Preparation and Reactions of α,β-Unsaturated and Cross-conjugated Diene Thiones

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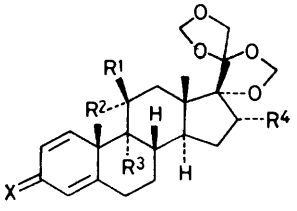
$\Delta^{1,4}$-Diene-3-thiones were prepared from corticosterone-1,4-dien-3-ones and phosphorus pentasulphide. Reaction with diphenyldiazomethane or 2-nitrobenzenesulphenyl chloride gave respectively the derived 3-diphenylmethylene-$\Delta^{1,5}$-dienes and 3-(2-nitrobenzenesulphenylthio)-$\Delta^{1,3,5}$-trienes. The less stable steroid Δ^{4}-ene-3-thiones were trapped with 2-nitrobenzenesulphenyl chloride as 3-(2-nitrobenzenesulphenylthio)-$\Delta^{3,5}$-dienes. Subsequent thiol exchange gave 3-ethane- and 3-benzene-sulphenylthio-$\Delta^{3,5}$-dienes. Warfarin and cyclocumarol were thionated with P_4S_{10} giving mono- and dithio-derivatives. Griseofulvin gave a stable enethione and thence with diphenyldiazomethane the diphenylmethylene derivative.

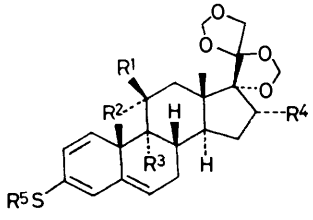
THE $\Delta^{1,4}$-dien-3-one unit of the corticosteroids is a structural feature of paramount importance for biological activity. The analogous $\Delta^{1,4}$-diene-3-thiones would be a novel class of corticosteroids which may possess interesting activities. In addition the increased reactivity of the thione function should make these derivatives useful intermediates for further transformations. Thiones are available from ketones by reaction with hydrogen sulphide catalysed by acid [1] or base [2] or with phosphorus pentasulphide,[3] silicon disulphide,[4] or boron sulphide.[4] Geminal dihalides,[5] vinyl halides,[6] imines,[7] and sulphides [8] are alternative precursors. Since corticosteroids are acid labile phosphorus pentasulphide was chosen for study.[9]

The dexamethasone derivative (1a) reacted smoothly with phosphorus pentasulphide in pyridine to give a purple crystalline product. Combustion analysis and spectral data supported formulation as the thione (1b).



(1)

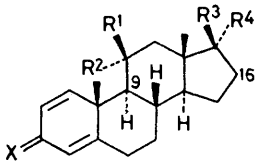
a; R^1 = HO, R^2 = H, R^3 = F, R^4 = Me, X = O
b; R^1 = HO, R^2 = H, R^3 = F, R^4 = Me, X = S
c; R^1R^2 = X = O, R^3 = R^4 = H
d; R^1R^2 = O, R^3 = R^4 = H, X = S
e; R^1R^2 = O, R^3 = R^4 = H, X = S–O; *syn*
f; R^1R^2 = O, R^3 = R^4 = H, X = S–O; *anti*
g; R^1R^2 = O, R^3 = R^4 = H, X = H_2



(2)

a; R^1 = HO, R^2 = R^5 = H, R^3 = F, R^4 = Me
b; R^1R^2 = O, R^3 = R^4 = H, R^5 = Et

Absence of the thiol function (i.r.), the presence of only three vinyl protons (n.m.r.), and the u.v. spectrum discounted the alternative trienethiol structure (2a).



(3)

a; R^1 = HO, R^2 = H, R^3 = $COCH_2OCOEt$, R^4 = OCOEt, X = O; 9α-F, 16β-Me
b; R^1 = HO, R^2 = H, R^3 = $COCH_2OCOEt$, R^4 = OCOEt, X = S; 9α-fluoro; 16β-Me
c; R^1 = HO, R^2 = H, R^3R^4 = $C(=O)(CH_2OC(Me)_2O$, X = O
d; R^1 = HO, R^2 = H, R^3R^4 = $C(=O)CH_2OC(Me)_2O$, X = S
e; R^1 = R^4 = HO, R^2 = H, R^3 = $COCH_2OAc$, X = O
f; R^1 = R^4 = HO, R^2 = H, R^3 = $COCH_2OAc$, X = S
g; R^1 = R^2 = H, R^3R^4 = X = O
h; R^1 = R^2 = H, R^3R^4 = O, X = S
i; R^1 = R^2 = R^4 = H, R^3 = $CH(Me)(CH_2)_3CHMe_2$, X = O; 6,7-didehydro
j; R^1 = R^2 = R^4 = H, R^3 = $CH(Me)(CH_2)_3CHMe_2$, X = S; 6,7-didehydro
k; R^1 = R^2 = H, R^3R^4 = O, X = CPh_2
l; R^1 = R^2 = H, R^3R^4 = O, X = $-SCPh_2N_2-$
m; R^1 = R^2 = H, R^3R^4 = O, X = $-SC(Ph_2)-$
n; R^1 = HO, R^2 = H, R^3R^4 = $C(=O)CH_2OC(Me)_2O$, X = CPh_2
o; R^1 = R^4 = HO, R^2 = H, R^3 = $COCH_2OAc$, X = CPh_2
p; R^1 = R^2 = R^4 = H, R^3 = $CH(Me)(CH_2)_3CHMe_2$, X = CPh_2; 6,7-didehydro

Similarly, the ketones (3a, 1c, and 3c, e, g, and i) gave the derived thiones (3b, 1d, and 3d, f, h, and j, respectively).

Clearly non-conjugate ketones, carboxylic esters, ketals, and bismethylenedioxy functions were compatible with phosphorus pentasulphide. Free hydroxy functions, although hindered (11β,17α), were detrimental to yield. The dienethiones were stable and neither appreciably enolised, readily oxidised by air, nor hydrolysed at pH 7.

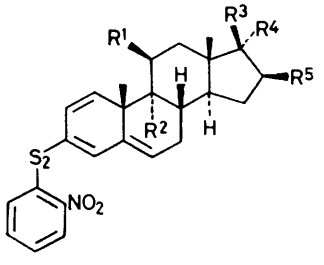
Dienethione (1d) was oxidised by 3-chloroperoxybenzoic acid to two yellow isomeric dienethione *S*-oxides (1e and f) sensitive to light. The products rapidly interconverted on attempted chromatography. Formulation as the *S*-oxides (1e and f) was consistent with analysis, spectral data, and the formation of the $\Delta^{1,4}$-dien-3-one (1c) on irradiation. Alternatively, dienethione (1d) was

ethylated by triethyloxonium tetrafluoroborate giving the air-sensitive trienethiol ether (2b).

Very hindered olefins have been prepared by the condensation of non-enolised thiones and diazoalkanes.[10] Pyrolysis of the intermediate 1,3,4-thiadiazolines and subsequent desulphurisation gave the olefins in high yield. The reaction should be applicable to the preparation of cross conjugated olefins from the corticosteroid dienethiones. Thione (3h) reacted readily with diphenyldiazomethane with discharge of colour. Formulation of the product as the 3-diphenylmethylene steroid (3k) (88%) followed from analysis and spectral data. Cross-conjugation was consistent with the n.m.r. (3 vinyl protons) and u.v. spectra. Presumably, formation of the extended conjugation diminished the stability of the intermediate 1,3,4-thiadiazoline (3l) and thiiran (3m); these were not observed. Similarly, thiones (3d, f, and j) were converted into the derived 3-diphenylmethylene steroids (3n, o, and p). Although cholesta-1,4,6-triene-3-thione (3j) could not be obtained, analytically pure 3-diphenylmethylenecholesta-1,4,6-triene (3p) was completely characterised.

Alper has described [11] the desulphurisation of diaryl thiones and adamantanethione using the hydridotetracarbonylferrate(−II) anion. When applied to the prednisone thione (1d) this reduction gave a complex mixture. Chromatography gave the expected novel skipped diene (1g) (12%). The u.v. spectrum discounted an alternative conjugated system.

The thione function is a soft nucleophile [12] and, as expected, dienethione (3b) was inert towards the hard toluene-4-sulphonyl chloride or methanesulphonyl chloride. In contrast dienethione (3b) rapidly reacted with the soft 2-nitrobenzenesulphenyl chloride giving a yellow product. The mass spectrum and analysis were consistent with a composition of $C_{25}H_{27}NO_3S_2$. The n.m.r. and u.v. spectra were in full agreement with the structure of the triene disulphide (4a). The generality of the reaction was demonstrated by the preparation of disulphides (4b and c). In these examples the hard

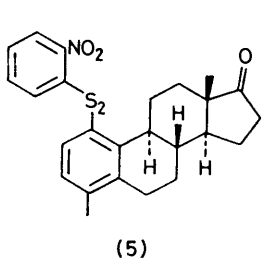


(4)

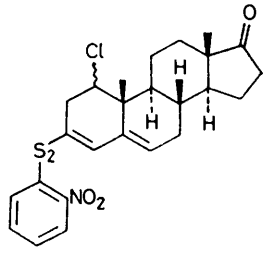
a; R^1 = HO, R^2 = F, R^3 = $COCH_2OCOEt$, R^4 = OCOEt, R^5 = Me
b; R^1 = HO, R^2 = R^5 = H, R^3 = $COCH_2OAc$, R^4 = HO
c; R^1 = R^2 = R^5 = H, R^3, R^4 = O

nucleophilic hydroxy functions were not able to compete with the thione functions.

In an attempt to trap the dienethione (3h) during the thionation of dienone (3g), an excess of 2-nitrobenzenesulphenyl chloride was added with the phosphorus pentasulphide. Two new compounds ($C_{25}H_{27}NO_3S_2$) and ($C_{25}H_{28}ClNO_3S_2$) were formed instead of disulphide (4c). The less polar product was formulated as the diaryl disulphide (5). The n.m.r. spectrum showed an aryl

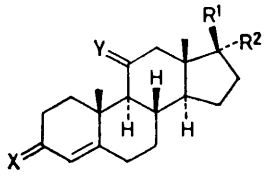


(5)



(6)

methyl resonance (δ 2.12) replacing the original C-10 methyl signal, and six aromatic and no vinyl protons. Since the two aromatic protons at δ 6.8 and 7.18 were *ortho* (*J* 8 Hz) this ruled out alternative structures. Most plausibly the other product was the 1-chlorodiene (6). This structure was consistent with the presence of $\Delta^{3,5}$ (u.v., n.m.r.) and only the 2-nitrobenzenesulphenyl aromatic protons. The proton α to chlorine was clearly not also allylic (δ 4.22) and was assigned to C1-H with C2-H_2 at δ 2.83. These products (5) and (6) were derived from disulphide (4c) with respective dienone–phenol type isomerisation and hydrogen chloride addition.



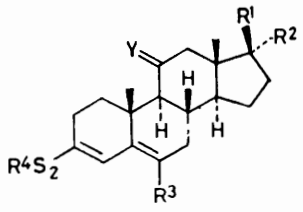
(7)

a; R^1 = $CH(Me)(CH_2)_3CHMe_2$, R^2 = H, X = S, Y = H_2
b; R^1 = OAc, R^2 = H, X = O, Y = H_2
c; R^1 = OAc, R^2 = H, X = S, Y = H_2
d; R^1R^2 = Y = X = O
e; R^1R^2 = Y = O, X = S

Although several simple alicyclic enethiones [13] have been prepared, cholest-4-ene-3-thione (7a) [14] remains the only characterised steroidal example. Reaction of testosterone acetate (7b) or androst-4-ene-3,11,17-trione (7d) with phosphorus pentasulphide gave the unstable derived enethiones (7c and e). Since neither could be isolated, the thionation was repeated in the presence of 2-nitrobenzenesulphenyl chloride. The enethiones were trapped *in situ* giving the expected diene disulphides (8a and b). The u.v. spectra ruled out the alternative $\Delta^{2,4}$ isomers. Since the products were dienes, complications arising from skeletal rearrangements did not take place. Again the 11 and 17 ketone functions were stable to the thionation reaction conditions. Further treatment of the diene disulphide (8b) with 2-nitrobenzene sulphenyl chloride and phosphorus pentasulphide gave a new product with the intact 11,17-dione. In this case, the sulphenyl chloride reacted with

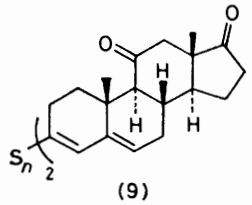
the diene giving the 6-(2-nitrobenzenesulphenyl) derivative (8c). The u.v. [$\lambda_{max.}$ 242 (ε 22 000) and 275 nm (16 000)] and n.m.r. [δ 6.93 (1 H, s)] spectra were consistent with 6- rather than 4-substitution.

Thiol–disulphide exchange is a well known process.[15] The diene disulphides (8a and b) reacted with ethanethiol or benzenethiol to give the exchanged disulphides (8d, e, f, and g) in good yields. The structures were all in good agreement with analyses and spectral data. It is conceivable that analogously diene disulphide (8b) would react with 11,17-dioxoandrost-4-ene-3-thione (7e) to give the symmetrical disulphide (9a). Surprisingly, reaction in the presence of triethylamine gave a new product, although little disulphide (8b) was consumed. Chromatography gave the product ($C_{38}H_{46}O_4S$). The structure was symmetrical (simple n.m.r.), the 11,17-dione intact (1 750 and 1 720 cm^{-1}), and $\Delta^{3,5}$ was present (n.m.r.). Clearly, the product was the sulphide (9b), presumably formed by a dienethiol enethione condensation. The product was also formed from enethione (7e) and triethylamine alone.



(8)

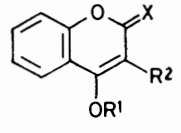
a; R^1 = OAc, R^2 = R^3 = H, R^4 = 2-$O_2NC_6H_4$, Y = H_2
b; R^1R^2 = Y = O, R^3 = H, R^4 = 2-$O_2NC_6H_4$
c; R^1R^2 = Y = O, R^3 = 2-$O_2NC_6H_4S$, R^4 = 2-$O_2NC_6H_4$
d; R^1 = OAc, R^2 = R^3 = H, R^4 = Et, Y = H_2
e; R^1 = OAc, R^2 = R^3 = H, R^4 = Ph, Y = H_2
f; R^1R^2 = Y = O, R^3 = H, R^4 = Et
g; R^1R^2 = Y = O, R^3 = H, R^4 = Ph



(9)

a; n = 2
b; n = 1

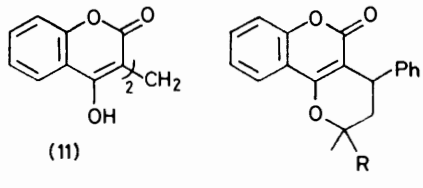
Some coumarin derivatives, including warfarin (10a), dicoumarol (11), and their derivatives, are powerful anticoagulants. In a search for compounds with improved activities, it was relevant to examine thione analogues. 4-Methoxy-4-methyl-2*H*-1-benzopyran-2-one (10b) was treated with phosphorus pentasulphide in toluene at 70 °C. Analysis, spectral data, and hydrolysis of the product to the parent pyranone (10b) with mercuric acetate were all consistent with formulation as the thione (10c). Dean has reported[4] that the pyran-2-one derivative (10d) and boron sulphide give a complex mixture resulting from loss of the 4-methoxy group. Presumably, introduction of the 3-methyl group in the analogue (10b) introduced sufficient steric hindrance and thus permitted clean thionation.



(10)

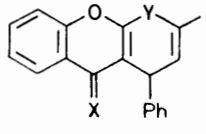
a; R^1 = H, R^2 = CH(Ph)CH_2COMe, X = O
b; R^1 = R^2 = Me, X = O
c; R^1 = R^2 = Me, X = S
d; R^1 = Me, R^2 = H, X = O
e; R^1 = R^2 = H, X = O
f; R^1 = Me, R^2 = CH(Ph)CH_2COMe, X = O

Cyclocumarol (12a) and phosphorus pentasulphide gave three novel heterocyclic compounds (A), (B), and (C) which were separated by careful chromatography. All three lacked carbonyl, methoxy, and C-3 methylene functions but contained a vinyl methyl and vinyl proton. High resolution mass spectra and microanalyses gave compositions for (A) and (B) of $C_{19}H_{14}OS_2$ and for (C) $C_{19}H_{14}O_2S$. Isomers (A) and (B) were assigned as compounds (13a) and (14a), respectively. The uniquely low field proton resonance (δ 8.37—8.57) in the n.m.r. spectrum of (A) was consistent with the aromatic proton deshielded by the adjacent thione function. In addition, mercuric acetate hydrolysis of (A) and (B) gave the carbonyl analogues (13b) and (14b) ($\nu_{max.}$ 1 640 and 1 710 cm^{-1}) respectively. The differences in the n.m.r. spectra of (A) and (B) and their respective hydrolysis products were consistent with the known[16] larger deshielding effect of a thiocarbonyl compared with a carbonyl function. The most polar fraction (C) was a thione (i.r. and u.v. spectra). The n.m.r. spectrum with the absence of a uniquely low field aromatic proton suggested formulation as the thione (14c) rather than (13c). Mercuric acetate hydrolysis of (C) gave the sulphur-free analogue (14d) ($\nu_{max.}$ 1 720 cm^{-1}).



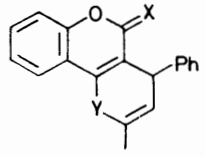
(11) (12)

a; R = OMe
b; R = SH



(13)

a; X = Y = S
b; X = O, Y = S
c; X = S, Y = O

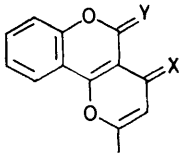


(14)

a; X = Y = S
b; X = O, Y = S
c; X = S, Y = O
d; X = Y = O

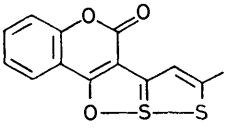
Cyclocumarol (12a) and phosphorus pentasulphide gave initially (t.l.c.) a colourless product. Analysis and spectral data were consistent with the benzopyranone derivative (14d) presumably formed *via* the acid-catalysed elimination of methanol. This intermediate (14d) was further converted into (C) (14c) and subsequently into (A) (13a) and (B) (14a). Under the reaction conditions (A) and (B) did not interconvert. Presumably (A) and (B) were formed *via* transient ring opened species. Warfarin (10a) with phosphorus pentasulphide gave the same three products (A), (B), and (C) *via* the intermediacy of the benzopyranone derivative (14d). During the isolation of intermediate (14d) from warfarin (10a), a thiol ($\nu_{max.}$ 2 560 cm^{-1}, δ 2.77, $C_{19}H_{16}O_3S$) was obtained in small yield. The n.m.r. spectrum exhibited an ABX multiplet centred at δ 2.31 and 4.1; consistent with the product being the thiol (12b). To verify the requirement for an initial acid-catalysed step warfarin (10a) was treated with phosphorus pentaoxide to give the same pyranone derivative (14d).

Dean has reported that the pyranopyranone derivative (15a) gave the monothione (15b) with freshly



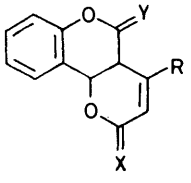
(15)

a; X = Y = O
b; X = S, Y = O
c; X = Y = S



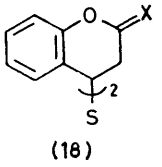
(16)

prepared silicon disulphide [4] but the oxadithiapentalene (16) with aged reagent. Since sulphur is more bulky than oxygen, the authors argued the dithione (15c) formation was less favourable than ring cleavage giving the pentalene derivative (16). Consistent with this, replacement of the thione function (van der Waals



(17)

a; X = S, Y = O, R = Me
b; X = Y = O, R = H
c; X = Y = S, R = H



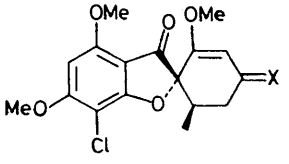
(18)

a; X = S
b; X = O

radius 1.9 Å) by a methyl group (2.0 Å) also prevented further thionation of monothione (17a) although the unhindered pyranopyrone (17b) gave a mixture of products including dithione (17c).[4] In the present study, the non-hindered carbonyl (models) of the benzopyranone (14d) was clearly being rapidly thionated.

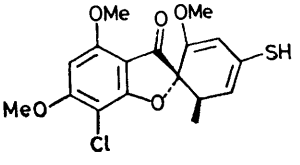
Attempts to thionate dicoumarol (11) with phosphorus pentasulphide gave a coloured intractable mixture. Possibly intermolecular condensations were taking place. 4-Hydroxy-2*H*-1-benzopyran-2-one (10e) reacted with phosphorus pentasulphide to give an orange dimeric product ($C_{18}H_{10}O_2S_3$). Clearly, the product was symmetrical (n.m.r.) and was assigned as the sulphide (18a). This was confirmed by 3-chloroperoxybenzoic acid or mercuric acetate oxidation giving the analogous dicarbonyl compound (18b)($C_{18}H_{10}O_4S$).

Griseofulvin (19a), an antifungal antibiotic, possesses an α,β-unsaturated carbonyl function. Reaction with phosphorus pentasulphide in benzene gave the derived thione (19b). Again, the tautomeric dienethiol (20) was not formed (n.m.r., i.r.). As expected, the product (19b) reacted with diphenyldiazomethane to give two



(19)

a; X = O
b; X = S
c; X = $-CPh_2-S-$
d; X = CPh_2



(20)

products. The major product ($C_{30}H_{27}ClO_5S$) was clearly one of the epimeric thiirans (19c). Subsequent treatment of this product with triphenylphosphine or pyrolysis (190 °C) gave the expected olefin (19d). The less polar product was inhomogeneous. By comparison with an authentic sample, the product was considered to be a mixture of olefin (19d) and the other thiiran (19c) epimer.

Phosphorus pentasulphide is clearly a useful reagent for the conversion of labile unsaturated ketones unto the thione analogues. The reaction should find wide application in the synthesis of potentially biologically active compounds.

EXPERIMENTAL

M.p.s were determined on a Kofler hot stage. Infrared, ultra violet, and n.m.r. spectra were recorded for solutions in chloroform, methanol, and deuteriochloroform, respectively, unless stated to the contrary. Preparative layer chromatography (p.l.c.) was carried out on Analtech GF silica gel.

9α-Fluoro-11β-hydroxy-16α-methyl-17α,20;20,21-bis-methylenedioxypregna-1,4-diene-3-thione (1b).—The dienone (1a) (1.0 g), phosphorus pentasulphide (150 mg), and pyridine (15 ml) were stirred at 90 °C for 1 h under argon. The solution was cooled and filtered and dichloromethane (100 ml) was added. The purple solution was washed with dilute hydrochloric acid (2 × 100 ml) and aqueous sodium hydrogen carbonate, dried, and evaporated. The residue in dichloromethane was filtered off through Florisil to give

the *dienethione* (1b) (290 mg, 28%), m.p. 212° (dec) (from dichloromethane–hexane), $\nu_{max.}$ (KBr) 3 500 and 1 630 cm^{-1}, $\lambda_{max.}$ (MeCN) 331 (ε 17 900) and 580 nm (25), δ 1.0 (3 H, d, *J* 6 Hz, 16-Me), 1.2 (3 H, s, 13-Me), 1.6 (3 H, s, 10-Me), 4.0 (2 H, s, 21-H), 4.3br (1 H, d, *J* 10 Hz, 11α-H), 4.9—5.3 (4 H, m, OCH_2O), 6.9br (1 H, s, 4-H), and 7.2 (2 H, s, 1-H, 2-H), *m/e* 450 (M^+) (Found: C, 63.85; H, 6.65; S, 7.25. $C_{24}H_{31}FO_5S$ requires C, 63.95; H, 6.95; S, 7.2%). Further elution of the column gave the dienone (1a) (205 mg).

9α-*Fluoro*-11β-*hydroxy*-16β-*methyl*-17α,21-*dipropionyloxy*-3-*thioxopregna*-1,4-*dien*-20-*one* (3b).—The dienone (3a) (1.0 g) in pyridine (15 ml) was stirred with phosphorus pentasulphide (2 × 100 mg) for 45 and 90 min, respectively, under argon to give the *dienethione* (3b) (200 mg, 19%), as blue plates, m.p. 113° (from dichloromethane–hexane), $\nu_{max.}$ (KBr) 3 570, 1 735, and 1 635 cm^{-1}, $\lambda_{max.}$ (MeCN) 330 nm (ε 19 000) and 575 nm (24), δ 1.0 (3 H, s, 13-Me), 1.6 (3 H, s, 10-Me), 4.5br (1 H, m, 11α-H), 4.6 (2 H, ABq, *J* 16 Hz, 21-H), 6.9br (1 H, s, 4-H), and 7.0 (2 H, s, 1- and 2-H), *m/e* 498 (M^+) (Found: C, 64.75; H, 7.2; S, 6.0. $C_{28}H_{37}FO_6S$ requires C, 64.6; H, 7.15; S, 6.15%).

17α,20;20,21-*Bismethylenedioxy*-3-*thioxopregna*-1,4-*dien*-11-*one* (1d).—The dienedione (1c) (4.0 g), phosphorus pentasulphide (4.0 g), and toluene (40 ml) were stirred under argon at 70 °C for 4 h. The mixture was cooled and filtered and the solids leached with toluene (15 ml). The filtrate was evaporated and chromatographed on Florisil (eluant dichloromethane) to give the *dienethione* (1d) (3.0 g, 72%), m.p. 184—187° (from dichloromethane–hexane), $\nu_{max.}$ (KBr) 1 710 and 1 630 cm^{-1}, $\lambda_{max.}$ (MeCN) 330 (ε 19 500) and 565 nm (20), δ 0.9 (3 H, s, 13-Me), 1.5 (3 H, s, 10-Me), 4.0 (2 H, s, 21-H), 5.0—5.4 (4 H, m, OCH_2O), 6.8—7.0 (2 H, m, 2- and 4-H), and 7.5 (1 H, d, *J* 10 Hz, 1-H), *m/e* 416 (M^+) (Found: C, 66.4; H, 6.7; S, 7.45. $C_{23}H_{28}O_5S$ requires C, 66.3; H, 6.8; S, 7.7%).

11β-*Hydroxy*-17α,21-[(1-*methylethylidene*)*dioxy*]-3-*thioxopregna*-1,4-*dien*-20-*one* (3d).—The dienedione (3c) [17] (1.21 g), phosphorus pentasulphide (1 g), toluene (50 ml), and chloroform (20 ml) were stirred at 75 °C for 6 h under argon. The mixture was filtered and the residue extracted with dichloromethane (2 × 15 ml). The combined filtrates were concentrated and chromatographed on Florisil (argon) to give (eluant chloroform) the purple *dienethione* (3d) (258 mg, 20%), m.p. 163—165 ° from methanol, $\nu_{max.}$ 3 700, 3 000, 1 725, 1 635, 1 185, 1 120, and 1 030 cm^{-1}, $\lambda_{max.}$ 332 nm (ε 19 000), δ 0.93 (3 H, s, 13-Me), 1.41 (6 H, s, CMe_2), 1.49 (3 H, s, 10-Me), 4.17 (2 H, ABq, *J* 18 Hz, 21-H), 4.5br (1 H, s, 11α-H), 6.92 (2 H, m, 1- and 2-H), and 7.02 (1 H, m, 4-H), *m/e* 416 M^+) (Found: C, 69.3; H, 7.5; S, 7.9. $C_{24}H_{32}O_4S$ requires C, 69.2; H, 7.75; S, 7.7%).

11β,17α-*Dihydroxy*-20-*oxo*-3-*thioxopregna*-1,4-*dien*-21-*yl Acetate* (3f).—Prednisolone 21-acetate (3e) (1.03 g) and phosphorus pentasulphide 1.0 g) in pyridine (20 ml) and benzene (60 ml) were stirred at 75 °C for 6 h under argon. The mixture was cooled and dichloromethane (80 ml) was added. Filtration and evaporation gave a purple residue which was chromatographed on Florisil (argon) (eluant ethyl acetate–dichloromethane 1 : 19) to give the purple 3-*thioxoprednisolone* 21-*acetate* (3f) (250 mg, 25%), m.p. 169—171° (dec) (from acetonitrile) $\nu_{max.}$ 3 750, 3 600, 3 000, 1 750, 1 730, 1 630, 1 240, 1 120, and 1 050 cm^{-1}, $\lambda_{max.}$ 334 nm (ε 22 000), δ 0.97 (3 H, s, 13-Me), 1.47 (3 H, s, 10-Me), 2.15 (3 H, s, OAc), 4.4 (1 H, m, 11α-H), 4.97 (2 H, ABq, *J* 18 Hz, 21-H), 6.92 (2 H, m, 1- and 2-H), and 7.02 (1 H, m, 4-H), *m/e* 418 (M^+) (Found: C, 63.5; H, 7.05; S, 7.05. $C_{23}H_{30}O_5S.H_2O$ requires C, 63.3; H, 7.4; S, 7.35%).

3-*Thioxoandrosta*-1,4-*dien*-17-*one* (3h).—Androsta-1,4-diene-3,17-dione (3 g) (570 mg), phosphorus pentasulphide (650 mg), and benzene (20 ml) were stirred at 70 °C for 6 h under argon. The mixture was filtered and the residue washed with dichloromethane (2 × 10 ml). Evaporation gave a purple residue which was chromatographed on Florisil (argon) (eluant ethyl acetate–dichloromethane 1 : 99) to give the *dienethione* (3h) (425 mg, 71%), m.p. 163—165 °C (from CCl_4), $\nu_{max.}$ 3 000, 1 750, 1 635, 1 160, and 1 140 cm^{-1}, $\lambda_{max.}$ 330 nm (ε 19 000), δ 0.88 (3 H, s, 13-Me), 1.27 (3 H, s, 10-Me), and 6.77 (3 H, m, 1-, 2-, and 4-H), *m/e* 300 (M^+) (Found: C, 75.95; H, 7.95; S, 10.3. $C_{19}H_{24}OS$ requires C, 75.95; H, 8.05; S, 10.65%).

Cholesta-1,4,6-*triene*-3-*thione* (3j).—Cholesta-1,4,6-trien-3-one (3i) [18] (765 mg), phosphorus pentasulphide (800 mg), and benzene (15 ml) were stirred at 25 °C for 24 h under argon. The mixture was filtered and the residue washed with benzene (2 × 10 ml). The concentrated filtrates were chromatographed on Florisil (argon) to give the thione (3j) as an unstable green foam (302 mg, 38%), $\nu_{max.}$ 3 000, 1 635, 1 470, 1 385, and 1 170 cm^{-1}, $\lambda_{max.}$ (hexane) 354 nm (ε 16 800), δ 0.8 (3 H, s, 13-Me), 0.83 and 0.93 (9 H, 2s, 20-Me and 25-Me_2), 1.23 (3 H, s, 10-Me), 6.2 (2 H, m, 6 and 7-H), and 6.73—6.83 (3 H, m, 1-, 2-, and 4-H), *m/e* 396 (M^+).

17α,20;20,21-*Bismethylenedioxy*-3-*thioxopregna*-1,4-*dien*-11-*one* S-*Oxide* (1e, f).—3-Chloroperoxybenzoic acid (50 mg, 1 equiv.) was added to the dienethione (1d) (104 mg) in dichloromethane (10 ml). The solution was washed with aqueous sodium hydrogen carbonate and water, dried, and evaporated to leave a yellow solid (two components by t.l.c.). After separation by p.l.c. the two separate isomers rapidly re-equilibrated. Recrystallisation gave the isomeric mixture of *dienethione* S-*oxides* (1e, f), m.p. 204° (dec), $[\alpha]_D$ +130° (*c* 1.25, CH_2Cl_2), $\nu_{max.}$ (KBr) 1 705 and 1 630 cm^{-1}, $\lambda_{max.}$ (MeCN) 358 nm (ε 16 000), δ 0.8 (3 H, s, 13-Me), 1.4 (3 H, s, 10-Me), 4.0 (2 H, s, 21-H), 5.0 (4 H, m, OCH_2O), and 6.2—7.2 (3 H, m, 1-, 2-, and 4-H), *m/e* 432 (M^+) (Found: C, 63.7; H, 6.4; S, 7.5. $C_{23}H_{28}O_6S$ requires C, 63.85; H, 6.55; S, 7.4%).

Conversion of Dienethione S-*Oxide* (1e, f) *into Ketone* (1c).—The *S*-oxide (1e, f) (100 mg) in dichloromethane was irradiated by a 1.5kW photoflood lamp for 1 h. Evaporation and recrystallisation from methanol–dichloromethane gave only ketone (1c) (n.m.r., t.l.c.). The *S*-oxide (1e, f) in dichloromethane was stable in the dark.

Alkylation of Dienethione (1d).—The dienethione (1d) (160 mg) and 4A molecular sieves in dichloromethane were stirred at room temperature under argon. After 1 h triethyloxonium tetrafluoroborate in dichloromethane (1M; 0.4 ml) was added. After 2 h 1,8-bisdimethylaminonaphthalene (60 mg) was added to the deep red solution. After 10 min the colourless solution was washed with dilute hydrochloric acid and water, dried, and evaporated. Chromatography on Florisil (eluant dichloromethane), and crystallisation from cold dichloromethane–hexane (argon) gave 3-*ethylthio*-17α,20;20,21-*bismethylenedioxypregna*-1,3,5-*trien*-11-*one* (2b), m.p. 183° (sealed tube), $\nu_{max.}$ (KBr) 1 700 cm^{-1}, $\lambda_{max.}$ (MeCN) 326 nm (ε 6 400), δ 0.8 (3 H, s, 13-Me), 1.25 (3 H, *t*, *J* 7 Hz, SCH_2CH_3), 1.3 (3 H, s, 10-Me), 2.75 (2 H, q, *J* 7 Hz, SCH_2CH_3), 4.0 (2 H, s, 21-H), 5.0—5.2 (4 H, m, OCH_2O), 5.3—5.8 (3 H, m, 2-, 4-, and 6-H), and 6.45 (1 H, d, *J* 10 Hz, 1-H), *m/e* 444 (M^+)

(Found: C, 67.8; H, 7.2; S, 7.1. $C_{25}H_{32}O_5S$ requires C, 67.55; H, 7.25; S, 7.2%).

3-(*Diphenylmethylene*)*androsta*-1,4-*dien*-17-*one* (3k).—3-Thioxoandrosta-1,4-dien-17-one (3h) (70 mg) and diphenyldiazomethane (50 mg) in dichloromethane (15 ml) were stirred at room temperature for 24 h under argon. Evaporation and p.l.c. gave the *trienone* (3k) (89 mg, 88%) as needles, m.p. 186—188° (from ethanol), $\nu_{max.}$ 3 000, 1 745, and 1 650 cm^{-1}, $\lambda_{max.}$ 313 (ε 23 000) and 248 nm (10 000), δ 0.87 (3 H, s, 13-Me), 1.19 (3 H, s, 10-Me), 5.77 (1 H, d, *J* 10 Hz, 1-H), 6.1 (1 H, d, *J* 1.5 Hz, 4-H), 6.31 (1 H, dd, *J* 10 and 1.5 Hz, 2-H), and 7.19 (10 H, m, aryl), *m/e* 434 (M^+) (Found: C, 88.4; H, 8.2. $C_{32}H_{34}O$ requires C, 88.45; H, 7.9%).

3-(*Diphenylmethylene*)-11β-*hydroxy*-17α,21-[(1-*methylethylidene*)*dioxy*]*pregna*-1,4-*dien*-20-*one* (3n).—The *trienone* (3n) prepared from the thione (3d) (66 mg) and diphenyldiazomethane (40 mg) was obtained as needles (73 mg, 81%), m.p. 187—188° (dec.) (from dichloromethane–hexane) $\nu_{max.}$ 3 750, 3 000, 1 730, and 1 655 cm^{-1}, $\lambda_{max.}$ 312 (ε 24 000) and 248 nm (11 000), δ 0.85 (3 H, s, 13-Me), 1.38 (6 H, s, CMe_2), 1.4 (3 H, s, 10-Me), 4.07 (2 H, ABq, *J* 18 Hz, 21-H), 4.45br (1 H, s, 11α-H), 5.7—6.55 (3 H, m, 1-, 2-, and 4-H), and 7.22 (10 H, m, aryl), *m/e* 550 (M^+) (Found: C, 80.65; H, 7.5. $C_{37}H_{42}O_4$ requires C, 80.7; H, 7.7%).

11β,17α-*Dihydroxy*-3-(*diphenylmethylene*)-20-*oxopregna*-1,4-*dien*-21-*yl Acetate* (3o).—3-Thioxoprednisolone 21-acetate (3f) (50 mg) and diphenyldiazomethane (30 mg) gave on p.l.c. the *triene* (3o) as needles (55 mg, 84%), m.p. 202—204° (dec.) (from dichloromethane–hexane), $\nu_{max.}$ 3 600, 3 000, 1 750, 1 730, and 1 650 cm^{-1}, $\lambda_{max.}$ 312 (ε 2 500) and 247 nm (11 500), δ 0.9 (3 H, s, 13-Me), 1.38 (3 H, s, 10-Me), 2.11 (3 H, s, OAc), 4.45br (1 H, s, 11α-H), 4.9 (2 H, ABq, *J* 18 Hz, 21-H), 6.0—6.8 (3 H, m, 1-, 2-, and 4-H), and 7.2 10 H, m, aryl), *m/e* 552 (M^+) (Found: C, 77.95; H, 7.6. ($C_{36}H_{40}O_5$ requires C, 78.2; H, 7.3%).

3-(*Diphenylmethylene*)*cholesta*-1,4,6-*triene* (3p).—The thione (3j) (100 mg) and diphenyldiazomethane (55 mg) gave on p.l.c. the *triene* (3p) as needles (101 mg, 76%), m.p. 141—142° (from methanol), $\nu_{max.}$ 3 000 and 1 640 cm^{-1}, $\lambda_{max.}$ 333 (ε 22 000), 250 (7 000), and 213 nm (20 000), δ 0.73 (3 H, s, 13-Me), 0.8 and 0.9 (9 H, 2d, 20- and 25-Me_2), 1.09 (3 H, s, 10-Me), 5.57 (1 H, d, *J* 10 Hz, 1-H), 5.86—6.16 (3 H, m, 4-, 6-, and 7-H), 6.38 (1 H, dd, *J* 10 and 1.5 Hz, 2-H), and 7.2 (10 H, m, aryl), *m/e* 530 (M^+) (Found: C, 90.35; H, 9.35. $C_{40}H_{50}$ requires C, 90.55; H, 9.45%).

17,20;20,21-*Bismethylenedioxypregna*-1,4-*dien*-11-*one* (1g).—The hydridotetracarbonylferrate anion [$HFe(CO_4)^-$] (4 equiv.) was generated *in situ* according to Alper's procedure.[11] Dienethione (1d) (500 mg, 1 equiv.) in 1,2-dimethoxyethane (25 ml) was added dropwise under argon and the mixture refluxed for 1 h. The mixture was cooled, filtered, and concentrated to give a brown residue which was extracted with benzene (4 × 30 ml) and ethyl acetate (2 × 20 ml). The combined extracts were washed with water, dried, concentrated, and chromatographed on Florisil (eluant dichloromethane) to give the *diene* (1g) (57 mg, 12%), m.p. 146—148° (dec.) (from methanol), $\nu_{max.}$ 3 000 and 1 715 cm^{-1}, δ 0.8 (3 H, s, 13-Me), 1.33 (3 H, s, 10-Me), 3.94 (2 H, s, 21-H), 4.98—5.17 (4 H, m, OCH_2O), 5.23—5.85 (2 H, m, 2- and 4-H), and 6.0—6.14 (1 H, m, 1-H), *m/e* 386 (M^+) (Found: C, 71.2; H, 7.8. $C_{23}H_{30}O_5$ requires C, 71.45; H, 7.8%). Similar reaction mixtures were obtained when the desulphurisation was repeated at room temperature and 0 °C.

9α-*Fluoro*-11β-*hydroxy*-20-*oxo*-17α,21-*dipropionyloxypregna*-1,3,5-*trien*-3-*yl* 2-*Nitrophenyl Disulphide* (4a).—The dienethione (3b) (400 mg) in dichloromethane (60 ml) was treated with 2-nitrobenzenesulphenyl chloride (154 mg) in small portions at 0 °C under argon. The yellow solution was evaporated and recrystallised under argon from dichloromethane–hexane to give the *disulphide* (4a) as yellow needles (485 mg, 90%), m.p. 98—100°, $\nu_{max.}$ 3 600, 3 050, 1 740, 1 665, 1 340, and 1 300 cm^{-1}, $\lambda_{max.}$ 340 (ε 10 500), 329 (11 000), and 270sh nm (10 200), δ 0.94 (3 H, s, 13-Me), 1.27 (3 H, s, 10-Me), 4.5br (1 H, s, 11α-H), 4.6 (2 H, ABq, *J* 16 Hz, 21-H), 5.66—6.25 (4 H, m, 1-, 2-, 4-, and 6-H), and 7.1—7.8 and 8.0—8.3 (4 H, m, aryl-H) (Found: C, 60.75; H, 5.95; N, 1.95; S, 9.5. $C_{34}H_{40}FNO_8S_2$ requires C, 60.6; H, 6.0; N, 2.05; S, 9.5%).

21-*Acetoxy*-11β,17α-*dihydroxy*-20-*oxopregna*-1,3,5-*trien*-3-*yl* 2-*Nitrophenyl Disulphide* (4b).—*The disulphide* (4b) (57 mg, 87%), prepared from 3-thioxoprednisolone 21-acetate (3f) (50 mg) and 2-nitrobenzenesulphenyl chloride (23 mg), was recrystallised under argon and in the cold from dichloromethane–hexane, m.p. 134—137° (dec.), $\nu_{max.}$ 3 700, 3 050, 1 735, 1 340, and 1 300 cm^{-1}, $\lambda_{max.}$ 340 (ε 10 000) and 330 nm (10 200), δ 0.88 (3 H, s, 13-Me), 1.2 (3 H, s, 10-Me), 2.1 (3 H, s, OAc), 4.43br (1 H, s, 11α-H), 4.91 (2 H, ABq, *J* 18 Hz, 21-H), 5.41—6.3 (4 H, m, 1-, 2-, 4-, and 6-H), and 7.1—8.3 (4 H, m, aryl-H) (Found: C, 60.85; H, 5.75; N, 2.5; S, 11.35. $C_{29}H_{33}NO_7S_2$ requires C, 60.9; H, 5.8; N, 2.45; S, 11.2%).

17-*Oxoandrosta*-1,3,5-*trien*-3-*yl* 2-*Nitrophenyl Disulphide* (4c).—The *disulphide* (4c) (284 mg, 85%), prepared from the dienethione (3h) (305 mg) and 2-nitrobenzenesulphenyl chloride (195 mg), was obtained as yellow needles, m.p. 136—139° (dec.) (from dichloromethane–hexane), $\nu_{max.}$ 3 000, 1 745, 1 665, 1 340, and 1 300 cm^{-1}, $\lambda_{max.}$ 339 (ε 10 000) and 328 nm (10 500), δ 0.88 (3 H, s, 13-Me), 1.02 (3 H, s, 10-Me), 5.5—6.17 (4 H, m, 1-, 2-, 4-, and 6-H), and 7.2—8.35 (4 H, m, aryl), *m/e* 453 (M^+) (Found: C, 66.05; H, 5.85; N, 3.1; S, 14.25. $C_{25}H_{27}NO_3S_2$ requires C, 66.2; H, 6.0; N, 3.1; S, 14.15%).

Reaction of Thione (3h) *with* 2-*Nitrobenzenesulphenyl Chloride in the Presence of Phosphorus Pentasulphide.*—Androsta-1,4-diene-3,17-dione (3g) (650 mg), phosphorus pentasulphide (800 mg), and benzene (60 ml) were stirred at 70 °C for 6 h under argon. The mixture was cooled to room temperature, 2-nitrobenzenesulphenyl chloride (500 mg) was added, and stirring continued for another 16 h. The yellow mixture was filtered and the concentrated filtrate purified by p.l.c. The least polar fraction was recrystallised from methanol to give 4-*methyl*-17-*oxoestra*-1,3,5(10)-*trien*-1-*yl* 2-*nitrophenyl disulphide* (5) (250 mg, 24%), m.p. 155—157°, $\nu_{max.}$ 3 000, 1 750, 1 340, and 1 305 cm^{-1}, $\lambda_{max.}$ 343 nm (ε 8 000), δ 0.95 (3 H, s, 13-Me), 2.12 (3 H, s, 4-Me), 6.8 and 7.18 (2 H, 2d, *J* 8.8 Hz, 2- and 3-H), and 7.2—8.25 (4 H, m, aryl), *m/e* 453 (M^+) (Found: C, 66.0; H, 5.9; N, 2.9; S, 14.3. $C_{25}H_{27}NO_3S_2$ requires C, 66.2; H, 6.0; N, 3.1; S, 14.15%). The more polar 1-*chloro*-17-*oxoandrosta*-3,5-*dien*-3-*yl* 2-*nitrophenyl disulphide* (6) (73 mg, 7%) was obtained as yellow prisms, m.p. 186—188° (dec.), $\nu_{max.}$ 3 000, 1 745, 1 645, 1 340, and 1 300 cm^{-1}, $\lambda_{max.}$ 247 (ε 25 000) and 350 nm (3 600), δ 0.88 (3 H, s, 13-Me), 1.0 (3 H, s, 10-Me), 2.83 (2 H, m, 2-H), 4.22 (1 H, m, 1-H), 5.7br (1 H, s, 6-H), 6.4 (1 H, s, 4-H), and 7.1—8.3 (4 H, m, aryl-H) (Found: C, 61,25; H, 5.75; N, 2.8; Cl, 6.95; S, 13.15. $C_{25}H_{28}ClNO_3S_2$ requires C, 61.25; H, 5.75; N, 2.85; Cl, 7.25; S, 13.1%).

1-*Chloro*-17-*oxoandrosta*-3,5-*dien*-3-*yl* 2-*Nitrophenyl Disulphide* (6).—The disulphide (4c) (100 mg) in benzene (30 ml) was treated with anhydrous hydrogen chloride at room temperature for 3 h. The solution was washed with aqueous sodium hydrogen carbonate, water, and dried. Evaporation and recrystallisation from methanol gave the disulphide (6) as yellow prisms (84 mg, 80%), m.p. 185—187°, identical with the sample previously obtained (mixed m.p., i.r., u.v., and n.m.r.).

17β-*Acetoxyandrosta*-3,5-*dien*-3-*yl* 2-*Nitrophenyl Disulphide* (8a).—Testosterone acetate (7b) (1 g), phosphorus pentasulphide (1 g), 2-nitrobenzenesulphenyl chloride (200 mg), and benzene (60 ml) were stirred at 75 °C under argon. Additional portions of 2-nitrobenzenesulphenyl chloride (3 × 130 mg) were added at 1.5 hourly intervals. The mixture was stirred for 1 h after the final addition and filtered. The concentrated filtrate was chromatographed on Florisil (eluant benzene) to give the yellow *disulphide* (8a) (1.03 g, 70%), m.p. 113—115° (dec.) (from methanol) $\nu_{max.}$ 3 000, 1 735, 1 360, and 1 300 cm^{-1}, $\lambda_{max.}$ 243 (ε 26 000) and 350 nm (5 500), δ 0.8 (3 H, s, 13-Me), 0.87 (3 H, s, 10-Me), 2.0 (3 H, s, OAc), 4.58 (1 H, t, *J* 8 Hz, 17α-H), 5.43br (1 H, s, 6-H), 6.27 (1 H, s, 4-H), and 7.1—8.3 (4 H, m, aryl), *m/e* 499 (M^+) (Found: C, 64.8; H, 6.6; N, 2.8; S, 12.9. $C_{27}H_{33}NO_4S_2$ requires C, 64.9; H, 6.65; N, 2.8; S, 12.85%).

11,17-*Dioxoandrosta*-3,5-*dien*-3-*yl* 2-*Nitrophenyl Disulphide* (8b).—Androst-4-ene-3,11,17-trione (7d) (610 mg), phosphorus pentasulphide (600 mg), 2-nitrobenzenesulphenyl chloride (150 mg), and toluene (60 ml) were stirred at 80 °C for 1.5 h under argon. Additional portions of 2-nitrobenzenesulphenyl chloride (4 × 65 mg) were added at hourly intervals. After a further hour the mixture was filtered and the concentrated filtrate chromatographed on Florisil. Elution with dichloromethane gave the yellow *disulphide* (8b) (668 mg, 73%), m.p. 134—136° (dec.) from methanol $\nu_{max.}$ 3 000, 1 750, 1 720, 1 340, and 1 300 cm^{-1}, $\lambda_{max.}$ 243 (ε 24 000) and 350 nm (6 000), δ 0.85 (3 H, s, 13-Me), 1.1 (3 H, s, 10-Me), 5.4br (1 H, s, 6-H), 6.2 (1 H, s, 4-H), and 7.2—8.3 (4 H, m, aryl), *m/e* 469 (M^+) (Found: C, 63.65; H, 5.8; N, 2.9; S, 13.65. $C_{25}H_{27}NO_4S_2$ requires C, 63.95; H, 5.8; N, 3.0; S, 13.65%).

6-(2-*Nitrophenylthio*)-11,17-*dioxoandrosta*-3,5-*dien*-3-*yl* 2-*Nitrophenyl Disulphide* (8c).—The disulphide (8b) was generated as described above from the trione (7d) (610 mg); additional 2-nitrobenzenesulphenyl chloride (400 mg) was added and stirring was continued for a further 6 h at 80 °C. The mixture was filtered, concentrated, chromatographed on Florisil (eluant ethyl acetate–dichloromethane 1 : 99), and separated by p.l.c. (dichloromethane) to give the less polar disulphide (8b) (365 mg, 36%) (i.r., n.m.r., u.v., and mixed m.p.) and the more polar *disulphide* (8c), (246 mg, 18%), m.p. 202—204° (from dichloromethane–hexane), $\nu_{max.}$ 3 000, 1 750, 1 720, 1 600, 1 340, and 1 300 cm^{-1}, $\lambda_{max.}$ 242 (ε 22 000), 275sh (16 000), and 355 nm (6 000), δ 0.88 (3 H, s, 13-Me), 1.28 (3 H, s, 10-Me), 6.93 (1 H, s, 4-H), and 7.0—8.28 (8 H, m, aryl) (Found: C, 59.7; H, 4.85; N, 4.5; S, 15.4. $C_{31}H_{30}N_2O_6S_3$ requires C, 59.8; H, 4.85; N, 4.5; S, 15.45%).

11,17-*Dioxoandrosta*-3,5-*dien*-3-*yl Ethyl Disulphide* (8b).—Ethanethiol (90 mg) was added dropwise with stirring under argon to the disulphide (8b) (470 mg) in dichloromethane (20 ml) and triethylamine (0.5 ml). After 2 h the solvent was evaporated off and the residue purified by p.l.c. (benzene–dichloromethane 2 : 3) to give the *disulphide* (8f) (238 mg, 64%), m.p. 155—157° (dec.) (from MeOH), $\nu_{max.}$ 3 000, 1 750, and 1 720 cm^{-1}, $\lambda_{max.}$ 248 nm (ε 18 000), δ 0.9 (3 H, s, 13-Me), 1.17 (3 H, s, 10-Me), 1.33 (3 H, t, *J* 7 Hz, C*H*$_3$-CH$_2$S), 2.77 (2 H, q, *J* 7 Hz, MeC*H*$_2$S), 5.54br (1 H, s, 6-H), and 6.4 (1 H, s, 4-H), *m/e* 376 (M^+) (Found: C, 66.85; H, 7.5; S, 16.9. $C_{21}H_{28}O_2S_2$ requires C, 66.95; H, 7.5; 17.05%).

11,17-*Dioxoandrosta*-3,5-*dien*-3-*yl Phenyl Disulphide* (8g).—Benzenethiol (130 mg) and the disulphide (8b) (470, mg) gave the *disulphide* (8g) (310 mg, 75%), m.p. 130—132° (dec.) (from MeOH), $\nu_{max.}$ 3 000, 1 750, and 1 720 cm^{-1}, $\lambda_{max.}$ 246 nm (ε 22 000), δ 0.88 (3 H, s, 13-Me), 1.15 (3 H, s, 10-Me), 5.5br (1 H, s, 6-H), 6.4 (1 H, s, 4-H), and 7.3—7.7 (5 H, m, Ph), *m/e* 424 (M^+) (Found: C, 70.95; H, 6.7; S, 15.15. $C_{25}H_{28}O_2S_2$ requires, C, 70.7; H, 6.65; S, 15.1%).

17β-*Acetoxyandrosta*-3,5-*dien*-3-*yl Ethyl Disulphide* (8d).—The disulphide (8a) (400 mg) and ethanethiol (80 mg) gave the *disulphide* (8d) (205 mg, 63%), m.p. 63.5—65° (dec.) (from MeOH), $\nu_{max.}$ 3 000 s and 1 740 s cm^{-1}, $\lambda_{max.}$ 248 nm (ε 16 000), δ 0.84 (3 H, s, 13-Me), 0.93 (3 H, s, 10-Me), 1.3 (3 H, t, *J* 7 Hz, C*H*$_3$CH$_2$S), 2.04 (3 H, s, OAc) 2.7 (2 H, q, *J* 7 Hz, MeC*H*$_2$S), 4.63 (1 H, m, 17α-H), 5.4br (1 H, s, 6-H), and 6.3 (1 H, s, 4-H), *m/e* 406 (M^+) (Found: C, 68.05; H, 8.15; S, 15.5. $C_{23}H_{34}O_2S_2$ requires C, 67.95; H, 8.4; S, 15.75%).

17β-*Acetoxyandrosta*-3,5-*dien*-3-*yl Phenyl Disulphide* (8e).—The disulphide (8a) (400 mg) and benzenethiol (110 mg) gave the *disulphide* (8e) (263 mg, 72%) (dec.) (from MeOH), $\nu_{max.}$ 3 000 and 1 740 cm^{-1}, $\lambda_{max.}$ 247 nm (ε 20 500) δ 0.83 (3 H, s, 13-Me), 0.91 (3 H, s, 10-Me), 2.01 (3 H, s, OAc), 4.6 (1 H, m, 17α-H), 5.4br (1 H, s, 6-H), 6.26 (1 H, s, 4-H), and 7.1—7.6 (5 H, m, Ph), *m/e* 454 (M^+) (Found: C, 71.3; H, 7.35; S, 14.1. $C_{27}H_{34}O_2S_2$ requires C, 71.3; H, 7.55; S, 14.1%).

Attempted Preparation of Bis-11,17-*dioxoandrosta*-3,5-*dien*-3-*yl Disulphide* (9a).—To 11,17-dioxoandrost-4-ene-3-thione (7e) [from androst-4-ene-3,11,17-trione (7d) (910 mg) and phosphorus pentasulphide (800 mg) in toluene (60 ml) at 80 °C under argon] 11,17-dioxoandrosta-3,5-dien-3-yl 2-nitrophenyl disulphide (8b) (500 mg) and triethylamine (2 ml) were added. After stirring for 6 h the mixture was filtered, concentrated, and chromatographed on Florisil to give (eluant dichloromethane) unchanged disulphide (8b) (430 mg) and (eluant ethyl acetate–dichloromethane 3 : 97) a fraction which was purified by p.l.c. to give *bis*-11,17-*dioxoandrosta*-3,5-*dien*-3-*yl sulphide* (9b) (402 mg), m.p. 196—198° (dec.) (from MeOH), $\nu_{max.}$ 3 000, 1 750, 1 720, and 1 605 cm^{-1}; $\lambda_{max.}$ 297sh (ε 8 500), 270 (13 100), 248 (17 000), and 239 nm (18 000), δ 0.9 (6 H, s, 13- and 13′-Me), 1.18 (6 H, s, 10- and 10′-Me), 5.5br (2 H, s, 6- and 6′-H), and 6.2 (2 H, s, 4- and 4′-H), *m/e* 598 (M^+) (Found: C, 76.35; H, 7.7; S, 5.1. $C_{38}H_{46}O_4S$ requires C, 76.2; H, 7.75; S, 5.35%).

Bis-11,17-*dioxoandrosta*-3,5-*dien*-3-*yl Sulphide* (9b).—Androst-4-ene-3,11,17-trione (7d) (750 mg), phosphorus pentasulphide (600 mg), triethylamine (2 ml), and toluene (50 ml) were stirred at 75 °C for 6.5 h under argon. The mixture was cooled and 2-nitrobenzenesulphenyl chloride (100 mg) and triethylamine (0.5 ml) were added. After 20 min the mixture was filtered, concentrated, and chromatographed on Florisil to give (eluant dichloromethane) 11,17-dioxoandrosta-3,5-dien-3-yl 2-nitrophenyl disulphide (8b) (112 mg) and (eluant ethyl acetate–dichloromethane 3 : 97) a more polar fraction. P.l.c. (ethyl acetate–dichloromethane 1 : 99) gave the title sulphide (9b) (394 mg, 54%), m.p. 196—

198° (dec.) (from MeOH) (identical with the sample previously obtained).

4-Methoxy-3-methyl-2H-1-benzopyran-2-thione (10c).—4-Methoxy-3-methyl-2*H*-1-benzopyran-2-one (10b) [19] (570 mg), phosphorus pentasulphide (1 g), and toluene (30 ml) were stirred at 70 °C for 20 h under argon. The mixture was filtered and the residue washed with dichloromethane (2 × 15 ml). The combined filtrates were concentrated and chromatographed on Florisil (eluant benzene), to give the *thione* (10c) (452 mg, 72%) as yellow needles, m.p. 115—116° (from benzene–hexane), $\nu_{max.}$ (KBr) 1 605, 1 560, and 1 130 cm^{-1}, $\lambda_{max.}$ (hexane) 384sh (ε 9 100), 370 (11 800), 360sh (10 700), 305 (1 800), 276 (8 300), and 244 nm (5 000), δ 2.38 (3 H, s, 3-Me), 4.0 (3 H, s, 4-OMe), and 7.14—7.83 (4 H, m, aryl), *m/e* 206 (M^+) (Found: C, 63.9; H, 5.05; S, 15.4. $C_{11}H_{10}O_2S$ requires C, 64.05; H, 4.9; S, 15.55%).

Hydrolysis of the Thione (10c).—The thione (10c) (155 mg), mercuric acetate (600 mg), acetone (25 ml), and acetic acid (0.5 ml) were stirred at room temperature until the mixture became colourless. The mixture was filtered, concentrated, and diluted with water. The resultant precipitate was washed thoroughly with water. Chromatography on silica gel (eluant diethyl ether) gave 4-methoxy-3-methyl-2*H*-1-benzopyran-2-one (10b) (126 mg) as needles, m.p. 42°, (identical with authentic material).

Reaction of Cyclocumarol (12a) *with Phosphorus Pentasulphide*.—Cyclocumarol (12a) (1.5 g), phosphorus pentasulphide (1.0 g), and benzene (40 ml) were stirred at 80 °C for 30 h under argon. Additional phosphorus pentasulphide (0.5 g) was added and reaction continued for another 28 h. The mixture was filtered and the residue washed with dichloromethane (2 × 15 ml). The combined concentrated filtrates were chromatographed on Florisil (eluant benzene) to give (in order of increasing polarity) *2-methyl-4-phenyl-4H,5H-thiopyrano*[2,3-b][1]*benzopyran-5-thione* (13a) (428 mg, 29%), as dark red crystals, m.p. 178—179.5° (from benzene–hexane), $\nu_{max.}$ (KBr) 1 660, 1 605, 1 590, 1 240, 1 170, and 1 100 cm^{-1}, $\lambda_{max.}$ 389 (ε 16 000), 353 (13 900), 305sh (4 000), 228sh (22 300), and 210 nm (37 100), δ 2.04 (3 H, s, 2-Me), 5.88 (2 H, m, 3-H and 4-H), 7.1—7.6 (8 H, m, aryl), and 8.37—8.57 (1 H, m, 6-H) (Found: C, 70.95; H, 4.45; S, 19.85; M^+, 322.048 4. $C_{19}H_{14}OS_2$ requires C, 70.75; H, 4.4; S, 19.9%; *M*, 322.048 5); *2-methyl-4-phenyl-4H,5H-thiopyrano*[3,2-c][1]*benzopyran-5-thione* (14a) (248 mg, 17%) as orange needles, m.p. 166—167° (from hexane), $\nu_{max.}$ (KBr) 1 610, 1 590, 1 260, and 1 170 cm^{-1}, $\lambda_{max.}$ 410 (ε 12 000), 390 (13 000), 368 (11 000), 355sh (9 100), 310 (5 100), 281 (9 500), 270sh (9 000), 246 (16 800), and 215 (16 500), δ 2.1 (3 H, d, *J* 1 Hz, 2-Me), 5.65 (1 H, *d*, *J* 7 Hz, 4-H), 5.98 (1 H, dq, *J* 1 and 7 Hz, 3-H), 7.1—7.53 (8H, m, aryl), and 7.58—7.82 (1 H, m, 10-H), (Found: C, 70.75; H, 4.5; S, 19.85%; M^+, 322.048 4. $C_{19}H_{14}OS_2$ requires C, 70.75; H, 4.4; S, 19.9%; *M*; 322.048 5); and *2-methyl-4-phenyl-4H,5H-pyrano*[3,2-c][1]*benzopyran-5-thione* (14c) (239 mg, 17%), m.p. 184—186° (from benzene–hexane), $\nu_{max.}$ (KBr) 1 605, 1 560, 1 205, 1 158, and 1 125 cm^{-1}, $\lambda_{max.}$ (hexane) 387 (ε 11 500), 371 (13 000), 310sh (4 600), and 278 nm (14 000), δ 2.03 (3 H, s, 2-Me), 4.77 (1 H, d, *J* 6 Hz, 4-H), 5.13 (1 H, d, *J* 6 Hz, 3-H), 7.01—7.5 (8 H, m, aryl), and 7.8—8.0 (1 H, m, 10-H), *m/e* 306 (M^+) (Found: C, 74.55; H, 4.8; S, 10.2. $C_{19}H_{14}O_2S$ requires C, 74.5; H, 4.6; S, 10.45%).

2-Methyl-4-phenyl-4H,5H-thiopyrano[2,3-b][1]*benzopyran-5-one* (13b).—2-Methyl-4-phenyl-4*H*,5*H*-thiopyrano[2,3-*b*][1]benzopyran-5-thione (13a) (97 mg), mercuric acetate (500 mg), and acetone (60 ml) were stirred at room temperature for 18 h. The mixture was filtered and the filtrate concentrated. Chromatography on Florisil (eluant benzene) gave the *pyranone* (13b) (81 mg, 88%) as needles, m.p. 117—118° (from benzene–hexane), $\nu_{max.}$ (KBr) 1 665, 1 640, 1 615, 1 565, 1 465, and 1 370 cm^{-1}, $\lambda_{max.}$ 314sh (ε 6 900), 302 (9 100), 294 (7 200), and 217 nm (23 500), δ 2.06 (3 H, d, *J* 1 Hz, 2-Me), 5.15 (1 H, d, *J* 6 Hz, 4-H), 5.83 (1 H, dd, *J* 1 and 6 Hz, 3-H), 7.07—7.6 (8 H, m, aryl), and 7.96—8.17 (1 H, m, 6-H) (Found: C, 74.6; H, 4.8; S, 10.6%; M^+, 306.071 8. $C_{19}H_{14}O_2S$ requires C, 74.5; H, 4.6; S, 10.45%; M^+, 306.071 4).

2-Methyl-4-phenyl-4H,5H-thiopyran[3,2-c][1]*benzopyran-5-one* (14b).—The *benzopyranone* (14b) (80 mg, 87%) was prepared from 2-methyl-4-phenyl-4*H*,5*H*-thiopyrano[3,2-*c*]-[1]benzopyran-5-thione (14a) (97 mg) and mercuric acetate (500 mg), m.p. 210—212° (from benzene–hexane), $\nu_{max.}$ (KBr) 1 710, 1 600, 1 455, and 1 270 cm^{-1}, $\lambda_{max.}$ 320sh (ε 9 400), 310 (9 900), 286 (11 300), 248 (14 500), 240 (15 000), and 213 nm (33 000), δ 2.1 (3 H, d, *J* 1.5 Hz, 2-Me), 4.97 (1 H, d, *J* 6 Hz, 4-H), 5.87 (1 H, dq, *J* 1.5 and 6 Hz, 3-H), 7.05—7.5 (8 H, m, aryl), and 7.5—7.7 (1 H, m, 10-H), (Found: C, 74.7; H, 4.95; S, 10.6%; M^+, 306.071 4. $C_{19}H_{14}O_2S$ requires C, 74.5; H, 4.6; S, 10.45%; M^+, 306.071 4).

Hydrolysis of the Thione (14c).—The thione (14c) (93 mg) was treated with mercuric acetate (500 mg) to give 2-methyl-4-phenyl-4*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one (14d) (73 mg, 85%), m.p. 145—146° (from methanol), identical with an authentic sample (see below).

Isolation of the Intermediate Pyranone (14d) *in the Reaction of Cyclocumarol* (12a) *with* P_4S_{10}.—Cyclocumarol (12a) (10 g), phosphorus pentasulphide (0.8 g), and benzene (35 ml) were stirred at 80 °C for 1.5 h under argon. The mixture was filtered, concentrated, and chromatographed on Florisil (eluant diethyl ether) to yield 2-methyl-4-phenyl-4*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one (14d) (756 mg, 86%), m.p. 146—147° (from methanol) (lit.,[21] m.p. 145—146°), $\nu_{max.}$ (KBr) 1 720, 1 630, and 1 610 cm^{-1}, $\lambda_{max.}$ 328sh (ε 4 800), 312 (8 000), 302sh (7 900), 273 (10 500), 267 (10 800), and 260 nm (11 600), δ 2.0 (3 H, s, 2-Me), 4.42 (1 H, d, *J* 6 Hz, 4-H), 4.97 (1 H, d, *J* 6 Hz, 3-H), 7.0—7.45 (8 H, m, aryl), and 7.67—7.87 (1 H, m, 10-H), *m/e* 290 (M^+) (Found: C, 78.6; H, 5.0. Calc. for $C_{19}H_{14}O_3$: C, 78.6; H, 4.9%).

Reaction of Pyranone (14d) *with Phosphorus Pentasulphide*.— 2-Methyl-4-phenyl-4*H*,5*H*-pyrano[3,2-c][1]benzopyran-5-one (14d) (650 mg), phosphorus pentasulphide (900 mg), and benzene (35 ml) were stirred at 80 °C for 25 h under argon. Additional phosphorus pentasulphide (400 mg) was added and stirring continued for another 30 h. The mixture was filtered, concentrated, and chromatographed on Florisil (eluant benzene) to give 2-methyl-4-phenyl-4*H*,5*H*-thiopyrano[2,3-*b*][1]benzopyran-5-thione (13a) (120 mg, 18%) and 2-methyl-4-phenyl-4*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-thione (14c) (391 mg, 59%) (identical with authentic samples).

Reaction of Thione (14c) *with Phosphorus Pentasulphide*.—The thione (14c) (465 mg), phosphorus pentasulphide (650 mg), and benzene (20 ml) were stirred at 80 °C for 48 h under argon. The mixture was filtered, concentrated, and chromatographed on Florisil (eluant benzene) to give (in order of increasing polarity) the benzopyranthione (13a) (204 mg, 42%), the dithio-compound (14a) (93 mg, 19%), and unchanged monothione (14c) (78 mg, 17%).

Reaction of Warfarin (10a) *with Phosphorus Pentasulphide*.—Warfarin (10a) (1 g), phosphorus pentasulphide (1.2 g), and benzene (60 ml) were stirred at 85 °C for 36 h under argon. Additional phosphorus pentasulphide (0.5 g) was added and the reaction continued for another 24 h. The mixture was filtered and the residue washed with dichloromethane (2 × 15 ml). The combined filtrates were concentrated and chromatographed on Florisil (eluant benzene) to give the benzopyranthiones (13a) (376 mg), (14a) (97 mg), and (14c) (159 mg). A similar reaction mixture was obtained with the 4-methoxy derivative (10f) of Warfarin (10a).

Isolation of Intermediates in the Reaction of Warfarin (10a) *with Phosphorus Pentasulphide*.—Warfarin (10a) (1.2 g), phosphorus pentasulphide (1.2 g), and benzene (80 ml) were stirred at 85 °C for 2 h (argon). The mixture was filtered, concentrated, and chromatographed on Florisil (eluant diethyl ether) to give a mixture of two products. Recrystallisation from methanol gave 2-methyl-4-phenyl-4*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one (14d) (620 mg, 55%), m.p. 146—147°. The mother liquor was separated by p.l.c. (diethyl ether) to give additional pyranone (14d) (96 mg, 18%) and a second product, 3,4-*dihydro*-2-*mercapto*-2-*methyl*-4-*phenyl*-2H,5H-*pyrano*[3,2-c][1]*benzopyran*-5-*one* (12b) (51 mg, 4%), m.p. 109—114° (dec.) (from benzene–hexane), $\nu_{max.}$ (KBr) 2 950, 2 560, 1 720, and 1 625 cm^{-1}, δ 1.95 (3 H, s, 2-Me), 1.87—2.75 (2 H, m, 3-H), 2.77 (1 H, s, exch. D_2O, SH), 3.95—4.25 (1 H, m, 4-H), 7.1—7.57 (8 H, m, aryl), and 7.7—7.92 (1 H, m, 10-H), (Found: M^+, 324.081 5. $C_{19}H_{15}O_3S$ requires *M* 324.082 0).

2-*Methyl*-4-*phenyl*-4H,5H-*pyrano*[3,2-c][1]*benzopyran*-5-*one* (14d).—Warfarin (10a) (3.5 g), phosphorus pentaoxide (4 g), and benzene (180 ml) were refluxed for 1 h. The mixture was filtered, concentrated, and chromatographed on Florisil (eluant diethyl ether) to yield the title compound (14d) (2.96 g, 86%), m.p. 146—147° (from methanol).

Reaction of 4-*Hydroxy*-2H-1-*benzopyran*-2-*one* (10e) *with Phosphorus Pentasulphide*.—4-Hydroxy-2*H*-1-benzopyran-2-one (10e) (1.62 g), phosphorus pentasulphide (1.8 g), and acetonitrile (100 ml) were refluxed with stirring for 24 h under argon. The mixture was filtered and the residue washed with dichloromethane (3 × 20 ml). The concentrated filtrates were chromatographed on Florisil (eluant benzene) to give bis(2-thioxo-2*H*-1-benzopyran-4-yl) sulphide (18a) (1.01 g, 57%) as orange needles, m.p. 206—209° (dec.) (from benzene–hexane), $\nu_{max.}$ (KBr) 1 605, 1 580, 1 530, 1 350, 1 215, 1 155, 1 135, and 1 105 cm^{-1}, $\lambda_{max.}$ (CH_3CN) 400sh (ε 10 000), 385 (12 000), 316 (7 000), and 273 nm (12 250), δ 7.07 (2 H, s, 3-H, 3′-H), and 7.2—7.8 (8 H, m, aryl), (Found: C, 61.2; H, 3.0; S, 27.05%; M^+ 354.983 1. $C_{18}H_{10}O_2S_3$ requires C, 61.0; H, 2.85; S, 27.15%; *M*, 354.984 3.

Bis(2-*oxo*-2-H-1-*benzopyran*-4-*yl*) *Sulphide* (18b).—(A) The dithione (18a) (100 mg) in dichloromethane (20 ml) was treated with 85% 3-chloroperoxybenzoic acid (120 mg, 2 equiv.) under argon. The solution was washed with aqueous sodium hydrogen carbonate and water, dried, and irradiated by a 1.5 kW photoflood lamp for 1 h. Evaporation and purification by p.l.c. (dichloromethane) gave the *sulphide* (18b) (70 mg, 77%), m.p. 258—260° (dec.) (from methanol), $\nu_{max.}$ 1 755sh, 1 725, 1 600, 1 555, and 1 345 cm^{-1}, $\lambda_{max.}$ 315 (ε 12 000) and 275 nm (18 000), δ 6.38 (2 H, s, 3-H, 3′-H) and 7.2—7.8 (8 H, m, aryl), *m/e* 322 (M^+) (Found: C, 67.0; H, 3.2; S, 10.15. $C_{18}H_{10}O_4S$ requires C, 67.05; H, 3.15; S, 9.95%). (B) Hydrolysis of the dithione (18a) (100 mg) with mercuric acetate (800 mg) gave the sulphide (18b) (75 mg, 82%), m.p. 258—260° (from methanol).

(2S-trans)-7-*Chloro*-2′,4,6-*trimethoxy*-6′-*methyl*-4′-*thioxo*-*spiro*[*benzofuran*-2(3H),1′-*cyclohex*-2-*en*]-3-*one* (19b).—Griseofulvin (19a) (1.5 g), phosphorus pentasulphide (1.8 g), and benzene (180 ml) were stirred at reflux temperature for 19 h under argon. The mixture was filtered and the residue washed with benzene (2 × 30 ml). The combined filtrates were evaporated and chromatographed on Florisil (argon) (eluant dichloromethane) to give the purple *griseofulvin*-4′-*thione* (19b) (790 mg, 51%), m.p. 156—157° from diethyl ether–hexane under argon, $\nu_{max.}$ 3 000, 1 715, 1 615, 1 580, and 1 260 cm^{-1}, $\lambda_{max.}$ 376 (ε 19 600), 323 (6 000), and 295 nm (20 000), δ 0.97 (3 H, d, *J* 6 Hz, 6′-Me), 2.3—3.43 (3 H, m, 5′ and 6′-H), 3.7 (3 H, s, 2′-OMe), 4.0 and 4.07 (6 H, 2s, 4- and 6-OMe), 6.22 (1 H, s, 5-H), and 6.52 (1 H, s, 3′-H) (Found: C, 55.55; H, 4.75; Cl, 9.5; S, 8.75%; M^+, 368.047 4. $C_{17}H_{17}ClO_5S$ requires C, 55.35; H, 4.65; Cl, 9.6; S, 8.7% *M*, 368.048 5).

Reaction of Griseofulvin-4′-*thione* (19b) *with Diphenyldiazomethane*.—Griseofulvin-4′-thione (19b) (220 mg) and diphenyldiazomethane (120 mg) in dichloromethane (15 ml) were stirred at room temperature under argon for 24 h. The two major components were separated by p.l.c. (benzene–dichloromethane 1 : 19) to give the more polar *thiiran* (19c) as needles (210 mg, 66%), m.p. 177—178° (dec.) (from methanol), $\nu_{max.}$ (KBr) 3 000, 1 710, 1 640, 1 610, and 1 580 cm^{-1}, $\lambda_{max.}$ 325 (ε 4 900), 290 (21 000), 237sh (29 500), and 214 nm (36 300), δ 0.77 (3 H, d, *J* 6 Hz, 6′-Me), 1.51 (1 H, m, 6′-H), 2.83—2.88 (2 H, m, 5′-H), 3.2 (3 H, s, 2′-OMe), 3.92—3.97 (6 H, 2s, 4- and 6-OMe), 4.55 (1 H, s, 3′-H), 6.1 (1 H, s, 5-H), and 7.1—7.7 (10 H, m, aryl) (Found: C, 67.05; H, 5.05; Cl, 6.65; S, 6.0%; M^+, 534.124 6. $C_{30}H_{27}ClO_5S$ requires C, 67.35; H, 5.1; Cl, 6.65; S, 6.0%; *M*, 534.126 8) and an inseparable mixture (104 mg), $\nu_{max.}$ (KBr) 3 000, 1 710, 1 610, and 1 580 cm^{-1}, δ 0.77 and 0.84 (3 H, 2d, *J* 6 and 6 Hz, 6′-Me), 1.7—3.15 (3 H, m, 5′-H_2 and 6′-H), 3.2 and 3.36 (3 H, 2s, 2′-OMe), 3.96 and 3.99 (6 H, 2s, 4- and 6-OMe), 4.63 and 5.8 (1 H, 2s, 3′-H), 6.08 and 6.11 (1 H, 2s, 5-H), and 7.2—7.7 (10 H, m, aryl), *m/e* 534, 502. This mixture (95 mg) was treated with triphenylphosphine (35 mg) in benzene (10 ml) in the dark for 3 days. Purification by p.l.c. (dichloromethane) gave (2S-trans)-7-*chloro*-4′-(*diphenylmethylene*)-2′,4,6-*trimethoxy*-6′-*methyl*-*spiro*[*benzofuran*-2(3H), 1′-*cyclohex*-2-*en*]-3-*one* (19d) as needles (85 mg), m.p. 233—235° (from ethanol), $\nu_{max.}$ (KBr) 3 000, 1 710, 1 610, and 1 580 cm^{-1}, $\lambda_{max.}$ 295 (ε 22 300) and 234sh nm (11 700), δ 0.84 (3 H, d, *J* 6 Hz, 6′-Me), 2.2—3.1 (3 H, m, 5′-H_2 and 6′-H), 3.36 (3 H, s, 2′-OMe), 3.97 and 3.99 (6 H, 2s, 4- and 6-OMe), 5.8 (1 H, s, 3′-H), 6.08 (1 H, s, 5-H), and 7.25 (10 H, m, aryl) (Found: C, 71.85; H, 5.45; Cl, 7.25%; M^+, 502.154 3. $C_{30}H_{27}ClO_5$ requires C, 71.65; H, 5.4; Cl, 7.05%; *M*, 502.154 7).

Desulphurisation of the Thiiran (19c).—(A) The thiiran (19c) (54 mg), triphenylphosphine (27 mg), and benzene (10 ml) were stirred in the dark for 3 days. The resulting mixture was separated by p.l.c. (dichloromethane) to give triphenylphosphine sulphide (28 mg), m.p. 160—161° (from EtOH) and the diene (19d) (46 mg, 90%), m.p. 232—235° (from EtOH). (B) The thiiran (19c) (54 mg) was heated to 190 °C for 5 min under argon. The residue was dissolved in dichloromethane and the product (19d) (41 mg, 80%) was separated from elemental sulphur by p.l.c. (dichloromethane).

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