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3-METHYLTHIO-1,2-DITHIOLYLIUM SALTS—II†

REACTION WITH 4-HYDROXY-3H-PYRAN-2,6-DIONE. 1,3-BIS-(1,2-DITHIOL-3-YLIDENE)-2-PROPANONES

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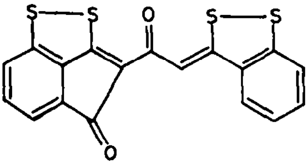
Abstract—A simple route to the hitherto unknown 1,3-bis-(1,2-dithiol-3-ylidene)-2-propanones is reported: 3-Methylthio-1,2-dithiolylium salts condense with 4-hydroxy-3H-pyran-2,6-dione to 3,5-bis-(1,dithiol-3-ylidene)pyran-2,4,6-triones, which are converted by acidic hydrolysis into the propanones.

Theoretically the $1,6,6a\lambda^4$-trithiapentalene system (**1**) may be extended to include compounds with four, five or even an infinite row of S atoms.[1] However, only extended structures of the types **2**[2] and **3**[3] have so far been reported. Stauvaux and Lozac'h[3] prepared **3** from the appropriate cyclohexanones in a multistep sequence, **4** and **5** being the important intermediates. The cyclohexane unit is, however, a prerequisite for the success of their route and we are currently investigating other methods.[4] We considered the hitherto unknown 1,3 - bis - (1,2 - dithiol - 3 - ylidene) - 2 - propanones (**6**, Scheme 1) key intermediates in an alternative procedure to the extended structures with five S atoms. In this paper a simple route to the compounds **6** from easily available starting material (3 - methylthio - 1,2 - dithiolylium salts and 4 - hydroxy - 3H - pyran - 2,6 - dione) is reported. Klingsberg[5] has previously prepared an azaanalog **7** (Y = 0) to the compounds **6** from 3 - chlor - 1,2 - benzodithiolylium chloride and urea. The fifth S atom (**7** (Y=S)) was introduced smoothly by the action of tetraphosphorous decasulfide.[5]

simple condensation reaction. Normally, condensations with 3 - methylthio - 1,2 - dithiolylium salts have been performed in glacial acetic acid with pyridinium acetate as base,[7] but recently we observed,[8] that especially in cases where the salt is substituted in position 4, the reactions proceeded better in dichloromethane (pyridine). Under these reaction conditions the salts **8a**–**8f** condensed with 4 - hydroxy - 3H - pyran - 2,6 - dione (acetonedicarboxylic acid anhydride) to give the bis-condensation products (**9a**–**9f**; Scheme 1). Previous attempts to obtain bis-condensation with the related reagents, acetonedicarboxylic acid and the corresponding diethyl ester, failed.[9,10]



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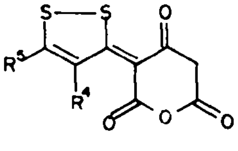

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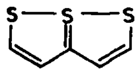

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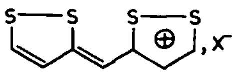

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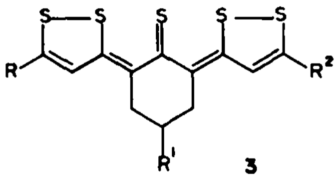

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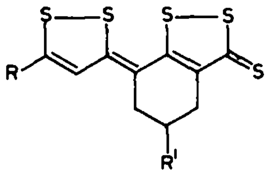

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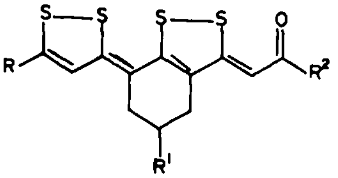

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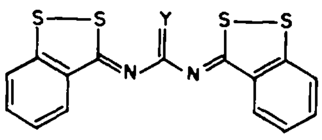

Y=O or S

7

RESULTS AND DISCUSSION

Depending on the substitution pattern and the reaction conditions the reaction of 1,2-dithiolylium salts with oxocompounds containing an α-methyl(ene) group yields α - (1,2 - dithiol - 3 - ylidene)ketones or aldehydes, $1,6,6a\lambda^4$-trithiapentalenes, 2H - thiopyran - 2 - ones or -thiones.[6] The two latter types of compounds are formed via a ringopening-elimination-ringclosure sequence, whereas the two former types result from a

Only compound **10** could be isolated in a poor but reproducible yield from the complex mixture of products, which resulted from the reaction of the salt **8g** with 4 - hydroxy - 3H - pyran - 2,6 - dione in dichloromethane. If the reaction, however, was performed in glacial acetic acid, the bis-condensation product **9g** was obtained in a good yield (Scheme 1). The compound **10** was not formed (TLC).

The products **9** derived from 4-unsubstituted salts (R^4 = H, Scheme 1) were very difficult to purify and two of them (**9d** and **9f**) could not be obtained analytically

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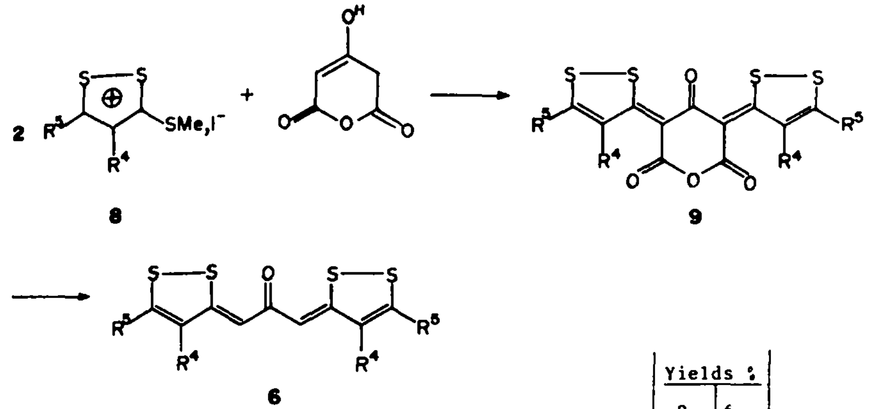
†Part I. E. G. Frandsen, *Tetrahedron* **33**, 869 (1977).



		Yields %	
		9	6
6a, 8a and 9a:	R^4, R^5 = H, C_6H_5	85	70
6b, 8b and 9b:	R^4, R^5 = H, p-BrC_6H_4	77	66
6c, 8c and 9c:	R^4, R^5 = CH_3, C_6H_5	60	74
6d, 8d and 9d:	R^4, R^5 = H, $C(CH_3)_3$	(54)	53
8e and 9e:	R^4, R^5 = C_6H_5, C_6H_5	61	—
8f and 9f:	R^4, R^5 = H, p-$CH_3OC_6H_4$	(91)	—
6g, 8g and 9g:	R^4, R^5 = CH = CH-CH = CH	57	22

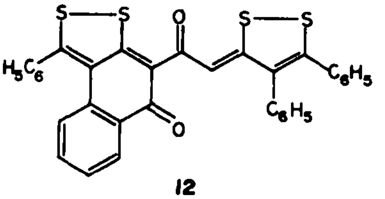
Scheme 1

pure. The difficulty was connected with their insolubility in organic solvents (9b, <1 mg/ml DMF at reflux temp.) and their great tendency to include solvent in the crystals.

Attempts to prepare the mono-condensation products 11, which might have been starting material for the prepartion of unsymmetrical compounds of type 9, did not succeed. When equimolar amounts of the reactants were used, high yields of the bis-condensation products were obtained.

The compounds 9 were surprisingly stable to acidic hydrolysis, e.g. 9a was recovered almost quantitatively after reflux for a week in concentrated hydrochloric acid. However, when 9a–9d were heated to *ca* 150° in sulfuric acid (80%), they were converted into 1,3 - bis - (1,2 - dithiol - 3 - yliden) - 2 - propanones (6, Scheme 1). The crude products (9) could be used in cases where the purification was difficult (Experimental). Complete hydrolysis-decarboxylation of 9g was achieved by heating the reaction mixture to 150–155° for 15 min. The main product was 6g, but 10 could be detected (TLC) in the crude product. Compound 9e gave 12 in a good yield on treatment with sulfuric acid (80%). No well-defined product could be isolated after hydrolysis of 9f. As it is known, the methyl group in a *para*-OMe group is rather easily lost,[7] an explanation for this failure may be, that the resulting phenolic compound polymerizes under the reaction conditions used.

In the mass spectra of 6 relative intense molecular ions were formed. The predominant fragmentation mode was in all cases α-cleavage with respect to the CO group giving rise to ions, which may be formulated as 13 (base peak) and 14. This observation is in agreement with results reported for 5 and simple α - (1,2 - dithiol - 3 - ylidene)ketones (15).[11,12]



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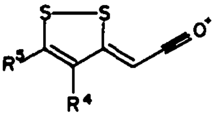

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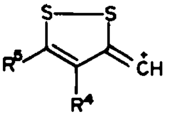

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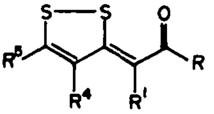

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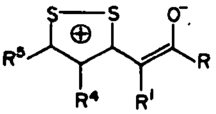
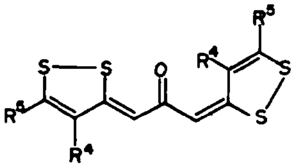


15a



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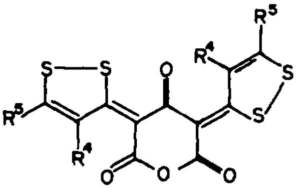
The prominent feature of the IR-spectra of 15 is the absence of the usual CO frequencies in the 1610–1750 cm^{-1} range, together with one or more strong bands in the 1500–1610 cm^{-1} range.[1,7] By comparison of the spectra of ^{16}O compounds with those of ^{18}O enriched compounds it was possible to locate the CO vibration (near 1575 cm^{-1} for α - (1,2 - dithiol - 3 - yliden)acetones and near 1550 cm^{-1} for -acetophenones). However, the isotopic displacement found was much smaller than the one observed with simpler ketones, due to the contribution of polar forms such as **15a**. In the IR spectra of **6a–6d** a strong band was observed in the 1558–1570 cm^{-1} range and this indicates that the structure of these compounds is similar to that of simpler α - (1,2 - dithiol - 3 - ylidene)ketones.

From the UV/spectra of **6a–6d** it could be concluded that the same chromophore is present. Two intense absorptions separated by 30–40 nm are observed in the visible (481–557 nm), and one (**6c** and **6d**) or two (**6a–6b**) are found in the UV (near 250 nm in all cases and near 310 nm). As observed for the related compounds **5**, the absorptions in the visible of the aryl substituted compounds **6a–6c** are situated at longer wavelengths than those of the t-Bu substituted compound **6d**.

Due to their insolubility in organic solvents ^{1}H and ^{13}C NMR spectra of **6a**, **6b** and **6g** could not be recorded. The spectra of **6c** and **6d** are in agreement with the symmetrical structure **6** and exclude the structure **16**.

Intense molecular ions were observed in the mass spectra of the compounds **10** and **12**. Important ions resulted from the elimination of small fragments (H, CO, S or S_2) or combinations of these from the molecular ions. α-Cleavage with respect to the *cis*-CO group gives rise to relative intense ions in the spectrum of **12**, whereas it is not observed in the fragmentation of **10**.

In the IR-spectra of α - (1,2 - dithiol - 3 - ylidene) - β - diketones the carbonyl stretching vibration of the *trans*-CO group is observed in the 1624–1638 cm^{-1} range, whereas the absorption of the *cis*-CO group is situated in the 1535–1547 cm^{-1} range.[7] The *trans*-CO group in **10** and **12** absorbs at 1620 and 1618 cm^{-1}, respectively. Two bands are situated in the 1500–1600 cm^{-1} range: 1530 and 1549 cm^{-1} in **10** and 1530 and 1588 cm^{-1} in **12**. Due to the insolubility of these compounds in organic solvents it was impossible to determine the solvent effect[7] on these bands and, therefore, a definite assignment of the *cis*-CO group absorption could not be made.



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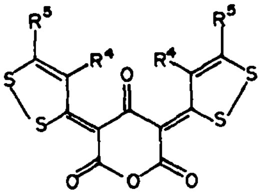

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Three isomeric structures **9**, **17** and **18** can be assigned to the bis-condensation products. It does not seem possible on the basis of the way of synthesis, their conversion into **6**, the MS, IR and UV spectra to make a definite choice between these structures. However, in view of the known preference for ketonic oxygen to participate in heterapentalene formation when ester oxygen is also available, structure **9** is considered most likely.[7]

EXPERIMENTAL

Microanalyses were carried out by Mr. P. Hansen, Microanalytical Department of the University of Copenhagen.

Instrumentation. IR: Perkin Elmer 457 and 580. ^{1}H and ^{13}C NMR: JEOL JMN-Fx 60. UV/VIS: Beckmann ACTA III. MS: Varian MAT 311A.

4 - Hydroxy - 3H - pyran - 2,6 - dione was prepared from acetonedicarboxylic acid (EGA Chemie) by the method published by Findlay.[13]

The 3 - methylthio - 1,2 - dithiolylium iodides were prepared from the appropriate 1,2-dithiole-3-thiones.[14]

The m.ps are uncorrected.

3,5 - *Bis* - (5 - *aryl* - 1,2 - *dithiol* - 3 - *ylidene*)*pyran* - 2,4,6 - *triones* (**9**). The appropriate compounds (**8a–8f**, 10^{-2} mol), 4 - hydroxy - 3H - pyran - 2,6 - dione (5 × 10^{-3} mol), and pyridine (20 ml) in CH_2Cl_2 (750 ml) were refluxed for *ca* 20 hr.

3,5 - *Bis* - (5 - *phenyl* - 1,2 - *dithiol* - 3 - *ylidene*)*pyran* - 2,4,6 - *trione* (**9a**). The precipitated red crystals were washed with CH_2Cl_2 followed by water, and dried, yield = 85%. A sample was purified by column chromatography (*ca.* 2.5 × 30 cm, silica (30–75 mesh), CH_2Cl_2: MeOH = 10 : 1), m.p. >320°; UV/VIS (dioxane): λ_{max} ($\epsilon \times 10^4$) = 513 (3.34), 490 (sh), 425 (0.87), 408 (sh), 360 (sh), 323 (1.79), 288 (1.29) and 240 nm (1.66). IR (KBr): ν_{max} = 1720, 1700, 1680, 1545, 1432 (broad), and 1370 cm^{-1}. MS: *m/z* (%) = 480 (100, M$^+$), 436 (30) and 408 (15). (Found: C, 57.10; H, 2.62; S, 26.85. $C_{23}H_{12}O_4S_4$ requires: C, 57.50; H, 2.50; S, 26.67%).

3,5 - *Bis* - (5 - p - *bromophenyl* - 1,2 - *dithiol* - 3 - *ylidene*)*pyran* - 2,4,6 - *trione* (**9b**). The precipitated red crystals were washed with CH_2Cl_2 followed by water and dried, yield: 77%, m.p. (DMF) > 320°; UV/VIS (dioxane): λ_{max} ($\epsilon \times 10^4$) = 518 (4.29), 500 (sh), 430 (1.10), 415 (sh), 333 (2.91), 288 (1.81) and 242 nm (2.64). IR (KBr): ν_{max} = 1720, 1687, 1582, 1490 and 1425 (broad) cm^{-1}. MS: *m/z* (%) = 640 (65), 638 (100), 636 (47), 596 (12), 594 (20), 592 (10), 568 (10), 566 (12) and 564 (7). (Found: C, 42.40; H, 1.58; S, 19.23; Br, 25.15. $C_{23}H_{10}O_4S_4Br_2$ requires: C, 43.27; H, 1.57; S, 20.07; Br, 25.06%).

3,5 - *Bis* - (4 - *methyl* - 5 - *phenyl* - 1,2 - *dithiol* - 3 - *ylidene*)*pyran* - 2,4,6 - *trione* (**9c**). The precipitated red crystals were washed with CH_2Cl_2 followed by water and dried. If the crude product was not analytically pure, it was recrystallized from N,N-dimethylformamide (DMF), yield = 60%, m.p. = 299–303° d; UV/VIS (dioxane): λ_{max} ($\epsilon \times 10^4$) = 526 (4.29), 501 (sh), 433 (1.35), 353 (sh), 305 (1.94) and 244 nm (3.20). IR (KBr): ν_{max} = 1732, 1711, 1690, 1530, 1435 and 1380 cm^{-1} (broad). MS: *m/z* (%) = 508 (100, M$^+$), 464 (80) and 436 (26). (Found: C, 58.95; H, 3.30; S, 25.18. $C_{25}H_{16}O_4S_4$ requires: C, 59.06; H, 3.15; S, 25.20%).

3,5 - *Bis* - (5 - *t* - *butyl* - 1,2 - *dithiol* - 3 - *ylidene*)*pyran* - 2,4,6 - *trione* (**9d**). The resulting soln was evaporated and the residue was partly purified by column chromatography (*ca.* 2.5 × 30 cm, silica, benzene, twice), yield = 54% (impure). Attempted further purification by recrystallization or chromatography did not succeed, but acidic hydrolysis of **9d** gave **6d** in a good yield.

3,5 - *Bis* - (4,5 - *diphenyl* - 1,2 - *dithiol* - 3 - *ylidene*)*pyran* - 2,4,6 - *trione* (**9e**). The resulting soln was extracted with 6M HCl (60 ml) followed by water (150 ml), dried (Na_2SO_4) and evaporated. The black-red crystals were purified by column chromatography (*ca.* 2.5 × 30 cm, silica, $CHCl_3$). Recrystallization from 2-methoxyethanol/water or DMF/abs EtOH gave brown-red needles, yield = 61%, m.p. 286–289°d; UV/VIS (dioxane): λ_{max} ($\epsilon \times 10^4$) = 536 (3.82), 514 (sh), 433 (1.07), 333 (sh), 278 (sh) and 243 nm (3.41). IR (KBr): ν_{max} = 1725, 1700, 1640, 1525 and 1380 cm^{-1} (broad). MS: *m/z* (%) = 632 (1, M$^+$), 588 (100) and 560 (12). (Found: C, 66.40; H, 3.12; S, 20.05. $C_{35}H_{20}O_4S_4$ requires: C, 66.45; H, 3.16; S, 20.25%).

3,5 - *Bis* - (5 - p - *methoxyphenyl* - 1,2 - *dithiol* - 3 - *ylidene*)*pyran* - 2,4,6 - *trione* (**9f**). The precipitated red crystals were washed with CH_2Cl_2, followed by water, and dried, yield = 91%. Attempted purification by recrystallization or chromatography did not succeed. (Found: C, 53.20; H, 2.94; S, 22.23. $C_{25}H_{16}O_6S_4$ requires: C, 55.56; H, 2.96; S, 23.70%). However, the spectroscopic properties of the product were as expected: UV/VIS (dioxane): λ_{max} ($\epsilon \times 10^4$) = 518 (3.65), 488 (sh), 425 (0.83), 405 (sh), 360 (1.94), 280 (0.80) and 242 nm (1.85). IR (KBr): ν_{max} = 1720, 1680, 1600, 1535 and 1425 (broad) cm^{-1}. MS: *m/z* (%) = 540 (100, M$^+$), 496 (32) and 468 (20).

3,5 - *Bis* - (1,2 - *benzodithiol* - 3 - *ylidene*)*pyran* - 2,4,6 - *trione* (**9g**). Compound **8g** (8 × 10^{-3} mol), 4 - hydroxy - 3H - pyran - 2,6 - dione (4 × 10^{-3} mol), pyridine (8 ml), in glacial AcOH (250 ml) were refluxed for *ca.* 21 hr. The precipitated black crystals were collected, washed with water followed by acetone and dried, yield = 57%, m.p. (DMF/abs EtOH) = 272–274° d; UV/VIS (dioxane): λ_{max} ($\epsilon \times 10^4$) = 543 (4.61), 513 (sh), 447 (1.72), 425 (sh), 336 (1.11), 310 (1.58), 275 (2.52) and 243 nm (3.33). IR (KBr): ν_{max} = 1727, 1700, 1520 and 1390 (broad) cm^{-1}. MS: *m/z* (%) =

428 (10, M$^+$), 384 (96), 356 (54) and 324 (100). (Found: C, 53.15; H, 1.97; S, 29.04. $C_{19}H_8O_4S_2$ requires: C, 53.27; H, 1.87; S, 29.91%).

1,3 - *Bis* - (5 - *aryl* - 1,2 - *dithiol* - 3 - *ylidene*) - 2 - *propanones* (**6**). The appropriate compound (**9a–9d** and **9g**, 10^{-3} mol) in 80% H_2SO_4 (45 ml) was heated to *ca* 150°, and the resulting homogenous mixture was poured on ice-water (300 ml).

1,3 - *Bis* - (5 - *phenyl* - 1,2 - *dithiol* - 3 - *ylidene*) - 2 - *propanone* (**6a**). The precipitated black-brown crystals were washed with water, 50% Na_2CO_3 aq, water and dried. Recrystallization from 2-methoxyethanol yielded black-violet crystals, yield = 70%, m.p. = 267–269° d; UV/VIS (dioxane): λ_{max} ($\epsilon \times 10^4$) = 557 (5.51), 520 (4.34), 488 (sh), 455 (sh), 383 (0.61), 304 (2.82) and 247 nm (4.90). IR (KBr): ν_{max} = 1558 and 1492 (broad) cm^{-1}. MS: *m/z* (%): 410 (24, M$^+$), 219 (100) and 191 (15). (Found: C, 61.50; H, 3.59; S, 31.32. $C_{21}H_{14}O_1S_4$ requires: C, 61.46; H, 3.41; S, 31.22%).

1,3 - *Bis* - (5 - p - *bromophenyl* - 1,2 - *dithiol* - 3 - *ylidene*) - 2 - *propanone* (**6b**). The precipitated brown-red crystals were washed with water, 50% Na_2CO_3 aq, water and dried. Recrystallization from DMF gave dark-red needles, yield = 66%, m.p. = 310–311° d; UV/VIS (dioxane): λ_{max} ($\epsilon \times 10^4$) = 563 (3.61), 525 (3.31), 495 (sh), 463 (sh), 380 (0.55), 323 (sh), 313 (3.14) and 255 nm (6.28). IR (KBr): ν_{max} = 1560 and 1498 (broad) cm^{-1}. MS: *m/z* (%) = 570 (18), 569 (11), 568 (43), 567 (11), 566 (41), 299 (100) and 297 (92). (Found: C, 44.25; H, 2.17; S, 22.35; Br. 28.25. $C_{21}H_{12}Br_2OS_4$ requires: C, 44.38; H, 2.11; S, 22.54; Br, 28.15%).

1,3 - *Bis* - (4 - *methyl* - 5 - *phenyl* - 1,2 - *dithiol* - 3 - *ylidene*) - 2 - *propanone* (**6c**). The precipitated dark-red crystals were washed with water, 50% Na_2CO_3 aq, water and dried. Recrystallization from 2-methoxyethanol gave brown-red needles, yield = 74%, m.p. 253–254°, UV/VIS (dioxane): λ_{max} ($\epsilon \times 10^4$) = 528 (6.01), 495 (3.83), 467 (sh), 443 (sh), 370 (0.60), 280 (sh) and 248 nm (4.16). IR (KBr): ν_{max} = 1568 and 1482 (broad) cm^{-1}. MS: *m/z* (%) = 438 (30, M$^+$), 233 (100) and 205 (14). ^{1}H NMR ($CDCl_3$): δ = 7.4 (5H), 6.6 (1H) and 2.1 ppm (3H). ^{13}C NMR ($CDCl_3$): δ = 181.4, 167.0, 153.3, 133.8, 129.3, 129.3, 128.2 (two poorly resolved signals), 110.5 and 15.3. (Found: C, 63.00; H, 4.25; S, 29.05. $C_{23}H_{18}O_1S_4$ requires: C, 63.01; H, 4.11; S, 29.22%).

1,3 - *Bis* - (5 - *t* - *butyl* - 1,2 - *dithiol* - 3 - *ylidene*) - 2 - *propanone* (**6d**). The precipitated red crystals were washed with water, 50% Na_2CO_3 aq, water and dried. Purification by column chromatography (*ca.* 2.5 × 30 cm, silica, toluene (twice)) yielded dark-red crystals, yield: 53%, m.p. = 170–172° d; (darkens at *ca.* 150°); UV/VIS (dioxane): λ_{max} ($\epsilon \times 10^4$) = 517 (6.66), 481 (3.72), 452 (sh), 428 (sh), 379 (0.42), 359 (0.51), 344 (0.53) and 245 nm (3.47). IR (KBr): ν_{max} = 1570 and 1490 (broad) cm^{-1}. MS: *m/z* (%) = 370 (24, M$^+$), 199 (100) and 171 (4). ^{1}H NMR ($CDCl_3$): δ = 6.73 (s, 1H), 6.50 (s, 1H) and 1.37 ppm (s, 9H). ^{13}C NMR ($CDCl_3$): δ = 181.1, 172.9, 166.7, 121.3, 109.5, 36.8 and 31.3 ppm. (Found: C, 54.50; H, 5.95; S, 34.05. $C_{17}H_{22}O_1S_4$ requires: C, 55.14; H, 5.95; S, 34.59%).

1,3 - *Bis* - (1,2 - *benzodithiol* - 3 - *ylidene*) - 2 - *propanone* (**6g**). The precipitated black-violet crystals were washed with water, 50% Na_2CO_3 aq, water and dried. Purified by column chromatography to yield red-brown crystals, yield = 22%, m.p. = 254–257° d; UV/VIS (dioxane): λ_{max} ($\epsilon \times 10^4$) = 528 (4.13), 493 (2.20), 463 (0.69), 413 (0.29), 388 (sh), 370 (sh), 324 (0.65), 309 (sh), 294 (1.21), 281 (1.55), 273 (sh) and 243 nm (2.67). IR (KBr): ν_{max} = 1590–1570 (three rather weak absorptions) and 1515 cm^{-1}. MS: *m/z* (%) = 358 (26, M$^+$), 193 (100) and 165 (25). (Found: C, 56.90; H, 3.05. $C_{17}H_{10}OS_4$ requires: C, 56.98; H, 2.79%).

3 - [2 - (1,2 - *Benzodithiol* - 3 - *ylidene*)*acetyl*]*indeno*[3,3a,4 - cd] - 1,2 - *dithiol* - 4 - *one* (**10**). Compound **8g** (4 × 10^{-3} mol), 4 - hydroxy - 3H - pyran - 2,6 - dione and pyridine (12 ml) in CH_2Cl_2 (600 ml) were refluxed for *ca.* 18 hr. The resulting homogenous soln was washed with 7M HCl (200 ml) followed by 50% Na_2CO_3 aq (200 ml), dried (Na_2SO_4) and evaporated. The residue was purified by column chromatography (*ca.* 2.5 × 30 cm, silica (30–75 mesh), benzene) to give red needles, yield = 20%, m.p. (2-methoxyethanol) = *ca.* 270° subl. UV/VIS (dioxane): λ_{max} ($\epsilon \times 10^4$) = 493 (2.41), 370 (sh), 340 (1.06), 331 (sh), 306 (1.62), 268 (sh), 256 (2.55), 253 (sh) and 242 nm (sh). IR (KBr): ν_{max} = 1620, 1549, 1530 and 1380 cm^{-1}. MS: *m/z* (%) = 384 (59, M$^+$), 383 (8), 356 (40), 355 (42), 352 (15), 324 (100) and 320 (35). (Found: C, 56.25; H, 2.13; S, 32.75. $C_{18}H_8O_2S_4$ requires: C, 56.25; H, 2.08; S, 33.33%).

4 - [2 - (4,5 - *Diphenyl* - 1,2 - *dithiol* - 3 - *ylidene*)*acetyl*] - 1 - *phenyl* - *naphtho*[2,1 - c][1,2] - *dithiol* - 5 - *one* (**12**). Compound **8e** (7.3 × 10^{-3} mol, purified material) in 80% H_2SO_4 (60 ml) was heated to *ca.* 150°. The resulting soln was poured on ice-water (200 ml). Extraction with $CHCl_3$ (2 × 150 ml), drying (Na_2SO_4) and evaporation afforded black-red crystals, which were recrystallized from DMF/abs EtOH to give red needles, yield = 70%, m.p. = 255–260° d; UV/VIS (dioxane): λ_{max} ($\epsilon \times 10^4$) = 517 (3.55), 488 (2.34), 443 (1.91), 417 (sh), 395 (sh), 350 (sh), 303 (sh), 265 (sh) and 239 nm (5.11). IR (KBr): ν_{max} = 1618, 1588, 1530, 1484, 1460 and 1420 (broad) cm^{-1}. MS: *m/z* (%) = 588 (100, M$^+$), 587 (60), 556 (20), 555 (40), 524 (18), 523 (27), 295 (20), 294 (69) and 293 (12). (Found: C, 69.30; H, 3.31; S, 21.60. $C_{34}H_{20}O_2S_4$ requires: C, 69.39; H, 3.40; S, 21.77%).

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REFERENCES

[1] Carl Th. Pedersen, Thesis, Odense (1976).
[2] C. Lamarie-Retour, M. Stavaux and N. Lozac'h, *Bull. Soc. Chim. Fr.* 1659 (1973); D. B. J. Easton, D. Leaver and D. M. McKinnon, *J. Chem. Soc.* (C), 462 (1968); E. Klingsberg, *Synthesis* 29 (1972); E, Klingsberg, *J. Heterocyclic Chem.* 3, 243 (1966).
[3] M. Stavaux, *Bull. Soc. Chim. Fr.* 4429 (1971); M. Stavaux and N. Lozac'h, *Ibid.* 4423 (1971).
[4] E. G. Frandsen, *J. Chem. Soc.* Chem. Comm. 851 (1977).
[5] E. Klingsberg, *Chem. & Ind.* 1813 (1968).
[6] E. G. Frandsen, Thesis, Odense (1978); and refs cited.
[7] N. Lozac'h, *Adv. Heterocyclic Chem.* 13, 161 (1971).
[8] E. G. Frandsen, *Tetrahedron* 33, 869 (1977).
[9] U. Schmidt, *Liebigs Ann.* 635, 109 (1960).
[10] E. G. Frandsen, unpublished results.
[11] C. Th. Pedersen, M. Stavaux and J. Møller, *Acta Chem. Scand.* 26, 3875 (1972).
[12] C. Th. Pedersen, N. L. Huaman, R. Pinel and J. Møller, *Ibid.* 26, 1305 (1972).
[13] S. P. Findlay, *J. Org. Chem.* 22, 1385 (1957).
[14] A. Brandin, C. Bouillon and J. Vialle, *Bull. Soc. Chim. Fr.* 4555 (1968); O. Coulibaly and Y. Mollier, *Ibid.* 3208 (1969).