*Acta Chemica Scandinavica, 1999: 53: 133–140*
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ACTA
CHEMICA SCANDINAVICA
*ISSN 0904–213X*

# New Reactions with Thiosulfines/Dithiiranes: Cycloadditions Leading to Dispiro Derivatives of 1,2,4-Trithiolane

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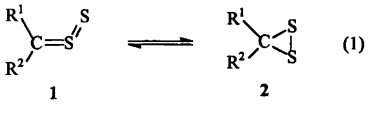
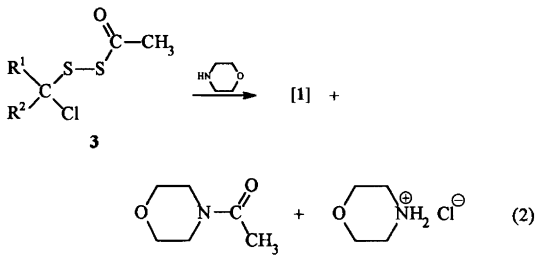
Hegab, M. I., Abdel-Megeid, F. M. E., Gad, F. A., Shiba, S. A., Søtofte, I., Møller, J. and Senning, A., 1999. New Reactions with Thiosulfines/Dithiiranes: Cycloadditions Leading to Dispiro Derivatives of 1,2,4-Trithiolane. – Acta Chem. Scand. 53: 133–140. © Acta Chemica Scandinavica 1999.

The β-oxo thiosulfines **8**, generated by 'unzipping' of the corresponding acetyl α-chloroalkyl disulfides **11** with morpholine, are partially converted into the corresponding thioketones **12** which then cycloadd to **8** to give the observed *cis*- and *trans*-1,2,4-trithiolanes **15**. The unsymmetrical Diels–Alder dimerization of **12** plays only a minor role. The new heterocycles thus obtained have been characterized spectroscopically and by X-ray crystallography.

Thiosulfines **1** and dithiiranes **2**, cf. eqn. (1), are compounds attracting much topical interest.[1–3] The generation of thiosulfines/dithiiranes **1/2** from α-chloroalkanesulfenyl chlorides **3** via acetyl α-chloroalkyl disulfides **4** by 'unzipping', eqn. (2), is a convenient and reliable preparative method.[4,5]

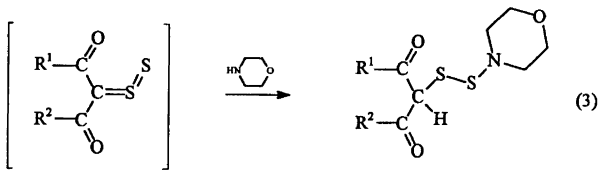


(1)

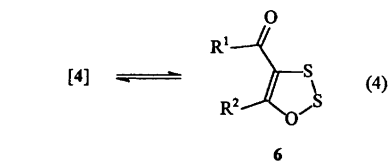


(2)

β,β′-Dioxo substituted compounds in the form of diaroylmethane derivatives exhibited characteristic behavior in that the otherwise predominant sulfur loss from the corresponding thiosulfine **4** was, by and large, suppressed. Furthermore, contrary to all other known **1/2** systems nucleophilic addition of morpholine to give **5**, eqn. (3), was observed which could be explained either in terms of inductive and mesomeric substituent effects on the electron distribution within the thiosulfine moiety (i.e., leading to a preponderance of the resonance contributor **1f**, cf. Scheme 1) or by invoking the intermediacy of a tautomer **6** formed by intramolecular ring closure of **4**, cf. eqn. (4).



(3)



(4)

In our present study we wished to examine the generation and reactive behavior of β-monooxo substituted **1/2** derived from 1-tetralone and its chalcogena analogs, i.e. **8**.

The required precursors of **8**, i.e. the ketones **7**, the α-chlorosulfenyl chlorides **10**, and the acetyl α-chloro-

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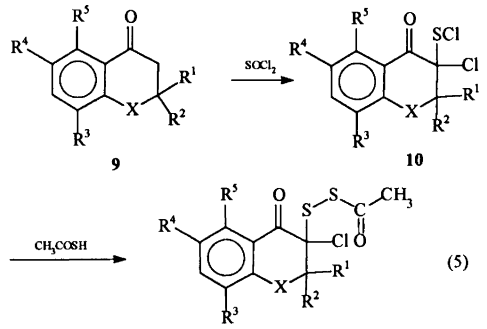
alkyl disulfides **11** were prepared according to standard procedures, cf. eqn. (5).

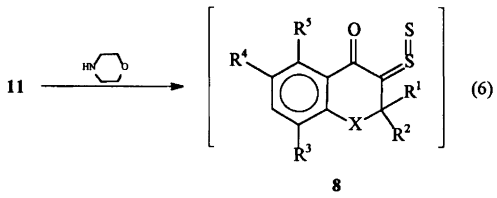


(5)

**11**

**a**, X=$CH_2$; $R^1$=Et, $R^2$=Me, $R^3$=$R^4$=$R^5$=H
**b**, X=$CH_2$; $R^1$=$R^2$=$R^3$=$R^5$=Me, $R^4$=H
**c**, X=$CH_2$; $R^1$=$R^2$=Et, $R^3$=$R^4$=$R^5$=H
**d**, X=O; $R^1$+$R^2$=$(CH_2)_5$, $R^3$=$R^4$=$R^5$=H
**e**, X=S, $R^1$=$R^2$=$R^4$=Me, $R^3$=$R^5$=H

When **8** was generated according to eqn. (6) it was immediately obvious that the corresponding thioketones **12** were formed as well, presumably via disproportionation, eqn. (7).[1,3] However, no products derived from the hypothetical thione *S*-disulfides **13** could be identified.



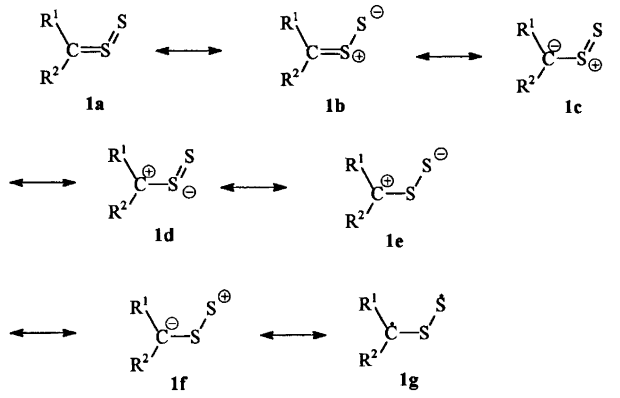
(6)

**8**

The yields of the cycloadditions following the liberation of **8** according to eqn. (6) are shown in Table 1.

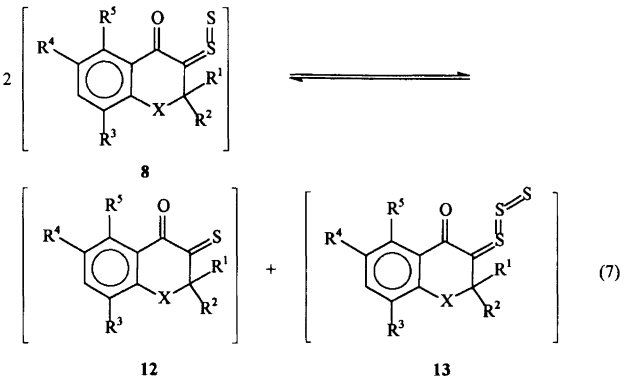
The Diels–Alder dimer of **12**, i.e. the spiro compound **14**, could be observed in only one case, namely in the shape of **14a**, cf. eqn. (8). Such dimers are otherwise known to be formed from α-oxo thioketones.[8]

The common denominator of the five reactions examined by us is the formation of the *trans*-1,2,4-trithiolanes, *trans*-**15**, formed from **8** and **12** according to eqn. (9),



**1a** **1b** **1c** **1d** **1e** **1f** **1g**

*Scheme 1.*



(7)

**8**

**12** **13**

*Table 1.* Yields (%) of cycloaddition products from **8**.

| Starting compound | **14** | *cis*-**15** | *trans*-**15** |
|---|---|---|---|
| **9a** | 0.7 | 2 | 15 |
| **9b** | — | — | 26 |
| **9c** | — | 2.6 | 20 |
| **9d** | — | — | 30 |
| **9e** | — | — | 14 |

cf. Table 1. In two cases, the isomeric *cis*-**15** could be isolated as a minor companion of *trans*-**15**. The nature of X in **8**, i.e. $CH_2$ (**8a–c**), O (**8d**), or S (**8e**) does not appear to influence the general course of the reactions.

In order to ascertain their *cis–trans* identity the new sulfur heterocycles obtained in our study were also examined by X-ray crystallography, cf. Figs. 1 and 2. A short summary of the crystal data is given in Table 2.

The NMR spectra of **15** only partially reflect the stereogenicity of the two carbon atoms of the 1,2,4-trithiolane ring. In the $^1$H NMR spectra the $CH_2$ protons of the ethyl groups (but not the $CH_3$ protons) exhibit the expected diastereotopy while the $^{13}$C NMR spectra fail to show corresponding effects on the carbon atoms.

The EI mass spectra of **15** all exhibit significant and relatively abundant molecular ion peaks; in the case of

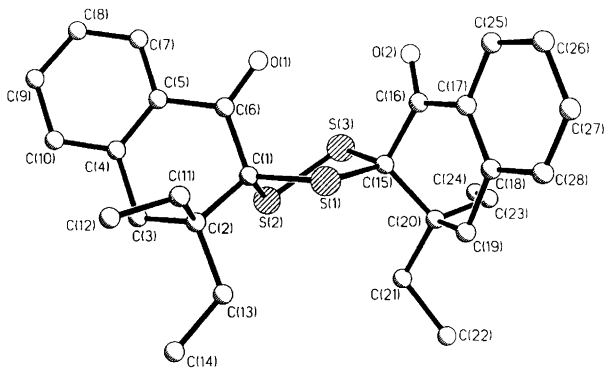



*Fig. 1.* The structure of *cis*-**15c** as determined by X-ray crystallography.

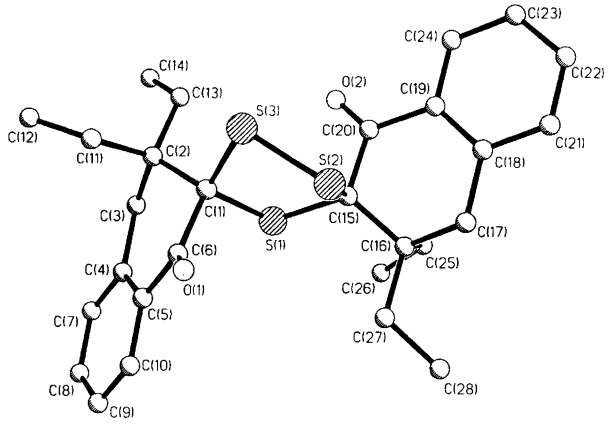
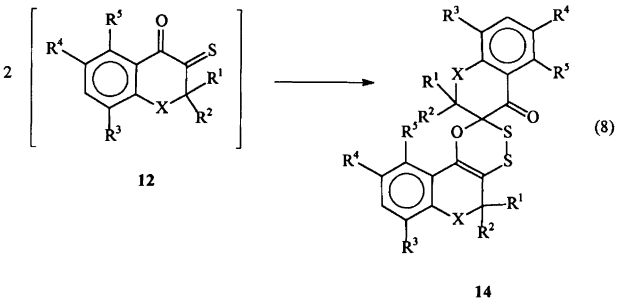



*Fig. 2.* The structure of *trans*-**15c** as determined by X-ray crystallography.




*trans*-**15d** the $M^{\cdot+}$ ion gives rise to the base peak. In the EI mass spectra of **15a–c** the base peaks correspond to loss of two sulfur atoms from the molecular ion. The EI mass spectra of corresponding *cis* and *trans* isomers are very similar and the small differences in the intensities of various ions in, for instance, the **15a** isomers do not allow any distinction.

Figure 3 shows the FAB spectra of *cis*- and *trans*-**15c** generated with a 3-nitrobenzyl alcohol matrix. A significant protonated molecular ion $(M+H)^+$ is present in both spectra at *m/z* 497 as well as peaks at *m/z* 519 corresponding to the sodiated molecular ions due to the presence of trace amounts of sodium salts in the samples. However, the intensity of this ion relative to that of the protonated molecular ion is much higher in the case of the *cis* than of the *trans* isomer. In addition, the spectrum of *cis*-**15c** exhibits a peak at *m/z* 1015 corresponding to an $(M_2+Na)^+$ ion. No corresponding peak of any significance is seen in the spectrum of *trans*-**15c**.

These differences could *a priori* either be due to unequal amounts of sodium salts in the two samples or to different abilities of these isomers to form such ions. In order to elucidate this point new spectra were recorded with a sodium chloride saturated matrix. The results are shown in Fig. 4. Quite clearly *cis*-**15c** is much better able than *trans*-**15c** to form sodiated molecular ions as well as $(M_2+Na)^+$ ions. Analogous results were obtained with the *cis–trans* isomers of **15a**.

Simple geometrical considerations readily lead to the conclusion that the spacing of the two carbonyl oxygen atoms in *cis*-**15** must be conducive to a gas phase $(M_2+Na)^+$ ion with a tetracoordinate sodium atom while the geometry of *trans*-**15** only allows the sodium

*Table 2.* Crystal data for 1,2,4-trithiolanes **15**.

| Crystal data[a] | Compound | | | | | | |
|---|---|---|---|---|---|---|---|
| | *cis*-**15a** | *trans*-**15a** | *trans*-**15b** | *cis*-**15c** | *trans*-**15c** | *trans*-**15d** | *trans*-**15e** |
| Formula | $C_{26}H_{28}O_2S_3$ | $C_{26}H_{28}O_2S_3$ | $C_{28}H_{32}O_2S_3$ | $C_{28}H_{32}O_2S_3$ | $C_{28}H_{32}O_2S_3$ | $C_{28}H_{28}O_4S_3$ | $C_{24}H_{24}O_2S_5$ |
| $M_W$ | 468.67 | 468.67 | 496.73 | 496.73 | 496.73 | 524.68 | 504.73 |
| M.p. | 167–170 °C | 162–165 °C | 218–220 °C | 148–150 °C | 190–192 °C | 280–282 °C | 198–201 °C |
| Crystal system | Monoclinic | Monoclinic | Monoclinic | Monoclinic | Triclinic | Tetragonal | Monoclinic |
| Space group | $P2_1/c$ | $P2_1/c$ | $P2_1/c$ | $P2_1/n$ | $P\bar{1}$ | $P4_32_12$ | $P2_1/n$ |
| *a*/Å | 11.0967(5) | 10.1910(4) | 18.8658(2) | 8.8167(2) | 9.8988(3) | 10.7929(2) | 11.7934(2) |
| *b*/Å | 16.8755(8) | 36.5703(14) | 11.1475(2) | 10.88230(10) | 10.1076(3) | 10.7929(2) | 17.4284(3) |
| *c*/Å | 12.4165(6) | 12.7772(5) | 12.1351(2) | 26.5226(6) | 14.4903(4) | 21.8689(4) | 12.1621(1) |
| α/° | — | — | — | — | 78.2660(1) | — | — |
| β/° | 99.0780(10) | 90.430(2) | 92.0880(10) | 90.7410(10) | 80.5360(1) | — | 107.812(1) |
| γ/° | — | — | — | — | 62.967(1) | — | — |
| $V$/Å$^3$ | 2296.0(2) | 4761.8(3) | 2550.40(7) | 2544.52(8) | 1260.10(6) | 2547.44(8) | 2379.97(6) |
| $Z$ | 4 | 8 | 4 | 4 | 2 | 4 | 4 |
| Total number of unique refl. | 4906 | 8349 | 6454 | 6446 | 6058 | 3389 | 6033 |
| $[I>2\sigma(I)]$ | 3708 | 4197 | 5370 | 4130 | 5436 | 2616 | 4732 |
| θ-range/° | 1.86–27.00 | 1.11–25.00 | 1.08–29.71 | 1.54–29.57 | 1.44–29.62 | 2.10–29.66 | 2.11–29.58 |
| *R* (obs. data) | 0.0810 | 0.1192 | 0.0386 | 0.0702 | 0.0381 | 0.0500 | 0.0406 |
| *wR*2 (all data) | 0.1863 | 0.2545 | 0.1140 | 0.1544 | 0.1013 | 0.0958 | 0.1080 |

[a]The data were collected at 296 K on a SMART diffractometer using Mo Kα radiation. The crystal-to-detector distance was 4.5 cm. The structures were solved by direct methods (SHELXTL) and refined with a full-matrix least-squares technique.

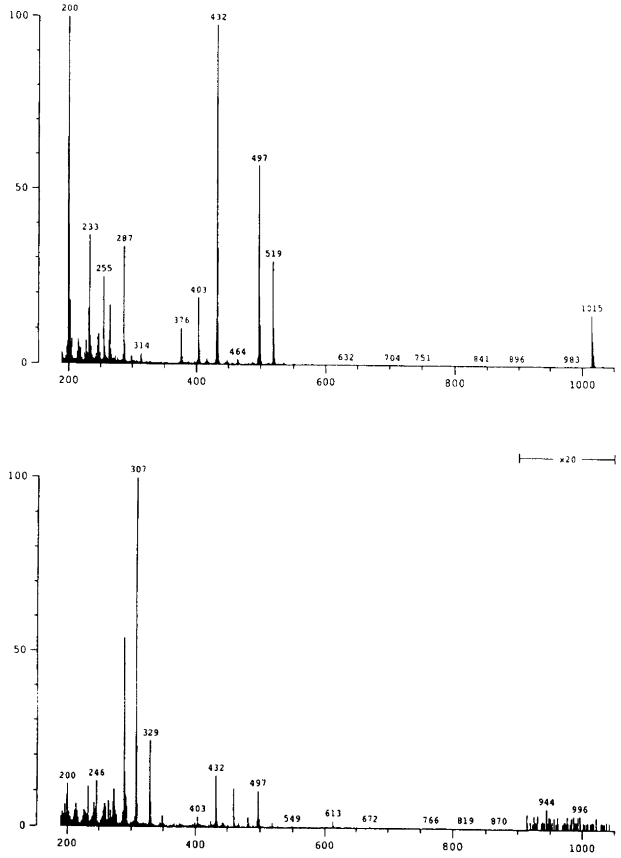


*Fig. 3.* The FAB mass spectra of *cis*-**15c** (top) and of *trans*-**15c** (bottom).

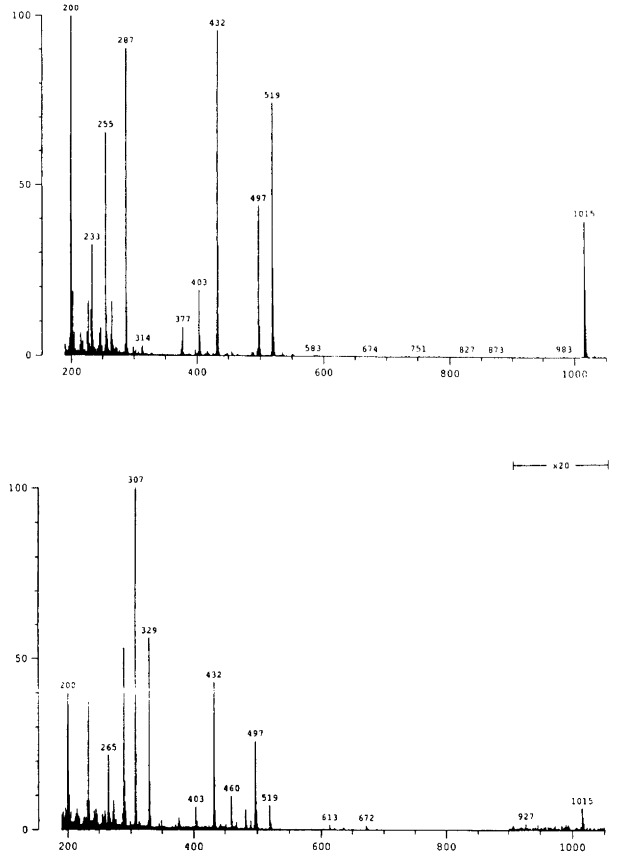


*Fig. 4.* The NaCl saturated FAB mass spectra of *cis*-**15c** (top) and of *trans*-**15c** (bottom).

atom to become dicoordinate. Analogous differences are to be expected for the sodiated molecular ions.

## Experimental

NMR spectra were taken for samples in $CDCl_3$ with TMS as an internal standard with a Bruker AC 250 or Bruker AM 500 apparatus. EI (70 eV) mass spectra were recorded on a Finnigan SSQ 710 quadrupole mass spectrometer by direct inlet. FAB mass spectra were obtained with a Kratos MS50 RF instrument with 3-nitrobenzyl alcohol as the matrix and 9 keV Xe atoms. IR spectra were obtained with a Perkin Elmer 1600 Series FTIR instrument for neat samples (for liquids) or KBr wafers (for solids).

Elemental analyses were performed by the Microanalytical Laboratory of the Department of Physical Chemistry, University of Vienna, A-1090 Vienna, Austria and by Institute of Organic Chemistry, Siberian Division of the Russian Academy of Sciences, RUS-664033 Irkutsk, Russia. The known compounds **9b**,[8] **9d**,[9,13] **9e**,[10] **10b**,[11] **10d**,[12] and **10e**[12] were prepared according to literature procedures. The single crystals for the X-ray work were obtained by slow evaporation of the corresponding hexane–ether (5:1) elutes from the column chromatographic separations.

*3,3-Diethyl-1,2,3,4-tetrahydronaphthalen-1-one* **9c**. A general procedure for the synthesis of substituted tetralones[6] was followed. Ethyl α-cyano-β,β-diethylacrylate[14] (158.0 g, 0.77 mol), dissolved in 150 ml dry ether, was added over 45 min at room temperature to a Grignard solution prepared from 103.7 (0.90 mol) benzyl chloride and 22.0 g (0.90 mol) magnesium turnings in 115 ml dry ether. When the spontaneous reflux had subsided the mixture was stirred and heated to reflux for another 1 h. The reaction mixture was cooled and poured onto 500 g cracked ice and then acidified with 20% sulfuric acid. After the usual work-up the combined ether phases were washed successively with 125 ml water and 125 ml saturated brine, filtered through a layer of anhydrous sodium sulfate, evaporated, and the residue distilled *in vacuo*. Yield of *ethyl 3-benzyl-2-cyano-3-ethylpentanoate* 165 g (79%), b.p. 155–165 °C/1.5 mmHg (bath temperature 200–210 °C). IR (neat): $\nu_{C\equiv N} = 2246$, $\nu_{C=O} = 1738\ cm^{-1}$. $^1H$ NMR (500 MHz): $\delta = 0.92$–$0.99$ (6 H, m, 3-$CH_3CH_2$ + 5-$CH_3$), 1.27 (3 H, t, $CH_3CH_2O$), 1.49–1.71 (4 H, m, 3-$CH_3CH_2$ + 4-$CH_2$), 2.79 (1 H, d, 3-$C_6H_5CH_aH_b$), 2.85 (1 H, d, 3-$C_6H_5CH_aH_b$), 3.41 (1 H, s, 2-CH), 4.19 (2 H, q, $CH_3CH_2O$), 7.19–7.28 (5 H, m, 5 ArH). MS (EI): *m/z* (%) 273 (*M*, 2), 228 (4), 200 (3), 160 (100), 131 (17), 91 (62). Anal. Calcd. for

$C_{17}H_{23}NO_2$ (273.25): C, 74.65, H, 8.48, N, 5.12. Found: C, 74.48, H, 8.26, N, 5.06.

Ethyl 3-benzyl-2-cyano-3-ethylpentanoate (172 g, 0.63 mol) was mixed with a solution of 67.0 g (1.0 mol) potassium hydroxide in 360 ml ethylene glycol and heated under reflux for 3 h (the reflux condenser was equipped with a rubber stopper). The cooled reaction mixture was diluted with 400 ml water and then extracted successively with 250, 100, and 100 ml ether. The combined ether extracts were washed with 100 ml water and 100 ml saturated brine and then filtered through a layer of anhydrous sodium sulfate. The solvent was evaporated off and the residue distilled *in vacuo*. This yielded 109 g (86%) *3-benzyl-3-ethylpentanenitrile*, b.p. 125–132 °C/2 mmHg. IR (neat): $\nu_{C=N}=2243\ cm^{-1}$. MS (EI): *m/z* (%) 201 (*M*, 38), 110 (9), 92 (80), 91 (100). Anal. Calc. for $C_{14}H_{19}N$ (201.29): C, 83.53, H, 9.51, N, 6.95. Found: C, 83.66, H, 9.43, N 6.81. This nitrile was converted, by being heated to reflux with a 3-molar excess of KOH and ethylene glycol for 6 h and subsequent conventional work-up, to give *3-benzyl-3-ethylpentanoic acid*, b.p. 165–170 °C/2 mmHg, yield 88%. IR (neat): $\nu_{OH}=$ 3250–3650, $\nu_{C=O}=1718\ cm^{-1}$. $^1H$ NMR (250 MHz): $\delta=$ 0.91 (6 H, t, 3-C*H*$_3$CH$_2$ + 5-CH$_3$), 1.31–1.55 (4 H, m, 3-CH$_3$C*H*$_2$ + 4-CH$_2$), 2.25 (2 H, s, 2-CH$_2$), 2.65 (2 H, s, 3-C$_6$H$_5$C*H*$_2$), 7.11–7.29 (5 H, m, 5 ArH), MS (EI): *m/z* (%) 220 (*M*, 61), 131 (27), 128 (68), 92 (76), 91 (100), 83 (35), 69 (53). Anal. Calc. for $C_{14}H_{20}O_2$ (220.30): C, 76.32, H, 9.15. Found: C, 75.87, H, 8.95.

Polyphosphoric acid (PPA) (250 g) was heated, on a steam bath, to 90 °C. Then it was removed from the steam bath and 99.0 g (0.45 mol) 3-benzyl-3-ethylpentanoic acid, preheated to 65 °C, added at once, and the reaction mixture stirred for 3 min. It was then placed on a steam bath, another 150 g PPA were added, stirring was continued for 30 min, and the temperature was maintained at 90 °C. After being cooled to room temperature the reaction mixture was poured, with stirring, into ice–water. A viscous brown oil precipitated and soon changed color to yellowish green. Subsequently, the crude product was extracted with ether (three times) and the combined ether extracts successively washed with 300 ml water, 2 × 200 ml 5% aqueous NaOH, 300 ml water, 200 ml 3% aqueous acetic acid, and 100 ml water. The organic phase was dried over magnesium sulfate, filtered, and evaporated. The residue was vacuum distilled to yield 60.0 g (71%), b.p. 145–155 °C/3 mmHg, yield 71%. IR (neat): $\nu_{C=O}=1677\ cm^{-1}$. $^1H$ NMR (250 MHz): $\delta=$ 0.85 [6 H, t, 3,3-(C*H*$_3$CH$_2$)$_2$], 1.42 [4 H, q, 3,3-(CH$_3$C*H*$_2$)$_2$], 2.49 (2 H, s, 2-CH$_2$), 2.84 (2 H, s, 4-CH$_2$), 7.25–7.98 (4 H, m, 4 Ar-H). $^{13}C$ NMR (125.7 MHz): $\delta=7.59$ (2 × 3-*C*H$_3$CH$_2$), 28.66 (2 × 3-CH$_3$*C*H$_2$), 38.88 (C-3), 39.20 (C-4), 48.77 (C-2), 126.38, 126.47, 129.30, 132.22, 133.60, 142.38 (C-4a, C-5, C-6, C-7, C-8, C-8a), 198.75 (C-1). MS (EI): *m/z* (%) 202 (*M*, 67), 173 (*M* − C$_2$H$_5$, 70), 145 (30), 131 (95), 118 (C$_8$H$_6$O, 100), 90 (C$_7$H$_6$, 22). Found: C, 82.91; H, 9.16; calc. for $C_{14}H_{18}O$ (202.28): C, 83.12; H, 8.96%.

*(RS)-3-Ethyl-1,2,3,4-tetrahydro-3-methylnaphthalen-1-one* **9a**, b.p. 134–136/4 mmHg), yield 71%. IR (neat): $\nu_{C=O}=1684\ cm^{-1}$. $^1H$ NMR (250 MHz): $\delta=0.95$ (3 H, t, C*H*$_3$CH$_2$), 1.04 (3 H, s, 3-Me), 1.43 (2 H, q, CH$_3$C*H*$_2$), 2.46 (1 H, d, 2-C*H*$_a$H$_b$), 2.55 (1 H, d, 2-CH$_a$*H*$_b$), 2.75 (1 H, d, 4-C*H*$_a$H$_b$), 2.91 (1 H, d, 4-CH$_a$*H*$_b$), 7.18–7.25 (1 H, m, Ar-H), 7.29–7.37 (1 H, m, Ar-H), 7.46–7.55 (1 H, m, Ar-H), 7.98–8.08 (1 H, m, Ar-H). $^{13}C$ NMR (62.9 MHz): $\delta=7.94$ (*C*H$_3$CH$_2$), 24.19 (3-CH$_3$), 33.31 (CH$_3$*C*H$_2$), 36.33 (C-3), 41.27 (C-4), 50.60 (C-2), 126.38, 128.21, 129.25, 131.88, 133.55, 142.44 (C-4a, C-5, C-6, C-7, C-8, C8a), 198.64 (C-1). MS (EI): *m/z* (%) 188 (*M*, 68), 173 (*M* − CH$_3$, 10), 159 (*M* − C$_2$H$_5$, 44), 131 (42), 118 (C$_8$H$_6$O, 100), 90 (24). Found: C, 82.80; H, 8.29; calc. for $C_{13}H_{16}O$ (188.26): C, 82.98; H, 8.51%.

*Sulfenyl chlorides* **10**. A general procedure for the conversion of 3,3-dialkyl-1-tetralones to α-chlorosulfenyl chlorides[8] was followed. The ketone **9** (0.10 mol) was dissolved in 37 ml thionyl chloride. The temperature rose to 35 °C and a brisk evolution of gas started after 2 min. The reaction mixture was allowed to stand for 3 h at room temperature. Excess thionyl chloride was removed on a rotatory evaporator to leave crude **10** which was then recrystallized from ligroin (b.p. 80–100 °C).

*(2RS,3SR)-2-Chloro-3-ethyl-1,2,3,4-tetrahydro-3-methyl-1-oxonaphthalene-2-sulfenyl chloride (2RS,3SR)*-**10a**. M.p. 115–117 °C, yield 43% (crude yield 65%). IR (KBr): $\nu_{C=O}=1692\ cm^{-1}$. $^1H$ NMR (250 MHz): $\delta=1.05$ (3 H, t, C*H*$_3$CH$_2$), 1.19 (3 H, s, 3-Me), 1.69–1.87 (1 H, m, CH$_3$C*H*$_a$H$_b$), 2.08–2.25 (1 H, m, CH$_3$CH$_a$*H*$_b$), 3.04 (1 H, d, 4-C*H*$_a$H$_b$), 3.20 (1 H, d, 4-CH$_a$*H*$_b$), 7.18–7.27 (1 H, m, ArH), 7.35–7.42 (1 H, m, ArH), 7.51–7.61 (1 H, m, ArH), 8.11–8.19 (1 H, m, ArH). $^{13}C$ NMR (62.9 MHz): $\delta=7.78$ (*C*H$_3$CH$_2$), 20.50 (3-CH$_3$), 30.84 (CH$_3$*C*H$_2$), 39.32 (C-4), 47.25 (C-3), 94.15 (C-2), 127.26, 128.80, 129.17, 129.17, 134.16, 138.83 (C-4a, C-5, C-6, C-7, C-8, C8a), 184.22 (C-1). MS (EI): *m/z* (%) 288 (*M*, 33), 253 (*M* − Cl, 56), 217 (34), 185 (39), 157 (38), 152 (100), 128 (45), 118 (C$_8$H$_6$O, 62), 115 (39), 90 (56). Found: C, 54.29; H, 4.85; Cl, 24.31; S, 11.15; calc. for $C_{13}H_{14}Cl_2OS$ (289.21): C, 53.98; H, 4.88; Cl, 24.51; S, 11.08%. The corresponding (2*RS*,3*RS*)-**10a** isomer could be observed in the crude product, but even repeated, painstaking column chromatography failed to provide a pure sample.

*2-Chloro-3,3-diethyl-1,2,3,4-tetrahydro-1-oxonaphthalene-2-sulfenyl chloride* **10c**. M.p. 52–55 °C, yield 48%. IR (KBr): $\nu_{C=O}=1698\ cm^{-1}$; $^1H$ NMR (250 MHz): $\delta=$ 0.82, 1.15 (6 H, t, 3,3-C*H*$_3$CH$_2$), 1.38–2.19 (4 H, m, 3,3-CH$_3$C*H*$_2$), 3.01–3.27 (2 H, q, 4-CH$_2$), 7.23 (1 H, d, ArH), 7.38 (1 H, t, ArH), 7.58 (1 H, t, ArH), 8.15 (1 H, d, ArH). $^{13}C$ NMR (62.9 MHz): $\delta=9.43$ (3-*C*H$_3$CH$_2$), 9.50 (3-*C*H$_3$CH$_2$), 27.61 (3-CH$_3$*C*H$_2$), 30.25 (3-CH$_3$*C*H$_2$), 36.79 (C-4), 49.36 (C-3), 94.49 (C-2), 127.19, 128.37, 129.02, 129.61, 134.14, 138.92 (C-4a, C-5,

C-6, C-7, C-8, C8a), 183.83 (C-1). MS (EI): *m/z* (%) 302 (*M*, 26), 267 (*M*−Cl, 65), 231 (24), 199 (59), 171 (47), 152 (100), 149 (62), 128 (53), 118 ($C_8H_6O$, 75). Found: C, 55.52; H, 5.28; Cl, 23.44; S, 10.73; calc. for $C_{14}H_{16}Cl_2OS$ (303.24): C, 55.44; H, 5.31; Cl, 23.38; S, 10.57%.

*Acetyl α-chloroalkyl disulfides* **11**. A general procedure for the conversion of α-chlorosulfenyl chlorides to acetyl α-chloroalkyl disulfides[4] was followed. Thioacetic acid (0.8 ml, 0.01 mol) was added to a solution of 0.01 mol **9** in 30 ml $CCl_4$ and the reaction mixture kept at 50–60 °C until completion of the reaction as judged by TLC (3 h). The solvent was then evaporated off and the oily residue treated with ligroin (b.p. 90–100 °C) until solidification. This crude solid was then recrystallized from ligroin (b.p. 90–100 °C).

*Acetyl (2RS,3SR)-2-chloro-3-ethyl-1,2,3,4-tetrahydro-3-methyl-1-oxonaphthalen-2-yl disulfide* **11a**. M.p. 86–88 °C (from petroleum ether, b.p. 40–60 °C), yield 60%. IR (KBr): $\nu_{C=O}$ = 1692 $cm^{-1}$. $^1H$ NMR (250 MHz): δ = 0.89 (3 H, s, 3-$Me_a$), 1.13 (3 H, s, 3-$Me_b$), 1.35–1.53 (1 H, m, $CH_3CH_aH_b$), 1.79–2.21 (1 H, m, $CH_3CH_aH_b$), 2.48 (3 H, s, $CH_3CO$), 3.09 (1 H, d, $PhCH_aH_b$), 3.47 (1 H, d, $PhCH_aH_b$), 7.21–7.31 (1 H, m, ArH), 7.41 (1 H, t, ArH), 7.61 (1 H, t, ArH), 7.61 (1 H, d, ArH). $^{13}C$ NMR (125.7 MHz): δ = 7.80 (3-$CH_3CH_2$), 20.60 (3-$CH_3$), 27.75 ($CH_3CO$), 28.89 (3-$CH_3CH_2$), 37.33 (C-4), 46.58 (C-3), 92.64 (C-2), 127.12, 127.18, 128.42, 128.96, 134.00, 138.69, (C-4a, C-5, C-6, C-7, C-8, C-8a), 184.12 (C-1), 191.50 ($CH_3CO$). MS (EI): *m/z* (%)264 (*M*−$S_2$, 29), 222 (*m/z* 264−$CH_2CO$, 33), 193 (*m/z* 222−$C_2H_5$, 100), 157 (14), 43 (20). Found: C, 55.09; H, 5.24; Cl, 10.79; S, 19.30; calc. for $C_{15}H_{17}ClO_2S_2$ (328.86): C, 54.78; H, 5.21; Cl, 10.78; S, 19.46%.

*Acetyl (RS)-2-chloro-1,2,3,4-tetrahydro-3,3,5,8-tetramethyl-1-oxonaphthalen-2-yl disulfide* **11b**. M.p. 118–120 °C (from ether–hexane), yield 91%. IR (KBr): $\nu_{C=O}$ = 1693 $cm^{-1}$. $^1H$ NMR (500 MHz): δ = 1.23 (3 H, s, 3-Me), 1.59 (3 H, s, 3-Me), 2.28 (3 H, s, 5-Me), 2.37 (3 H, s, 8-Me), 2.56 (3 H, s, MeCO), 2.88 (1 H, d, 4-$H_a$), 3.22 (1 H, d, 4-$H_b$), 7.13 (1 H, d, ArH), 7.29 (1 H, d, ArH). $^{13}C$ NMR (125.7 MHz): δ = 19.39 (5-$CH_3$), 22.99 (8-$CH_3$), 25.91, 25.12 (2 × 3-$CH_3$), 28.38 ($CH_3CO$), 40.72 (C-4), 42.79 (C-3), 93.41 (C-2), 127.83, 130.39, 133.77, 134.44, 138.05, 140.52 (C-4a, C-5, C-6, C-7, C-8, C-8a), 186.58 (C-1), 192.33 ($CH_3CO$). MS (EI): *m/z* (%) 342 (*M*, 0.3), 278 (*M*−$S_2$, 55), 236 (*m/z* 278−$CH_2CO$, 82), 221 (*m/z* 236−$CH_3$, 100), 185 (4), 43 (25). Found: C, 56.35; H, 5.68; Cl, 10.49; S, 18.59; calc. for $C_{16}H_{19}ClO_2S_2$ (342.88): C, 56.04; H, 5.58; Cl, 10.34; S, 18.70%.

*Acetyl 2-chloro-3,3-diethyl-1,2,3,4-tetrahydro-1-oxonaphthalen-2-yl disulfide* **11c**. The crude product obtained from **10c** and thioacetic acid was used immediately for the reaction with morpholine (*vide infra*).

*Acetyl 3'-chloro-4'-oxospiro[cyclohexane-1,2'-chroman]-3'-yl disulfide* **11d**. M.p. 132–133 °C (from ether), yield 89%. IR (KBr): $\nu_{C=O}$ = 1692 $cm^{-1}$. $^1H$ NMR (250 MHz): δ = 1.18–2.62 (10 H, m, 5 $CH_2$), 2.51 (3 H, s, $CH_3CO$), 6.99–7.17 (2 H, m, 2 ArH), 7.52–7.62 (1 H, m, ArH), 7.85–7.95 (1 H, dd, ArH). $^{13}C$ NMR (62.9 MHz): δ = 20.77, 21.23, 24.99, 27.70, 31.04 (C-2, C-3, C-4, C-5, C-6), 28.86 ($CH_3CO$), 86.22, 86.60 (C-2', C-3'), 118.06 (C-8'), 119.35 (C-6', 122.15 (C-4a'), 128.54 (C-5'), 136.35 (C-7'), 156.36 (C-8a'), 180.49 (C-4'), 191.19 ($CH_3CO$). MS (EI): *m/z* (%) 292 (*M*−$S_2$, 70), 250 (100), 207 (67), 121 (22), 43 (51). The FAB spectrum exhibits a significant $MH^+$ ion at *m/z* 357 as well as ions at *m/z* 292, 250, and 207, all including chlorine as indicated by their isotopic patterns. Found: C, 53.95; H, 4.69; Cl, 10.03; S, 17.79; calc. for $C_{16}H_{17}ClO_3S_2$ (356.87): C, 53.84; H, 4.80; Cl, 9.93; S, 17.96%.

*Acetyl 3-chloro-4-oxo-2,2,6-trimethylthiochroman-3-yl disulfide* **11e**. M.p. 100–102 °C (from ether–petroleum ether, b.p. 40–60 °C), yield 89%. IR (KBr): $\nu_{C=O}$ = 1701 $cm^{-1}$. $^1H$ NMR (250 MHz): δ = 1.61 (3 H, s, 2-$Me_a$), 1.85 (3 H, s, 2-$Me_b$), 2.38 (3 H, s, 6-Me), 2.41 (3 H, s, $CH_3CO$), 7.12 (1 H, d, ArH), 7.25–7.31 (1 H, m, ArH), 7.95–8.00 (1 H, m, ArH). $^{13}C$ NMR (125.7 MHz): δ = 20.79 (2-$Me_a$), 25.12, 25.26 (2-$Me_b$, 6-Me), 52.39 (C-2), 91.76 (C-3), 126.90 (C-6), 127.85 (C-8), 131.38 (C-5), 133.78 (C-8a), 134.83 (C-7), 135.70 (C-4a), 181.20 (C-4), 191.38 ($CH_3CO$). MS: *m/z* (%) 346 (*M*, 3.4), 282 (*M*−$S_2$, 57), 267 (*m/z* 282−$CH_3$, 6), 247 (*m/z* 282−Cl, 7), 240 (14), 239 (9), 225 ($C_{11}H_{10}ClOS$, 100), 205 (65), 204 (70), 121 (29), 43 (54). Found: C, 48.81; H, 4.35; Cl, 10.02; S, 27.61; calc. for $C_{14}H_{15}ClO_2S_3$ (346.89): C, 48.47; H, 4.35; Cl, 10.21; S, 27.72%.

*Reaction of* **11** *with morpholine*. The following 'unzipping' reactions were carried out according to a literature procedure for the generation of **1**/**2**.[3] Disulfide **11** (2.3 g, 7 mmol) was dissolved in 50 ml ether and treated, with stirring, with 6.0 ml (60 mmol) morpholine, dissolved in 30 ml ether. The rate of the addition was adjusted so as to avoid any appreciable rise in temperature. The reaction mixture was then extracted three times with water, dried over anhydrous $CaCl_2$, and evaporated *in vacuo*. The oily residue was separated by column chromatography (aluminium oxide Merck 90, particle size 0.063–0.200 mm; ether–hexane 1:5). For each reaction the products are described in the order of their elution from the chromatographic column.

*3,5'-Diethyl-3,5'-dimethyl-3,4,5',6'-tetrahydrospiro-{naphthalene-2,2'-naphtho[2,1-e][1,3,4]oxadithiin}-1-one* **14a**. M.p. 113–115 °C. IR (KBr): $\nu_{C=O}$ = 1696 $cm^{-1}$. MS: *m/z* (%) 436 (*M*, 16), 404 (*M*−S, 4), 372 (*M*−$S_2$, 14), 218 ($C_{13}H_{14}OS$, 100), 185 (80), 176 (47), 118 (87), 115 (32), 90 (60). The sample size was insufficient for NMR spectroscopy and elemental analysis.

trans-*3,3″-Diethyl-1,1″,2,2″,3,3″,4,4″-octahydro-3,3″-methyldispiro{naphthalene-2,3′-[1,2,4]trithiolane-5′,2″-naphthalene}-1,1″-dione* trans-**15a**. M.p. 162–165 °C. IR (KBr): $\nu_{C=O}$ = 1687 $cm^{-1}$. $^1H$ NMR (250 MHz): δ = 0.78–0.89 (6 H, m, 3-C$H_3$CH$_2$, 3″-C$H_3$CH$_2$), 1.02 (6 H, t, 3-Me, 3″-Me), 1.21–1.41 (2 H, m, 3-CH$_3$C$H_a$H$_b$, 3″-CH$_3$C$H_a$H$_b$), 1.51–1.65 (2 H, m, 3-CH$_3$CH$_a$$H_b$, 3″-CH$_3$CH$_a$$H_b$), 3.05 (2 H, d, 4-H$_a$, 4″-H$_a$), 3.05 (2 H, d, 4-H$_b$, 4″-H$_b$), 7.12–7.21 (2 H, m, 2 ArH), 7.28–7.39 (2 H, m, 2 ArH), 7.44–7.49 (2 H, m, 2 ArH), 8.09–8.19 (2 H, m, 2 ArH). $^{13}C$ NMR (50.32 MHz): δ = 8.31 (CH$_3$CH$_2$), 22.55 (3-CH$_3$), 31.45 (CH$_3$C$H_2$), 39.28 (C-4, C-4″), 50.64 (C-3, C-3″), 95.70 (C-2, C-2″), 126.57, 126.99, 128.70, 130.54, 133.53, 138.89 (C-4a, C-4a″, C-5, C-5″, C-6, C-6″, C-7, C-7″, C-8, C-8″, C-8a, C-8a″), 185.95 (C-1, C-1″). MS: *m/z* (%) 468 (*M*, 13), 436 (*M* − S, 7), 404 (*M* − $S_2$, 100), 375 (*m/z* 404 − $C_2H_5$, 37), 347 (4), 286 (7), 250 (9), 218 (44), 186 (46), 185 (77), 157 (41), 145 (32), 128 (31), 118 (48), 90 (46). Found: C, 66.77; H, 6.43; S, 19.76; calc. for $C_{26}H_{28}O_2S_3$ (468.67): C, 66.62; H, 6.02, S 20.52%.

cis-*3,3″-Diethyl-1,1″,2,2″,3,3″,4,4″-octahydro-3,3″-dimethyldispiro{naphthalene-2,3′-[1,2,4]trithiolane-5′,2″-naphthalene}-1,1″-dione* cis-**15a**. M.p. 167–170 °C (from ethyl acetate), yield 2%. IR (KBr): $\nu_{C=O}$ = 1696 $cm^{-1}$. $^1H$ NMR (250 MHz): δ = 0.77–0.99 (6 H, m, 3-C$H_3$CH$_2$, 3″-C$H_3$CH$_2$), 1.19–1.72 (4 H, m, 3-CH$_3$C$H_2$, 3″-CH$_3$C$H_2$), 2.21 (6 H, s, 2 × 3-CH$_3$), 2.92–3.29 (4 H, 4-H$_a$, 4-H$_b$, 4″-H$_a$, 4″-H$_b$), 7.13 (2 H, d, 2 ArH), 7.23–7.39 (2 H, m, 2 ArH), 7.45–7.52 (2 H, m, 2 ArH), 8.11–8.22 (2 H, m, 2 ArH). $^{13}C$ NMR (125.7 MHz): δ = 8.49 (3-C$H_3$CH$_2$, 3″-C$H_3$CH$_2$), 21.71 (3-CH$_3$, 3″-CH$_3$), 29.91 (3-CH$_3$C$H_2$, 3″-CH$_3$C$H_2$), 38.89 (C-4, C-4″), 45.63 (C-3, C-3″), 95.87 (C-2, C-2″), 126.83, 128.41, 128.69, 128.98, 133.31, 138.81 (C-4a + C-4a″, C-5 + C-5″, C-6 + C-6″, C-7 + C-7″, C-8 + C-8″, C-8a + C-8a″), 206.69 (C-1, C-1″). MS: *m/z* (%) 468 (*M*, 8), 404 (*M* − $S_2$, 100), 375 (*m/z* 404 − $C_2H_5$, 40), 347 (3), 286 (4), 250 (3), 218 (18), 186 (39), 185 (58), 157 (32), 145 (23), 128 (23), 118 (28), 90 (25). Found: C, 67.01; H, 6.19; S, 19.86; calc. for $C_{26}H_{28}O_2S_3$ (468.67): C, 66.62; H, 6.02, S 20.52%.

trans-*1,1″,2,2″,3,3″,4,4″-octahydro-3,3,3″,3″,5,5″,8,8″-octamethyldispiro{naphthalene-2,3′-[1,2,4]trithiolane-5′,2″-naphthalene}-1,1″-dione* trans-**15b**. M.p. 218-220 °C. IR (KBr): $\nu_{C=O}$ = 1684 $cm^{-1}$. $^1H$ NMR (250 MHz): δ = 1.35 (12 H, s, 3-Me$_a$, 3-Me$_b$, 3″-Me$_a$, 3″-Me$_b$), 2.18 (6 H, s, 5-CH$_3$, 5″-CH$_3$), 2.58 (6 H, s, 8-CH$_3$, 8″-CH$_3$), 2.84 (2 H, d, 4-H$_a$, 4″-H$_a$), 2.84 (2 H, d, 4-H$_b$, 4″-H$_b$), 7.05 (2 H, d, 6-H, 6″-H, ArH), 7.21 (2 H, d, 7-H, 7″-H, ArH). $^{13}C$ NMR (125.7 MHz): δ = 19.36 (3-CH$_3$ or 3″-CH$_3$), 22.40 (3-CH$_3$ or 3″-CH$_3$), 26.49 (5-CH$_3$, 5″-CH$_3$), 27.36 (8-CH$_3$, 8″-CH$_3$), 40.28 (C-4, C-4″), 43.35 (C-3, C-3″), 95.49 (C-2, C-2″), 129.65, 130.02, 133.58, 133.74, 137.80, 139.44 (C-4a + C-4a″, C-5 + C-5″, C-6 + C-6″, C-7 + C-7″, C-8 + C-8″, C-8a + C-8a″), 189.52 (C-1 + C-1″). MS: *m/z* (%) 496 (*M*, 11), 464 (*M* − S, 7), 432 (*M* − $S_2$, 100), 417 (*m/z* 432 − $CH_3$, 6), 404 (4), 389 (3), 286 (6), 232 (23), 217 (21), 200 (29), 185 (18), 173 (20), 146 (30), 117 (25). Found: C, 67.66; H, 6.93; S, 19.27; calc. for $C_{28}H_{32}O_2S_3$ (496.73): C, 67.69; H, 6.49; S, 19.36%.

trans-*1,1″,2,2″,3,3″,4,4″-Octahydro-3,3,3″,3″-tetraethyldispiro{naphthalene-2,3′-[1,2,4]trithiolane-5′,2″-naphthalene}-1,1″-dione* trans-**15c**. M.p. 190–192 °C (from petroleum ether, b.p. 40–60 °C). IR (KBr): $\nu_{C=O}$ = 1695 $cm^{-1}$. $^1H$ NMR (250 MHz): δ = 0.89 (6 H, t, 3-Me$_a$, 3″-Me$_a$), 1.11 (6 H, t, 3-Me$_b$, 3″-Me$_b$), 1.85–2.28 (8 H, m, 2 × 3-CH$_3$C$H_2$, 2 × 3″-CH$_3$C$H_2$), 3.15 (4 H, s, 4-CH$_2$, 4″-CH$_2$), 7.15–7.57, 8.17 (8 H, m, 8 ArH). $^{13}C$ NMR (125.7 MHz): δ = 9.69, 9.98 (2 × 3-CH$_3$CH$_2$ + 2 × 3″-C$H_3$CH$_2$), 28.32, 29.59 (2 × 3-CH$_3$C$H_2$ + 2 × 3″-CH$_3$C$H_2$), 39.51 (C-4 + C-4″), 47.48 (C-3 + C-3″), 96.70 (C-2 + C-2″), 126.98, 128.59, 128.67, 130.77, 133.29, 139.02 (C-4a + C-4a″, C-5 + C-5″, C-6 + C-6″, C-7 + C-7″, C-8 + C-8″, C-8a + C-8a″), 186.73 (C-1 + C-1″). MS: *m/z* (%) 496 (*M*, 8), 464 (*M* − S, 1), 432 (*M* − $S_2$, 100), 375 (3), 314 (3), 285 (2), 264 (8), 232 (14), 217 (7), 200 (35), 199 (47), 171 (24), 159 (14), 118 (11), 90 (11). Found: C, 67.57, H, 6.67, S, 18.80; calc. for $C_{28}H_{32}O_2S_3$ (496.73): C, 67.69, H, 6.49, S, 19.36%.

cis-*1,1″,2,2″,3,3″,4,4″-Octahydro-3,3,3″,3″-tetraethyldispiro{naphthalene-2,3′-[1,2,4]trithiolane-5′,2″-naphthalene}-1,1″-dione* cis-**15c**. M.p. 148–150 °C (from petroleum ether, b.p. 40–60 °C). IR (KBr): $\nu_{C=O}$ = 1693 $cm^{-1}$. $^1H$ NMR (250 MHz): δ = 0.90 (6 H, t, 3-Me$_a$, 3″-Me$_a$), 1.06 (6 H, t, 3-Me$_b$, 3″-Me$_b$), 1.69–2.21 (8 H, m, 2 × 3-CH$_3$C$H_2$, 2 × 3″-CH$_3$C$H_2$), 3.05 (2 H, d, 4-C$H_a$H$_b$, 4″-C$H_a$H$_b$), 3.17 (2 H, d, 4-CH$_a$$H_b$, 4″-CH$_a$$H_b$), 7.15–7.20 (2 H, dd, 2 ArH), 7.22–7.38 (2 H, m, 2 ArH), 7.41–7.52 (2 H, dd, 2 ArH), 8.11–8.19 (2 H, dd, 2 ArH). $^{13}C$ NMR (125.7 MHz): δ = 9.66, 9.90 (2 × 3-C$H_3$CH$_2$, 2 × 3″-C$H_3$CH$_2$), 27.98 (2 × 3-CH$_3$C$H_2$, 2 × 3″-CH$_3$C$H_2$), 38.91 (C-4, C-4″), 47.81 (C-3, C-3″), 95.66 (C-2, C-2″), 126.88, 128.50, 128.69, 130.98, 133.35, 138.94 (C-4a, C-4a″, C-5, C-5″, C-6, C-6″, C-7, C-7″, C-8, C-8″, C-8a, C-8a″), 186.73 (C-1, C-1″). MS: *m/z* (%) identical with the above-mentioned EI spectrum of *trans*-**15c**. Found: C, 67.67, H, 6.73, S, 18.84; calc. for $C_{28}H_{32}O_2S_3$ (496.73): C, 67.69, H, 6.49, S, 19.36%.

trans-*Tetraspiro{cyclohexane-1,2′-chroman-3′,3″-[1,2,4]-trithiolane-5″,3‴-chroman-2‴,1⁗-cyclohexane}-4′,4‴-dione* trans-**15d**. M.p. 280–282 °C (from ether). IR (KBr): $\nu_{C=O}$ = 1697 $cm^{-1}$. $^1H$ NMR (250 MHz): δ = 1.18–1.59 (8 H, m, 3-CH$_2$, 3⁗-CH$_2$, 5-CH$_2$, 5⁗-CH$_2$), 1.61–1.98, 2.17–2.45 (8 H, m, m, 2-CH$_2$, 2⁗-CH$_2$, 6-CH$_2$, 6⁗-CH$_2$), 2.59–2.85 (4 H, m, 4-CH$_2$, 4⁗-CH$_2$), 6.98–7.09 (2 H, m, 2 ArH), 7.27 (2 H, s, 2 ArH), 7.49–7.59 (2 H, m, 2 ArH), 7.98–8.07 (2 H, dd, 2 ArH). $^{13}C$ NMR (62.9 MHz): δ = 21.00, 21.83, 25.16, 31.64, 32.63 (C-2 + C-2⁗, C-3 + C-3⁗, C-4 + C-4⁗, C-5 + C-5⁗,

C-6+C-6‴), 85.18 (C-2′+C-2″), 91.71 (C-3′+C-3‴), 118.01, 119.53, 121.94, 128.15, 135.85, 156.55 (C-4a′+C-4a‴, C-5′+C-5‴, C-6′+C-6‴, C-7′+C-7‴, C-8′+C-8‴, C-8a′+C-8a‴), 182.21 (C-4′+C-4‴). MS: *m/z* (%): 524 (*M*, 100), 492 (*M*−S, 2), 460 (*M*−$S_2$, 10), 404 (11), 340 (13), 247 (10), 213 (22), 201 (60), 126 (22), 121 (25). Found: C, 63.87, H, 5.49, S, 18.34; calc. for $C_{28}H_{28}O_4S_3$ (524.68): C, 64.09, H, 5.38, S, 18.33%.

trans - *2,2,2″,2″,6,6″ - Hexamethyldispiro{thiochroman - 3,3′ - [1,2,4]trithiolane - 5′,3″ - thiochroman} - 4,4″ - dione* trans-**15e**. M.p. 198–201 °C (from petroleum ether, b.p. 40–60 °C). IR (KBr): $\nu_{C=O}=1693\ cm^{-1}$. $^1H$ NMR (250 MHz): δ = 1.59 (6 H, s, 2-$Me_a$+2″-$Me_a$), 2.15 (6 H, s, 2-$Me_b$+2″-$Me_b$), 2.35 (6 H, s, 6-Me+6″-Me), 7.05–7.28 (4 H, m, 4 ArH), 8.09 (2 H, d, 2 ArH). $^{13}C$ NMR (50.32 MHz): δ = 20.87 [(2-$CH_3$)$_a$+(2″-$CH_3$)$_a$], 26.53 [(2-$CH_3$)$_b$+(2″-$CH_3$)$_b$], 28.19 (6-$CH_3$+6″-$CH_3$), 51.55 (C-2+C-2″), 98.57 (C-3+C-3″), 126.86, 128.16, 131.17, 134.32, 134.45, 135.65 (C-4a+C-4a″, C-5+C-5″, C-6+C-6″, C-7+C-7″, C-8+C-8″, C8a+C-8a″), 183.40 (C-4+C-4″). MS: *m/z* (%) 504 (*M*, 16), 472 (*M*−S, 3), 440 (*M*−$S_2$, 2), 425 (3), 334 (22), 290 (8), 236 (22), 204 (100), 150 (52), 121 (13). Found: C, 57.21, H, 4.64, S, 31.77; calc. for $C_{24}H_{24}O_2S_5$ (504.73): C, 57.10, H, 4.79, S, 31.76%.

*Acknowledgements.* A grant from the Egyptian Government under the Channel System for M. I. Hegab is gratefully acknowledged. This work was also supported by the Danish Research Council (SNF). The technical support of Mrs. Jytte Grove-Rasmussen, Department of Organic Chemistry, Technical University of Denmark is gratefully acknowledged.

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Received July 27, 1998.