Synthesis and Reactions of a New Cyclobutanethione Derivative

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The 3,3-dichloro-2,2,4,4-tetramethylcyclobutanethione (**4b**) was prepared from the parent diketone by successive reaction with PCl_5 and *Lawesson* reagent in pyridine. This new thioketone **4b** was transformed into 1-chlorocyclobutanesulfanyl chloride **5** and chloro 1-chlorocyclobutyl disulfide **9** by treatment with PCl_5 and SCl_2, respectively, in chlorinated solvents (*Schemes 1* and *2*). These products reacted with S- and P-nucleophiles by substitution of Cl^- at the S-atom; *e.g.*, the reaction with **4b** yielded the di- and trisulfides **6b** and **11**, respectively. Surprisingly, only pentasulfide **12** was formed in the reaction of **9** with thiobenzophenone (*Scheme 3*). In contrast to **5** and **9**, the corresponding chloro 1-chlorocyclobutyl trisulfide **13** could not be detected, but reacted immediately with the starting thioketone **4b** to give the tetrasulfide **14** (*Scheme 4*). Oxidation of **4b** with 3-chloroperbenzoic acid (*m*CPBA) yielded the corresponding thione oxides (=sulfine) **15**, which underwent 1,3-dipolar cycloadditions with thioketones **3a** and **4b** (*Scheme 5*). Furthermore, **4b** was shown to be a good dipolarophile in reactions with thiocarbonylium methanides (*Scheme 6*) and iminium ylides (=azomethine ylides; *Scheme 7*). In the case of phenyl azide, the reaction with **4b** gave the symmetrical trithiolane **25** (*Scheme 8*).

1. Introduction. – Despite their interesting chemical and physicochemical properties, thioketones were considered as unstable compounds, which are accessible only with difficulty. Whereas aromatic thioketones show enhanced stability, aliphatic representatives are much less stable and easily undergo enolization and oligomerization [1][2][4]). At present, it is known that their stability increases significantly by the introduction of bulky substituents or other sterically stabilizing effects. In addition to adamantanethione (**1**) [3] and the only recently described 'cage thioketone' **2** [4], thioxo derivatives **3** of 2,2,4,4-tetramethylcyclobutane-1,3-dione, *i.e.*, 2,2,4,4-tetramethyl-3-thioxocyclobutane-1-one [5] and 2,2,4,4-tetramethylcyclobutane-1,3-dithione [6], belong to the most useful and relatively easily available cycloaliphatic thioketones. Generally, the synthesis of thioketones is carried out by replacement of the O-atom of a carbonyl group by an S-atom with *Lawesson*'s reagent, a mixture of H_2S and HCl, or with P_4S_{10} as thionating reagents (for reviews, see [7]).

In a recent paper, we reported on the reaction of 2,2,4,4-tetramethylcyclobutane-1,3-dione with PCl_5 which leads to 3,3-dichloro-2,2,4,4-tetramethylcyclobutan-1-one (**4a**) [8]. Now we present the preparation of the corresponding thione **4b** and reactions of this new and stable chlorinated thioketone.

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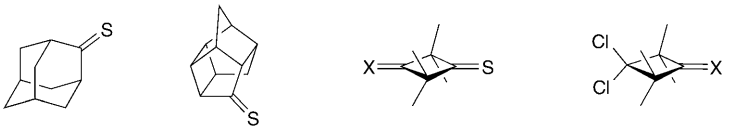
[1]) Part of the planned Ph.D. thesis of *A. M.*, Universität Zürich.
[2]) In part from the Diploma thesis of *M. R.*, University of Łódź, 2003.
[3]) Part of the planned Ph.D. thesis of *M. W.*, University of Łódź.
[4]) Furthermore, thioketones are known as substances with very unpleasant odor.



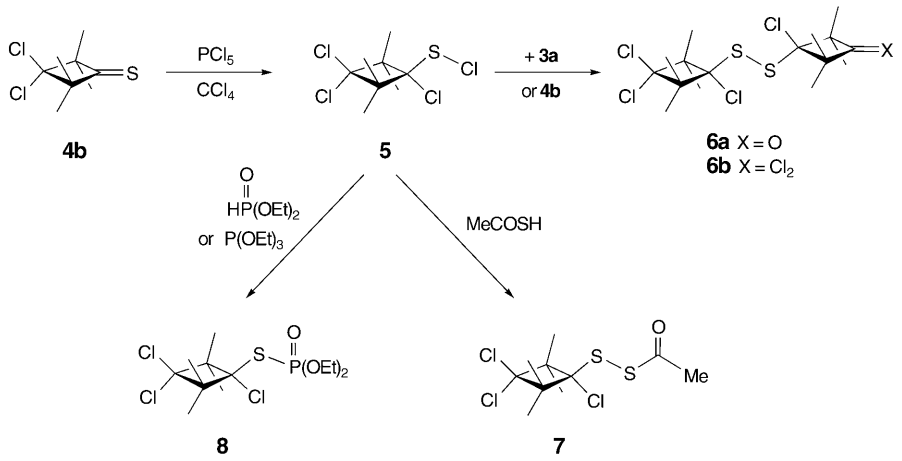
1 **2** **3a** X = O **3b** X = S **4a** X = O **4b** X = S

2. Results and Discussion. – Heating of **4a** with P_4S_{10} in pyridine for 6 h led to the thioketone **4b** as a red solid, which was stable at room temperature, similar to the thioketones **3a** and **3b**. Typically, the C=S group of **4b** absorbed in the ^{13}C-NMR spectrum ($CDCl_3$) at 273.0 ppm. In analogy to the corresponding reactions of **3a** and **3b** [9], the new thioketone **4b** reacted with PCl_5 to yield the relatively stable 1-chlorocyclobutanesulfanyl chloride **5**, which was used for further reactions without purification. Treatment of **5** in CH_2Cl_2 at room temperature with thioketones **3a** and **4b** led smoothly to the disulfides **6a** and **6b**, respectively, in high yield (*Scheme 1*). In this reaction, the S-atom of the thioketone acts as a soft nucleophile towards the sulfanyl chloride.

The substitution of chloride in the SCl group was easily achieved by the reaction of **5** with thioacetic acid, which afforded the carbo(dithioperoxoic) acid **7** (*cf.* [9][10]). Compounds of this type have been shown to undergo a deacetylation in the presence of morpholine, and a subsequent intramolecular substitution of chloride is believed to yield a reactive dithiirane [11]. Alternatively, the corresponding thiocarbonylium sulfide can be formed by elimination of chloride. In the case of **7**, the experiment with morpholine led, unexpectedly, to **4b**, which probably was formed from the intermediate disulfide by elimination of sulfur and Cl^-.

The reaction of chlorosulfenyl chloride **5** with diethyl phosphonate or triethyl phosphite yielded exclusively **8**, which is the substitution product formed by the nucleophilic attack of the P-atom in analogy to the *Arbuzov* reaction [12] (*Scheme 1*).

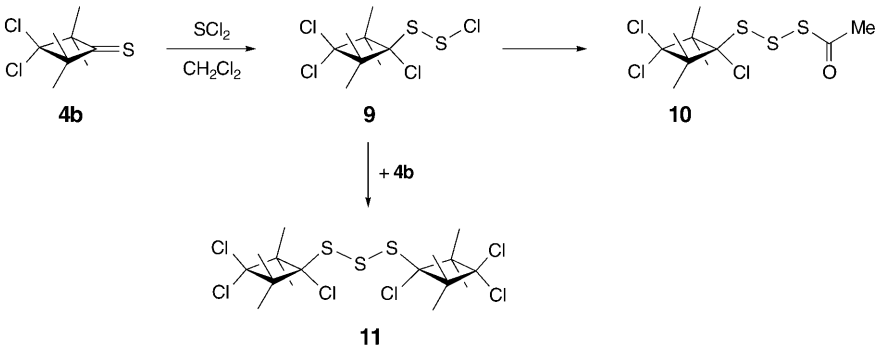
Scheme 1



4b **5** **6a** X = O **6b** X = Cl_2 **8** **7**

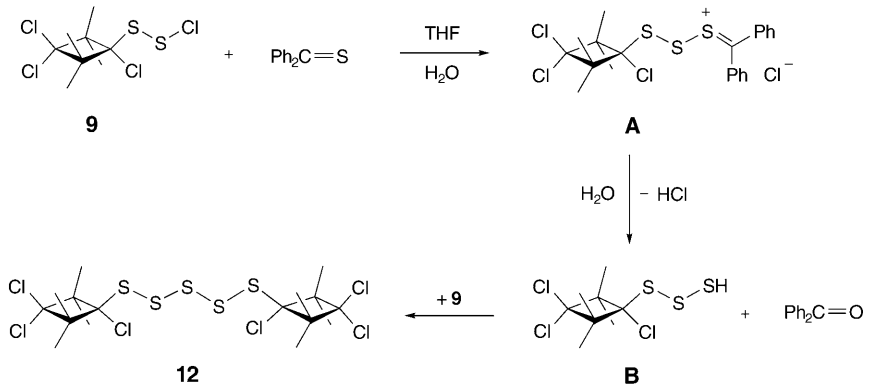
The treatment of **4b** with SCl_2 in CH_2Cl_2 gave the adduct **9**, *i.e.*, a chloro 1-chlorocyclobutyl disulfide (*Scheme 2*). The reaction of the latter with thioacetic acid led to the trisulfide **10** by an extension of the S-chain. Similar to the reaction with **5**, **9** also underwent an addition with the parent thioketone **4b** to give the symmetrical trisulfide **11**.

Scheme 2



To test the ability of aromatic thioketones to form nonsymmetric trisulfides of type **11**, an experiment with **9** and thiobenzophenone (=diphenylmethanethione) was carried out. When the reagents were used in a 1:1 molar ratio, only benzophenone (=diphenylmethanone) was isolated after chromatographic workup. Therefore, the reaction was repeated with an excess of **9** (2:1 ratio) in wet THF. Under these conditions, the symmetrical pentasulfide **12** was isolated along with comparable amounts of benzophenone. A likely reaction pathway leading to **12** is outlined in *Scheme 3*. The first step is the formation of the thiocarbonylium ion **A** by a nucleophilic substitution of the Cl-atom. In contrast to similar intermediates appearing in reactions with cycloaliphatic thioketones, which lead to the formation of **6** and **11**, **A** is easily hydrolyzed to give benzophenone and the hydrotrisulfide derivative **B**. The excess of **9** intercepts **B** immediately forming the pentasulfide **12**.

Scheme 3



The molecular formula of **12** was confirmed by the elemental analysis. As the spectroscopic data were not indicative for the structure, an X-ray crystal-structure determination was performed (*Fig. 1*).

In accordance with the results obtained with other polysulfides [14], the S-chain adopts a helical conformation with torsion angles close to 90° and, as observed in a previously described pentasulfide structure [15], it completes one full helical turn along its length. However, unlike the similar pentasulfide with terminal cyclobutanone groups [15], there is no disorder in the crystal structure.

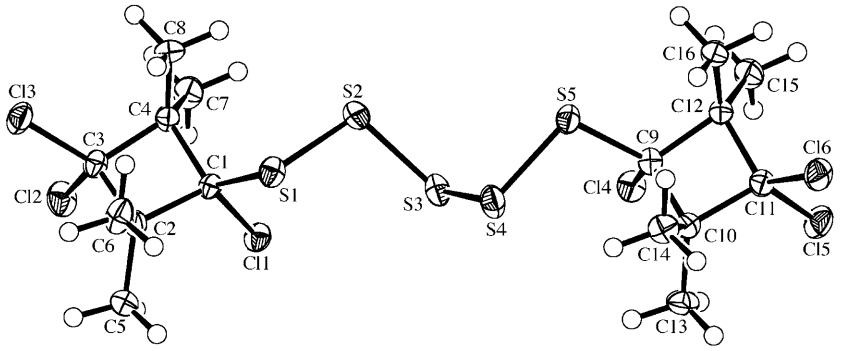
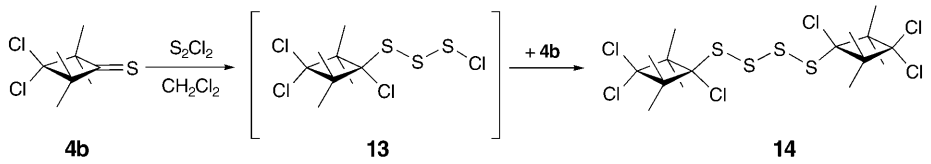


Fig. 1. *ORTEP Plot* [13] *of the molecular* structure *of* **12**. Arbitrary numbering of atoms; 50% probability ellipsoids.

With the aim of preparing the corresponding chloro 1-chlorocyclobutyl trisulfide **13**, **4b** was treated with freshly distilled S_2Cl_2 in CH_2Cl_2 at room temperature. The decoloration of the mixture was significantly slower than in the reaction with SCl_2, and after usual workup, the tetrasulfide **14** was isolated exclusively (*Scheme 4*). Apparently, the slowly formed **13** instantaneously reacts with thioketone **4b** to give the final product in almost quantitative yield.

Scheme 4



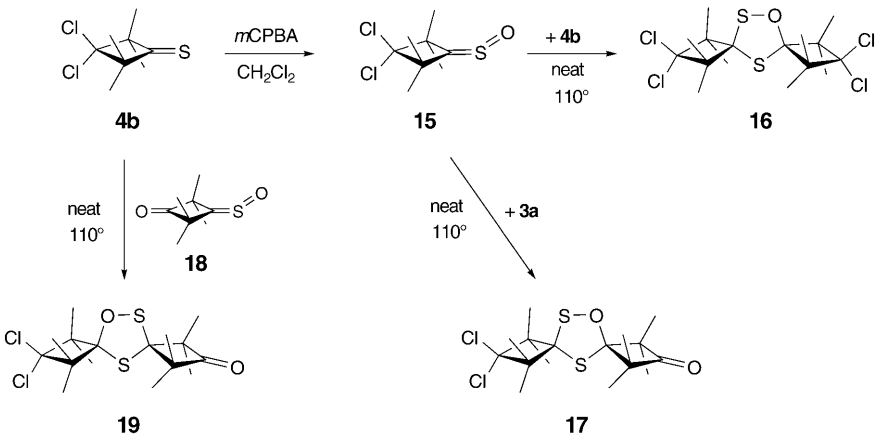
4b **13** **14**

The oxidation of thiocarbonyl compounds leads to their *S*-oxides *i.e.*, to so-called sulfines, which differ in stability significantly, depending on the substitution pattern [16]. It is well established that sulfines react smoothly with 1,3-dienes and 1,3-dipoles along the activated C=S bond to give the corresponding six- or five-membered heterocyclic *S*-oxides [17]. On the other hand, it has been shown recently that sulfines also behave as 1,3-dipoles in [3+2] cycloadditions with thioketones [18][19]. Treatment of **4b** with 3-chloroperbenzoic acid (*m*CPBA) in CH_2Cl_2 gave the expected sulfine **15** as a crystalline material (*Scheme 5*). The reaction of **15** with the parent thioketone **4b** and the oxo analogue **3a**, respectively, was carried out by heating a mixture of equimolar

amounts of the reagents without solvent to 110°. The red color of the thioketones disappeared within *ca.* 30 min, and 1,2,4-oxadithiolanes **16** and **17**, respectively, were obtained after crystallization from MeOH. The molecular structure of **17** was established by X-ray crystallography (*Fig. 2*). The reaction between **4b** and the known sulfine **18** [20] was performed in an analogous manner leading to **19**, which is an isomer of **17**.

The parent thioketone **4b** was also tested as a dipolarophile in reactions with thiocarbonylium methanides, which were generated by thermal N_2 extrusion from the corresponding 2,5-dihydro-1,3,4-thiadiazoles **20a** and **20b** (*Scheme 6*). The analysis of the reaction mixture by ^{1}H-NMR spectroscopy showed that the cycloaddition occurred regioselectively leading to the 2,2,4,4-substituted 1,3-dithiolanes **21**. These products revealed the characteristic CH_2 absorption in the ^{13}C-NMR spectrum at 41.9 and 43.3 ppm, respectively. The regioselectivity observed in these reactions fits well with

Scheme 5



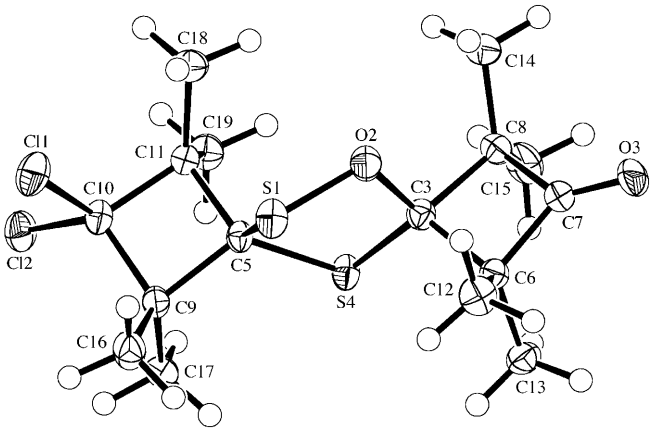
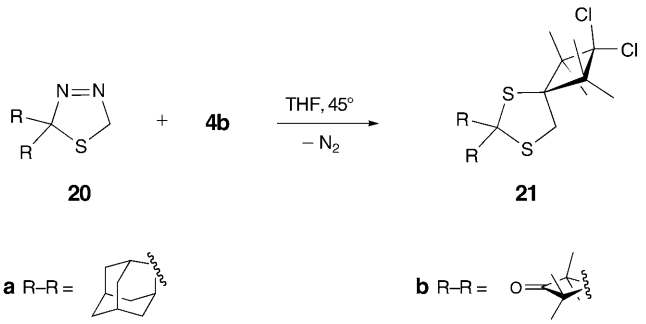


Fig. 2. *ORTEP Plot* [13] *of the molecular structure of* **17**. Arbitrary numbering of atoms; 50% probability ellipsoids.

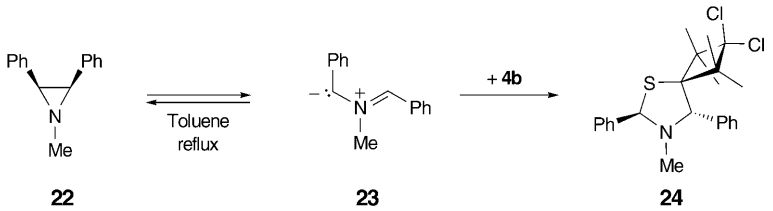
Scheme 6



the general rules for [3+2] cycloadditions of cycloaliphatic thiocarbonylium methanides with cycloaliphatic thioketones [21].

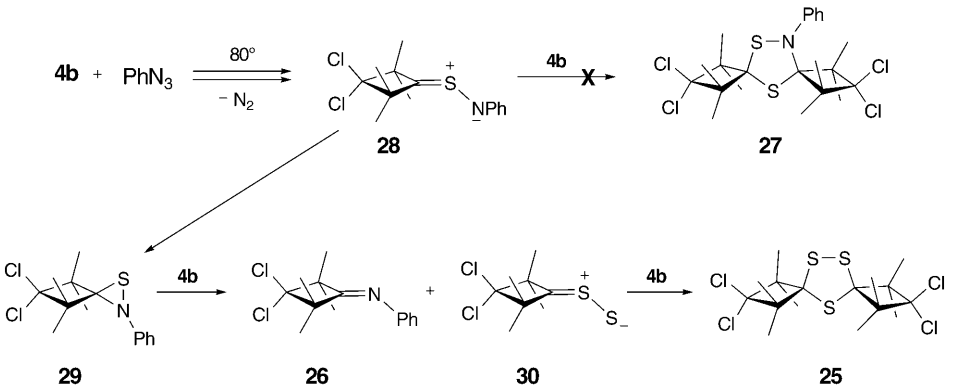
The thermal electrocyclic ring opening of aziridines was widely explored for the synthesis of thiazolidines *via* [3+2] cycloadditions of the reactive iminium ylides (=azomethine ylides) with C=S dipolarophiles (*cf.* [22–24]). Thermolysis of *cis*-1-methyl-2,3-diphenylaziridine (**22**) in boiling toluene in the presence of **4b** afforded a single product **24** whose structure was again established by X-ray crystallography [25] (*Scheme 7*). In accordance with the expected reaction course, the Ph groups are *trans* oriented, *i.e.*, the intermediate 1,3-dipole **23** has been generated by a conrotatory ring opening of **22**.

Scheme 7



In analogy to a previously reported experiment with **3a** and phenyl azide [26], a mixture of **4b** and phenyl azide was heated to 80°. The reaction was significantly slower than with **3a** and, after evaporation of excess phenyl azide, the residue was analyzed by ^{1}H-NMR spectroscopy. The presence of two sets of *s* located at 1.58 and 1.51 ppm, and 1.49 and 1.20 ppm revealed the formation of two products in comparable amounts. After chromatographic workup, only the product with the signals at lower field was obtained as a colorless solid, which was identified as the symmetric 1,2,4-trithiolane **25** (*Scheme 8*). The second set of signals can be attributed to the imine **26**, which decomposed during chromatography. In contrast to the reaction with **3a** [26], no 1,4,2-dithiazolidine **27** was formed. Obviously, the proposed intermediate thiocarbonylium aminide (=thiocarbonyl imide) **28** undergoes a fast electrocyclic ring closure to give the thiaziridine **29**. Sulfur transfer to **4b** yields the reactive thiocarbonylium sulfide **30**

Scheme 8



and imine **26**. Finally, interception of **30** by **4b** leads to the isolated trithiolane **25**. This result shows that the replacement of the C=O group of **3a** by CCl_2 influences remarkably the reactivity of the intermediate thiocarbonylium aminide.

In summary, the presented results show that the new chlorinated thioketone **4b**, which can easily be prepared, is an attractive model for studies focused on the reactivity of thiocarbonyl groups. Of special interest are the chlorinated sulfanyl chloride **5** and the corresponding chlorinated chloro disulfide **9**, which are suitable for the preparation of polysulfides and other S-rich products. The replacement of the C=O group in **3a** by the CCl_2 unit ($\rightarrow$ **4b**) does not change significantly the properties of the C=S function, *e.g.*, the dipolarophilicity of **4b** was demonstrated in cycloadditions with sulfonium ylides, sulfines, and iminium ylides. However, the lack of the stabilizing transannular effect of the C=O group influences the reactivity of the thiocarbonylium aminide **28** in comparison with the analogous 1,3-dipole generated from **3a** [27].

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Experimental Part

1. *General.* See [28]. M.p.: *Meltemp 2* apparatus; in capillary; uncorrected. ^{1}H- and ^{13}C-NMR Spectra *Tesla BS-687* instrument (80 and 20 Mhz, resp.) or *Bruker-300* spectrometer (300 and 75 Mhz, resp.); in $CDCl_3$ with $SiMe_4$ (=0 ppm) as an internal standard. IR Spectra (KBr pellets or film): *Nexus* spectrophotometer. MS (EI or CI): *Finnigan-Mat-90* or *Finnigan-SSQ-700* spectrometer. Elemental analyses were performed in the Analytical Laboratory of the University of Zurich or in the Laboratory of the Polish Academy of Sciences (CBMiM) in Łódź.

2. *Starting Materials.* The 2,2,4,4-tetramethylcyclobutane-1,3-dione was prepared from isobutyryl chloride (=2-methylpropanoyl chloride) and Et_3N in CH_2Cl_2 [29]. The 2,5-dihydro-1,3,4-thiadiazoles **20a** and **20b** were synthesized from the corresponding thioketones and CH_2N_2 in pentane at 0–5° following known protocols [30][31]. *cis*-1-Methyl-2,3-diphenylaziridine (**22**) was available from *erythro*-2-(methylamino)-1,2-diphenylethanol by treatment with $SOCl_2$ and subsequent cyclization by using Et_3N or KOH as a base [32]. Phenyl azide was prepared by diazotation of phenylhydrazine as described in [33]. Thioacetic acid, diethyl phosphonate and

triethyl phosphite, sulfur chloride (SCl_2), and disulfur dichloride (S_2Cl_2; b.p. 134–136°) were carefully distilled prior to their use. The 2,2,4,4-tetramethyl-3-(oxidothioxo)cyclobutanone (**18**) was obtained by oxidation of **3a** with 3-chloroperbenzoic acid (*m*CPBA) in CH_2Cl_2 following the protocol in [34].

3. *3,3-Dichloro-2,2,4,4-tetramethylcyclobutanone* (**4a**). A mixture of 2,2,4,4-tetramethylcyclobutane-1,3-dione (9.8 g, 0.07 mol) and PCl_5 (29.2 g, 0.14 mol) in CCl_4 (50 ml) was heated under reflux for 1.5 h. After cooling to r.t., the soln. was diluted with CH_2Cl_2 (20 ml) and washed with sat. aq. $NaHCO_3$ soln. and H_2O (3×). The org. layer was dried ($MgSO_4$) and evaporated. CC (SiO_2, hexane containing increasing amounts of $CHCl_3$) gave the less polar, colorless *1,1,3,3-tetrachloro-2,2,4,4-tetramethylcyclobutane* (2.68 g, 15%; m.p. 240–241° ([35]: 234–236°)) and the more-polar **4a** (8.07 g, 59%). Colorless crystals. M.p. 69–71° ([35]: 72–73°).

4. *3,3-Dichloro-2,2,4,4-tetramethylcyclobutanethione* (**4b**). To a vigorously stirred (magnetic stirrer) soln. of **4a** (2.93 g, 0.015 mol) in freshly distilled pyridine (15 ml), P_2S_5 (3.33 g, 0.015 mol) was added in small portions. The mixture was heated to 130° (oil bath) for 6 h. After cooling to r.t., the mixture was poured into H_2O and extracted with hexane (3×5 ml). The org. layer was washed with 2N HCl and H_2O (3×), dried ($MgSO_4$), and evaporated and the red solid residue purified by CC (SiO_2, hexane with increasing amounts of CH_2Cl_2): crude **4b** (2.79 g, 88%). M.p. 140–144°[5]). Crystallization from petroleum ether in dry ice gave red crystals. M.p. 133–135°. IR (KBr): 2990*m*, 1466*m*, 1306*s*, 1145*m* (C=S), 1003*w*, 915v*s*, 827v*s*. ^{1}H-NMR: 1.50 (*s*, 4 Me). ^{13}C-NMR: 26.8 (*q*, 4 Me); 73.1 (*s*, C(2), C(4)); 98.0 (*s*, CCl_2); 273.0 (*s*, C=S). EI-MS: 212 (24), 211 (3), 210 (39), 175 (50), 139 (27), 86 (100, $Me_2C{=}C{=}S^+$), 71 (55). Anal. calc. for $C_8H_{12}Cl_2S$ (211.15): C 45.50, H 5.73, S 15.19; found: C 45.65, H 5.84, S 15.38.

5. *1,3,3-Trichloro-2,2,4,4-tetramethylcyclobutanesulfanyl Chloride* (**5**). A soln. of **4b** (211 mg, 1 mmol) and PCl_5 (416 mg, 2 mmol) in CCl_4 (5 ml) was heated under reflux. After 45 min, another portion of PCl_5 (832 mg, 4 mmol) was added, and heating was continued for 15 min until the red color of the soln. disappeared. The mixture was diluted with CCl_4 (10 ml), the soln. washed with sat. aq. Na_2CO_3 soln. and H_2O (2×), dried ($MgSO_4$), and evaporated, and the oily residue was used for further reactions without purification: 272.0 mg (96%) of **5**. Colorless, thick oil. IR (neat): 3007*m*, 2981*s*, 2940*s*, 1469v*s*, 1453*s*, 1385v*s*, 1371*s*, 1190*m*, 943*m*, 871v*s*, 835v*s*, 803*s*. ^{1}H-NMR: 1.56 (*s*, 2 Me); 1.58 (*s*, 2 Me). ^{13}C-NMR: 24.3 (*q*, 2 Me); 27.4 (*q*, 2 Me); 60.1 (*s*, C(2), C(4)); 89.6 (*s*, C(1)); 97.9 (*s*, CCl_2).

6. *Reaction of* **5** *with Cyclobutanethiones* **3a** *and* **4b**: *General Procedure.* To a magnetically stirred soln. of freshly prepared **5** (136 mg, 0.48 mmol) in CH_2Cl_2 (2 ml), the red soln. of the corresponding thioketone (0.48 mmol) was added dropwise at r.t. After 30 min, the solvent was evaporated and the oily residue triturated with MeOH to yield crystalline products. Anal. pure samples were obtained by recrystallization.

3-Chloro-2,2,4,4-tetramethyl-3-[(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutyl)dithio]cyclobutanone (**6a**): Yield 57 mg (30%). Colorless crystals. M.p. 116–118° (MeOH). IR (KBr): 2984*w*, 2936*w*, 1789v*s*, 1445*m* (br.), 1366*w*, 1023*w*, 834*m*. ^{1}H-NMR: 1.38, 1.51, 1.52, 1.64 (4*s*, 4 Me). ^{13}C-NMR ($CDCl_3$): 23.0, 23.2 (2*q*, 4 Me); 26.4, 26.6 (2*q*, 4 Me); 60.6 (*s*, 2 Me_2C); 69.7 (*s*, 2 Me_2C); 84.8 (*s*, SCCl); 87.2 (*s*, SCCl); 98.9 (*s*, CCl_2); 217.2 (*s*, C=O). EI-MS: 438 (1), 368 (20), 366 (15), 213 (31), 177 (44), 159 (43), 141 (85), 131 (100), 105 (26), 86 (86). Anal. calc. for $C_{16}H_{24}Cl_4OS_2$ (438.31): C 43.84, H 5.52, S 14.63; found C 43.72, H 5.56, S 14.65.

Bis(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutyl) Disulfide (**6b**): Yield 143 mg (60%). Colorless crystals. M.p. 182–184° (MeOH/CH_2Cl_2). IR (KBr): 3012*s*, 2984*s*, 2942*s*, 1466v*s*, 1443v*s*, 1383v*s*, 1370*s*, 1197*s*, 992*s*, 942*s*, 868v*s*, 833v*s*, 796*s*, 554*s*. ^{1}H-NMR: 1.49 (*s*, 4 Me); 1.62 (*s*, 4 Me). ^{13}C-NMR: 26.48, 26.51 (2*q*, 4 Me each); 60.5 (*s*, 4 Me_2C); 87.2 (*s*, 2 SCCl); 98.7 (*s*, 2 CCl_2). CI-MS: 459 (72), 457 (100), 455 (61). Anal. calc. for $C_{16}H_{24}Cl_6S_2$ (493.21): C 38.96, H 4.90, S 13.00; found: C 38.67, H 4.78, S 12.92.

7. *Ethane(dithioperoxoic) Acid 1,3,3-Trichloro-2,2,4,4-tetramethylcyclobutyl Ester* (**7**). To a stirred soln. of **5** (282 mg, 1 mmol) in CCl_4 (5 ml), thioacetic acid (83 mg, 1.1 mmol) in CCl_4 (2 ml) was added in small portions at r.t. After complete addition, stirring was continued for 30 min, the solvent evaporated, and the residual thick oil crystallized from hexane: 59 mg (38%) of **7**. Colorless crystals. M.p. 48–50° (hexane). IR (KBr): 2980*w*, 2940*w*, 1740v*s* (C=O), 1470*m*, 1110*s*, 943*m*, 870*m*, 833*s*, 595*s*. ^{1}H-NMR: 1.52 (*s*, 2 Me); 1.61 (*s*, 2 Me); 2.49 (*s*, MeCO). ^{13}C-NMR: 26.1 (*q*, 2 Me); 27.1 (*q*, 2 Me); 28.7 (*q*, *Me*CO); 60.1 (*s*, 2 Me_2C); 89.4 (*s*, SCCl); 98.3 (*s*, CCl_2); 193.5 (*s*, Me*C*O). CI-MS: 340 (5), 338 (5), 289 (16), 287 (72), 286 (13), 285 (100). Anal. calc. for $C_{10}H_{15}Cl_3OS_3$ (321.71): C 37.33, H 4.69, S 19.93; found: C 37.44, H 4.72, S 19.65.

8. *Treatment of* **7** *with Morpholine.* A soln. of morpholine (652.5 mg, 7.5 mmol) in Et_2O (3 ml) was cooled to −40° (acetone/dry ice). To the stirred soln. was added dropwise a soln. of **7** (482 mg, 1.5 mmol) in Et_2O (3 ml).

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[5]) During the storage at r.t., a slow decomposition of **4b** was observed, and the ^{1}H-NMR spectrum confirmed the formation of growing amounts of dichloro ketone **4a**.

The mixture was stirred at −40° (acetone, dry ice) for 4 h and then allowed to reach r.t. (orange → red). After addition of Et_2O (15 ml), the mixture was washed with H_2O (2×30 ml), the org. phase dried ($MgSO_4$) and evaporated, and the residue (180 mg) analyzed by ^{1}H-NMR (no signals of the expected product). Then, the mixture was separated by prep. TLC (SiO_2, CH_2Cl_2/hexane 1:1). Only **4b** (68 mg, 21%) and decomposition products were obtained.

9. O,O-*Diethyl* S-*(1,3,3-Trichloro-2,2,4,4-tetramethylcyclobutyl Phosphorothioate* (**8**). $P(OEt)_3$ (166 mg, 1 mmol) was slowly added to a stirred soln. of **5** (282 mg, 1 mmol) in CH_2Cl_2 (7 ml) at 0°. (→ pale red). After additional stirring for 30 min at r.t., the solvent was evaporated: **8** (*ca.* 97%) as a crude oil. Crystallization from hexane (−78°) afforded anal. pure **8** (282 mg, 73%).

As an alternative, $HP(O)(OEt)_2$ (138 mg, 1 mmol) in CH_2Cl_2 (3 ml) was added to a stirred soln. of **5** (501 mg, 1.77 mmol) in CH_2Cl_2 (3 ml). After keeping for 3 d at r.t., the solvent was evaporated and the crude oil crystallized from hexane in dry ice: pure **8** (186 mg, 31%).

Colorless crystals. M.p. 48–50° (hexane, dry ice). IR (KBr): 3004*m*, 2984*m*, 2942*m*, 1473*s*, 1384*m*, 1263v*s*, 1161*s*, 1052v*s*, 1019v*s*, 831*s*, 742v*s*, 564*s*, 547*s*. ^{1}H-NMR: 1.36 (*td*, *J*(H,H) = 7.1, *J*(H,P) = 0.8, 2 *Me*CH_2); 1.57 (*s*, 2 Me); 1.67 (*s*, 2 Me); 4.12–4.28 (*m*, MeCH_2). ^{13}C-NMR: 15.9 (*dq*, *J*(C,P) = 7.3, Me); 25.0 (*q*, 2 Me); 27.4 (*q*, Me); 60.4 (*d*, *J*(C,P) = 5.2, 2 Me_2C); 64.3 (*td*, *J*(C,P) = 7.1, MeCH_2O); 85.4 (*s*, SCCl); 98.9 (*s*, CCl_2). CI-MS: 404 (33), 402 (100), 400 (96), 385 (49), 383 (47). Anal. calc. for $C_{12}H_{22}Cl_3O_3P$ (383.70): C 37.56, H 5.78, Cl 27.71, S 8.35; found: C 37.58, H 5.63, Cl 27.42, S 8.17.

10. *Chloro 1,3,3-Trichloro-2,2,4,4-tetramethylcyclobutyl Disulfide* (**9**). To a stirred soln. of SCl_2 (536 mg, 5.2 mmol) in CH_2Cl_2 (5 ml), a soln. of **4b** (1.0 g, 4.74 mmol) in CH_2Cl_2 (5 ml) was added dropwise, and the stirring was continued for 30 min. The solvent was evaporated, and the crude thick, pale yellow oil (1.41 g, 95%) was bulb-to-bulb distilled at 100°/0.5 Torr to give: **9**. Colorless thick oil. IR (neat): 3005*s*, 2977v*s*, 2940v*s*, 1469v*s*, 1385v*s*, 1371*s*, 1200*s*, 1171*m*, 994*m*, 871v*s*, 834v*s*, 801*s*. ^{1}H-NMR: 1.52 (*s*, 2 Me); 1.53 (*s*, 2 Me). ^{13}C-NMR: 26.4 (*q*, 2 Me); 27.5 (*q*, 2 Me); 59.9 (*s*, 2 Me_2C); 89.9 (*s*, SCCl); 98.2 (*s*, CCl_2).

11. *Acetyl 1,3,3-Trichloro-2,2,4,4-tetramethylcyclobutyl Trisulfide* (**10**). To a stirred soln. of freshly distilled **9** (314 mg, 1 mmol) in CH_2Cl_2 (5 ml) at r.t., thioacetic acid (84 mg, 1.1 mmol) in CH_2Cl_2 (2 ml) was added dropwise. After complete addition, stirring was continued for 15 min at r.t., and the solvent was evaporated. The crude colorless, thick oil crystallized slowly: 243 mg (69%) of **10**. Colorless crystals. M.p. 72–74°. IR (KBr): 3007*w*, 2983*m*, 2941*w*, 1732v*s* (C=O), 1466*s*, 1383*m*, 1107v*s*, 944v*s*, 867v*s*, 829v*s*, 800*m*, 591v*s*, 564*s*. ^{1}H-NMR: 1.54 (*s*, 2 Me); 1.55 (*s*, 2 Me); 2.47 (s, *Me*CO). ^{13}C-NMR: 26.3 (*q*, 2 Me); 27.0 (*q*, 2 Me); 29.3 (*q*, *Me*CO); 60.0 (*s*, 2 Me_2C); 90.3 (*s*, SCCl); 98.2 (*s*, CCl_2); 192.3 (*s*, MeCO). CI-MS: 319 (78), 317 (100), 287 (28), 285 (38), 200 (77), 175 (53). Anal. calc. for $C_{10}H_{15}Cl_3OS_3$ (353.78): C 33.95, H 4.27, Cl 30.06, S 27.18; found: C 34.29, H 4.09, Cl 30.06, S 26.34.

12. *Bis(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutyl) Trisulfide* (**11**). To a stirred soln. of **9** (314 mg, 1 mmol) in CH_2Cl_2 (4 ml) at r.t., a soln. of **4b** (211 mg, 1 mmol) in CH_2Cl_2 (2 ml) was added in small portions. After additional stirring for 30 min, the colorless soln. was evaporated to give a solid material. Crystallization from MeOH/CH_2Cl_2 afforded the anal. pure **11** (296 mg, 56%). Colorless crystals. M.p. 238–240°. IR (KBr): 3010*s*, 2978*s*, 2939*s*, 1469v*s*, 1442*m*, 1385*s*, 1370*s*, 1200*m*, 993*m*, 946*m*, 870v*s*, 833v*s*, 559*s*. ^{1}H-NMR: 1.54 (*s*, 4 Me); 1.55 (*s*, 4 Me). ^{13}C-NMR: 26.8 (*q*, 4 Me); 27.1 (*q*, 4 Me); 60.1 (*s*, 4 Me_2C); 90.7 (*s*, 2 SCCl); 98.3 (*s*, 2 CCl_2). CI-MS: 493 (29), 491 (48), 490 (21), 489 (100), 487 (59), 457 (46), 455 (26). Anal. calc. for $C_{16}H_{24}Cl_6S_3$ (525.28): C 36.58, H 4.60, Cl 40.50, S 18.31; found: C 36.58, H 4.49, Cl 40.44, S 18.07.

13. *Bis(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutyl) Pentasulfide* (**12**). To a stirred soln. of blue thiobenzophenone (99 mg, 0.5 mmol) in wet THF (2 vol-% H_2O; 1 ml), a soln. of **9** (314 mg, 1 mmol) in abs. THF (1 ml) was added in small portions. The mixture was cooled in a H_2O/ice bath, and stirring was continued for 10 min. The colorless soln. was evaporated and the pale yellow, oily residue crystallized from MeOH/CH_2Cl_2: 94 mg (32%) of **12**. Colorless crystals. M.p. 157–159°. IR (KBr): 2997v*s*, 2974*s*, 2935*m*, 1466v*s*, 1450*s*, 1383*s*, 1371*s*, 1198*m*, 1170*m*, 991*m*, 944*m*, 870v*s*, 835v*s*, 800*m*, 559*s*. ^{1}H-NMR: 1.54 (*s*, 6 Me); 1.55 (*s*, 2 Me). ^{13}C-NMR: 26.4 (*s*, 2 Me); 26.5 (*s*, 2 Me); 27.0 (*s*, 4 Me); 60.1 (*s*, 4 Me_2C); 89.8 (*s*, SCCl); 90.1 (*s*, SCCl); 98.4 (*s*, 2 CCl_2). CI-MS: 555 (2), 523 (14), 519 (10), 197 (26), 195 (39), 177 (37), 176 (12), 175 (100). Anal. calc. for $C_{16}H_{24}Cl_6S_5$ (589.41): C 32.60, H 4.10, Cl 36.10, S 27.20; found: C 32.50, H 3.90, Cl 35.70, S 27.04.

Suitable crystals for an X-ray crystal-structure determination were grown from MeOH/CH_2Cl_2 by slow evaporation of the solvent.

14. *Bis(1,3,3-trichloro-2,2,4,4-tetramethylcyclobutyl) Tetrasulfide* (**14**). A soln. of freshly distilled S_2Cl_2 (149 mg, 1.1 mmol) in CH_2Cl_2 (1 ml) was added at r.t. in small portions to a stirred soln. of **4b** (211 mg, 1 mmol) in CH_2Cl_2 (1 ml). After complete addition, the solvent was evaporated and the crude colorless solid crystallized from MeOH/CH_2Cl_2: 253 mg (91%) of pure **14**. Colorless crystals. M.p. 218–220° (MeOH/CH_2Cl_2). IR

(KBr): 3010*s*, 2972v*s*, 2937*s*, 1467v*s*, 1442v*s*, 1384*s*, 1372*s*, 1199s, 1169*m*, 993*m*, 831v*s*, 799*s*, 557*s*. ^{1}H-NMR: 1.54 (*s*, 8 Me). ^{13}C-NMR: 26.4 (*q*, 4 Me); 27.0 (*q*, 4 Me); 60.0 (*s*, 4 Me_2C); 90.1 (*s*, 2 SCCl); 98.3 (*s*, 2 CCl_2). CI-MS: 525 (31), 524 (15), 523 (74), 522 (21), 521 (100), 519 (56), 175 (90). Anal. calc. for $C_{16}H_{24}Cl_3S_4$ (557.35): C 34.48, H 4.34, Cl 38.17, S 23.01; found: C 34.04, H 4.07, Cl 37.96, S 23.13.

15. *3,3-Dichloro-2,2,4,4-tetramethylcyclobutanethione* S-*Oxide* (**15**). To a stirred soln. of **4b** (1.0 g, 4.7 mmol) in CH_2Cl_2 (15 ml) at 0° (ice-water bath), *m*CPBA acid was added in small portions until the red color of the soln. completely vanished. After 10 min, the soln. was diluted with CH_2Cl_2 (10 ml), washed with sat. aq. $NaHCO_3$ soln., 2% aq. NaOH soln., and brine, dried ($MgSO_4$), and evaporated and the crude thick colorless oil crystallized from hexane in dry ice: 460 mg (43%) of **15**[6]). Colorless crystals. M.p. 149–152° (hexane). IR (KBr): 2992*s*, 2934*s*, 2868*w*, 1795*m*, 1467*s*, 1450*s*, 1383*m*, 1368*m*, 1299*s*, 1222*m*, 1150*m*, 1072v*s*, 1015*m*, 916v*s*, 825v*s*, 607*m*. ^{1}H-NMR: 1.61 (*s*, 2 Me); 1.76 (*s*, 2 Me). ^{13}C-NMR: 25.1 (*q*, 2 Me); 28.8 (*q*, 2 Me); 57.8, 61.5 (2*s*, 2 Me_2C); 98.5 (*s*, CCl_2); 204.1 (*s*, C=S). CI-MS: 248 (13), 246 (69), 245 (10), 244 (100). Anal. calc. for $C_8H_{12}Cl_2OS$ (227.15): C 42.30, H 5.32, S 14.11; found: C 42.44, H 5.75, S 14.16.

16. *1,3-Dipolar Cycloadditions of Sulfines* **15** *and* **18** *with* **3a** *and* **4b**: *General Procedure.* A soln. of **15** or **18** (1 mmol) and **3a** or **4b** (1 mmol) in toluene (0.5 ml) was heated to 110° (oil bath) for 1.5 h. After cooling to r.t., the solvent was evaporated, the residual solid material triturated with MeOH, and the solid product filtered and purified by crystallization.

2,2,8,8-Tetrachloro-1,1,3,3,7,7,9,9-octamethyl-10-oxa-5,11-dithiadispiro[3.1.3.2]undecane (**16**): Yield 236 mg (54%). Colorless crystals. M.p. 162–163° (MeOH/CH_2Cl_2). IR (KBr): 2976*s* (br.), 2938*s* (br.), 1452*s*, 1375*s*, 1056*w*, 946*m*, 881v*s*, 802v*s* (br.), 778*s*, 570*m*. ^{1}H-NMR: 1.33 (*s*, 4 Me); 1.47 (*s*, 2 Me); 1.58 (*s*, 2 Me). ^{13}C-NMR: 21.4 (*q*, 2 Me); 24.5 (*q*, 2 Me); 28.3 (*q*, 2 Me); 28.7 (*q*, 2 Me); 58.2 (*s*, 2 Me_2C); 59.4 (*s*, 2 Me_2C); 81.8 (*s*, SCS); 98.4, 99.0 (2*s*, 2 CCl_2); 112.3 (*s*, OCS). CI-MS: 456 (8), 455 (6), 405 (25), 404 (12), 403 (65), 401 (61), 171 (100). Anal. calc. for $C_{16}H_{24}Cl_4OS_2$ (438.31): C 43.84, H 5.52, S 14.63; found: C 43.64, H 5.48, S 14.79.

2,2-Dichloro-1,1,3,3,7,7,9,9-octamethyl-10-oxa-5,11-dithiadispiro[3.1.3.2]undecan-8-one (**17**): Yield 242 mg (63%). Colorless crystals. M.p. 100–101° (MeOH/CH_2Cl_2). IR (KBr): 2974v*s*, 2935*s*, 1772v*s* (C=O), 1456*s*, 1376*s*, 1252*m* (br.), 1046*s*, 1012*s*, 888*s*, 800*s*. ^{1}H-NMR: 1.23 (*s*, 2 Me); 1.33 (*s*, 2 Me); 1.37 (*s*, 2 Me); 1.61 (*s*, 2 Me). ^{13}C-NMR: 17.4 (*q*, 2 Me); 24.6 (*q*, 4 Me); 28.7 (*q*, 2 Me); 58.4 (*s*, 2 Me_2C); 66.1 (*s*, 2 Me_2C); 82.5 (*s*, SCS); 99.0 (*s*, CCl_2); 110.2 (*s*, OCS); 218.7 (*s*, C=O). CI-MS: 402 (22), 400 (31), 385 (75), 383 (100). Anal calc. for $C_{16}H_{24}Cl_2O_2S_2$ (383.40): C 50.12, H 6.31, S 16.73; found: C 49.95, H 6.45, S 16.62.

Suitable crystals for an X-ray crystal-structure determination were grown from MeOH/CH_2Cl_2 by slow evaporation of the solvent.

8,8-Dichloro-1,1,3,3,7,7,9,9-octamethyl-10-oxa-5,11-dithiadispiro[3.1.3.2]undecan-2-one (**19**): Yield: 196 mg (51%). Colorless crystals. M.p. 103–105° (MeOH). IR (KBr): 2966*s*, 2927*m*, 1790v*s* (C=O), 1451*s* (br.), 1374*m*, 1027*w*, 943*m*, 894*m*, 810*m* (br.), 771*s*. ^{1}H-NMR: 1.25 (*s*, 2 Me); 1.35 (*s*, 2 Me); 1.44 (*s*, 2 Me); 1.52 (*s*, 2 Me). ^{13}C-NMR: 20.9 (*q*, 2 Me); 21.1 (*q*, 2 Me); 25.2 (*q*, 2 Me); 28.4 (*q*, 2 Me); 59.6 (*s*, 2 Me_2C); 65.5 (*s*, 2 Me_2C); 79.2 (*s*, SCS); 98.5 (*s*, CCl_2); 113.5 (*s*, OCS); 217.9 (*s*, C=O). CI-MS: 402 (4), 401 (3), 400 (5), 189 (100), 175 (20). Anal calc. for $C_{16}H_{24}Cl_2O_2S_2$ (383.40): C 50.12, H 6.31, Cl 18.49, S 19.73; found: C 49.73, H 6.10, Cl 18.44, S 16.52.

17. *Reactions of* **4b** *with Thiocarbonylium Methanides: General Procedure.* A stirred red soln. of **4b** (211 mg, 1 mmol) and the corresponding 2,5-dihydro-1,3,4-thiadiazole **20** (1.1 mmol) in abs. THF (1 ml) was heated to 45° (oil bath). The evolution of N_2 was monitored with a fitted gas burette. After 5 h, the red color had disappeared and the evolution of N_2 ceased (collected N_2: *ca.* 25 ml, as expected). After cooling to r.t., the solvent was evaporated and the residue was triturated with MeOH. After 2 h in the refrigerator, the crude product was filtered and purified by crystallization.

3″3″-Dichloro-2″,2″,4″,4″-tetramethyldispiro[adamantane-2,2′-[1,3]dithiolane-4′,1″-cyclobutane] (**21a**): Yield: 230 mg (59%). Colorless crystals. M.p. 92–94° (MeOH). IR (KBr): 2997v*s*, 2977v*s*, 2914v*s* (br.), 2854*s*, 1470*s*, 1451*s*, 1382*m*, 1097*w*, 966*w*, 917*m*, 879*m*, 803*s*. ^{1}H-NMR: 1.35 (*s*, 2 Me); 1.49 (*s*, 2 Me); 1.71–1.81 (*m*, 8 H); 2.02–2.17 (*m*, 6 H); 3.31 (*s*, CH_2). ^{13}C-NMR: 23.3 (*q*, 2 Me); 29.1 (*q*, 2 Me); 26.2, 26.5, 42.1 (3*d*, 4 CH); 36.4, 36.6, 37.5 (3*t*, 5 CH_2); 41.8 (*t*, CH_2S); 55.0 (*s*, 2 Me_2C); 73.4, 74.5 (*s*, 2 quat. C); 100.8 (*s*, CCl_2). CI-MS: 395 (17), 393 (71), 391 (100). Anal. calc. for $C_{19}H_{28}Cl_2S_2$ (391.47): C 58.30, H 7.21, Cl 18.11, S 16.38; found: C 58.19, H 7.21, Cl 18.36, S 16.53.

2,2-Dichloro-1,1,3,3,7,7,9,9-octamethyl-5,10-dithiadispiro[3.1.3.2]undecan-8-one (**21b**): Yield 148 mg (39%). Colorless crystals. M.p. 143–145° (hexane). IR (KBr): 2971v*s*, 2928*m*, 1773v*s* (C=O), 1453*s* (br.), 1381*m*, 1248*w*, 1170*w*, 1024*s* (br.), 906*m*, 885*m*, 806*s* (br.). ^{1}H-NMR: 1.29 (*s*, 2 Me); 1.53 (*s*, 2 Me); 3.16 (*s*,

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[6]) During storage at r.t., **15** decomposed slowly by elimination of S and was converted to **4a**.

CH_2). ^{13}C-NMR: 21.9, 23.5, 25.0, 28.9 (4*q*, 4 Me); 43.3 (*t*, CH_2); 56.2 (*s*, 2 Me_2C); 66.2 (*s*, 2 Me_2C); 73.1 (*s*, SCS); 74.3 (*s*, quat. C); 100.5 (*s*, CCl_2); 219.9 (*s*, C=O). CI-MS: 385 (18), 383 (75), 381 (100). Anal. calc. for $C_{17}H_{26}Cl_2OS_2$ (381.43): C 53.53, H 6.87, Cl 18.59, S 16.81; found: C 53.59, H 6.98, Cl 18.37, S 16.58.

18. trans-*2,2-Dichloro-1,1,3,3,7-pentamethyl-6,8-diphenyl-5-thia-7-azaspiro[3.4]octane* (**24**). A soln. of **22** (209 mg, 1 mmol) in abs. toluene (2 ml) was heated under reflux for 30 min. Then, **4b** (211 mg, 1 mmol) was added in small portions, and the mixture was heated under reflux for 6 h. The solvent was evaporated and the solid residue purified by crystallization: 200 mg (50%) of **24**. Colorless crystals. M.p. 194–196° (MeOH/CH_2Cl_2). IR (KBr): 3025*m*, 2977*m*, 2946*s*, 2844*m*, 2797*m*, 1490*m*, 1454*s* (br.), 1381*s*, 1240*m*, 1024*m*, 1142*m*, 1074*m* (br.), 906*s*, 873*s*, 806v*s*, 758*s*, 727*s*, 711*s*, 695*s*. ^{1}H-NMR: 0.87, 1.28, 1.55, 1.69 (4*s*, 4 Me); 1.83 (*s*, MeN); 4.63 (br. *s*, 2 CH); 7.10–7.60 (*m*, 8 arom. H); 8.20–8.50 (2 arom. H). ^{13}C-NMR: 25.5, 27.0, 27.4, 28.7 (4*q*, 4 Me); 35.5 (*q*, MeN); 54.9, 58.3, 71.0 (3*s*, 3 quat. C); 71.1, 76.3 (2*d*, 2 CH); 102.1 (*s*, CCl_2); 128.2, 128.4, 128.5, 128.6, 128.8, 132.3 (6*d*, 10 arom. CH); 135.5, 139.8 (2*s*, 2 arom. C). CI-MS: 424 (15), 422 (69), 420 (100), 386 (12). Anal. calc. for $C_{23}H_{27}Cl_2NS$ (420.45): C 65.71, H 6.47, Cl 16.86, N 3.33, S 7.63; found: C 65.65, H 6.67, Cl 16.36, N 3.30, S 7.44.

19. *2,2,8,8-Tetrachloro-1,1,3,3,7,7,9,9-octamethyl-5,10,11-trithiadispiro[3.1.3.2]undecane* (**25**). A stirred soln. of **4b** (422 mg, 2 mmol) in freshly distilled PhN_3 (0.5 ml) was heated to 80° (oil bath) and the evolution of N_2 monitored with a fitted gas burette. After 10 h, the N_2 evolution ceased (collected N_2: *ca.* 17 ml, 1/3 of the stochiometric amount). The excess of PhN_3 was removed at 50°/0.1 Torr in a 'Kugelrohr'. The residual oil was analyzed by ^{1}H-NMR: 2*s* at 1.20 and 1.49 ppm; 2*s* at 1.51 and 1.57 ppm; the first two signals were attributed to the *N*-phenylimine **26**, which decomposed during prep. TLC (SiO_2). Prep. TLC (SiO_2, hexane) followed by recrystallization yielded 110 mg (36%) of anal. pure **25**. Colorless crystals. M.p. 183–184° (MeOH/CH_2Cl_2). IR (KBr): 2994*s*, 2979*s*, 2937*m*, 1470*s*, 1452*m*, 1442*m*, 1382*s*, 1368*m*, 947*m*, 871*s*, 800v*s*, 566*m*. ^{1}H-NMR: 1.51 (*s*, 4 Me); 1.58 (*s*, 4 Me). ^{13}C-NMR: 25.4 (*q*, 4 Me); 29.4 (*q*, 4 Me); 59.1 (*s*, 4 Me_2C); 88.0 (*s*, 2 SCS); 100.0 (*s*, 2 CCl_2). CI-MS: 456 (59), 454 (100), 419 (82). Anal. calc. for $C_{16}H_{24}Cl_4S_3$ (454.38): C 42.30, H 5.32, S 21.17; found: C 42.64, H 5.23, S 19.48.

20. *X-Ray Crystal-Structure Determination of* **12** *and* **17** (*Table* and *Figs. 1* and *2*)[7]). All measurements were performed on a *Nonius-KappaCCD* diffractometer [36] by using graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford-Cryosystems Cryostream-700* cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in *Figs. 1* and *2*. Data reduction was performed with HKL Denzo and Scalepack [37]. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method [38] was applied. Equivalent reflections, other than the *Friedel* pairs for **12**, were merged. The structures were solved by direct methods with SIR92 [39], 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 by using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me groups). The refinement of each structure was carried out on F^2 by full-matrix least-squares procedures, which minimized the function $\sum w(F_o^2 - F_c^2)^2$. Corrections for secondary extinction were not applied. In **12** and **17**, three and one reflections, resp., whose intensities were considered to be extreme outliers, were omitted from the final refinement. Refinement of the absolute structure parameter [40] of **12** yielded a value of $-0.03(5)$, which confidently confirms that the refined coordinates correspond with the true absolute structure. Neutral-atom scattering factors for non-H-atoms were taken from [41a], and the scattering factors for H-atoms were taken from [42]. Anomalous dispersion effects were included in F_c [43]; the values for f' and f'' were those of [41b]. The values of the mass attenuation coefficients are those of [41c]. All calculations were performed with the SHELXL97 [44] program.

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[7]) CCDC-271077–271078 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.

Table. *Crystallographic Data for Compounds* **12** *and* **17**

		12	**17**
Crystallized from		$MeOH/CH_2Cl_2$	$MeOH/CH_2Cl_2$
Empirical formula		$C_{16}H_{24}Cl_6S_5$	$C_{16}H_{24}Cl_2O_2S_2$
M_r		589.38	383.39
Crystal color, habit		colorless, prism	colorless, tablet
Crystal dimensions [mm]		$0.13\times0.15\times0.20$	$0.10\times0.23\times0.25$
T [K]		160(1)	160(1)
Crystal system		monoclinic	orthorhombic
Space group		*Pc*	*Pbca*
Z		2	8
Reflections for cell determination		20425	56713
2θ range for cell determination [°]		4–55	4–60
Unit cell parameters	a [Å]	12.9819(2)	11.0298(1)
	b [Å]	6.9384(1)	13.3380(2)
	c [Å]	14.7339(3)	25.1125(4)
	β [°]	112.8723(9)	90
	V [Å^3]	1222.79(4)	3694.44(9)
D_x [g cm^{-3}]		1.601	1.378
$\mu(MoK_\alpha)$ [mm^{-1}]		1.132	0.581
Scan type		ϕ and ω	ϕ and ω
$2\theta_{(max)}$ [°]		55	60
Transmission factors [min; max]		0.721; 0.883	0.750; 0.947
Total reflections measured		27585	64184
Symmetry-independent reflections		5533	5407
Reflections with $I>2\sigma(I)$		5023	4040
Reflections used in refinement		5530	5406
Parameters refined; restraints		252; 2	207; 0
Final	$R(F)$ [$I>2\sigma$ (I) reflections]	0.0314	0.0425
	$wR(F^2)$ (all data)	0.0735	0.1164
Weighting parameters (a; b)[a]		0.0406; 0	0.0583; 2.0602
Goodness of fit		1.053	1.036
Final Δ_{max}/σ		0.001	0.001
$\Delta\rho$ (max; min) [e Å^{-3}]		0.53; −0.55	0.79; −0.45

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

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