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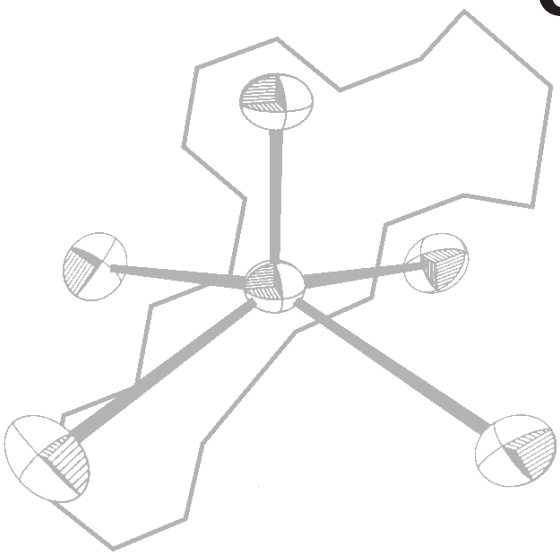

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The Synthesis of Sulfur-Containing Spiro Orthocarbonates

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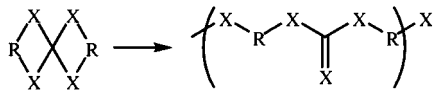
New sulfur-containing spiro orthocarbonates (SOCs) were prepared by using dichlorodiphenoxymethane. Mercapto alcohols were employed to yield O,S SOCs, and O,S diphenoxy intermediates in a one-step procedure. By adopting a two-step synthesis under basic conditions, a range of sulfur-containing heteroatom SOCs was produced. Preliminary studies indicate that this methodology is applicable to different ring sizes.

Introduction

Interest in minimal shrinkage polymerization has focused attention on the synthesis of spiro orthocarbonates (SOCs) (1a) and related compounds. Furthermore, double ring-opening polymerization of SOCs (1a) offers the opportunity of yielding polymers which contain ether and carbonate groups within the backbone (2a) (Scheme 1). Therefore these polymers could potentially be useful as biodegradable materials. The usefulness of SOCs (1a) and spiro tetrathio orthocarbonates (STOCs) (1b) has been claimed in areas as varied as accelerating the vulcanization of rubber,[1] to the production of dental resins with reduced shrinkage during hardening.[2]

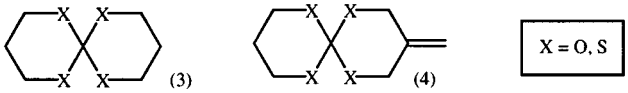


(1a) X = O
(1b) X = S

(2a) X = O
(2b) X = S

Scheme 1

Whilst the polymerization of SOCs has received considerable attention culminating in the preparation of a monograph,[3] relatively little work has been published[4,5] on analogous series in which oxygen has been replaced with different heteroatoms. Studies[6] have shown that many SOCs are inherently unstable molecules, being particularly sensitive to trace amounts of acid causing rapid decomposition. In contrast, STOCs (1b) are more stable, but can be difficult to polymerize cationically.[4] It was envisaged that the substitution of two oxygen atoms with sulfur atoms in the SOC would produce compounds of greater stability, yet maintain reactivity towards ionic polymerization. In addition, the presence of sulfur in the resulting polymer offers the potential to improve its mechanical and optical properties. Also of interest was the incorporation of a methylidene group into sulfur-containing SOCs, thus making them amenable to free-radical, as well as cationic, polymerization. In this paper we report methodology toward the synthesis of new sulfur-containing SOCs (3) and (4).



(3) (4) X = O, S

Results and Discussion

Our interest focused on sulfur-containing SOCs (3) and (4) consisting of six-membered rings. Early studies[7] suggested that the cationic polymerization of six-membered, rather than five- or seven-membered, ring SOC monomers proceeded without fragmentation. Various routes leading to the synthesis of SOCs and STOCs have been reported. Limitations of a number of these procedures include the inability to efficiently produce unsymmetrical monomers[8] and the use of highly toxic thiophosgene and tin intermediates.[9] Gross and coworkers[10] avoided these problems by synthesizing a variety of spiro orthocarbonates via dichlorodiphenoxymethane (6). More recently, work completed in this laboratory[11] demonstrated that this methodology could provide access to 3,9-dimethylidene-1,5,7,11-tetrathiaspiro[5.5]undecane (7) (Scheme 2).

Modification of literature procedures,[10,12] yielded the precursors dichloro-diphenoxymethane (6) and 2-methylidenepropane-1,3-dithiol (5) in near quantitative yields.[11]

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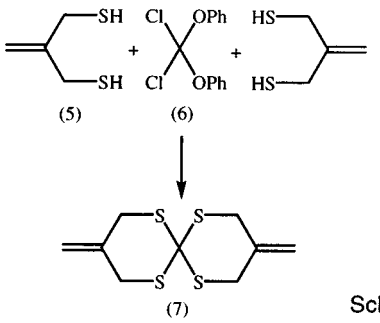
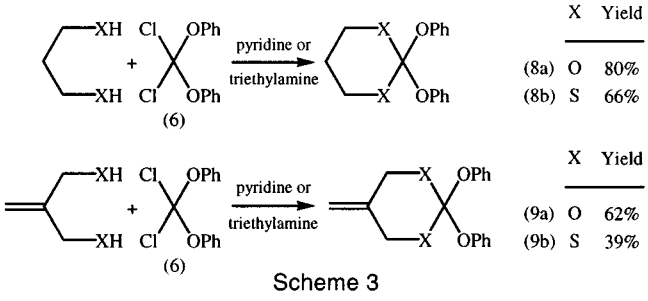


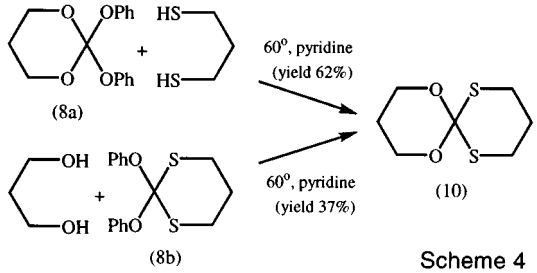
Scheme 2

A range of precursor diphenoxy acetals and thioacetals was synthesized. The addition of 1 equiv. of the appropriate diol or dithiol to (6) in the presence of a non-nucleophilic base yielded the corresponding acetals (8a,b) and (9a,b) (Scheme 3). Higher yields of the diphenoxy acetals (8a) and (9a) were obtained when compared with the corresponding diphenoxy thioacetals (8b) and (9b).



Scheme 3

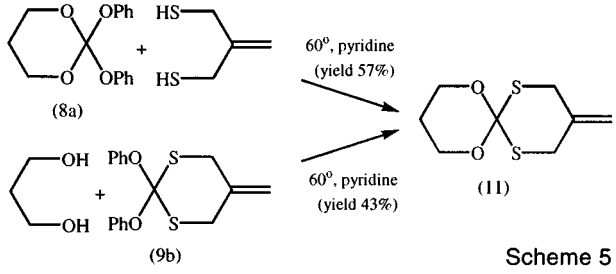
Transesterification of the diphenoxy intermediates (8a) or (9a) with a diol has traditionally been accomplished via an acid-catalysed mechanism.[8] However, work undertaken in these laboratories and reports in the literature[13] suggest that, under acidic conditions, both the six-membered ring and the diphenoxy groups of the acetals (8a) or (9a) are susceptible to attack. This results in the production of unwanted SOCs, resulting in lower yields of the required SOCs and complicating the purification process. In an effort to avoid these problems, transesterification under basic conditions was investigated.



Scheme 4

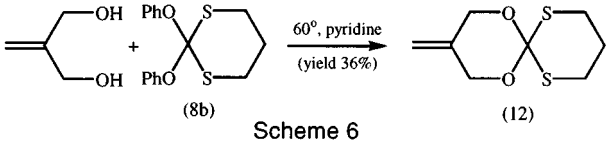
Initial studies involving the addition of different diphenoxy acetals and diols (or dithiols), in the presence of various quantities of pyridine and solvent, resulted in recovery of starting material. Eventually, in the presence of pyridine at elevated temperatures, a sulfur-containing SOC (10) was isolated in viable yields (Scheme 4). The more efficient pathway, as judged by overall yields, was via the diphenoxy acetal (8a).

Under similar conditions to those employed above, the methylidene sulfur-containing SOC (11) was produced from both the diphenoxy acetal (8a) and the methylidene diphenoxy thioacetal (9b) (Scheme 5). As in the previous synthetic pathway, the diphenoxy acetal intermediate (8a) produced the required material (11) in a higher yield.



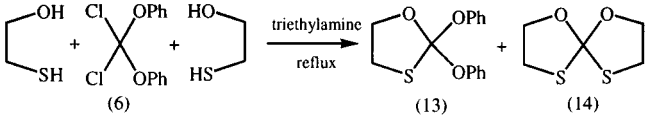
Scheme 5

Compound (12)* was synthesized from the diphenoxy thioacetal (8b) and 2-methylidenepropane-1,3-diol (Scheme 6). Synthesis of (12) was also attempted from 5-methylidene-2,2-diphenoxy-1,3-dioxan (9a) and propane-1,3-dithiol. However, it appears that at elevated temperatures the propane-1,3-dithiol can also add across the double bond of the diphenoxy acetal (9a) yielding a range of unidentified products observed in the crude ^{1}H n.m.r. spectrum.



Scheme 6

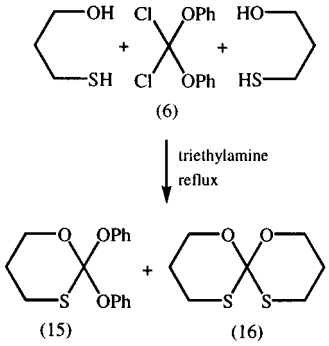
In the sulfur-containing SOCs contained in this report to date, each ring contains either oxygen or sulfur. Due to the ready availability of 2-mercaptoethanol, the first mixed heteroatom ring SOC target was 2,2-diphenoxy-1,3-oxathiolan (13). Two equivalents of 2-mercaptoethanol were added to dichlorodiphenoxymethane (6) in the presence of triethylamine, and the mixture was refluxed overnight (Scheme 7). From the resulting reaction mixture the diphenoxy oxygen/sulfur acetal (13) and the oxygen/sulfur SOC (14) were isolated; however, due to the highly unstable nature of (14), only ^{1}H n.m.r. spectral data were obtained.



Scheme 7

* 3-Methylidene-1,5-dioxa-7,11-dithiaspiro[5.5]undecane.

Synthesis (Scheme 8) of the six-membered O,S SOC (16) was also completed in a one-step procedure from dichlorodiphenoxymethane (6) and 3-mercaptopropan-1-ol. The diphenoxy O,S acetal intermediate (15) was also isolated from the reaction mixture. When compared with the all-sulfur or all-oxygen systems, the mixed O,S SOCs (14) and (16) appear more reluctant to form.



Scheme 8

Conclusion

The methodology for the synthesis of a range of new sulfur-containing SOCs from dichlorodiphenoxymethane (6) is reported. The diphenoxy O,S acetal intermediates (13) and (15) were isolated in a one-step procedure which was designed to synthesize the O,S SOCs (14) and (16). The diphenoxy acetal intermediates (8a,b) and (9a,b) were also produced, and by use of these intermediates various sulfur-containing SOCs (10)–(12) were obtained. In addition, preliminary studies indicate that this methodology can be successfully applied to a variety of ring size SOCs.

Experimental

Instrumentation

N.m.r. spectra were obtained in (D)chloroform (99·9%) (Cambridge Isotope Laboratories) by using a Varian Unity Plus 400 MHz spectrometer unless otherwise specified. Due to the long relaxation time of the spiro carbon the pulse delay was increased to 30 s. Mass spectrometric data were obtained with a V.G. Micromass 7070F spectrometer or on a Kratos Analytical Concept ISQ instrument. Infrared (i.r.) spectra were recorded on a Biorad FTS-60A Fourier-transform i.r. spectrometer. Microanalyses were performed by Central Science Laboratory, Hobart. Melting points were performed on an Electrothermal melting point apparatus and are uncorrected.

Reagents and Conditions

Propane-1,3-diol, 2-methylidenepropane-1,3-diol, 3-mercaptopropan-1-ol, 2-mercaptoethanol and propane-1,3-dithiol were obtained from Aldrich Chemical Company. A.R. grade solvents were used after purification by standard literature procedures.[14] The (D)chloroform was stored over potassium carbonate, and all reactions were conducted under an atmosphere of argon.

2,2-Diphenoxy-1,3-dioxan (8a)

A solution of dichlorodiphenoxymethane (6) (3·54 g, 13·2 mmol) in dichloromethane (20 ml) was added dropwise over 0·5 h to a stirred solution of propane-1,3-diol (2·00 g, 26·3 mmol) and triethylamine (5·32 g, 52·6 mmol) in dichloromethane (20 ml). After the addition was complete, the reaction mixture was stirred for a further 4 h.

The organic extract was washed with 1 M NaOH (3×50 ml) and water (50 ml). The organic layer was collected, dried ($MgSO_4$) and concentrated under reduced pressure to afford a pale red solid (this is a typical purification or treatment of the reaction mixture and will be referred to in the following experimental section).

Recrystallization from ethanol yielded 2,2-diphenoxy-1,3-dioxan (8a) as a crystalline white powder (5·71 g, 80%), m.p. 95–96° (lit.[15] 96–97°) (Found: C, 70·7; H, 6·0. Calc. for $C_{16}H_{16}O_4$: C, 70·6; H, 5·9%). I.r. ν_{max} (KBr) 2994, 2888, 1951, 1748, 1592, 1489, 1221, 1189, 1135, 1079, 984, 756 cm^{-1}. ^1H n.m.r. δ 7·29–7·28, m, 8H, ArH; 7·09–7·05, m, 2H, ArH; 4·18, t, 4H, J 5·6 Hz, OC**H**$_2$; 1·86, quin, 2H, J 5·6 Hz, $OCH_2C\mathbf{H}_2$. ^{13}C n.m.r. δ 152·3; 129·0; 123·4; 119·8; 117·0, C 2; 63·3, C 4/6; 23·3, C 5. Mass spectrum (c.i., NH_4^+) m/z 273 (4·4%), 179 (97), 120 (100), 102 (22), 94 (25).

5-Methylidene-2,2-diphenoxy-1,3-dioxan (9a)

To a stirred solution of 2-methylidenepropane-1,3-diol (3·00 g, 34·1 mmol) and pyridine (5·51 ml, 68·1 mmol) in dichloromethane (15 ml) was added dropwise a solution of dichlorodiphenoxymethane (6) (9·16 g, 34·1 mmol) in dichloromethane (15 ml) over 0·5 h. The solution was stirred at room temperature for a further 20 h and following normal workup distilled to afford 5-methylidene-2,2-diphenoxy-1,3-dioxan (9a) as a colourless oil (5·01 g, 62%), b.p. 130–132°/0·05 mmHg (lit.[13] 162–168°/0·25 mmHg) (Found: C, 71·9; H, 5·9. Calc. for $C_{17}H_{16}O_4$: C, 71·8; H, 5·7%). I.r. ν_{max} (NaCl) 3069, 3038, 2984, 2922, 2872, 1593, 1487, 1210, 1158, 1066, 888, 752 cm^{-1}. ^1H n.m.r. δ 7·28–7·27, m, 8H, ArH; 7·09–7·06, m, 2H, ArH; 5·00, s, 2H, C=C**H**$_2$; 4·55, s, 4H, OCH_2. ^{13}C n.m.r. δ 152·2; 136·6, C 5; 129·0; 123·5; 119·8; 117·6, C 2; 110·5, C=**C**H_2; 66·5, C 4/6. Mass spectrum (c.i., NH_4^+) m/z 302 (0·8%), 286 (0·6), 285 (1·9), 192 (12), 191 (100), 94 (8).

2,2-Diphenoxy-1,3-dithian (8b)

A solution of dichlorodiphenoxymethane (6) (10·0 g, 37·0 mmol) in dichloromethane (20 ml) was added dropwise over 0·5 h to a stirred solution of propane-1,3-dithiol (4·02 g, 37·0 mmol) and pyridine (5·85 g, 74·0 mmol) in dichloromethane (20 ml). The mixture was stirred at room temperature for 20 h and after workup yielded a yellow solid. Recrystallization of the crude solid from dichloromethane/ethanol afforded 2,2-diphenoxy-1,3-dithian (8b) as off-white *crystals* (7·43 g, 66%), m.p. 110–112° (Found: C, 63·2; H, 5·3. $C_{16}H_{16}O_2S_2$ requires C, 63·1; H, 5·3%). I.r. ν_{max} (KBr) 3054, 2911, 2906, 1589, 1486, 1196, 1166, 1028, 993, 951, 759 cm^{-1}. ^1H n.m.r. δ 7·37–7·30, m, 8H, ArH; 7·18–7·14, m, 2H, ArH; 3·04–3·02, m, 4H, SCH_2; 2·14–2·08, m, 2H, $SCH_2C\mathbf{H}_2$. ^{13}C n.m.r. δ 153·0; 129·1; 124·5; 121·2; 113·3, C 2; 30·3, C 4/6; 24·8, C 5. Mass spectrum (c.i., NH_4^+) m/z 305 (3·4%), 231 (20), 212 (13), 211 (100), 106 (14), 94 (57).

5-Methylidene-2,2-diphenoxy-1,3-dithian (9b)

A solution of dichlorodiphenoxymethane (6) (1·12 g, 4·2 mmol) in dichloromethane (10 ml) was added dropwise over 0·5 h to a stirred solution of 2-methylidenepropane-1,3-dithiol (0·5 g, 4·2 mmol) and triethylamine (1·21 ml, 8·7 mmol) in dichloromethane (10 ml). The mixture was stirred at room temperature for 20 h and following normal workup yielded a yellow solid. The solid was sublimed (50°/0·05 mmHg) and a small amount of diphenyl carbonate was isolated as a white powder. The sublimation residue was extracted with hot hexane (3×50 ml), and the solvent removed in vacuum to yield an off-white powder. Recrystallization of this material from dichloromethane/ethanol afforded 5-methylidene-

2,2-diphenoxy-1,3-dithian (9b) as fine white *crystals* (0·51 g, 39%), m.p. 93–95° (Found: C, 64·5; H, 5·0. $C_{17}H_{16}O_2S_2$ requires C, 64·5; H, 5·1%). I.r. ν_{max} (KBr) 3072, 1641, 1587, 1489, 1205, 1191, 1169, 1030, 947, 850, 753 cm^{-1}. ^1H n.m.r. δ 7·37–7·31, m, 8H, ArH; 7·19–7·16, m, 2H, ArH; 5·08, s, 2H, C=CH_2; 3·53, s, 4H, SCH_2. ^{13}C n.m.r. δ 153·2; 137·9, C 5; 129·2; 124·7; 121·2; 114·5, C=**C**H_2; 113·8, C 2; 35·3, C 4/6. Mass spectrum (c.i., NH_4^+) *m/z* 317 (4·8%), 231 (77), 223 (100), 94 (60).

1,5-Dioxa-7,11-dithiaspiro[5.5]undecane (10)

Method A. A solution of 2,2-diphenoxy-1,3-dioxan (8a) (10·0 g, 36·8 mmol), propane-1,3-dithiol (4·38 g, 40·5 mmol) and pyridine (8·93 ml, 110·4 mmol) was stirred at 60° for 36 h. The mixture underwent normal workup to yield an amorphous yellow material. This material was extracted with hot hexane (3×50 ml) and the solvent removed in vacuum to afford an off-white solid. This material was sublimed (50°/0·05 mmHg) to yield 1,5-dioxa-7,11-dithiaspiro[5.5]undecane (10) as small white *crystals* (4·362 g, 62%), m.p. 60–62° (Found: C, 43·7; H, 6·1; S, 33·4. $C_7H_{12}O_2S_2$ requires C, 43·7; H, 6·3; S, 33·4%). I.r. ν_{max} (KBr) 2930, 2886, 1424, 1378, 1282, 1245, 1089, 1022, 921, 862, 800 cm^{-1}. ^1H n.m.r. δ 4·15, t, 4H, *J* 5·6 Hz, OCH_2; 3·00–2·97, m, 4H, SCH_2; 2·08–2·03, m, 2H, $SCH_2C\mathbf{H}_2$; 1·85, quin, 2H, *J* 5·6 Hz, $OCH_2C\mathbf{H}_2$. ^{13}C n.m.r. δ 110·5, C 6; 61·8, C 2/4; 29·5, C 8/10; 25·8, C 9; 24·6, C 3. Mass spectrum (c.i., NH_4^+) *m/z* 195 (9·5%), 194 (11), 193 (100), 192 (16), 119 (28), 118 (25), 106 (21).

Method B. A solution of 2,2-diphenoxy-1,3-dithian (8b) (0·50 g, 1·64 mmol), propane-1,3-diol (0·125 g, 1·64 mmol) and pyridine (0·266 ml, 3·28 mmol) was stirred at 60° for 20 h. The mixture was treated by the standard method producing a yellow solid. This material was recrystallized from ethyl acetate/hexane to yield 1,5-dioxa-7,11-dithiaspiro[5.5]undecane (10) as small white crystals (0·117 g, 37%), m.p. 60–62°. The spectroscopic data were identical to those of the authentic material obtained in method A.

9-Methylidene-1,5-dioxa-7,11-dithiaspiro[5.5]undecane (11)

Method A. A solution of 2,2-diphenoxy-1,3-dioxan (8a) (9·068 g, 33·3 mmol), 2-methylidenepropane-1,3-dithiol (4·00 g, 33·3 mmol) and pyridine (5·38 ml, 66·5 mmol) was stirred at 60° for 24 h. The mixture was treated in the standard manner yielding a yellow solid. Recrystallization from ethyl acetate/hexane afforded 9-methylidene-1,5-dioxa-7,11-dithiaspiro[5.5]undecane (11) as white *crystals* (3·87 g, 57%), m.p. 81–83° (Found: C, 47·4; H, 6·0; S, 31·8. $C_8H_{12}O_2S_2$ requires C, 47·0; H, 5·9; S, 31·4%). I.r. ν_{max} (KBr) 2964, 2920, 2876, 1866, 1747, 1638, 1458, 1413, 1242, 1088, 1030, 912, 869, 835, 750 cm^{-1}. ^1H n.m.r. ($CDCl_3$) δ 5·03, s, 2H, C=CH_2; 4·17, t, 4H, *J* 5·6 Hz, OCH_2; 3·50, s, 4H, SCH_2; 1·88, quin, 2H, *J* 5·6 Hz, $OCH_2C\mathbf{H}_2$. ^{13}C n.m.r. ($CDCl_3$) δ 139·0, C 9; 113·0, C=**C**H_2; 111·9, C 6; 62·2, C 2/4; 34·4, C 8/10; 24·5, C 3. Mass spectrum (c.i., NH_4^+) *m/z* 207 (10%), 206 (12), 205 (100), 204 (6·8), 140 (29), 119 (44), 118 (15).

Method B. A solution of 2,2-diphenoxy-5-methylidene-1,3-dithian (9b) (0·200 g, 0·63 mmol), propane-1,3-diol (0·04 g, 0·63 mmol) and pyridine (0·12 ml, 1·26 mmol) was stirred at 60° for 24 h. The mixture underwent a typical workup yielding a yellow solid. Recrystallization from ethyl acetate/hexane provided 9-methylidene-1,5-dioxa-7,11-dithiaspiro[5.5]undecane (11) as white crystals (0·056 g, 43%). The spectroscopic data were identical to those of the authentic material obtained in method A.

3-Methylidene-1,5-dioxa-7,11-dithiaspiro[5.5]undecane (12)

A solution of 2,2-diphenoxy-1,3-dithian (8b) (5·22 g, 17·1 mmol), 2-methylidenepropane-1,3-diol (1·51 g, 17·1 mmol) and pyridine (2·77 ml, 34·3 mmol) was stirred at 60° for 24 h. The mixture was treated in the standard manner to yield an orange viscous oil. This material was sublimed (50°/0·05 mmHg) affording a white crystalline product. Following recrystallization from ethyl acetate/hexane, 3-methylidene-1,5-dioxa-7,11-dithiaspiro[5.5]undecane (12) was isolated as white *crystals* (1·26 g, 36%), m.p. 48–49° (Found: C, 47·2; H, 5·9. $C_8H_{12}O_2S_2$ requires C, 47·0; H, 5·9%). ^1H n.m.r. δ 4·93, s, 2H, C=CH_2; 4·51, s, 4H, OCH_2; 3·03–3·00, m, 4H, SCH_2; 2·09–2·04, m, 2H, $SCH_2C\mathbf{H}_2$. ^{13}C n.m.r. ($CDCl_3$) δ 139·0, C 3; 111·9, C 6; 109·3, C=**C**H_2; 65·3, C 2/4; 29·6, C 8/10; 25·3, C 9. Mass spectrum (c.i., NH_4^+) *m/z* 207 (21%), 206 (14), 205 (100), 204 (8), 106 (20).

2,2-Diphenoxy-1,3-oxathiolan (13)/1,6-Dioxa-4,9-dithiaspiro[4.4]nonane (14)

A solution of dichlorodiphenoxymethane (6) (1·72 g, 6·4 mmol) in dichloromethane (10 ml) was added dropwise over 0·5 h to a stirred solution of 2-mercaptoethanol (1·00 g, 12·8 mmol) and triethylamine (1·78 ml, 12·8 mmol) in dichloromethane (10 ml). After the addition was complete, the reaction mixture was refluxed overnight. The organic extract underwent a typical workup to afford a waxy solid (0·580 g). A portion (0·29 g) of this material was recrystallized from ethyl acetate and yielded 2,2-diphenoxy-1,3-oxathiolan (13) as a crystalline white *powder* (0·08 g), m.p. 114–114·5° (Found: C, 65·7; H, 5·1; S, 11·8. $C_{15}H_{14}O_2S_2$ requires C, 65·7; H, 5·2; S, 11·7%). I.r. ν_{max} (KBr) 3114, 3069, 2996, 2943, 2891, 1736, 1586, 1484, 1230, 1198, 1108, 1034, 984, 752 cm^{-1}. ^1H n.m.r. δ 7·31–7·22, m, 8H, ArH; 7·12–7·08, m, 2H, ArH; 4·36, t, 2H, *J* 6·0 Hz, OCH_2; 3·11, t, 2H, *J* 6·0 Hz, SCH_2. ^{13}C n.m.r. δ 153·2; 132·4, C 2; 129·1; 124·1; 120·8; 70·7, C 5; 33·9, C 4. Mass spectrum (c.i., NH_4^+) *m/z* 292 (1%), 275 (1), 232 (19), 182 (12·5), 181 (100).

The other portion of this material (0·290 g) was sublimed (50°/0·1 mmHg) and the liquid collected allowed to solidify in the freezer overnight providing 1,6-dioxa-4,9-dithiaspiro[4.4]nonane (14) as white crystals (0·122 g). ^1H n.m.r. δ 4·52, t, 4H, *J* 6·95 Hz, OCH_2; 3·57, t, 4H, SCH_2. ^{13}C n.m.r. δ 173·4, C 5; 68·4, C 2/7; 32·0, C 3/8.

1,7-Dioxa-5,11-dithiaspiro[5.5]undecane (16)/2,2-Diphenoxy-1,3-oxathian (15)

A solution of dichlorodiphenoxymethane (6) (1·460 g, 5·43 mmol) in dichloromethane (10 ml) was added dropwise over 0·5 h to a stirred solution of 3-mercaptopropan-1-ol (1·0 g, 10·85 mmol) and triethylamine (1·098 g, 10·85 mmol) in dichloromethane (10 ml). The mixture was stirred at reflux for 24 h, and the organic extract underwent typical treatment to yield a creamy solid. The solid was extracted with hot hexane (4×50 ml) and solvent removed in vacuum affording a white solid. This material, when sublimed (50°/0·2 mmHg), yielded 1,7-dioxa-5,11-dithiaspiro[5.5]undecane (16) as fine white *crystals* (0·195 g, 19%), m.p. 44–45° (Found C, 43·8; H, 6·2. $C_7H_{12}O_2S_2$ requires C, 43·7 H, 6·3%). I.r. ν_{max} (KBr) 2960, 2913, 2831, 1452, 1424, 1279, 1198, 1182, 1087, 1056, 1016, 975, 955, 905, 847, 813 cm^{-1}. ^1H n.m.r. δ 4·16, ddd, 2H, *J* 11·8, 9·1, 3·3 Hz, OCH_a; 4·07, ddd, 2H, *J* 11·7, 5·1, 4·9 Hz, OCH_b; 3·07, ddd, 2H, *J* 13·2, 9·7, 3·4, SCH_a; 2·79, ddd, 2H, *J* 13·1, 6·6, 3·6 Hz, SCH_b; 2·07–1·97, m, 2H; 1·87–1·79, m, 2H. ^{13}C n.m.r. δ 108·4, C 6; 63·7, C 2/8; 26·2, C 4/10; 24·2, C 3/9. Mass spectrum (c.i., NH_4^+) *m/z* 195 (11%), 194 (10), 193 (100), 192 (10), 74 (30).

The residual material from the sublimation was recrystallized from hexane to yield 2,2-diphenoxy-1,3-oxathian (15) as white crystals (0·100 g), m.p. 101–102°. I.r. ν_{max} (KBr) 3062, 2966, 2923, 1591, 1488, 1202, 1105, 1077, 1047, 1006, 955, 899, 847, 813 cm^{-1}. ^1H n.m.r. δ 7·33–7·28, m, 8H, ArH; 7·14–7·10, m, 2H, ArH; 4·82, dd, *J* 5·2, 5·6 Hz, OCH_2; 2·95, dd, 2H, *J* 5·6, 6·0 Hz, SCH_2; 1·97, m, 2H, $OCH_2C\mathbf{H}_2$. ^{13}C n.m.r. δ

152·6; 129·1; 124·0; 120·7; 119·0, C 2; 66·1, C 6; 27·0, C 4; 23·9, C 5. Mass spectrum (c.i., NH_4^+) *m/z* 289 (5%), 195 (73), 193 (100), 192 (21), 119 (83).

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