On the Reaction of Thioacetals with Sulphuryl Chloride

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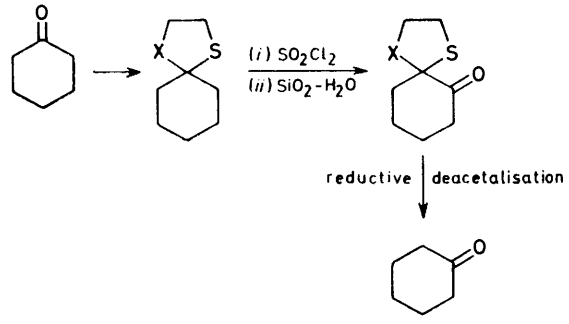
Sulphuryl chloride reacts with 1,3-oxathiolans and 1,3-dithiolans to afford unstable intermediate *trans*-2,3-dichloro-1,4-oxathians or *trans*-2,3-dichloro-1,4-dithians. Some of these intermediates can be converted on hydrolytic work up to α-ketothioacetals in reasonable yield. Intermediates in the rearrangement pathway have been identified. Reaction of 6-oxospiro[cyclohexane-1,2'-1',3'-oxathiolan] (4) with toluene-*p*-sulphonic acid gave 2,14-dioxa-11-thiatetracyclo[7.5.3.0^{1,10}.0^{3,8}]heptadec-3-en-4-one (20), a novel tetracyclic compound whose structure was determined by *X*-ray crystallography.

SULPHURYL CHLORIDE has found a large number of applications in organic synthesis, not only as a chlorinating reagent, but also as an oxidising [1,2] or sulphurating species.[3-5]

Chlorination may take place in a variety of ways; for example, on nitrogen [6] or on sulphur,[1,2,7-10] by displacement of a hydroxy-group,[11] and by addition to a double



SCHEME 1

bond [12] or an aromatic nucleus.[13-15] Chlorination may also occur on carbon atoms α to sulphides,[16,17] sulphoxides,[18-20] ethers,[21,22] carbonyl moeties,[12,23] and aromatic rings.[24,25]

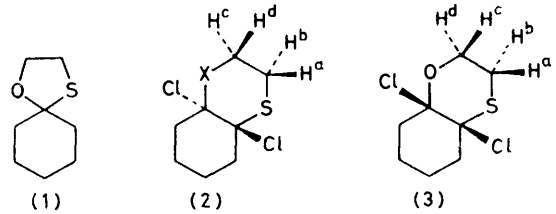
A chance observation in these laboratories indicated that α-ketothioacetals were formed by the successive action of sulphuryl chloride and wet silica gel on oxathiolans and dithiolans. This procedure appeared to have synthetic potential as a 1,2-ketone transposition reaction after reductive removal of the thioacetal group (Scheme 1).

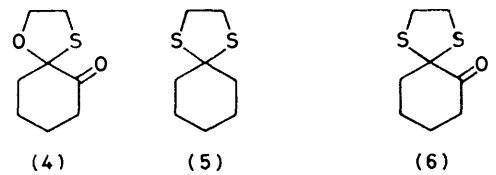
RESULTS AND DISCUSSION

Hence, treatment of the oxathiolan (1) with 2 mol. equiv. of sulphuryl chloride in carbon tetrachloride solution at 0 °C led to complete formation of an unstable intermediate after 30—60 min. The 60-MHz ^{1}H n.m.r. spectrum of this intermediate was complex; however, at 100 MHz it was shown to consist of a simple four-spin system, along with other resonances which are in accord with the structure (2a). Analysis of the spectrum together with ^{1}H n.m.r. computer-spectral simulation shows two large *gem* coupling constants and a third large coupling arising from a *transoid-vic* proton arrangement, marked H^b and H^d in the structure. The coupling between H^a and H^c is only 1.7 Hz, indicating a dihedral angle of *ca.* 60° (or 120°). Had the intermediate been *cis*-fused, as in (3), the dihedral angles H^a–H^c and H^b–H^d would have been the same and therefore would be expected to have similar-sized coupling constants.

Work-up of the intermediate by removal of the solvents and excess of reagents under reduced pressure gave (2a) as a colourless solid contaminated with small amounts (5—10%) of (4).

Alternatively, addition of 2 mol equiv. of triethylamine to the CCl_4 solution of (2a) at 0 °C, followed by hydrolysis with wet silica gel (or preparative layer chromatography), gave the α-keto-oxathiolan (4) in 95% yield. This yield compares well with the literature figure of 40% for the preparation of (4) by a different route.[26] The ^{1}H n.m.r. spectrum of (4) shows two multiplets centred at δ 2.9 and 4.1, corresponding to the intact oxathiolan ring.



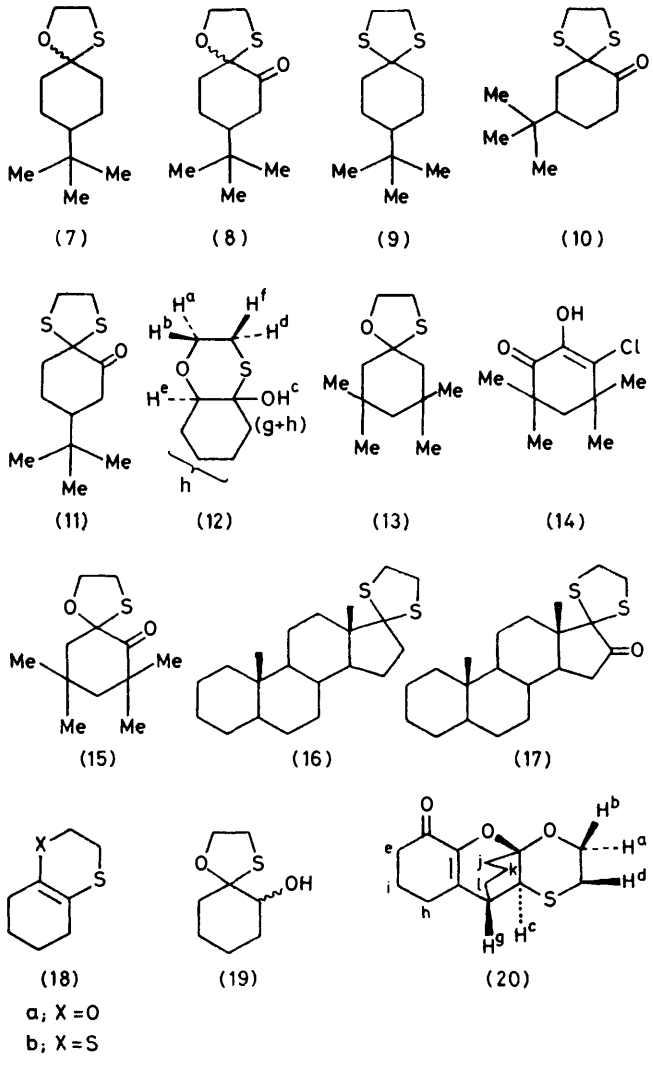


On reaction of the 1,3-dithiolan derivative (5) with sulphuryl chloride an intermediate corresponding to (2b) was similarly formed. The ^{1}H n.m.r. of (2b) showed two pairs of doublets centred at δ 2.8 and 3.74.

Work-up with triethylamine and wet silica gel afforded the α-ketodithiolan (6) in 86% yield.

Encouraged by these results we then investigated substituted examples of oxathiolans and dithiolans.

Thus, treatment of the 4-t-butyloxathiolans (7) with sulphuryl chloride gave, on hydrolytic work-up, a 65% yield of the desired α-keto-oxathiolans (8). However,



similar treatment of the dithiolan derivative (9) gave an inseparable mixture of products, which after Raney nickel desulphurisation, gave largely 4-t-butylcyclohexanone by g.l.c. thus implying that the major product of the sulphuryl chloride reaction was (10) rather than the desired product (11).

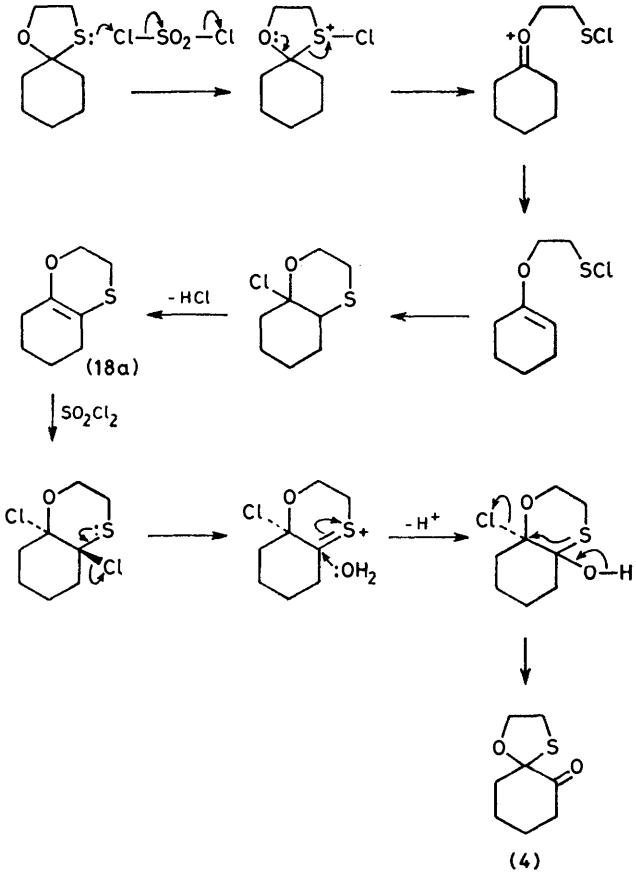
Various methods for reductive removal of the oxathiolan moiety were unsuccessful. For example, calcium–liquid ammonia reduction of (4) afforded only a 21% yield of a product characterised as (12). Sodium amalgam reduction gave rise to a mixture of products containing *ca.* 50% cyclohexanone by g.l.c.

The tetramethyloxathiolan (13), on reaction with SO_2Cl_2 followed by wet silica gel, gave a 61% yield of the crystalline chloro-derivative (14) plus other minor products but none of the desired keto-oxathiolan (15).

Reaction of the androstan-17-one dithiolan (16) disappointingly gave a complicated mixture of reaction products which could not be separated cleanly by preparative-layer chromatography, although one fraction did show an i.r. carbonyl stretching frequency at 1 750 cm^{-1}, which could correspond to (17).

In order to explain the formation of the α-ketoacetals from the corresponding acetals, we propose a mechanism as outlined in Scheme 2. The possible intermediacy of the dihydro-oxathiin (18a) in Scheme 2 was tested by preparing an authentic sample and subjecting it to the reaction conditions. Hence borohydride reduction of (4) gave the alcohols (19) which on reaction with P_2O_5 produced (18a) in high yield.[27] This then with 1 mol equiv. of SO_2Cl_2 rapidly gave (2a) quantitatively (by ^1H n.m.r.). If (1) was reacted with only 0.5 mol equiv. of sulphuryl chloride it was possible to observe the intermediacy of (18a) spectroscopically.

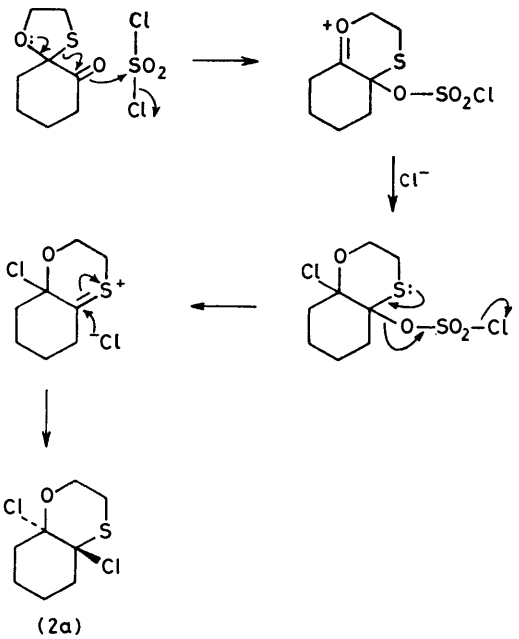
In a similar series of reactions we also prepared (18b) which readily afforded the intermediate (2b) with SO_2Cl_2, and on hydrolytic work-up gave (6) in 87%



SCHEME 2

yield. We further showed that (4) reacted with SO_2Cl_2 at room temperature in CCl_4 to give the intermediate (2a), which was identified by ^1H n.m.r. spectroscopy (Scheme 3).

Finally, the α-keto-oxathiolan (4) was found to be unstable to acid and on heating in benzene with

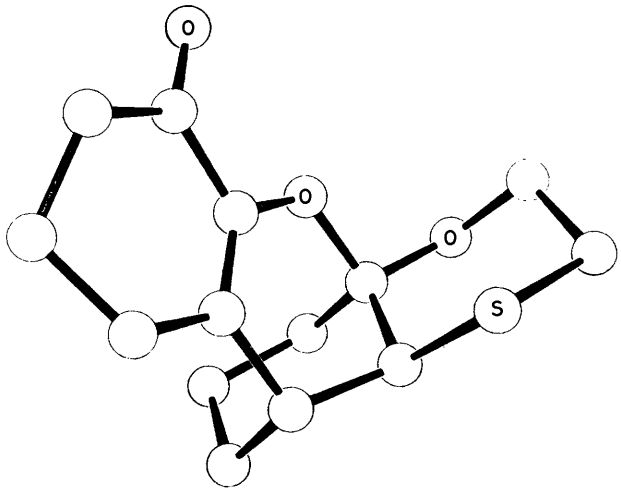


(2a)

SCHEME 3

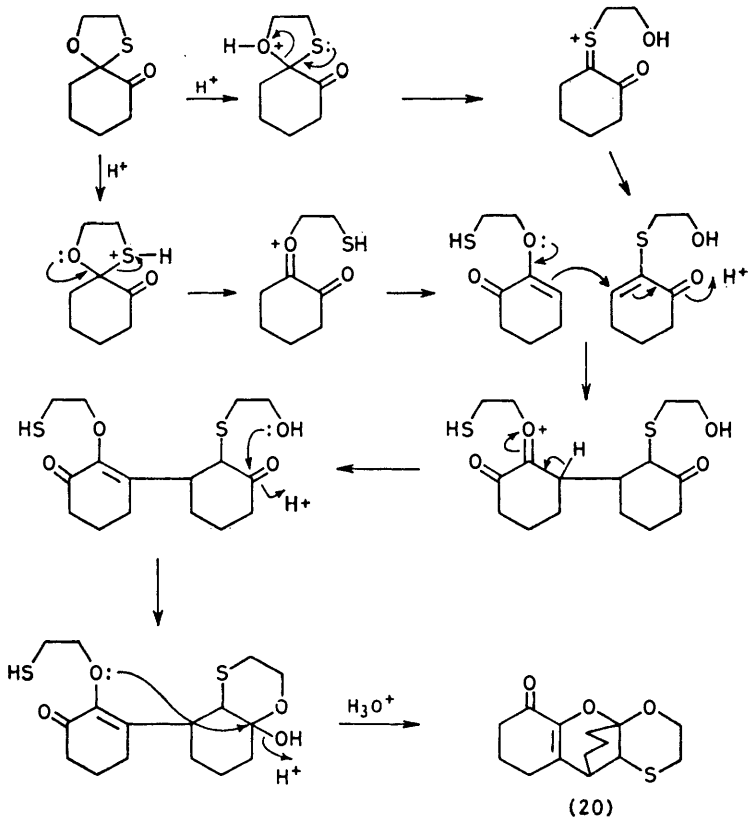
toluene-*p*-sulphonic acid a novel tetracyclic species (20) could be isolated (83%). The structure of (20) was confirmed by *X*-ray crystallography (Figure).

A possible rationale for the formation of (20) is shown in Scheme 4. The form in which the final two-carbon unit is lost is not known. Corresponding rearrangement of (6) was not observed. Molecules of the general



structure (2) do not appear to have been previously reported, although α-ketothioacetals have found some application in synthesis.[28]

We hope our brief incursion into the area will highlight some of the potential pitfalls.



(20)

SCHEME 4

EXPERIMENTAL

Melting points were recorded using a Kofler hot stage apparatus. Infra-red spectra were recorded on Perkin Elmer 197 and 298 spectrometers; nuclear magnetic resonance spectra were recorded using Varian EM 360 and XL-100 and Bruker WM 250 machines. Mass spectra were recorded on a V.G. Micromass 7070 spectrometer. ^{1}H N.m.r. spectral simulations were carried out using an Imperial College STEK programme.

General Procedure for Reaction of Thioacetals with Sulphuryl Chloride.—A solution of sulphuryl chloride (2.7 g, 20 mmol) in carbon tetrachloride (10 ml) was added dropwise to a stirred solution of thioacetal (10 mmol) in carbon tetrachloride (50 ml) at 0 °C over a period of 30—60 min (removal of the solvent at this point gave the intermediate dichlorides, which could be examined spectroscopically). A solution of triethylamine (2.0 g, 20 mmol) in carbon tetrachloride (10 ml) was added dropwise to the above solution of the intermediate at 0 °C. The mixture was allowed to warm to room temperature, filtered, washed with water (3 × 50 ml), and concentrated *in vacuo*. Silica gel (5 g, Merck Kieselgel H, type 60) and water (5 ml) were added and the mixture stirred until hydrolysis was complete. The mixture was filtered, washed with water (50 ml), dried over $MgSO_4$, and the solvent was removed under reduced pressure to afford the product.

Reaction of (1).—Spiro[cyclohexane-1,2′-1′,3′-oxathiolan] (1) (10.0 g) with sulphuryl chloride (17.1 g) in CCl_4 gave (2a); $\nu_{max.}$ 2 900, 1 450, 1 405, 1 380, 1 310, 1 300, 1 250, 1 250, 1 240, 1 220, 1 195, 1 155, 1 100, 1 045, 1 020, 985, 960, 940, 920, 850, and 845 cm^{-1}; δ (CCl_4, 100 MHz) 1.4—2.4 (8 H, m), 2.50 (1 H, ddd, *J* 1.7, 2.7, and 13.7 Hz, H^a), 3.74 (1 H, ddd, *J* 4.0, 12.8, and 13.7 Hz, H^b), 4.12 (1 H, ddd, *J* 1.7, 4.0, and 12.2 Hz, H^c), and 4.59 (1 H, ddd, *J* 2.7, 12.2, and 12.8 Hz, H^d); *m/e* 228, 227, 226, 225, 193, 191, 172, 156, 155, and 154. Hydrolysis of (2a) gave 6-*oxospiro*[*cyclohexane*-1,2′-1′,3′-*oxathiolan*] (4) (10.3 g, 94.8%), b.p. 74—77 °C at 0.7 mmHg; $\nu_{max.}$ 2 900, 1 720, 1 445, 1 430, 1 340, 1 300, 1 260, 1 220, 1 150, 1 110, 1 080, 1 010, 950, 910, 890, and 840 cm^{-1}; δ ($CDCl_3$, 100 MHz) 1.4—2.7 (8 H, m), 2.8—3.0 (2 H, m), and 4.0—4.4 (2 H, m) (Found: C, 55.6; H, 7.1; S, 18.6. $C_8H_{12}O_2S$ requires C, 55.76; H, 7.03; S, 18.62%).

Reaction of (5).—Spiro[cyclohexane-1,2′-1′,3′-dithiolan] (5) (1.36 g, 7.8 mmol) with sulphuryl chloride (2.11 g, 16 mmole) in CCl_4 gave (2b); $\nu_{max.}$ 2 900, 1 440, and 1 428 cm^{-1}; δ ($CDCl_3$, 100 MHz) 1.45—2.6 (8 H, m), 2.8 (2 H, d, *J* 12 Hz), and 3.74 (2 H, d, *J* 12 Hz). Hydrolysis of (2b) gave an oil which on trituration with light petroleum afforded 6-oxospiro[cyclohexane-1,2′-1′,3′-dithiolan] (6) (1.15 g, 79%) as white crystals, m.p. 55—57 °C (lit.,[29] 56—57 °C); $\nu_{max.}$ 2 940, 2 860, 1 715, 1 680, 1 450, 1 438, 1 425, 1 270, 1 220, and 1 120 cm^{-1}; δ (CCl_4) 1.71—2.21 (4 H, m), 2.21—2.6 (2 H, m), 2.6—2.91 (2 H, m), and 3.39 (4 H, s).

Reaction of (7).—8-t-Butylspiro[cyclohexane-1,2′-1′,3′-oxathiolan] (7) (1.25 g) with sulphuryl chloride (1.6 g) in CCl_4 gave the intermediate; δ (CCl_4) 1.0 (9 H, s), 1.1—2.3 (7 H, m), 2.5 (1 H, m), and 3.3—5.0 (3 H, m). Hydrolysis gave 8-*t-butyl*-6-*oxospiro*[*cyclohexane*-1,2′-1′,3′-*oxathiolan*] (8) (0.43 g, 32%); $\nu_{max.}$ 2 900, 1 725, 1 480, 1 470, 1 440, 1 420, 1 395, 1 365, 1 265, 1 235, 1 145, 1 090, 1 045, 1 110, 970, 960, 915, 880, and 800 cm^{-1}; δ ($CDCl_3$) 0.8 (9 H, m) 1.1—2.6 (7 H, m), 2.9—3.1 (2 H, m), and 4.1—4.3 (2 H, m) (Found: C, 62.85; H, 9.0. $C_{12}H_{20}O_2S$ requires C, 63.11; H, 8.83%).

Reaction of (13).—7,7,9,9-Tetramethylspiro[cyclohexane-1,2′-1′,3′-oxathiolan] (13) (1.0 g) under the usual conditions gave pale yellow crystals after hydrolytic work-up. Sublimation at 15 mmHg gave 8-*chloro*-3,3,5,5-*tetramethylcyclohexane*-1,2-*dione* (14) (0.48 g, 61%) as colourless crystals, m.p. 73—74 °C; $\nu_{max.}$ 3 420, 2 900, 1 680, 1 645, 1 460, 1 375, 1 365, 1 320, 1 245, 1 070, and 640 cm^{-1}; δ ($CDCl_3$) 1.2 (7 H, s), 1.3 (6 H, s), and 2.05 (2 H, s) (Found: C, 59.0; H, 7.45; Cl, 17.55. $C_{10}H_{15}ClO_2$ requires C, 59.26; H, 7.46; Cl, 17.49%).

Preparation of 1-*Thia*-4-*oxa*-10-*hydroxy*-trans-*decalin* (12).—Spiro[cyclohexanone-2,2′-1′,3′-oxathiolan] (4) (799 mg) was added to a stirred solution of calcium (1.84 g) in liquid ammonia (100 ml) and THF (20 ml). After re-appearance of a deep violet colour, ethanol (50 ml) was added and the mixture allowed to reach room temperature overnight. Work-up followed by preparative-layer chromatography resulted in the isolation of colourless crystals of 1-*thia*-4-*oxa*-10-*hydroxy*-trans-*decalin* (12) (170 mg, 21%); $\nu_{max.}$ 3 400, 2 960, 2 930, 2 855, 1 460, 1 375, 1 310, 1 295, 1 265, 1 255, 1 240, 1 230, 1 210, 1 190, 1 150, 1 140, 1 110, 1 090, 990, 950, 910, 840, and 830 cm^{-1}; δ ($CDCl_3$, 250 MHz) 4.25 (1 H, ddd, *J* 11.8, 3.5, and 1.8 Hz, H^a), 3.86 (1 H, ddd, *J* 11.8, 12.3, and 2.2 Hz, H^b), 3.72 (1 H, dd, *J* 5 and 11 Hz, H^c), 3.32 (1 H, ddd, *J* 3.5, 12.3, and 14.0 Hz, H^d), 3.19 (1 H, br s, H^e), 2.40 (1 H, ddd, *J* 1.8, 2.2, and 14.0 Hz, H^f), 1.90—2.02 (1 H, m, H^g), and 1.15—1.83 (7 H, m, H^h) (Found: C, 55.05; H, 8.25; $C_8H_{14}O_2S$ requires C, 55.14; H, 8.10%).

Preparation of 6-*Hydroxyspiro*[*cyclohexane*-1,2′-1′,3′-*oxathiolan*] (19).—6-Oxospiro[cyclohexane-1,2′-1′,3′-oxathiolan] (4) (946 mg) was dissolved in methanol (100 ml) and sodium borohydride (0.2 g) added over 30 min. The mixture was concentrated, water (50 ml) added, and the products extracted with chloroform (2 × 50 ml). The solvent was removed under reduced pressure to give an oil which was purified by low-pressure column chromatography to afford 6-*hydroxyspiro*[*cyclohexane*-1,2′-1′,3′-*oxathiolan*] (19) (629 mg, 70%) as a colourless oil; $\nu_{max.}$ 3 470, 2 940, 2 860, 1 460, 1 445, 1 435, 1 390, 1 350, 1 265, 1 240, 1 220, 1 150, 1 070, 1 010, and 990 cm^{-1} (Found: C, 55.0; H, 8.3; $C_8H_{14}O_2S$ requires C, 55.14; H, 8.1%).

Preparation of 2-*Oxa*-5-*thiabicyclo*[4.4.0]*dec*-1-*ene* (18a).—Compound (19) (503 mg) was dissolved in benzene (50 ml) and P_2O_5 (2 g) was added. The mixture refluxed for 2 h, cooled, and washed with water (2 × 50 ml). Removal of the solvent under reduced pressure gave 2-*oxa*-5-*thiabicyclo*[4.4.0]*dec*-1-*ene* (18a) (358 mg, 79%) as a pale yellow oil; $\nu_{max.}$ 2 950, 2 930, 2 880, 2 860, 2 840, 1 660, 1 450, 1 440, 1 375, 1 335, 1 295, 1 230, 1 140, 1 045, 1 020, and 995 cm^{-1}; δ 4.1—4.3 (2 H, m), 2.8—3.0 (2 H, m), and 1.1—2.2 (8 H, m) (Found: M^+, 156.060 7. $C_8H_{12}OS$ requires *M*, 156.060 9).

Reaction of (18a) *with Sulphuryl Chloride.*—The dihydro-1,4-oxathiin (18a) (357 mg) was dissolved in CCl_4 (20 ml), cooled to 0 °C, and SO_2Cl_2 (0.3 ml) added. After 30 min ^{1}H n.m.r. showed that (18a) had been quantitatively converted to (2a).

Reaction of (18b) *with Sulphuryl Chloride.*—The dihydro-1,4-dithiin (18b) [27] (280 mg, 1.63 mmol) in CCl_4 (15 ml) with with SO_2Cl_2 (0.26 ml, 3.26 mmol) after 30 min, gave a solution which by ^{1}H n.m.r. contained (2b) as the only organic product. Work-up of the mixture in the usual way gave (6) (0.29 g, 99%) which on trituration with light petroleum gave crystalline (6) (0.26 g, 87%) identical by t.l.c., m.p., and ^{1}H n.m.r. to previous samples.

Reaction of (4) *with Sulphuryl Chloride.*—The α-keto

oxathiolan (1.0 g) (4) was dissolved in CCl_4 (20 ml) cooled to 0 °C and sulphuryl chloride (1 ml) was added. After 30 min, ^1H n.m.r. showed that (4) had been quantitatively converted to (2a).

Rearrangement of (4) *with Toluene*-p-*sulphonic Acid.*—Compound (4) (120 mg) was refluxed in benzene (15 ml) in the presence of toluene-*p*-sulphonic acid (10 ml) for 3 days. The cooled solution was washed with water, and solvent removed under reduced pressure to give *2,14-dioxa-11-thiatetracyclo*[7.5.3.$0^{1,10}$.$0^{3,8}$]*heptadec-3-en-4-one* (20) (77 mg, 83%), m.p. 207—209 °C; $\nu_{max.}$ 2 900, 1 670, 1 630, 1 460, 1 420, 1 370, 1 300, 1 190, 1 185, 1 150, 1 140, 1 110, 1 070, 1 050, 995, 960, 950, and 920 cm^{-1}; δ_H ($CDCl_3$) (250 MHz) 1.34—1.94 (8 H, m, $H^{i,j,k}$), 2.07—2.21 (4 H, m, $H^{f,g,h}$), 2.32 (2 H, dd, *J* 6.0 and 7.5 Hz, H^e), 2.85 (1 H, ddd, *J* 3.2, 12.25, and 12.4 Hz, H^d), 3.01 (1 H, s, H^c), 3.64 (1 H, ddd, *J* 2.2, 3.2, and 12.0 Hz, H^b), and 4.03 (1 H, ddd, *J* 2.0, 12.0, and 12.25 Hz, H^a), δ_C [$(CD_3)_2SO$ (25 MHz)] 207.0 (C-14), 190.9 (C-8), 144.3 (C-3), 129.5 (C-1), 95.4 (C-13), 60.7 (C-10), 40.8, 39.4, 37.7, 28.7, 27.4, 26.2, 22.0, and 18.8 (Found: C, 62.8; H, 6.8; S, 12.1. $C_{14}H_{18}O_3S$ requires C, 63.13; H, 6.81; S, 12.04%).

Crystallographic Data.—$C_{14}H_{18}O_3S$, $M = 266.4$. Triclinic, $a = 8.986(1)$, $b = 11.319(1)$, $c = 6.930(1)$ Å, $\alpha = 75.86(1)$, $\beta = 95.60(1)$, $\gamma = 109.44(1)°$, $U = 644.4$ Å^3, $F(000) = 284$, $Z = 2$, $D_c = 1.378$ g cm^{-3}, space group $P\bar{1}$, $\mu(Cu\text{-}K_\alpha) = 21$ cm^{-1}. 2 204 Reflections were measured on a diffractometer (to $\theta \leqslant 65°$) with Cu-K_α radiation; of these 97 were reckoned unobserved and 3 removed for extinction. The structure was solved using the program MULTAN and refined to *R* 0.039 using the '*X*-Ray '72' program system. No absorption corrections were applied. The two S–C(sp^3) distances do not differ significantly and have an average value of 1.812 Å.

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