Polyketo-enols and Chelates. Synthesis of Acetyl- and Alkoxycarbonyl-xanthyrones

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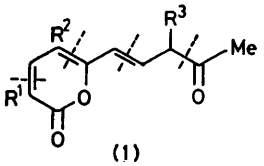
New xanthyrones having acetyl and alkoxycarbonyl substituents have been prepared by addition of anions from substituted 6-methylpyran-2-ones to alkoxymethylene β-dicarbonyl compounds, and also by the ' melt ' assembly procedure. Reaction of xanthyrones with boiling water gives substituted phenols, the position of the substituents in the latter enabling substitution assignments to the pyrone ring to be confirmed. Spectral (n.m.r., u.v., and i.r.) data for the sixteen currently available xanthyrones are considered.

MEMBERS of the xanthyrone (6-propenylpyran-2-one) group of compounds described in this and our earlier papers [1-3] may be viewed as having a doubly reduced and dehydrated pentaketide chain carrying pendant acetyl or ester groups (or no substituents), R^1, R^2, and R^3 in (1). These synthetic compounds are thus not



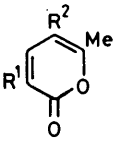
(1)

direct models for biosynthetic polyketides, even though the ester groups can be imagined as undecarboxylated residues from a malonate chain-extender, and the side-chain acetyls as inserted additional acetate units. Nevertheless their chemistry is evocative of biosynthetic processes, and the pendants to the chain, with their chelating possibilities and additional participation in cyclisation and other reactions, provide a varied potential for chemical investigation. As a basis for chemical exploration, a number of new xanthyrones are now reported.

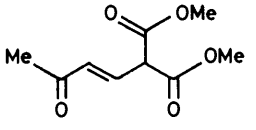
RESULTS AND DISCUSSION

For synthetic purposes pyranones (2)—(7) carrying ester and acetyl side chains were required. The pyranone (2) was made by treatment of 2,4-diacetylglutaconate in benzene with methanolic magnesium methoxide (1 mol) [2] whilst the 3-ester (3) was obtained by cyclising the ketodiester (8). The latter is accessible by condensation between 4-chlorobuten-2-one and magnesiomalonic ester at −10 °C.[4] The isomeric pyranone (4) was made from 3,3-dichloroacrylaldehyde, accessible from the radical addition of carbon tetrachloride to butyl vinyl ether:[5] condensation with acetoacetic ester gave (9), which formed the required pyranone on distillation.[6] The diester pyranone (5) was obtained when methyl cyanoacetate and methoxymethylene acetoacetate were condensed in the presence of sodium methoxide.[7] From the condensation of methyl cyanoacetate with methoxymethyleneacetylacetone, the pyranone (6) was not isolated, but 5-acetyl-3-methoxycarbonyl-6-methyl-2-pyridone was formed: a more detailed study of this reaction will be reported later. The pyranone (7) was formed in good yield, though it was rather difficult to purify, from triacetic lactone:[8] an alternative method using (10)[9] gave very pure material though yields were low.

N.m.r. data for the pyranones (Table 1 of SUP) † display the expected shieldings for the 4-H and 6-Me. A 3-ester ‡ is more effective in shielding the 4-H than a 5-ester: this is expected as the former is conjugated with the 4-H, and in addition, the time-averaged long-range shielding of the 3-ester, relative to the 5-ester, may be different because of dipolar repulsion with the pyranone carbonyl. In the u.v. pyranone (4) absorbs at a distinctly shorter wavelength ($\lambda_{max.}$ 295, ε 5 400) than the 3-substituted isomer (3) ($\lambda_{max.}$ 322, ε 9 700), reflecting



(2) R^1 = COMe; R^2 = CO_2Me
(3) R^1 = CO_2Me; R^2 = H
(4) R^1 = H; R^2 = CO_2Me
(5) R^1 = CO_2Me; R^2 = CO_2Me
(6) R^1 = CO_2Me; R^2 = COMe
(7) R^1 = R^2 = H



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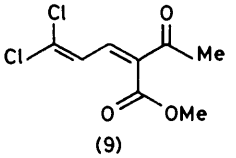

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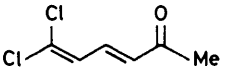


(10)

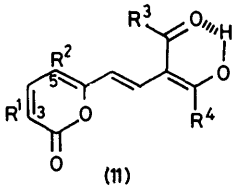
conjugation effects. As noted previously,[10] the presence of a 3-acyl or ester substituent raises the frequency of the pyranone carbonyl.

The eight new xanthyrones prepared in this paper, along with those available from earlier work, are listed.[1] Condensation of dimethyl 6-methyl-2-oxo-2*H*-pyran-3,5-dicarboxylate (5) with methyl methoxy-

† Tables 1—4 are available as Supplementary Publication No. SUP 22363; for details see Notice to Authors No. 7, *J.C.S. Perkin I*, 1977, Index issue.

‡ In the discussion, 3- and 5-substituents refer to formula (11). Systematic numbering may interchange 3- and 5- depending on whether the pyranone is correctly referred to as 2*H* or 6*H*.

methyleneacetoacetate in the presence of sodium methoxide [2] gave the yellow xanthyrone (12) whilst a similar



(11)

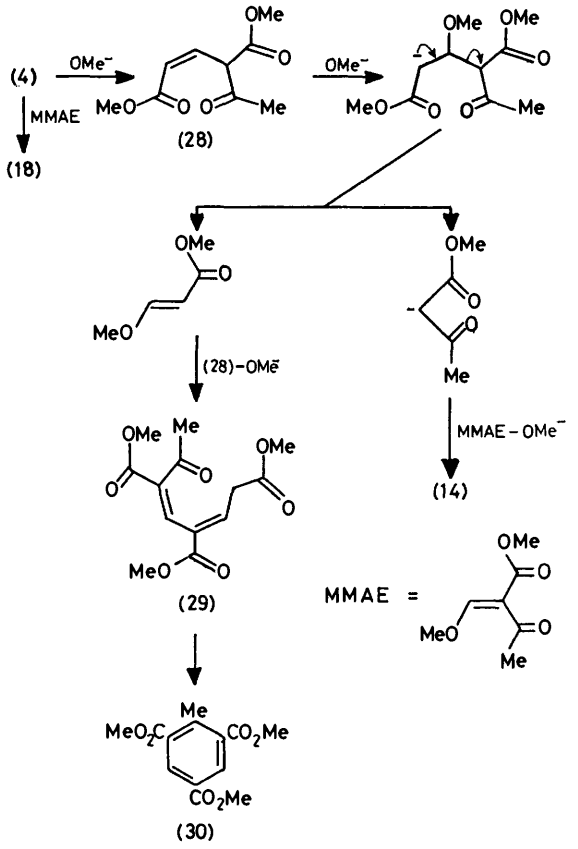
	R^1	R^2	R^3	R^4
(12)	CO_2Me	CO_2Me	Me	OMe
(13)	CO_2Me	CO_2Me	Me	Me
(14)	COMe	CO_2Me	Me	OMe
(15)	COMe	CO_2Me	Me	Me
(16)	CO_2Me	COMe	Me	Me
(17)	COMe	COMe	Me	Me
(18)	H	CO_2Me	Me	OMe
(19)	H	CO_2Me	Me	OEt
(20)	H	CO_2Et	Me	OEt
(21)	CO_2Me	H	Me	OEt
(22)	CO_2Et	COMe	Me	Me
(23)	COMe	CO_2Me	Me	OEt
(24)	COMe	CO_2Et	Me	OMe
(25)	CO_2Et	CO_2Et	Me	OEt
(26)	COMe	CO_2Et	Me	OEt
(27)	COMe	CO_2Et	Ph	OEt

Available xanthyrones

condensation using methoxymethyleneacetylacetone provided (13). The 3-acetylxanthyrone (14) was made from the corresponding pyran (2),[2] as was the 3',3'-diacetylxanthyrone (15), which formed red-brown crystals. When methyl 2-methyl-6-oxo-6*H*-pyran-3-carboxylate (4) was treated with methyl methoxymethyleneacetoacetate only a small yield of the required xanthyrone (18) was obtained. The major product was trimethyl methyltrimesate (30) [11] along with dimethyl xanthophanic enol (14).[1] These products can be explained as indicated in Scheme 1. Methoxide opening of the pyran gives (28) which degrades to methyl methoxymethyleneacetate and acetoacetic ester anion. Reaction of the former by Michael addition with the anion of (28), and elimination of methoxide ion gives (29) which cyclises to (30). With methyl methoxymethyleneacetoacetate and the methyl acetoacetate anion available, the necessary components for the formation of dimethylxanthophanic enol (14) by ' melt ' type reaction are present. Improved, though still modest, yields of (18) were obtained by using potassium t-butoxide in benzene as the base. Two ester variants of this xanthyrone, (19) and (20), were made.

Condensation of 6-methyl-2-oxo-2*H*-pyran-3-carboxylate (3) with ethyl ethoxymethyleneacetoacetate, to give the xanthyrone (21), could be effected in the presence of potassium t-butoxide, but the unsubstituted 6-methylpyran-2-one (7) reacted slowly under these conditions. No examples of xanthyrones with a malonate terminus were formed in the present work. Doubtless the enolised acetoacetate and acetylacetone enol groups give additional stabilisation to the xanthyrone system, and this matter will be returned to in a later paper.

Although preparation of xanthyrones *via* initial formation of the appropriate pyrones is more controlled and logical,[2] the ' melt ' assembly reaction [1] is still very convenient in a number of cases. Thus heating methoxymethyleneacetylacetone with sodioacetylacetone gives, with evolution of methanol, the tetraacetylxanthyrone (17) very conveniently.[1] Heating together either methoxymethylenemalonic ester and sodio-acetylacetone, or methoxymethyleneacetylacetone and sodio-malonic ester gave the triacetylxanthyrone (16). Dimethyl methoxymethylenemalonate and methyl sodio-acetoacetate gave the 3'-acetyltrismethoxycarbonylxanthyrone (12): no tetracarbomethoxyxanthyrone (malonate end group) was found.

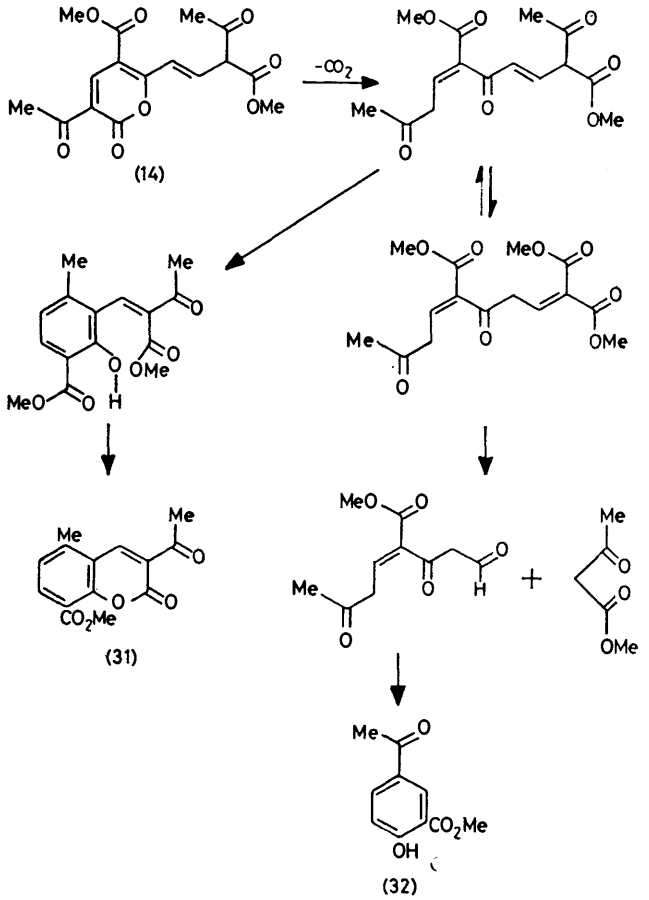


SCHEME 1 Formation of trimethyl methyltrimesate and xanthyrones (18) and (14) from pyran (4)

In earlier work [1] we showed that dimethyl xanthophanic enol (14), on heating with water, decarboxylates; it apparently releases a reactive chain which undergoes cyclisation to the coumarin (31), and methyl 3-acetyl-6-hydroxybenzoate (32), along with formation of methyl acetoacetate. It is represented in Scheme 2. A number of xanthyrones have now been subjected to this aqueous decarboxylation and the formation scheme is supported by the structures of the various phenols isolated (Scheme 3). Formation of these phenols gives a very convenient additional check on xanthyrone structures, particularly as the relative positioning of mixed acetyl and ester groups in the 3- and 5-pyran positions is not readily decided by n.m.r. spectroscopy.

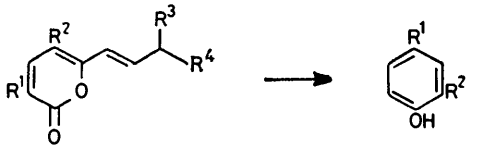
Spectroscopic data have been obtained for the

majority of the xanthyrones at present known, and a few general comments are made here. N.m.r. assignments



SCHEME 2 Reaction of dimethylxanthophanic enol with boiling water

for the series (12)—(27) are given in Table 2 of SUP 22363. In 6-methylpyran-2-one (7), the 4-proton resonates at τ 2.87 and is lowered by a 5-methoxycarbonyl



	R^1	R^2	R^3	R^4		R^1	R^2
(14)	COMe	CO_2Me	COMe	CO_2Me	(32)	COMe	CO_2Me
(12)	CO_2Me	CO_2Me	COMe	CO_2Me	(33)	CO_2Me	CO_2Me
(13)	CO_2Me	CO_2Me	COMe	COMe	(33)	CO_2Me	CO_2Me
(15)	COMe	CO_2Me	COMe	COMe	(32)	COMe	CO_2Me
(16)	CO_2Me	COMe	COMe	COMe	(34)	CO_2Me	COMe
(17)	COMe	COMe	COMe	COMe	(35)	COMe	COMe

SCHEME 3 Substituted phenols from the reaction of xanthyrones with boiling water

substituent to 2.22 (4). Xanthyrones (18)—(20) have this 4-proton at only slightly lower field (τ 2.14—2.17). The 3-methoxycarbonylxanthyrone (21) 4-proton resonates at τ 1.86, fairly close to the 4-proton resonance in (3) (τ 1.78), but slightly upfield. When carrying both 3- and 5-acetyl or -ester substituents, the 4-proton in the xanthyrone generally resonates at lower field (τ 0.2—0.3) than in the corresponding 6-methylpyran-2-one. Differentiation between an acetylacetone and an acetoacetic ester terminated side chain is clearly given by the chelated proton signal of the enolised residue, τ −8.05 to −7.90 for the former and −4.30 to −4.75 for the latter. The *trans*-1′,2′-protons form an AB system, J 15—16.5 Hz with, when the terminus is an enolised acetylacetone residue, the low-field doublet at τ 2.05—2.15 and the high-field one at τ 2.43—2.56. Replacement of the terminal residue in the 3,5-disubstituted xanthyrones by an enolised acetoacetic ester residue causes a shift mainly to the high-field line; the AB signals are now at τ 1.98—2.19 and 2.22—2.42. In the single example available (21), loss of the 5-substituent raises the AB resonances to τ 2.66 and 3.35 as a result of the removal of carbonyl deshielding and electron withdrawal.

In the i.r. (Table 3 of SUP) most of the pyran ring carbonyl absorptions (in chloroform) are in the range 1 745—1 775 cm^{-1}, pyran ester carbonyls at 1 700—1 730 cm^{-1}, and pyran acetyl carbonyls at 1 680—1 690 cm^{-1}. Unsaturation is represented by absorptions at 1 640—1 650 (weak) and 1 600—1 630 cm^{-1} (more intense): the former, ascribed to the side-chain double bond vibration, is not always clearly observed but tends to merge with the pyran ring double bond vibration. The chelated terminus in the xanthyrones is represented by two strong absorptions at 1 565—1 595 and 1 500—1 530 cm^{-1}.

In the u.v. (Tables 4A—C of SUP 22363) xanthyrones having 3-ester, 5-acetyl, or 3-acetyl-5-ester substitution on the pyran have two major bands in 0.01N acid–ethanol, one near 300 nm (ε *ca.* 10 000—14 000) and the other near 430 nm (ε *ca.* 13 000—25 000). There is also an inflection near 520—530 nm (ε *ca.* 1 500—5 000). When a 3-acetyl or ester is absent as a substituent on the xanthyrone, the long wave-length absorption near 430 nm is absent and there is absorption in the 385—390 nm region. In 0.01N alkaline ethanol there is development of a strong absorption in the 510—540 nm region (ε 40 000—70 000) in the xanthyrones having carbonyl or ester substitution in the 3- and 5-pyran positions. Xanthyrones lacking 3-substitution [(18)—(20)] show a similar alkaline absorption at 500 nm (ε 45 000—55 000). These absorptions in the 500—540 nm region are present at intermediate ε values in neutral ethanol and suggest that the xanthyrones are appreciably ionised in neutral and even 0.01N acid–ethanol. All u.v. data were recorded exactly 10 min after addition of acid or base: control experiments show the ε values gradually fall in 0.01N base, but the error is small under the conditions employed.

EXPERIMENTAL

Methyl 5-Acetyl-2-methyl-6-oxo-6H-pyran-3-carboxylate (2).—Dimethyl 2,4-diacetylglutaconate (2 g) in benzene (10 ml) was added to a magnesium methoxide solution [from magnesium (0.201 g) and anhydrous methanol (30 ml)] and set aside for 3 days. Water (40 ml) was added, and the solution acidified and extracted with benzene. The benzene extracts were washed, dried, and evaporated

to dryness to give *compound* (2) (1.37 g), m.p. 60 °C [from light petroleum (b.p. 40—60 °C)] (Found: C, 57.15; H, 4.90. Calc. for $C_{10}H_{10}O_5$: C, 57.15; H, 4.80%) (lit.,[2] m.p. 58 °C); M^+ 210.

Methyl 6-*Methyl*-2-*oxo*-2H-*pyran*-3-*carboxylate* (3).—The magnesio-derivative of dimethyl malonate [from magnesium (4.8 g) and dimethyl malonate (31.8 g)] was dissolved in dry benzene (100 ml), cooled, and a cooled solution of methyl β-chlorovinylketone [12] (15.7 g) in benzene (100 ml) added. After setting aside (18 h), water and acid were added and the benzene layer separated. Two distillations gave material (4.8 g), b.p. 119—123 °C at 2 mmHg, which solidified; *compound* (3) (4.5 g) had m.p. 88 °C after crystallisation from chloroform–ether (Found: C, 57.10; H, 4.75%, M^+ 168. $C_8H_8O_4$ requires C, 57.15; H, 4.80%).

Methyl 2-*Methyl*-6-*oxo*-6H-*pyran*-3-*carboxylate* (4).—3,3-Dichloroacrylaldehyde [5] (10 g) and methyl acetoacetate (30.6 g) were stirred and heated, first at 65 °C and finally at 85 °C for 10 h. Distillation (140—180 °C at 13 mmHg) gave the pyran (4) (40%), m.p. 81—82 °C [from chloroform–light petroleum (b.p. 60—80 °C)] (lit.,[6] m.p. 82 °C).

Dimethyl 6-*Methyl*-2-*oxo*-2H-*pyran*-3,5-*dicarboxylate* (5).—(*a*) Methyl cyanoacetate (9.9 g) was added to sodium methoxide [from sodium (2.3 g) and methanol (50 ml)]; methyl methoxymethyleneacetoacetate (15.3 g) was then added to the solution, keeping the temperature below 30 °C. The solution was set aside for 5 min; ice was then added and the solution acidified with 4N hydrochloric acid and filtered. The solid was washed, and then recrystallised from ether–light petroleum (b.p. 40—60 °C) (1 : 1) to give the *dicarboxylate* (5) (10 g), m.p. 93 °C (Found: C, 52.85; H, 4.40. $C_{10}H_{10}O_6$ requires C, 53.10; H, 4.36%); M^+ 226.

(*b*) Dimethyl malonate (6.6 g) was added to a solution of sodium methoxide [from sodium (1.15 g) and methanol (50 ml)]. Addition of methyl methoxymethyleneacetoacetate (7.9 g) as above yielded an oily solid which was chromatographed from benzene on silica gel to give (5) (4.0 g), identical with that from (*a*).

3′-*Acetyl*-3,3′,5-*trismethoxycarbonylxanthyrone* (12).—Compound (5) (11.3 g) was added to sodium methoxide [from sodium (1.2 g) and methanol (50 ml)]. Methyl methoxymethyleneacetoacetate (7.9 g) was then added and the solution was heated under reflux. The red-violet precipitate was filtered off, washed with methanol, and dissolved in water (100 ml). Acidification (0 °C) gave 3′-*acetyl*-3,3′,5-*trismethoxycarbonylxanthyrone* (12) (4.3 g), m.p. 193—194 °C, yellow crystals from chloroform (Found: C, 54.70; H, 4.60. $C_{16}H_{16}O_9$ requires C, 54.55; H, 4.58%); M^+ 352.

3′,3′-*Diacetyl*-3,5-*bismethoxycarbonylxanthyrone* (13).—Treatment of (5) (11.3 g) with sodium methoxide [from sodium (1.15 g) in methanol (50 ml)], and methoxymethyleneacetylacetone (14.2 g) as above yielded 3′,3′-*diacetyl*-3,5-*bismethoxycarbonylxanthyrone* (13) (3.8 g), yellow, m.p. 168 °C (from benzene) [Found: C, 57.15; H, 4.80%; M^+ 336.085 9(16). $C_{16}H_{16}O_8$ requires C, 57.14; H, 4.80%; *M*, 336.084 52].

3,3′,3′-*Triacetyl*-5-*methoxycarbonylxanthyrone* (15).—Compound (2) (10.5 g) was added to a solution of sodium methoxide [from sodium (1.15 g) and methanol (50 ml)]. Methoxymethyleneacetylacetone (14.2 g) was added and the solution heated for 1.5 h. The methanol was removed, water (100 ml) was added, the solution cooled to 0 °C, and acidified with 4N hydrochloric acid. The solid was filtered off, and dissolved in chloroform. Drying and evaporation yielded 3′,3′,3-*triacetyl*-5-*methoxycarbonylxanthyrone* (15) (2.6 g), red-brown, m.p. 159 °C (from benzene) [Found: C, 60.1; H, 5.05%; M^+ 320.091 0(16). $C_{16}H_{16}O_7$ requires C, 60.00; H, 5.04%; *M*, 320.089 6].

3′,3′,5-*Triacetyl*-3-*methoxycarbonylxanthyrone* (16).—Methoxymethyleneacetylacetone (9.4 g) and dimethyl sodiomalonate (3.6 g) were heated on a steam-bath; the melt was dark red possessing a green sheen. The melt was cooled, water was added, and the resulting solution further cooled to 0 °C. Addition of 4N hydrochloric acid (25 ml) gave a green precipitate, which was filtered off and washed with methanol until the green colour had been removed. The precipitate was crystallised from benzene, yielding red-brown crystals of 3′,3′,5-*triacetyl*-3-*methoxycarbonylxanthyrone* (16) (1.4 g), m.p. 180 °C [Found: C, 59.80; H, 5.05%; M^+ 320.089 6(16). $C_{16}H_{16}O_7$ requires C, 60.00; H, 5.04%; *M*, 320.089 6].

Reaction of Methyl 2-*Methyl*-6-*oxo*-6H-*pyran*-3-*carboxylate with Methyl Methoxymethyleneacetoacetate in the Presence of Sodium Methoxide*.—The pyran (2.1 g), methoxymethylene ester (1.75 g), and sodium methoxide [6.25 ml of a 1M methanolic solution] were refluxed together (30 min). Water was added and the mixture acidified and extracted with ether. The ether-soluble product (3.4 g) was chromatographed on silica-gel using benzene–chloroform–methanol gradient elution. Starting pyran eluted first, followed by trimethyl methyltrimesate (1.05 g), m.p. 105—106 °C, from ether–light petroleum (b.p. 40—60 °C) (lit.,[11] m.p. 107 °C) [M^+ 266.078 7(12). $C_{13}H_{14}O_6$ requires *M* 266.079 0]. Rechromatography gave dimethylxanthophanic enol (232 mg), m.p. and mixed m.p. 178 °C, and 3′-acetyl-5,3′-bismethoxycarbonylxanthyrone (18), m.p. 169—170 °C (see below).

3′-*Acetyl*-3′,5-*bismethoxycarbonylxanthyrone* (18).—To a solution of (4) (6.7 g) and methyl methoxymethyleneacetoacetate (7.4 g) in benzene (10 ml), a slurry of potassium t-butoxide (4.5 g) in benzene (20 ml), was added. The deep red solution was shaken for 1 h. The product was poured into water (40 ml) and 4N hydrochloric acid was added. Chloroform extraction gave a dark orange liquid, which was dissolved in chloroform–ether (1 : 1) and set aside. Red-brown 3-*acetyl*-3′,5-*bismethoxycarbonylxanthyrone* (18) (2.3 g), m.p. 172 °C, was obtained (Found: C, 57.25; H, 4.65. $C_{14}H_{14}O_7$ requires C, 57.14; H, 4.80%); M^+ 294.

In a similar way, (4) (6.7 g) and ethyl ethoxymethyleneacetoacetate (7.4 g) gave 3′-*acetyl*-3′-*ethoxycarbonyl*-5-*methoxycarbonylxanthyrone* (19) (1.4 g), yellow plates, m.p. 172—174 °C (Found: C, 58.9; H, 5.35. $C_{15}H_{16}O_7$ requires C, 58.45; H, 5.25%). The corresponding *diethyl ester* (20), yellow needles, had m.p. 144 °C (Found: C, 59.6; H, 5.63. $C_{16}H_{18}O_7$ requires C, 59.7; H, 5.7%); M^+ 322.

3′-*Acetyl*-3′-*ethoxycarbonyl*-3-*methoxycarbonylxanthyrone* (21).—Using (3) (670 mg) in the procedure above, the xanthyrone (21) (38 mg) was isolated as orange crystals, m.p. 126—128 °C, M^+ 308 ($C_{15}H_{16}O_7$ requires *M*, 308).

Boiling Water on 3′-*Acetyl*-3,5,3′-*trimethoxycarbonylxanthyrone* (12).—The xanthyrone (3 g) was refluxed in water (100 ml) until the solution was pale yellow (4 h). Extraction with ether gave dimethyl 4-hydroxyisophthalate (1.73 g), identified by m.p. and mixed m.p. 94—95 °C, and by spectral comparison.

Boiling Water on 3′,3′-*Diacetyl*-3,5-*bismethoxycarbonylxanthyrone* (13).—The xanthyrone (3 g), similarly refluxed with water (100 ml), gave dimethyl 4-hydroxyisophthalate (1.76 g), m.p. and mixed m.p. 94—95 °C.

Boiling Water on 3,3′-*Diacetyl*-3′,5-*bismethoxycarbonyl*-

xanthyrone (14).—The xanthyrone (2 g) treated as above yielded white crystals of 3-acetyl-5-methyl-8-methoxycarbonylcoumarin (0.28 g), m.p. and mixed m.p. 159 °C (lit.,[1] m.p. 161—162 °C). When light petroleum (b.p. 40—60 °C) was added to the mother liquors and the solution set aside at 0 °C, methyl 3-acetyl-6-hydroxybenzoate (0.16 g), m.p. and mixed m.p. 53 °C (lit.,[1] m.p. 54 °C), was obtained.

Boiling Water on 3,3′,3′-*Triacetyl*-5-*methoxycarbonylxanthyrone* (15).—The xanthyrone (1.2 g) treated as above gave methyl 3-acetyl-6-hydroxybenzoate (0.2 g), identified by m.p. and mixed m.p. and spectral comparison.

Boiling Water on 3′,3′,5-*Triacetyl*-3-*methoxycarbonylxanthyrone* (16).—The xanthyrone (1.8 g), treated as above, gave methyl 3-acetyl-4-hydroxybenzoate (0.18 g), m.p. 97 °C (lit.,[13] m.p. 98 °C) (Found: C, 61.80; H, 5.01. Calc. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.01%); M^+ 194; $\nu_{max.}$ 1 728 (aryl ester), 1 680, 1 643 (bonded ketone), 1 595 (aryl), and 1 488 cm^{-1}; $\lambda_{max.}$ (0.01N ethanolic sulphuric acid) 232 (ε 34 700), 254 (11 300), and 320 (2 700) nm; $\lambda_{max.}$ (0.01N ethanolic potassium hydroxide) 245 (ε 21 400), 296 (26 000), and 360 (7 900) nm; n.m.r., τ 7.34 (3 H, CH_3CO), 6.12 (3 H, CH_3O), 3.07 (1 H, d, *J* 8.6 Hz), 1.97 (1 H, dd, *J* 1.9 and 8.6 Hz, aryl), 1.59 (1 H, d, *J* 1.9 Hz, aryl), and −2.65 (1 H, chelated OH).

Boiling Water on 3,5,3′,3′-*Tetra-acetylxanthyrone* (17).—The xanthyrone (1.2 g), treated as above gave an oil which when sublimed under reduced pressure yielded 5-acetyl-2-hydroxyacetophenone (0.13 g), m.p. 72 °C, after repeated recrystallisations from chloroform–ether, m.p. 72 °C (lit.,[14] 92—93 °C) (Found: C, 67.65; H, 5.70. Calc. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66%); M^+ 178; $\nu_{max.}$ 1 687 (aryl ketone) 1 647 (bonded ketone), 1 595 (aryl), and 1 492 cm^{-1}; $\lambda_{max.}$ (0.01N ethanolic sulphuric acid) 240 (ε 25 800), 272 (12 300) and 318 (3 000) nm; $\lambda_{max.}$ (0.01N ethanolic potassium hydroxide) 247 (ε 13 700) and 320 (24 100) nm; n.m.r., τ (carbon tetrachloride) 7.52, 7.32 (6 H, 2 × CH_3CO), 3.05 (1 H, d, *J* 8.6 Hz, aryl), 2.05 (1 H, dd, *J* 2.0 and 8.6 Hz, aryl), 1.66 (1 H, d, *J* 2.0 Hz, aryl), and −2.58 (1 H, chelated OH).

In view of the discrepant m.p. an authentic sample was prepared by the literature method [14] and the literature m.p. 93 °C was confirmed. This sample was spectroscopically the same as that above and a mixed m.p. of 85 °C was recorded.

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