1,3-Dipolar Cycloadditions, 97[1]

Some Cycloadditions of Aromatic Thione *S*-Oxides☆

Rolf Huisgen*, Grzegorz Mloston[2], Kurt Polborn, and Francisco Palacios-Gambra[3]

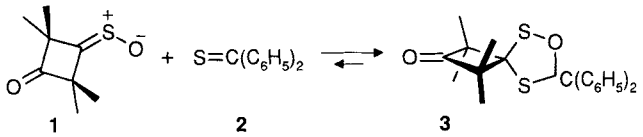
Institut für Organische Chemie der Universität München,
Karlstr. 23, D-80333 München, Germany

Received August 2, 1996

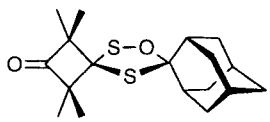
Keywords: 1,2,4-Oxadithiolanes / 1,2,4-Trithiolanes / Thione *S*-oxides (sulfines) / Thione *S*-sulfides (thiosulfines)

Surprisingly, thiobenzophenone *S*-oxide (**5**) and thione **6** afforded the spiro-1,2,4-trithiolane **7** (86%) instead of the expected spiro-1,2,4-oxadithiolane **16**. Structure **7** was established via spectra, single-crystal X-ray analysis, and an independent synthesis from thiobenzophenone *S*-sulfide (**15**) and **6**. On accepting the formation of **16** by 1,3-cycloaddition as a first step, we reduced the mechanistic problem to the conversion **16** + **6** → **15** + dione **8**; three conceivable pathways are discussed. Thiofluorenone *S*-oxide (**25**) combines with **6** to the trithiolane **27** in low yield; the spontaneous conversion of **25** to 9,9′-bifluorenylidene (**26**) takes precedence. No 1,3-cycloaddition is involved in the 1:1 reaction of **5** with (*E*)-cyclooctene (**28**); **5** combines as a hetero-1,3-diene with **28** to a Diels-Alder type adduct **30**.

In a preceding paper it was shown that the alicyclic thione *S*-oxide (sulfine) **1** reacted with thiobenzophenone (**2**) at room temp., furnishing the spiro-1,2,4-oxadithiolane **3**; a small equilibrium concentration of the reactants occurred in solution alongside **3**[4]. The cycloadducts of **1** with alicyclic thioketones, e.g., **4**, are thermodynamically more favored[5].



1 **2** **3**

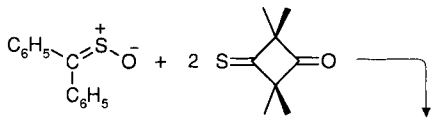


4

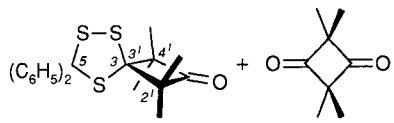
Thiobenzophenone *S*-Oxide and Thione 6

Thiobenzophenone *S*-oxide (**5**) and 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**6**) correspond to the reactant pair **1** and **2** with exchanged functions. Much to our surprise, the slow reaction afforded the spiro-1,2,4-trithiolane **7** instead of the expected 1,2,4-oxadithiolane. The stoichiometry has changed: 2 equiv. of thioketone **6** are consumed and dione **8** appears as desulfurized product. When **5** was reacted with 1.1 equiv. of **6** in $CDCl_3$ at room temp. for 30 d, the ^{1}H-NMR spectrum indicated a 74% consumption of **6** and a molar ratio of 1:1.2 for **7**/**8**. Crystalline **7** was isolated in 86% yield.

Elemental analyses were in accordance with $C_{21}H_{22}OS_3$, and the NMR spectra agreed with **7**. Conspicuously, nearly all of the cationic fragments in the MS of **7** contain the aromatic rings. The peak *m/z* 230 (18%) is ascribed to **9**,

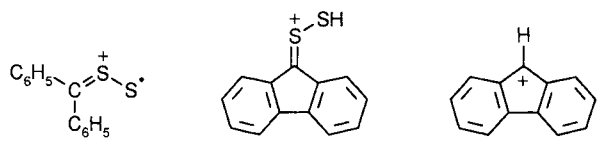


5 **6**



7 **8**

suggesting a cycloreversion of $7^{+\bullet}$ into **9** + neutral **6**; the peak of $6^{+\bullet}$ is missing. Species **9** is the ionization product of thiobenzophenone *S*-sulfide (**15**), mentioned below. The radical cation of thiobenzophenone ($2^{+\bullet}$, *m/z* 198) appears as the base peak, while the fluorenyl cation (**11**, *m/z* 165, 48%) and $C_6H_5C{\equiv}S^+$ (*m/z* 121, 19%) occur as further fragments down the line. In the MS of thiobenzophenone (**2**) itself, fluorenyl$^+$ is the parent peak, and the product of α-cleavage, $C_6H_5C{\equiv}S^+$, occurs with 67%. The structure **10** is tentatively assigned to *m/z* 229 (20%) in the MS of **7**; it suggests that the cyclization to the fluorene backbone already starts at **9**. The S and C contents of the fragments were secured by the intensities of the isotope peaks.



9 **10** **11**

The deep-seated structural change in the reaction of **5** with **6** was confirmed by the X-ray diffraction pattern of

  0947–3440/97/0101–0187 $ 15.00+.25/0

7. The heterocycle approximates an *envelope* conformation modified so as to resemble a *half-chair* (Figure 1).

Figure 1. X-ray structure of spiro-1,2,4-trithiolane **7**; ORTEP plot

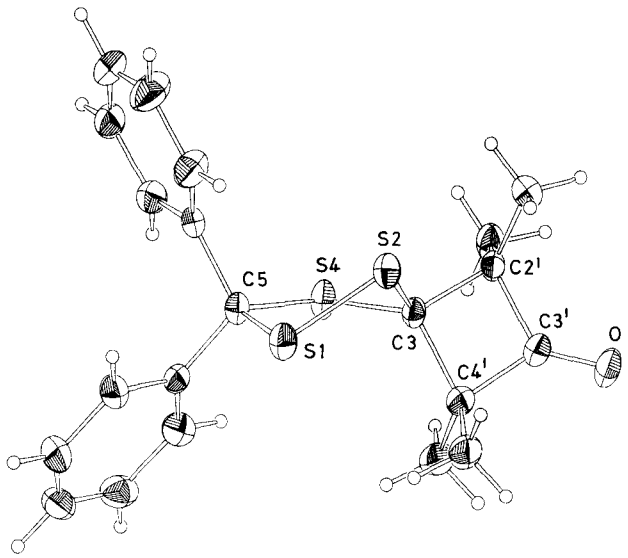
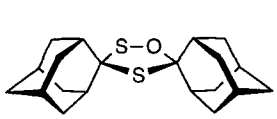


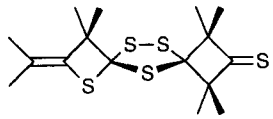
Table 1. Selected bond lengths and angles for the spiro-1,2,4-trithiolane **7** (standard deviations of the last significant digit)

Bond lengths (Å)			
S1–S2	2.031(1)	C1′–C2′	1.518(3)
S2–C3	1.814(2)	C2′–C3′	1.589(3)
C3–S4	1.831(2)	C3′–C4′	1.594(3)
S4–C5	1.855(2)	C4′–C1′	1.515(3)
C5–S1	1.836(2)	C1′–O	1.203(2)
Bond angles (°)			
S1–S2–C3	93.9(1)	C1′–C2′–C3′	86.4(1)
S2–C3–S4	106.0(1)	C2′–C3′–C4′	90.1(1)
C3–S4–C5	103.5(1)	C3′–C4′–C1′	86.3(1)
S4–C5–S1	106.4(1)	C4′–C1′–C2′	95.9(2)
C5–S1–S2	97.5(1)		
Torsion angle in heterocyclic ring (°)			
C5–S1–S2–C3	−53.4(1)		
S1–S2–C3–S4	50.8(1)		
S2–C3–S4–C5	−29.6(1)		
C3–S4–C5–S1	−8.8(1)		
S4–C5–S1–S2	38.3(1)		

The torsion angle of the S1–S2 bond of **7** is 53.4°; thus, the repulsion of the filled *n*-orbitals at S1 and S2 enforces a torsion angle almost as high as that observed for the O–S bond of the spiro-1,2,4-oxadithiolane **12** (54.5°)[5]. On the other hand, the dihedral angle at S2–C3–S4–C5, the base of the envelope, is the smallest (9.8°, Table 1) in the hetero-ring; for a true envelope it should be zero. The angle of observation chosen in Figure 1 suggests a half-chair in which S1 and S2 are expected to be equidistant from the C3–S4–C5 plane, one sitting above, one below. However, this is an illusion; in fact, the torsion angles at C3–S4 and S4–C5 differ by as much as 20.8°, thus indicating a mongrelization of envelope and half-chair. In the literature, the PE spectra of the 1,2,4-trithiolane parent and its tetramethyl derivative were explained by postulating the exclusive occurrence of the half-chair in the gas phase[6]. For the 1,2,4-trithiolane **13**, X-ray analysis revealed a torsion angle at the S–S bond of 50.2° and a S–S bond length of 2.044 Å[7].



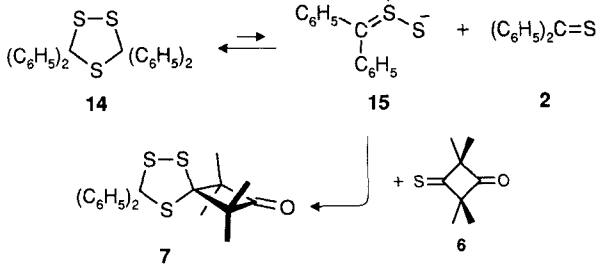
12



13

Bock et al. based a linear relation between the torsion angle at the S–S bond and its length on structural data of many disulfides[8]. The angle of 53.4° for **7** would correspond to a S–S bond length of 2.057 Å; the observed value of 2.031 Å deviates noticeably from this. Much smaller S–S torsion angles have been reported for 1,2-dithiolane-4-carboxylic acid (26°)[9] and *rac*-α-lipoic acid (35°)[10]. The bonds C3–S4 and S4–C5 in **7** (1.83, 1.85 Å) are longer than the C–C bonds in 1,2-dithiolanes. The increased flexibility in the trithiolane ring permits the mentioned repulsive forces to pull through more clearly, leading to greater torsion at the S1–S2 bond.

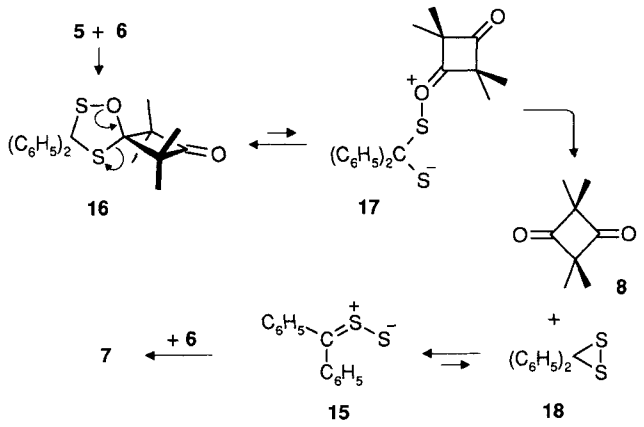
A distinct difference in the bond angles is seen for O1 in **12** (108.1°) and S1 in **7** (97.5°); with the higher *p* character of sulfur bonds[11] they reflect the bond angles in water (104.5°) and hydrogen sulfide (92.3°). The four-membered ring in **7** slightly deviates from planarity; the puckering angle is 12°.



We conjecture that the 1,3-dipolar cycloaddition of thiobenzophenone *S*-sulfide (**15**) to thione **6** is the concluding step in the formation of **7** from **5** + **6**. In 1987, **15** was presented as the first secured member of the thiocarbonyl sulfide (thiosulfine) family in a paper of our laboratory[12]. In 2,2-diphenylthiirane a sulfur donor was encountered which attaches a formal sulfur atom to the sulfur of thiobenzophenone (**2**); in situ **15** undergoes a fast cycloaddition to a second molecule of **2**, giving rise to tetraphenyl-1,2,4-trithiolane (**14**). The colorless crystals of **14** are the storage form of the non-isolable *S*-sulfide **15**. In a warm solution of **14** in inert solvents, the blue color of **2** reveals the equilibration with a small concentration of the dissociation products.

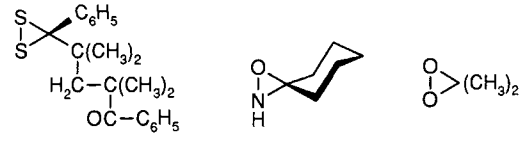
When this equilibrium was established in $CDCl_3$ at 80 °C in the presence of **6**, the irreversible cycloaddition of **15** furnished the "mixed" trithiolane **7**, identical with the specimen obtained from sulfine **5**. The ^{1}H-NMR integrals of the methyl signals indicated only **7** and the excess of **6**; the isolation was less productive (63%) since thiobenzophenone and the excess of **6** had to be removed by chromatography.

In our reaction solution the thiones **2** and **6** compete for the elusive **15**; **6** wins, as shown by the nearly complete conversion to **7**. The reason is that the conjugation energy of thiobenzophenone diminishes the cycloaddition enthalpy in the formation of **14** compared with that of **7**.

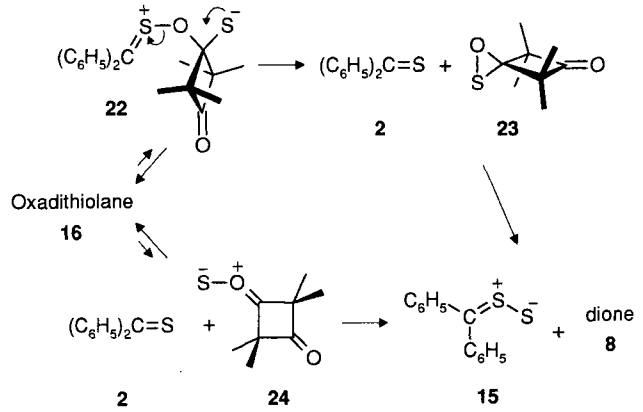


^{1}H-NMR monitoring of the reaction **5** + **6** did not allow us to detect intermediates; admittedly, the crowded region of methyl signals does not offer much chance of differentiation. In a conceivable pathway, the 1,3-cycloaddition of thione *S*-oxide **5** to **6** proceeds as usual affording **16**. The postulated 1,2,4-oxadithiolane **16** harbors *S,O*- and *S,S*-acetal groups. An ionization equilibrium may provide some oxonium thiolate zwitterion **17**. We chose to illustrate formula **17** in such a way that the next step, the closure of the dithiirane ring, can be recognized as an intramolecular nucleophilic substitution; the dione **8** is the leaving group. Although the S–S bond may be the weakest in diphenyldithiirane (**18**), the breaking of the C–S bond is partially compensated by bond making in the transition state of the electrocyclic ring opening, **18** → **15**. Whether the 1,3-dipole **15** has a higher bond energy than **18**, is uncertain. An equilibrium of cyclic and open-chain tautomers is conceivable, and the phenyl conjugation contributes to the stabilization of **15**. The latter is captured by the second molecule of **6**, giving **7**.

Assuming the intermediacy of a dithiirane is no longer as daring as it might have been in the past. The first crystalline dithiirane, **19**, encumbered by phenyl and *tert*-alkyl groups, was prepared by Nakayama et al. in 1994 and confirmed by X-ray analysis[13]; its thermal conversion was interpreted as involving an electrocyclic ring opening.



Two alternative pathways for the conversion of the oxadithiolane **16** into the thione *S*-sulfide **15** deserve discussion. Instead of an ionization at the *S,O*-acetal, **16** ⇄ **17**, the *dithio*-acetal system of **16** (C-3) could equilibrate with the sulfonium thiolate zwitterion **22**. An intramolecular substitution, analogous to that of **17** above, would afford the spiro-oxathiirane **23**. The capacity of **23** to transfer sulfur to thione **2** (the reaction yielding thione *S*-sulfide **15** + dione **8**) should far exceed that of diphenylthiirane[12].



In contrast to the oxathiirane **23**, which is unknown, the spiro-oxaziridine **20** is isolable; it is a reagent for electrophilic amination[14]. The splendid studies by E. Schmitz et al. include the transfer of NH to the thione function of thioamides, thioureas and related compounds. The oxygen transfer from dioxiranes, e.g., **21**, has been exploited in recent years[15]; thioethers were oxidized to sulfoxides. The high bond energy of the carbonyl group formed (176 kcal mol^{-1}) contributes to the driving force of all these cheletropic transfer reactions.

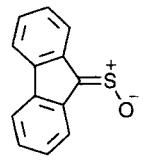
Oxathiiranes of type **23** are the hypothetical intermediates in the conversion of thiocarbonyl *S*-oxides into carbonyl compounds; a sulfur acceptor (**2** in our scheme) is required, since the elimination of a *sulfur atom* is thermochemically unfeasible. At 130 °C thiobenzophenone *S*-oxide furnishes benzophenone (95%)[16], and *tert*-thioamide *S*-oxides yield *tert*-amides even at 30–50 °C[17]. The same process occurs in the radical cations of diaryl thioketone *S*-oxides (MS), and the electrocyclization to an oxathiirane$^{+\bullet}$ was proposed as the initiating step[18].

In a variant of the above scheme, oxadithiolane **16** might enter a cycloreversion/cycloaddition equilibrium with **6** and the carbonyl sulfide **24**, a representative of an unknown class of 1,3-dipoles. Again, a sulfur transfer would provide **15** + **8**, and the interception of **15** by **6** would then conclude the reaction sequence.

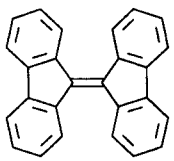
Neither the spiro-1,2,4-oxadithiolanes of type **4**, prepared by cycloaddition at 80–110 °C, nor the 5,5-diphenyl-spiro-oxadithiolane **3** (up to 70 h at room temp.) reacted with thiones to furnish 1,2,4-trithiolanes. The phenyl groups in the 3-position of the oxadithiolane **16** appear to be a requirement for the cleavage reaction that furnishes the thiocarbonyl *S*-sulfide **15**. The stabilization of an intermediate by phenyl conjugation is likely to play a determining role. Although the pathway via **17** appears to be the most straightforward, only the second and third mechanisms can profit from phenyl conjugation in an early step of the reaction sequence. We feel that a clarification of the mechanism merits further experiments.

Further Reactions of Aromatic Thione *S*-Oxides with Thiones

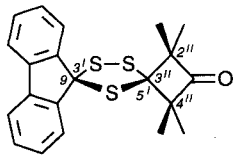
The interaction of thiobenzophenone *S*-oxide (**5**) with adamantanethione did not follow the same pattern as that of **6**. After several days in $CDCl_3$ at room temp., 74% of the colorless trimer of adamantanethione was isolated. Greidanus effected the trimerization to the 1,3,5-trithiane derivative by methanesulfonic acid[19]. The nature of the catalysis by **5** is unknown.



25



26



27

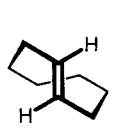
Some exploratory experiments were carried out with thiofluorenone *S*-oxide (**25**). Sheppard and Diekmann observed the formation of 9,9′-bifluorenylidene (**26**) on storing crystalline **25**[20]; we did not confirm the claimed stability in hot solvents. In contrast, we noticed a deep-red coloration in refluxing $CDCl_3$, accompanied by evolution of SO_2; monitoring by ^1H NMR indicated 89% of **26** after 6 h.

Reaction of **25** with 1.1 equiv. of thione **6** (refluxing $CDCl_3$, 20 h) afforded the dispiro-1,2,4-trithiolane **27** in 16% isolated yield. Quantitative ^1H-NMR analysis of an experiment with 2.2 equiv. of **6** resulted in 15% of **27** and 26% of dione **8**; 43% of **26** demonstrated that the self-decomposition of **25** is faster than its interaction with **6**.

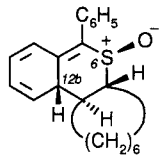
The NMR spectra of **27** are in accordance with a C_s plane. The radical cation of thiofluorenone (*m/z* 196) is the parent peak in the MS of **27**. An amusing detail: the fluorenyl cation (**11**, *m/z* 165) is a major peak in the MS of **7**, and even the base peak in the MS of thiobenzophenone (**2**), as mentioned above. By contrast, in the MS of **27** (the fluorene framework preformed) *m/z* 165 occurs only at a level of 1.5%; the 9-H of the fluorenyl cation (**11**) must be provided *intermolecularly* to $\mathbf{27}^{+\bullet}$ or thiofluorenone$^{+\bullet}$. In the case of $\mathbf{2}^{+\bullet}$, the 2H atoms set free by *o*-condensation of the phenyl groups allow the hydrogenolysis $\mathbf{2}^{+\bullet} \rightarrow$ fluorenyl$^+$ + HS$^\bullet$) by transfer *within* the molecule. A plausible mechanism with the sequence of steps was given in 1968[21].

Thiobenzophenone *S*-Oxide and (*E*)-Cyclooctene

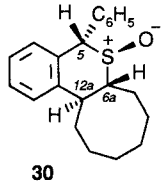
Cycloaddition reactions of (*E*)-cyclooctene (**28**) profit from the relief of ring strain[22]. When **5** was warmed with 1.1 equiv. of **28** in chloroform to 50°C for 4 d, most of the starting material was still present. The yield of the crystalline 1:1 adduct, 73%, was based on the consumed **5**. The strong IR absorption at 1038 cm^{-1} signals a sulfoxide, and the ^1H-NMR spectrum (5-H at δ = 4.71) is in accordance with the Diels-Alder adduct **30**. Thus, we are not dealing with the rare 1,3-cycloaddition of thione *S*-oxides, but rather with a [4 + 2] addition in which the C=S bond of **5** plus an aromatic C–C bond constitute a hetero-1,3-diene.



28

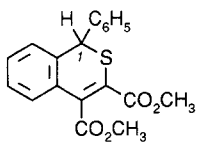


29

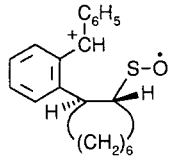


30

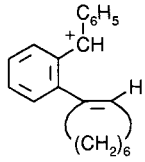
There is no evidence for a mixture of diastereomers. If the planar diene system approaches the dienophile **28** from above, the oxygen will come to the front in the pyramidalization at sulfur, i.e., 12b-H and 6-O are *cis* in the *primary* cycloadduct **29**. In the subsequent 1,3-prototropy, a sulfoxide function of **5** or **30** could be the carrier for the intermolecular proton transfer; we tend to favor the proton delivery on the upper face. The configuration **30** for the rearomatized cycloadduct is plausible.



31



32



33

Thiobenzophenone (**2**) combines as a 1,3-diene with dimethyl acetylenedicarboxylate at room temp. to provide **31**, as described by Gotthardt and Nieber[23]; the δ(1-H) of **31** at 5.14 compares well with 5-H at 4.71 in **30**. The Diels-Alder reaction of "diene" **2** was extended to further activated acetylenes[24] and also to **28** in our laboratory[25]; even the nonaromatic intermediate of type **29** was isolated[24].

Although the loss of the 5-H from the radical cation of **30** would offer optimal stabilization of positive charge, [M$^+$ − 1] is missing in the MS. M$^+$ (14%) may well be the *distonic*[26] ring-opened species **32** in which the centers of spin density and positive charge are separated. For [M$^+$ − SOH] (13%), cation **33** appears possible. The base peak is $C_6H_{13}^+$, which comes from the saturated ring of **32**.

Gratefully we acknowledge the support of the project by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie*. We thank *Helmut Huber* for his help in the NMR analyses and *Helmut Schulz* for the elemental analyses.

Experimental Section

For methods and instruments, see ref.[5]. All NMR spectra were taken in $CDCl_3$ (stored over dry solid potassium carbonate) with TMS as internal standard. In the evaluation of the MS (70 eV, electron impact), the percent intensity of the isotope peak (^{13}C, ^{34}S) was calculated on the basis of the intensity of the main isotopic composition and compared with the one found, e.g., ^{13}C calcd./found.

Thiobenzophenone S-Oxide (**5**)[27]: after column chromatography (silica gel, dichloromethane/ether, 9:1) m.p. 33–35°C (30–32°C[27]). – MS (25°C); *m/z* (%): 214 (19%) [M$^+$], 213 (14) [M$^+$ − H], 198 (2) [**2**$^+$], 182 (59) [benzophenone$^+$; ^{13}C 8.6/8.4], 181

(8) [fluorenone + H^+], 165 (18) [**11**], 121 (5) [$C_6H_5C{\equiv}S^+$], 105 (100) [$C_6H_5C{\equiv}O^+$; ^{13}C 7.8/7.6].

Thiofluorenone S-Oxide (**25**)[27]: after chromatography orange crystals, m.p. 112–113°C (dec., 111–112°C[27]). – *Decomposition:* 424 mg of **25** in 2 ml of $CDCl_3$ were refluxed for 6 h. After cooling, 1,1,2,2-tetrachloroethane (δ = 5.92) was added as an internal standard; ^1H-NMR analysis: 89% of **26** (δ = 8.38, d). In an experiment with 3 h refluxing, 68% of **26** and 30% of **25** were analyzed. – *9,9'-Bifluorenylidene* (**26**): red needles (ethanol/diethyl ether), m.p. 192–193°C (187–188°C[28]). – ^1H NMR: δ = 7.18–7.35 (m, 8H), 7.69 (d, *J* = 8.0 Hz, 4H), 8.38 (d, *J* = 8.0 Hz, 4H). – ^{13}C NMR: δ = 119.9, 126.7, 126.8, 129.1 (4 d, 16 CH), 138.3, 141.0, 141.3 (3 s, 10 C_q). – MS (80°C); *m/z* (%): 328 (100) [M^+], 327 (92) [M^+ – 1], 326 (46), 165 (11) [**11**].

2',2',4',4'-Tetramethyl-5,5-diphenyl-(1,2,4)-trithiolane-3-spiro-3'-cyclobutanone (**7**): (a) 429 mg (2.0 mmol) of **5** and 344 mg (2.2 mmol) of **6**[29,30] in 1 ml of $CDCl_3$ were reacted at room temp. in an NMR tube. After 3 d new CH_3 signals were observed at δ = 1.42 and 1.51 for **7**, and at 1.27 for dione **8**. The signals grew slowly and after 30 d the ^1H-NMR spectrum indicated the molar ratio **7**/**8**/**6** = 33:41:26 when the sum of the methyl integrals was set to 100. Work-up by thick-layer chromatography (dichloromethane/pentane, 1:1) provided 270 mg (86% based on 1.63 mmol of consumed **6**) of colorless crystals of **7**, m.p. 100–102°C, as the first fraction ($R_f \approx 0.5$). The second fraction ($R_f \approx 0.2$), 170 mg of a colorless oil, crystallized from pentane at –78°C; it was a mixture of **8** and benzophenone. Trithiolane **7**, recryst. from ethanol, showed m.p. 101–102°C. – IR (KBr): $\tilde{\nu}$ = 652 cm^{-1} m, 696 s, 740, 752 m (C_6H_5 wagging); 1455 s, 1463, 1489 m (δ CH_3), 1790 vs (C=O). – ^1H NMR: δ = 1.42, 1.51 (2 s, 2 CH_3 each); 7.25–7.33, 7.61–7.63 (2 m, 2 C_6H_5). – ^{13}C NMR: δ = 21.43, 26.19 (2 q, 2 CH_3 each), 67.37 (s, C-2', C-4'); 88.85, 89.48 (2 s, C-3, C-5), 127.90, 127.99, 128.92 (3 d, 3 aromat. CH), 142.01 (s, aromat. C_q), 218.80 (C=O). – MS (30°C); *m/z* (%): 316 (2.8) [M^+ – dimethylketene], 230 (18) [15% of **9** + 3% of ^{13}C of 229; ^{13}C of 230 + ^{34}S of 229 4.4/4.7; ^{34}S of 230 1.3/1.5], 229 (20) [$C_{13}H_9S_2^+$, probably **10**], 198 (100) [**2**$^+$; ^{13}C 15/15; ^{34}S 4.4/5.3], 165 (48) [$C_{13}H_9^+$, **11**; ^{13}C 6.9/7.5], 121 (19) [C_6H_5-$C{\equiv}S^+$; ^{13}C 1.5/1.6, ^{34}S 0.85/0.85], 86 (5) [dimethylthioketene$^+$], 77 (4) ($C_6H_5^+$). – $C_{21}H_{22}OS_3$ (386.6): calcd. C 65.24, H 5.74, S 24.88; found C 65.42, H 5.80, S 24.28. – (b) 107 mg (0.50 mmol) of **5** and 172 mg (1.10 mmol) of **6**, dissolved in 0.5 ml of $CDCl_3$, were kept in a sealed NMR tube in a 60°C bath for 4 d. 2,6-Dimethylnaphthalene (δ = 2.45) served as an internal standard for the quantitative ^1H-NMR analysis: 0.27 mmol of **7** (δ = 1.51), 0.54 mmol of dione **8** (δ = 1.27), and 0.27 mmol of unreacted **6** (δ = 1.34). The yield of **7** amounts to 65% of the consumed **6**; the excess of **8** points to a side reaction.

X-ray Data of Trithiolane **7**[31]: $C_{21}H_{22}OS_3$, mol. mass 386.6, triclinic, space group *P*1, No. 2. Unit cell dimensions: *a* = 6.637(2), *b* = 8.085(3), *c* = 18.563(4) Å, and α = 82.89(2)°, β = 89.24(2)°, γ = 81.59(2)°; volume 977.8(5) Å^3, *Z* = 2; D_x = 1.313 mg/ml. *F*(000) = 408, *T* = 293(2) K; μ(Mo-K_α) = 0.385 mm^{-1}. Data collection: CAD4 diffractometer, colorless crystal (size 0.17 × 0.33 × 0.53 mm) mounted in a glass capillary, cell constants from 25 centered reflexions, Mo-K_α radiation, graphite monochromator, λ = 0.71073 Å, ω-scan with profile fitting, scan width (0.90 + 0.35 tanΘ)°, maximum measuring time 120 s; intensity of three standard reflexions checked after every h, 2Θ range 4–46° for all ±*h*/±*k*/+*l*, 2821 reflexions measured, 2721 unique and 2545 with $I > 2\sigma(I)$. Structure solution by SHELXS-86 and refinement by SHELXL-93; non-hydrogen atoms refined anisotropically, hydrogens riding with $U_i = 1.2\ U_{eq}$ of the adjacent carbon atom. Full matrix refinement against F^2. Final *R*1 = 0.0289 and *wR*2 = 0.0830 for 2545 reflexions with $I > 2\sigma(I)$ and 230 variables. *R*1 = 0.0312 and *wR*2 = 0.0893 for all data. Weights: SHELXL-93. Maximum and minimum of the final difference Fourier synthesis: 0.259 and 0.188 eÅ^3.

Independent Synthesis of **7**: 429 mg (1.0 mmol) of **14**[12] and 312 mg (2.0 mmol) of **6** in 1 ml of $CDCl_3$ were sealed in an NMR tube. On warming at 80°C, the blue color of **2** appeared several min later. After 4 h at 80°C, the integrals of the ^1H-NMR methyl signals revealed a 91:109 ratio of **7** (δ = 1.42, 1.51) to **6** (δ = 1.34). Separation from **2** and the excess **6** by thick-layer chromatography (dichloromethane/pentane, 1:1) furnished 270 mg of a colorless oil which crystallized and was washed with ice-cold pentane: 220 mg (63%, based on consumed **6**) of **7**, m.p. 102–103°C; mixed m.p., IR and ^1H-NMR spectra established the identity with the specimen prepared from **5** + **6**.

S-Oxide **5** *and Adamantanethione:* 236 mg (1.1 mmol) of **5** and 166 mg (1.0 mmol) of adamantanethione[19] were dissolved in 1 ml of $CDCl_3$; soon the precipitation of colorless needles began. After 3 d at room temp. 123 mg (74%) of the trimer of adamantanethione with m.p. 352–355°C (dec.) was isolated. It was insoluble in the usual solvents. The IR spectrum (KBr) agreed with the description by Greidanus (m.p. 354°C, dec.)[19].

2'',2'',4'',4''-Tetramethyldispiro[fluorene-9,3'-(1,2,4)-trithiolane-5',1''-cyclobutane]-3'-one (**27**): (a) 637 mg (3.0 mmol) of **25** and 516 mg (3.3 mmol) of **6** in 3 ml of $CDCl_3$ were refluxed for 20 h under argon. In the thick-layer separation on silica gel (dichloromethane/pentane, 1:1), the excess of the red thione appeared as the first fraction. The second with $R_f \approx 0.6$ consisted of 110 mg of a colorless viscous oil that crystallized from pentane in fine pale-yellow needles (103 mg, 16%) of **27**, m.p. 153–154°C. According to the ^1H-NMR spectrum, the third fraction (210 mg of pale-yellow oil) contained unreacted sulfine **25**, fluorenone and an unidentified product with δ(CH_3) = 1.42, 1.46. – (b) 106 mg (0.50 mmol) of **25** and 172 mg (1.1 mmol) of **6** in $CDCl_3$ were sealed in an NMR tube and heated for 4 d in a 60°C bath. The tube, cooled to –20°C, was opened (SO_2 pressure) and ^1H-NMR-analyzed after addition of 2,6-dimethylnaphthalene (δ = 2.45) as internal standard: 302 μmol of **6** (δ = 1.32, s, 12H), 57.9 μmol of **27** (δ = 1.62, s, 12H, 15%), 109 μmol of **8** (δ = 1.29, s, 12H, 27%), 108 μmol of **26** (δ = 8.38, d, 4H, 43%), 104 μmol of the unknown compound, supposedly the dispiro-1,2,4-oxadithiolane (δ = 1.42, 1.45, 4 CH_3); yields based on 798 μmol of consumed **6**. – Properties of **27**: IR (KBr): $\tilde{\nu}$ = 739 cm^{-1} s (aromat. CH wagging, *o*-disubst.), 1461 m (δ CH_3), 1784 s (C=O). – ^1H NMR: δ = 1.62 (br. s, 4 CH_3); 7.17–7.42, 7.47–7.70, 7.77–7.80 (m, 8 aromat. H). – ^{13}C NMR: δ = 21.4, 26.6 (2 q, 2 CH_3 each), 67.5 (s, C-2'', C-4''), 77.4 (s, C-5'), 90.3 (s, C-3'); 120.0, 124.8, 128.2, 129.4 (4 d, 8 aromat. CH); 138.6, 146.7 (2 s, 4 aromat. C_q), 218.1 (C=O). – MS (110°C); *m/z* (%): 384 (1.7) [M^+], 314 (2.8) [M^+ – dimethylketene], 228 (17) [$C_{13}H_8S_2^+$; ^{13}C 2.5/3.4, ^{34}S 1.5/1.4], 196 (100) [$C_{13}H_8S^+$, thiofluorene$^+$; ^{13}C 15/15, ^{34}S 4.4/5.0], 188 (2) [$C_8H_{12}OS_2^+$], 165 (1.5) [**11**], 152 (12) [$C_{12}H_8^+$, biphenylene$^+$; ^{13}C 1.5/1.5], 86 (7) [dimethylthioketene$^+$]. – $C_{21}H_{20}OS_3$ (384.6): calcd. C 65.58, H 5.24, S 25.02; found C 65.62, H 5.38, S 25.07.

6a,7,8,9,10,11,12,12a-Octahydro-5-phenyl-5H-benzo[d]cycloocta[b]thiopyran S-Oxide (**30**): 214 mg (1.0 mmol) of **5** and 121 mg (1.10 mmol) of (*E*)-cyclooctene (**28**)[32] in 0.4 ml of $CDCl_3$ were heated to 50°C for 4 d. After removal of the solvent (0°C bath, 25 torr), unconsumed **28** (64 mg) was distilled (receiver cooled with liq. N_2). Trituration of the green-yellow residue with 1 ml of diethyl ether left 102 mg of crude **30**, m.p. 183–184°C. From the mother

liquor 131 mg of crystalline **5** was obtained. Recrystallization of **30** from benzene gave 92 mg (73% of consumed **5**) of colorless needles, m.p. 186–187°C. – IR (KBr): $\tilde{\nu}$ = 705 cm^{-1}, 710 s (C_6H_5 wagg.); 754 s, 778 m (C_6H_4 wagg.), 1038, 1042 vs (S–O), 1454 m (δ CH_2), 1605 w (arom. ring vibr.) – ^1H NMR: δ = 1.51–2.31 (m, 6 CH_2), 2.85 (m_c, 6a-H), 3.45 (m_c, 12a-H), 4.71 (s, 5-H), 6.6–7.6 (m, 9 arom. H). – MS (110°C); *m/z* (%): 324 (14) [M^+, **32**; ^{13}C 3.3/3.2], 307 (15) [M^+ – OH; ^{13}C 3.5/4.5, ^{34}S 0.7/0.9], 292 (9) [M^+ – S; ^{13}C 2.2/2.5], 275 (13) [M^+ – SOH; $C_{21}H_{23}^+$, **33**; ^{13}C 2.9/3.4], 193 (25) [$C_{15}H_{13}^+$, ethylfluorenyl$^+$; ^{13}C 4.2/4.5], 179 (23) [$C_{14}H_{11}^+$, methylfluorenyl$^+$], 165 (11) [$C_{13}H_9^+$, fluorenyl$^+$, **11**], 105 (62) [$C_6H_5C{\equiv}O^+$; ^{13}C 4.9/4.9], 91 (42) [tropylium, ^{13}C 3.3/3.4], 85 (100) [$C_6H_{13}^+$], 83 (75) [$C_6H_{11}^+$], 77 [phenyl$^+$; ^{13}C 2.6/3.5]. $C_{21}H_{24}OS$ (324.5): calcd. C 77.73, H 7.55, S 9.88; found C 77.38, H 7.52, S 9.95.

☆ Dedicated to Professor *Hans Suschitzky*, Salford, on the occasion of his 80th birthday.

[1] For part 96 see ref.[4].

[2] Present address: Institute of Organic and Applied Chemistry, University of Lodz, Poland.

[3] Present address: Departamento Quimica Organica, Facultad de Farmacia, Universidad de Pais Vasco, Vitoria, Spain.

[4] R. Huisgen, G. Mloston, K. Polborn, *J. Org. Chem.*, **1996**, *61*, 6570–6574.

[5] R. Huisgen, G. Mloston, K. Polborn, R. Sustmann, W. Sicking, *Liebigs Ann.* **1997**, 179–185, preceding publication.

[6] M. F. Guimon, C. Guimon, G. Pfister-Guillouzo, *Tetrahedron Lett.* **1975**, *16*, 441–444.

[7] C. D. Shirrell, D. E. Williams, *Acta Cryst. Sect.B* **1973**, *29*, 2128–2133.

[8] H. Bock, U. Stein, A. Semkow, *Chem. Ber.* **1980**, *113*, 3208–3220.

[9] O. Foss, O. Tjomsland, *Acta Chem. Scand.* **1958**, *12*, 1810–1818.

[10] I. L. Karle, J. A. Estlin, K. Britts, *Acta Cryst.* **1967**, *22*, 567–573; R. M. Stroud, C. H. Carlisle, *Acta Cryst. Sect. B* **1972**, *28*, 304–307.

[11] W. Kutzelnigg, *Angew. Chem.* **1984**, *96*, 262–286; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 272–296.

[12] R. Huisgen, J. Rapp, *J. Am. Chem. Soc.* **1987**, *109*, 902–903.

[13] A. Ishii, T. Akazawa, T. Maruta, J. Nakayama, M. Hoshino, M. Shiro, *Angew. Chem.* **1994**, *106*, 829–830; *Angew. Chem. Int. Engl.* **1994**, *33*, 777–779. A. Ishii, T. Maruta, K. Teramoto, J. Nakayama, *Sulfur Lett.* **1995**, *18*, 237–242.

[14] Review: S. Andreae, E. Schmitz, *Synthesis* **1991**, 327–341.

[15] R. W. Murray, *Chem. Rev.* **1989**, *89*, 1187–1201. W. Adam, R. Curci, J. O. Edwards, *Acc. Chem. Res.* **1989**, *22*, 205–211. W. Adam, L. Hadjiarapoglou, *Top. Curr. Chem.* **1993**, *164*, 47–62.

[16] L. Carlsen, A. Holm, E. Koch, B. Stilkerieg, *Acta Chem. Scand. B* **1977**, *31*, 679–682.

[17] W. Walter, O. H. Bauer, *Liebigs Ann. Chem.* **1976**, 1584–1597.

[18] A. Tangerman, L. Thijs, A. P. Anker, B. Zwanenburg, *J. Chem. Soc., Perkin Trans. 2* **1973**, 458–460.

[19] J. W. Greidanus, *Can. J. Chem.* **1970**, *48*, 3530–3536.

[20] W. A. Sheppard, J. Diekmann, *J. Am. Chem. Soc.* **1964**, *86*, 1891–1892.

[21] D. Schumann, E. Frese, A. Schönberg, *Chem. Ber.* **1969**, *102*, 3192–3204.

[22] D. Boeckh, Ph. D. Thesis, University of Munich 1986.

[23] H. Gotthardt, S. Nieberl, *Liebigs Ann. Chem.* **1980**, 867–872.

[24] R. Huisgen, J. Rapp, *Tetrahedron*, submitted.

[25] Experiments by F. Palacios Gambra, University of Munich, 1981.

[26] B. F. Yates, W. J. Bouma, L. Radom, *J. Am. Chem. Soc.* **1984**, *106*, 5805–5808; *Tetrahedron* **1986**, *42*, 6225–6234.

[27] B. Zwanenburg, L. Thijs, J. Strating, *Rec. Trav. Chim. Pays-Bas* **1967**, *86*, 577–588.

[28] C. Graebe, *Ber. Dtsch. Chem. Ges.* **1892**, *25*, 3146–3149.

[29] D. St. C. Black, K. G. Watson, *Aust. J. Chem.* **1973**, *26*, 2491–2504.

[30] R. Huisgen, L. Fisera, H. Giera, R. Sustmann, *J. Am. Chem. Soc.* **1995**, *117*, 9671–9678.

[31] Further details may be obtained from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD-405878 (compound **7**), the names of the authors, and the journal citation.

[32] A. J. Bridges, G. H. Witham, *J. Chem. Soc., Chem. Commun.* **1974**, 142–143.

[96228]