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# Reactions of 9*H*-Fluorene-9-thione with (Trimethylsilyl)-diazomethane*

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*Dedicated to Prof. Jacek Młochowski on the occasion of his 70th birthday*

The [3+2]-cycloaddition of (trimethylsilyl)diazomethane (**7**) with 9*H*-fluorene-9-thione (**1**) at –60°C yields the spirocyclic 2,5-dihydro-5-trimethylsilyl-1,3,4-thiadiazole **10**, which eliminates nitrogen at room temperature to give the 1,4-dithiane derivative **13** by dimerization of the intermediate fluorenethione (trimethylsilyl)methanide (**11**). This thiocarbonyl ylide can be trapped by **1** to give the 2-trimethylsilyl-1,3-dithiolane **14** via [3+2]-cycloaddition. Furthermore, the 1,3-dipole **11** undergoes successfully [3+2]-cycloadditions with the C=S group of the phosphonyldithioformate **15** as well as with the C=C dipolarophiles maleic anhydride (**18a**) and *N*-(cyclohexyl)maleimide (**18b**). The structures of **13** and **14** have been established by X-ray crystallography.

**Key words**: 1,3-dipolar cycloaddition, thiocarbonyl ylides, diazo compounds, 1,4-dithianes, 1,3-dithiolanes

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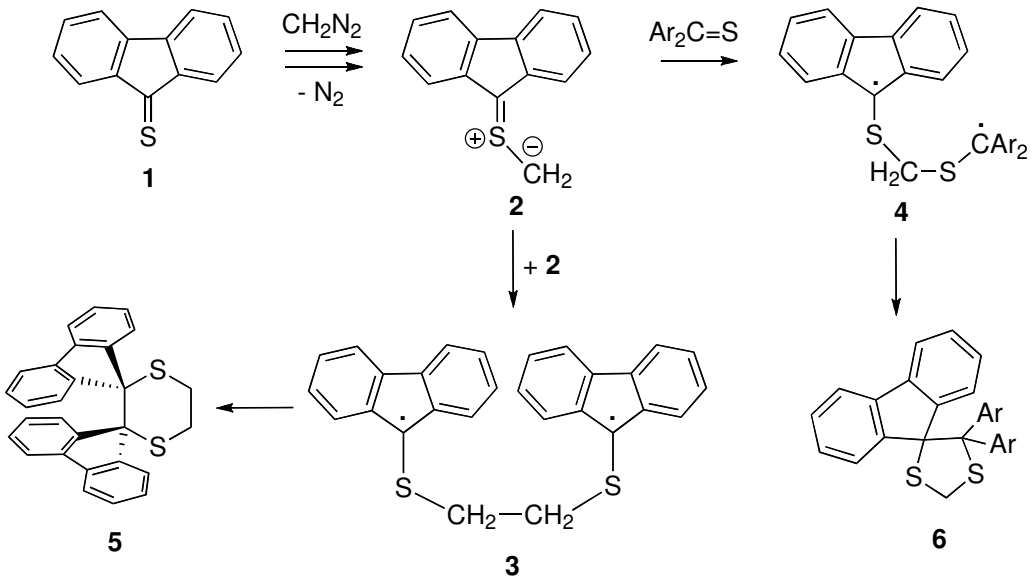
Aromatic thioketones are known as versatile starting materials for the synthesis of sulfur-containing heterocycles [1,2]. Especially important are cycloaddition reactions leading to five- or six-membered products, in which aromatic thioketones act as excellent dipolarophiles and dienophiles, respectively[***]. [2+3]-Cycloadditions with diazomethane and its derivatives yield regioselectively 2,5-dihydro-1,3,4-thiadiazoles, which spontaneously eliminate $N_2$ below 0°C, and thiocarbonyl ylides were identified as reactive intermediates. Depending on the reaction conditions, the latter undergo 1,3-dipolar electrocyclization to give thiiranes, head-to-head dimerization yielding 1,4-dithianes, or react with a suitable dipolarophile to afford five-membered heterocycles [5,6].

Numerous studies showed that among aromatic thioketones, 9*H*-fluorene-9-thione (thiofluorenone, **1**) is most reactive in cycloaddition reactions [3,4]. The regioselectivity observed in the dimerization of thiofluorenone *S*-methylide (**2**) and in [2+3]-cycloadditions with aromatic thioketones is plausibly rationalized by the formation of intermediate 1,6- (**3**) and 1,5-biradicals, (**4**) respectively [7], which cyclize to yield 1,4-dithiine **5** or 1,3-dithiolanes **6** [8] (Scheme 1).

**Scheme 1**



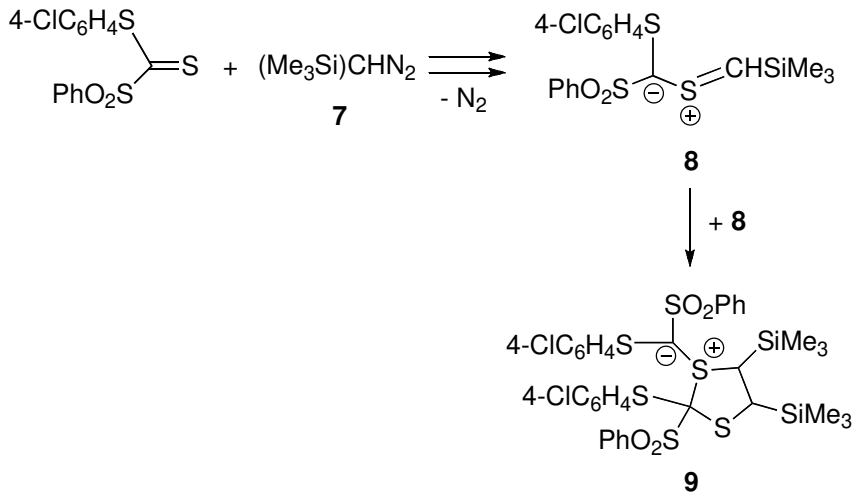

*** Aromatic thioketones are called ‘superdipolarophiles’ (Huisgen [3]) and ‘superdienophiles’ (Sauer [4])

The reactivity of the diazo compound depends on the type of substituents; *e.g.*, diazomethane reacts with **1** already at –78°C [8], and in the case of methyl diazoacetate the reaction occurs only at 20°C [9]. Similarly, the reaction of **1** with 2-diazo-1-phenylethanone was performed at room temperature, and $N_2$ was eliminated instantenously leading to the corresponding (1,3-dithiolan-2-yl)(phenyl)methanone [10]. Sterically hindered diazo compounds are less reactive in [2+3]-cycloadditions, and in some instances, the initially formed 1,3,4-thiadiazole derivatives undergo the cycloreversion without evolution of $N_2$ [11].

(Trimethylsilyl)diazomethane ($TMSCHN_2$, **7**) is well known as a safe and relatively stable analogue of diazomethane. On the other hand, it is a reactive 1,3-dipole [12a] and a useful source of trimethylsilylmethylene in cyclopropanation reactions [12b]. Its synthetic application also includes conversions of the carbanion, which is easily generated by treatment with strong bases [12c]. Subsequent desilylation of the products offers the possibility to use **7** as a synthetic equivalent of diazomethane. Surprisingly little is known about reactions of **7** with thiocarbonyl compounds. To the best of our knowledge, there are only three papers reporting on reactions of non-deprotonated $TMSCHN_2$ with compounds containing the C=S group. For example, treatment of di(*tert*-butyl)thioketone with **7** at 0°C gave a product, which upon heating *in vacuo* was converted into 2,2-bis(*tert*-butyl)-3-trimethylsilyl)thiirane [13].

Reactions of **7** with C-sulfonylated dithioformates were carried out at –78°C. Subsequent warming to room temperature resulted in the formation of a transient thiocarbonyl ylide **8**, which dimerizes to give the zwitterion **9** [14] (Scheme 2). The detailed mechanism of this dimerization is not known to date.

**Scheme 2**



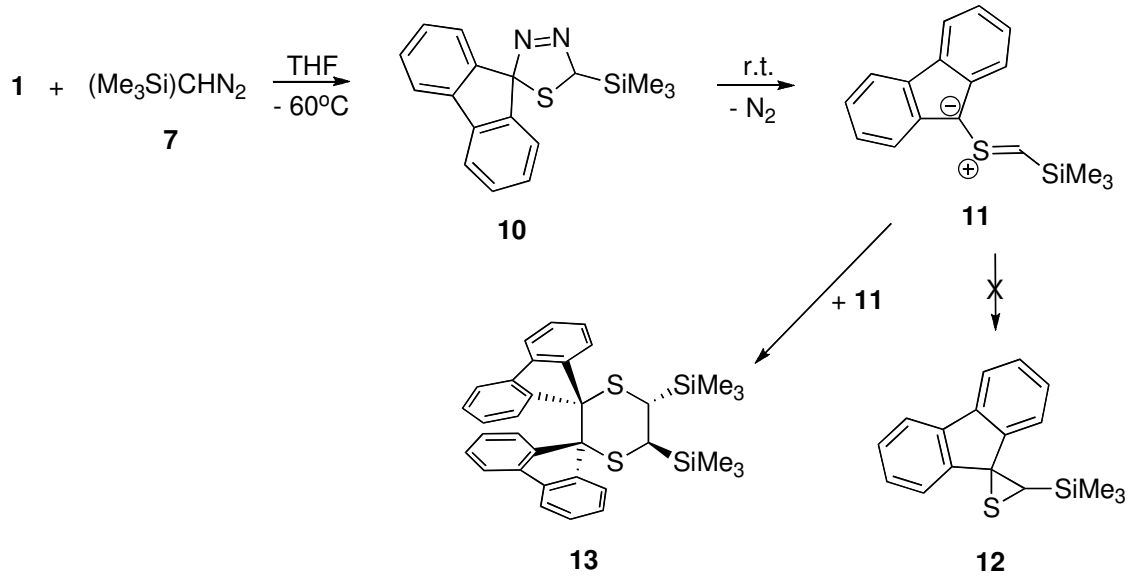

Depending on the substitution pattern of the aromatic ring of the intermediate **8**, an intramolecular cyclization of the thiocarbonyl ylide can occur [15].

The aim of the present study was to examine reactions of **7** with thiofluorenone (**1**), the most reactive thioketone.

## RESULTS AND DISCUSSION

Addition of an equimolar amount of **7** to a solution of **1** in THF at –60°C resulted in immediate disappearance of the green color without release of $N_2$. During slow warming of the mixture to room temperature, the evolution of $N_2$ was observed. After typical workup, the crude product was examined by $^1$H-NMR spectroscopy, which revealed the presence of only one product with characteristic singlets at 3.75 ppm for CH and at 0.31 ppm for $Me_3Si$. The aromatic H-atoms absorb as broad multiplets at 6.18–7.62 and 9.20–9.22 ppm in a ratio of 7:1. The comparison of the integrals of the signals led to the assumption that the stoichiometry of the formation of the product from **1** and **7** is 1:1. The CI-MS showed the base peak at m/z 565, which corresponds to the $[M+1]^+$ peak of the dimer of the expected silylated thiocarbonyl ylide **11** (Scheme 3).

**Scheme 3**




Obviously, the dimerization of **11** is much faster than the alternative 1,3-dipolar electrocyclization leading to the thiirane **12**. In contrast, other thiocarbonyl ylides derived from aromatic thioketones, which are substituted at the methanide terminus (Ph or Me), undergo the 1,3-dipolar electrocyclization [8,16].

In order to establish the structure of the dimer, an X-ray single-crystal analysis was carried out. It turned out that the dimerization proceeded in a head-to-head fashion, and the two bulky $Me_3Si$ groups located at C(2) and C(3) are *trans* configured (Figure 1).

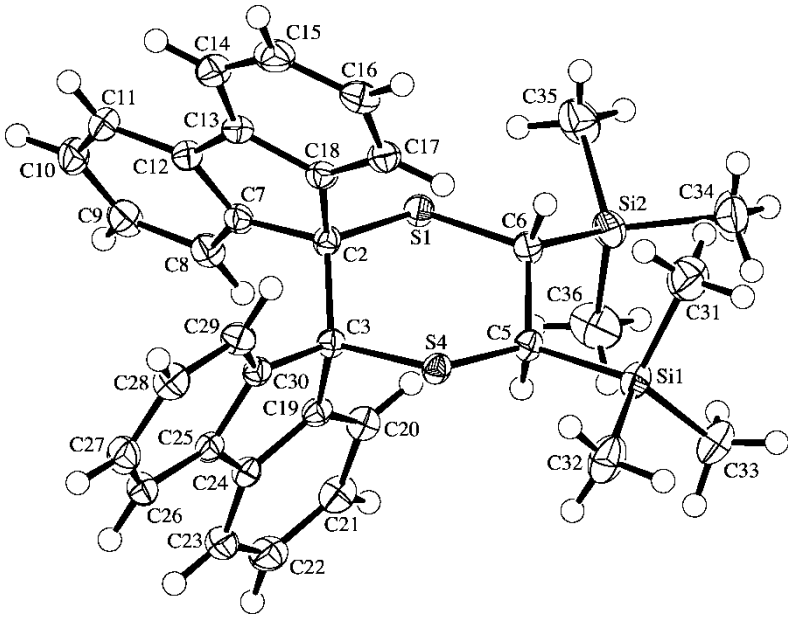


**Figure 1**. ORTEP-Plot [17] of the molecular structure of **13** (50% probability ellipsoids, arbitrary numbering of atoms)

This result shows that the dimerization of thiocarbonyl ylide **11** occurs analogously to that of the parent dipol **2** (Scheme 1) and yields the sterically more crowded product. Thus, the intermediacy of the diradical of type **3** is very likely and corresponds to the generally observed pathway for the dimerization of thiocarbonyl ylides (cf. [18]).

When the decomposition of **10** was carried out in THF solution and in the presence of **1**, the intermediate ylide **11** was trapped by the thioketone to afford the 1,3-dithiolane **14** (Scheme 4). The [2+3]-cycloaddition is very fast, and the dimerization of **11** is completely suppressed ($^1$H-NMR). Furthermore, the presence of only one signal for $CHSiMe_3$ as well as for $Me_3Si$ evidenced the formation of only one regioisomer. Again, the structure of **14** was unambigously established by X-ray crystallography (Figure 2).

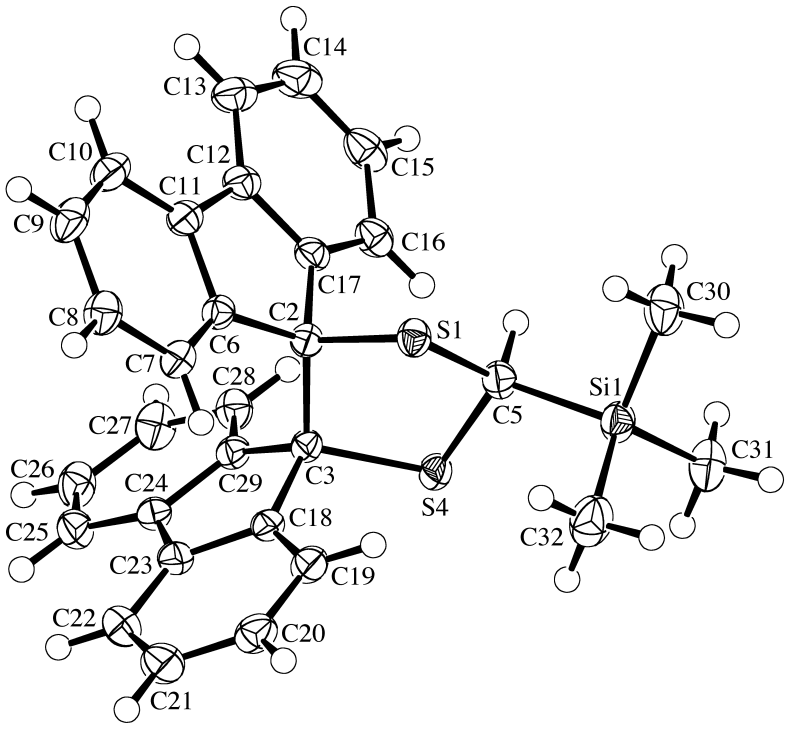
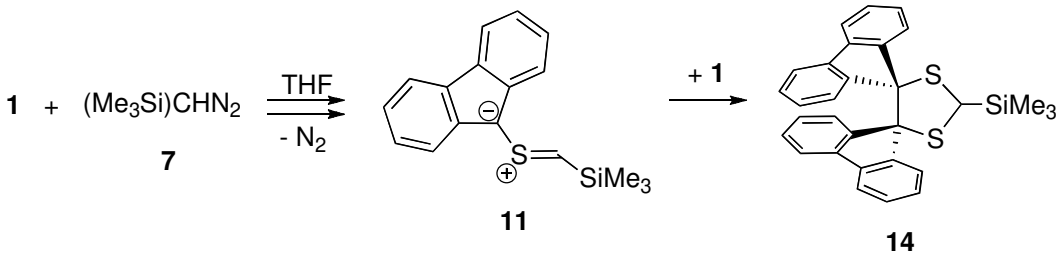



**Figure 2**. ORTEP-Plot [17] of the molecular structure of **14** (50% probability ellipsoids, arbitrary numbering of atoms)

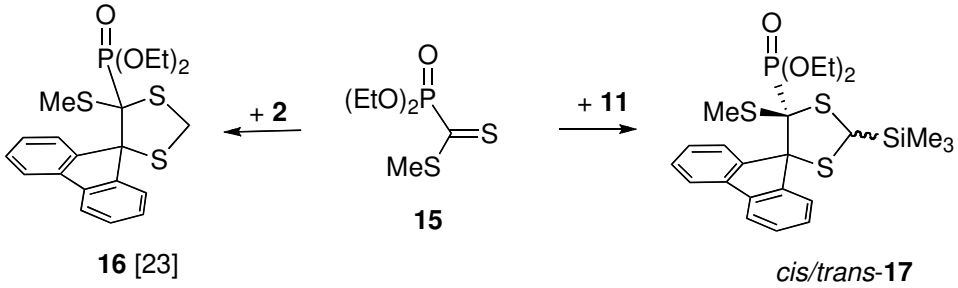
**Scheme 4**




The formation of sterically crowded 1,3-dithiolanes from aromatic thioketones and their *S*-methylides was established independently by *Bergmann* et al. [19] and *Schönberg* et al. [20] in 1930/31. The mechanism of the reaction was elucidated by *Huisgen* and coworkers some 50 years later [21] (see also [8]). Recently published results of computational studies show that the mechanism of this [2+3]-cycloaddition can be explained by the assumption of a biradical intermediate of type **4** [22] (see also [7]) (Scheme 1).

Another dipolarophile with an active C=S bond, which was included in this study, was the phosphonylated diithioformate **15**. In a recent study, thiofluorenone *S*-methylide (**2**) was efficiently trapped with **15** to give the sterically more crowded 1,3-dithiolane **16** [23]. The generation of the thiocarbonyl ylide **11** in the presence of **15** led to a mixture of two isomeric 1,3-dithiolanes, which show similar chemical shifts for the absorption of C*H*$SiMe_3$ (4.35 and 4.41ppm) in a ratio of 1:2. Based on the earlier described results [23], we propose that both products are of the 'more crowded' type **17** and differ by their relative configuration, *i.e.*, they are *cis*/*trans*-isomers (Scheme 5). The mixture of the two isomers could not be separated by column chromatography nor by layer chromatography.

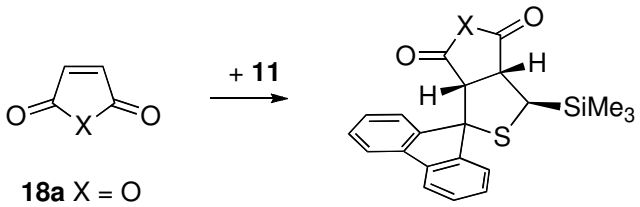
**Scheme 5**




**16** [23] **15** *cis/trans*-**17**

Along with C=S dipolarophiles, maleic anhydride (**18a**) and *N*-(cyclohexyl)maleimide (**18b**) were tested in reactions with **11**. In both cases, the expected [2+3]-cycloadducts **19** were obtained in good yields (Scheme 6). The analysis the $^1$H-NMR spectra indicated the formation of only one stereoisomer in each case (only one $Me_3Si$ signal). Tentatively, the relative configuration of the trimethylsilyl group has been assigned *exo*, but no convincing proof is available so far.

**Scheme 6**




**18a** X = O
**b** X = $NC_6H_{11}$

**19a** X = O
**b** X = $NC_6H_{11}$

Tetracyanoethylene (TCNE) and dimethyl acetylenedicarboxylate (DMAD) are frequently used for the interception of thiocarbonyl ylides [5,6]. In the case of **11**, TCNE reacted efficiently with the intermediate, and no dimer **13** was detected in the NMR spectra of the mixture. However, spontaneous decomposition of the product was observed during attempted chromatographic purification. On the other hand, the experiment carried out with DMAD resulted in the formation of the dimer **13**, which indicates that this dipolarophile is not reactive enough to trap **11**.

In conclusion, the 'superdipolarophilic' fluorenethione (**1**) easily reacts with $TMSCHN_2$ (**7**) at low temperature, and the [2+3]-cycloadduct formed in this reaction can be used as a convenient source of the novel silylated thiocarbonyl ylide **11**. The

reactivity of the latter is in part comparable with that of thiofluorenone *S*-methylide (**2**), *e.g.*, with respect to the dimerization or the interception with very reactive C=S dipolarophiles. However, its reactivity towards C,C-dipolarophiles is reduced compared with **2**. These results show that $TMSCHN_2$ can replace $CH_2N_2$ in the procedure aimed at the generation of the corresponding thiocarbonyl ylide, but the advantages are limited to the handling of a safer reagent.

## EXPERIMENTAL

**1. General**. Melting points were determined in a capillary using a MEL-TEMP II apparatus (*Aldrich*) and are uncorrected. The IR spectra were recorded with a FT-IR NEXUS instrument as KBr pellets or as films, and the position of absorption bands are given in $cm^{-1}$. The $^1$H-NMR, $^{13}$C-NMR and $^{31}$P-NMR spectra were recorded on a BRUKER-AC-300 ($^1$H at 300 MHz, $^{13}$C at 75 MHz and $^{31}$P at 121 MHz) instrument in $CDCl_3$ solutions using TMS ($\delta$ = 0 ppm) as an internal standard; chemical shifts ($\delta$) in ppm. The $^{13}$C-NMR spectra were recorded by using DEPT registration. The CI-MS and ESI-MS spectra were registered with a Finnigan-TSQ-700 triple quadrupole instrument (CI-MS; with $NH_3$) and an Esquire-LC-00028 instrument, respectively; *m/z* (rel. %). Elemental analyses were performed in the Analytical Laboratory of the University of Zurich.

**2. Starting material:** 9*H*-Fluorene-9-thione (**1**) was prepared by thionation of the commercial 9*H*-fluoren-9-one in MeOH solution with a mixed stream of $H_2S$ and HCl [24]. (Trimethylsilyl)diazomethane was used as a commercial reagent from *Sigma-Aldrich* as a 2 M solution in diethyl ether. Methyl(diethoxy)phosphonyldithioformate (**15**) was prepared from diethyl phosphite and carbon disulfide by following a known protocol [25]. *N*-(Cyclohexyl)maleimide (**18b**) was synthesized according to [26]. Maleic anhydride (**18a**) was purchased from *Sigma-Aldrich* and used without further purification.

**3. Reaction of 9*H*-fluorenone-9-thione (1) with (trimethylsilyl)diazomethane (7)**. A solution of **1** (196 mg, 1 mmol) in dry THF (1 ml) was placed in a flask equipped with a magnetic stirring bar. The solution was cooled in an acetone/dry ice bath to –65°C. While stirring, a solution of (trimethylsilyl)diazomethane in diethyl ether was added drop-wise until the green color of the starting material disappeared completely (step-wise decolorization of the mixture was observed after each drop of added solution

of diazocompound). The mixture was stirred and allowed to warm to room temperature. Elimination of $N_2$ was observed at ca. –45°C. The solvent was evaporated and the oily residue was purified by crystallization.

*Dispiro[*trans-*5,6-bis(trimethylsilanyl)-1,4-dithiane-2,9',3,9''-bis(fluorene)]* (**13**; 150 mg, 53%). Colorless crystals (MeOH/$CH_2Cl_2$ or hexane/$CH_2Cl_2$), m.p. 282–286°C (decomp.). IR (KBr): 3058*m*, 2952*m*, 2892*m*, 1635*m*, 1618*m*, 1445*s*, 1252*s*, 856*vs*, 841*vs*, 736*vs*, 670*m*, 654*m*. $^1$H-NMR: 9.22–9.20 (*m*, 2 arom. H); 6.62–7.18 (*m*, 14 arom. H); 3.76 (*s*, 2 CHSi); 0.31 (*s*, 2 $Me_3Si$). $^{13}$C-NMR: 150.0, 144.8, 140.5, 139.9 (8 arom. $C_q$); 128.2, 128.1, 126.5, 126.3, 125.5, 120.2, 119.2 (16 arom. CH); 54.8 (2 $C_q$); 29.9 (2 CHSi); 0.40 (2 $Me_3Si$). CI-MS ($NH_3$): 567 (27), 566 (51), 565 (100, $M^{+\cdot}$), 361 (13), 349 (16), 348 (55), 330 (12), 329 (38), 197 (9), 180 (7), 90 (32). Anal. Calcd for $C_{34}H_{36}S_2Si_2$ (564.96): C 72.28, H 6.42, S 11.35; found: C 72.64, H 6.51, S 11.60.

Suitable crystals for an X-ray crystal structure determination were obtained after crystallization from hexane/$CH_2Cl_2$ mixture.

**4. Reactions of 11 with dipolarophiles 1, 15, 18a, and 18b; general procedure**. A solution of **1** (196 mg, 1 mmol) in dry THF (1 ml) was placed in a flask equipped with a magnetic stirring bar. The solution was cooled in an acetone/dry ice bath to –65°C. While stirring, a solution of (trimethylsilyl)diazomethane in diethyl ether was added drop-wise until the green color of the starting material disappeared completely (step-wise decolorization of the mixture was observed after each drop of added solution of diazocompound). After decolorization, 1 mmol of the corresponding dipolarophile was added to the mixture at –65°C and the magnetically stirred solution was allowed to warm to room temperature. Elimination of $N_2$ was observed at ca. –45°C. The solvent was evaporated and the crude products were purified either by crystallization or chromatographically on a column packed with silica gel.

*Dispiro[2-trimethylsilanyl-1,3-dithiolane-4,9',5,9''-bis(fluorene)]* (**14**). Reaction with 9*H*-fluorene-9-thione (**1**); yield of **14**: 380 mg (80%). Colorless crystals (hexane/$CH_2Cl_2$); m.p. 257–260°C (decomp.). IR (KBr): 3060*m*, 2953*m*, 2856*m*, 1636*m*, 1603*m*, 1445*s*, 1251*s*, 1157*m*, 1034*m*, 856*s*, 841*s*, 740*vs*, 651*m*, 634*w*. $^1$H-NMR: 7.77–7.03 (*m*, 16 arom. H); 4.72 (*s*, CHSi); 0.38 (*s*, $Me_3Si$). $^{13}$C-NMR: 144.9, 144.6, 140.4, 140.1 (8 arom. $C_q$); 128.6, 128.5, 127.6, 126.8, 126.7, 126.6, 119.8, 119.4 (16 arom. CH); 75.3 (2 $C_q$); 37.1 (CHSi); –1.3 ($Me_3Si$). CI-MS ($NH_3$): 496 (11, $[M+NH_4]^+$), 479 (21, $[M+1]^+$), 348 (32), 330 (29), 329 (100), 328 (16), 282 (19), 197 (57), 165 (10), 151 (13), 90 (81).

Anal. Calcd for $C_{30}H_{26}S_2Si_2$ (478.75): C 75.26, H 5.47, S 13.40; found: C 74.96, H 5.45, S 13.17.

Suitable crystals for an X-ray crystal structure determination were obtained after crystallization from hexane/$CH_2Cl_2$ mixture.

*Diethyl 2-trimethylsilanyl-5-(methylsulfanyl)spiro[1,3-dithiolane-4,9'-[9*H*]fluorene]-5-phosphonate* (mixture of *cis*/*trans*-**17**). Reaction with methyl [(diethoxy)phosphonyl]dithioformate (**15**); yield of **17**: 350 mg (73%). Yellow oil, after purification by column chromatography (hexane/AcOEt 3.5:1.5 as the eluent). IR (film): 2979*s*, 2959*s*, 2925*s*, 2864*m*, 1717*m*, 1474*m*, 1447*s*, 1390*m*, 1281*s* (P=O), 1248*s* (P=O), 1163*m*, 1100*s* (P-O-C), 1050*s* and 1028*s* (P-O-C), 973*s*, 843*s*, 739*s*. $^1$H-NMR*: 8.29, 8.08 (2*d*, $J \approx 6$, 2 arom. H (minor)); 8.22, 8.18 (2*d*, $J \approx 6$, 2 arom. H (major)); 7.69 (*t*-like, $J \approx 5$, 2 arom. H (minor)); 7.59, 7.56 (2*d*, $J \approx 5$, 2 arom. H (major)); 7.41–7.18 (*m*, 4 arom. H); 4.41, 4.35 (2*s*, ratio *ca*. 2:1, H-C(2')); 3.88–3.37 (*m*, 2 MeC*H*$_2$O); 2.48, 2.38 (2*s*, ratio *ca*. 1:2, MeS); 1.21, 0.94, 0.82, 0.81 (4*t*, $J \approx 7.1$, 2 *Me*CH$_2$O); 0.32, 0.29 (2*s*, ratio *ca*. 2:1, Me$_3$Si). $^{13}$C-NMR: 149.8, 142.4, 142.2, 139.6 (4 arom. $C_q$ (major)); 146.8, 141.7, 140.2, 138.9 (4 arom. $C_q$ (minor)); 130.2, 129.3, 129.0, 128.7, 126.7, 126.1, 119.4, 118.8 (8 arom. CH (major)); 129.2, 128.8, 127.7, 127.1, 126.6, 119.6, 119.5 (8 arom. CH (minor)); 64.8, 62.8 (2*d*, 2 Me*C*H$_2$O (major)); 64.4, 63.2 (2*d*, Me*C*H$_2$O (minor)); 37.4, 35.4 (*C*HSi, ratio *ca*. 1:2); 17.9, 16.3, 16.0, 15.9 (MeS, 2 *Me*CH$_2$O); –1.8, –2.0 (Me$_3$Si, ratio *ca*. 2:1)**. $^{31}$P-NMR: 20.44, 19.70 (ratio *ca*. 1:2). ESI-MS ($CH_2Cl_2$/MeOH/NaI): 533 (100, [*M*+Na]$^+$), 337 (14), 251 (21). Anal. Calcd for $C_{23}H_{31}O_3PS_3Si$ (510.75): C 54.09, H 6.12, S 18.83; found: C 54.14, H 5.97, S 18.57.

*(3a'*S*R, 6'*S*R, 6a'*R*S)-6'-(Trimethylsilanyl)spiro[9*H*-fluorene-9,4'-tetrahydro-thieno[3,4-*c*]furan]-1',3'-dione* (**19a**). Reaction with maleic anhydride (**18a**); yield of **19a**: 200 mg (53%). Colorless crystals (hexane/$CH_2Cl_2$); mp 240–246°C (decomp.). IR (KBr): 3061*w*, 3041*w*, 2987*w*, 2952*w*, 1870*m*, 1794*vs* (C=O), 1628*m*, 1449*s*, 1253*s*, 1235*m*, 1092*m*, 998*s*, 987*s*, 927*s*, 848*s*, 765*s*, 742*s*, 751*s*, 616*m*. $^1$H-NMR: 7.71 (*td*-like, $J \approx 7$ and 1, 2 arom. H); 7.45–7.30 (*m*, 6 arom. H); 4.32 (*dd*, $J$ = 7.9 and 5.6, H–C(6a')); 3.91 (*d*, $J$ = 7.9, H–C(3a')); 3.41 (*d*, $J$ = 5.6, H–C(6')); 0.31 (*s*, Me$_3$Si). $^{13}$C-NMR: 171.7, 168.6 (2 CO); 152.9, 141.4, 139.8, 138.2 (4 arom. $C_q$); 129.5, 128.8, 128.4, 128.0, 126.1, 121.8, 120.6, 120.1 (8 arom. CH); 67.4 (C(4')); 58.8, 57.2 (C(3a'), C(6a')); 39.5 (C(6')); –1.2 (Me$_3$Si). ESI-MS (MeCN): 381 (100, [*M*+1]$^+$); CI-MS

* The ratio of the two isomers is *ca*. 1:2.
** C(4) and C(5) of the 1,3-dithiolane could not be detected.

($NH_3$): 398 (100, $[M+NH_4]^+$), 381 (4, $[M+1]^+$), 197 (15). Anal. Calcd for $C_{21}H_{20}O_3SSi$ (380.54): C 66.28, H 5.30, S 8.43; found: C 66.24, H 5.13, S 8.57.

*(1*SR*, 3a*SR*, 6a*RS*)-5-Cyclohexyl-1-(trimethylsilanyl)spiro-[9*H*-fluorene-9,3'-tetrahydrothieno[3,4-*c*]pyrrole-4,6-dione* (**19b**). Reaction with *N*-(cyclohexyl)maleimide (**18b**); yield of **19b**: 280 mg (61%). Yellow oil, after purification by column chromatography (hexane/AcOEt 3.5:1.5 as the eluent). Crystallization (hexane/$Et_2O$) gave colorless crystals; m.p. 219–222°C (decomp.). IR (KBr): 3063*w*, 2935*m*, 2858*m*, 1702*vs* (C=O), 1449*m*, 1371*m*, 1347*m*, 1257*m*, 1249*m*, 1192*m*, 1148*w*, 1036*w*, 858*m*, 848*m*, 744*m*, 734*m*, 634*w*. $^1$H-NMR: 7.72–7.19 (*m*, 8 arom. CH); 4.08–3.91 (*m*, CHN, CH); 3.58 (*d*, $J_{HH}$ = 7.4 Hz, CH); 3.40 (*d*, $J_{HH}$ = 6.4 Hz, CH); 2.27–1.26 (*m*, 5 $CH_2$); 0.28 (*s*, $Me_3Si$). $^{13}$C-NMR: 177.2, 174.7 (2 CO); 153.9, 142.3, 140.1, 138.4 (4 arom. $C_q$); 129.1, 128.6, 128.3, 127.5, 127.3, 122.2, 120.5, 120.1 (8 arom. CH); 66.9 ($C_q$); 57.6, 55.5, 52.6, 39.3 (4 CH); 29.4, 29.1, 26.2, 26.1, 25.2 (5 $CH_2$); –0.60 ($Me_3Si$). CI-MS ($NH_3$): 481 (16), 480 (38), 479 (100, $[M+NH_4]^+$), 463 (10), 462 (28, $[M+1]^+$), 408 (10), 407 (34), 390 (7), 375 (7), 358 (8). Anal. Calcd for $C_{27}H_{31}NO_2SSi$ (461.70): C 70.24, H 6.71, N 3.03, S 6.95; found: C 70 75, H 6.62,N 2.83, S 6.63.

**5. X-Ray Crystal-Structure Determination of 13 and 14** (see Table 1 and Figs. 1– 2)[*]). All measurements were made on a Nonius KappaCCD diffractometer [27] using graphite-monochromated Mo$K_\alpha$ radiation ($\lambda$ 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with HKL Denzo and Scalepack [28]. The intensities were corrected for Lorentz and polarization effects, and an absorption correction based on the multi-scan method [29] was applied. Equivalent reflections were merged. Data collection and refinement parameters are given in Table 1, and views of the molecules are shown in Figs. 1 and 2. The structures of **13** and **14** were solved by direct methods using SIR92 [30], which revealed the positions of all non-H-atoms. The non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal

[*]) CCDC-643228–643229 contain 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.

to $1.2U_{eq}$ of its parent C-atom ($1.5U_{eq}$ for the Me groups). Refinement of each structure was carried out on $F^2$ using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_O^2-F_C^2)^2$. Corrections for secondary extinction were applied for **13** and **14**. Two and three reflections, respectively, whose intensities were considered to be extreme outliers, were omitted from the final refinement. Neutral atom scattering factors for non-H-atoms were taken from [31a], and the scattering factors for H-atoms were taken from [32]. Anomalous dispersion effects were included in $F_C$ [33]; the values for $f'$ and $f''$ were those of [31b]. The values of the mass attenuation coefficients are those of [31c]. All calculations were performed using the SHELXL97 [34] program.

**Table 1**. Crystallographic Data for Compounds **13** and **14**

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Table 1. Crystallographic Data for Compounds **13** and **14**

| | **13** | **14** |
|---|---|---|
| Crystallized from | $MeOH/CH_2Cl_2$ | $hexane/CH_2Cl_2$ |
| Empirical formula | $C_{34}H_{36}S_2Si_2$ | $C_{30}H_{26}S_2Si$ |
| Formula weight [g $mol^{-1}$] | 564.94 | 478.74 |
| Crystal color, habit | colorless, needle | colorless, prism |
| Crystal dimensions [mm] | 0.10 × 0.10 × 0.25 | 0.17 × 0.25 × 0.25 |
| Temperature [K] | 160(1) | 160(1) |
| Crystal system | triclinic | monoclinic |
| Space group | $P\bar{1}$,1 | $P2_1/n$ |
| $Z$ | 2 | 4 |
| Reflections for cell determination | 26454 | 72844 |
| $2\theta$ range for cell determination [°] | 4–60 | 4–60 |
| Unit cell parameters $a$ [Å] | 9.1242(2) | 9.5748(1) |
| $b$ [Å] | 12.9142(3) | 15.3358(3) |
| $c$ [Å] | 13.5209(2) | 17.1129(4) |
| α [°] | 97.542(1) | 90 |
| $\beta$ [°] | 91.510(1) | 103.207(1) |
| γ [°] | 108.573(1) | 90 |
| $V$ [$Å^3$] | 1493.21(5) | 2446.35(8) |
| $D_X$ [g $cm^{-3}$] | 1.257 | 1.300 |
| $\mu$(Mo$K\alpha$) [$mm^{-1}$] | 0.281 | 0.284 |
| Scan type | $\phi$ and $\omega$ | $\phi$ and $\omega$ |
| $2\theta$(max) [°] | 60 | 60 |
| Transmission factors (min; max) | 0.839; 0.980 | 0.844; 0.948 |
| Total reflections measured | 42598 | 63597 |
| Symmetry independent reflections | 8735 | 7113 |
| Reflections with $I > 2\sigma(I)$ | 6748 | 5417 |
| Reflections used in refinement | 8733 | 7110 |
| Parameters refined | 350 | 302 |
| Final $R(F)$ [$I>2\sigma(I)$ reflections] | 0.0489 | 0.0476 |
| $wR(F^2)$ (all data) | 0.1286 | 0.1219 |
| Weights:[a)] a; b | 0.0613; 0.6508 | 0.0558; 1.2392 |
| Goodness of fit | 1.057 | 1.058 |
| Secondary extinction coefficient | 0.071(3) | 0.040(2) |
| Final $\Delta_{max}/\sigma$ | 0.001 | 0.001 |

| | | |
|---|---|---|
| $\Delta\rho$ (max; min) [e Å$^{-3}$] | 0.64; –0.39 | 0.48; –0.44 |

a) $w = [\sigma^2(F_o^2) + (aP)^2 + bP]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$