373*s*, 1350*w*, 1300*w*, 1280*w*, 1178*m*, 1070*w*, 1025*w*, 920*w*. ^{1}H-NMR: 7.8–6.55 (*m*, 18 arom. H); 3.48 (*s*, MeN). ^{13}C-NMR: 169.7 (*s*, C=O); 142.5, 140.7, 137.9, 137.2, 137.1, 136.1, 135.5 (7*s*, 6 arom. C, 2 =C); 129.2, 129.0, 128.8, 128.5, 128.2, 127.7, 127.5, 126.7, 126.5, 125.3, 125.0, 124.2, 119.7, 119.3 (14*d*, 18 arom. CH); 37.2 (*q*, MeN). CI-MS: 389 (28), 388 (100, $[M + 1]^+$).

4.7. *Reactions with* **2e**. *3-(*tert*-Butyl)-*N*-methyl-*N*-phenylspiro[thiirane-2,9′-[9*H*]xanthene]-3-carboxamide* (**11h**). According to *4.1*, in the presence, of $LiClO_4$; **2e** (106 mg, 0.5 mmol), **1d** (139 mg, 0.6 mmol), 60°, 7 h. CC (hexane/AcOEt 6:1): 137 mg (66%) of **11h**. Colorless crystals. M.p. 175.6–177.2°. IR: 3000*m*, 2960*m*, 1640*s*, 1600*s*, 1495*s*, 1470*s*, 1460*s*, 1450*s*, 1365*s*, 1300*m*, 1250*s*, 1105*m*, 970*w*, 900*m*, 710*m*, 700*s*. ^{1}H-NMR (2 rotamers): 7.6–6.8 (*m*, 13 arom. H); 3.57, 2.84 (2*s*, MeN); 1.033, 1.027 (2*s*, *t*-Bu). ^{13}C-NMR (2 rotamers): 167.4, 167.1 (2*s*, C=O); 157.5, 156.6, 156.5, 145.3, 144.1 (5*s*, 5 arom. C); 130.3, 129.7, 129.0, 128.8, 128.5, 126.8, 126.4, 125.9,

125.2, 125.0, 122.8, 122.5, 122.4, 122.3, 116.6, 116.5, 116.4 (17*d*, 13 arom. CH); 67.0, 66.3, 51.9, 51.7 (4*s*, 2 C_q); 41.1, 40.2 (2*q*, MeN); 37.3, 36.7 (2*s*, Me_3C); 30.9, 29.9 (2*q*, Me_3C). CI-MS: 417 (28), 416 (100, $[M+1]^+$). Anal. calc. for $C_{26}H_{25}NO_2S$ (415.56): C 75.15, H 6.06, N 3.37, S 7.72; found: C 74.60, H 6.12, N 3.25, S 7.84.

Suitable crystals for the X-ray crystal-structure determination were grown from $MeOH/CH_2Cl_2$.

N-Methyl-N,3-diphenylspiro[thiirane-2,9'-[9H]xanthene]-3-carboxamide (**11i**). According to *4.1*, in the presence of $LiClO_4$; **2e** (106 mg, 0.5 mmol), **1e** (240 mg, 0.96 mmol), 60°, 40 h. CC (hexane/CH_2Cl_2 1:1): 177 mg (81%) of **11i**. Colorless crystals. M.p. 183.1–185.1°. IR (KBr): 3060*w*, 3040*w*, 1650*s*, 1592*s*, 1572*m*, 1538*w*, 1495*s*, 1470*s*, 1445*s*, 1415*m*, 1368*s*, 1308*m*, 1292*m*, 1270*m*, 1250*s*, 1200*m*, 1120*m*, 1100*m*, 1070*m*, 1035*m*, 968*w*, 890*w*, 860*m*, 790*m*, 770*s*, 750*s*, 730*m*, 700*s*, 650*m*. ^{1}H-NMR: 7.55–6.95 (*m*, 16 arom. H); 6.5–6.45 (*m*, 2 arom. H); 2.99 (*s*, MeN). ^{13}C-NMR: 167.1 (*s*, C=O); 154.7, 154.3, 143.5, 135.6, 129.8, 120.2 (6*s*, 6 arom. C); 130.8, 129.1, 129.0, 128.3, 128.0, 127.5, 127.4, 127.2, 126.0, 122.9, 121.9, 116.5, 115.6 (13*d*, 18 arom. CH); 63.1, 53.8 (2*s*, 2 C_q); 38.7 (*q*, MeN). CI-MS: 436 (29, $[M+1]^+$), 405 (31), 404 (100). Anal. calc. for $C_{28}H_{21}NO_2S$ (435.55): C 77.22, H 4.86, N 3.22; found: C 77.29, H 4.88, N 3.14.

5. *X-Ray Crystal-Structure Determination of Compounds* **4a**, **11h**, *and* **12a** (see *Table* and *Figs. 1–3*).[7]). All measurements were made on a *Rigaku AFC5R* diffractometer in the $\omega/2\theta$-scan mode using graphite-monochro-

Table. *Crystallographic Data for Compounds* **4a**, **11h**, *and* **12a**

	4a	**11h**	**12a**
Crystallized from	hexane/Et_2O	$MeOH/CH_2Cl_2$	$MeOH/CH_2Cl_2$
Empirical formula	$C_{27}H_{20}OS$	$C_{26}H_{25}NO_2S$	$C_{21}H_{29}N_2O_2S$
Formula weight	392.51	415.55	387.54
Crystal color, habit	pale-green, prism	colorless, prism	colorless, prism
Crystal dimensions [mm]	$0.10\times0.24\times0.45$	$0.30\times0.45\times0.45$	$0.27\times0.35\times0.45$
Temp. [K]	173(1)	173(1)	173(1)
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	$P2_1/n$	$P2_12_12_1$	$P2_1/c$
Z	4	4	4
Reflections for cell determination	25	25	25
2θ range for cell determination [°]	22–37	39–40	37–40
Unit cell parameters a [Å]	9.615(5)	12.888(3)	11.626(2)
b [Å]	16.408(4)	16.806(3)	10.603(2)
c [Å]	13.039(3)	10.156(3)	17.130(2)
β [°]	101.68(3)	90	90.41(1)
V [Å^3]	2014(1)	2199.7(8)	2111.6(5)
D_x [g cm^{-3}]	1.294	1.255	1.219
$\mu(MoK_\alpha)$ [mm^{-1}]	0.176	0.169	0.173
Scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
$2\theta_{(max)}$ [°]	55	55	55
Total reflections measured	5085	4604	5364
Symmetry independent reflections	4644	3900	4855
Reflections used [$I > 2\sigma(I)$]	2564	3441	3767
Parameters refined	282	372	361
Final R	0.0583	0.0351	0.0403
wR	0.0512	0.0327	0.0396
Weights: p in $w=[\sigma^2(F_o)+(pF_o)^2]^{-1}$	0.005	0.005	0.005
Goodness of fit	1.766	1.821	1.820
Secondary extinction coefficient	–	$2.24(9)\times10^{-6}$	$1.96(8)\times10^{-6}$
Final Δ_{max}/σ	0.0001	0.0005	0.0007
$\Delta\rho$(max; min) [e Å^{-3}]	0.59; −0.29	0.25; −0.25	0.29; −0.21
Range of $\sigma(d(C-C))$ [Å]	0.005–0.007	0.003–0.004	0.002–0.003

[7]) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the *Cambridge Crystallographic Data Centre* as deposition No. CCDC-100843. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge CB1 1EZ, U.K. (fax: + 44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

mated 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 listed in the *Table*, views of the molecules are shown in *Figs. 1–3*. The structures were solved by direct methods using SHELXS86 [25], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms of **11h** and **12a** were located in difference electron-density maps, and their positions were allowed to refine together with individual isotropic displacement parameters. All H-atoms of **4a** were fixed in geometrically calculated positions with a C–H distance of 0.95 Å, but their isotropic displacement parameters were refined independently. All refinements were carried out on F using full-matrix least-squares procedures. A correction for secondary extinction was applied for **11h** and **12a**. For **11a**, the data collection included measurement of the *Friedel* opposites of all unique reflections with $2\theta < 40°$, and the absolute configuration was confirmed by the refinement of the absolute structure parameter [26] to 0.04(8). Neutral atom scattering factors for non-H-atoms were taken from [27a] and the scattering factors for H-atoms from [28]. Anomalous dispersion effects were included in F_{calc} [29]; the values for f' and f'' were those of [27b]. All calculations were performed using the TEXSAN crystallographic software package [30].

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