Studies of Heterocyclic Compounds. Part XVII.[1] Synthesis of 1,6-Dioxa-6a-thia- and 1,6-Dioxa-6a-selena-pentalenes [2]

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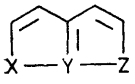
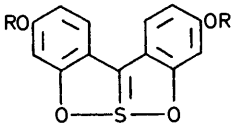
1,6-Dioxa-6a-thia- and 1,6-dioxa-6a-selena-pentalenes, two new classes of hypervalent heterocyclic compound, have been synthesised by the reaction of pyran-4-thiones and -4-selones, respectively, with thallium(III) trifluoroacetate, and treatment of the resulting labile thallium-containing pyrylium trifluoroacetates with water. 1,6-Dioxa-6a-thiapentalene was also formed in low yield by ring-opening of pyran-4-thione with sodium hydroxide in aqueous dimethyl sulphoxide, and intramolecular oxidative coupling of the resulting anion with potassium ferricyanide. ^{1}H N.m.r. spectra of symmetrically substituted 1,6-dioxa-6a-thia- and 1,6-dioxa-6a-selena-pentalenes show real or time averaged C_{2v} symmetry. The pattern of the spectrum of 1,6-dioxa-6a-thiapentalene was unaffected by change of solvent ($CDCl_3$, CS_2, or CD_3CN) or by lowering the temperature of a solution in $CDCl_3$ (to −50°) or CS_2 (to −90°). The i.r. spectra of 1,6-dioxa-6a-thiapentalene, 1,6-dioxa-6a-selenapentalene, and their 2,5-dimethyl derivatives show no absorption in the double bond region above 1515 cm^{-1}. The significance of the ^{1}H n.m.r. and i.r. spectra of 1,6-dioxa-6a-thia- and 1,6-dioxa-6a-selena-pentalenes is discussed in relation to structure. Thionation of 1,6-dioxa-6a-thiapentalene with phosphorus pentasulphide gave 6a-thiathiophthen. 1,6-Dioxa-6a-thiapentalene underwent sulphur–oxygen exchange in boiling thioacetic acid to give a mixture of 6a-thiathiophthen and 1-oxa-6,6a-dithiapentalene. Thionation of 1,6-dioxa-6a-selenapentalene with phosphorus pentasulphide afforded 6a-selenathiophthen.

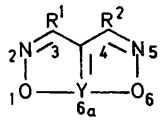
THE concept of electron-rich three-centre bonding has been used [3] to explain the unusual structure and bonding of the heteroatom sequence (X–Y–Z) in compounds of the 6a-thiathiophthen type (1). In the three-centre bonding scheme the non-bonding orbital concentrates negative charge on the end atoms, and this type of bond is strongest when the central atom is relatively electropositive and the end atoms have high electronegativities. The heteroatom sequence (O–Y–O) in oxygen analogues (1; X = Z = O) of 6a-thiathiophthen (1; X = Y = Z = S) should therefore be a



(1)



(2) R = H
(3) R = Me
(4) R = MeCO



(5)

stable one. At the beginning of our work, three complex derivatives (2)—(4) of the 1,6-dioxa-6a-thiapentalene system (1; X = Z = O, Y = S) had been prepared,[4] and a crystallographic structure determination of compound (3) had been carried out.[5] The preparation of a 1,6-dioxa-6a-thia-2,5-diazapentalene (5; R^1R^2 = $CH_2{\cdot}CMe_2{\cdot}CH_2$, Y = S) [6] and of numerous selenium (5; Y = Se) † [7] and tellurium analogues (5; Y = Te) [7c] had also been described, and structure (5) has been confirmed by *X*-ray crystallographic structure determinations of the thia-compound (5; R^1R^2 = $CH_2{\cdot}CMe_2{\cdot}CH_2$, Y = S) [8] and the selena-compound (5; R^1R^2 = $CH_2{\cdot}CMe_2{\cdot}CH_2$, Y = Se).[7a,9] We wished, however, to obtain the simplest possible 1,6-dioxa-analogues for structural studies and for studies of reactivity. In this paper we describe syntheses of 1,6-dioxa-6a-thia- (1; X = Z = O, Y = S) and 1,6-dioxa-6a-selena-pentalenes (1; X = Z = O, Y = Se) which involve intramolecular sulphur–oxygen and selenium–oxygen oxidative coupling.

Syntheses.—Recent work involving thallium(III) compounds in synthesis [10] suggested that the energetically favourable process $Tl^{III} \longrightarrow Tl^{I}$ (E° − 1·25 V) could be harnessed as a driving force to effect sulphur–oxygen oxidative coupling. We have found that pyran-4-thione (6) reacts immediately with thallium(III) trifluoroacetate in acetonitrile to give a pale brown solution containing the labile pyrylium salt (11) (Scheme 1). This salt is ring-opened instantaneously by water, and the resulting intermediate (12) spontaneously loses thallium(I) trifluoroacetate, with concomitant sulphur–oxygen bond formation, to give 1,6-dioxa-6α-thiapentalene (13) in good yield (61%). At an early stage of the investigation, sodium hydroxide was tried in place of water in order to facilitate the ring-opening process (11) ⟶ (12), but the yield of 1,6-dioxa-6a-thiapentalene (56%) was not substantially different, although the crude product was cleaner and easier to purify.

Thallium(III) nitrate was also investigated as oxidant. However, the yield of 1,6-dioxa-6a-thiapentalene was only 35%, and in all subsequent work the trifluoroacetate was used.

The reaction sequence in Scheme 1 constitutes a

† 1,6-Dioxa-6a-selena-2,5-diazapentalenes (5; Y = Se) were first prepared in 1949 (F. E. King and D. G. I. Felton, *J. Chem. Soc.*, 1949, 274) but were incorrectly formulated.

[1] Part XVI, R. M. Christie, A. S. Ingram, D. H. Reid, and R. G. Webster, *J.C.S. Perkin I*, 1974, 722.

[2] Preliminary communication, D. H. Reid and R. G. Webster, *J.C.S. Chem. Comm.*, 1972, 1283.

[3] R. Gleiter and R. Hoffmann, *Tetrahedron*, 1968, **24**, 5899.

[4] I. H. Pomerantz, L. J. Miller, E. Lustig, D. Mastbrook, E. Nansen, R. Barron, N. Oates, and J.-Y. Chen, *Tetrahedron Letters*, 1969, 5307; I. H. Pomerantz, L. J. Miller, R. Barron, D. Mastbrook, and I. Egry, *Tetrahedron*, 1972, **28**, 2183.

[5] R. D. Gilardi and I. L. Karle, *Acta Cryst.*, 1971, **B27**, 1083.

[6] R. J. S. Beer and A. J. Poole, *Tetrahedron Letters*, 1972, 1835.

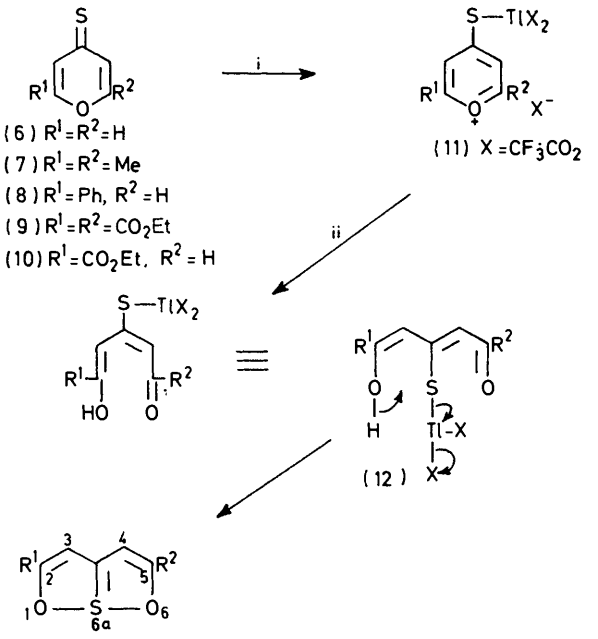
[7] (*a*) R. J. S. Beer, J. R. Hatton, E. C. Llaguno, and I. C. Paul, *Chem. Comm.*, 1971, 594; (*b*) D. Paquer, M. Perrier, and J. Vialle, *Bull. Soc. chim. France*, 1970, 4517; (*c*) M. Perrier and J. Vialle, *ibid.*, 1971, 4591.

[8] E. C. Llaguno and I. C. Paul, *Tetrahedron Letters*, 1973, 1565.

[9] E. C. Llaguno and I. C. Paul, *J.C.S. Perkin II*, 1972, 2007.

[10] E. C. Taylor and A. McKillop, *Accounts Chem. Res.*, 1970, **3**, 338.

general synthesis of 1,6-dioxa-6a-thiapentalenes, and the derivatives (14)—(17) were readily obtained from the corresponding thiones (7)—(10). It is necessary to use water in the ring opening–cyclisation steps for the



(13) $R^1 = R^2 = H$
(14) $R^1 = R^2 = Me$
(15) $R^1 = Ph$, $R^2 = H$
(16) $R^1 = R^2 = CO_2Et$
(17) $R^1 = CO_2Et$, $R^2 = H$
(18) $R^1 = R^2 = CO_2H$
(19) $R^1 = CO_2H$, $R^2 = H$

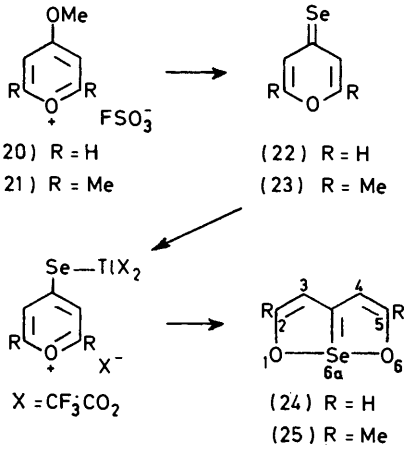
SCHEME 1 Reagents: i, TlX_3; ii, H_2O(NaOH)

preparation of the esters (16) and (17), since these compounds are rapidly hydrolysed by cold alkali. The acids (18) and (19) were subsequently obtained by brief treatment of the esters (16) and (17) with dilute aqueous ethanolic sodium hydroxide.

Attempts to isolate crystalline salts from solutions of the intermediate trifluoroacetate (11; $R^1 = R^2 = H$) in acetonitrile, for example by the addition of 70% perchloric acid, were unsuccessful. It was later found that the intermediate (11; $R^1 = R^2 = H$) is very sensitive to traces of water absorbed from the atmosphere by acetonitrile during the usual laboratory operations. An attempted spectroscopic identification of the intermediate (11; $R^1 = R^2 = H$) was also unsuccessful. The ^1H n.m.r. spectrum of a solution of pyran-4-thione (6) in CD_3CN shows two multiplets centred at δ 7·10 (3- and 5-H) and 7·64 (2- and 6-H), together with a small water peak at δ 2·09. Addition of a slight excess of thallium(III) trifluoroacetate in CD_3CN to this solution gave a solution whose spectrum showed only two doublets arising from 1,6-dioxa-6a-thiapentalene (13) [δ 7·05 (3- and 4-H) and 8·73 (2- and 5-H) (J 2·7 Hz)].*

We have successfully modified the foregoing synthesis to provide a route to 1,6-dioxa-6a-selenapentalenes (1; X = Z = O, Y = Se) by using pyran-4-selones in place of the 4-thiones (Scheme 2). The usefulness of this modification is unfortunately limited by the poor stability of pyran-4-selones, which lose selenium with varying ease to form 4,4′-bipyranylidene derivatives (*cf.* the instability of thiopyran-4-selones [11]). The moderately stable selones (22) and (23) gave 1,6-dioxa-6a-selenapentalene (24) (15%) and its dimethyl derivative (25) (1·9%), respectively. Compound (22), previously unknown, and its known dimethyl derivative (23),[12] were prepared by a minor modification of the method of Traverso,[12] involving the methylation of 4-pyrone and 2,6-dimethyl-4-pyrone with methyl fluorosulphonate, and treatment of the resulting pyrylium fluorosulphonates (20) and (21) with aqueous sodium hydrogen selenide.

An attempt to synthesise 6-methyl-1-oxa-6a-thia-6-azapentalene (26) by treating a solution of the intermediate (11; $R^1 = R^2 = H$) in acetonitrile with aqueous methylamine gave 1,6-dioxa-6a-thiapentalene (13) (48%) as the only detectable product. Since the intermediate (11; $R^1 = R^2 = H$) is rapidly attacked by traces of water to give compound (13), the experiment was repeated, but with the intermediate (11; $R^1 = R^2 = H$) prepared in the presence of molecular sieves. 1,6-Dioxa-6a-thiapentalene was again the only product,



SCHEME 2

but its yield was lower (3·4%). 1-Oxa-6a-thia-6-azapentalenes, for example (27) and (28), are stable substances,[13] and in view of the mildness of the reaction conditions we conclude that compound (26) had not been formed.

We have previously shown [14] that pyran-4-thione (6) reacts with sodium sulphide in aqueous dimethyl

* See Table, footnotes *a* and *b*.

[11] D. H. Reid, *J. Chem. Soc.* (*C*), 1971, 3187.

[12] G. Traverso, *Ann. Chim.* (*Italy*), 1957, **47**, 3.

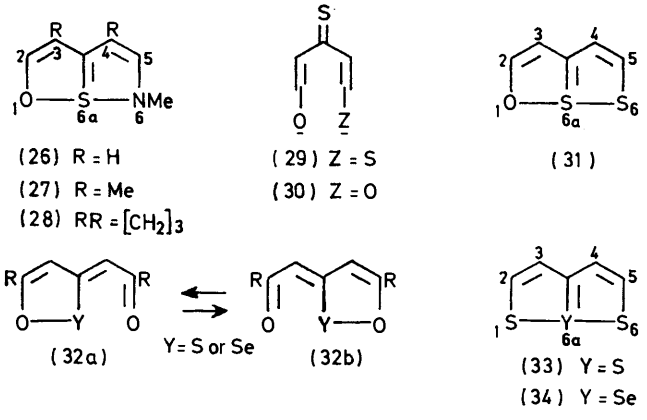
[13] D. H. Reid and J. D. Symon, unpublished data.

[14] D. H. Reid and R. G. Webster, *J.C.S. Perkin I*, 1972, 1447.

sulphoxide to form the intermediate (29) which, when oxidised with potassium ferricyanide, gives 1-oxa-6,6a-dithiapentalene (31) in a preparatively useful synthesis. We attempted to adapt this synthesis to furnish 1,6-dioxa-6a-thiapentalene (13) *via* the intermediate (30), by using sodium hydroxide in place of sodium sulphide for ring opening of pyran-4-thione. 1,6-Dioxa-6a-thiapentalene was indeed formed, but in low yield (2·3%). Further work using potassium ferricyanide to effect sulphur–oxygen oxidative coupling was therefore abandoned.

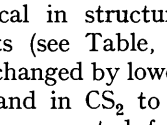
Structural and Spectral Studies.—The dioxathiapentalenes (13)—(19) and the dioxaselenapentalenes (24) and (25) represent two new classes of hypervalent [15] heterocyclic compound. 1,6-Dioxa-6a-thiapentalene (13), 1,6-dioxa-6a-selenapentalene (24), and the corresponding dimethyl derivatives (14) and (25) are colourless, volatile, low-melting solids, which are very soluble in organic solvents including cold petroleum. They become brown on prolonged exposure to sunlight but are stable indefinitely in the dark below room temperature. The pale yellow dioxathiapentalenes (15)—(19) are stable.

The ^{1}H n.m.r. spectra of the dioxathiapentalenes (13), (14), (16), and (18), and of the dioxaselenapentalenes (24) and (25) (Table) show magnetic equivalence of



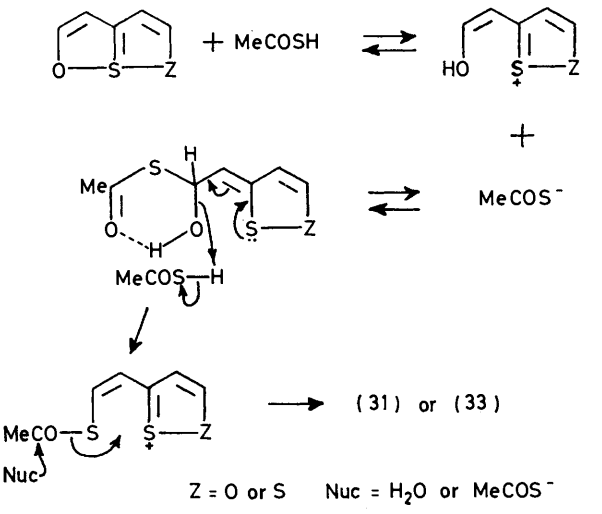
ring protons or substituents at the pairs of sites C-2, C-5 and C-3, C-4. 1,6-Dioxa-6a-thiapentalene (13) was studied in detail. Its spectra in $CDCl_3$, CS_2, and CD_3CN were identical in structure and consisted of one pair of doublets (see Table, footnotes *a* and *b*). This pattern was unchanged by lowering of temperature, in $CDCl_3$ to −50° and in CS_2 to −90°, below which decreasing solubility prevented further study. These results demonstrate that symmetrically substituted di-

† This conclusion is valid unless (*a*) the interconversion (32a) ⇌ (32b) is extremely fast on the i.r. time-scale or (*b*) the carbonyl group is so highly polarised [structure (i)] that the C····O absorption falls below 1500 cm^{-1}.


(i)

[15] J. I. Musher, *Angew. Chem. Internat. Edn.*, 1969, **8**, 54.

oxathiapentalenes and dioxaselenapentalenes in solution possess real or time-averaged C_{2v} symmetry. The i.r. spectra (CCl_4) of the dioxathiapentalenes (13) and (14) and of the dioxaselenapentalenes (24) and (25) show



SCHEME 3

no absorption in the double bond region above 1515 cm^{-1}.

Chemical shifts (δ) in the 100 MHz ^{1}H n.m.r. spectra of the 1,6-dioxa-6a-thiapentalenes (13)—(19) and the 1,6-dioxa-6a-selenapentalenes (24) and (25) (solutions in $CDCl_3$ unless otherwise stated; *J* in Hz)

	Proton signals (δ) *			
	R^1/R	3-H	4-H	R^2/R
(13)	8·64(d) [a] $J_{2,3}$ 2·8 [b]	6·90(d) [a] $J_{3,2}$ 2·8 [b]	6·90(d) [a] $J_{4,5}$ 2·8 [b]	8·64(d) [a] $J_{5,4}$ 2·8 [b]
(13) [c]	8·54(d) [a] $J_{2,3}$ 2·7 [b]	6·81(d) [a] $J_{3,2}$ 2·7 [b]	6·81(d) [a] $J_{4,5}$ 2·7 [b]	8·54(d) [a] $J_{5,4}$ 2·7 [b]
(13) [d]	8·72(d) [a] $J_{2,3}$ 2·7 [b]	7·04(d) [a] $J_{3,2}$ 2·7 [b]	7·04(d) [a] $J_{4,5}$ 2·7 [b]	8·72(d) [a] $J_{5,4}$ 2·7 [b]
(14)	2·32(d) $J_{2\text{-Me},3}$ 0·4	6·49(q) $J_{3,2\text{-Me}}$ 0·4	6·49(q) $J_{4,5\text{-Me}}$ 0·4	2·32(d) $J_{5\text{-Me},4}$ 0·4
(15)	7·40— 7·47(m) [e] 7·86— 7·96(m) [f]	7·23	6·85(d) $J_{4,5}$ 2·6	8·58(d) $J_{5,4}$ 2·6
(16)	1·42 (t, Me) 4·43 (q, CH_2) J_{Me,CH_2} 7·2	7·65	7·65	1·42 (t, Me) 4·43 (q, CH_2) J_{Me,CH_2} 7·2
(17)	1·41 (t, Me) 4·41 (q, CH_2) J_{Me,CH_2} 7·2	7·51	7·10(d) $J_{4,5}$ 2·5	8·75(d) $J_{5,4}$ 2·5
(18) [g,h]	5·51br [i]	7·87	7·87	5·51br [i]
(19) [h]	7·15br [j]	7·65	7·34(d) $J_{4,5}$ 2·5	8·95(d) $J_{5,4}$ 2·5
(24)	8·90(d) [a] $J_{2,3}$ 2·6 [b]	7·10(d) [a] $J_{3,2}$ 2·6 [b]	7·10(d) [a] $J_{4,5}$ 2·6 [b]	8·90(d) [a] $J_{5,4}$ 2·6 [b]
(25)	2·30	6·72	6·72	2·30

* Unless otherwise stated, values refer to singlet absorptions.

[a] Components show satellite signals arising from long-range 2,4(5,3)-coupling. 2-H,5-H, and 3-H,4-H comprise an AA′,XX′ system. [b] *J* Value approximate; see footnote *a*. [c] In CS_2. [d] In CD_3CN. [e] 2 *m*- + *p*-protons of 2-Ph. [f] 2 *o*-protons of 2-Ph. [g] Monohydrate. [h] In $(CD_3)_2CO$. [i] CO_2H–H_2O signal. [j] Disappears on addition of D_2O.

The absence of carbonyl absorption rules out † the presence of a rapid, degenerate, valence isomerisation

(32a) ⇌ (32b), which would show time-averaged C_{2v} symmetry.

The structural relationship of 1,6-dioxa-6a-thiapentalene (13) to 1-oxa-6,6a-dithiapentalene (31) and to 6a-thiathiophthen (33) was shown by thionation experiments. 1,6-Dioxa-6a-thiapentalene reacted with phosphorus pentasulphide to give 6a-thiathiophthen (33) (20%). It also underwent oxygen–sulphur exchange in boiling thioacetic acid to give both 6a-thiathiophthen (33) (12%) and 1-oxa-6,6a-dithiapentalene (31) (38%) according, we suggest, to Scheme 3. Thionation of 1,6-dioxa-6a-selenapentalene (24) with phosphorus pentasulphide likewise afforded 6a-selenathiophthen (34) [11] (37%).

Crystallographic structure determinations of selected 1,6-dioxa-6a-thiapentalenes are in progress.[16]

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. U.v. spectra were measured with a Unicam SP 800 spectrophotometer. Electronic absorption data refer to solutions in cyclohexane unless otherwise stated. I.r. spectra were recorded with a Perkin-Elmer 621 spectrometer. ^{1}H N.m.r. spectra were determined at 100 MHz with a Varian HA100 spectrometer. Solutions in deuteriochloroform were 0·4M; those in trifluoroacetic acid were 0·6M. Tetramethylsilane was used as internal reference and J values were measured on the 100 Hz scale. Unless otherwise stated, values refer to singlet absorptions. Mass spectra were obtained with an A.E.I. MS902 spectrometer. Criteria used in the identification of products included m.p., t.l.c. behaviour, and n.m.r. and mass spectra. Petroleum was of boiling range 40—60°, unless otherwise stated. Acetonitrile was boiled over sodium hydride for 30 min, distilled, then boiled over phosphoric anhydride for 1 h, distilled, and redistilled. Column chromatography was carried out with Spence grade H alumina, unless otherwise indicated. Solvent mixtures are described in ratios by volume. Solutions were dried over sodium sulphate and evaporated under reduced pressure.

Preparation of Pyran-4-thiones.—Methods for the preparation of three thiones in quantity were improved.

2,6-*Dimethylpyran-4-thione* (7). A stirred mixture of 2,6-dimethyl-4-pyrone (18·6 g, 150 mmol), phosphorus pentasulphide (33·3 g, 150 mmol), and benzene (500 ml) was boiled for 1 h, cooled, and decanted. The residual solid was hydrolysed with water, and the resulting mixture was extracted with benzene (×3). The extracts were added to the decanted benzene solution, and the combined solutions were washed with water, dried, and evaporated. Chromatography [alumina (15 × 3·8 cm)] of the residue with benzene gave red eluates which yielded 2,6-dimethylpyran-4-thione (14·1 g, 67%), yellow spars from methanol, m.p. 145—146° (lit.,[17] 145°).

Diethyl 4-thioxopyran-2,6-dicarboxylate (9). A stirred mixture of diethyl 4-oxopyran-2,6-dicarboxylate [18] (12 g, 50 mmol), phosphorus pentasulphide (11·1 g, 50 mmol), and benzene (150 ml) was boiled for 1 h, cooled, and filtered through Celite (7 × 1 cm). The Celite was washed with benzene, and the combined benzene filtrates were washed with water, dried, and evaporated. Chromatography [alumina (25 × 2·5 cm)] of the residual solid with benzene gave green eluates which afforded diethyl 4-thioxopyran-2,6-dicarboxylate (9·50 g, 74%), green needles from petroleum, m.p. 51—52° (lit.,[19] 51°), δ 1·45 (6H, t, J_{Me,CH_2} 7·2 Hz, 2- and 6-CO_2·CH_2*Me*), 4·49 (4H, q, $J_{CH_2,Me}$ 7·2 Hz, 2- and 6-CO_2·CH_2Me), and 7·81 (2H, 3- and 5-H).

Ethyl 4-thioxopyran-2-carboxylate (10). Ethyl 4-oxopyran-2-carboxylate [18] (6·72 g, 40 mmol) was thionated with phosphorus pentasulphide (8·9 g, 40 mmol) in benzene (150 ml) according to the procedure of the preceding experiment. Chromatography [alumina (10 × 2·5 cm)] with benzene gave inhomogeneous red eluates which were evaporated, and the residual solid was rechromatographed in the same way. Recrystallisation of the product from hexane gave ethyl 4-thioxopyran-2-carboxylate (2·88 g, 39%) as red needles, m.p. 66—68° (lit.,[20] 66—67°), δ 1·39 (3H, t, J_{Me,CH_2} 7·2 Hz, CO_2·CH_2*Me*), 4·41 (2H, q, $J_{CH_2,Me}$ 7·2 Hz, CO_2·CH_2Me), 7·18 (1H, dd, $J_{5.6}$ 5·4, $J_{5.3}$ 2·3 Hz, 5-H), 7·56 (1H, dd, $J_{6.5}$ 5·4, $J_{6.3}$ 0·5 Hz, 6-H), and 7·74 (1H, dd, $J_{3.5}$ 2·3, $J_{3.6}$ 0·5 Hz, 3-H).

Synthesis of 1,6-Dioxa-6a-thiapentalenes: Sulphur–Oxygen Coupling by Thallium(III) *Trifluoroacetate.*—1,6-*Dioxa-6a-thiapentalene* (13). (*a*) A solution of thallium(III) trifluoroacetate [21] (59·8 g, 110 mmol) in acetonitrile (300 ml) was added to a solution of pyran-4-thione (6) [14] (11·2 g, 100 mmol) in acetonitrile (300 ml). After 1 min water (500 ml) was added to the pale brown solution. The resulting mixture was extracted with ether (×4), and the extracts were washed with water (×3), dried, and evaporated. Chromatography [alumina (10 × 3·8 cm)] of the residue with benzene gave inhomogeneous eluates which were evaporated, and the residual solid was rechromatographed [alumina (50 × 2·8 cm)] with petroleum–benzene (1 : 1). The colourless eluates yielded 1,6-*dioxa-6a-thiapentalene* (7·80 g, 61%), volatile spars from petroleum (b.p. 40—50°), m.p. 61—62·5° (Found: C, 46·7; H, 3·0; S, 25·0. $C_5H_4O_2S$ requires C, 46·9; H, 3·1; S, 25·0%); M^+ 127·9931; $\lambda_{max.}$ 339 (log ε 4·06), 257 (3·35), and 222 nm (3·38).

(*b*) The procedure was identical with that of the preceding experiment, with aqueous M-sodium hydroxide (500 ml) in place of water. Chromatography [alumina (10 × 3·8 cm)] with benzene gave 1,6-dioxa-6a-thiapentalene (7·19 g, 56%).

2,5-*Dimethyl*-1,6-*dioxa*-6a-*thiapentalene* (14). (*a*) A solution of thallium(III) trifluoroacetate (59·8 g, 110 mmol) in acetonitrile (300 ml) was added to a solution of 2,6-dimethylpyran-4-thione (7) (14·0 g, 100 mmol) in acetonitrile (300 ml). Water (500 ml) was added after 1 min and the mixture was shaken with much ether before being filtered through Celite (9 × 1 cm). The Celite was washed with ether and the washings were added to the original two-phase filtrate. The aqueous layer was extracted with ether (×3), and the combined extracts were washed with water, dried, and evaporated. Purification of the residue [2 chromatograms: alumina (10 × 3·8 cm), benzene; alumina (20 × 2·5 cm), petroleum–benzene (1 : 1)] gave 2,5-*dimethyl*-1,6-*dioxa*-6a-*thiapentalene* (1·15 g, 7·4%), spars

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from petroleum (b.p. 40—50°), m.p. 70—71° (Found: C, 53·7; H, 5·1. $C_7H_8O_3S$ requires C, 53·8; H, 5·2%); M^+ 156·0250; $\lambda_{max.}$ 338 (log ε 4·24), 260 (3·32), and 220 nm (3·35).

(*b*) The procedure was identical with that of the preceding experiment, with aqueous M-sodium hydroxide (500 ml) in place of water. Chromatography [alumina (10 × 3·8 cm)] with benzene yielded 2,5-dimethyl-1,6-dioxa-6a-thiapentalene (1·37 g, 8·7%).

2-Phenyl-1,6-dioxa-6a-thiapentalene (15). A solution of thallium(III) trifluoroacetate (12·0 g, 22 mmol) in acetonitrile (60 ml) was added to a solution of 2-phenylpyran-4-thione (8) [17,22] (3·77 g, 20 mmol) in acetonitrile (60 ml). Aqueous M-sodium hydroxide (100 ml) was added after 1 min, and the resulting mixture was extracted with ether (×4). The residue from the washed, dried, and evaporated extracts was chromatographed twice [alumina (10 × 2·5 cm), benzene; alumina (40 × 2·2 cm), petroleum–benzene (1 : 1)]. The final pale yellow eluates afforded *2-phenyl-1,6-dioxa-6a-thiapentalene* (2·00 g, 49%), pale yellow spars from hexane, m.p. 97—98° (Found: C, 64·6; H, 3·8. $C_{11}H_8O_2S$ requires C, 64·7; H, 4·0%): M^+ 204·0240; $\lambda_{max.}$ 365 (log ε 4·36), 291sh (3·69), 286 (3·71), 233 (4·15), 229sh (4·12), and 213 nm (4·05).

Diethyl 1,6-dioxa-6a-thiapentalene-2,5-dicarboxylate (16). A solution of thallium(III) trifluoroacetate (5·98 g, 11 mmol) in acetonitrile (30 ml) was added to a solution of diethyl 4-thioxopyran-2,6-dicarboxylate (9) (2·56 g, 10 mmol) in acetonitrile (30 ml). Water (50 ml) was added after 1 min and the mixture was extracted with ether (×4). The residue from the washed, dried, and evaporated extracts was dissolved in benzene and adsorbed on alumina [Woelm neutral, activity I (5 × 2·5 cm)]. *Rapid* elution with benzene–ether (4 : 1) brought through yellow eluates which yielded *diethyl 1,6-dioxa-6a-thiapentalene-2,5-dicarboxylate* (1·65 g, 61%), pale yellow needles from methanol, m.p. 97—98·5° (Found: C, 48·3; H, 4·4. $C_{11}H_{12}O_6S$ requires C, 48·5; H, 4·4%); M^+ 272·0358; $\lambda_{max.}$ 373 (log ε 4·16), 263 (3·50), and 220 nm (3·96); $\nu_{max.}$ (CCl_4) 1757 and 1736 cm^{-1} (C=O). When the foregoing reaction was carried out with aqueous M-sodium hydroxide (50 ml) in place of water for solvolysis, the yield of the ester (16) was only 573 mg (21%) owing to rapid hydrolysis.

Ethyl 1,6-dioxa-6a-thiapentalene-2-carboxylate (17). The procedure was identical with that of the preceding experiment, with ethyl 4-thioxopyran-2-carboxylate (10) (1·84 g, 10 mmol) in place of the thione (9). For recrystallisation a solution of the product in petroleum (b.p. 40—50°) was left overnight at −20°. *Ethyl 1,6-dioxa-6a-thiapentalene-2-carboxylate* (1·725 g, 86%) was obtained as pale yellow spars, m.p. 43—44° (Found: C, 47·7; H, 4·1. $C_8H_8O_4S$ requires C, 48·0; H, 4·0%); M^+ 200·0144; $\lambda_{max.}$ 359 (log ε 4·11), 271 (3·44), 245 (3·40), and 206 nm (3·89); $\nu_{max.}$ (CCl_4) 1754 and 1734 cm^{-1} (C=O).

1,6-Dioxa-6a-thiapentalene-2,5-dicarboxylic acid (18). Aqueous M-sodium hydroxide (10 ml) was added to a solution of the ester (16) (544 mg, 2 mmol) in ethanol (100 ml) at 50°. A precipitate appeared and redissolved when water (200 ml) was added after 5 min. The solution was kept for a further 5 min before being acidified with 2M-hydrochloric acid (20 ml). The mixture was extracted with ether (×3), and the residue from the dried and evaporated extracts was recrystallised from water (charcoal). *1,6-Dioxa-6a-thiapentalene-2,5-dicarboxylic acid monohydrate* (324 mg, 69%) was obtained as pale yellow needles which decompose gradually above 270° (Found: C, 35·9; H, 2·7. $C_7H_6O_7S$ requires C, 35·9; H, 2·6%); M^+ 215·9731; $\lambda_{max.}$ (MeOH) 370 (log ε 4·20), 259 (3·53), and 217 nm (3·92); $\nu_{max.}$ (KBr) 3540, 3440 (CO_2H and H_2O, O–H), and 1702br cm^{-1} (C=O).

1,6-Dioxa-6a-thiapentalene-2-carboxylic acid (19). Aqueous M-sodium hydroxide (10 ml) was added to a solution of the ester (17) (400 mg, 2 mmol) in ethanol (40 ml), whereupon a flocculent yellow precipitate appeared. After 5 min the mixture was diluted with water and extracted with ether (×3). The extracts were discarded, and the aqueous layer was acidified with 2M-hydrochloric acid (10 ml) before being extracted with ether (×3). The dried extracts were evaporated, and the residue was recrystallised from water (charcoal). *1,6-Dioxa-6a-thiapentalene-2-carboxylic acid* (267 mg, 78%) was obtained as pale yellow spars which gradually decompose above 180° (Found: C, 42·2; H, 2·5. $C_6H_4O_4S$ requires C, 41·9; H, 2·3%); M^+ 171·9838; $\lambda_{max.}$ (MeOH) 355 (log ε 4·11), 267 (3·40), 242 (3·35), and 208 nm (3·77); $\nu_{max.}$ (KBr) 1698br cm^{-1} (C=O).

A ^{1}H N.m.r. Study of the Reaction of Pyran-4-thione (6) *with Thallium*(III) *Trifluoroacetate*.—The spectrum of a solution of pyran-4-thione (28 mg, 0·25 mmol) in CD_3CN (0·5 ml) showed two multiplets centred at δ 7·10 (3- and 5-H) and 7·64 (2- and 6-H), together with a weak water signal at δ 2·09. To this solution was added a solution of thallium(III) trifluoroacetate (152 mg, 0·28 mmol) in CD_3CN (0·5 ml). The spectrum of the resulting solution, recorded immediately, showed only a pair of doublets arising from 1,6-dioxa-6a-thiapentalene (13) [δ 7·05 (3- and 4-H) and 8·83 (2- and 5-H) (*J* 2·7 Hz)].* The water signal at δ 2·09 had disappeared.

Other Syntheses of 1,6-Dioxa-6a-thiapentalene (13).—(a) *By using thallium*(III) *nitrate*. A solution of thallium(III) nitrate [23] (5·55 g, 12·5 mmol) in acetonitrile (20 ml) was added to a solution of pyran-4-thione (1·12 g, 10 mmol) in acetonitrile (20 ml). After 1 min aqueous M-sodium hydroxide (50 ml) was added, and the mixture was extracted with benzene (×3). The extracts were washed with water, dried, and evaporated. Chromatography [alumina (10 × 2·5 cm)] with benzene yielded 1,6-dioxa-6a-thiapentalene (443 mg, 35%).

(b) *By using potassium ferricyanide*. Aqueous M-sodium hydroxide (20 ml) was added to a solution of pyran-4-thione (1·12 g, 10 mmol) in dimethyl sulphoxide (100 ml) at room temperature. After 10 min benzene (125 ml) was added to the purple-brown solution followed by aqueous M-potassium ferricyanide (60 ml) with swirling. The mixture was diluted with water, and the aqueous layer was extracted with benzene (×2). The combined extracts were washed with water (×6), dried, and evaporated. Chromatography [alumina (15 × 2·2 cm)] of the residue with benzene yielded 1,6-dioxa-6a-thiapentalene (30 mg, 2·3%)

Attempted Synthesis of 6-Methyl-1-oxa-6a-thia-6-azapentalene (26).—A solution of thallium(III) trifluoroacetate (5·98 g, 11 mmol) in acetonitrile (30 ml) was added to a solution of pyran-4-thione (1·12 g, 10 mmol) in acetonitrile (30 ml). After 1 min, aqueous methylamine (25—30% w/v; 25 ml) was added, and the resulting mixture was diluted with water and extracted with ether. The extracts

* See Table, footnotes *a* and *b*.

[22] G. Traverso and M. Sanesi, *Ann. Chim.* (*Italy*), 1953, **43**, 795.

[23] A. McKillop, J. D. Hunt, E. C. Taylor, and F. Kienzle, *Tetrahedron Letters*, 1970, 5275.

were washed with water, dried, and evaporated. Chromatography [alumina (15 × 2·2 cm)] of the residue with benzene gave 1,6-dioxa-6a-thiapentalene (13) (614 mg, 48%). No other product was detected in the residue before chromatographic purification.

The reaction was repeated, with molecular sieves present in the acetonitrile solutions before and after mixing, in order to prevent hydrolysis of the intermediate (11; $R^1 = R^2 = H$) by traces of water in the solvent. 1,6-Dioxa-6a-thiapentalene (44 mg, 3·4%) was the only product.

Preparations of Pyran-4-selones.—Pyran-4-selone (22). Methyl fluorosulphonate (8·8 ml, 110 mmol) was added to a solution of 4-pyrone [14] (9·61 g, 100 mmol) in dichloromethane (200 ml). After 1 h the colourless oil which had separated was induced to crystallise, and a large quantity of ether was added. Successive filtration, washing with ether, and drying *in vacuo* gave 4-methoxypyrylium fluorosulphonate (20) (14·4 g, 69%) as a hygroscopic powder, m.p. 26—30°, for which satisfactory analytical data could not be obtained; δ ($CF_3{\cdot}CO_2H$) 4·44 (3H, OMe), 7·67 (2H, m, 3- and 5-H), and 9·06 (2H, m, 2- and 6-H). The corresponding fluoroborate was an oil and the perchlorate, m.p. 77—78°, was explosive.

Aqueous M-sodium hydrogen selenide (40 ml) was added to an ice-cold solution of the fluorosulphonate (20) (4·20 g, 20 mmol) in water (40 ml). The mixture was kept at 0° for 2 h and filtered, and the solid was washed with water before being dried *in vacuo*. Five such experiments gave pyran-4-selone (5·14 g, 32%) as blue needles contaminated with traces of selenium. Recrystallisation was impracticable owing to thermal instability of the selone, but the product was satisfactory for further work. The ^1H n.m.r. spectrum showed two multiplets centred at δ 7·46 (3- and 5-H) and 7·59 (2- and 6-H).

2,6-Dimethylpyran-4-selone (23). Methylation of 2,6-dimethyl-4-pyrone (12·4 g, 100 mmol) by the foregoing procedure gave *4-methoxy-2,6-dimethylpyrylium fluorosulphonate* (21) (23·4 g, 98%), small prisms from methanol (ether), m.p. 123—129° (Found: C, 40·3; H, 4·9. $C_8H_{11}FO_5S$ requires C, 40·3; H, 4·7%); δ ($CF_3{\cdot}CO_2H$) 2·77 (6H, 2- and 6-Me), 4·28 (3H, OMe), and 7·20 (2H, 3- and 5-H).

Aqueous M-sodium hydrogen selenide (200 ml) was added to an ice-cold solution of the fluorosulphonate (21) (23·8 g, 100 mmol) in water (200 ml), and the resulting mixture was kept at 0° for 2 h before being filtered. Washing with water and drying *in vacuo* gave 2,6-dimethylpyran-4-selone (12·5 g, 67%) as red needles, m.p. 137—138° (lit.,[12] 137—138°); δ 2·07 (6H, 2- and 6-Me) and 7·32 (2H, 3- and 5-H).

Synthesis of 1,6-Dioxa-6a-selenapentalenes.—1,6-Dioxa-6a-selenapentalene (24). A solution of thallium(III) trifluoroacetate (14·94 g, 25 mmol) in acetonitrile (75 ml) was added to a solution of the selone (22) (3·98 g, 25 mmol) in acetonitrile (75 ml). After 1 min the solution was diluted with water (125 ml) and extracted with ether (×4). The extracts were washed with water, dried, and evaporated. Chromatography [alumina (20 × 2·2 cm)] of the product with benzene gave yellow eluates which were evaporated. Sublimation of the residue at 90—95° and 16 mmHg afforded *1,6-dioxa-6a-selenapentalene* (646 mg, 15%), volatile crystals, m.p. 43—44° (Found: C, 34·2; H, 2·3; Se, 44·8. $C_5H_4O_2Se$ requires C, 34·3; H, 2·3; Se, 45·1%); M^+ 175·9373; $\lambda_{max.}$ 353 (log ε 4·11), 288 (3·45), and 211infl nm (3·26).

2,5-Dimethyl-1,6-dioxa-6a-selenapentalene (25). A solution of thallium(III) trifluoroacetate (59·8 g, 110 mmol) in acetonitrile (300 ml) was added to a solution of the selone (23) (18·7 g, 100 mmol) in acetonitrile (300 ml). After 1 min the solution was diluted with water (500 ml) and extracted with ether (×3). The extracts were washed with water, dried, and evaporated. Chromatography [alumina (15 × 3·8 cm)] with benzene gave yellow eluates which were evaporated. The residue was rechromatographed twice in the same manner [alumina (25 × 2·2 cm), petroleum–benzene (1 : 1); alumina (50 × 2·2 cm), petroleum–benzene (3 : 1)]. Sublimation of the residue from the final pale yellow eluates at 145—150° and 16 mmHg gave *2,5-dimethyl-1,6-dioxa-6a-selenapentalene* (391 mg, 1·9%), light-sensitive crystals, m.p. 55—56° (Found: C, 41·6; H, 4·0. $C_7H_8O_2Se$ requires C, 41·4; H, 4·0%); M^+ 203·9686; $\lambda_{max.}$ 352 (log ε 4·32), 258 (3·57), and 219infl nm (3·45).

Thionation of 1,6-Dioxa-6a-thiapentalene (13).—*With phosphorus pentasulphide.* A stirred mixture of 1,6-dioxa-6a-thiapentalene (1·28 g, 10 mmol), phosphorus pentasulphide (4·44 g, 20 mmol), and benzene (200 ml) was boiled for 1 h. The cooled mixture was filtered through Celite (5·5 × 1 cm) which was then washed with benzene. The combined benzene filtrates were washed with water, dried, and evaporated. Chromatography [alumina (70 × 2·8 cm)] of the residue with petroleum–benzene (3 : 1) brought through red eluates which yielded 6a-thiathiophthen (33) [14] (324 mg, 20%).

With thioacetic acid. A solution of 1,6-dioxa-6a-thiapentalene (641 mg, 5 mmol) in thioacetic acid (25 ml) was boiled for 1 h, cooled, and poured into water. The mixture was basified with sodium carbonate before being extracted with ether (×3). The extracts were washed with water, dried, and evaporated, and the residue was chromatographed [alumina (25 × 2·5 cm)]. Elution with petroleum–benzene (1 : 1) gave red eluates from which 6a-thiathiophthen (33) (97 mg, 12%) was isolated. Continued elution with benzene gave pale yellow eluates which were discarded. Subsequent elution with benzene–ether (9 : 1) brought through yellow eluates which were evaporated, and the residual oil was rechromatographed [alumina (25 × 2·2 cm)]. Elution with benzene gave pink eluates containing a trace of 6a-thiathiophthen. Continued elution with benzene–ether (9 : 1) brought through yellow eluates which yielded 1-oxa-6,6a-dithiapentalene (31) [14] (274 mg, 38%) as a yellow oil.

Thionation of 1,6-Dioxa-6a-selenapentalene (24) *with Phosphorus Pentasulphide.*—The procedure was identical with that for the thionation of 1,6-dioxa-6a-thiapentalene. 1,6-Dioxa-6a-selenapentalene (350 mg, 2 mmol), phosphorus pentasulphide (888 mg, 4 mmol), and benzene (40 ml) were used. Chromatography [alumina (70 × 2·2 cm)] of the product with petroleum–benzene (3 : 1) gave orange eluates which yielded 6a-selenathiophthen (34) [11] (155 mg, 37%).

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