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Highly Sulfurated Heterocycles via Dithiiranes and Trithietanes as Key Intermediates

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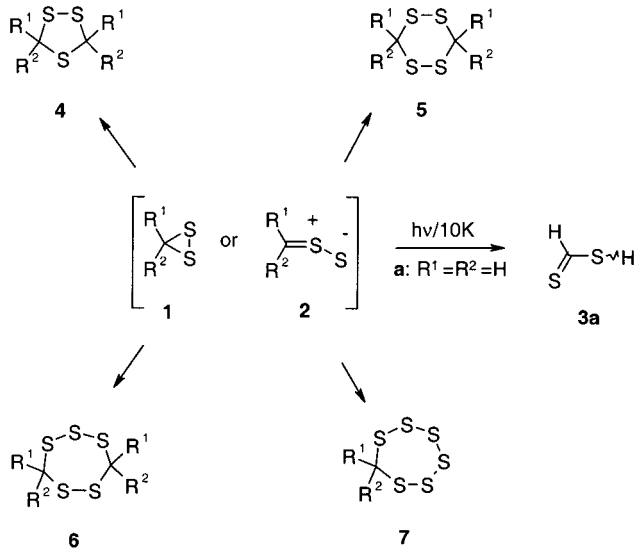
2,2,4,4-Tetramethyl-3-thioxocyclobutanone (**8b**) easily reacts with gaseous chlorine to yield the stable α-chloro sulfenyl chloride **10**. The same product was obtained when **8b** was treated either with phosphorus pentachloride (PCl_5) or sulfuryl chloride (SO_2Cl_2) in CCl_4 solution. Sulfur dichloride (SCl_2) reacts with **8b** to give the α-chloro thiosulfenyl chloride **12** along with an almost equimolar amount of the trisulfide **13b**. The less reactive disulfur dichloride (S_2Cl_2) was shown to react slowly with **8b** and the symmetrical tetrasulfide **15** was found as the exclusive product. The pure thiosulfenyl chloride **12** added to adamantanethione (**8c**) yielded the unsymmetrical trisulfide **13c**. When **12** was treated with thioacetic acid, the acetylated trisulfide **17** was formed in high yield. "Unzipping" reactions with the acetylated disulfide **16** and trisulfide **17** with morpholine in THF at −40 °C led to the formation of mixtures of two sulfur-rich heterocycles identified as the pentathiepane **6b** and the hexathiepane **7b**. A mixture of analogous products was obtained when α-chloro sulfenyl chloride **10** was treated with sodium sulfide in anhydrous THF at −40 °C. The formation of **6b** and **7b** is believed to occur via the intermediate dithiirane **1b** and/or the isomeric thiosulfine **2b**. In the case of **17** the reaction starts probably with the formation of a nonisolable tetrathiane **18b** as presented in Scheme 5.

Introduction

The intermediacy of the dithiiranes **1** and of their valence isomers, the thiosulfines **2**, has been proposed by many authors to explain a number of reaction mechanisms leading to sulfur-rich heterocycles such as 1,2,4-trithiolanes **4**, 1,2,4,5-tetrathianes **5**, 1,2,3,5,6-pentathiepanes **6**, and hexathiepanes **7**.[1] Recently, the matrix isolation of the parent thiosulfine **2a** and dithiirane **1a** with subsequent photolysis at 10 K delivered clear-cut evidence for the possible transformation of **1a** and **2a** to dithioformic acid (**3a**).[2]

The isolation of a series of stable dithiiranes **1** by Ishii and Nakayama was a milestone in the development of the chemistry of small-ring heterocycles and allowed a physicochemical characterization of sulfur-containing strained ring systems.[3]



(1) (a) Fabian, J.; Senning, A. *Sulfur Rep.* **1998**, *21*, 1−42. (b) Huisgen, R.; Rapp, J. *Tetrahedron* **1997**, *53*, 939−960. (c) Huisgen, R.; Rapp, J.; Huber, H. *Liebigs Ann./Recl.* **1997**, 1517−1523. (d) Mloston, G.; Heimgartner, H. *Helv. Chim. Acta* **1996**, *79*, 1305−1314. (e) Mloston, G.; Romanski, J.; Heimgartner, H. *Pol. J. Chem.* **1996**, *70*, 437−445. (f) El-Essawy, F. A. G.; Yassin, S. M.; El-Sakka, I. A.; Khattab, A. F.; Søtofte, I.; Madsen, J. Ø.; Senning, A. *J. Org. Chem.* **1998**, *63*, 9840−9845. (g) Hegab, M. I.; Abdel-Megeid, F. M. E.; Gad, F. A.; Shiba, S. A.; Søtofte, I.; Møller, J.; Senning, A. *Acta Chem. Scand.* **1999**, *53*, 133−140. (h) Hawata, M. A.; El-Torgoman, A. M.; El-Kousy, S. M.; Ismail El-Hamid, A.; Madsen, J. Ø.; Søtofte, I.; Lund, T.; Senning, A. *Eur. J. Org. Chem.* **2000**, 2583−2592.

(2) (a) Mloston, G.; Romanski, J.; Reisenauer, H. P.; Maier, G. *Angew. Chem.* **2001**, *113*, 401−404. (b) Senning, A. *Angew. Chem.* **1979**, *91*, 1006−1008. Cf.: Vivekanda, S.; Srinivas, R.; Manoharan, M.; Jemmis, E. D. *J. Phys. Chem.* **1999**, *103*, 5123−5128.

(3) (a) Ishii, A.; Nakayama, J. *Rev. Heteroat. Chem.* **1999**, *19*, 1−34. (b) Ishii, A.; Nakayama, J. *Adv. Heterocycl. Chem.* **2000**, *77*, 221−284 and papers cited therein.

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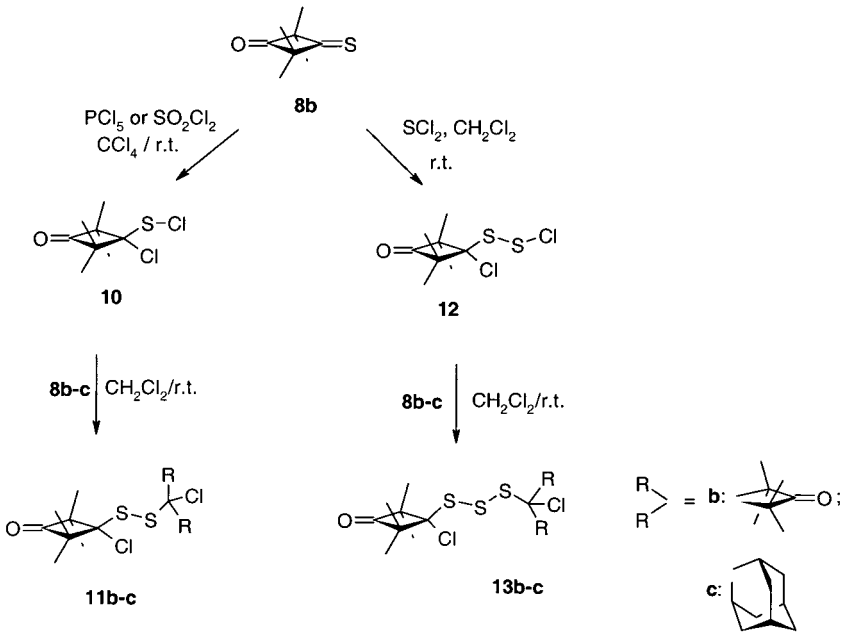
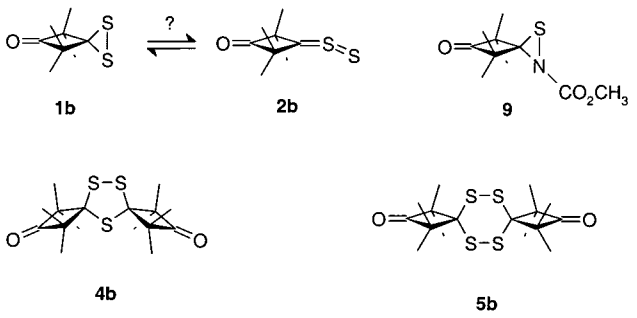
SCHEME 1



The stability of the isolable dithiiranes[3,4] is believed to be due to thermodynamic factors and thus bulky substituents must be present. According to Shimada et al.[4a] treatment of thiocamphor derived sulfines (thiocarbonyl *S*-oxides) with Lawesson's reagent also leads to isolable dithiiranes. Our attempts to apply this methodology to 2,2,4,4-tetramethyl-3-thioxocyclobutanone *S*-oxide or adamantanethione *S*-oxide, respectively, were unsuccessful and only desulfurated products could be detected.[4c] No examples of dithiiranes stabilized by electronic effects have been reported so far.[1a,3] By definition, dithiiranes useful for mechanistic studies and for synthetic purposes must be highly reactive.

2,2,4,4-Tetramethyl-3-thioxocyclobutanone *S*-sulfide (**2b**), a promising precursor of the sterically encumbered dithiirane **1b**, has so far been generated in two ways: (1) The formation (in 36% yield, together with other products) of the 1,2,4-trithiolane **4b** upon heating of the thioketone **8b** with methyl azidoacetate was interpreted in terms of sulfur transfer from the postulated thiaziridine **9** to **8b**; subsequent [3+2] cycloaddition of **2b** to **8b** would then yield **4b**.[1e] (2) The reaction of **8b** with elemental sulfur (in the presence of sodium benzenethiolate) leads, according to Huisgen et al.,[1c] to **2b** which, depending on the reaction conditions, is further converted to **5b** and/or **6b**. The intermediacy of **2b** was not explicitly acknowledged by these authors.



The aim of the present paper is to explore the role of the dithiirane **1b**, presumably existing in equilibrium with the thiosulfine **2b**, in the formation of sulfur-rich heterocycles under mild conditions (ethereal solutions, −40 °C).

Results and Discussion

Recently we reported the synthesis of the α-chloro sulfenyl chloride **10** from **8b** and chlorine.[5] Now we are pleased to present an even more convenient protocol for the preparation of **10** from **8b** and either phosphorus pentachloride (PCl_5) or sulfuryl chloride (SO_2Cl_2) as chlorinating agents. Investigating an early claim by Schönberg et al.[6] to the effect that thioketones react with thionyl chloride ($SOCl_2$) with formation of the corresponding dichloromethylene compounds (readily hydrolyzed to the corresponding ketones) we treated **8b** with excess thionyl chloride, both at ambient temperature and under reflux conditions, but no reaction could be observed. It is tempting to assume that what Schönberg et al. actually encountered was the acid hydrolysis of aromatic thioketones after the aqueous workup.

Little has been reported about reactions of thioketones with sulfur chlorides[7a] and sulfenyl chlorides.[7b] In our hands, thioketone **8b** neatly added dilute sulfur dichloride at room temperature to form a mixture of almost equal amounts of 3-chloro-3-chlorodisulfanyl-2,2,4,4-tetramethylcyclobutanone (**12**) and the trisulfide **13b** (Scheme 1). Both products were separated by distillative workup; however, the crude **12** was satisfactory for some

(4) (a) Shimada, K.; Kodaki, K.; Aoyagi, S.; Takikawa, Y.; Kabuto, C. *Chem. Lett.* **1999**, 695−696. (b) Ishi, A.; Saito, M.; Murata, M.; Nakayama, J. *Eur. J. Org. Chem.* **2002**, 979−982. (c) Mloston, G.; Celeda, M. Unpublished results, University of Lodz, 2000.

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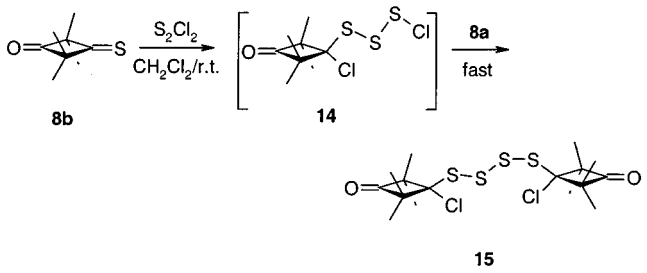
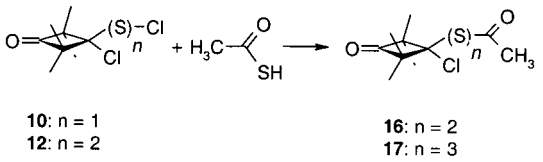
(6) Schönberg, A.; Asker, W. *J. Chem. Soc.* **1946**, 604−608.

(7) (a) Still, I. W. J.; Kutney, G. W.; McLean, D. *J. Org. Chem.* **1982**, *47*, 555−560. (b) Williams, Ch. R.; Harpp, D. N. *Tetrahedron Lett.* **1991**, *32*, 7633−7636.

SCHEME 2



SCHEME 3



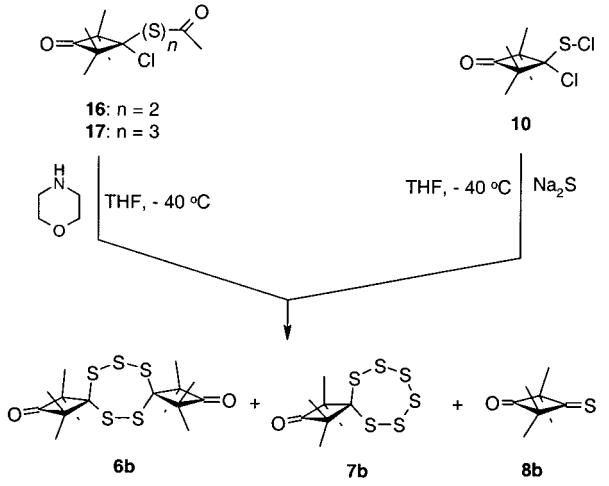
synthetic purposes (the same was true of crude **10**).[5] The sulfenyl chloride **10** reacted smoothly with thioketones **8b** and **8c** to give the corresponding disulfides **11b** and **11c**, respectively, in high yields. In their ^{13}C NMR spectra the symmetrical compound **11b** exhibits one signal at 84.8 ppm for the equivalent carbon atoms C-α and C-α′ while the mixed product **11c** shows two singlets at 85.7 and 91.5 ppm, respectively. The disulfane **12** readily added to an equimolar amount of **8b** to form the corresponding symmetrical trisulfide **13b**. In this case the C-α/C-α′ ^{13}C NMR signal appears at 88.3 ppm. Similarly there occurred a reaction between freshly distilled **12** and **8c**, and the trisulfide **13c** was isolated as the sole product in high yield. Two quaternary C-atoms substituted with sulfur and chlorine atoms exhibited their resonance signals at 88.6 and 93.4 ppm, respectively (Scheme 1).

Disulfur dichloride is known to be less reactive than sulfur dichloride.[5b,8] This rule of thumb was confirmed in the corresponding reactions with **8b**. While addition of SCl_2 to **8b** at ambient temperature led to immediate discharge of the characteristic purple thioketone color the corresponding decoloration after the addition of S_2Cl_2 required several minutes. The latter reaction mixture yielded, after evaporation of the solvent, a crystalline product that could be shown to be bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl) tetrasulfide (**15**), i.e., a 2:1 adduct of **8b** and disulfur dichloride. Interestingly, the ^1H NMR spectrum of **15** contains two sharp singlets at 1.40 and 1.41 ppm, respectively, each integrating for 12 protons. While it is inconceivable that the 1:1 adduct **14** should not be an intermediate in the formation of **15** we were unable to directly observe or trap **14** in the presence of **8c** (Scheme 2).

The sulfenyl chlorides **10** and **12** smoothly react with thioacetic acid to afford the corresponding unsymmetrical disulfide **16** and the trisulfide **17**, respectively (Scheme 3).

While earlier work with the "unzipping" of acetyl α-chloroalkyl disulfides typically yielded 1,2,4-trithiolanes **4** and/or 1,2,4,5-tetrathianes **5** as the dominant products (or mainly led to a trivial loss of sulfur),[1a] we

SCHEME 4



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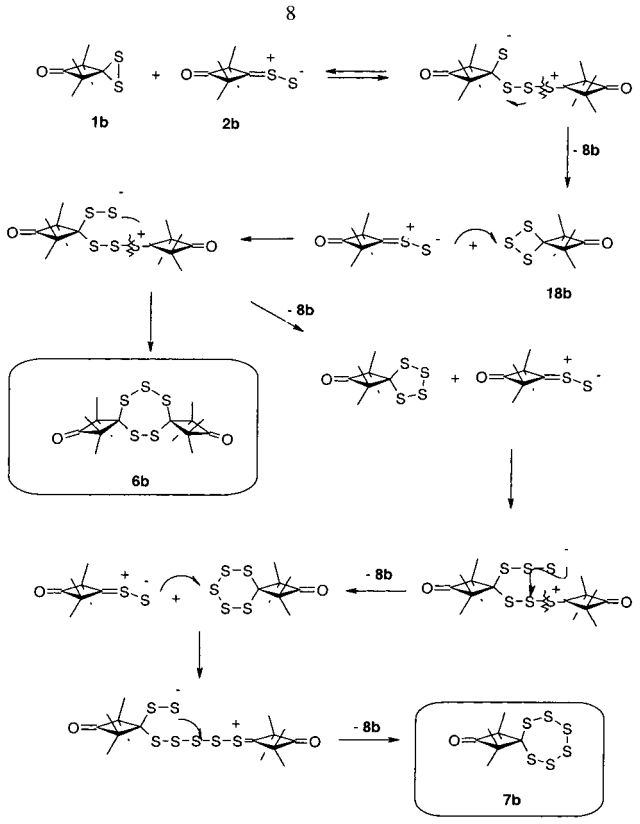

now find that the corresponding treatment of **16** and **17** with morpholine probably leads to the near-exclusive formation of the dithiirane **1b** in the former case and of the trithietane **18b** in the latter (Scheme 5). Thus, treatment of 3-(acetyldisulfanyl)-3-chloro-2,2,4,4-tetramethylcyclobutanone (**16**) with morpholine in ethereal solution at −40 °C caused an orange coloration of the reaction mixture.

It should be noted that authentic dithiiranes **1** described by Ishi and Nakayama are orange and in dichloromethane solution exhibit absorption maxima around 460 nm.[9] On the other hand, the parent thiosulfine **2a** has calculated UV−vis absorptions at 300 ($\pi \rightarrow \pi^*$) and 373 ($n \rightarrow \pi^*$) nm[1a] and **2b** should thus be rather colorless.

(8) Austad, B. C. In *Encyclopedia of Reagents for Organic Synthesis*; Paquette, L. A., Ed.; John Wiley & Sons: New York, 1995; Vol. 4, pp 2306−2307 (see for S_2Cl_2) and Vol. 7, pp 4686−4688 (see for SCl_2).

When the reaction mixture was allowed to reach ambient temperature the primarily formed 1,1,3,3-tetramethyl-5,6-dithiaspiro[3.2]bicyclohexan-2-one (**1b**) entered into secondary reactions which afforded a mixture of the pentathiepane **6b**,[1c] the hitherto unknown hexathiepane **7b**, and the monothione **8b**. Due to the notorious volatility of **8b** it was impossible to determine the exact **6b**:**7b**:**8b** ratio in the reaction mixture. The products **6b** (yield 66%)[10] and **7b** (yield 11%) could be separated by column chromatography on silica gel, the latter constituting the less polar component. Apart from the standard spectroscopic identification both **6b** (whose structure had not been rigorously established in previous work[1c]) and **7b** (Scheme 4) were subjected to single-crystal X-ray structure determinations.

Interestingly, the same orange color could be observed when the α-chloro sulfenyl chloride **10** was treated with sodium sulfide at −40 °C. This color disappeared upon warming to approximately −20 °C. After standard work-up and column chromatography **6b**, **7b**, and variable amounts of **8b** could be isolated. In this case the **6b**:**7b** molar ratio was determined as 10:90[11] (based on the ^{1}H NMR spectrum of the crude reaction mixture, Scheme 4).

In conclusion, the "unzipping" of the acetyl oligosulfides **16** and **17** with morpholine leads to the formation of **6b** and **7b**, the key intermediates probably being the dithiirane **1b** in the case of **16** and the trithietane **18b** in the case of **17**. The same products, but in an inverted molar ratio, were formed when **10** was treated with sodium sulfide according to a somewhat less developed literature method.[12]

The practically exclusive formation of oligothiepanes from dithiiranes appears to be unique for cyclobutanone derivatives such as those used in the present study. In comparable systems lacking the combination of steric crowding and small-ring strain or where the dominating intermediate S_2 species is the thiosulfine, oligothiepanes are formed as minor byproducts, if at all.[1c,f,h,13] It should also be noted that earlier studies focused on the "unzipping" of acyl α-chloroalkyl trisulfides failed to generate isolable trithietanes or straightforward trapping products of trithietanes.[14]

As presented in Scheme 5 the strong preference for the build-up of the "magic" seven-membered sulfur heterocycles **6b** and **7b** appears to be the result of a *domino* reaction involving both the dithiirane **1b** and the thiosulfine **2b** with several ring closure−ring opening sequences.

It is deemed plausible, on the basis of their analogy with thiocarbonyl *S*-methylides, that thiosulfines are basic and nucleophilic species.[13]

At the same time Ishii and Nakayama[16] have reported that dithiiranes readily undergo ring opening upon treatment with nucleophiles. Similar *domino* reactions would appear feasible starting with the interaction between the α-chloro sulfenyl chlorides **10** and excess sodium sulfide.

Experimental Section

General Methods. Melting points were determined in a capillary and are uncorrected. The IR spectra of solids were taken with KBr wafers and spectra of liquids between NaCl; the absorption maxima are shown in cm^{-1}. ^{1}H NMR spectra (100 MHz) and ^{13}C NMR spectra (25.16 MHz) were obtained with TMS as internal standard ($\delta_{TMS} = 0$ ppm). The mass spectra were registered as EI or ESI (MeOH, NaI). The elemental microanalyses were performed in the laboratory of the Polish Academy of Sciences (CBMiM) in Lodz. The single crystals for the X-ray work (cf. Supporting Information) were obtained by crystallization from petroleum ether in a refrigerator (vide infra).

Starting Materials. Commercial thioacetic acid was used as received while commercial sodium sulfide nonahydrate was dried in vacuo according to a literature procedure.[17] The thioketones **8b**[18] and **8c**[19] were prepared according to published protocols. Commercial sulfur dichloride (SCl_2) and disulfur dichloride (S_2Cl_2) were distilled prior to use according to literature protocols.[8]

Conversions of the Monothione 8b to the α-Chloro Sulfenyl Chloride 10. (a) With phosphorus pentachloride: To a solution of **8b**[18] (156 mg, 1.00 mmol) in 2 mL of tetrachloromethane was added, in small portions, 418 mg (2.00 mmol) of phosphorus pentachloride. The reaction mixture was heated with reflux until it became colorless (10−20 min) and then, after cooling, poured into ice/water. The organic layer was diluted with 20 mL of dichloromethane, extracted three times with 20-mL portions of water, and dried over anhydrous magnesium sulfate. After filtration and evaporation of the solvent in vacuo crude **10** was obtained as a viscous pale yellow oil, yield 205 mg (90%). **(b) With sulfuryl chloride:** To a solution of **8b** (156 mg, 1.00 mmol) in 2 mL of tetrachloromethane was added, under argon atmosphere, 270 mg (2.00 mmol) of freshly distilled sulfuryl chloride. After 4 h at ambient temperature complete decoloration had taken place. Tetrachloromethane (10 mL) was added and the mixture was poured into ice/water. The organic layer was separated, shaken with 5% aqueous sodium carbonate then with water, dried over anhydrous magnesium sulfate, and filtered. After evaporation of the solvent 170 mg (75%) of **10** was obtained as a viscous pale yellow oil. Both preparations were subsequently used without further purification. Their spectral properties (IR, ^{1}H NMR) corresponded to the literature data for **10**.[5]

Attempted Reaction of 8b with Thionyl Chloride. Under an atmosphere of argon, a solution of **8b** (156 mg, 1.00 mmol) in 2 mL of tetrachloromethane was kept under reflux

(9) Ishii, A.; Maruta, T.; Teramoto, K.; Nakayama, J. *Sulfur Lett.* **1995**, *18*, 237−242.

(10) The calculation of the yields for **6b** and **7b** in the "unzipping" reactions was based on the following stoichiometric relations: 5 mol of **16** → 1 mol of **7b** + 4 mol of **8b**; 3 mol of **16** → 1 mol of **6b** + 1 mol of **8b**; 5 mol of **17** → 2 mol of **7b** + 3 mol of **8b**; 2 mol of **17** → 1 mol of **6b** + $^1/_8$ mol of S_8.

(11) The calculation of the yields for **6b** and **7b** in the reactions of the α-chloro sulfenyl chloride **10** with excess sodium sulfide was based on the following stoichiometric relations: 2 mol of **10** → 1 mol of **6b** + 1 mol of **8b** and 2 mol of **10** → 1 mol of **7b** + 1 mol of **8b**.

(12) Dubs, P.; Joho, M. *Helv. Chim. Acta* **1978**, *61*, 1404−1407.

(13) (a) Okazaki, R.; Inoue, K.; Inamoto, N. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 3541−3545. (b) Jin, Y.-N.; Ishii, A.; Sugihara, Y.; Nakayama, J. *Heterocycles* **1997**, *44*, 255−262. (c) Hartke, K.; Wagner, U. *Chem. Ber.* **1996**, *129*, 663−669.

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(15) Mloston, G.; Heimgartner, H. *Pol. J. Chem.* **2000**, *74*, 1503−1532.

(16) Ishii, A.; Omata, T.; Umezawa, K.; Nakayama, J. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 729−737.

(17) Hermann, W. A.; Zybill, Ch. E. Sulfur, Selenium, Tellurium. In *Synthetic Methods of Organometallic and Inorganic Chemistry*; Hermann, W. A., Ed.; G. Thieme Verlag: Stuttgart, Germany, 1997; Vol. 4, p 41.

(18) (a) Elam, E. U.; Davis, H. E. *J. Org. Chem.* **1967**, *32*, 1562−1565. (b) Mloston, G.; Romanski, J.; Linden, A.; Heimgartner, H. *Helv. Chim. Acta* **1993**, *76*, 2147−2154.

(19) (a) Huisgen, R.; Mloston, G. *Pol. J. Chem.* **1999**, *73*, 635−644. (b) Greidanus, J. W. *Can. J. Chem.* **1970**, *48*, 3530−3534.

with 714 mg (6.00 mmol) of thionyl chloride. The purple color of **8b** persisted for 2 h.

Reaction of 8b with Sulfur Dichloride. Thioketone **8b** (936 mg, 6.00 mmol) was dissolved in 5 mL of tetrachloromethane. To the stirred solution was added a solution of freshly distilled SCl_2 in 5 mL of dichloromethane until the purple color of **8b** had disappeared. After an additional 10 min of stirring the solvent was stripped off, leaving a crude mixture of **12** and **13b** as 1.42 g of a viscous yellow oil. The ^{1}H NMR analysis showed that **12** and **13b** were present in a ratio of ca. 1:1. The crude mixture was triturated with a portion of petroleum ether and after 1 h at room temperature 272 mg (0.65 mmol) of colorless crystals of trisulfide **13b** were filtered off. The solvent was evaporated from the mother liquor and the residual thick oil was distilled in a kugelrohr apparatus to yield pure **12** as a pale yellow oil.

3-Chloro-3-(chlorodisulfanyl)-2,2,4,4-tetramethylcyclobutanone (12): 464 mg (30%) of a pale yellow oil, kugelrohr distilled at 100 °C/0.4 Torr; IR (neat) 2981 (s), 2933 (m), 1792 (C═O, vs), 1464 (br s), 1383 (m), 1365 (m), 1024 (s), 916 (m), 833 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.44 (s, Me), 1.49 (s, 2 Me); ^{13}C NMR δ 24.0 (2 Me), 22.9 (2 Me), 69.2 (C-2, C-4), 87.8 (C-3), 215.1 (C-1). Anal. Calcd for $C_8H_{12}Cl_2OS_2$ (259.22): C, 37.07; H, 4.67; S, 24.74. Found: C, 37.52; H, 4.66; S, 24.55.

Reaction of 8b with Disulfur Dichloride. Disulfur dichloride (810 mg, 6.00 mmol) was dissolved in 7 mL of dichloromethane. To the stirred solution was added dropwise 936 mg (6.00 mmol) of **8b**,[18] dissolved in 7 mL of dichloromethane. When the addition was complete (after ca. 15 min) the reaction mixture was stirred for another 20 min whereafter the purple color of **8b** had disappeared. The solution was evaporated in vacuo to yield **15** as a yellow solid, yield 2.49 g (93%). Recrystallization from petroleum ether gave 1.38 g (55%) of colorless crystals.

Bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl) tetrasulfide (15): mp 132−134 °C; IR 1770 (vs, C═O), 1420 (s), 1350 (s), 1120 (vs), 1000 (s), 870 (s), 800 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 4 Me), 1.41 (s, 4 Me); ^{13}C NMR ($CDCl_3$) δ 22.9 (4 Me), 23.6 (4 Me), 69.5 (C-2, C-2′, C-4, C-4′), 87.9 (C-1, C-1′), 215.9 (C-3, C-3′); MS (EI) *m*/*z* (%) 447 (<1, M$^+$), 43 (100). Anal. Calcd for $C_{16}H_{24}Cl_2O_2S_4$ (447.53): C, 42.94; H, 5.41; S, 28.66. Found: C, 42.93; H, 5.48; S, 29.03.

Reactions of the α-Chloro Sulfenyl Chloride 10 with the Thioketones 8b and 8c. To a stirred solution of 1.00 mmol of **8b** or **8c** in 2 mL of dichloromethane was added 227 mg (1.00 mmol) of crude **10**, dissolved in 1 mL of dichloromethane. In the case of **8b** immediate decoloration took place while the reaction with **8c** required ca. 8 h at room temperature. The solvent was evaporated and the solid residue purified by recrystallization from petroleum ether. The yields shown are of recrystallized products.

Bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl) disulfide (11b): yield 470 mg (61%); mp 98−100 °C; IR 1795 (vs, C═O), 1460 (vs), 1370 (s), 1240 (m), 1160 (m), 1120 (w), 1020 (s), 910 (s), 820 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 4 Me), 1.51 (s, 4 Me); ^{13}C NMR ($CDCl_3$) δ 22.9 (4 Me), 23.3 (4 Me), 69.9 (2 C-2, C-2′, C-4, C-4′), 84.8 (C-1, C-1′), 216.6 (C-3, C-3′); MS (ESI) *m*/*z* (%) 407 (68, [(M + 1) + Na]$^+$, 406 (16, [M + Na]$^+$), 405 (100, [(M − 1) + Na]$^+$, 319 (53), 163 (71), 131 (49). Anal. Calcd for $C_{16}H_{24}Cl_2O_2S_2$ (383.40): C, 50.12; H, 6.31; S, 16.73. Found: C, 50.35; H, 6.34; S, 16.27.

(2-Chloroadamantan-2-yl)(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl) disulfide (11c): yield 240 mg (61%); mp 90−92 °C; IR 1770 (vs, C═O), 1420 (vs), 1350 (m), 1000 (s), 940 (m), 790 (s), 760 (vs) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.36 (br s, 2 Me), 1.51 (s, 2 Me), 1.78 (m, 7H), 2.45 (m, 7H); ^{13}C NMR ($CDCl_3$) δ 23.2 (2 Me), 23.3 (2 Me), 26.7 (C-5, adamantane), 26.9 (C-7, adamantane), 34.5 (C-4, C-9, adamantane), 35.1 (C-1, C-3, adamantane), 38.5 (C-8, C-10, adamantane), 40.3 (C-6, adamantane), 69.8 (C-2, C-4, cyclobutane), 85.7 (C-1, cyclobutane), 91.5 (C-2, adamantane), 216.8 (C-3, cyclobutane); MS (EI) *m*/*z* (%) 393 (4, M$^+$), 392 (12, M$^+$ − 1), 359 (12), 357 (27, $C_{18}H_{26}ClOS_2$), 324 (5), 322 (7, $C_{18}H_{26}OS_2$), 171 (98), 169 (99), 133 (100). Anal. Calcd for $C_{18}H_{26}Cl_2OS_2$ (393.44): C, 54.95; H, 6.66; S, 16.30. Found: C, 55.35; H, 7.00; S, 16.39.

Reaction of 3-Chloro-3-chlorodisulfanyl-2,2,4,4-tetramethylcyclobutanone (12) with the Thioketones 8b and 8c. To a stirred solution of 518.5 mg (2.00 mmol) of freshly distilled **12** in 5 mL of dichloromethane was slowly added a solution of 2.00 mmol of the appropriate **8** dissolved in 5 mL of dichloromethane. The color of each portion of **8b** was immediately discharged after the addition. The analogous reaction with **8c** was slower and the orange color of the thioketone disappeared only after ca. 2 h at ambient temperature. The solvent was stripped off in vacuo, leaving the crude products **13b**,**c** as colorless solids in nearly quantitative yields. Recrystallization from petroleum ether provided analytically pure products.

1,3-Bis(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl) trisulfide (13b): yield 673 mg (81%); mp 110−112 °C; IR 3000 s, 1790 (vs, C═O), 1450 (s), 1380 (s), 1360 (s), 1230 (s), 1155 (s), 1120 (s), 1010 (vs), 900 (s), 870 (s), 810 (s), 780 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.45 (s, 4 Me), 1.47 (s, 4 Me); ^{13}C NMR ($CDCl_3$) δ 22.6 (4 Me), 23.5 (4 Me), 69.2 (C-2, C-2′, C-4, C-4′), 88.2 (C-1, C-1′), 216.9 (C-3, C-3′); MS (ESI) *m*/*z* (%) 439 (67, [(M + 1) + Na]$^+$, 438 (28, [M + Na]$^+$), 437 (100, [(M − 1) + Na]$^+$), 413 (37), 304 (33), 280 (41), 179 (48). Anal. Calcd for $C_{16}H_{24}Cl_2O_2S_3$ (415.47): C, 46.26; H, 5.82; S, 23.15. Found: C, 46.20; H, 5.77; S, 22.26.

(2-Chloroadamantan-2-yl)(1-chloro-2,2,4,4-tetramethyl-3-oxocyclobutan-1-yl) trisulfide (13c): yield 580 mg (68%); mp 197−199 °C; IR (KBr) 2907 (s), 1788 (vs, C═O), 1450 (m), 1020 (m), 960 (w), 821 (w), 790 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (s, 2 Me), 1.42 (s, 2 Me), 1.60−2.05, 2.10−2.65 (2 m, 14H, adamantane); ^{13}C NMR ($CDCl_3$) δ 22.9 (2 Me), 23.6 (2 Me), 26.8 (C-5, adamantane), 27.1 (C-7, adamantane), 34.2 (C-4, C-9, adamantane), 34.9 (C-1, C-3, adamantane), 38.6 (C-8, C-10, adamantane), 39.8 (C-6, adamantane), 69.5 (C-2, C-4, cyclobutane), 88.6 (C-3, cyclobutane), 93.4 (C-2, adamantane), 216.5 (C-3, cyclobutane); MS (CI, isobutane) *m*/*z* (%) 390 (M$^+$ − Cl, 21), 389 (100), 335 (25), 169 (26), 167 (57). Anal. Calcd for $C_{18}H_{26}Cl_2OS_3$ (425.51): C, 50.81; H, 6.16; S, 22.61. Found: C, 50.56; H, 6.17; S, 22.06.

Synthesis of the Acetyl Oligosulfides 16 and 17: General Procedure. To a stirred solution of 1.50 mmol of **10** or **12** was added 15 mL of tetrachloromethane thioacetic acid (122 mg, 1.60 mmol). In the case of **10** the reaction was complete after 5 min at room temperature. The less reactive **12** required heating in a bath kept at 50 °C for 30 min under a reflux condenser. The solvent was then removed in vacuo and the residue crystallized from petroleum ether. The stated yields refer to recrystallized material.

3-(Acetyldisulfanyl)-3-chloro-2,2,4,4-tetramethylcyclobutanone (16): yield 212 mg (53%); mp 52−54 °C (reported as colorless oil[5]); IR 1795 (vs, ketone C═O), 1700 (vs, thioacyl C═O), 1360 (s), 1110 (vs), 1010 (s), 940 (s), 900 (s), 810 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.40 (br s, 2 Me), 1.50 (2 Me), 2.52 (s, CH_3CO); ^{13}C NMR ($CDCl_3$) δ 22.4 ($2CH_3$), 23.6 ($2CH_3$), 28.7 (CH_3-CO), 69.3 (C-2 + C-4), 86.9 (C-3), 192.9 (CH_3-*C*O), 215.5 (C═O); MS (CI) *m*/*z* (%) 283 (100, M$^+$ + NH_3). Anal. Calcd for $C_{10}H_{15}ClO_2S_2$ (266.81): C, 45.02; H, 5.67; Cl, 13.29; S, 24.04. Found: C, 44.95; H, 5.48; Cl, 13.46; S, 23.82.

3-(Acetyltrisulfanyl)-3-chloro-2,2,4,4-tetramethylcyclobutanone (17): yield 206 mg (46%); mp 76−78 °C; IR 1790 (vs, ketone C═O), 1740 (vs, thioacyl C═O), 1460 (s), 1380 (w), 1100 (s), 1020 (m), 940 (m), 910 (m), 820 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.44 (s, 2 Me), 1.45 (s, 2 Me), 2.49 (s, CH_3CO); ^{13}C NMR ($CDCl_3$) δ 22.5 (2 Me), 23.4 (2 Me), 29.2 (CH_3CO), 69.2 (C-2, C-4), 87.7 (C-3), 192.1 (CH_3*C*O), 215.8 (C-1); MS (ESI) *m*/*z* (%) 323 (36, [(M + 1) + Na]$^+$), 322 (13, [M + Na]$^+$), 321 (100, [(M − 1) + Na]$^+$), 166 (37), 165 (74). Anal. Calcd for $C_{10}H_{15}ClO_2S_3$ (298.88): C, 40.19; H, 5.06; Cl, 11.86; S, 32.19. Found: C, 40.38; H, 5.00; Cl, 11.57; S, 31.89.

"Unzipping" of 16 and 17 with Morpholine. Morpholine (653 mg, 7.50 mmol) was dissolved in 3 mL of diethyl ether and the solution placed in an acetone/dry ice bath kept at −40 °C. To the stirred solution was added dropwise a solution of 1.50 mmol of **16** or **17** in 2 mL of diethyl ether. After the addition cooling and stirring was continued for 4 h where TLC showed complete consumption of the starting material. In the case of **16** the reaction mixture assumed an *orange* color that changed to red upon warming to room temperature. After the addition of 15 mL of diethyl ether the reaction mixture was shaken with 2 × 30 mL of water. The organic phase was dried over anhydrous sodium sulfate, the solvent evaporated, and the residue analyzed by ^{1}H NMR. The ratios between **6b** and **7b** (85:15 starting with **16** and 35:65 starting with **17**) were established by comparison of the singlets at 1.65 (2 Me for **6b**) and 1.42 ppm (4 Me for **7b**). The crude products were purified by preparative TLC or by column chromatography, the mobile phase being petroleum ether with increasing amounts of dichloromethane. The stated yields refer to pure, chromatographed, and recrystallized material.

1,1,3,3,8,8,10,10-Octamethyl-5,6,11,12,13-pentathiadispiro[3.3.3.2]tridecane-2,9-dione (6b): yields 134 mg (66%) from **16** and 48 mg (16%) starting from **17**; mp 154−156 °C (from petroleum ether; lit.[1c] mp 148−150 °C); IR 1780 (vs, C=O), 1460 (s), 1380 (m), 1360 (m), 1240 (m), 1160 (s), 1130 (m), 1015 (s), 870 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.38 (s, 2 Me), 1.45 (s, 2 Me), 1.52 (s, 6H, 2 Me), 1.65 (s, 2 Me); ^{13}C NMR ($CDCl_3$) δ 21.9 (Me), 22.8 (Me), 23.5 (br, Me), 24.0 (Me), 67.6 (C-1, C-3, C-8, C-10), 216.5 (C-2, C-9), the signal of C-4 and C-7 cannot be observed at 25 °C, for a discussion of this phenomenon see ref 1c. Anal. Calcd for $C_{16}H_{24}O_2S_5$ (408.70): C, 47.02; H, 5.92; S, 39.23. Found: C, 47.27; H, 5.98; S, 39.67.

1,1,3,3-Tetramethyl-5,6,7,8,9,10-hexathiaspiro[3.6]decan-2-one (7b): yields 10 mg (11%) from **16** and 145 mg (76%) starting from **17**; mp 117−119 °C (from petroleum ether mixed with a small amount of dichloromethane); IR 1785 (vs, C=O), 1455 (s), 1380 (m), 1360 (m), 1240 (m), 1160 (m), 1120 (m), 1030 (m), 870 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.42 (br s, 4 Me); ^{13}C NMR ($CDCl_3$) δ 23.7 (br, 4 Me), 68.2 (C-1, C-3), 92.2 (C-4), 215.7 (C-2); MS (EI) *m*/*z* (%) 316 (12, M^+), 252 (100, $M^+ - S_2$), 188 (66, $M^+ - S_4$), 156 (24, $C_8H_{12}OS$), 86 (47, C_4H_6S). Anal. Calcd for $C_8H_{12}OS_6$ (316.58): C, 30.35; H, 3.82; S, 60.77. Found: C, 30.45; H, 3.78; S, 61.13.

Reactions of 10 with Sodium Sulfide. Anhydrous sodium sulfide[17] (936.5 mg, ca. 12 mmol) was placed in a flask with 5 mL of tetrahydrofuran. The colorless suspension was kept at −50 °C in an acetone/dry ice bath and, with magnetic stirring, 2.20 mmol of **10**, dissolved in 3 mL of tetrahydrofuran, was added at once. Then the bath temperature was raised to −20 °C and stirring was continued for 1 h. The reaction mixture was brought to room temperature and evaporated to dryness. The solid residue was triturated with 30 mL of dichloromethane, and the liquid phase was shaken with 2 × 30 mL of water. After drying over anhydrous magnesium sulfate and evaporation of the solvent, the workup was continued as above. The ratios between **6b** and **7b** (10:90) were established by comparison of the singlets at 1.65 ($2CH_3$ for **6b**) and 1.42 ppm ($4CH_3$ for **7b**).

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Supporting Information Available: X-ray crystallographic data and X-ray structures for **6b** and **7b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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