Pyranopyran Derivatives Related to Citromycetin, and their Sulphurization to give Derivatives of 1-Oxa-6,6-dithia(6a-S^{IV})pentalene and 1,6,6a-Trithia(6a-S^{IV})pentalene

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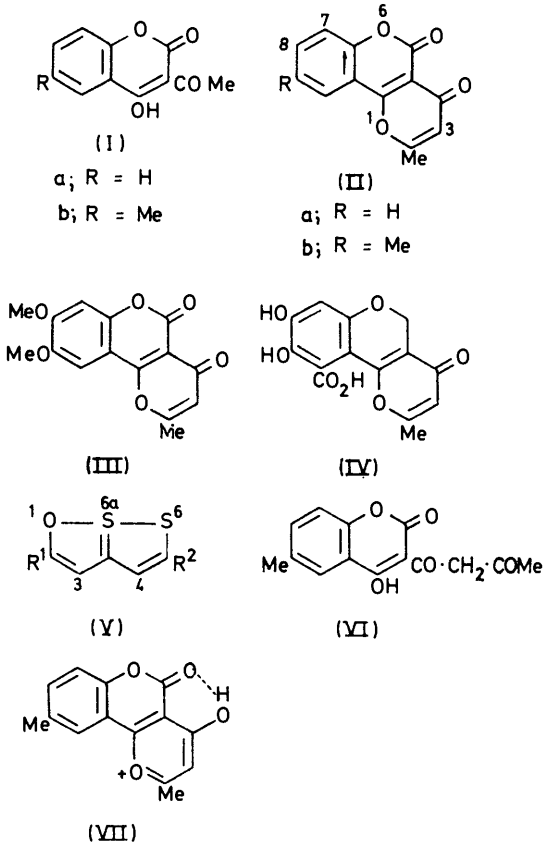
Acetic anhydride and perchloric acid convert 3-acetyl-4-hydroxy-6-methylcoumarin into the half perchlorate of 2,9-dimethylpyrano[3,2-*c*][1]benzopyran-4,5-dione (IIb). Di-*O*-methylcitromycinone (III) has been obtained similarly. On treatment with boron sulphide, 2-methylpyrano[3,2-*c*][1]benzopyran-4,5-dione (IIa) gives 8-methyl-5,10-dioxa-9,9a-dithia(9a-S^{IV})pentaleno[2,1-*a*]naphthalen-6-one (VIII). With phosphorus pentasulphide this gives a trithiapentalene derivative (XII), converted by acidic hydrolysis into 8-methyl-5,9-dioxa-9a,10-dithia(9a-S^{IV})pentaleno[2,1-*a*]naphthalen-6-one (XIV).

Silicon disulphide transforms the dione (IIb) into a mixture of compounds (VIII) and (XII), along with a compound believed to have structure (XXII) containing the rare 1,6-dioxa-6a-thia(S^{IV})pentalene nucleus.

The reference dioxadithia- and oxatrithia-pentalenonaphthalenones (XVIII) and (XIX) were obtained by condensing 4-hydroxycoumarin with 3-methylthio-5-phenyl-1,2-dithiolium sulphate and sulphurizing the product. A similar condensation of the salt with 4-hydroxy-6-methylchromen-2-thione afforded 6-methyl-2-phenyl-9-oxa-1,10,10a-trithia(10a-S^{IV})pentaleno[1,2-*b*]naphthalen-4-one (XXI), a thionester sulphur atom participating in heterapentalene formation in preference to a benzoyl oxygen atom.

PRAILL and WHITEAR [1] found that acetic anhydride and perchloric acid acylate 3-acetyl-4-hydroxycoumarin (Ia), giving the pyronocoumarin derivative (IIa). We have prepared by this method di-*O*-methylcitromycinone (III), a degradation product of the fungal metabolite citromycetin [2] (IV), but to elaborate the method into a synthesis of the pyranopyrone nucleus that characterizes citromycetin itself we required a selective carbonyl reduction for which no adequate technique appeared to be available. Since thiocarbonyl chemistry offers more scope for manoeuvre we examined the sulphurization of the model pyronocoumarin (IIa) only to find that the 4-pyrone ring is broken and that the chief product is not a simple thione but a derivative of 1-oxa-6,6a-dithia(6a-S^{IV})pentalene (V).

A mixture of 3-acetyl-4-hydroxy-6-methylcoumarin [3] (Ib), acetic anhydride, and perchloric acid deposited a salt from which hot water liberated the pyronocoumarin (IIb). The structure was confirmed by gentle acidic hydrolysis to 3-acetoacetyl-4-hydroxy-6-methylcoumarin (VI), ring closure of which regenerated the pyronocoumarin. Gentle alkaline hydrolysis of either of these compounds gave acetone, which does not result from hydrolysis of the simple 3-acetylcoumarin derivative (Ib). I.r. absorption at 1746 (2-pyrone) and at 1657 cm^{-1} (4-pyrone [4]) and the detailed analysis of the mass spectrum recorded previously [5] were also in accord with structure (IIb). On the other hand, the salt did not correspond well to the perchlorate $C_{13}H_8O_4,HClO_4$ described by the earlier authors.[1] When 2,6-dimethyl-4-pyrone adds hydrogen bromide,[4] the i.r. band near 1660 is destroyed and a hydroxylic band appears at 2380 cm^{-1}; and since 2-pyrones are relatively non-basic we expected our salt to have structure (VII), to retain the 2-pyrone but not the 4-pyrone band, and to show hydroxylic absorption modified to some extent by the hydrogen bonding indicated. In fact the salt showed no recognisable hydroxylic absorption; indeed, it had much the same i.r. spectrum as the base, and was proved analytically to be a half perchlorate, $(C_{14}H_{10}O_4)_2,HClO_4$. The compound behaves as a salt and not as an ester; for example double decomposition with potassium acetate liberates the pyronocoumarin immediately. Moreover



[1] P. F. G. Praill and A. L. Whitear, *Proc. Chem. Soc.*, 1961, 112; and personal communications.
[2] A. Robertson and W. B. Whalley, *J. Chem. Soc.*, 1949, 848.
[3] G. G. Badcock, F. M. Dean, A. Robertson, and W. B. Whalley, *J. Chem. Soc.*, 1950, 903.
[4] D. Cook, *Canad. J. Chem.*, 1961, **39**, 1184.
[5] R. A. W. Johnstone, B. J. Millard, F. M. Dean, and A. W. Hill, *J. Chem. Soc.* (*C*), 1966, 1712.

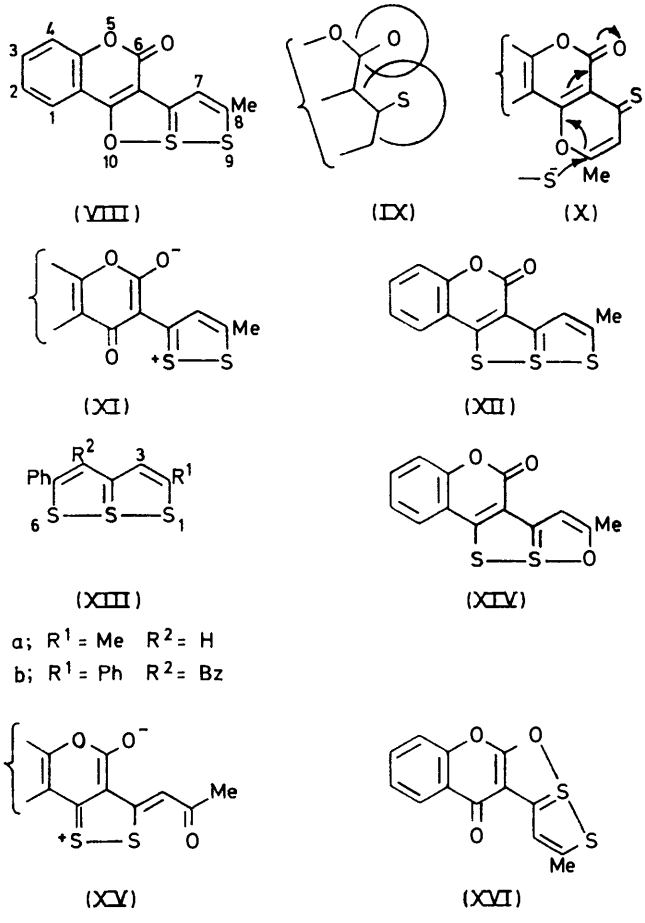
perchloric acid, which reacts with neither the 3-acetylcoumarin (Ib) nor the 3-acetoacetylcoumarin (VI), at once precipitates the pyronocoumarin half perchlorate from a solution of the base in acetic acid. But since the situation seems to be further confused by polymorphism we do not consider the nature of the salt to be established unequivocally.

A parallel acylation of 3-acetyl-4-hydroxy-6,7-dimethoxycoumarin [3] supplied another half perchlorate from which was obtained 8,9-dimethoxy-2-methylpyrano[3,2-*c*][1]benzopyran-4,5-dione (III), identical with di-*O*-methylcitromycinone from citromycetin.[2]

The action of phosphorus pentasulphide on the pyronocoumarin (IIa) proved to be complex, so we examined the reactions with boron and silicon sulphides instead. Although these reagents readily convert 4-pyrones into thiones,[6] the chief product from the boron sulphide reaction was not a thione but the heterapentalene derivative (VIII). Consideration of van der Waals' radii for the expected thione (IX) discloses a compression between the sulphur atom and the lactone carbonyl oxygen atom that would be relieved by ring fission; moreover, diagram (X) further indicates that the lactone carbonyl group would promote the nucleophilic attack by sulphide required to bring about the fission itself. Thus the general result can be accounted for readily even though the details cannot be formulated precisely.

The heterapentalene (VIII) is yellow, but is shown not to be a simple thione by its failure to react with mercury(II) acetate. An i.r. band at 1690 cm^{-1} could correspond to a benzoyl carbonyl group, but can be attributed to the lactonic carbonyl group provided that allowance is made for some interaction with the dithiole system, the sulphur atoms being *trans*.[7] Diagram (XI) suggests that a flow of electrons into the lactone carbonyl group is likely, since it would leave behind the dithiolium ion with aromatic character. A band at 1600 can be attributed to aromatic absorption, and another at 1550 cm^{-1} is typical[7] of oxadithiapentalene derivatives (V) bearing an aryl substituent at position 2. In the n.m.r. spectrum the methyl protons resonate at τ 7·2, the lactonic carbonyl group inducing a shift to lower field. This resonance also shows the presence of the adjacent proton by a small splitting (*J ca.* 1 Hz) normal in this arrangement.[7] The proton itself resonates at unusually low field (τ 0·87) because it is rigidly held in the plane of the lactone carbonyl group and is therefore subject to both electron withdrawal and anisotropic deshielding.

However, in the absence of sufficiently close analogies these spectral interpretations are not conclusive, and the mechanistic arguments summarized in diagrams (IX) and (X) are admittedly speculative. We have therefore sought to eliminate alternative structures. First, phosphorus pentasulphide was used to convert the boron sulphide product into the trithiapentalene (XII), which exhibits an appropriate electronic absorption spectrum and retains the i.r. carbonyl absorption at 1700 but not that at 1550 cm^{-1}. Then this compound was hydrolysed with sulphuric acid to replace one sulphur atom by an



oxygen. It is known that in unsymmetrical trithiapentalene derivatives such as (XIIIa) the sulphur atom at position 1 (*i.e.* that nearest the alkyl substituent) is replaced selectively;[8] on the other hand, it is known [9] that an acyl substituent at position 4 as in (XIIIb) directs the selective exchange of the sulphur atom at position 6. In (XII) both features are present and their directive effects conflict. In practice, a new oxadithiapentalene was obtained and its properties accord well with structure (XIV).

Treatment with phosphorus pentasulphide regenerated the trithiapentalene (XII). Aromatic absorption persisted at 1605 cm^{-1} but there was no absorption near 1550; instead, a band appeared at 1590 cm^{-1} in agreement with the shift usually observed [7,10] when an oxadithiapentalene system (V) carries an alkyl rather than an aryl substituent at position 2. That the lactonic absorption appears at the relatively high frequency 1720 cm^{-1}

[6] F. M. Dean, J. Goodchild, and A. W. Hill, *J. Chem. Soc.* (*C*), 1969, 2192.

[7] N. Lozac'h, *Adv. Heterocyclic Chem.*, 1971, **13**, 161; R. Pinel and Y. Mollier, *Bull. Soc. chim. France*, 1972, 1385.

[8] F. Arndt, *Rec. Fac. Sci. Univ. Istanbul*, 1948, **13***A*, 57; H. Behringer, H. Reinmann, and M. Ruff, *Angew. Chem.*, 1960, **72**, 415.

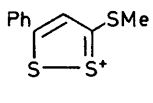
[9] J. Bignebat and H. Quiniou, *Compt. rend.*, 1970, **270***A*, 83; C. Trebaul and J. Teste, *Bull. Soc. chim. France*, 1966, 3790.

[10] D. Festal and Y. Mollier, *Tetrahedron Letters*, 1970, 1259.

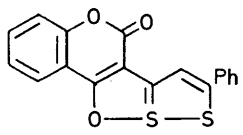
fits in well with structure (XIV) since interaction with the dithiole ring has to be as shown in (XV) and would not be supported by dithiolium ion formation. For the same reason the lactonic carbonyl group cannot exert direct electronic effects on either the methyl substituent or the adjacent proton, so that the associated n.m.r. peaks are at higher field (τ 7·52 and 1·85, respectively) than in the isomer. There is now no sign of splitting between the methyl group and the adjacent proton, and it seems that none has been recorded for any comparable arrangement.[7]

In view of the known preference for ketonic oxygen to participate in heterapentalene formation when ester oxygen is also available,[11] structure (XVI) might be considered unlikely. Again, however, the properties of the boron sulphide product do not exclude it unequivocally, and additional allowances have to be made for the special character of the 4-hydroxy-2-pyrone nucleus, which can undergo reactions at the lactonic site as readily as at any other.[1,12] We have been unable to synthesize the isomer with this structure but offer strong indirect evidence for its elimination.

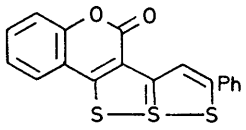
The dithiolium salt (XVII) condensed readily with 4-hydroxycoumarin giving an oxadithiapentalene derivative formulated as (XVIII) and having i.r. absorption



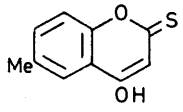
(XVII)



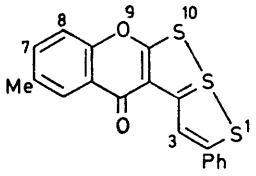
(XVIII)



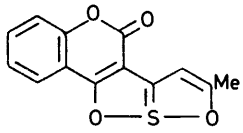
(XIX)



(XX)



(XXI)



(XXII)

bands at 1695 (lactonic), 1600 (aromatic), and 1550 cm^{-1} in satisfactory correspondence with those of the boron sulphide product. The heterapentalene proton resonates at τ 0·33, the additional downfield shift registering the influence of the aryl substituent. Sulphurization with phosphorus pentasulphide gave (XIX), with i.r. bands at 1695 (lactone) and 1595 (aromatic) but none near 1550 cm^{-1}, and with a detailed and characteristic electronic absorption spectrum appropriate to a trithiapentalene derivative.[7] This compound provides the key to the orientational problem, for condensation of the dithiolium salt with 4-hydroxychromen-2-thione [13] (XX) affords the isomeric arrangement in (XXI), as expected since a thionester sulphur atom has been observed to engage in heterapentalene formation in preference to a ketonic oxygen atom.[14] This isomer is red, has an electronic absorption spectrum appropriate to a trithiapentalene derivative (though more complex than most), and absorbs at 1635, 1615, and 1560 but not near 1700 cm^{-1}. Hence there is no longer doubt that an i.r. band near this last frequency does indicate a lactonic carbonyl group in isomer (XIX) and thus in all the other heterapentalene derivatives. Hence structure (VIII) for the boron sulphide product is justified.

Silicon sulphide reacts less readily than boron sulphide with the pyronocoumarin (IIa) and gives not only compounds (VIII) and (XII) but also a yellow product containing only one sulphur atom. Lack of material prevented a detailed study and structure (XXII) is assigned on a tentative basis only. Derivatives of 1,6-dioxa-6a-thia(S^{IV})pentalene are rare, and the single fully established example [15] known to us is not properly comparable because its oxygen atoms are phenoxide in origin.* However, structure (XXII) can reasonably be expected from a situation as in diagram (X) but with ring opening by nucleophilic oxygen instead of sulphur, and it explains the spectroscopic data satisfactorily. Thus there is no i.r. band appropriate to hydroxy or thiol groups but there are strong bands at 1725 (lactone), 1605 (aromatic), and 1585 and 1525 cm^{-1}. Of these last two bands, the former might be held to indicate the alkyl-substituted terminus and the other the aryl terminus of the heterapentalene system; at all events, none of the other oxadithiapentalene derivatives considered here show more than one band in this region. N.m.r. peaks at τ 7·44 and 2·19 are due to the methyl protons and the pentalene proton, respectively, and no coupling was seen.

EXPERIMENTAL

Electronic spectra were usually obtained from 10^{-4}M-solutions in ethanol and i.r. spectra from potassium bromide discs.

2,9-*Dimethylpyrano*[3,2-c][1]*benzopyran*-4,5-*dione* (IIb).—To 3-acetyl-4-hydroxy-6-methylcoumarin (1·7 g) in freshly distilled acetic anhydride (31·8 ml), perchloric acid (72% w/v; 0·68 ml) was added dropwise at 40°. After 2 h at that temperature the solution was kept at 23° for 1·5 days

* *Added in proof:* Comparable compounds are now available; see D. H. Reid and R. G. Webster, *J.C.S. Chem. Comm.*, 1972, 1283.

[11] R. Pinel, Y. Mollier, and N. Lozac'h, *Bull. Soc. chim. France*, 1966, 1049; G. Duguay, H. Quiniou, and N. Lozac'h, *ibid.*, 1967, 2763.

[12] F. M. Dean, J. Goodchild, and S. Murray, unpublished observations; I. Chmielewska and J. Cieślak, *Tetrahedron*, 1958, **4**, 36, 135.

[13] F. M. Dean, D. B. Frankham, N. Hatam, and A. W. Hill, *J. Chem. Soc.* (*C*), 1971, 218.

[14] S. M. Johnson, M. G. Newton, I. C. Paul, R. J. S. Beer, and D. Cartwright, *Chem. Comm.*, 1967, 1170; S. M. Johnson, M. G. Newton, and I. C. Paul, *J. Chem. Soc.* (*B*), 1969, 986.

[15] I. Pomerantz, L. Miller, E. Lustig, D. Mastbrook, E. Hansen, R. Barron, N. Oates, and J.-Y. Chen, *Tetrahedron Letters*, 1969, 5307; R. D. Gilardi and I. L. Karle, *Acta Cryst.*, 1971, **B27**, 1073.

while an orange-yellow solid separated. Further quantities obtained after slight evaporation of the mother liquor brought the yield up to 1·52 g. This product could not be crystallised from acetic acid containing perchloric acid but it crystallised from nitromethane giving the *half perchlorate* as faintly pink prisms (0·96 g), m.p. 264° (decomp.) [Found: C, 57·4; H, 3·6; Cl, 6·2; O, 32·6. $(C_{14}H_{10}O_4)_2,HClO_4$ requires C, 57·5; H, 3·6; Cl, 6·1; O, 32·8%].

A solid separated when a solution of the perchlorate (0·5 g) in water (5 ml) was heated on a steam-bath for 2 h, and after purification from aqueous acetic acid supplied the *pyranopyrandione* as needles (0·3 g), m.p. 220° (decomp.), $\lambda_{max.}$ 242, 279, 289sh, and 327 nm (log ε 4·16, 4·08, 4·03, and 4·79) [Found: C, 69·4; H, 4·4%; *M* (mass spec.), 442. $C_{14}H_{10}O_4$ requires C, 69·4; H, 4·4%; *M*, 242]. In another preparation the perchlorate (1·0 g) in acetic acid (40 ml) was mixed with potassium acetate (0·5 g) in water (2 ml) and acetic acid (20 ml) and left for 2 days until precipitation of potassium perchlorate was complete; filtration and slight concentration of the solution then induced crystallisation of the pyranopyrandione in the form of golden-yellow plates (0·5 g), m.p. 282° (decomp.), having an i.r. spectrum not distinguishable from that of a colourless specimen (Found: C, 69·5; H, H, 4·2%).

When the pyranopyrandione (either form; 0·7 g) in acetic acid (40 ml) was treated with perchloric acid (72%; 1·2 ml) a precipitate (0·8 g) appeared immediately. After being washed with acetic acid and crystallized from nitromethane this solid gave the perchlorate as pink needles, m.p. >360°, which regenerated the pyranopyrandione when heated with water [Found: C, 57·3; H, 3·55; Cl, 6·2. $(C_{14}H_{10}O_4)_2,HClO_4$ requires C, 57·5; H, 3·5; Cl, 6·1%]. The i.r. spectrum of the perchlorate prepared thus was very similar to that of a specimen prepared by acylation of 3-acetyl-4-hydroxy-6-methylcoumarin but differed in detail at several points.

3-*Acetoacetyl*-4-*hydroxy*-6-*methylcoumarin* (VI).—A solution of the foregoing pyranopyrandione (1·0 g) in ethanol (80 ml) and 2N-hydrochloric acid (75 ml) was heated under reflux on a steam-bath for 3 h and then concentrated a little and cooled. The solid (0·83 g) which separated was purified from aqueous ethanol to give the *acetoacetylcoumarin* as needles (0·6 g), m.p. 162°, $\lambda_{max.}$ 227, 306, 332sh, 350, and 360sh nm (log ε 4·09, 4·10, 4·11, 4·16, and 4·10), $\nu_{max.}$ 1721 (coumarin C:O), 1618 (aromatic and ethylenic), and 1555 cm^{-1} (chelated C:O), which were readily soluble in aqueous sodium hydrogen carbonate and gave an intense orange colour with ethanolic iron(III) chloride [Found: C, 64·6; H, 4·5%; *M* (mass spec.), 260. $C_{14}H_{12}O_5$ requires C, 64·6; H, 4·65%; *M*, 260].

This compound was recovered when a solution in cold sulphuric acid was poured into water, but when warmed to 80° for 5 min before being poured into water the sulphuric acid solution supplied the pyranopyrandione, m.p. and mixed m.p. 220°, further identified spectroscopically.

The acetoacetylcoumarin or the pyranopyrandione (0·5 g) was warmed on a steam-bath with 2N-sodium hydroxide (20 ml) and a stream of nitrogen was used to carry volatile products into 2,4-dinitrophenylhydrazine in 5N-hydrochloric acid. The yellow precipitate (0·27 g) was identified as acetone 2,4-dinitrophenylhydrazone by m.p. and mixed m.p. and spectroscopically.

8,9-*Dimethoxy*-2-*methylpyrano*[3,2-c][1]*benzopyran*-4,5-*dione* (*Di*-O-*methylcitromycinone*) (III).—3-Acetyl-4-hydroxy-6,7-dimethoxycoumarin (0·5 g) gradually dissolved in acetic anhydride (15·5 ml) at 50° as perchloric acid (72%; 0·33 ml) was added dropwise. After 2 h the mixture was left at room temperature for 4 months while a brownish deposit formed. This possessed no i.r. lactonic carbonyl absorption and was discarded. Then the mixture was concentrated under reduced pressure to about two thirds of its bulk and again left. Further deposits did exhibit lactonic absorption and were collected (0·15 g) and heated with a little water for 3 h. The product crystallised from acetic acid to give the pyranopyrandione as faintly fawn needles (0·1 g), m.p. 325° (decomp.), $\nu_{max.}$ 1745 (lactone C:O), 1668 (4-pyrone C:O), and 1615 cm^{-1} (aromatic and ethylenic), identical with an authentic sample [Found: C, 62·0; H, 4·2%; *M* (mass spec.), 288. $C_{15}H_{12}O_6$ requires C, 62·5; H, 4·2%; *M*, 288 (the difficulty of obtaining satisfactory elemental analyses has been noted [2] before with this compound)].

Addition of perchloric acid (72%; 1·2 ml) to this pyronocoumarin (0·7 g) in acetic acid (40 ml) gave an immediate precipitate that was washed with acetic acid and then crystallized from nitromethane to give the *perchlorate* as pink needles, m.p. 360°, which reverted to the pyronopyrandione when heated with water [Found: C, 57·3; H, 3·55; Cl, 6·2. $(C_{15}H_{12}O_6)_2,HClO_4$ requires C, 57·5; H, 3·5; Cl, 6·1%].

8-*Methyl*-5,10-*dioxa*-9,9a-*dithia*-(9a-S^{IV})*pentaleno*[2,1-a]-*naphthalen*-6-*one* (VIII).—The pyranopyrandione (IIa) (0·20 g) and boron sulphide (1 g) were stirred together in chloroform (50 ml) for 35 min. The solution was filtered and the solute recovered by evaporation under reduced pressure and chromatographed on silica from light petroleum (b.p. 40—60°) (which removed sulphur) and then benzene, which gave the crude product. Crystallized from ethanol, this supplied the *dioxadithiapentalenonaphthalene* as deep yellow needles (0·12 g), m.p. 219—220°, $\lambda_{max.}$ 232, 264, and 418 nm (log ε 4·42, 4·11, and 4·54) [Found: C, 56·8; H, 3·0; S, 23·5%; *M* (mass spec.), 244. $C_{13}H_8O_3S_2$ requires C, 56·5; H, 2·9; S, 23·2%; *M*, 244]. This compound was recovered quantitatively after having been warmed with mercury(II) acetate in ethanol for 15 min.

8-*Methyl*-5-*oxa*-9,9a,10-*trithia*(9a-S^{IV})*pentaleno*[2,1-a]-*naphthalen*-6-*one* (XII).—Compound (VIII) (35 mg) was heated with phosphorus pentasulphide (0·2 g) in refluxing toluene (30 ml) for 35 min. Evaporation of the solvent under reduced pressure left an orange solid that was dissolved in chloroform and washed with water, dried ($MgSO_4$), and recovered. The product was induced to crystallise by dissolving it in a small volume of dichloromethane, adding cyclohexane, and keeping hot so that the former solvent was gradually and selectively lost. Crystallisation was completed by cooling and furnished the *trithiapentalenonaphthalene* as orange-red needles (30 mg), m.p. 220° (softens at 209°), $\lambda_{max.}$ 266, 313, 356, and 467 nm (log ε 4·67, 4·23, 3·87, and 3·97), τ 7·18 (CH_3), 0·25 (4-H), and 2·6 (m, ArH) [Found: C, 53·2; H, 2·9; S, 33·0%; *M* (mass spec.), 292. $C_{13}H_8O_2S_3$ requires C, 53·4; H, 2·8; S, 32·9%; *M*, 292].

8-*Methyl*-5,9-*dioxa*-9a,10-*dithia*(9a-S^{IV})*pentaleno*[2,1a]-*naphthalen*-6-*one* (XIV).—The trithiapentalene (XII) (30 mg) in sulphuric acid (2 ml) was heated on a steam-bath for 3 h and then added to aqueous sodium hydrogen carbonate. The product was extracted into chloroform, washed with water, dried ($MgSO_4$), recovered from the solvent, and purified by thick-layer chromatography on silica plates with benzene–light petroleum (b.p. 60—80°) (first 1 : 1 v/v, then

3 : 1 v/v). The *dioxadithiapentalenonaphthalene* formed yellow needles (22 mg), m.p. 233—236° [Found: *M* (mass spec.), 275·994817. $C_{13}H_8O_3S_2$ requires *M*, 275·994817].

With phosphorus pentasulphide in refluxing xylene this compound regenerated the trithiapentalene (XII), identified by t.l.c., and i.r. spectroscopy.

8-*Methyl*-5,9,10-*trioxa*-9a-*thia*(S^{IV})*pentaleno*[2,1-a]-*naphthalen*-6-*one* (XXII).—2-Methylpyrano[3,2-*c*][1]benzopyran-4,5-dione (0·20 g) was attacked by silicon disulphide (1 g) in boiling chloroform (10 ml) during 6 h and the soluble material was chromatographed on a silica column, sulphur being removed first by light petroleum and the organic products sequentially by gradually increasing the proportion of benzene in the eluant. Further purification of the three main fractions was effected on thick silica plates giving (i) the 5,10-dioxa-9,9a-dithiapentalene (VIII) (47 mg), (ii) the 5-oxa-9,9a,10-trithiapentalene (XII) (20 mg), and (iii) the 5,9,10-*trioxa*-9a-*thiapentalene*, which crystallised from ethanol as yellowish needles (34 mg), m.p. 230—235° [Found: C, 59·9; H, 3·0; S, 12·6%; *M* (mass spec.), 260. $C_{13}H_8O_4S$ requires C, 60·0; H, 3·1; S, 12·3%; *M*, 260].

8-*Phenyl*-5,10-*dioxa*-9,9a-*dithia*(9a-S^{VI})*pentaleno*[2,1-a]-*naphthalen*-6-*one* (XVIII).—4-Hydroxycoumarin (0·11 g) reacted with methyl 3-methylthio-5-phenyl-1,2-dithiolium sulphate (0·23 g) in refluxing acetic acid (15 ml) containing pyridine (1·5 ml) during 25 min. Removal of the solvents and crystallisation of the residue from benzene gave the *phenylpentalenonaphthalenone* as yellow needles, and chromatography of the mother liquor gave more pure material (total 0·23 g), m.p. 255—256°, $\lambda_{max.}$ 231, 250, 280, 293, 327, and 436 nm (log ε 4·46, 4·34, 4·18, 4·18, 4·15, and 4·53) [Found: C, 63·8; H, 3·0; S, 18·2%; *M* (mass spec.), 338. $C_{18}H_{10}O_3S_2$ requires C, 63·9; H, 3·0; S, 18·95%; *M*, 338].

8-*Phenyl*-5-*oxa*-9,9a,10-*trithia*(9a-S^{IV})*pentaleno*[2,1-a]-*naphthalen*-6-*one* (XIX).—The foregoing phenylpentalenonaphthalene (0·11 g) and phosphorus pentasulphide (0·8 g) were heated together in boiling toluene (25 ml) for 1·75 h and the products were recovered by removing the solvent *in vacuo*. The products in chloroform were washed with much water, dried ($MgSO_4$), and transferred to dichloromethane. Cyclohexane was added to this solution which was kept warm to facilitate selective loss of the dichloromethane; gradually, the *phenyltrithiapentalene* separated as red needles (0·11 g), m.p. 199—200°, $\lambda_{max.}$ 258, 280, 325, and 479 nm (log ε 4·64, 4·47, 4·38, and 4·08), $\nu_{max.}$ 1700 (lactone C:O) and 1595 cm^{-1} (aromatic), τ −0·32 (pentalene H) and 2·2 (m, ArH) [Found: C, 60·8; H, 3·1; S, 27·2%; *M* (mass spec.), 354. $C_{18}H_{10}O_2S_3$ requires C, 61·0; H, 2·8; S, 27·1%; *M*, 354].

6-*Methyl*-2-*phenyl*-9-*oxa*-1,10,10a-*trithia*(10a-S^{IV})*pentaleno*[1,2-b]*naphthalen*-4-*one* (XXI).—4-Hydroxy-6-methylchromen-2-thione (0·10 g) in ethanol (7 ml) was neutralised with sodium hydrogen carbonate (40 mg) in water (7 ml) and the mixture was stirred until dissolution was complete. Then methyl 3-methylthio-5-phenyl-1,2-dithiolium sulphate (0·20 g) in ethanol–water (1 : 1 v/v; 20 ml) was added dropwise with vigorous agitation. After some hours brown amorphous material had separated and was removed, whereafter an orange solid crystallised out and was purified from ethyl acetate to give the *trithiapentalene* as orange needles (30 mg), m.p. 261—263·5°, $\lambda_{max.}$ 245, 270, 293, 321, 356, and 460 nm (log ε 4·78, 4·63, 4·59, 4·51, 4·40, and 4·03), $\nu_{max.}$ 1640 (benzoyl C:O) and 1610 cm^{-1} (aromatic), τ 7·54 ($ArCH_3$), −0·53 (trithiapentalene H), and 2·3 (m, ArH) [Found: C, 61·9; H, 3·5; S, 26·2%; *M* (mass spec.), 367·999942. $C_{19}H_{12}O_2S_3$ requires C, 61·95; H, 3·3; S, 26·1%; *M*, 367·999965].

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