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Grzegorz Mlostoń, Paulina Pipiak, Anthony Linden, Heinz Heimgartner

Institutions: University of Zurich

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Mlostoń, Grzegorz ; Pipiak, Paulina ; Linden, Anthony ; Heimgartner, Heinz

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Prof. Dr. H. Heimgartner
Tel. 044 635 4282
Fax 044 635 6836
e-mail: heinz.heimgartner@chem.uzh.ch

Studies on the Reactions of Thiocarbonyl *S*-Methanides with Hetaryl Thioketones

by **Grzegorz Mlostoń***[a]), **Paulina Pipiak**[a])[1]), **Anthony Linden**[b]), and **Heinz Heimgartner***[b])

[a]) University of Łódź, Department of Organic and Applied Chemistry, Tamka 12, PL-91-403 Łódź (phone: +48 42 6355761; fax: +48 42 6655162; e-mail: gmloston@uni.lodz.pl)

[b]) University of Zürich, Department of Chemistry, Winterthurerstrasse 190, CH-8057 Zürich (phone:+41 44 6354282; fax: +41 44 6356812; e-mail: heinz.heimgartner@chem.uzh.ch)

[1]) Part of the planned PhD thesis of *P. P.*, University of Łódź

Bishetaryl thioketones react with thiocarbonyl ylides to give 1,3-dithiolanes in high yields. No competitive side reactions of the thiocarbonyl ylides are observed, evidencing the 'superdipolarophilic' character of this little-known group of thioketones. Depending on the type of substituents present in both the thiocarbonyl ylide and the thioketone, formal [3+2] cycloadditions occur with complete regioselectivity or with formation of a mixture of both regioisomers. Regioselective formation of the sterically more crowded 1,3-dithiolanes is explained *via* a mechanism involving stabilized 1,5-biradicals. In systems with less efficient radical stabilization, *e.g.*, in the case of adamantanethione *S*-methanide, substantial violation of the regioselectivity is observed as a result of steric hindrance.

1. Introduction. – Thiocarbonyl ylides belong to the class of the so-called S-centered 1,3-dipoles, and they are widely applied for the preparation of S-heterocycles with diverse sizes of the formed ring [1]. The reactive thiocarbonyl S-methanides, generated *via* thermal N_2-elimination from 2,5-dihydro-1,3,4-thiadiazoles, easily react with diverse dipolarophiles, and special attention is focused on their reactions with 'superdipolarophilic' thioketones [2]. These reactions leading to 1,3-dithiolane derivatives (*Schönberg* reaction [3]) are of interest not only as a method for the preparation of these products, but also for studies on organic reaction mechanisms. Important features of these reactions are the regioselectivity and the nature of the postulated intermediates. Whereas S-methanides of cycloaliphatic thioketones, *e.g.*, adamantanethione S-methanide (**1a**), react with adamantanethione (**2a**) to give the sterically less hindered 2,2,4,4-tetrasubstituted 1,3-dithiolane of type **3a**, its reaction with thiofluorenone (**2b**) gave a *ca.* 1:3 mixture of the regioisomeric 1,3-dithiolanes **3b** and **4b** in favor of the sterically more crowded isomer [4] (*Scheme 1*). On the other hand, S-methanides derived from aromatic thioketones, *e.g.*, thiobenzophenone S-methanide (**1b**), react with thiobenzophenone (**2c**) to give the 4,4,5,5-tetrasubstituted 1,3-dithiolane of type **4c** as the sole product [3b].

Scheme 1

In a recent publication, we described the synthesis and selected reactions of aryl/hetaryl and bishetaryl thioketones [5]. Unexpectedly, the experiments with diazomethane demonstrated that the presence of a hetaryl substituent such as thiophen-2-yl, selenophen-2-yl, or furan-2-yl results in a spontaneous evolution of N_2 even at –60°. In contrast to thiobenzophenone, the precursor of the corresponding S-methanides

of type **1**, *i.e.*, 2,5-dihydro-2,2-diaryl-1,3,4-thiadiazoles **5**, could not be prepared in solution. Instead, a reactive intermediate trapped the starting thioketone **2** and yielded the sterically more crowded 1,3-dithiolane in a regioselective manner. However, in the case of phenyl (selenophen-2-yl) thioketone (**2d**), the formation of a second product, a novel macrocyclic dimer of the thiocarbonyl S-methanide was observed [6]. Based on these results, we proposed that the intermediate 'thiocarbonyl ylide' displays a biradical character. Thus, the formation of the 12-membered cyclodimer can be considered as experimental evidence for the appearance of a delocalized biradical. An earlier computational study suggested the participation of a 1,5-diradical in the formation of 1,3-dithiolane derivatives *via* formal [3+2] cycloaddition of thioketones with thiocarbonyl S-methanides [7].

The goal of the present study was the investigation of the formation of 1,3-dithiolanes *via* formal [3+2] cycloaddition of thiocarbonyl S-methanides and aryl/hetaryl and bishetaryl thioketones. Of special interest is the regioselectivity of the ring formation.

2. Results and Discussion. – The thermal decomposition of 2,2-disubstituted 2,5-dihydro-1,3,4-thiadiazoles **5** is considered as a straightforward method for the *in situ* generation of reactive thiocarbonyl S-methanides of type **1** [1a][8]. The stability of these precursors depends strongly on the type of substitutents, and the presence of bulky cycloaliphatic groups allows them to be prepared as crystalline, shelf-stable compounds. On the other hand, 2,2-diaryl-substituted 2,5-dihydro-1,3,4-thiadiazoles **5** can be prepared only at low temperature and have to be used as thiocarbonyl S-methanide precursors at –40° without isolation.

Based on the typical procedure for the generation of diaryl-substituted thiocarbonyl S-methanides of type **1b**, solutions of thiobenzophenone (**2c**) or thiofluorenone (**2b**) in THF were treated with CH_2N_2 at –60°. Equimolar amounts of hetaryl/phenyl (**2d**, **2e**) or bishetaryl thioketones (**2f**, **2g**) were added to the colorless solutions and the mixtures were warmed to –40°. After complete evolution of N_2, the crude products were analyzed by ^{1}H-NMR spectroscopy with a weighed amount of 1,1,2,2-tetrachloroethane as a standard. In all reactions, only one product was detected in good yields and identified as the sterically crowded 4,4,5,5-tetrasubstituted 1,3-dithiolanes **4** (*Scheme 2*). The proposed structures of the products were elucidated from the characteristic absorption of $H_2C(2)$ in the ^{13}C-NMR spectra at 30.5–32.5 ppm [3].

Scheme 2

In the second series, adamantanethione S-methanide (**1a**) was generated from its precursor **5a** at 45° in THF in the presence of equimolar amounts of thioketones **2**. In all cases, the formation of mixtures of regioisomeric 1,3-dithiolanes was shown by ^{1}H-NMR spectroscopy (weighed standard). In analogy to earlier reported products obtained from **1a** and aromatic thioketones **2b** and **2c** (*Scheme 1*), the major products were identified as the sterically more crowded 4,4,5,5-tetrasubstituted 1,3-dithiolanes of type **4** (*Scheme 3*). The ratios of the isomers **3** and **4** established by NMR spectroscopy were between *ca*. 1:3 and 1:4, and in the case of the mixtures of **3e/4k** and **3h/4n** the major products **4k** and **4n**, respectively, were isolated as pure crystalline compounds and fully characterized.

Scheme 3

Reactions with the 2,2,4,4-tetramethyl-3-oxocyclobutanethione S-methanide (**1c**) with hetaryl phenyl thioketones **2d** and **2e** as well as with the bishetaryl thioketone **2h** led also to mixtures of regioisomeric 1,3-dithiolanes **3** and **4** with the sterically more congested product of type **4** as the major component (*Scheme 4*). In comparison with the series of 1,3-dithiolanes obtained in the case of **1a** (*Scheme 3*), the ratio of isomers increased in favor of the more crowded isomers of type **4**. However, the analogous reactions with bis(thiophen-2-yl) thioketone (**2f**) and bis(selenophen-2-yl) thioketone (**2g**) led to the sterically more crowded 1,3-dithiolanes **4r** and **4s**, respectively, as the sole products.

Scheme 4

Finally, the structure of compound **4r**, which had been deduced from the NMR data, was unambiguously confirmed by X-ray crystallography (*Figure*). Although the molecule is achiral, the compound has crystallized in a chiral space group and the absolute structure has been determined by the diffraction experiment. There are two symmetry-independent molecules in the asymmetric unit. Both molecules show disorder of the thiophene rings due to 180° rotation of each ring around its parent C–C bond. The 5-membered dithiolane ring in each molecule has a half-chair conformation twisted on the C–C bond.

Figure. *ORTEP plot* [9] *of the molecular structure of one of the two symmetry-independent molecules of* **4r** (with 50% probability ellipsoids; arbitrary numbering of the atoms; only the major conformations of the disordered thiophene rings are shown).

It is worth mentioning that the thiocarbonyl ylides **1a**-**1d** reacted with hetaryl thioketones **2** without competitive formation of 1,4-dithianes or thiiranes (see [1a][8]). These results confirm that hetaryl thioketones belong to the group of 'superdipolarophiles' in reactions with thiocarbonyl S-methanides [2]. According to *Huisgen*'s reactivity scale, the most reactive thioketone is thiofluorenone (**2b**), followed by thiobenzophenone (**2c**). For comparison reasons, the competition experiments of thiobenzophenone S-methanide (**1b**) with equimolar amounts of **2b** and bis(thiophen-2-yl) thioketone (**2f**), as well as with **2c** and **2f**, were performed in THF at *ca*. –40°. The obtained products were analyzed by ^{1}H-NMR spectroscopy. In the first case, the only product formed was the sterically crowded 1,3-dithiolane **4h**. In the second experiment, however, the ratio of **4c** (*Scheme 1*) to **4f** was determined to be *ca*. 5:4. These results demonstrate that the symmetrical hetaryl thioketone **2f** is less reactive than thiofluorenone (**2b**) but almost as reactive as thiobenzophenone (**2c**).

3. Conclusions. – The present study showed that hetaryl thioketones extend the group of 'superdipolarophiles' in reactions with thiocarbonyl S-methanides **1**. The observed regioselectivity of the 1,3-dithiolane formation suggests that the formal [3+2] cycloaddition occurs, most likely, *via* biradical intermediates. The latter mechanism leads to complete regioselectivity only when the substituents stabilize the biradical structure, *e.g.*, *via* delocalization in tetraaryl-substituted systems (*cf.* [6]). In such systems, the intermediate 1,5-diradical **6a** is the precursor of the sterically crowded 4,4,5,5-tetrasubstituted 1,3-dithiolane, such as **4d-4h** [7] (*Scheme 2*). The same regioisomers were only obtained as sole products in the reaction of 2,2,4,4-tetramethyl-3-oxocyclobutanethione S-methanide (**1c**) with bishetaryl thioketones **2f** and **2g**, which

possess S or Se atoms in both heterocycles. In these cases, the stabilization of the 1,5-biradical intermediate **6b** results from delocalization within the hetaryl rings and, likely, from an additional stabilizing effect across the cyclobutanone ring [10]. The presence of Se or S atoms in the five-membered heteroaromatic rings is essential for the exclusive formation of an intermediate of type **6b** (see also [6]). Both heteroatoms are known to stabilize radicals in the α-position.

Formulae **6a** and **6b**

In the presented cases, electronic effects are decisive, but in the reactions with adamantanethione S-methanide (**1a**), no radical stabilization is possible at the adamantane-substituted terminus of the intermediate. For that reason, the influence of steric factors is of increasing importance and the formation of the sterically less crowded 1,3-dithiolanes as minor products is also observed in all cases.

In summary, the results discussed in this publication, additionally supported by computational studies [7], evidence that in the case of S-centered thiocarbonyl ylides some of the formal [2+3] cycloadditions occur stepwise *via* biradical intermediates. This conclusion supports the concept of the radical character of '1,3-dipolar cycloaddition reactions' formulated by *Firestone* [11], at least for some systems with the required structural features.

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Experimental Part

1. *General*. M.p.: *MEL-TEMP. II* (*Aldrich*); uncorrected. Column chromatography (CC): silica gel (70–230 mesh, *Merck*). IR Spectra: *NEXUS FT-IR* instrument; in KBr; absorptions in cm^{-1}. ^{1}H-NMR and ^{13}C-NMR Spectra: *BRUKER AVANCE III* instrument (^{1}H at 600 and ^{13}C at 150 MHz) using the solvent signal as reference; in $CDCl_3$; chemical shifts (δ) in ppm; coupling constants *J* in Hz. ESI-MS: *Varian 500 MS* LC Ion Trap spectrometer. Elemental analyses were performed in the Laboratory of the Faculty of Chemistry, University of Łódź.

2. *Starting Materials. 1,1,3,3-Tetramethyl-5-thia-7,8-diazaspiro[3.4]oct-7-en-2-one* (**5d**) [12] and *2,5-Dihydrospiro[1,3,4-thiadiazole-2,2'-tricyclo[3.3.1.1^{3,7}]decane]* (**5a**) [13] were prepared by known methods according to the literature protocols. Thiobenzophenone (**2b**), fluorene-9-thione **(2c**), the nonsymmetrical heteroaromatic thioketones *phenyl(selenophen-2-yl)methanethione* (**2d**), *phenyl(selenophen-2-yl)methanethione* (**2e**), and *(furan-2-yl) (thiophen-2-yl)methanethione* (**2h**), as well as the symmetrical heteroaromatic thioketones *bis(thiophen-2-yl)methanethione* (**2g**) and *bis(selenophen-2-yl)methanethione* (**2h**) were obtained from the corresponding ketones using the known thionation procedure with *Lawsson*'s reagent [5]. Other reagents used in the present study were commercially available.

3. *Reactions of Hetaryl Phenyl Thioketones* **2d**–**2e** *or Bishetaryl Thioketones* **2f**–**2g** *with 2,5-Dihydro-2,2-diphenyl-1,3,4-thiadiazole* (**5b**). – *General Procedure.* Thiobenzophenone (**2b**, 1 mmol) dissolved in 2 ml of THF was cooled to –70° and treated with small portions of ethereal CH_2N_2 soln. until the dark-blue color disappeared. A soln. of the corresponding thioketone **2d**–**g** (1 mmol) in 2 ml of THF was added at –70° and the reaction mixture was kept in a cold bath (–45° to –40°, acetone/dry ice) for 2.5 h. Then, the mixture was allowed to warm slowly to r.t. During

the reaction, a colorless precipitate was formed. The mixture was kept at r.t. for *ca*. 30 min. Then, the solvent was evaporated; the crude product was purified by crystallization or by treatment with small portions of hexane.

3.1. *4,5,5-Triphenyl-4-(thiophen-2-yl)-1,3-dithiolane* (**4d**). Reaction with **2d**; the crude product was purified by crystallization from CH_2Cl_2/hexane. Yield: 320 mg (77%). Colorless crystals. M.p. 175.2–176.5° (CH_2Cl_2/hexane). IR (KBr): 3050*w*, 1597*w*, 1488*m*, 1440*m*, 1233*m*, 1033*w*, 747*m*, 722*m*, 708*s*. ^{1}H-NMR ($CDCl_3$): 3.01, 3.89 (*AB*, J_{AB} = 9.6, CH_2); 6.76–6.77 (*m*, 1 arom. H); 6.85 (*d*, *J* = 3.6, 1 arom. H); 7.10–7.20 (*m*, 10 arom. H); 7.39–7.43 (*m*, 4 arom. H); 7.50 (*d*, *J* = 8.4, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 30.5 ($H_2C(2)$); 74.5, 78.3 (C(4), C(5)); 125.1, 125.6, 126.3, 126.4, 126.6, 126.7, 126.8, 127.0, 130.0, 130.6, 131.4, 131.8 (18 arom. CH); 142.3, 143.0 (br., 4 arom. C). HR-ESI-MS: 416.072719 (calc. for $C_{25}H_{20}S_3$ 416.073100, M^+).

3.2. *4,5,5-Triphenyl-4-(selenophen-2-yl)-1,3-dithiolane* (**4e**). Reaction with **2e**; the crude product was purified by crystallization from CH_2Cl_2/hexane. Yield: 320 mg (70%). Colorless crystals. M.p. 177.4–178.8° (CH_2Cl_2/hexane). IR (KBr): 3049*w*, 1597*w*, 1489*m*, 1439*m*, 1232*m*, 1186*w*, 1083*w*, 1034*w*, 746*m*, 716*s*, 696*s*. ^{1}H-NMR ($CDCl_3$): 3.81, 3.90 (*AB*, J_{AB} = 9.6, CH_2); 7.00–7.01 (*m*, 2 arom. H); 7.07–7.19 (*m*, 9 arom. H); 7.37 (*d*, *J* = 7.2, 2 arom. H); 7.46–7.50 (*m*, 4 arom. H); 7.89 (*dd*, *J* = 4.8, 1.8, 1 arom. H). ^{13}C-NMR ($CDCl_3$): 30.6 ($H_2C(2)$); 76.4, 78.2 (C(4), C(5)); 126.2, 126.6, 126.7, 126.7, 126.9, 127.1, 127.9, 130.6, 131.6, 131.8, 131.9 (18 arom. CH); 142.7, 142.8 (br., 4 arom. C). Anal. calc. for $C_{25}H_{20}S_2Se$ (463.53): C 64.78, H 4.35, S 13.83; found: C 64.55, H 4.38, S 13.75.

3.3. *5,5-Diphenyl-4,4-bis(thiophen-2-yl)-1,3-dithiolane* (**4f**). Reaction with **2f**; the crude product was purified by repeated treatment with small portions of hexane. Yield: 320 mg (76%). Colorless crystals. M.p. 192.7–193.4°. IR (KBr): 3095*w*, 3068*w*,

1595*w*, 1488*m*, 1440*m*, 1238*m*, 1086*w*, 849*w*, 747*s*, 734*m*, 707*s*. ^{1}H-NMR ($CDCl_3$): 3.94 (*s*, CH_2); 6.80 (*dd*, *J* = 5.4, 3.6, 2 arom. H); 7.03 (*dd*, *J* = 3.6, 1.2, 2 arom. H); 7.10–7.18 (*m*, 8 arom. H); 7.40–7.41 (*m*, 4 arom. H). ^{13}C-NMR ($CDCl_3$): 31.4 ($H_2C(2)$); 71.4, 79.1 (C(4), C(5)); 125.6, 125.7, 126.5, 126.9, 129.1, 131.4 (16 arom. CH); 142.2, 147.9 (4 arom. C). ESI-MS (MeOH): 461 (55, $[M+K]^+$), 445 (45, $[M+Na]^+$), 423 (100, $[M+H]^+$). Anal. calc. for $C_{23}H_{18}S_4$ (422.64): C 65.36, H 4.29, S 30.35; found: C 64.81, H 4.39, S 30.32.

3.4. *5,5-Diphenyl-4,4-bis(selenophen-2-yl)-1,3-dithiolane* (**4g**). Reaction with **2g**; the crude product was purified by repeated treatment with small portions of hexane. Yield: 310 mg (58%). Colorless crystals. M.p. 184.8–185.3°. IR (KBr): 3096*w*, 3050*w*, 1624*w*, 1487*w*, 1439*m*, 1227*m*, 1033*w*, 729*m*, 697*s*. ^{1}H-NMR ($CDCl_3$): 3.99 (*s*, CH_2); 7.08–7.09 (*m*, 2 arom. H); 7.13–7.19 (*m*, 6 arom. H); 7.30 (*dd*, *J* = 4.2, 1.2, 2 arom. H); 7.45–7.46 (*m*, 4 arom. H); 7.89 (*dd*, *J* = 5.4, 1.2, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 31.6 ($H_2C(2)$); 75.2, 78.9 (C(4), C(5)); 126.5, 127.0, 128.3, 130.9, 131.5, 132.1 (16 arom. CH); 142.4, 145.0 (br., 4 arom. C). Anal. calc. for $C_{23}H_{18}S_2Se_2$ (516.44): C 53.49, H 3.51, S 12.42; found: C 53.58, H 3.65, S 12.63.

4. *Reaction of 2,5-Dihydrospiro[1,3,4-thiadiazole-2,9'-[9*H*]fluorene]* (**5c**) *with Bis(thiophen-2-yl)methanethione* (**2f**). A soln. of fluorene-9-thione (**2c**, 1 mmol) in 2 ml of THF was cooled to –70° and treated with small portions of a soln. of CH_2N_2 in Et_2O, until the green soln. became yellow. Then, a soln. of **2f** (1 mmol) in 2 ml of THF was added at –70° and the mixture was kept in a cold bath (–45° to –40°, acetone/dry ice) for 1 h. Then, the mixture was allowed to warm slowly to r.t., whereby a colorless precipitate was formed. The mixture was kept at r.t. for *ca.* 30 min, then the solvent was evaporated, and the residue was crystallized from CH_2Cl_2/hexane.

*5,5-Diphenylspiro[1,3-dithiolane-4,9'-[9*H*]fluorene]* (**4h**). Yield: 295 mg (70%). Colorless crystals. M.p. 216.4–218.0° (CH_2Cl_2/hexane). IR (KBr): 3066*w*, 2924*w*, 1624*w*, 1446*m*, 1427*w*, 1227*m*, 1239*m*, 1048*w*, 1034*w*, 851*w*, 789*s*, 745*s*, 736*s*, 719*s*, 706*s*. ^{1}H-NMR ($CDCl_3$): 4.50 (*s*, CH_2); 6.61 (*dd*, *J* = 3.6, 1.2, 2 arom. H); 6.74 (*dd*, *J* = 5.4, 3.6, 2 arom. H); 7.07–7.13 (*m*, 6 arom. H); 7.32–7.35 (*m*, 2 arom. H); 7.69 (*d*, $^2J_{H,H}$ = 7.2, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 32.5 (H_2C(2)); 70.3, 75.5 (C(4), C(5)); 119.8, 125.3, 125.7, 125.9, 127.5, 127.8, 128.6 (14 arom. CH); 140.2, 144.1, 147.9 (6 arom. C). ESI-MS (MeOH): 443 (100, $[M+Na]^+$).

5. *Reactions of Hetaryl Phenyl Thioketones* **2d**–**2e** *or Bishetaryl Thioketones* **2f**-**2h** *with 2,5-Dihydrospiro[1,3,4-thiadiazole-2,2'-tricyclo[3.3.1.1^{3,7}]decane]* (**5a**). – *General Procedure.* The thiadiazoline **5a** (1.1 mmol) and a corresponding thioketone **2** (1.05 mmol) were dissolved in freshly distilled THF (2.5 ml). The mixture was heated in an oil bath (45–50°) until the intense color of the thioketone vanished; the gas burette combined with the flask indicated the evolution of stoichiometric amounts of N_2. After removal of the solvent under vacuum, the residue was subjected to ^{1}H-NMR analysis in $CDCl_3$ soln. with a weighed amount of 1,1,2,2-tetrachloroethane as standard. Crude products were purified by CC (CH_2Cl_2/petroleum ether 4:6). In all cases, formation of mixtures of regioisomeric 1,3-dithiolanes **3** and **4** was observed.

5.1. *Reaction with* **2d***: 5-Phenyl-5-(thiophen-2-yl)spiro[1,3-dithiolane-4,2'-tricyclo[3.3.1.1^{3,7}]decane]* (**4i**; major) *and 4-Phenyl-4-(thiophen-2-yl)spiro[1,3-dithiolane-2,2'-tricyclo[3.3.1.1^{3,7}]decane]* (**3d**; minor); crude product ratio: 75:25. Reaction time: 8 h. Isolated as a mixture of isomers. Yield: 332 mg (82%). Yellow crystals. M.p.139.8–141.0°. IR (KBr): 2905*s*, 2855*s*, 1443*m*, 1233*w*, 1220*w*, 1099*w*, 743*w*, 708*w*. ^{1}H-NMR ($CDCl_3$): 1.19–3.04 (*m*, 28 H); 3.50, 3.56 (*AB*, J_{AB} = 9.0, CH_2 of **4i**); 3.83, 3.94 (*AB*, *J* = 12.6, CH_2 of **3d**); 6.78–7.94 (*m*, 16 arom. H). ^{13}C-NMR

($CDCl_3$): 26.3, 26.4, 26.6, 26.8, 36.4, 36.8, 42.0, 42.1 (8 $CH_{(ad)}$); 27.2 ($H_2C(2)$ of **4i**); 33.2, 33.6, 36.5, 36.5, 36.6, 36.9, 37.6, 38.2, 38.9, 40.5 (10 $CH_{2(ad)}$); 50.2 ($H_2C(5)$ of **3d**); 70.5, 75.4, 77.6, 78.5 (2 C(4), 2 C(5)); 124.8, 125.0, 126.0, 126.1, 126.6, 127.2, 127.4, 127.9, 128.1, 128.8, 130.8 (16 arom. CH); 140.8, 148.5 (2 arom. C of **4i**); 144.0, 151.2 (2 arom. C of **3d**). Anal. calc. for $C_{22}H_{24}S_3$ (384.63): C 68.70 H 6.29 S 25.01; found: C 68.37 H 6.00 S 25.01.

5.2. *Reaction with* **2e**: *5-Phenyl-5-(selenophen-2-yl)spiro[1,3-dithiolane-4,2'-tricyclo[3.3.1.1^{3,7}]decane]* (**4k**; major) and *4-Phenyl-4-(selenophen-2-yl)spiro[1,3-dithiolane-2,2'-tricyclo[3.3.1.1^{3,7}]decane]* (**3e**; minor); crude product ratio: 78:22. Reaction time: 7 h. After chromatography, **4k** and **3e** were isolated as a mixture of regioisomers. Yield: 358 mg (80%). After repeated crystallization from hexane, the major product **4k** was isolated in pure form. Colorless crystals. M.p. 152.1–153.0° (hexane). IR (KBr): 2903*s*, 2858*m*, 1441*m*, 1231*m*, 1221*m*, 709*s*, 695*m*, 684*s*. ^{1}H-NMR ($CDCl_3$): 1.04–3.05 (*m*, 14 H); 3.54, 3.60 (*AB*, J_{AB} = 8.4, CH_2); 7.17–7.96 (*m*, 4 arom. H); 7.59 (*d*, $^2J_{H,H}$ = 3.6, 1 arom. H); 7.83 (*d*, $^2J_{H,H}$ = 6.6, 1 arom. H); 7.96 (br. *s*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 26.7, 26.9, 36.4, 37.1 (4 $CH_{(ad)}$); 27.5 ($H_2C(2)$); 33.2, 33.3, 38.0, 39.0, 40.8 (5 $CH_{2(ad)}$); 77.5, 77.6 (C(4), C(5)); 127.5, 128.0, 129.1, 130.5, 130.9 131.0 (8 arom. CH); 140.8, 157.2 (2 arom. C). Anal. calc. for $C_{22}H_{24}S_2Se$ (431.52): C 61.24, H 5.61, S 14.86; found: C 61.17, H 5.39, S 15.16.

Spectroscopic data of **3e**, collected from the spectra of a mixture of **3e** with the major product **4k**: ^{1}H-NMR ($CDCl_3$): 1.04–3.05 (*m*, 14 H); 3.78–3.96 (*m*, CH_2); 7.17–7.96 (*m*, 8 arom. H). ^{13}C-NMR ($CDCl_3$): 26.3, 26.4, 41.9, 42.0 (4 $CH_{(ad)}$); 36.3, 36.6, 36.6, 37.0, 37.6 (5 $CH_{2(ad)}$); 50.6 ($H_2C(5)$); 72.5, 78.5 (C(2), C(4)); 127.1, 127.4, 127.8, 127.9, 129.0, 130.7 (8 arom. CH); 144.2, 159.3 (2 arom. C).

5.3. *Reaction with* (**2f**): *5,5-Bis(thiophen-2-yl)spiro[1,3-dithiolane-4,2'-tricyclo[3.3.1.1^{3,7}]decane]* (**4l**; major) and *4,4-Bis(thiophen-2-yl)spiro[1,3-dithiolane-2,2'-tricyclo[3.3.1.1^{3,7}]decane]* (**3f**; minor); crude product ratio: 82:18. Reaction time: 9 h. Isolated as a mixture of isomers. Yield 309 mg (76%). Yellow crystals. M.p. 127.0–128.7°. IR (KBr): 2899*s*, 2851*s*, 1628*w*, 1442*m*, 1425*m*, 1225*m*, 1097*m*, 707*s*, 697*s*. ^{1}H-NMR ($CDCl_3$): 1.48–2.82 (*m*, 28 H); 3.78 (*s*, CH_2 of **4l**); 3.93 (*s*, CH_2 of **3f**); 7.00–7.41 (*m*, 12 arom. H). ^{13}C-NMR ($CDCl_3$): 26.2, 26.3, 26.9, 35.6, 42.0 (8 $CH_{(ad)}$); 26.8 (H_2C(2) of **4l**); 32.9, 36.4, 36.7, 37.5, 38.8, 39.1 (10 $CH_{2(ad)}$); 52.4 (H_2C(5) of **3f**); 67.3, 72.0, 76.5, 79.0 (2 C(4), 2 C(5)); 125.1, 125.1, 125.9, 126.6, 127.7, 127.0 (12 arom. CH); 147.9 (2 arom. C of **4l**); 150.0 (2 arom. C of **3f**). ESI-MS (MeOH): 391 (100, $[M+H]^+$).

5.4. *Reaction with* **2g**: *5,5-Bis(selenophen-2-yl)spiro[1,3-dithiolane-4,2'-tricyclo[3.3.1.1^{3,7}]decane]* (**4m**; major) and *4,4-Bis(selenophen-2-yl)spiro[1,3-dithiolane-2,2'-tricyclo[3.3.1.1^{3,7}]decane]* (**3g**; minor); crude product ratio: 74:26. Reaction time: 8 h. Isolated as a mixture of isomers. Yield: 325mg (64%). M.p. 151.8–153.0°. IR (KBr): 2926*s*, 2899*s*, 2845*s*, 1625*w*, 1439*m*, 1234*m*, 1220*m*, 1097*m*, 717*m*, 695*s*, 703*s*. ^{1}H-NMR ($CDCl_3$): 1.39–2.76 (*m*, 28H); 3.72 (*s*, CH_2 of **4m**); 3.82 (*s*, CH_2 of **3g**); 7.07–7.81 (*m*, 12 arom. H). ^{13}C-NMR ($CDCl_3$): 26.3, 26.4, 27.0, 27.1, 35.7, 41.9 (8 $CH_{(ad)}$); 27.3 (H_2C(2) of **4m**); 33.1, 38.9, 39.1, 36.5, 36.7, 37.5 (10 $CH_{2(ad)}$); 53.4 (H_2C(5) of **3g**); 71.5, 79.3, 76.4, 76.4 (2 C(4), 2 C(5)); 127.7, 129.3, 131.0, 129.2, 130.1, 131.6 (12 arom. CH); 156.7 (2 arom. C of **3g**), 158.0 (2 arom. C of **4m**). Anal. calc. for $C_{20}H_{22}S_2Se_2$ (484.45): C 49.59 H 4.58 S 13.24; found: C 49.81 H 4.45 S 13.66.

5.5. *Reaction with* **2h**: *5-(Furan-2-yl)-5-(thiophen-2-yl)spiro[1,3-dithiolane-4,2'-tricyclo[3.3.1.1^{3,7}]decane]* (**4n**; major) and *4-(Furan-2-yl)-4-(thiophen-2-yl)spiro[1,3-dithiolane-2,2'-tricyclo[3.3.1.1^{3,7}]decane]* (**3h**; minor); crude product ratio:

77:23. Reaction time: 5 h. After CC, **4n** and **3h** were isolated as a mixture of regioisomers. Yield: 340 mg (86%). After repeated crystallization from hexane, the major product **4n** was isolated in pure form. Yellow crystals. M.p. 120.2–121.2°. IR (KBr): 2899*s*, 2853*s*, 1636*w*, 1449*m*, 1235*m*, 1149*m*, 1097*m*, 1021*m*, 751*m*, 727*s*, 693*s*. ^{1}H-NMR ($CDCl_3$): 1.02–2.74 (*m*, 14 H); 3.73, 3.84 (*AB*, J_{AB} = 9.0, C*H*$_2$); 6.33 (*dd*, *J* = 3.0, 1.8, 1 arom. H); 6.75 (*dd*, *J* = 3.6, 1.2, 1 arom. H); 6.99 (*dd*, *J* = 5.4, 3.6, 1 arom. H); 7.20 (*dd*, *J* = 4.8, 1.2, 1 arom. H); 7.43–7.44 (*m*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 26.4 ($H_2C(2)$); 26.9, 27.2, 35.0, 35.7 (4 $CH_{(ad)}$); 32.6, 33.1, 38.3, 39.2, 40.0 (5 $CH_{2(ad)}$); 69.8, 77.1 (C(4), C(5)); 111.0, 112.3, 124.8, 126.6, 127.5, 141.4 (6 arom. CH); 146.5, 152.1 (2 arom. C). Anal. calc. for $C_{20}H_{22}OS_3$ (374.59): C 64.13 H 5.92 S 25.68; found: C 64.05 H 6.00 S 25.65.

Spectroscopic data of **3h**, collected from the spectra from a mixture of **3h** with the major product **4n**. ^{1}H-NMR ($CDCl_3$): 1.02–2.74 (*m*, 14 H); 3.75–4.03 (*m*, CH_2); 6.32–7.38 (*m*, 6 arom. H). ^{13}C-NMR ($CDCl_3$): 26.2, 26.4, 42.0, 42.1 (4 $CH_{(ad)}$); 36.3, 36.5, 36.7, 36.9, 37.6 (5 $CH_{2(ad)}$); 48.8 ($H_2C(5)$); 65.5, 78.8 (C(2), C(4)); 109.0, 110.3, 125.1, 125.7, 126.6, 142.1 (6 arom. CH); 147.6, 155.8 (2 arom. C).

6. *Reactions of Hetaryl Phenyl Thioketones* **2d**–**2e** *or Bishetaryl Thioketones* **2f**-**2h** *with 1,1,3,3-Tetramethyl-5-thia-7,8-diazaspiro[3.4]oct-7-en-2-one* (**5d**). – *General Procedure.* A soln. of **5d** (1.1 mmol) and a thioketones **2d**–**2h** (1.05 mmol) in freshly distilled THF (2.5 ml) was heated in an oil bath (45–50°) until the color of the thioketone disappeared; a gas burette indicated the liberation of a stoichiometric amount of N_2. After removal of the solvent under vacuum, the residue was subjected to ^{1}H NMR analysis in $CDCl_3$ with a weighed amount of 1,1,2,2-tetrachloroethane as a standard.

6.1. *Reaction with* **2d**: *1,1,3,3-Tetramethyl-8-phenyl-8-(thiophen-2-yl)-5,7-dithiaspiro[3.4]octan-2-one* (**4o**; major) and *1,1,3,3-Tetramethyl-6-phenyl-6-(thiophen-2-yl)-5,8-dithiaspiro[3.4]octan-2-one* (**3i**; minor); crude product ratio: 86:14. Reaction time: 3.5 h. The crude mixture was purified by CC (CH_2Cl_2/hexane 4:6). Product isolated as a 86:14 mixture of regioisomers. Yield: 372 mg (94%). Colorless crystals. M.p. 109.0–112.0°. IR (KBr): 1778*s* (C=O), 1636*w*, 1597*w*, 1443*m*, 1230*m*, 1164*m*, 1022*m*, 744*m*, 707*s*. ^{1}H-NMR ($CDCl_3$): 1.26, 1.33, 1.36, 1.38, 1.47, 1.58, 1.65, 1.72 (8*s*, 8 Me); 3.62–3.66 (*m*, CH_2 of **4o**); 3.83, 3.92 (*AB*, J_{AB} = 12.0, CH_2 of **3i**); 6.86–7.82 (*m*, 16 arom. H). ^{13}C-NMR ($CDCl_3$): 22.3, 22.5, 24.6, 24.8, 24.8, 25.5, 25.68, 25.70 (8 Me); 26.8 (H_2C(6) of **4o**); 51.7 (H_2C(7) of **3i**); 66.5 (br.), 66.6, 67.0, 68.8 (br.) (2 C(1), 2 C(3)); 71.0, 74.5, 75.8, 76.1 (C(4), C(8) of **4o**, C(4), C(7) of **3i**); 125.2, 126.1, 126.3, 126.6, 127.4, 127.6, 127.7, 127.9, 128.1, 128.4, 129.1, 130.2 (16 arom. CH); 132.2, 134.1 (2 arom. C of **3i**); 143.4, 150.3 (2 arom. C of **4o**); 219.9 (C=O of **4o**); 220.1 (C=O of **3i**). Anal. calc. for $C_{20}H_{22}OS_3$ (374.59): C 64.13 H 5.92 S 25.68; found: C 64.02 H 5.93 S 25.95.

6.2. *Reaction with* **2e**: *1,1,3,3-Tetramethyl-8-phenyl-8-(selenophen-2-yl)-5,7-dithiaspiro[3.4]octan-2-one* (**4p**; major) and *1,1,3,3-Tetramethyl-6-phenyl-6-(selenophen-2-yl)-5,8-dithiospiro[3.4]octan-2-one* (**3k**; minor); crude product ratio: 96:4. Reaction time: 6.5 h. The crude product was crystallized from CH_2Cl_2/MeOH. Yield: 420 mg (95%). Colorless crystals. M.p. 140.0–142.0°. IR (KBr): 1170*s* (C=O), 1443*m*, 1227*m*, 1164*w*, 1020*w*, 706*s*, 695*s*. ^{1}H-NMR ($CDCl_3$): 1.23, 1.25, 1.28, 1.31, 1.47, 1.61, 1.62, 1.71 (8*s*, 8 Me); 3.70–3.74 (*m*, CH_2 of **4p**); 3.78–3.92 (*m*, CH_2 of **3k**); 7.13–7.97 (*m*, 16 arom. H). ^{13}C-NMR ($CDCl_3$): 22.1, 22.5, 24.5, 24.8, 25.2, 25.5, 25.7, 25.8 (8 Me); 27.0 (H_2C(6) of **4p**); 52.1 (H_2C(7) of **3k**); 60.2, 65.4, 66.2, 69.7 (2 C(1), 2 C(3)); 67.1, 73.0, 76.1, 76.7 (C(4), C(8) of **4p**, C(4), C(7) of **3k**); 127.4, 127.5, 127.8,

128.0, 128.3, 128.4 (br.), 128.9, 129.1, 130.8 (br.), 130.9, 131.3, 131.7 (16 arom. CH); 140.8, 160.8, 143.5, 158.1 (4 arom. C); 219.7, 219.9 (2 C=O). Anal. calc. for $C_{20}H_{22}OS_2Se$ (421.49): C 56.99 H 5.26 S 15.21; found: C 56.55 H 5.12 S 15.17.

6.3. *Reaction with* **2h**: *1,1,3,3-Tetramethyl-8-(furan-2-yl)-8-(thiophen-2-yl)-5,7-dithiaspiro[3.4]octan-2-one* (**4q**; major) and *1,1,3,3-Tetramethyl-6-(furan-2-yl)-6-(thiophen-2-yl)-5,8-dithiospiro[3.4]octan-2-one* (**3l**; minor); crude product ratio: 91:9. Reaction time: 4 h. The crude product was purified by CC (CH_2Cl_2/hexane 4:6). Yield: 370 mg (96%). Yellow crystals. M.p. 130.0–132.4°. IR (KBr): 1784*s* (C=O), 1464*m*, 1381*s*, 1227*s*, 1130*m*, 1074*m*, 1027*s*, 1016*s*, 808*s*, 742*s*, 695*s*, 593*m*. ^{1}H-NMR ($CDCl_3$): 0.81, 1.24, 1.29, 1.34, 1.38, 1.45, 1.57, 1.59 (8*s*, 8 Me); 3.61–3.92 (*m*, CH_2 of **3l**); 3.86–3.90 (*m*, CH_2 of **4q**); 6.35–7.44 (*m*, 12 arom. H). ^{13}C-NMR ($CDCl_3$): 19.3, 22.1, 22.4, 23.3, 24.6, 24.7 28.3, 28.9 (8 Me); 29.1 ($H_2C(6)$ of **4q**); 50.6 ($H_2C(7)$ of **3l**); 65.6, 66.6, 67.0, 67.3 (2 C(1), 2 C(3)); 65.0, 67.2, 76.8, 77.3 (C(4), C(8) of **4q**, C(4), C(7) of **3l**); 109.1, 110.4, 111.6, 112.0, 125.3, 125.7, 126.0, 126.2, 126.4, 126.8, 140.8, 142.4 (12 arom. CH); 146.8, 148.1, 155.0, 152.2 (4 arom. C); 219.4, 219.7 (2 C=O). Anal. calc. for $C_{18}H_{20}O_2S_3$ (364.55): C 59.31 H 5.53 S 26.39; found: C 58.93 H 5.19 S 26.04.

6.4. *Reaction with* **2f**: *1,1,3,3-Tetramethyl-8,8-bis(thiophen-2-yl)-5,7-dithiaspiro[3.4]octan-2-one* (**4r**). The reaction was complete after 2 h. The solvent was evaporated, and the crude product was purified by CC (CH_2Cl_2/hexane 4:6). Yield: 320 mg (81%). Colorless crystals. M.p. 140.6–141.5°. IR (KBr): 1774*s* (C=O), 1630*w*, 1385*w*, 1234*m*, 710*s*. ^{1}H-NMR ($CDCl_3$): 1.45, 1.64 (2*s*, 4 Me); 3.80 (*s*, CH_2,); 6.94–6.95 (*m*, 2 arom. H); 7.24–7.25 (*m*, 2 arom. H); 7.29–7.30 (*m*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 24.1, 26.5 (4 Me); 28.3 ($H_2C(6)$); 67.0 (C(1), C(3)); 70.1, 76.6 (C(4), C(8)); 125.7, 126.3, 127.8 (6 arom. CH); 148.2 (2 arom. C); 219.5 (C=O). Anal. calc. for $C_{18}H_{20}OS_4$ (380.62): C 56.80 H 5.30 S 33.70; found: C 57.02 H 5.52 S 33.68.

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

6.5. *Reaction with* **2g**: *1,1,3,3-Tetramethyl-8,8-bis(selenophen-2-yl)-5,7-dithiaspiro[3.4]octan-2-one* (**4s**). The reaction was complete after 4 h. The crude product was crystallized from MeOH. Yield: 323 mg (85%). Pale yellow crystals. M.p. 157.0–158.0° (MeOH). IR (KBr): 1770*s* (C=O), 1442*m*, 1383*m*, 1232*s*, 1012*m*, 808*m*, 696*s*. ^{1}H-NMR ($CDCl_3$): 1.45, 1.63 (2*s*, 4 Me); 3.86 (*s*, CH_2); 7.17–7.18 (*m*, 2 arom. H); 7.37–7.38 (*m*, 2 arom. H); 7.95–7.96 (*m*, 2 arom. H). ^{13}C-NMR ($CDCl_3$): 24.4, 26.8 (4 Me); 28.9 (H_2C(6)); 66.9 (C(1), C(3)); 74.2, 76.5 (C(4), C(8)); 129.0, 129.2, 132.4 (6 arom. CH); 156.6 (2 arom. C); 219.4 (C=O). Anal. calc. for $C_{18}H_{20}OS_2Se_2$ (474.41): C 45.57 H 4.25 S 13.52; found: C 45.84 H 4.32 S 13.55.

7. *Competition Experiments.* – a) *Bis(thiophen-2-yl)methanethione* (**2f**) *versus 9*H- *Fluorene-9-thione* (**2c**) *with 2,5-Dihydro-2,2-diphenyl-1,3,4-thiadiazole* (**5b**). A soln. of thiobenzophenone (**2b**, 1 mmol) in 2 ml of THF was cooled to –70° and treated with small portions of a soln. of CH_2N_2 in Et_2O, until the dark-blue color disappeared. Then, equimolar amounts of **2f** (1 mmol) and **2c** (1 mmol) dissolved in 3 ml of THF were added at –70° and the mixture was kept at –45° to –40° (acetone/dry ice bath) for 2 h. After that time the soln. was allowed to warm slowly to r.t. and kept at r.t. for *ca.* 30 min, and then the solvent was evaporated. The residue was subjected to ^{1}H-NMR analysis in $CDCl_3$ with a weighed amount of 1,1,2,2-tetrachloroethane as standard. The only observed product was the known 5,5'-diphenylspiro[9*H*-fluorene-9,4'-[1,3]dithiolane] [3b]. Yield: 99% (^{1}H NMR).

b) *Bis(thiophen-2-yl)methanethione* (**2f**) *versus Thiobenzophenone* (**2b**) *with* **5b**. In analogy to the procedure described above, a soln. of **2b** (0.57 mmol) in 2 ml of THF at –70° was treated with an ethereal CH_2N_2 soln., followed by a soln. of **2f** (0.57 mmol)

and **2c** (0.57 mmol) in 3 ml of THF. The mixture was stirred at –45° to –40° for 2 h and then allowed to warm slowly to r.t. After 30 min. at r.t., the solvent was evaporated and the residue was subjected to ^{1}H-NMR analysis ($CDCl_3$, 1,1,2,2-tetrachloroethane as standard). The crude product was identified as a mixture of the known 4,4,5,5-tetraphenyl-1,3-dithiolane [3b] (40%) and 5,5-diphenyl-4,4-bis(thiophen-2-yl)-1,3-dithiolane (**4f**) (29%, ^{1}H NMR).

8. *X-Ray Crystal Structure Determination of* **4r** (*Table* and *Figure*)[2]). All measurements were made on an *Agilent Technologies SuperNova* area-detector diffractometer [14] using Mo$K\alpha$ radiation (λ = 0.71073 Å) from a micro-focus X-ray source and an *Oxford Instruments Cryojet XL* cooler. Data reduction was performed with *CrysAlisPro* [14]. The intensities were corrected for *Lorentz* and polarization effects, and an empirical absorption correction using spherical harmonics [14] was applied. Equivalent reflections, other than *Friedel* pairs, were merged. The data collection and refinement parameters are given in the *Table*. A view of the molecule is shown in the *Figure*. The structure was solved by direct methods using *SHELXS-2013* [15], which revealed the positions of all non-H-atoms. There are two symmetry-independent molecules in the asymmetric unit. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher symmetry space group using the program *PLATON* [16], but none could be found. Both molecules show disorder of both thiophene rings due to 180° rotation of each ring around its parent C–C bond which swaps the positions of the S- and C-atoms in the 2,5-positions of the ring.

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[2]) CCDC-1052007 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre*, *via* www.ccdc.cam.ac.uk/data_request/cif.

Two positions were defined for these S- and C-atoms in each disordered ring and the site occupation factors of the major orientations of these rings refined to 0.680(4) and 0.845(3) in molecule A and 0.954(3) and 0.794(3) in molecule B. Similarity restraints were applied to the chemically equivalent bond lengths involving all disordered S- and C-atoms. In addition, the bond lengths involving disordered C-atoms were restrained to 1.40(1) Å. Neighboring disordered atoms between each orientation of the disordered thiophene rings were restrained to have similar atomic displacement parameters. One thiophene ring was additionally restrained to be planar. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent C-atom ($1.5U_{eq}$ for the Me groups). The refinement of the structure was carried out on F^2 by using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. A correction for secondary extinction was not applied. Refinement of the absolute structure parameter [17] yielded a value of 0.01(1), which confidently confirms that the refined model represents the true absolute structure. Neutral atom scattering factors for non-H-atoms were taken from [18a], and the scattering factors for H-atoms were taken from [19]. Anomalous dispersion effects were included in F_c [20]; the values for f' and f'' were those of [18b]. The values of the mass attenuation coefficients are those of [18c]. The *SHELXL-2014* program [21] was used for all calculations.

Table. *Crystallographic Data for Compound* **4r**

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Table. *Crystallographic Data for Compound* **4r**

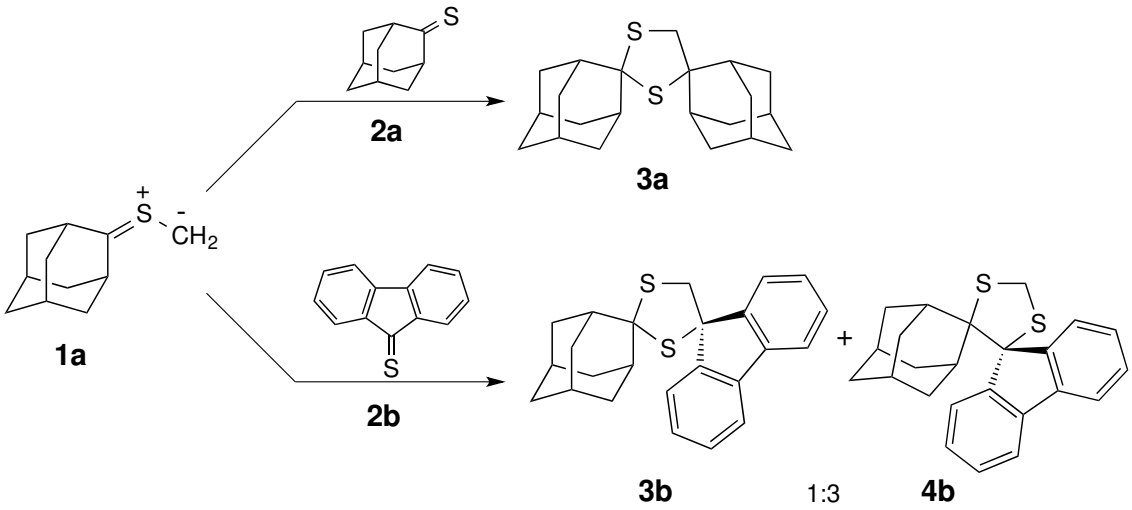
Crystallized from		MeOH
Empirical formula		$C_{18}H_{20}OS_4$
Formula weight [g mol^{-1}]		380.60
Crystal color, habit		colorless, prism
Crystal dimensions [mm]		0.23 × 0.24 × 0.37
Temperature [K]		160(1)
Crystal system		monoclinic
Space group		$P2_1$
Z		4
Reflections for cell determination		14706
2θ range for cell determination [°]		5–60
Unit cell parameters	a [Å]	8.69316(11)
	b [Å]	12.82765(15)
	c [Å]	15.94089(19)
	β [°]	90.7785(11)
	V [Å^3]	1777.45(4)
D_X [g cm^{-3}]		1.422
μ(Mo$K\alpha$) [mm^{-1}]		0.535
Scan type		ω
$2\theta_{(max)}$ [°]		60.9
Transmission factors (min; max)		0.932; 1.000
Total reflections measured		23111
Symmetry independent reflections		9322
Reflections with $I > 2\sigma(I)$		8753
Reflections used in refinement		9322
Parameters refined; restraints		499; 319
Final $R(F)$ [$I > 2\sigma(I)$ reflections]		0.0301
$wR(F^2)$ (all data)		0.0708
Weights:	$w = [\sigma^2(F_o^2) + (0.0314P)^2 + 0.4989]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$	
Goodness of fit		1.039
Final Δ_{max}/σ		0.001
$\Delta\rho$ (max; min) [e Å^{-3}]		0.55; –0.43

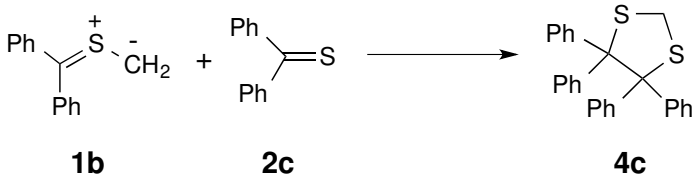
Legends

Figure. *ORTEP plot* [9] *of the molecular structure of one of the two symmetry-independent molecules of* **4r** (with 50% probability ellipsoids; arbitrary numbering of the atoms; only the major conformations of the disordered thiophene rings are shown).

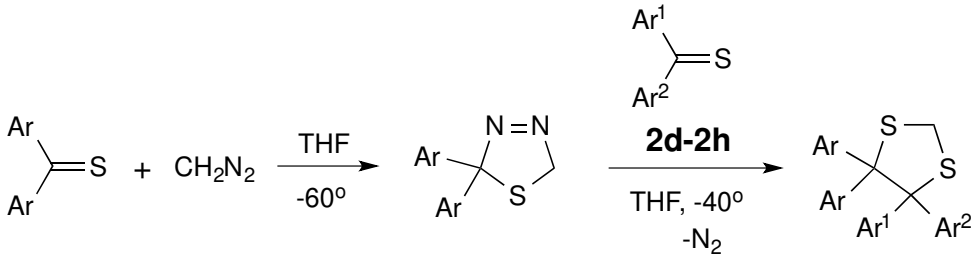
Table. *Crystallographic Data for Compound* **4r**

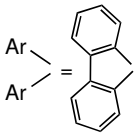
Scheme 1

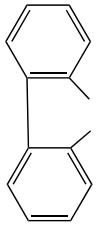
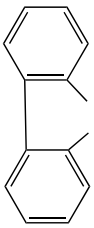

S
2a
S
S
3a
+
S
-
CH2
1a
S
2b
S
S
3b
1:3
S
S
4b


Ph
+
S
-
CH2
Ph
1b
Ph
S
Ph
2c
S
Ph
S
Ph
Ph
Ph
4c

Scheme 2



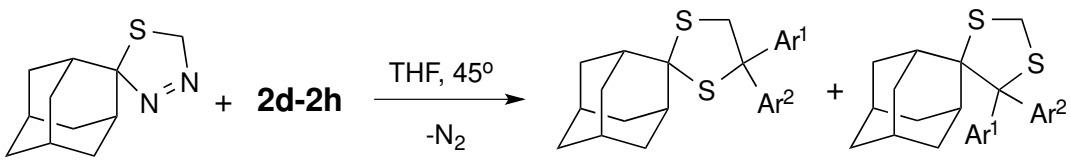
b: Ar = Ph; **c**: 

5	**2** Ar^1 Ar^2	**4** Ar Ar^1 Ar^2	Yield (%)
b Ar = Ph	**d** Ph Thiophen-2-yl	**d** Ph Ph Thiophen-2-yl	79[a]) (77)[b])
	e Ph, Selenophen-2-yl	**e** Ph Ph Selenophen-2-yl	88 (70)
	f Thiophen-2-yl Thiophen-2-yl	**f** Ph Thiophen-2-yl Thiophen-2-yl	82 (76)
	g Selenophen-2-yl Selenophen-2-yl	**g** Ph Selenophen-2-yl Selenophen-2-yl	66 (58)
c Ar, Ar = 	**f** Thiophen-2-yl Thiophen-2-yl	**h** Thiophen-2-yl Thiophen-2-yl 	(70)

[a]) Yields determined by ^{1}H-NMR with a weighed amount of 1,1,2,2-tetrachloroethane as a standard

[b]) Yields of isolated product

Scheme 3



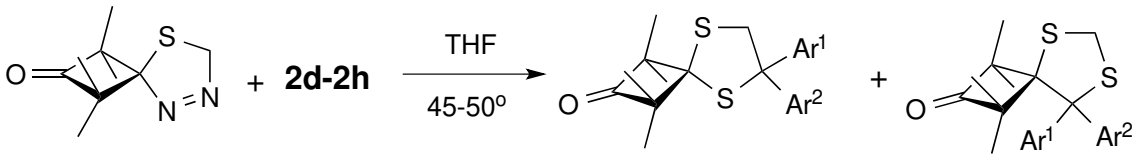
5a **3d-3h** **4i-4n**

2	Ar^1	Ar^2	Yield (%)[a]		Yield (%)[b]
			3	**4**	
d	Ph	Thiophen-2-yl	**d** 23	**i** 70	82
e	Ph	Selenophen-2-yl	**e** 21	**k** 71	80
f	Thiophen-2-yl	Thiophen-2-yl	**f** 16	**l** 75	76
g	Selenophen-2-yl	Selenophen-2-yl	**g** 22	**m** 63	64
h	Thiophen-2-yl	Furan-2-yl	**h** 21	**n** 70	86

[a]) Yields determined by ^{1}H-NMR with a weighed amount of 1,1,2,2-tetrachloroethane as a standard

[b]) Yields of isolated products (as mixtures of **3** and **4**)

Scheme 4



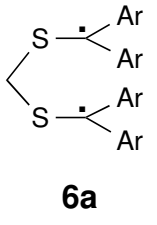
5d **3i-e** **4o-s**

2	Ar^1	Ar^2	Yield (%)[a]		Yield (%)[b]
			3	**4**	
d	Ph	Thiophen-2-yl	**i** 13	**o** 84	94
e	Ph	Selenophen-2-yl	**k** 8	**p** 91	95
h	Thiophen-2-yl	Furan-2-yl	**l** 6	**q** 91	96
f	Thiophen-2-yl	Thiophen-2-yl	**-**	**r** 83	81
g	Selenophen-2-yl	Selenophen-2-yl	**-**	**s** 95	85

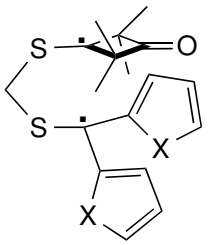
[a]) Yields determined by ^{1}H-NMR with a weighed amount of 1,1,2,2-tetrachloroethane as a standard

[b]) Yields of isolated products (as mixtures of **3** and **4** or as pure compounds **4r** and **4s**)

Formulae

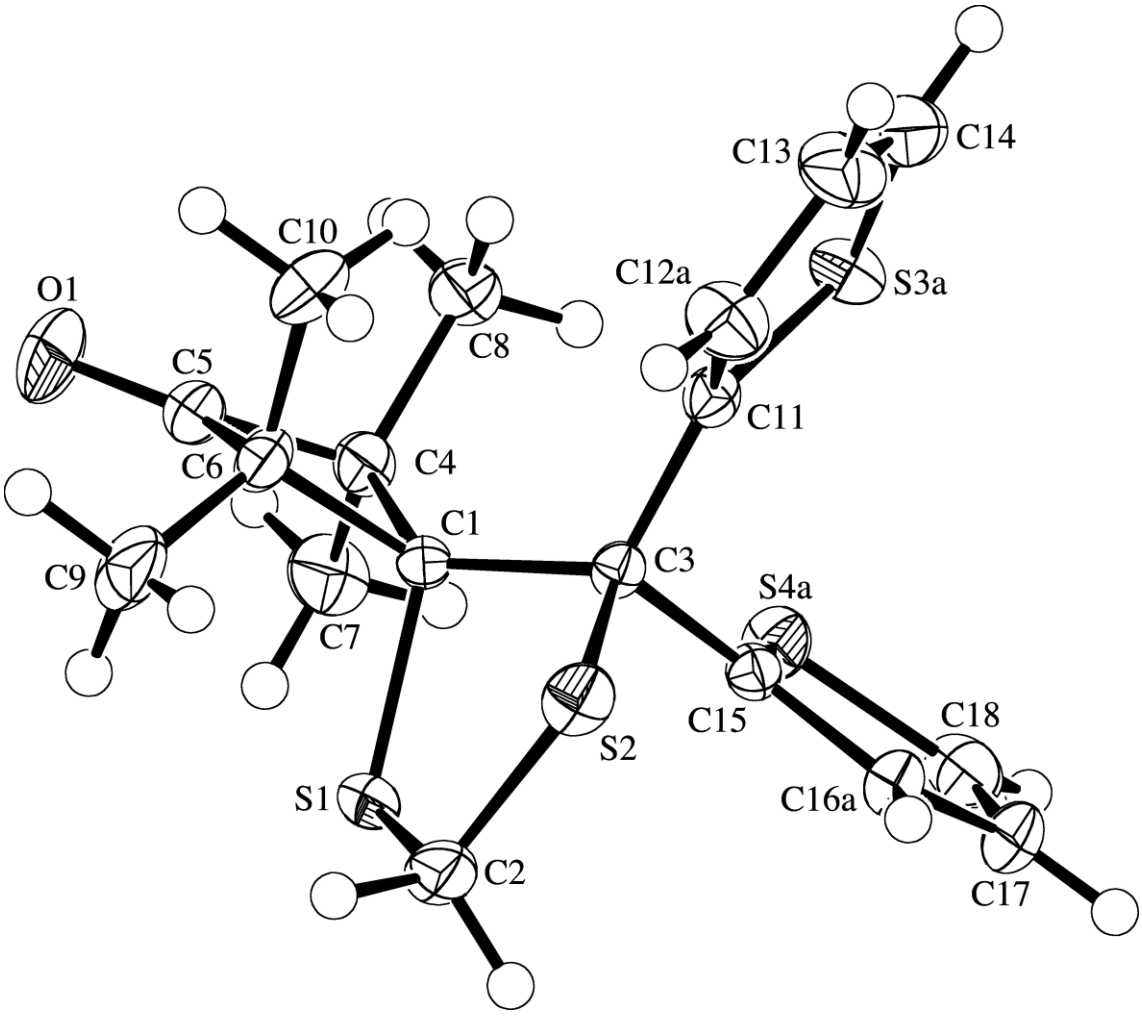


6a



6b X = Se, S

Figure



Graphical Abstract