Polyketoenols and Chelates. New Types of Xanthyrones lacking Enolised Side-chain Termini: their Reactions with Magnesium Methoxide

By **S. Richard Baker, Leslie Crombie,* and Roderick V. Dove,** Department of Chemistry, University of Nottingham, Nottingham NG7 2RD

Xanthyrones (4) and (8) as well as (9), (11), and (13) have been synthesised: blocking the side-chain terminus, which is normally enolised as in (5), by dicyano or cyano-ester end groups, leads to enolisation of the 3-acetylpyrone end as shown by n.m.r. data in $CDCl_3$. The dicyanobismethoxycarbonyl representative (9) exists in the 1'-H form in $CDCl_3$–CF_3CO_2H whilst in $CDCl_3$ the tetraester (13) is a 3'-H form. Xanthyrone (11) is present mainly in the 3'-H form in $CDCl_3$ but some enolate (12) is observed. All the xanthyrones are highly ionised in ethanol, (9) especially so. Treated with excess ($\geqslant$6 mol. equiv.) magnesium methoxide, xanthyrones (4) and (8) cyclise by an aldol pathway and (9) and (13) by an analogous Claisen pathway. This contrasts with dimethylxanthophanic enol (5) which undergoes a different type of Claisen cyclisation. The results accord with the view that cyclisation in the latter case involves a bischelate (20) and in the other cases monochelates, *e.g.* (22) and (25). Reactions of xanthyrones (4) and (8) with boiling water follow expected pathways.

ALL xanthyrones synthesised up to the present have enolised side-chain termini which doubtless contribute to their stability.[1] Thus, in the 'melt reaction' between ethyl ethoxymethylenemalonate and ethyl sodioacetoacetate, the components assemble [2,3] as (2; R = OEt) rather than (1; R = OEt). This is caused by ethoxymethylene interchange with the anion, leading ultimately to the more stable structure (2).[2] Replacement of sodioacetoacetate by sodioacetylacetone similarly leads to (2; R = Me) rather than (1; R = Me).[2] The present paper deals with the synthesis of xanthyrones lacking enolised propenyl side-chains, and certain of their reactions.

Condensation of the anion of pyrone (3), formed in the presence of methanolic sodium methoxide, with methyl methoxymethylenecyanoacetate gave a new xanthyrone (4) in 89% yield as dark red plates. Its structure in $CDCl_3$ solution, the pyrone-acetyl enolised form, was shown by n.m.r. examination: in addition to the expected resonances it showed a chelated hydroxy, τ −3.85, and an AB quartet, τ 1.55, 2.83 (J 12 Hz). Sixteen examples having propenyl side-chains of type (2) have J 15.0—16.3 Hz, *e.g.* (5) has resonances at τ 2.03, 2.23 (J 15.4 Hz). The pyrone carbonyl vibration of (4) also has a lowered value in the i.r., $\nu(CHCl_3)$ 1 730 cm^{-1}, due to hydrogen bonding: the range for xanthyrones of type (2) or (5) in $CHCl_3$ is 1 745—1 775 cm^{-1}.[1] The u.v. spectrum in chloroform is simple ($\lambda_{max.}$ 425 nm), but in neutral ethanol compound (4) is almost completely ionised [delocalised (7)] as shown by the long wavelength absorption at 522 nm in neutral and alkaline solution (Table): even in 0.01M-acid it is *ca.* 36% ionised. Comparative data for the typical xanthyrone (5), *ca.* 40% ionised in ethanol, are given in the Table.

A further example involving enolisation of the pyrone acetyl was provided when the anion from (3) condensed with methoxymethylenemalononitrile. The new purple-black crystalline compound, formed in 83% yield, had $\lambda_{max.}$ ($CHCl_3$) 431 nm, and in $CDCl_3$ n.m.r. examination showed a chelated hydroxy, τ −3.60, and an AB quartet, τ 1.92 and 2.73 (J 12.5 Hz). It had $\nu_{max.}$ ($CHCl_3$) 1 725 cm^{-1} for the pyrone carbonyl and is thus formulated as (8). The u.v. spectrum is the same in neutral ethanol as in 0.01M-alkali, with the long wavelength absorption at 521 nm. It is thus fully ionised in neutral ethanol and even in 0.01M-acid ethanol (8) is nearly 80% ionised. The compound is strongly acidic, more so than (4). In these two examples, if enolisation at the side-chain terminus is blocked, enolisation of the pyrone acetyl clearly supervenes. Consequently a structure was prepared to suppress both such enolisation possibilities.

Refluxing 3,5-bismethoxycarbonyl-6-methyl-2-pyrone (6) with methoxymethylenemalononitrile in the presence of methanolic sodium methoxide gave a violet sodium salt which on work-up formed a compound (55%) crystallising in red needles or plates (methanol solvate). Unfortunately it was too insoluble in $CDCl_3$ for satisfactory n.m.r. examination, but it was sufficiently soluble in $CDCl_3$–trifluoroacetic acid (TFA) (9 : 1). In this solvent there was, apart from the pyrone 4-H, only one olefinic proton at τ 2.50 (t, J 8 Hz), coupled to the methylene signals at τ 5.48 (d). Its structure is thus the 1'-H form (9). On the other hand, in [$^2H_6$]DMSO the compound apparently exists as the delocalised anion form (10). Thus, whilst one proton is missing, an AB quartet is present, τ 2.36, 3.24 (J 13 Hz) (in this solvent the 1 mol equiv. of methanol present in the crystal lattice can be observed). The delocalised ion from (10) must thus protonate at C-1' in this case. In $CHCl_3$–TFA (9 : 1) the u.v. spectrum shows $\lambda_{max.}$ at 317 with a weaker absorption at 460 nm. Compared with the u.v. data for (4) and (8) in $CHCl_3$, the former band appears consistent with methylene interruption of the longer conjugated system. In ethanol, however, the complete spectrum is the same whether in neutral, 0.01M-basic, or acidic ethanol. Xanthyrone (9) must thus be strongly acidic, virtually fully ionised in all three solvents with long wavelength absorption at 507 nm.

Successful isolation of (4), (8), and (9) encouraged us to see if xanthyrones having malonate-terminated side chains could be obtained as these had earlier eluded us.[1] A 'melt reaction' [3] between (3), dry sodium methoxide, and dimethylmethoxymethylene malonate gave substantial quantities of 3,3'-diacetyl-5,5'-bismethoxycar-

U.v. data for xanthyrones

Xanthyrone	Solvent	$\lambda_{max.}$ ($\varepsilon \times 10^{-3}$)/nm								
(5)	0.01M-HCl [a]			301 (13.1)			437 (19.8)			530infl (3.9)
	0.01M-KOH [a]		253 (12.3)	297 (12.0)	320infl (10.4)	366 (12.0)		498infl (39.7)		525 (48.9)
	EtOH			298 (11.1)			439 (19.1)			526 (19.5)
	$CHCl_3$ [b]			297 (18.7)			440 (18.7)			
(4)	0.01M-HCl [a]			295 (6.4)	325 (7.6)		444 (25.5)	493infl (25.5)		522 (28.0)
	0.01M-KOH [a]	227 (10.5)	250 (9.1)	300infl (5.7)	325 (7.6)	363 (10.2)		493infl (48.0)		522 (77.4)
	EtOH	227 (10.5)	250 (9.1)	300infl (5.7)	325 (7.6)	363 (10.2)		493infl (43.0)		522 (75.8)
	$CHCl_3$ [b]						425 (25.1)			
(8)	0.01M-HCl [a]			295 (6.4)	326 (9.2)	358 (10.9)		493infl (44.5)		521 (71.0)
	0.01M-KOH [a]	236 (4.6)	247 (5.2)	295 (6.4)	326 (9.2)	358 (10.9)		493infl (52.7)		521 (90.0)
	EtOH	236 (4.4)	247 (5.2)	295 (6.4)	326 (9.2)	358 (10.9)		493infl (52.7)		521 (90.0)
	$CHCl_3$ [b]						431 (45.7)			
(9)	0.01M-HCl [a] / 0.01M-KOH [a] / EtOH	229 (10.7)	247 (12.4)		317 (7.0)	352 (10.2)				507 (79.0) [c]
	$CHCl_3$–TFA (9 : 1)				317 (7.9)		460 (1.6)			
(11)—(12)	0.01M-HCl [a]			270 (5.3)		385 (13.5)				
	0.01M-KOH [a]		246 (18.4)	294 (8.5)		365 (8.5)		483infl (30.7)		510 (33.8)
	EtOH		246 (18.4)	294 (5.6)	323infl (6.8)	365 (11.3)	400infl (8.15)	483infl (12.7)		510 (13.5)
	$CHCl_3$ [b]		253 (11.7)	273infl (7.3)		364 (6.6)				
(13)	0.01M-HCl [a]		256 (17.3)		328 (9.2)					
	0.01M-KOH [a]		250 (18.4)	307 (6.9)		357 (15.3)		476infl (34.3)		503 (42.9)
	EtOH		250 (18.4)	307 (6.9)		357 (7.7)		476infl (20.0)		503 (26.0)
	$CHCl_3$ [b]		253 (15.5)			349 (12.7)				

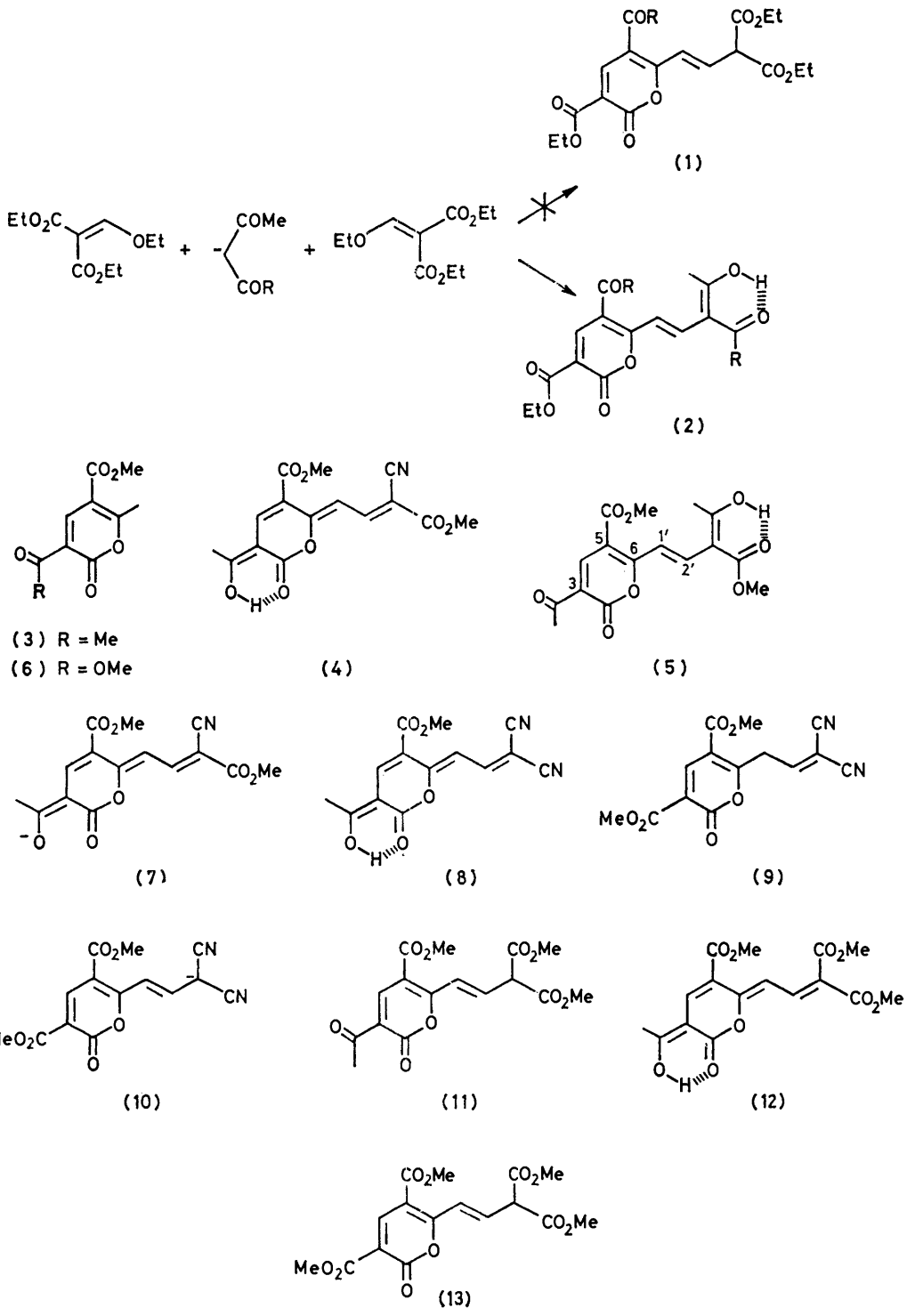
[a] Ethanolic solution. [b] Ethanol-free. [c] Inflection at *ca.* 483 nm.

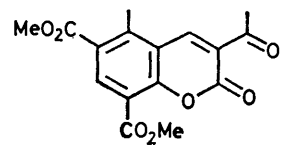
bonylglaucyrone which was removed as its sodium salt. From the remaining product, 3-acetyl-3′,3′,5-trismethoxycarbonylxanthyrone was isolated in low yield as yellow crystals. The n.m.r. spectrum ($CDCl_3$) showed that this xanthyrone was present mainly in the form (11). It had a proton at τ 5.63 (d, *J* 8 Hz) coupled to the higher field proton of an AB quartet, τ 2.74 (*J* 16, 8 Hz) and 2.36 (*J* 16 Hz). On the other hand the sample also showed a second set of lines corresponding to *ca.* 20% of the enolised structure (12). Thus it showed a chelated hydroxy at τ −3.50, and an AB quartet, τ 1.92, 2.74 (*J* 12 Hz), along with an enolised acetyl methyl at τ 7.61. It thus appears that the compound exists in $CDCl_3$ as a mixture of unenolised and enolised forms, the former predominating (*ca.* 4 : 1). U.v. data in ethanol indicate that the equilibrium is substantially altered in this solvent and the compound is *ca.* 60% ionised as judged by $\lambda_{max.}$ 510 nm: in 0.01M-acid ethanol, however, it is not ionised (Table). It is of interest that the side-chain of (9) is apparently more stable in the 1′-H form, whilst (11) is more stable in the 3′-H form: this reflects enhanced conjugation by the 3′,3′-dinitrile groups.

In pursuit of a tetraester xanthyrone (1; R = OEt), mentioned at the outset of the paper, attempts were made to form the system as the tetramethyl ester. A ' melt ' type reaction between 3,5-bismethoxycarbonyl-6-methyl-2-pyrone, dimethyl methoxymethylenemalonate, and sodium methoxide gave, on work-up, 3,3′,5,5′-tetrakismethoxycarbonylglaucyrone as the major product. From the residues however, a small yield of 3,3′,3′,5-tetrakismethoxycarbonylxanthyrone was isolated as golden needles. In $CDCl_3$, the n.m.r. spectrum showed four methyl esters, the pyrone 4-H (τ 1.24) and a proton at τ 5.63 (d, *J* 9 Hz), coupled to a higher field component of an AB quartet, τ 2.30, 2.70 (*J* 16 Hz). It thus has structure (13) which is in agreement with the u.v. data in $CHCl_3$ (Table). In neutral ethanol, however, the compound is ionised to the extent of 60% as judged by the extinction of the long wavelength absorption (503 nm) in 0.01M-alkali. In 0.01M-acid it exists essentially in the un-ionised form (13). Again, with a malonate end group, the 3′H-form is more stable than the 1′H-form in chloroform.

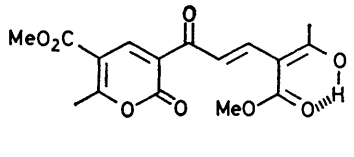
In earlier work [4] it was shown that the xanthyrone (5) gave different products when treated with different

initial molarities of magnesium methoxide at 20°. With <1 mol equiv. of reagent the xanthyrone was recovered unchanged on acid work-up, the terminal β-keto-ester being complexed. At about the 1 mol equiv. level of reagent 80—85% of the product was the aldol-derived (14), but when 2 mol equiv. of magnesium methoxide were used, the major product was the pyrone (15). An initial molarity of 2.5 gave 65—70% of the products as (15) with none of the aldol-derived (14): the remainder of the material was the Claisen product (16), none of which was found when 2 mol equiv., or less, of magnesium methoxide was employed. Addition of 6 mol equiv. of magnesium methoxide however gave almost entirely (16). These results were explained by

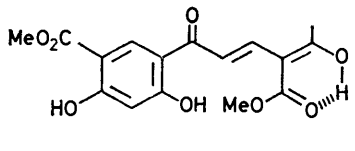




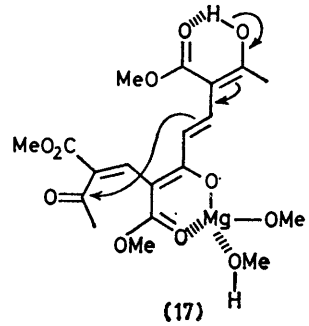
(14)



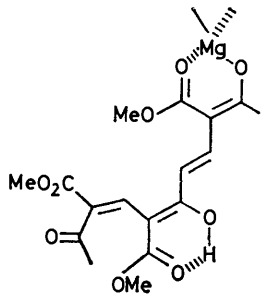
(15)



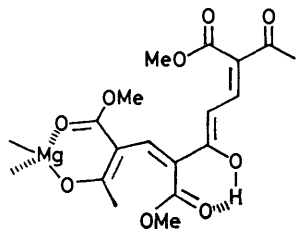
(16)



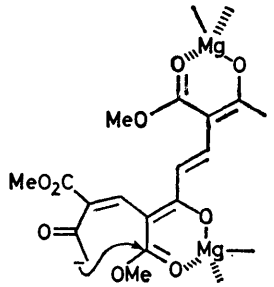
(17)



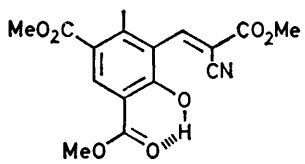
(18)



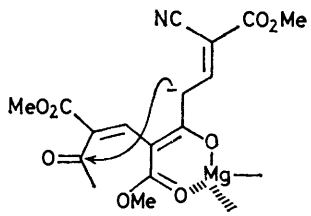
(19)



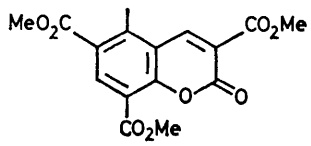
(20)



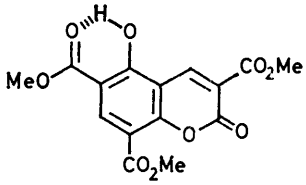
(21)



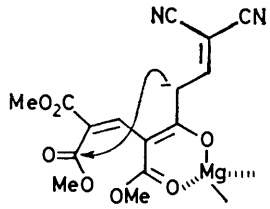
(22)



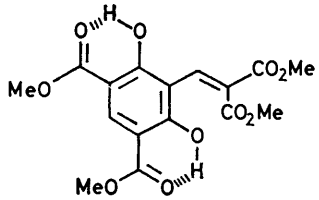
(23)



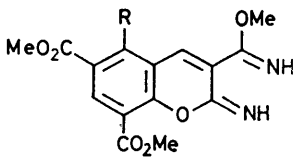
(24)



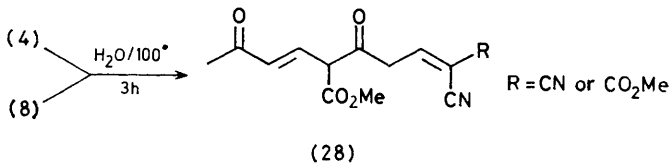
(25)



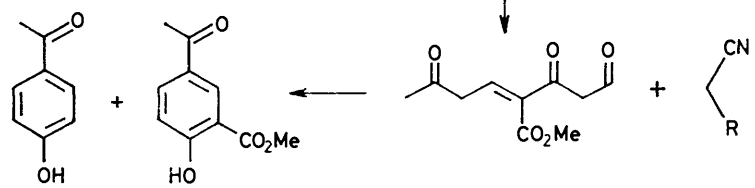
(26)



(27)



(28)



(30) (29)

postulating that pyrone ring-opening by methanolysis led to a monoconjugated chelate (17) from which the aldol product (14) was derived. Because of charge retention by the chelate, (18) is unlikely to be the precursor of (14), and (19) is considered unlikely since evidence indicates that whereas Claisen attack by an

anion on the chelate system is effective, aldol attack is an ineffective process.[3] With 2 mol equiv. of magnesium methoxide present, a doubly capped magnesium chelate (20; without charge) is present as the substrate and it appears comparatively stable to disposal by aldol or Claisen reaction, releasing pyrone (15) on work-up. With further base present, however, the terminal anion forms and cyclises by internal Claisen attack on the magnesio-chelated ester as shown [(20)].[4]

Since the cyanoxanthyrone (4) lacks a chelating propenyl side-chain terminus and can only give a mono-conjugated chelate, after opening of the pyrone ring, one would thus expect only aldol product even at high, molarities of magnesium methoxide. This proved to be the case. Treatment of (4) with 6 mol equiv. of magnesium methoxide in methanol–benzene at 20° overnight gave the isophthalate (21) in 73% yield. In the i.r. (KBr) it had a nitrile vibration (2 220 cm^{-1}), esters (1 725 cm^{-1}), and chelated ester (1 680 cm^{-1}). The n.m.r. ($CDCl_3$) showed an aromatic methyl (τ 7.40), three ester methyls (τ 6.01, 6.05, 6.11), an aromatic and an olefinic proton (τ 1.42, 1.60), and a chelated hydroxy (τ −1.74). It is likely that pyrone opening proceeds as Claisen-like attack by alkoxide ion on the magnesio-chelate of (4), but chelate exchange is expected between the sites of the opened form. Aldol cyclisation then proceeds using chelate (22). Under similar reaction conditions, the dinitrile (8) was incompletely attacked and the only compound isolated from gummy product, the coumarin (23), was again a product from the parallel aldol cyclisation.

3′,3′-Dicyano-3,5-bismethoxycarbonylxanthyrone (9) was refluxed (2 h) with 6.6 mol equiv. of magnesium methoxide in methanol and gave the coumarin (24) in 34% yield. Necessarily, this is a product of Claisen (25) rather than aldol reaction, but the pattern of attack is the same as in the aldol examples above and is different from that leading to the Claisen product (16) which has a requirement for an acetyl substituent on the pyrone [*cf.* (20)]. Prolonged refluxing of the 3,3′,3′,5-tetramethoxyxanthyrone (13) with a large excess of magnesium methoxide also gave (24) together with the corresponding uncyclised tetraester (26) which was readily converted into (24). This indicates that the malonate terminus complexes inefficiently with magnesium methoxide as compared with an acetoacetate terminus. Search by t.l.c. failed to show the presence of (26) in the reaction product from treatment of (9) with excess of magnesium methoxide. Possibly an imidolactone is involved in the latter case with the other nitrile being hydrolysed *via* an imidate ester [*cf.* (27; R = OH)]: 1,1-dinitriles appear to be more prone to nucleophilic attack at the nitrile by anions than are 1-cyano-esters.[5]

Apart from the magnesium alkoxide chemistry, the reactions of (4) and (8) with boiling water [1,6] also confirm their structures. According to their termini, methyl cyanoacetate or malononitrile are found along with the two acetophenones (29) and (30) *via* a species related to (28).

EXPERIMENTAL

N.m.r. data are given as τ values.

3-Acetyl-3′-cyano-3′,5-bismethoxycarbonylxanthyrone (4).— 3-Acetyl-5-methoxycarbonyl-6-methyl-2-pyrone (3) [1,3] (2.0 g) was added to sodium methoxide solution [from sodium (0.22 g) and methanol (15 ml)] followed by methyl methoxymethylenecyanoacetate (1.35 g), and the mixture was refluxed (90 min). Evaporation and addition of water and 4M-hydrochloric acid gave, on extraction with chloroform, *3-acetyl-3′-cyano-3′,5-bismethoxycarbonylxanthyrone* (4) (2.7 g, 89%), dark red needles from benzene, m.p. 185 °C (Found: C, 56.45; H, 4.45; N, 4.6%; M^+, 319. $C_{15}H_{13}NO_7$ requires C, 56.45; H, 4.1; N, 4.4%; *M*, 319); $\nu_{max.}$ ($CHCl_3$) 2 225 (nitrile), 1 730 (pyrone carbonyl), 1 715, 1 695 (ester carbonyls), 1 610, and 1 575 cm^{-1}; τ($CDCl_3$) −3.85 (1 H, chelated OH), 1.55 and 2.83 (2 × 1 H, *J* 12 Hz), 2.20 (1 H, pyrone 4-H), 6.11 (6 H, 2 × CO_2CH_3), and 7.55 [3 H, $CH_3C(O)$=].

3-Acetyl-3′,3′-dicyano-5-methoxycarbonylxanthyrone (8).—3-Acetyl-5-methoxycarbonyl-6-methyl-2-pyrone (3) (2.0 g) was added to sodium methoxide solution [from sodium (0.22 g) and methanol (15 ml)] followed by methoxymethylenemalononitrile (1.3 g) and the mixture was refluxed (1.5 h). Work-up as above gave *3-acetyl-3′,3′-dicyano-5-methoxycarbonylxanthyrone* (8) (2.25 g, 83%), purple-black crystals from methanol–benzene, m.p. 197 °C (Found: C, 58.7; H, 3.5; N, 9.7%; M^+, 286. $C_{14}H_{10}N_2O_5$ requires C, 58.75; H, 3.5; N, 9.8%; *M*, 286); $\nu_{max.}$ ($CHCl_3$) 2 215 (nitrile), 1 725 (pyrone carbonyl), and 1 690 (ester carbonyl) cm^{-1}; $\nu_{max.}$ (mull) 2 215, 1 715, 1 700, and 1 580 cm^{-1}; τ($CDCl_3$) −3.60 (1 H, chelated OH), 1.92 and 2.73 (2 × 1 H, *J* 12.5 Hz), 2.05 (1 H, pyrone 4-H), 6.08 (3 H, CO_2CH_3), and 7.52 ([3 H, $CH_3C(O)$=]; τ([$^2H_6$]DMSO) 2.20 and 3.12 (each 1 H, *J* 14 Hz), 1.52 (1 H, pyrone 4-H), 6.27 (3 H, CO_2CH_3), and 7.59 [3 H, $CH_3C(O)$=].

3′,3′-Dicyano-3,5-bismethoxycarbonylxanthyrone (9).—3,5-Bismethoxycarbonyl-6-methyl-2-pyrone (6) [1] (4.52 g) was added to sodium methoxide solution [from sodium (0.46 g) and methanol (25 ml)], followed by methoxymethylenemalononitrile (2.16 g) in methanol (50 ml) and the mixture was refluxed (30 min). On cooling in ice, red crystals of the sodium salt deposited and were filtered off and washed with chloroform. The salt was decomposed with 8M-hydrochloric acid to give *3′,3′-dicyano-3,5-bismethoxycarbonylxanthyrone* (9) (3.65 g, 55%), red needles and plates from methanol, m.p. 300 °C (decomp.) (Found: C, 53.55; H, 3.85; N, 8.15. $C_{14}H_{10}N_2O_6$·CH_3OH requires C, 53.9; H, 4.2; N, 8.4%); $\nu_{max.}$ (KBr) 2 240 (nitrile), 1 745 (pyrone carbonyl), and 1 687 (ester carbonyls) cm^{-1}; τ($CDCl_3$–TFA, 9 : 1) 1.18 (1 H, pyrone 4-H), 2.50 (1 H, t, *J* 8 Hz), 5.48 (2 H, d, *J* 8 Hz), and 5.97, 6.00 (6 H, 2 × CO_2CH_3); τ([$^2H_6$]DMSO) 1.64 (1 H, pyrone 4-H), 2.36 and 3.24 (2 × 1 H, *J* 13 Hz), 6.32, 6.34 (2 × CO_2CH_3), and 6.60 (CH_3OH of solvation). The n.m.r. spectrum in [$^2H_6$]acetone was similar in form to the latter.

3,3′,3′,5-Tetrakismethoxycarbonylxanthyrone (13) *and 3,3′-5,5′-Tetrakismethoxycarbonylglaucyrone.*— 3,5-Bismethoxycarbonyl-6-methyl-2-pyrone (11.3 g), dimethylmethoxymethylenemalonate (8.7 g), and dry sodium methoxide (2.7 g) were mixed, and melted together at 100 °C (3 h). Methanol was evolved and the mixture became viscous, setting to a black solid having a green sheen. The solid was cooled and 4M-acetic acid (100 ml) was added, followed by chloroform (100 ml). The black solid was ground up,

filtered, and washed with chloroform to give sodio-3,3′,5,5′-tetrakismethoxycarbonylglaucyrone (4.3 g) (which will be discussed in a later paper). The chloroform layer was separated and the aqueous layer further extracted with chloroform. After combination, all the chloroform extracts were shaken with saturated aqueous sodium acetate (3 × 50 ml) and a red precipitate formed. The red precipitate plus sodium acetate washings were acidified with 4M-hydrochloric acid and extracted with chloroform. After washing, drying, and evaporation 3,3′,3′,5-*tetrakismethoxycarbonylxanthyrone* (13) (321 mg) was isolated as pale golden needles from chloroform–ether, m.p. 138—139 °C (Found: C, 51.8; H, 4.6%; M^+, 368.073 2. $C_{16}H_{16}O_{10}$ requires C, 52.2; H, 4.4%; *M*, 368.074 3); $\nu_{max.}$ (KBr) 1 780 (pyrone carbonyl), 1 730, 1 710 (ester carbonyls), and 1 640 (olefin) cm^{-1}; $\tau(CDCl_3)$ 1.24 (1 H, pyrone 4-H), 2.30 (1 H, *J* 16 Hz), 2.70 (1 H, *J* 16 and 9 Hz), 5.63 (1 H, *J* 9 Hz), and 6.03, 6.04, 6.16, 6.16 (12 H, 4 × CO_2CH_3).

3-*Acetyl*-3′,3′,5-*trismethoxycarbonylxanthyrone* (11) *and* (12) *and* 3,3′-*Diacetyl*-5,5′-*bismethoxycarbonylglaucyrone*.—3-Acetyl-5-methoxycarbonyl-6-methyl-2-pyrone (0.45 g), dimethyl methoxymethylenemalonate (0.35 g), and sodium methoxide (0.1 g) were heated together (3 h). Work-up similar to that above gave sodio-3,3′-diacetyl-5,5′-bismethoxycarbonylglaucyrone (to be discussed later) and 3-*acetyl*-3′,3′,5-*trismethoxycarbonylxanthyrone* (11) and (12) (53 mg), pale yellow crystals from ether–n-hexane, m.p. 90—92 °C (Found: C, 54.75; H, 4.6%; M^+, 352.070. $C_{16}H_{16}O_9$ requires C, 54.55; H, 4.6%; *M*, 352.079); $\nu_{max.}$ (KBr) 1 710 (carbonyls) and 1 575 cm^{-1}; $\tau(CDCl_3)$ [mixed forms (11)—(12)] 3.50 (chelated OH), 1.36, 1.38 (pyrone 4-H) 2.36, 2.74 (*J* 16 Hz) and 1.95, 2.74 (*J* 12 Hz) (1′- and 2′-H), 5.63 (d, *J* 8 Hz, 3′-H), 6.10, 6.16, 6.19 (3 × CO_2CH_3), 7.38 ($COCH_3$), and 7.61 [$CH_3C(O)$=]; n.m.r. estimate of unenolised : enolised forms, 4 : 1.

Treatment of 3-*Acetyl*-3′-*cyano*-3′,5-*bismethoxycarbonylxanthyrone* (4) *with Magnesium Methoxide* (6 mol equiv.).—Xanthyrone (4) (3.0 g) in benzene (75 ml) was treated with magnesium methoxide solution [from magnesium (1.4 g) and methanol (25 ml)]. The mixture was kept (18 h) at 20° and water and 2M-hydrochloric acid was added with thorough shaking. Extraction with chloroform followed by chromatography on alumina gave the *isophthalate* (21) (2.3 g, 73%), needles from cyclohexane–chloroform, m.p. 141° (decomp.) (Found: C, 57.8; H, 4.4; N, 4.15%; M^+, 333. $C_{16}H_{15}NO_7$ requires C, 57.65; H, 4.55; N, 4.2%; *M*, 333); $\nu_{max.}$ (KBr) 2 220 (CN), 1 725 (ester carbonyls), and 1 680 (chelated ester carbonyl) cm^{-1}; $\tau(CDCl_3)$ −1.74 (1 H, chelated OH), 1.42 and 1.60 (2 × 1 H, aromatic and olefinic −CH=), 6.01, 6.05, 6.11 (3 × 3 H, CO_2CH_3), and 7.40 (aromatic CH_3) $\lambda_{max.}$ (EtOH) 224 (ε 25 500), 251 (18 000), 297 (6 800), 319infl. (5 600), 334infl. (4 600) nm; $\lambda_{max.}$ (M/100 ethanolic NaOH) 236 (ε 22 600), 284 (25 900), and 425 (6 400) nm.

Treatment of 3-*Acetyl*-3′,3′-*dicyano*-5-*methoxycarbonylxanthyrone* (8) *with Magnesium Methoxide* (6 mol equiv.).—Xanthyrone (8) (3.0 g) in benzene (50 ml) and methanol (75 ml) was treated with magnesium methoxide solution [from magnesium (1.54 g) and methanol (25 ml)]. After keeping at 20° (18 h) water and 2N-hydrochloric acid were added. The precipitate which formed was unchanged xanthyrone (8) (1.8 g). The aqueous phase was extracted with ether and evaporation of the ethereal solution gave a red gum. Preparative t.l.c. gave the *coumarin* (23) (12 mg), needles from carbon tetrachloride, m.p. 174 °C (Found: C, 57.55; H, 4.2%; M^+, 334. $C_{16}H_{14}O_8$ requires C, 57.5; H, 4.2%; *M*, 334); $\nu_{max.}$ (KBr) 1 775 (pyrone carbonyl), 1 730 (ester carbonyls), and 1 590 (aromatic) cm^{-1}; $\tau(CDCl_3)$ 1.11 (1 H, coumarin 4-H), 1.35 (1 H, aromatic −CH=), 5.99, 6.02, 6.04 (3 × 3 H, CO_2CH_3), and 7.10 (3 H, aromatic CH_3); $\lambda_{max.}$ (EtOH) 224 (ε 25 500), 251 (18 100), 297 (6 800), 319infl. (5 600), and 334 (4 800) nm; $\lambda_{max.}$ (M/100 ethanolic NaOH) 236 (ε 22 600), 284 (25 900), and 425 (6 400) nm.

Treatment of 3′,3′-*Dicyano*-3,5-*bismethoxycarbonylxanthyrone* (9) *with Magnesium Methoxide* (8 mol equiv.).—Xanthyrone (9) (203 mg) was refluxed (2 h) with magnesium methoxide solution [from magnesium (120 mg) and methanol (25 ml)]. Treatment with 4M-hydrochloric acid and extraction with chloroform gave the *coumarin* (24) (74 mg, 34%), pale yellow needles from methanol, m.p. 209—211 °C (decomp), and after vacuum sublimation, m.p. 220—230 °C (decomp.) (Found: C, 53.15; H, 3.65%; M^+, 336.049 7. $C_{15}H_{12}O_9$ requires C, 53.55; H, 3.6%; *M*, 336.048 1); $\nu_{max.}$ (KBr) 1 760 (coumarin carbonyl), 1 700 (ester carbonyls), and 1 685 (chelated ester carbonyl cm^{-1}); $\tau(CDCl_3)$ −1.95 (1 H, chelated OH), 1.03 (1 H, 4-H), 1.27 (1 H ,7-H), and 5.99, 6.04, 6.08 (3 × 3 H, CO_2CH_3).

Treatment of 3,3′,3′,5-*Tetrakismethoxycarbonylxanthyrone* (13) *with Magnesium Methoxide* (15 mol equiv.).—Xanthyrone (13) (37 mg) was refluxed (7 h) with magnesium methoxide solution [from magnesium (36 mg) and methanol (25 ml)]. Treatment with 4M-hydrochloric acid and extraction ($CHCl_3$) gave a solid which analytical t.l.c. (silica HF254; 1% acetic acid and chloroform) showed to be a mixture of coumarin (24) and a less polar compound. After washing with ether and crystallisation of the undissolved material, the coumarin (24) was isolated (mixed m.p. and i.r. comparison). The tetraester (26) isolated from the ether washings underwent a change at 130—139 °C and melted at 220—230 °C (decomp.) apparently as the coumarin (24). It was changed to the latter on prolonged contact with silica and on attempted crystallisation from methanol. The tetraester had M^+, 368 ($C_{16}H_{16}O_{10}$ requires *M*, 368) but the ion was too weak for accurate mass measurement. The tetraester had $\nu_{max.}$ (KBr) 1 725 (ester carbonyls) and 1 680 (chelated ester carbonyls) cm^{-1}; $\tau(CDCl_3)$ −1.80 (2 H chelated hydroxys), 1.28 and 1.47 (2 × 1 H, 4- and 7-H), 6.21 (6 H, 2 × CO_2CH_3), and 6.00 (6 H, 2 × chelated CO_2CH_3).

Treatment of 3-*Acetyl*-3′-*cyano*-3′,5-*bismethoxycarbonylxanthyrone* (4) *with Boiling Water*.—Xanthyrone (4) (3.0 g) was refluxed with water (200 ml) for 3 h. Extraction with ether gave an oil which was shown to contain methyl cyanoacetate by t.l.c. The oil was chromatographed on Florisil (100—200 mesh) and the polar component, crystallised from light petroleum (b.p. 40—60 °C), was identified as methyl 3-acetyl-6-hydroxybenzoate (29) (0.75 g, 41%), m.p. and mixed m.p. 58 °C with an authentic specimen, and spectral comparison (lit.,[2] 54 °C). The less polar component crystallised from chloroform–cyclohexane and was identified as *p*-hydroxyacetophenone (30) (0.2 g, 16%) by its n.m.r. spectrum and m.p. and mixed m.p. 106 °C (lit.,[7] 109 °C).

Treatment of 3-*Acetyl*-3′,3′-*dicyano*-5-*methoxycarbonylxanthyrone* (8) *with Boiling Water*.—Xanthyrone (8) (3.0 g) was refluxed as above. Extraction with chloroform gave an oil in which the presence of malononitrile was confirmed by t.l.c. The remaining components were separated by p.l.c. to give methyl 3-acetyl-6-hydroxybenzoate (0.55 g, 26%), m.p. and mixed m.p. 57 °C, and *p*-hydroxyacetophenone (0.15 g, 11%), m.p. and mixed m.p. 109°.

We thank the University of Nottingham (S. R. B.) and Shell Research (R. V. D.) for studentships.

[0/489 *Received*, 31*st March*, 1980]

REFERENCES

[1] L. Crombie, M. Eskins, D. E. Games, and C. Loader, *J.C.S. Perkin I*, 1979, 478; preliminary communication, S. R. Baker, L. Crombie, and R. V. Dove, *J.C.S. Chem. Comm.*, 1979, 666.

[2] L. Crombie, D. E. Games, and M. H. Knight, *J. Chem. Soc.* (*C*), 1967, 757.

[3] L. Crombie, D. E. Games, and A. W. G. James, *J.C.S. Perkin I*, 1979, 464.

[4] L. Crombie, M. Eskins, D. E. Games, and C. Loader, *J.C.S. Perkin I*, 1979, 472; L. Crombie, M. Eskins, and D. E. Games, *Chem. Comm.*, 1968, 1015.

[5] R. Baker, L. Crombie, R. V. Dove, and D. A. Slack, *J.C.S. Perkin I*, 1979, 677.

[6] L. Crombie, D. E. Games, and M. H. Knight, *J.C.S. Perkin I*, 1967, 763.

[7] 'Handbook of Chemistry and Physics,' The Chemical Rubber Co., Cleveland 1964, 45th edn.