125. 4,10a-(Epidithio)-4,4a,10,10a-tetrahydro-1*H*-5-oxaanthracen-1-ones, Tetracycles with a Novel Heterocyclic Ring System

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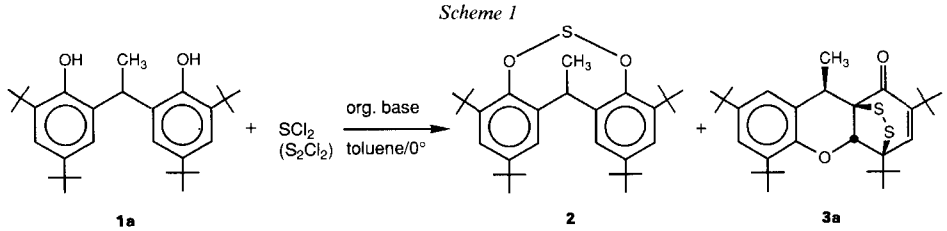
(2.V.88)

The 4,4′,6,6′-tetrasubstituted 2,2′-alkylidene-bisphenols **1** reacted with sulfur monochloride to give 4,10a-(epidithio)-4,4a,10,10a-tetrahydro-1*H*-5-oxaanthracen-1-ones (**3** and **4**). The structures of the products were elucidated by a combination of X-ray crystal-structure analysis and ^{1}H- and ^{13}C-NMR spectroscopy.

Introduction. – In search for novel antioxidants, a series of medium-ring heterocycles has been prepared and investigated, which are derived from sterically hindered phenols [1]. In this context, we prepared **2** by a condensation reaction between the bisphenol **1a** and sulfur dichloride [2]. Besides the expected product **2**, compound **3a** was formed *(Scheme 1)*. This report describes its structure determination and possible mode of formation.

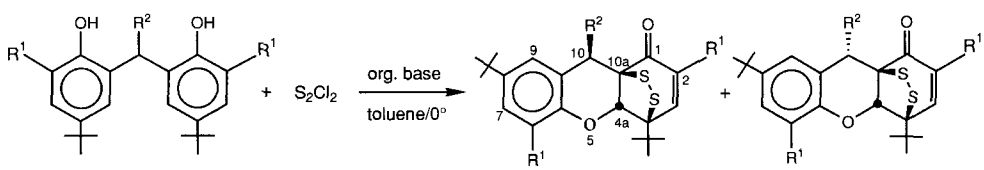
Scheme 1



1a **2** **3a**

Preparation. – Compound **3a** contains one additional S-atom as compared with **2**. This indicates that it is formed by a reaction with S_2Cl_2 *(Scheme 2)*, an impurity often present in SCl_2. Consequently, we prepared compound **3a** and its homologues **3b–e**

Scheme 2



1 **3** **4**

a R^1 = *t*-Bu, R^2 = Me
b R^1 = *t*-Bu, R^2 = Et
c R^1 = R^2 = Me
d R^1 = *t*-Bu, R^2 = H
e R^1 = *t*-Bu, R^2 = i-Pr

directly from the corresponding bisphenols **1a–e** and sulfur monochloride (S_2Cl_2). At 0°, a toluene solution of S_2Cl_2 was added dropwise to a toluene solution of the bisphenol **1** and pyridine (molar ratio 1:1:2), and the mixture was stirred at r.t. Pure **3a–e** could be obtained from the crude filtrate by recrystallisation from hexane or repeated chromatography on silica gel in yields of 13–45% (see *Exper. Part*). Besides **3a**, a minor amount of the epimer **4a** was isolated in pure form. As the yields of **3b–3c** and **3e** were rather low (13–30%), no epimers **4b–4c** or **4e** could be isolated. The NMR spectra of the crude products showed mixtures precluding an estimate of the amount of epimers of type **4a** formed.

Structures of 3a–e and 4a. – The structure of **3a** was established by X-ray crystal structure analysis. The molecular structure and numbering scheme are illustrated in *Fig. 1*. Bond distances are listed in *Table 1*. They lie within experimental limits. Selected torsion angles are given in *Table 2*. Both, the cyclohexenone and the pyrane ring adopt half-chair conformations. The torsion angle over the disulfide bridge is 18.9°, *i.e.* the 5-membered ring is strongly twisted. The angle between the keto group and the double bond is 13°.

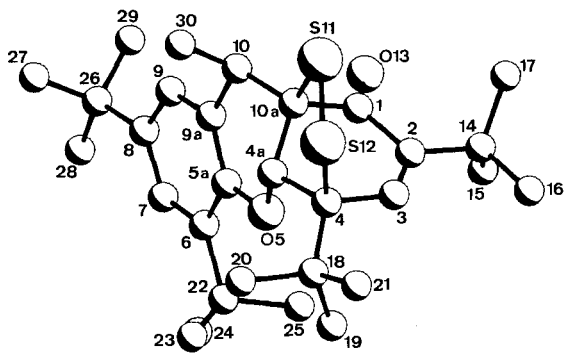


Fig. 1. *A view* (PLUTO plot [3]) *of molecule* **3a** *with the atom-numbering scheme.* H-Atoms are omitted for clarity.

Table 1. *Bond Distances* (in Å) *of* **3a**[a])

Atom 1, 2	Distance	Atom 1, 2	Distance	Atom 1, 2	Distance
C(1)–C(2)	1.499(4)	C(5a)–C(9a)	1.390(4)	C(14)–C(16)	1.531(5)
C(1)–C(10a)	1.532(4)	C(6)–C(7)	1.396(4)	C(14)–C(17)	1.533(5)
C(1)–O(13)	1.214(4)	C(6)–C(22)	1.543(4)	C(18)–C(19)	1.536(5)
C(2)–C(3)	1.331(4)	C(7)–C(8)	1.389(4)	C(18)–C(20)	1.523(4)
C(2)–C(14)	1.530(4)	C(8)–C(9)	1.384(4)	C(18)–C(21)	1.540(4)
C(3)–C(4)	1.491(3)	C(8)–C(26)	1.537(4)	C(22)–C(23)	1.539(4)
C(4)–C(4a)	1.539(4)	C(9)–C(9a)	1.390(4)	C(22)–C(24)	1.538(4)
C(4)–S(12)	1.871(3)	C(9a)–C(10)	1.525(4)	C(22)–C(25)	1.532(3)
C(4)–C(18)	1.567(4)	C(10)–C(10a)	1.534(4)	C(26)–C(27)	1.513(5)
C(4a)–O(5)	1.436(3)	C(10)–C(30)	1.527(4)	C(26)–C(28)	1.506(5)
C(4a)–C(10a)	1.525(4)	C(10a)–S(11)	1.840(3)	C(26)–C(29)	1.542(5)
O(5)–C(5a)	1.400(3)	S(11)–S(12)	2.070(1)		
C(5a)–C(6)	1.405(4)	C(14)–C(15)	1.532(5)		

[a]) Numbers in parentheses are estimated standard deviations in the least significant digits.

Table 2. *Selected Torsion Angles* (in °) *of* **3a**

C(10a)–C(1)–C(2)–C(3)	13.8(4)	C(10a)–C(4a)–O(5)–C(5a)	–51.6(3)	S(12)–C(4)–C(4a)–C(10a)	61.9(2)
C(1)–C(2)–C(3)–C(4)	–0.2(4)	C(4a)–O(5)–C(5a)–C(9a)	17.8(3)	C(4)–C(4a)–C(10a)–S(11)	–47.8(2)
C(2)–C(3)–C(4)–C(4a)	19.3(4)	O(5)–C(5a)–C(9a)–C(10)	1.3(4)	C(4a)–C(10a)–S(11)–S(12)	12.0(2)
C(3)–C(4)–C(4a)–C(10a)	–50.1(3)	C(5a)–C(9a)–C(10)–C(10a)	15.1(3)	C(10a)–S(11)–S(12)–C(4)	18.9(1)
C(4)–C(4a)–C(10a)–C(1)	63.4(3)	C(9a)–C(10)–C(10a)–C(4a)	–48.0(3)	C(4a)–C(4)–S(12)–S(11)	–45.3(2)
C(2)–C(1)–C(10a)–C(4a)	–45.8(3)	O(5)–C(4a)–C(10a)–C(10)	68.6(3)		

Table 3. *^{13}C-NMR Data of* **3a–e** *and* **4a** ($CDCl_3$ solution)

	3a	**4a**	**3b**	**3c**	**3d**	**3e**
C(1)	188.7	191.3	188.2	188.9	188.9	187.5
J	11, 5, 3	11, 8, 4.5	10.5, 5.5, 2.5		10, 7.5, 5.5, 3	10.5, 5.5, 2.5
C(2)	145.5	145.6	145.6	134.2	144.8	145.5
C(3)	131.1	130.8	131.1	133.8	132.6	131.0
J	160, 5.5	160, 5.5	160, 5.5	160, 6, 6	160, 5.5	160, 5.5
C(4)	68.7	70.5	68.5	67.8	68.3	68.3
C(4a)	78.6	85.9	79.0	78.7	83.2	78.6
J	158, 5, 5	158, 5, 3	158, 5, 5, 5	158, 5, 5	158.5, 5, 5	157.2, 5, 5
C(5a)	148.4	149.1	148.1	147.8	149.1	148.3
C(6)	136.5	136.0	136.1	124.7	136.7	135.5
C(7)	122.6	122.5	122.4	126.2	122.5	122.1
C(8)	143.3	143.3	142.7	143.8	143.5	142.0
C(9)	125.0	121.1	125.3	124.1	124.2	125.1
C(9a)	125.5	125.3	124.1	124.1	119.1	121.7
C(10)	33.0	43.0	39.7	32.1	34.2	43.4
C(10a)	64.3	63.8	64.9	63.0	58.8	65.6
Substituent at C(10)	21.8	17.9	28.4 14.0	21.8	–	30.8 26.1 22.0
Substituents at C(2), C(4), C(6), and C(8)						
CH_3	31.5	31.6	31.4	31.4	31.4	31.4
	29.7	29.8	29.7		29.7	29.7
	29.2	29.4	29.1		29.1	29.1
	27.7	27.6	27.7	27.2	27.5	27.7
				17.2		
				16.5		
$(CH_3)_3C$	35.7	35.6	35.6	35.6	35.5	35.5
	34.92	34.9	34.9		34.8	34.9
	34.87	34.9	34.8		34.8	34.7
	34.2	34.4	34.1	34.0	34.1	34.0

The structures of **3b–e** and **4a** are based upon the structures of the starting materials **1a–e** and a comparison of their ^{1}H-coupled ^{13}C-NMR spectra with that of **3a** (*cf. Table 3;* for the ^{1}H-NMR and FD mass spectra and other analytical data, see *Exper. Part*). Thus, the NMR data of **3a** and **4a** allow an independent deduction of the relative configuration of both compounds.

First, the W-coupling observed for *H*–C(3) and *H*–C(4a) (^4J = 2.5 Hz in all compounds) requires a planar coupling path between the two protons [4] and defines, therefore, the configuration at C(4a), since the dithio bridge between C(4) and C(10a) is only possible in a *cis* arrangement for steric reasons. C(10) and O(5) are, consequently,

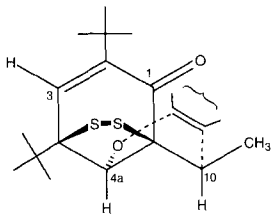


Fig. 2. *Partial structure of* **4a** *showing the antiperiplanar arrangement of C(1) and H–C(10)*

cis to each other. This is in agreement with the observation of a *trans* vicinal coupling between *C*(3) and *H*–C(4a) (J = 5.5 Hz in both **3a** and **4a**).

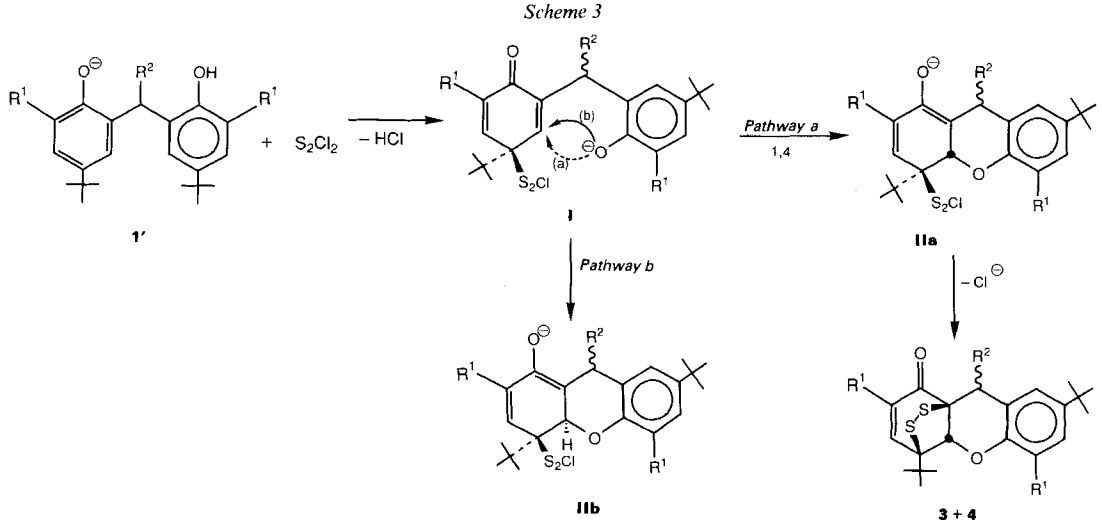
The configuration at the remaining centre, C(10), can be assigned on the basis of the long-range H,C-coupling constants of C(1) and C(4a) using their angle dependence [5]. In detail, ^3J(C(1), H–C(10)) amounts to 3 Hz in **3a** and to 8 Hz in **4a**, representing a synclinal and a antiperiplanar arrangement [5], respectively, of C(1) and H–C(10) (see *Fig. 2, cf.* also the same J's (3 and 7.5 Hz) in **3d**, the compound without a substituent at C(10)). The same argument holds for ^3J(C(4a), *H*–C(10)) (5 Hz in **3a**, 3 Hz in **4a** as compared with 5 and < 1 Hz in **3d**).

An additional argument for the configuration at C(10) is based on the ^{13}C-NMR-chemical shifts of the CH_3 group and C(9) in **3a** (21.8 and 125.0 ppm resp.) as compared with that in **4a** (17.9 and 121.1 ppm, resp.). This upfield shift represents the *syn*-γ-effect between CH_3 and C(9) and defines the position of the CH_3 group in **4a** as equatorial, since the half-chair conformation of the tetrahydropyran ring is given by the value of ^3J(C(1), *H*–C(10)) (8 Hz or 7.5 Hz in **3d**, antiperiplanar arrangement). Furthermore, the axial position of the substituent at C(10) in **3a** is shown by the γ-upfield shift of C(4a) (δ 78.6 ppm (**3a**) as compared with 83.2 ppm (**3d**) or 85.9 ppm (**4a**)).

Comparison of the ^{13}C-NMR data of **3a** and **4a** with those of **3b–e** *(Table 3)* shows that **3b–e** have the same configuration as **3a**, since the chemical shifts agree well with those of **3a** (standard substituent effects evaluated according to [6]) and since the coupling constants are identical or very similar. Besides the coupling constants already discussed, this is true for ^3J(C(1), *H*–C(3)) (10–11 Hz, *cf. e.g.* [7]), ^3J(C(1), *H*–C(4a)) (5–5.5 Hz, *cf.* [5]) and ^3J(C(4a), *H*–C(3)) (5 Hz). As these antiperiplanar vicinal coupling constants [5] are practically identical in all compounds, they possess the same steric arrangement in the cyclohexenone ring, namely the half-chair conformation dictated by the presence of the dithio bridge and the annellated pyrane ring, a conformation which can also be deduced from the W-coupling mentioned above.

Mode of Formation. – A possible mode of formation of compounds **3** and **4** is represented in *Scheme 3*. Intermediate **I** cyclises preferentially *trans* to the bulky $-S_2Cl$ substituent *(Pathway a)* to give selectively the enolate **IIa** which then – by a further

Scheme 3



cyclisation – can only lead to compound **3** and its epimer at C(10), **4**. Depending on the reaction conditions, the ratio **3a**/**4a** varies between 78:22 and 59:41 (for **1a**/S_2Cl_2/pyridine 1:1:2 and 1:1.5:2, resp.). No explanation can be forwarded for this observation.

Experimental Part

1. *General.* Flash chromatography (FC) [8]: silica gel (*Merck 60;* 230–400 mesh). M.p.: *Tottoli (Büchi);* uncorrected. UV spectra (λ in nm (ε)): *Shimadzu Graphicord UV 240.* IR spectra (cm^{-1}): *Nicolet 20SX* or *Perkin Elmer 983G;* unless specified otherwise, in KBr. *Raman* spectra (shift in cm^{-1}, at 90° illumination): *Cary 83;* if not specified otherwise, as neat powder. ^{1}H- and ^{13}C-NMR spectra: *Bruker WP 100 SY* (100-MHz ^{1}H-NMR), *Bruker WM 250* (250-MHz ^{1}H-NMR), and *Varian XL 300* (75.4-MHz ^{13}C-NMR); $CDCl_3$ soln.; chemical shifts δ *vs.* TMS (= 0 ppm), *J* in Hz. High-resolution (HR) MS: *CEC 21-110B* high-resolution mass spectrometer. FD-MS: *VARIAN CH5* mass spectrometer.

2. *Starting Materials.* The bisphenols **1a** and **1d** are commercially available (= *Isonox 129* and *128,* resp., from *Schenectady Chemicals,* US). The bisphenols **1b**, **1c**, and **1e** can be prepared by the following general procedure: To a stirred soln. of 1 mol of the corresponding 2,4-disubstituted phenol and of 0.5 mol of the corresponding aldehyde in 250 ml of AcOH were added dropwise at 0° 75 g (0.53 mol) of $BF_3 \cdot Et_2O$. The soln. was stirred at r.t. for 23 h. The white precipitate was filtered off and recrystallised (hexane): **1b**, m.p. 142–144°; **1c**, m.p. 126–127°; **1e**, m.p. 188–190°.

3. *4,10a-(Epidithio)-4,4a,10,10a-tetrahydro-1*H*-5-oxaanthracen-1-ones. General Procedure.* To a stirred soln. of 0.04 mol of **1** and 0.088 mol of pyridine in 50 ml of toluene at 0°, a soln. of 0.0405 mol of S_2Cl_2 in 50 ml of toluene was added dropwise within 30 min. The suspension was stirred for 1 h at 0° and for 1.5–5 h at r.t. Then, the pyridine hydrochloride was filtered off, the filtrate evaporated, and the crude product purified. *Purification method A:* The major product was obtained by recrystallisation from hexane. *Purification method B:* Repeated column chromatography on silica gel with CS_2, hexane, or CCl_4 and hexane/AcOEt 49:1 or hexane/CH_2Cl_2 49:1. R_f values given for hexane/AcOEt 49:1.

*2,4α,6,8-Tetra(*tert*-butyl)-4β,10aβ-(epidithio)-4,4aβ,10,10a-tetrahydro-10β-methyl-1*H*-5-oxaanthracen-1-one* (**3a**). Purification method A. Yield 45%. M.p. 218–220°. UV ($CHCl_3$): 348 (sh, 1360), 312 (2240), 282 (2640), 244 (6570); min. 291 (1500), 266 (1840). IR (KBr): 1681 (C=O, conj.), 1602 (non-arom. C=C, weak). *Raman:* 1681 (C=O, conj.), 1602 (non-arom. C=C), 525 (S–S). ^{1}H-NMR: 7.14, 7.05 (2*d*, *J* = 2, H–C(9), H–C(7)); 6.68 (*d*, *J* = 2.5, H–C(3)); 4.39 (*d*, *J* = 2.5, H–C(4a)); 3.80 (*q*, *J* = 7.5, H–C(10)); 1.58 (*d*, *J* = 7.5, CH_3–C(10)); 1.38, 1.30, 1.29, 1.20 (*t*-Bu). FD-MS: 500. HR-MS: 500 (2, $C_{30}H_{44}O_2S_2$, M^+), 436 (24, $C_{30}H_{44}O_2$, $M^+ - S_2$), 421 (20, $C_{29}H_{41}O_2$, $M^+ - S_2 - CH_3$), 419 (17, $C_{30}H_{43}O$, $M^+ - S_2 - OH$), 380 (23, $C_{26}H_{36}O_2$, $M^+ - S_2 - C_4H_8$), 379 (14, $C_{26}H_{35}O_2$, $M^+ - S_2 - C_4H_9$), 244 (100, $C_{17}H_{24}O$), 229 (93, $C_{16}H_{21}O$). Anal. calc. for $C_{30}H_{44}O_2S_2$ (500.81): C 71.95, H 8.86, O 6.39, S 12.80; found: C 71.96, H 8.87, O 6.52, S 12.68.

*2,4α,6,8-Tetra(*tert*-butyl)-4β,10aβ-(epidithio)-4,4aβ,10,10a-tetrahydro-10α-methyl-1*H*-5-oxaanthracen-1-one* (**4a**). Purification method B gave, besides **3a**, a small amount of pure **4a** (0.6%). M.p. 175°. R_f (**3a**) 0.51, R_f (**4a**) 0.61. UV ($CHCl_3$): 351 (sh, 1030), 314 (1820), 284 (2170), 243 (6115); min. 294 (1470), 266 (1620). IR: 1686. ^{1}H-NMR: 7.15 (*m*, H–C(7), H–C(9)); 6.63 (*d*, *J* = 2.5, H–C(3)); 4.47 (*d*, *J* = 2.5, H–C(4a)); 3.52 (*q*, *J* = 7.5, H–C(10)); 1.80 (*d*, *J* = 7.5, CH_3–C(10)); 1.36, 1.30, 1.20 (*t*-Bu). FD-MS: 500. Anal. calc. for $C_{30}H_{44}O_2S_2$ (500.81): C 71.95, H 8.86, S 12.80; found: C 71.62, H 8.93, S 12.55.

Mixture **3a**/**4a**. Purification method B. Collecting all mixed and pure fractions containing exclusively **3a** and/or **4a** yielded 62% of **3a**/**4a** (75:25 by ^{1}H-NMR).

*2,4α,6,8-Tetra(*tert*-butyl)-4β,10aβ-(epidithio)-10β-ethyl-4,4aβ,10,10a-tetrahydro-1*H*-5-oxaanthracen-1-one* (**3b**). Purification method A. Yield 30%. R_f (**3b**) 0.46. M.p. 206–207°. UV ($CHCl_3$): 348 (sh, 1380), 316 (2040), 284 (2390), 244 (6210); min. 295 (1600), 268 (1730). IR (KBr): 1682. *Raman:* 1683 (C=O), 1605 (C=C), 528 (S–S). ^{1}H-NMR: 7.10, 7.00 (2*d*, *J* = 2, H–C(9), H–C(7)); 6.65 (*d*, *J* = 2.5, H–C(3)); 4.39 (*d*, *J* = 2.5, H–C(4a)); 3.43 (*dd*, *J* = 7.5, 4.5, H–C(10)); 2.26, 1.61, 1.20 (Et); 1.37, 1.27, 1.17 (*t*-Bu). FD-MS: 514. Anal. calc. for $C_{31}H_{46}O_2S_2$ (514.84): C 72.32, H 9.01, S 12.43; found: C 72.36, H 9.14, S 12.43.

*4α,8-Di(*tert*-butyl)-4β,10aβ-(epidithio)-4,4aβ,10,10a-tetrahydro-2,6,10β-trimethyl-1*H*-5-oxaanthracen-1-one* (**3c**). Purification method B. R_f (**3c**) 0.37. Yield 19%. M.p. 96°. UV ($CHCl_3$): 344 (sh, 1760), 318 (2130), 284 (2870), 246 (6120); min. 297 (1920), 268 (2060). IR (KBr): 1681 (C=O). ^{1}H-NMR: 7.05, 6.98 (2 br. *d*, *J* = 2, H–C(9), H–C(7)); 6.69 (*m*, H–C(3)); 4.34 (*d*, *J* = 2.5, H–C(4a)); 3.96 (*q*, *J* = 7.5, H–C(10)); 2.10 (br. *s*, CH_3–C(6)); 1.98

(*d*, *J* = 1.5, CH_3–C(2)); 1.53 (*d*, *J* = 7.5, CH_3–C(10)); 1.33, 1.28 (*t*-Bu). FD-MS: 416. Anal. calc. for $C_{24}H_{32}O_2S_2$ (416.64): C 69.19, H 7.74, S 15.39; found: C 69.19, H 7.91, S 15.19.

2,4α,6,8-Tetra(tert-*butyl)-4β,10aβ-(epidithio)-4,4aβ,10,10a-tetrahydro-1*H-*5-oxaanthracen-1-one* (**3d**). Purification by recrystallisation from i-PrOH/H_2O 96:4 and FC on silica gel using hexane/AcOEt 49:1. R_f (**3d**) 0.24. Yield 15%. M.p. 172–174°. UV ($CHCl_3$): 350 (sh, 1180), 316 (1830), 283 (2910), 244 (6080); min. 298 (1630), 267 (2360). IR (KBr): 1680. ^{1}H-NMR: 7.13, 6.99 (2 br. *d*, *J* = 2, H–C(9), H–C(7)); 6.76 (*d*, *J* = 2.5, H–C(3)); 4.43 (*d*, *J* = 2.5, H–C(4a)); 3.81, 3.22 (*AB*, *J* = 16, H–C(10)); 1.37, 1.30, 1.28, 1.22 (*t*-Bu). FD-MS: 486. Anal. calc. for $C_{29}H_{42}O_2S_2$ (486.64): C 71.56, H 8.70, S 13.17; found: C 71.47, H 8.79, S 12.90.

2,4α,6,8-Tetra(tert-*butyl)-4β,10aβ-(epidithio)-4,4aβ,10,10a-tetrahydro-10β-isopropyl-1*H-*5-oxaanthracen-1-one* (**3e**). Purification method **B**. R_f (**3e**) 0.28. Yield 13%. M.p. 200°. IR: 1678. ^{1}H-NMR: 7.10, 6.92 (2*d*, *J* = 2, H–C(9), H–C(7)); 6.68 (*d*, *J* = 2.5, H–C(3)); 4.43 (*d*, *J* = 2.5, H–C(4a)); 3.47 (*d*, *J* = 3, H–C(10)); 2.35 (*dsept.*, $(CH_3)_2CH$); 1.39, 1.28, 1.18 (*t*-Bu); 1.30, 0.70 (*d*, *J* = 7, $(CH_3)_2CH$). FD-MS: 528. Anal. calc. for $C_{32}H_{48}O_2S_2$ (528.86): C 72.68, H 9.15, S 12.12; found: C 72.88, H 9.49, S 11.91.

4. *Reaction of* **1a** *with 50% Excess of* S_2Cl_2. Following the general procedure, **1a** was allowed to react with *1,5 equiv.* (50% excess) of S_2Cl_2. Purification method **B**. Collecting all the fractions containing **3a** and/or **4a** yielded 68% of **3a**/**4a** (59:41 by ^{1}H-NMR).

5. *Crystal-Structure Analysis of* **3a**. *Crystal Data:* Formula, $C_{30}H_{44}O_2S_2$; crystal size, 0.30 × 0.30 × 0.40 mm; diffractometer, *Enraf-Nonius CAD 4;* space group, triclinic P_1 (No. 2); a = 9.720(2), b = 11.706(2), c = 13.633(3) Å, α = 102.85(2), β = 104.85(2), γ = 98.88(2)°; V = 1425 Å^3; $d_{calc.}$ = 1.167 g/cm^3; Z = 2; No. of reflections, 3462 ($I > 2\sigma(I)$); No. of parameters, 483; final R factors, R = 0.052, R_w = 0.049; max. residual electron density, 0.38 e/Å^3.

The structure was solved by direct methods using MULTAN 11/82 [9] and *Fourier* methods. Full matrix least squares minimized $\Sigma w(\Delta F)^2$. All non-H refined anisotropically, H isotropically. Programs used were those of *Enraf-Nonius* SDP [10]. *Table 4* gives the atomic coordinates.

Table 4. *Positional Parameters of* **3a** *and their Estimated Standard Deviations*[a])

Atom	*x*	*y*	*z*	*B(A2)*
C(1)	0.6995(3)	0.3333(2)	0.1005(2)	2.96(6)
C(2)	0.5638(3)	0.2703(2)	0.1163(2)	2.93(6)
C(3)	0.5728(3)	0.2477(2)	0.2089(2)	3.06(6)
C(4)	0.7071(3)	0.2789(2)	0.3011(2)	2.66(6)
C(4a)	0.8247(3)	0.3775(2)	0.2927(2)	2.57(6)
O(5)	0.7787(2)	0.4893(1)	0.3041(1)	2.69(4)
C(5a)	0.8648(3)	0.5801(2)	0.2799(2)	2.45(5)
C(6)	0.8491(3)	0.6982(2)	0.3154(2)	2.53(6)
C(7)	0.9390(3)	0.7882(2)	0.2937(2)	2.74(6)
C(8)	1.0389(3)	0.7667(2)	0.2389(2)	2.70(6)
C(9)	1.0443(3)	0.6480(2)	0.2014(2)	2.87(6)
C(9a)	0.9592(3)	0.5540(2)	0.2211(2)	2.55(6)
C(10)	0.9741(3)	0.4264(2)	0.1770(2)	3.06(6)
C(10a)	0.8430(3)	0.3397(2)	0.1832(2)	2.68(6)
S(11)	0.86012(9)	0.18220(6)	0.15713(6)	3.72(2)
S(12)	0.79637(9)	0.14830(6)	0.28351(6)	3.68(2)
O(13)	0.7005(2)	0.3724(2)	0.0253(2)	4.30(5)
C(14)	0.4216(3)	0.2328(3)	0.0249(2)	3.69(7)
C(15)	0.3706(4)	0.3445(3)	0.0025(3)	5.8(1)
C(16)	0.3009(4)	0.1560(4)	0.0510(3)	5.46(9)
C(17)	0.4448(4)	0.1555(3)	–0.0736(3)	5.4(1)
C(18)	0.6756(3)	0.2964(2)	0.4099(2)	3.11(6)
C(19)	0.5700(3)	0.3807(3)	0.4171(2)	3.97(7)
C(20)	0.8157(4)	0.3493(3)	0.5014(2)	4.23(8)
C(21)	0.6020(4)	0.1755(3)	0.4208(2)	4.68(8)
C(22)	0.7395(3)	0.7296(2)	0.3757(2)	3.08(6)
C(23)	0.7855(3)	0.7034(3)	0.4837(2)	3.65(7)

Table 4 (cont.)

Atom	*x*	*y*	*z*	*B(A2)*
C(24)	0.7360(3)	0.8636(3)	0.3974(2)	4.44(7)
C(25)	0.5847(3)	0.6586(3)	0.3099(2)	3.85(7)
C(26)	1.1410(3)	0.8676(2)	0.2195(2)	3.12(6)
C(27)	1.2977(4)	0.8692(4)	0.2754(4)	7.4(1)
C(28)	1.1073(5)	0.9886(3)	0.2548(3)	8.0(1)
C(29)	1.1233(5)	0.8401(4)	0.1004(3)	6.5(1)
C(30)	1.1222(3)	0.4067(3)	0.2335(3)	4.64(8)

[a]) Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)\cdot[a^2\cdot B_{11} + b^2\cdot B_{22} + c^2\cdot B_{33} + ab(\cos\gamma)\cdot B_{12} + ac(\cos\beta)\cdot B_{13} + bc(\cos\alpha)\cdot B_{23}]$.

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