

Studies of Heterocyclic Compounds. Part XII.¹ A Three-step Synthesis of 6a-Thiathiophthen from γ -Pyrone

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6a-Thiathiophthen has been synthesised in 12% overall yield by the sequence γ -pyrone \longrightarrow 4*H*-pyran-4-thione \longrightarrow 1-oxa-6,6a-dithiapentalene \longrightarrow 6a-thiathiophthen.

RECENTLY² we described a preparatively useful synthesis of 6a-thiathiophthen (7) in which the key step involved the ring-opening of 4*H*-thiopyran-4-thione (1) with sodium sulphide in aqueous dimethyl sulphoxide and oxidative cyclisation of the resulting anion (3) with potassium ferricyanide. The thione (1) had previously been obtained^{3,4} by a four-step synthesis³⁻⁵ from dimethyl thiodipropionate⁶ in 43–58% overall yield. We now describe a rapidly effected three-step synthesis

of 6a-thiathiophthen from γ -pyrone, based on a similar synthetic approach.

Large-scale thionation of γ -pyrone with phosphorus pentasulphide gave 4*H*-pyran-4-thione (2)^{4,7} (48%) together with a small amount (0.45%) of 6a-thiathiophthen (7). The origin of the 6a-thiathiophthen was not established. A possible precursor is 1,3-diformylacetone or a derivative thereof produced under the reaction conditions. Oxidative thionation leading to 6a-thiathiophthen is a well-established reaction of 1,3,5-tricarbonyl compounds.

¹ Part XI, J. G. Dingwall, A. R. Dunn, D. H. Reid, and K. O. Wade, *J.C.S. Perkin I*, 1972, 1360.

² J. G. Dingwall, D. H. Reid, and J. D. Symon, *J. Chem. Soc. (C)*, 1970, 2412; *Chem. Comm.*, 1969, 466.

³ G. Traverso, *Chem. Ber.*, 1958, **91**, 1224.

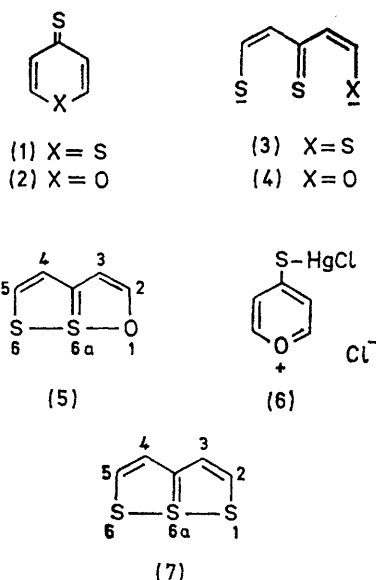
⁴ G. Pfister-Guillouzo and N. Lozac'h, *Bull. Soc. chim. France*, 1964, 3254.

⁵ E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, 1948, **70**, 1813.

⁶ L. L. Gershbein and C. D. Hurd, *J. Amer. Chem. Soc.*, 1947, **69**, 241.

⁷ F. Arndt, P. Nachtwey, and E. Scholz, *Ber.*, 1924, **57**, 1903.

The thione (2) was ring-opened by sodium sulphide in dimethyl sulphoxide-water (4:1 v/v) giving deep red solutions containing the anion (4) and/or related species. Intramolecular oxidative coupling of the anion (4) by aqueous potassium ferricyanide gave impure 1-oxa-6,6a-dithiapentalene (5).³ A small quantity of unchanged



thione in the oxidation product was removed as the ether-insoluble salt (6) by treatment with mercury(II) chloride. Thionation³ of the resulting pure 1-oxa-6,6a-dithiapentalene (5) (23%) with phosphorus pentasulphide afforded 6a-thiathiophthen (7) (58%). For the purpose of preparing 6a-thiathiophthen it is unnecessary to isolate 1-oxa-6,6a-dithiapentalene, and the reactions (2) \rightarrow (5) \rightarrow (7) are expediently combined into a single operation. Thionation of the crude oxidation product gave 6a-thiathiophthen in 25% yield from 4H-pyran-4-thione. 6a-Thiathiophthen is thereby available from γ -pyrone in three steps comprising two operations in 12% overall yield.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. ¹H N.m.r. spectra were obtained with a Varian HA100 spectrometer operating at 100 MHz. Chemical shifts (δ) are given in p.p.m. downfield from tetramethylsilane as internal reference; *J* values were measured on the 100 Hz scale. Mass spectra were obtained with an A.E.I. MS902 spectrometer. Column chromatography was carried out with Spence grade H alumina. The compositions of solvent mixtures are described as ratios of volumes. Solutions were dried over sodium sulphate and evaporated with a rotary film evaporator. Criteria used in the identification of products included m.p.s, t.l.c. behaviour, and n.m.r. and mass spectra.

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† γ -Pyrone has been thionated previously,^{4,7} but experimental details are lacking.

‡ A small quantity of material remained undissolved.

Materials.—Light petroleum was of boiling range 40–60°. γ -Pyrone (56 g), b.p. 108–110° at 18 mmHg, was prepared⁸ by the copper-catalysed decarboxylation of practical grade chelidonic acid*⁹ (225 g; conveniently in 25 g batches).

Thionation of γ -Pyrone.†—A stirred mixture of γ -pyrone (24 g, 250 mmol), phosphorus pentasulphide (55.5 g, 250 mmol), and benzene (750 ml) was boiled for 1 h. The benzene solution was decanted and the residual solid was extracted with a fresh portion (100 ml) of boiling benzene. The extract was decanted and combined with the parent benzene solution. The residual solid was solvolysed with aqueous 0.4M-sodium sulphide (100 ml), and the resulting mixture was extracted with benzene-ether (1:1; 3 \times 300 ml). The extracts were added to the parent benzene solution. The combined extracts were washed with water (\times 3), dried, and concentrated to 150 ml. Light petroleum (150 ml) was added and the resulting solution was adsorbed on to a column of alumina (40 \times 5.7 cm). Elution with light petroleum-benzene (1:1) gave red eluates from which 6a-thiathiophthen (7) (178 mg, 0.45%) was isolated. Further elution with light petroleum-benzene (1:1) and then benzene gave pale yellow eluates which were discarded. Continued elution, with benzene-ether (9:1), brought through purple eluates which yielded 4H-pyran-4-thione (2) (13.65 g, 48%), orange needles from light petroleum-acetone (8:1), m.p. 47–49° (lit.,⁴ 44°; lit.,⁷ 49°).

6a-Thiathiophthen (7).—(a) *Directly from 4H-pyran-4-thione.* Aqueous 0.8M-sodium sulphide (250 ml) was added to a solution of 4H-pyran-4-thione (11.22 g, 100 mmol) in dimethyl sulphoxide (1 l) at room temperature. After 10 min benzene (1.25 l) was added to the deep red solution, followed by aqueous M-potassium ferricyanide (600 ml) with vigorous swirling. The mixture was diluted with water (1 l) and filtered through Celite (12 \times 1 cm). The Celite was washed with hot benzene (3 \times 200 ml) and the washings were added to the two-phase filtrate. The aqueous layer was extracted with benzene-ether (9:1; 5 \times 500 ml), and the extracts were added to the orange benzene layer. The combined extracts were washed with water (\times 6), dried, and evaporated. A stirred solution of the residue in benzene (1 l) was boiled for 1 h with phosphorus pentasulphide (22.2 g, 100 mmol). The solution was filtered through a bed of Celite (12 \times 1 cm) which was then washed with hot benzene (4 \times 200 ml). The combined benzene filtrates were evaporated. The residual solid, in light petroleum-benzene (2:1),‡ was chromatographed on a column of alumina (70 \times 3.8 cm). Elution with light petroleum-benzene (3:1) removed sulphur and was continued until red eluates emerged. Subsequent elution with benzene gave red eluates which were evaporated. The residue was rechromatographed in the same manner. Evaporation of the final red eluates and recrystallisation from cyclohexane gave 6a-thiathiophthen (3.90 g, 24%) as red plates, m.p. 113–114° (lit.,² 112–113°).

(b) *From 1-oxa-6,6a-dithiapentalene.* A stirred solution of 1-oxa-6,6a-dithiapentalene (1.44 g, 10 mmol) in benzene (100 ml) was boiled for 1 h with phosphorus pentasulphide (2.22 g, 10 mmol). The solution was filtered through Celite (7.5 \times 1 cm) which was then washed with benzene (200 ml). The combined benzene filtrates were evaporated. Subsequent purification (2 chromatograms; 60 \times

⁸ P. L. Pauson, G. R. Proctor, and W. J. Rodger, *J. Chem. Soc.*, 1965, 3037.

⁹ E. R. Riegel and F. Zwillmeyer, *Org. Synth.*, 1947, **17**, 40.

2.5 cm) as in the preceding experiment gave 6a-thiathiophthen (921 mg, 58%).

1-Oxa-6,6a-dithiapentalene (5).—4H-Pyran-4-thione (5.61 g, 50 mmol) in dimethyl sulphoxide (500 ml) was ring-opened with aqueous 0.8M-sodium sulphide (125 ml), benzene (625 ml) was added, and oxidation with m-potassium ferricyanide (300 ml) was carried out as in the preceding experiment (a). A solution of mercury(II) chloride (6.80 g, 25 mmol) in ether (400 ml) was added to a solution of the product in ether (200 ml). 4-Chloromercurithiopyrylium chloride (6) was precipitated as a greenish black powder, which was filtered off. The filtrate was diluted with benzene (200 ml), washed with water ($\times 9$) until the washings no longer gave a precipitate with aqueous sodium hydrogen sulphide, dried, and evaporated. The residual oil in benzene was chromatographed on a column of alumina (10×2.5 cm) with benzene as eluant. The yellow eluates were evaporated and the residual oil, in light petroleum-

benzene (1 : 1), was rechromatographed on a column of alumina (20×2.5 cm). Initial elution with light petroleum-benzene (1 : 1) gave pale yellow eluates which were discarded. Continued elution with benzene brought through bright yellow eluates which afforded 1-oxa-6,6a-dithiapentalene (1.673 g, 23%) as a yellow oil, b.p. 115—120° at 0.5 mmHg (block) (lit.,³ 160—180° at 1 mmHg) (Found: C, 42.0; H, 2.9. Calc. for $C_5H_4OS_2$: C, 41.7; H, 2.8%); M^+ , 144; λ_{max} (cyclohexane) 428sh (log ϵ 3.95), 412 (4.03), 227 (4.20), and 194 nm (4.10); ν_{max} (film) 1583 (ring C=O) cm^{-1} ; δ ($CDCl_3$) 6.86 (1H, d, $J_{3,2}$ 1.6 Hz, 3-H), 7.23 (1H, d, $J_{4,5}$ 5.9 Hz, 4-H), 7.98 (1H, d, $J_{5,4}$ 5.9 Hz, 5-H), and 9.38 (1H, d, $J_{2,3}$ 1.6 Hz, 2-H).

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