Convenient procedure for converting 1,3-dithiolane-2-thiones into 1,3-dithiolan-2-ones

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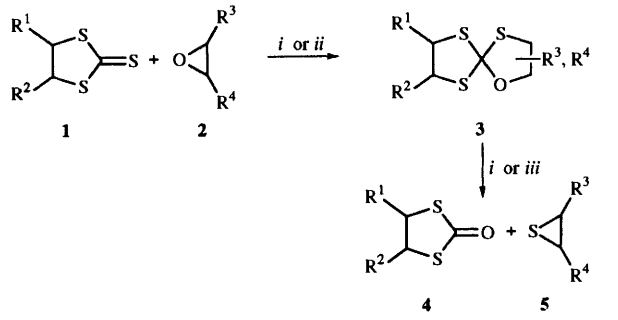
1,3-Dithiolan-2-ones have been obtained by reaction of 1,3-dithiolane-2-thiones and epoxides in the presence of HBF_4·Et_2O. The reactions, carried out in anhydrous CH_2Cl_2 at 0–5 °C→room temperature (Procedure A) or in anhydrous chlorobenzene at 0–5→80 °C (Procedure B), gave product yields of 63–95%. By Procedure B it was also possible to isolate the intermediates 1-oxa-4,6,9-trithiaspiro[4.4]nonanes in good yields (66–85%). Reaction pathways are proposed.

1,3-Dithiolan-2-ones **4** are a class of compounds of notable interest because (*a*) they are endowed with specific biological properties, (fungicidal,[1] insecticidal,[2] antibacterial,[3] plant growth regulatory,[4] choleretic and hepatoprotective[5] activities), and (*b*) they can be used as intermediates for the preparation of acyclic and cyclic compounds containing two sulfur functional groups on vicinal carbon atoms (dithiols,[6] disulfonyl chlorides, disulfonic acids and their derivatives[7]). Numerous methods for their preparation have been reported but the most significant are: (*i*) reactions between dithiols and phosgene;[8] (*ii*) cyclizations of dithiocyanates;[6,8] (*iii*) rearrangements of 1,3-oxathiolane-2-thiones;[8] (*iv*) reactions between epoxides and carbon sulfide or episulfides and carbon oxysulfide;[8,9] (*v*) conversions of 1,3-dithiolane-2-thiones into 1,3-dithiolan-2-ones using either different oxidants[8,10] or *via* carbenium salts.[11] A preliminary comparative evaluation of the different methods shows that whenever large quantities of product are needed, most of the methods, particularly those in points *i–iv*, are greatly limited due to the poor accessibility of the starting compounds, the toxicity of the reagents to be used or the poor yield. In fact these methods have been mainly used to prepare the parent compound, 1,3-dithiolan-2-one, and some of its simple derivatives. However, with regard to point *v* above, 1,3-dithiolane-2-thiones **1** can be obtained relatively easily and on a large scale, by reactions under PTC conditions between alkaline trithiocarbonates and aliphatic vicinal dihalides or disulfonates.[12] Furthermore, from among the numerous procedures proposed the one based on the intermediate formation of 2-methylsulfanyl-1,3-dithiolanylium salts and successive hydrolyses is particularly advantageous in that it is easy to carry out, of general use and inexpensive. The 1,3-dithiolan-2-ones are obtained in high yield, making the method also suitable for large-scale preparation.[11]

In this paper we propose an alternative to this last mentioned method. It is equally valid for any preparative scale and is based on the reaction of 1,3-dithiolane-2-thiones **1** with epoxides **2** (Scheme 1). 1,3-Dithiolane-2-thione **1a** has been converted into the corresponding 1,3-dithiolan-2-one **4a** by treating it, in a sealed tube at 170–180 °C, with propylene oxide in the presence of catalytic amounts of BF_3·Et_2O.[13] However, such conditions have precluded its synthetic use even on a reduced scale. Subsequent studies of the reactions between **1a** and the epoxides **2** in the presence of Lewis acids [BF_3·Et_2O, $Mg(ClO_4)_2$ or $TiCl_4$] in 1,2-dichloroethane at −20 °C[14] failed to produce **4a**, the reactions stopping at the formation of 1-oxa-4,6,9-trithiaspiro[4.4]nonanes **3** obtained in poor yields. Such spirocyclic compounds have been proposed as intermediates of the conversion, realized in the absence of solvents, of the thiocarbonyl group to the carbonyl group.[13]



1, 4	R^1	R^2	2, 5	R^3	R^4
a	H	H	**a**	H	H
b	H	Me	**b**	H	Me
c	H	$C_{10}H_{21}$	**c**	H	$C_{10}H_{21}$
d	$CH_2(CH_2)_2CH_2$		**d**	$CH_2(CH_2)_2CH_2$	
e	Me	Me (*cis*)	**e**	Me	Me (*cis*)
f	Me	Me (*trans*)	**f**	Me	Me (*trans*)

Scheme 1 *Reagents and conditions: i*, Procedure A: HBF_4·Et_2O, dry CH_2Cl_2, 0–5 °C→room temp.; *ii*, Procedure B: HBF_4·Et_2O, dry chlorobenzene, 0–5 °C→room temp.; *iii*, Procedure B: HBF_4·Et_2O, 80 °C

In our work we treated, in methylene dichloride or chlorobenzene and in the presence of HBF_4·Et_2O, a number of 1,3-dithiolane-2-thiones **1a–f** with the commercially available epoxides **2a–f**. We found that in both solvents the reaction proceeds in two steps: the first gives the spirocyclic intermediates **3** through cycloaddition; the second gives the 1,3-dithiolan-2-ones **4** by elimination of the episulfide **5**. Depending on the reaction conditions (nature of solvent, amount of catalyst and temperature) the reaction can be stopped either at stage one or be allowed to proceed to completion. For the preparation of 1,3-dithiolan-2-ones **4** the reaction conditions were optimized by realizing the two steps in succession in the same pot, the reactions being carried out in methylene dichloride (procedure A) or in chlorobenzene (procedure B). By procedure A compounds **1** (10 mmol) and **2** (12 mmol) were allowed to react in the presence of catalytic amounts (0.15 mmol) of HBF_4·Et_2O at 0–5 °C (smaller amounts of catalyst afforded unsatisfactory results). After the starting compounds **1** had disappeared, the reaction mixture was found to contain both the spirocyclic intermediates **3** and considerable amounts

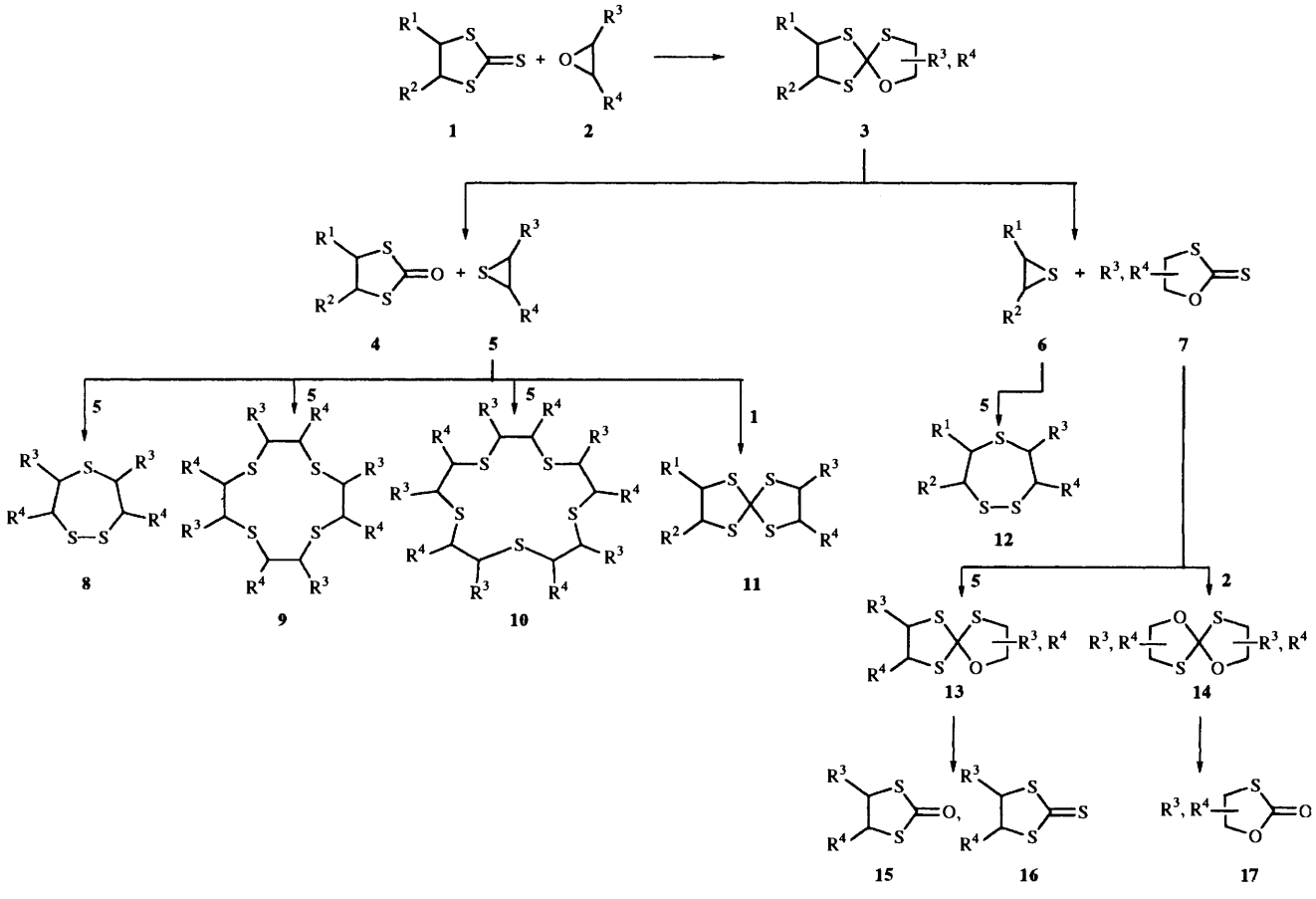
of 1,3-dithiolan-2-ones **4**; then the reactions were brought to completion at room temperature. For procedure B the first step utilized less catalyst (0.015 mmol) but the same reagent amounts and temperature as in procedure A and after the disappearance of the starting compounds **1** the reaction mixture contained only the intermediates **3**. The reactions were then brought to completion by adding a second portion of catalyst and raising the temperature to 80 °C. Depending on the two reagents involved both procedures resulted in good to excellent yields of 1,3-dithiolan-2-ones **4** (Table 1). In other reactions carried out using procedure B the spirocyclic compounds **3** were also isolated in good yield. These afforded almost quantitative yields of compounds **4**, when heated at 80 °C in chlorobenzene in the presence of a catalytic amount of HBF_4·Et_2O.

In the present work an effort was made to isolate and/or identify the numerous by-products formed along with the desired 1,3-dithiolan-2-ones **4** (Scheme 2). As stated earlier, compounds **4** originated from the spirocyclic intermediates **3** through the elimination of the episulfides **5**. Nevertheless, only the 1,2-epithiododecane **5c** was isolated in the reactions between **1a–f** and 1,2-epoxydodecane **2c** (entries 5, 10, 13 and 17). In all the other cases derivatives from successive episulfide transformations were isolated, even in high yield. These were trithiepanes **8** and macrocyclic oligomers **9** and **10** of known interest. The obtained products are essentially the same as those that originate from episulfides through polymerizations and subsequent degradation to oligomers.[15] In two cases (entries 7 and 19) a further addition product of the episulfide **5d** with the starting compounds **1a** and **1d**, *i.e.* the 1,4,6,9-tetrathiaspiro[4.4]nonanes **11b** and **11c**, were isolated. Among the by-products identified by GC–MS, as being present in very small amount in the reaction mixture were: 1,3-oxathiolane-2-thiones **7**, trithiepanes **12**, 1,3-dithiolan-2-ones **15**, 1,3-dithiolane-2-thiones **16** and 1,3-oxathiolan-2-ones **17**. Scheme 2 shows the formation of the various products and by-products. It should be understood that despite the complexity of the reaction there is no difficulty in isolating the desired products **4** from the reaction mixtures.

In conclusion, the reaction conditions are mild, the reagents are inexpensive and, in certain cases, there is the possibility of obtaining consistent amounts of derived oligomers from the episulfides. Thus, from a synthetic point of view, the procedure for converting 1,3-dithiolane-2-thiones **1** into 1,3-dithiolan-2-ones **4** is competitive with those already known, especially for large-scale preparations.

Experimental

^1H and ^{13}C NMR spectra were recorded on a Bruker WP 80 SY spectrometer for solutions in deuteriochloroform. ^1H NMR spectra of compounds **3** were obtained with a JEOL EX-400 instrument (9.4 T). The chemical shifts are expressed in ppm (δ) relative to internal tetramethylsilane and J values are given in Hz. Mass spectra were recorded on a quadrupole MS Engine HP 5989 B instrument, operating with a direct-inlet system at 70 eV for compounds **3** and **8c**, and on an HP 5970 B mass selective detector connected to an HP 5890 GC, cross-linked methyl silicone capillary column (70 eV), for the other compounds. IR spectra were recorded in the gas phase on a Bruker IFS 85 IR Fourier spectrophotometer equipped with a GC–IR coupling system and a cross-linked methyl silicone capillary column for compounds **17** and on a Perkin-Elmer 599 B spectrophotometer for solutions in tetrachloromethane for the other compounds. Column chromatography and TLC were performed on Merck silica gel 60 (70–230 mesh ASTM) and GF 254, respectively. Light petroleum refers to the fraction boiling in the range 40–70 °C and is abbreviated as LP. Anhydrous dichloromethane and chlorobenzene were purchased from Aldrich.



Scheme 2 *Reaction mechanism* (compounds **6**, **13**, **14** were not identified)

Table 1 1,3-Dithiolan-2-ones **4a–f**

Entry no.	Product 4	Starting compounds 1	2	Yields (%)[a] Proc. A	Proc. B	Chromatographic solvent[b]	Mp (°C) (solvent)[b] or bp (°C)/mmHg	Lit. data or formula
1	**4a**	**1a**	**2a**	63		LP–EE (3:2)	35–36 (LP)	35[22]
2					63			
3		**1a**	**2b**	70				
4					80			
5		**1a**	**2c**	65				
6					66			
7		**1a**	**2d**	90				
8					75			
9	**4b**	**1b**	**2b**	64		LP–A (9:1)	113–114/10	82–85/2[27]
10		**1b**	**2c**	56				
11		**1b**	**2d**	60				
12	**4c**	**1c**	**2b**	66		LP–A (9.8:0.2)	197–198/2	$C_{13}H_{24}OS_2$
13		**1c**	**2c**	95				
14		**1c**	**2d**	61				
15	**4d**	**1d**	**2a**	66		LP–EE (9:1)	109–110 (E)	109–110[28]
16		**1d**	**2b**	90				
17		**1d**	**2c**	92				
18					70			
19		**1d**	**2d**	85				
20					75			
21	**4e**	**1e**	**2e**	61		LP–EE (9:1)	87–88/1	oil[23]
22		**1e**	**2f**	76				
23	**4f**	**1f**	**2d**	78		LP–EE (9:1)	41–42 (LP)	41–41.5[23]
24		**1f**	**2e**	81				
25		**1f**	**2f**	76				

[a] Yields of pure products. [b] LP = light petroleum; EE = diethyl ether; A = acetone; E = ethanol.

1,2-Dibromododecane,[16] 1,2-dimethylethylene dimethanesulfonate (+, − and *meso*),[17] 1,3-dithiolane-2-thione **1a**[12] and *trans*-3a,4,5,6,7,7a-hexahydro-2*H*-1,3-benzodithiole-2-thione **1d**[18] were prepared as described in the literature.

Synthesis of compounds 1b, 1c, 1e and 1f

According to the procedure previously reported for the synthesis of **1a**,[12] a red solution of sodium trithiocarbonate was prepared from sodium sulfide nonahydrate (24.02 g, 0.1 mol), carbon disulfide (7.61 g, 0.1 mol), water (30 cm^3) and tricaprylmethylammonium chloride (Aliquat 336; 0.20 g), to which the appropriate vicinal dihalide or dimethanesulfonate (0.1 mol) was added. The mixture was slowly heated to 70–90 °C at which temperature it was maintained until completion of the reaction (colourless solution). After work-up, the crude reaction mixture was column chromatographed to afford the virtually pure title compounds (TLC, NMR, GC–MS).

Reagents, reaction times and reaction temperatures, chromatographic solvents, yields and NMR spectra are reported below.

4-Methyl-1,3-dithiolane-2-thione 1b. 1,2-Dibromopropane (20.18 g); 5 h at 70 °C; LP–Et_2O (3:2); 85% (12.75 g); bp 112–113 °C/0.5 mmHg (lit.,[19a] 157 °C/10 mmHg); ^1H NMR spectrum identical with that reported.[19b]

4-Decyl-1,3-dithiolane-2-thione 1c. 1,2-Dibromododecane (32.81 g); 1 h at 70 °C; LP–benzene (4:1); 85% (23.50 g); mp 32–33 °C (from EtOH) (lit.,[20] 31–33 °C); δ_H 0.77–1.07 (3 H, m, Me), 1.07–1.75 [16 H, m, $CH_2(CH_2)_8Me$], 1.75–2.12 (2 H, m, $CH_2C_9H_{19}$), 3.55–4.12 (2 H, m, CH_2S) and 4.20–4.60 (1 H, m, CH); δ_C 13.79 (q, *J* 125, Me), 22.31, 27.97, 28.94, 29.17, 31.52 and 33.22 (t, *J* 140, CH_2), 48.04 (t, *J* 140, CH_2S), 60.77 (d, *J* 140, CH) and 220.85 (s, C=S); *m/z* 276 (M^+).

***cis*-4,5-Dimethyl-1,3-dithiolane-2-thione 1e and *trans*-4,5-dimethyl-1,3-dithiolane-2-thione 1f.** 1,2-Dimethylethylene dimethanesulfonate (+, − and *meso*; 24.63 g); 2.5 h at 90 °C; LP–acetone (9:1); 84% (13.80 g); bp 161–162 °C/8 mmHg; *m/z* 164 (M^+). GC and GC–MS analyses showed that the substance was a mixture of *cis* and *trans* isomers in a 1:3 ratio. These were separated by column chromatography (several times) using LP–Et_2O (9:1) as eluent. Compound **1e** had mp 42–43 °C (from LP) (lit.,[21] 41–42 °C); δ_H 1.52 (6 H, d, *J* 6.00, 2 × Me) and 4.40 (2 H, dq, *J* 4.90 and 1.75, 2 × CH); δ_C 13.93 (q, *J* 130, Me), 58.03 (d, *J* 145, CH) and 219.80 (s, C=S). Compound **1f** had mp 40–41 °C (from LP) (lit.,[21] 39–41 °C); δ_H 1.47 (6 H, d, *J* 6.00, 2 × Me) and 4.16 (2 H, dq, *J* 5.00 and 2.00, 2 × CH); δ_C 18.17 (q, *J* 130, Me), 60.85 (d, *J* 145, CH) and 221.00 (s, C=S).

1,3-Dithiolan-2-ones 4a–f from 1,3-dithiolane-2-thiones 1a–f: general procedures

Procedure A. For entries 3, 5, 9–14, 16, 17, 21–25 (Table 1), HBF_4·Et_2O complex (54% in Et_2O, ρ 1.19; 0.21 cm^3, 0.15 mmol) was added to a solution of 1,3-dithiolane-2-thione **1** (10 mmol) in anhydrous CH_2Cl_2 (20 cm^3) previously cooled to 0–5 °C in an ice-bath. After this mixture had been stirred for 5 min, a solution of epoxide **2** (12 mmol) in anhydrous CH_2Cl_2 (20 cm^3) was added dropwise over 1 h at such a rate that the temperature was maintained at 0–5 °C. Cooling and stirring were continued until a GC test showed the disappearance of the starting compound **1** (0.5–1 h). At this point the major product (determined by GC–MS and TLC) was 1,3-dithiolan-2-one **4** although the intermediate 1-oxa-4,6,9-trithiaspiro[4.4]nonane **3** was always present in varying amounts. To complete the conversion of **3** into **4** the cooling bath was removed and the reaction mixture was allowed to warm gradually to room temperature at which it was maintained until disappearance of the intermediate **3** (1–2 h). The reaction mixture was then treated with aq. $NaHCO_3$ (5%; 50 cm^3) after which the aqueous layer was separated and extracted with CH_2Cl_2 (3 × 50 cm^3). The combined extracts were washed with water (50 cm^3), dried (Na_2SO_4) and evaporated under reduced pressure. Column chromatography of the crude residue afforded virtually pure product **4** (GC, TLC, NMR); yields and chromatographic solvents are reported in Table 1.

For entry 7 the initial amount of HBF_4·Et_2O was 0.42 cm^3 (0.3 mmol); moreover for entries 7 and 19 a second portion of HBF_4·Et_2O (0.21 cm^3, 0.15 mmol) was added after the disappearance of **1a** and **1d** to complete the conversion of the

intermediates **3** into **4a** and **4d** (1–2 h at room temperature). For entries 1 and 15 the molar ratio **1a**, **1d**:**2a** was 1:1.4 and the reaction was started at −10 °C. MS, IR and NMR data of compounds **4a–f** are reported below together with the analytical data for the new compound **4c**.

1,3-Dithiolan-2-one 4a. IR and ^{1}H NMR spectra identical with those reported;[22] *m/z* 120 (M^+).

4-Methyl-1,3-dithiolan-2-one 4b. IR and ^{1}H NMR spectra identical with those reported;[9] *m/z* 134 (M^+).

4-Decyl-1,3-dithiolan-2-one 4c. (Found: C, 59.95; H, 9.3; S, 24.6%; M^+, 260. $C_{13}H_{24}OS_2$ requires C, 59.95; H, 9.29; S, 24.62%; *M*, 260); ν_{max}/cm^{-1} 1660 (CO); δ_H 0.62–0.90 (3 H, m, Me), 0.91–1.34 [16 H, m, $CH_2(CH_2)_8Me$], 1.61–1.90 (2 H, m, $CH_2C_9H_{19}$), 3.15–3.70 (2 H, m, CH_2S) and 3.70–4.15 (1 H, m, CH); δ_C 13.94 (q, *J* 125, Me), 22.53, 28.02, 29.20, 29.37, 31.75 and 34.55 (t, *J* 140, CH_2), 41.06 (t, *J* 145, CH_2S), 53.49 (d, *J* 140, CH) and 194.90 (s, CO).

***trans*-3a,4,5,6,7,7a-Hexahydro-2*H*-1,3-benzodithiol-2-one 4d.** IR and ^{1}H NMR spectra identical with those reported;[9] *m/z* 174 (M^+).

***cis*-4,5-Dimethyl-1,3-dithiolan-2-one 4e.** IR data identical with those reported;[23] δ_H 1.50 (6 H, d, *J* 6.00, 2 × Me) and 4.10 (2 H, dq, *J* 6.00 and 1.90, 2 × CH); δ_C 15.02 (q, *J* 130, Me), 50.88 (d, *J* 145, CH) and 195.87 (s, CO); *m/z* 148 (M^+).

***trans*-4,5-Dimethyl-1,3-dithiolan-2-one 4f.** IR data identical with those reported;[23] δ_H 1.60 (6 H, d, *J* 6.00, 2 × Me) and 3.85 (2 H, dq, *J* 6.00 and 2.00, 2 × CH); δ_C 13.90 (q, *J* 127, Me), 54.03 (d, *J* 143, CH) and 195.87 (s, CO); *m/z* 148 (M^+).

In some reactions the significant by-products which are listed below were isolated, *i.e.* compounds **5c**, **7**, **8** and **11** or identified by GC–MS and GC–FTIR, *i.e.* compounds **5d**, **12**, **15**, **16** and **17**. Episulfides **6**, 1-oxa-4,6,9-trithiaspiro[4.4]nonanes **13** and 1,6-dioxa-4,9-dithiaspiro[4.4]nonanes **14** were never identified.

Episulfides 5

1,2-Epithiododecane 5c. Obtained in 5–15% yield (0.1–0.3 g) by chromatography of the crude reaction mixtures from entries 5, 10, 13 and 17 (the eluents are reported in Table 1); bp 120–121 °C/0.4 mmHg (lit.,[24] 80 °C/0.02 mmHg). Its structure was confirmed by MS and NMR spectral data; δ_H 0.85–1.05 (3 H, m, Me), 1.05–1.70 (18 H, m, 9 × CH_2), 2.10 and 2.45 (2 H, 2 d, *J* 6.00, CH_2S) and 2.65–3.00 (1 H, m, CH); δ_C 14.02 (q, *J* 119, Me), 22.64 (t, *J* 125, CH_2Me), 26.87 (d, CHS), 29.33 and 29.60 (t, *J* 125, CH_2) and 31.88 (t, *J* 125, CH_2S); *m/z* 200 (M^+).

1,2-Epithiocyclohexane 5d. Traces, identified by GC–MS on the crude reaction mixtures from entries 7, 11, 14, 19 and 23; *m/z* 114 (M^+). The structure was confirmed by comparison with an authentic sample (Aldrich).

1,2,5-Trithiepanes 8

1,2,3,4,4a,6a,7,8,9,10,10a,11a-Dodecahydrodibenzo[1,2,5]trithiepine 8a. [R^3, R^4 = $CH_2(CH_2)_2CH_2$]. By chromatography (LP–Et_2O, 9:1) of the crude reaction mixture from entry 19, a white solid substance was obtained (90%, 2.34 g); mp 165–195 °C; δ_H 1.25–1.90, 1.90–2.66 and 2.66–3.35 (20 H, 3 m, 8:1:1); δ_C 21.73, 22.09, 22.36, 22.84, 26.27, 28.17, 28.54, 28.94 and 30.90 (t, CH_2) and 43.01, 46.40, 48.40, 49.72, 52.36 and 53.12 (d, CH); *m/z* 260 (M^+). The broad melting range and complex NMR spectra indicated that the product was a mixture of geometrical isomers, similar to that obtained from the reaction of 1,2-epithiocyclohexane in the presence of boron trifluoride–diethyl ether (physical and spectroscopic data are not reported).[15d] Attempts to separate the isomers by fractional crystallizations from propanol failed.

Similar mixtures of trithiepanes were obtained also from entries 7, 11 and 14; yields were 74 (1.92 g), 82 (2.13 g) and 80% (2.08 g), respectively. In entry 23, GC–MS analysis showed a mixture of **8a** and **12a**; the first was the major product. The two products could not be separated.

3,4,6,7-Tetramethyl-1,2,5-trithiepane 8b. (R^3 = R^4 = Me). By chromatography (LP–Et_2O, 9:1) of the crude reaction mixture from entry 25, an oily substance was obtained (Found: C, 46.1; H, 7.8; S, 46.1%; M^+, 208. $C_8H_{16}S_3$ requires C, 46.11; H, 7.73; S, 46.16%; *M*, 208); (81%, 1.68 g). GC–MS analysis indicated that the product was a mixture of geometrical isomers similar to that described for the reaction of 2,3-epithiobutane in the presence of triethyloxonium tetrafluoroborate.[15c] A comparison of the ^{1}H NMR spectrum with those reported showed that the major product was a *cis-cis-cis* or a *cis-trans-cis* isomer.[15c] After several days, a crystalline compound separated from the oil, the ^{1}H NMR spectrum of which was essentially identical with that of the oil.

3,4-Dimethyl-3,4,5a,6,7,8,9,9a-octahydro-1,2,5-benzotrithiepine 12a. [R^1 = R^2 = Me; R^3, R^4 = $CH_2(CH_2)_2CH_2$]. Identified by GC–MS analysis from entry 23; *m/z* 234 (M^+).

1,4,6,9-Tetrathiaspiro[4.4]nonanes 11

2-Methyl-1,4,6,9-tetrathiaspiro[4.4]nonane 11a. (R^1 = R^2 = R^3 = H, R^4 = Me). Traces, identified by GC–MS analysis from entry 3; *m/z* 210 (M^+).

Spiro[3a,4,5,6,7,7a-hexahydro-1,3-benzodithiole-2,2′-[1,3]-dithiolane] 11b. [R^1 = R^2 = H; R^3, R^4 = $CH_2(CH_2)_2CH_2$]. From entry 7 (5%, 0.12 g); mp 118–120 °C (from EtOH) (lit.,[25] 117.5–120 °C); ^{1}H NMR spectrum identical to that reported;[25] *m/z* 250 (M^+).

2,2′-Spirobi[3a,4,5,6,7,7a-hexahydro-1,3-benzodithiole] 11c. [R^1, R^2 = R^3, R^4 = $CH_2(CH_2)_2CH_2$]. From entry 19 (4%, 0.12 g); mp 199–201 °C (from LP) (Found: C, 51.2; H, 6.55; S, 42.1%; M^+, 304. $C_{13}H_{20}S_4$ requires C, 51.27; H, 6.62; S, 42.11%; *M*, 304); δ_H 1.07–2.22 (16 H, m, 8 × CH_2) and 3.09–3.35 (4 H, m, 4 × CH); δ_C 25.26 and 29.02 (t, CH_2), 61.37 (d, CH) and 105.04 (s, C spiro).

1,3-Oxathiolane-2-thiones 7

4- or 5-Methyl-1,3-oxathiolane-2-thione 7a. (R^3 = H, R^4 = Me). Traces, identified by GC–MS analysis from entry 3; *m/z* 134 (M^+).

***trans*-3a,4,5,6,7,7a-Hexahydro-2*H*-1,3-benzoxathiole-2-thione 7b.** [R^3, R^4 = $CH_2(CH_2)_2CH_2$]. Isolated in 4–6% yield (0.07–0.10 g) from entries 7, 11, 14 and 19; mp 58–59 °C (from LP) (lit.,[21] 58.5–60.5 °C for *trans* derivative); *m/z* 174 (M^+); ^{1}H NMR data identical with those reported.[26]

***trans*-3a,4,5,6,7,7a-Hexahydro-2*H*-1,3-benzodithiol-2-one 15a**

[R^3, R^4 = $CH_2(CH_2)_2CH_2$]. Traces, identified by GC–MS analysis from entries 11 and 14; *m/z* 174 (M^+); identical with **4d**.

***trans*-3a,4,5,6,7,7a-Hexahydro-2*H*-1,3-benzodithiole-2-thione 16a**

[R^3, R^4 = $CH_2(CH_2)_2CH_2$]. Traces, identified by GC–MS analysis from entries 11 and 14; *m/z* 190 (M^+); identical with **1d**.

1,3-Oxathiolan-2-ones 17

4- or 5-Methyl-1,3-oxathiolan-2-one 17a. (R^3 = H, R^4 = Me). Oil; traces from entries 3 and 9; GC–FTIR: ν_{max}/cm^{-1} 1790 (CO); *m/z* 118 (M^+).

4- or 5-Decyl-1,3-oxathiolan-2-one 17b. (R^3 = H, R^4 = $C_{10}H_{21}$). Oil; traces from entries 5, 10, 13 and 17; GC–FTIR: ν_{max}/cm^{-1} 1786 (CO); *m/z* 244 (M^+).

3a,4,5,6,7,7a-Hexahydro-2*H*-1,3-benzoxathiol-2-one 17c. [R^3, R^4 = $CH_2(CH_2)_2CH_2$]. Oil; traces from entries 7 and 19; GC–FTIR: ν_{max}/cm^{-1} 1790 (CO); *m/z* 158 (M^+).

Procedure B. In entries 4, 6, 8, 18 and 20 HBF_4·Et_2O (54% in Et_2O, *ρ* 1.19; 0.02 cm^3, 0.015 mmol) was added to a solution of 1,3-dithiolane-2-thione **1** (10 mmol) in anhydrous chlorobenzene (20 cm^3) previously cooled at 0–5 °C in an ice-bath. After the mixture had been stirred for 5 min, a solution of epoxide **2** (11 mmol) in chlorobenzene (20 cm^3) was added dropwise over *ca.* 1 h at such a rate that the temperature was maintained at

0–5 °C. After the addition was complete, the cooling bath was removed and the reaction mixture was allowed to warm to room temperature at which it was stirred until the starting compound **1** had disappeared (0.5–1 h). At this point the intermediate 1-oxa-4,6,9-trithiaspiro[4.4]nonane **3** was present as almost the only product (GC–MS, TLC). To convert **3** into **4** a second portion of HBF_4·Et_2O (0.14 cm^3, 0.10 mmol) was added and the reaction mixture was gradually heated to 80 °C over 20 min. After a further 10 min at 80 °C the intermediate **3** had disappeared and the major product was 1,3-dithiolan-2-one **4**. Work-up identical with that described above afforded virtually pure product **4** (GC, TLC, NMR); yields and chromatographic solvents are reported in Table 1.

In entry 2 the molar ratio **1a**:**2a** was 1:2 and the reaction was started at −10 °C. The two portions of HBF_4·Et_2O were 0.21 cm^3 (0.15 mmol) and 0.42 cm^3 (0.30 mmol). In entry 4 the molar ratio **1a**:**2b** was 1:1.3 and the initial amount of HBF_4·Et_2O was 0.21 cm^3 (0.15 mmol).

In some reactions the significant by-products which are listed below were isolated.

Oligomers 9 and 10

2,5,8,11-Tetramethyl-1,4,7,10-tetrathiacyclododecane 9a (R^3 = H, R^4 = Me) and 2,5,8,11,14-pentamethyl-1,4,7,10,13-pentathiacyclopentadecane 10a (R^3 = H, R^4 = Me). GC analysis of the oil obtained by chromatography (LP–Et_2O, 3:2) of the crude reaction mixture from entry 4, showed the presence of two substances. These were separated by successive chromatography with LP–Et_2O (9.6:0.4) as eluent. The first eluted substance was the tetramer **9a** (29%, 0.21 g); mp 128–129 °C (white crystals, from propanol–water) (lit.,[15b] 135 °C for one probable stereoisomer); GC–MS analysis indicated a mixture of several geometrical isomers; *m*/*z* 296 (M^+). The second eluted substance was the pentamer **10a**; 34% yield (0.25 g); viscous oil (lit.,[15b] viscous oil); GC–MS analysis indicated a mixture of several geometrical isomers; *m*/*z* 370 (M^+). ^1H NMR spectra of **9a** and **10a** were identical with those reported in the literature for the same products obtained in the polymerization of epithiopropane in the presence of triethyloxonium tetrafluoroborate or boron trifluoride–diethyl ether.[15b]

1,2,5-Trithiepanes 8

Compound 8a [R^3, R^4 = $CH_2(CH_2)_2CH_2$]. Obtained from entries 8 and 20 (90%, 2.34 g). Physical and spectroscopic properties were identical with those of the same product obtained in Procedure A.

Compound 8c (R^3 = H or $C_{10}H_{21}$, R^4 = $C_{10}H_{21}$ or H). By chromatography of the crude reaction mixture from entries 6 and 18 (the eluents are reported in Table 1), a polymeric substance was obtained. MS analysis showed the presence of the title compound **8c**: *m*/*z* 432 (M^+).

1-Oxa-4,6,9-trithiaspiro[4.4]nonanes 3

The reaction described in Procedure B could be stopped after the first step. Work-up and column chromatography of the crude mixtures afforded pure title compounds **3**.

Entries, chromatographic solvents, yields and physical and spectroscopic properties for compounds **3** are reported below.

1-Oxa-4,6,9-trithiaspiro[4.4]nonane 3a. (R^1 = R^2 = R^3 = R^4 = H). Entry 2; LP–Et_2O (4:1); (66%, 1.18 g); mp 71–72 °C (from EtOH) (Found: C, 33.3; H, 4.4; S, 53.4%; M^+, 180. $C_5H_8OS_3$ requires C, 33.34; H, 4.48; S, 53.29%; *M*, 180); δ_H 3.17 (2 H, t, *J* 6.00, CH_2S), 3.47 [4 H, br s, $S(CH_2)_2S$] and 4.27 (2 H, t, *J* 6.00, CH_2O); δ_C 34.29 (t, *J* 145, CH_2S), 41.26 [t, *J* 145, $S(CH_2)_2S$], 71.42 (t, *J* 145, CH_2O) and 100.11 (s, C spiro).

2-Methyl-1-oxa-4,6,9-trithiaspiro[4.4]nonane 3b. (R^1 = R^2 = R^3 = H, R^4 = Me). Entry 4; LP–Et_2O (3:2); (85%, 1.65 g). GC–MS analysis showed a mixture of the title compound and 3-methyl-1-oxa-4,6,9-trithiaspiro[4.4]nonane **3** (R^1 = R^2 = R^3 = H, R^4 = Me) in an 8:1 ratio. After several extractions of the mixture with pentane at room temperature, the first compound **3b** was obtained pure: mp 66.5–68 °C (from LP) (lit.,[14] 63–66 °C); ^1H and ^{13}C NMR spectra were identical with those reported; *m*/*z* 194 (M^+). The second product could not be isolated pure; its structure was confirmed by MS: *m*/*z* 194 (M^+) and ^1H and ^{13}C NMR that were identical with those reported.[14]

As confirmatory proof, the reaction between **1a** and **2b** was carried out at −45 °C. The above two products were obtained in a 15:1 ratio and with a lower yield (61%, 1.18 g).

2-Decyl-1-oxa-4,6,9-trithiaspiro[4.4]nonane 3c. (R^1 = R^2 = R^3 = H, R^4 = $C_{10}H_{21}$). Entry 6; LP–Et_2O (4:1); (66%, 2.12 g); mp 28.5–29.5 °C (from EtOH) (Found: C, 56.15; H, 8.85; S, 30.1; M^+, 320. $C_{15}H_{28}OS_3$ requires C, 56.20; H, 8.80; S, 30.00%; *M*, 320); δ_H 0.88 (3 H, t, *J* 6.70, Me), 1.26 [16 H, m, $CH_2(CH_2)_8Me$], 1.63–1.71 and 1.82–1.90 (2 H, 2 m, 1:1, $CH_2C_9H_{19}$), 2.88 (1 H, t, *J* 10.11, 3-H), 3.10 (1 H, dd, *J* 9.67 and 4.84, 3-H), 3.36 and 3.52 (4 H, 2 m, 1:1, 7-H_2 and 8-H_2) and 4.18–4.23 (1 H, m, 2-H); δ_C 13.75 (q, *J* 123, Me), 22.29, 24.95, 28.91, 29.09, 31.50 and 32.53 (t, CH_2), 38.40, 40.28 and 41.37 (t, CH_2 cyclo), 83.97 (d, *J* 143, CH) and 111.50 (s, C spiro).

Spiro[3a,4,5,6,7,7a-hexahydro-1,3-benzoxathiole-2,2′-[1,3]-dithiolane] 3d. [R^1 = R^2 = H, R^3, R^4 = $CH_2(CH_2)_2CH_2$]. Entry 8; LP–Et_2O (4:1); (75%, 1.76 g); mp 119.5–120 °C (from CH_2Cl_2–LP) (Found: C, 46.15; H, 6.1; S, 41.1%; M^+, 234. $C_9H_{14}OS_3$ requires C, 46.12; H, 6.02; S, 41.03%; *M*, 234); δ_H 1.25–1.66, 1.78–1.90 and 2.08–2.25 (8 H, 3 m, 2:1:1, 4 × CH_2 cyclo), 3.07–3.15 (1 H, m, 3a-H), 3.34–3.40 and 3.51–3.56 (4 H, 2 m, 1:1, 4′-H_2 and 5′-H_2) and 3.56–3.64 (1 H, m, 7a-H); δ_C 23.45, 24.89, 28.53 and 29.37 (t, CH_2 cyclo), 40.10 and 41.44 (t, C-4′ and C-5′), 53.74 (d, *J* 141, C-3a), 87.42 (d, *J* 137, C-7a) and 111.77 (s, C spiro).

5′-Decylspiro[3a,4,5,6,7,7a-hexahydro-1,3-benzodithiole-2,2′-[1,3]oxathiolane] 3e. [R^1 = R^2 = $CH_2(CH_2)_2CH_2$, R^3 = H, R^4 = $C_{10}H_{21}$]. Entry 18; LP–Et_2O (9.5:0.5); (70%, 2.62 g); mp 56.5–57 °C (from LP) (Found: C, 61.0; H, 9.2; S, 25.6; M^+, 374. $C_{19}H_{34}OS_3$ requires C, 60.91; H, 9.15; S, 25.67%; *M*, 374); mixture of diastereoisomers; δ_H 0.89 (3 H, t, *J* 6.37, Me), 1.27–1.58 [20 H, m, $CH_2(CH_2)_8Me$ and 2 × CH_2 cyclo], 1.62–1.72, 1.84–1.92 and 2.07–2.20 (6 H, 3 m, 1:3:2, $CH_2C_9H_{19}$ and 2 × CH_2 cyclo), 2.86 and 2.90 (1 H, 2 t, 1:1, *J* 9.69 and 9.89, 4′-H), 3.07 and 3.20 (1 H, 2 dd, 1:1, *J* 4.61 and 9.66 and *J* 4.83 and 9.88, 4′-H), 3.28–3.34, 3.48–3.55 and 3.55–3.63 (2 H, 3 m, 1:2:1, 3a-H and 7a-H) and 4.17–4.22 and 4.22–4.28 (1 H, 2 m, 1:1, 5′-H); δ_C 13.94 (q, Me), 22.47, 25.28, 25.92, 28.60, 28.84, 29.15, 29.29, 29.37, 30.08, 30.29, 31.70, 32.86 and 33.14 (t, CH_2), 38.67 and 39.13 (t, C-4′), 59.75, 60.18, 62.26 and 62.87 (d, C-3a and C-7a), 83.94 and 84.64 (d, C-5′) and 110.26 (s, C spiro). Complicated NMR spectra indicated a mixture of stereoisomers.

Spiro[3a,4,5,6,7,7a-hexahydro-1,3-benzodithiole-2,2′-(3a′,4′,5′,6′,7′,7a′-hexahydro-1′,3′-benzoxathiole)] 3f. [R^1, R^2 = R^3, R^4 = $CH_2(CH_2)_2CH_2$]. Entry 20; LP–Et_2O (9:1); (75%, 2.17 g); mp 121–122 °C (from LP) (Found: C, 54.2; H, 7.1; S, 33.25%; M^+, 288. $C_{13}H_{20}OS_3$ requires C, 54.13; H, 6.99; S, 33.34%; *M*, 288); δ_H 1.25–1.65, 1.75–1.92 and 2.02–2.27 (16 H, 3 m, 2:1:1, 8 × CH_2 cyclo), 3.05–3.15, 3.28–3.35, 3.47–3.63 and 3.63–3.72 (4 H, 4 m, 1:0.5:2:0.5, 4 × CH); δ_C 23.79, 25.24, 28.50, 28.79, 29.43, 29.68, 29.98 and 30.53 (t, CH_2 cyclo), 53.87, 54.62, 59.64, 60.15, 62.21 and 63.11 (d, SCH), 87.48 and 87.73 (d, OCH), and 109.04, 110.03 and 113.10 (s, C spiro). Complicated NMR spectra indicated a mixture of stereoisomers.

1,3-Dithiolan-2-ones 4 from 1-oxa-4,6,9-trithiaspiro[4.4]-nonanes 3

***trans*-3a,4,5,6,7,7a-Hexahydro-2*H*-1,3-benzodithiol-2-one 4d: typical procedure.** HBF_4·Et_2O (0.14 cm^3, 0.10 mmol) was added to a solution of compound **3f** (2.88 g, 10 mmol) in anhydrous chlorobenzene (20 cm^3) and the reaction mixture was gradually

heated to 80 °C over 20 min. The temperature was maintained for a further 10 min until all the starting compound had reacted. After work-up, the reaction mixture was chromatographed using LP–Et_2O (9 : 1) as eluent. Two products were obtained in almost quantitative yields: compound **8a** (0.87 g) and the title compound **4d** (1.74 g). With the same procedure **4a** and **4d** were also obtained starting from **3b** and **3e**, respectively.

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