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STUDIES IN THE XANTHONE SERIES—III*

PREPARATION AND REACTIONS OF 1-ACETYL-2-HYDROXYXANTHONE

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Abstract The orientation and reactions of 1-acetyl-2-hydroxyxanthone (I; R_1 = Ac, R_2 = R_3 = H) leading to the synthesis of angular furanoxanthones (III; R = Me) and (IV) and pyronoxanthones of the type (V) are described. The ultra-violet spectra of these extended xanthone systems are discussed.

REACTIONS of 1-acetyl-2-hydroxyxanthone (I; R_1 = Ac, R_2 = R_3 = H) were studied in an attempt to prepare physiologically active molecules of simple chemical structure, analogous to biologically active chromones such as khellin.[1] The ketone itself could not be obtained from 2-hydroxyxanthone (I; R_1 = R_2 = R_3 = H) (or from its acetyl or methyl derivative) which, unlike the 1-hydroxy-isomer,[2] did not undergo acetylation under Fries or Friedel-Crafts conditions. In another unsuccessful attempt at preparing the ketone, the diphenyl ether (II; R_1 = R_2 = H, R_3 = OMe) (obtained from *o*-chlorobenzoic acid and *p*-methoxyphenol)[10] was treated with a mixture of aluminium chloride and acetyl chloride, but gave only 2-methoxyxanthone (I; R_2 = Me, R_1 = R_3 = H). When, in order to prevent this premature cyclisation, the ethyl ester (II; R_1 = Et, R_2 = H, R_3 = OMe) was used, the following products were obtained: Two diphenyl ethers (II; R_1 = Et, R_2 = Ac, R_3 = OH and R_1 = H, R_2 = Ac, R_3 = OH), a diacetyldiphenyl ether of unknown constitution, and the required ketone (I; R_1 = Ac, R_2 = R_3 = H), but in small yield only. The incidental formation of the ketone under Friedel-Crafts conditions prompted cyclisation of the acetyl compound (II; R_1 = H, R_2 = Ac, R_3 = OH) with aluminium chloride-acetyl chloride which gave the ketone in 37% yield. *Poly*phosphoric acid, could also be used as a cyclising agent when the reaction temperature was kept within the range of 60–80°. No reaction occurred below 60°, while above 80° phosphono-2-oxyxanthone (I; R_1 = R_3 = H, R_2 = $P(O)(OH)_2$) together with some 2-hydroxyxanthone (I; R_1 = R_2 = R_3 = H) were the main products. The latter two products were also formed when 1-acetyl-2-hydroxyxanthone was heated with *poly*phosphoric acid above 80°, thus demonstrating the lability of the 1-acetyl-group. By contrast, the 2-acetyl and the 4-acetyl-1-hydroxyxanthone proved to be stable to hot *poly*phosphoric acid.[3] De-acylation in sterically hindered aromatic ketones by *poly*phosphoric acids[4] and other acids[5] has been reported previously.

* Part II was published in *J. Chem. Soc.* 1790 (1958).

[1] C. P. Huttrer and E. Dale, *Chem. Rev.* **48**, 543 (1951).
[2] J. S. H. Davies, F. Scheinmann and H. Suschitzky, *J. Chem. Soc.* 2140 (1956).
[3] F. Scheinmann and H. Suschitzky, Unpublished results.
[4] H. R. Snyder and R. W. Roeske, *J. Amer. Chem. Soc.* **74**, 5820 (1952).
[5] W. M. Schubert and H. K. Latourette, *J. Amer. Chem. Soc.* **74**, 1829 (1952).

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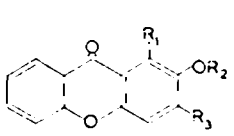

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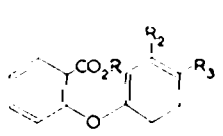

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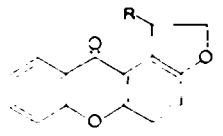


III

Since cyclisation of the diphenyl ether (II; R_1 = H, R_2 = Ac, R_3 = OH) may occur in two directions yielding two isomers (I; R_1 = Ac, R_2 = R_3 = H or R_1 = R_2 = H, R_3 = Ac), the resulting ketone had to be orientated. It was not possible to show the presence of a 1:4-diketone structure by means of hydrazine or *o*-phenylenediamine. In an unsuccessful attempt to prepare the 1-acetyl-isomer (I; R_1 = Ac, R_2 = R_3 = H) unambiguously, 1-formyl-2-hydroxyxanthone (I; R_1 = CHO, R_2 = R_3 = H) was made to react with diazomethane yielding the oxide (I; R_1 = $\overset{O}{\diagdown\diagup}$CH—$CH_2$ R_2 = R_3 = H) which, on treatment with 2-N-sulphuric acid gave the furanoxanthone (III; R = H). The reaction of diazomethane with *o*-hydroxy-aldehydes as a preparative route to furanocompounds is being investigated by us. Formation of furanostructures by hydrolysis of ethylene oxides in the case of a benzene and also a phenanthrene ethylene oxide[6,7] has been observed previously. In another unsuccessful synthesis of the 1-acetyl compound the acid chloride (I; R_1 = COCl, R_2 = Ac, R_3 = H), obtained by permanganate oxidation of the aldehyde (I; R_1 = CHO, R_2 = Ac, R_3 = H) followed by treatment with thionyl chloride, could not be made to react with dimethyl cadmium or with diazomethane.

Structural assignment of the ketone was next attempted by oxidation experiments but none of the standard methods applicable to ketones was of any avail. A modified hypobromite oxidation described recently for sterically hindered ketones[8] afforded a 1-tribromo-acetyl-2-methoxyxanthone (I; R_1 = $CO{\cdot}CBr_3$, R_2 = Me, R_3 = H). Formation of an *ω*-halo acetophenone type of compound actually supports placing the acetylgroup in the 1-position, since only methyl arylketones with two *ortho*-substituents are known to form stable trihalo-acetyl-derivatives in haloform reactions.[9] Attempts to hydrolyse the tribromocompound proved abortive. When, however, a cold solution of the methoxyketone (I; R_1 = Ac, R_2 = Me, R_3 = H) in concentrated sulphuric acid was treated with chromium trioxide 2-methoxy-xanthone-1 carboxylic acid (I; R_1 = CO_2H, R_2 = Me, R_3 = H) identical with the oxidation-product of 1-formyl-2-methoxyxanthone (I; R_1 = CHO, R_2 = Me, R_3 = H) was obtained. Additional constitutional evidence for the structure of the hydroxy ketone also follows from its lack of reactivity towards ketonic reagents, the absence of chelation (negative ferric reaction), the ease of de-acylation (cf. above) and finally from the similarity between the ultra-violet spectrum of its methyl ether and that of 1-formyl-2-methoxyxanthone (Fig. 1).

The hydroxyketone proved a useful starting material for the preparation of angular furano- and pyrono-xanthones. It condensed readily with ethyl bromoacetate to give the xanthyloxyacetate (I; R_1 = Ac, R_2 = $CH_2{\cdot}CO_2Et$, R_3 = H) and by

[6] J. W. Cook and W. H. S. Thomson, *J. Chem. Soc.* 395 (1945).
[7] V. I. Pansevich-Kolyada and Z. B. Idel'chik, *Zh. obshch. khim.* **25**, 2215 (1955).
[8] J. D. Edwards, Jr. and J. L. Cashaw, *J. Amer. Chem. Soc.* **78**, 3821 (1956).
[9] R. C. Fuson and B. A. Bull, *Chem. Rev.* **15**, 275 (1934).

hydrolysis of the latter the corresponding acid (I; R_1 — Ac, R_2 = $CH_2 \cdot CO_2H$, R_3 = H). Cyclisation and decarboxylation occurred when the latter compound was heated with a mixture of sodium acetate and acetic anhydride yielding 4′-methylfurano(3′:2′–1:2)xanthone (III; R = Me). Its ultra-violet absorption spectrum (Fig. 2) resembles that of the angular furano(3′:2′–1:2)xanthone (III; R = H) prepared unambiguously[10] from 1-formyl-2-hydroxyxanthone. This incidentally

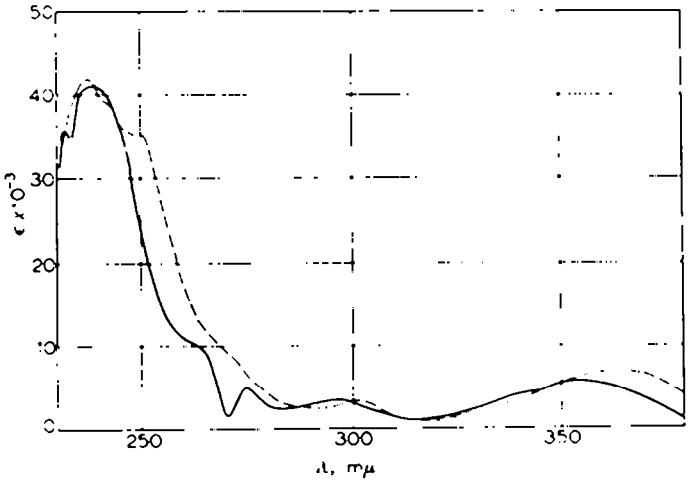


FIG. 1. Ultra-violet absorption spectra of 1-acetyl-2-methoxyxanthone (· ·) and of 1-formyl-2-methoxyxanthone (· · ·) in methanol.

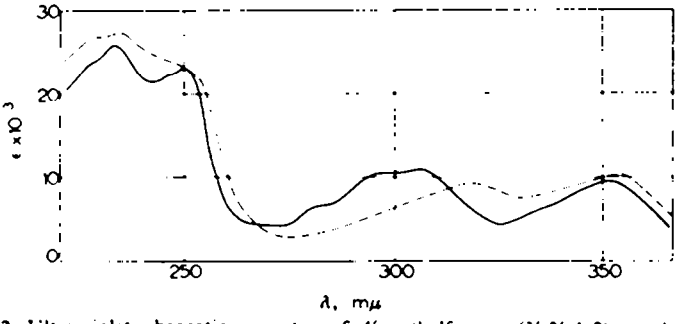


FIG. 2. Ultra-violet absorption spectra of 4′-methylfurano (3′:2′ 1:2) xanthone (– – –) and of furano(3′:2′–1:2)xanthone (———) in methanol.

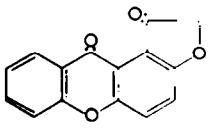
affords additional confirmation for the constitution of the hydroxyketone (I; R_1 Ac, R_2 — R_3 — H).

Bromination of the ketone in acetic acid gave the ω-bromocompound (I; R_1 = $CO \cdot CH_2Br$, R_2 = R_3 — H) which was readily cyclised with sodium acetate in boiling aqueous ethanol to 4′:5′-dihydro-4′-oxofurano(3′:2′–1:2)xanthone (IV).

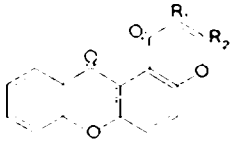
Two methods for making angular γ-pyronoxanthones from the ketone were examined. In the first the impure ester (I; R_1 = $CO \cdot CH_2 \cdot CO \cdot CO_2Et$, R_2 — R_3 = H) obtained by a Claisen condensation with diethyl oxalate, was ring-closed in ethanol with hydrochloric acid to the γ-pyronoxanthone (V; R_1 = H, R_2 — CO_2Et). In

[10] J. S. H. Davis, F. Lamb and H. Suschitzky, *J. Chem. Soc.* 1790 (1958).

the second, the γ-pyronoxanthone (V; R_1 = COPh, R_2 = Ph) was prepared by a Kostanecki-Robinson reaction from the ketone with benzoic anhydride and sodium benzoate.



IV.



V

Comparison between the ultra-violet absorption spectrum of xanthone and those of its extended ring-systems possessing a conjugated angular ring in the 1:2-positions reveals an interesting feature: the latter compounds show a marked depression in the intensity of the principal absorption band without appreciable change in the location of the maximal absorption (see Table 1), e.g. xanthone absorbs maximally at 238 mμ, ε = 44,200, while furano(3′:2′-1:2)xanthone (III; R = H) absorbs maximally at 233 mμ, ε = 25,800. A similar spectral behaviour is observed in 1-formyl-2-hydroxyxanthone which, owing to chelation, may be regarded as equivalent to a xanthone with a fused conjugated angular ring. The intensity depression in the oxofuranoxanthone (IV; see Table 1) suggests predominance of the conjugated enol- over the

TABLE 1. MAIN ABSORPTION MAXIMA OF XANTHONE AND RELATED COMPOUNDS IN METHANOL

Compound	λ_{max} (mμ)	ε_{max}
Xanthone	238	44,200
Furano(3′:2′-1:2)xanthone	233	25,800
4′-Methylfurano(3′:2′-1:2)xanthone	235	27,300
4′:5′-Dihydro-4′oxofurano(3′:2′ 1:2)xanthone	229	29,500
1-Formyl-2-hydroxyxanthone	241	32,600
1-Formyl-2-methoxyxanthone	239	41,000
1-Acetyl-2-hydroxyxanthone	237	35,700
1-Acetyl-2-methoxyxanthone	238	41,800
6′-Ethoxycarbonyl-4′-pyrono(3′:2′ 1:2)xanthone	218	26,000
4′-Pyrono(3′:2′ 1:2)xanthone-6′-carboxylic acid, hydrate	221	24,600
6′-Pyrono(3′:2′- 1:2)xanthone	245	44,600
5′-Methyl-6′-pyrono(3′:2′-1:2)xanthone	246	42,700

keto-form. In contrast 6′-pyrono(3′:2′-1:2)xanthone and its methyl-homologue[10] which have a non-conjugated angular ring and also 1-formyl- and -acetyl-2-methoxyxanthone in which chelation is prevented, show no significant reduction in the intensity of their chief absorption band relative to that of xanthone. The absence of any marked intensity changes in 1-acetyl-2-hydroxyxanthone is probably due to steric effects which interfere with effective chelation by dislodging the acetyl-group from the plane of the xanthone ring.

Inspection of molecular models (Courtaulds) reveals that the presence of a conjugated angular ring next to the xanthone carbonyl group moderately opposes adoption

of uniplanarity of the xanthone system, thus causing the molecule to assume a non-planar structure. This steric hindrance of resonance is associated with intensity decreases which are more pronounced than the change in the wavelength of maximum absorption (cf. Table 1). The spectroscopic behaviour of 1:2-substituted xanthones appears to be analogous to that of *ortho*-substituted ketones related to acetophenones in which similar changes in their electronic spectra on *ortho*-substitution are interpreted as moderate spatial interference with a uniplanar arrangement of the molecule.[11,12] Benzo- and naphtho-cyclenones have recently been found to show on substitution similar changes in their ultra-violet spectra, which is taken as indicative of steric interference with mesomerism.[13,14]

EXPERIMENTAL

Ultra-violet absorption spectra were measured in methanol and are quoted as λ_{max} (mμ) with ϵ in parentheses.

Fries rearrangements of 2-acetoxyxanthone

2-Acetoxyxanthone[15] did not undergo rearrangement in nitrobenzene with aluminium chloride at room temperature nor in the absence of a solvent at 100–110°, nor on treatment in acetic acid with BF_3-ether catalyst at 90° for 2 hr. Starting material and 2-hydroxyxanthone were the only products.

Attempted Friedel–Crafts acetylation

(a) 2-Acetoxy-, 2-hydroxy-, and 2-methoxyxanthone gave only starting material on acetylation under Friedel–Crafts conditions.

(b) To a solution of 2′-carboxy-4-methoxydiphenyl ether[10] (2·44 g) in *sym*-tetrachloroethane (50 ml) was added a suspension of powdered aluminium chloride (3·2 g) in the same solvent (70 ml) containing acetyl chloride (0·94 g). The mixture was stirred for 4·5 hr at room temperature and then allowed to stand for 3 days. Starting material and 2-methoxyxanthone[10] (74%) only were obtained.

2′-Ethoxycarbonyl-4-methoxydiphenyl ether

The parent acid[10] (56·2 g) in ethanol (215 ml) was esterified with dry hydrochloric acid gas for 12 hr. The solvent was driven off, and the residue taken up in chloroform (150 ml) and starting material removed by extraction with sodium hydroxide solution (2 N). Evaporation of the organic layer gave the crude ester (84%) m.p. 39–42°. On distillation (210°/9 mm) the *ester* solidified as white crystals, m.p. 43° (Found: C, 70·2; H, 5·9. $C_{16}H_{16}O_4$ requires C, 70·6; H, 5·9%).

3-Acetyl-4-hydroxy-2′-ethoxycarbonyldiphenyl ether

Powdered aluminium chloride (64 g) carbon disulphide (550 ml), acetyl chloride (14·4 ml) and crude ester (25 g) were refluxed with stirring for 3 hr and then left standing overnight. The residual gum, obtained by driving off the solvent, was treated with hydrochloric acid (30 ml) and crushed ice, and the resulting reaction

[11] E. A. Braude, F. Sondheimer and W. F. Forbes, *Nature, Lond.* **173**, 117 (1954).
[12] G. D. Hedden and W. G. Brown, *J. Amer. Chem. Soc.* **75**, 3744 (1953).
[13] R. Huisgen, I. Ugi, E. Rauenbusch, V. Vossius and H. Oertel, *Ber. Dtsch. Chem. Ges.* **90**, 1946 (1957).
[14] R. Huisgen and U. Rietz, *Ber. Dtsch. Chem. Ges.* **90**, 2768 (1957).
[15] St. von Kostanecki and R. Rutishauser, *Ber. Dtsch. Chem. Ges.* **25**, 1648 (1892).

mixture extracted with chloroform (230 ml), leaving an insoluble substance A (1·42 g). From the chloroform layer an alkaline extract B was produced with 2 N-sodium-hydroxide (3 × 250 ml). Removal of the chloroform and fractional distillation of the residue furnished pure *3-acetyl-2'-ethoxycarbonyl-4-hydroxydiphenyl ether* as a yellow liquid (14·7 g), b.p. 199–200°/2 mm (Found: C, 68·3; H, 5·4. $C_{17}H_{16}O_5$ requires C, 68·0; H, 5·4%). It gave a green-brown ethanolic ferric reaction and a red precipitate with Brady's reagent.

1-Acetyl-2-hydroxyxanthone

(a) Acidification of the alkaline extract B (see above) gave a solid which, after trituration with sodium hydrogen carbonate, left *1-acetyl-2-hydroxyxanthone* as pale-yellow needles (0·61 g) (ethanol), m.p. 237°, identical with the insoluble substance A (see above) λ_{max} 237 (35,700), 303 (3600), 366 (6700) (Found: C, 71·0; H, 4·0. $C_{15}H_{10}O_4$ requires C, 70·9; H, 4·0%). It had a negative ferric reaction and gave no precipitate with Brady's reagent. Its *acetyl* derivative obtained from acetic anhydride and pyridine or by the boric acid-acetic anhydride method crystallised as white needles (ethanol), m.p. 160° (Found: C, 69·2; H, 4·2. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·1%). Its *methyl ether* prepared with dimethyl sulphate had m.p. 185° λ_{max} 238 (41,800), 300 (3600), 363 (6900) (Found: C, 71·5; H, 4·6. $C_{16}H_{12}O_4$ requires C, 71·6; H, 4·5%).

(b) 3-Acetyl-2'-carboxy-4-hydroxydiphenyl ether (see next experiment) (2·72 g), aluminium chloride (6·92 g), and acetyl chloride (1·72 g) in carbon disulphide (50 ml) were heated under reflux with agitation for 3 hr and then set aside over-night. After decantation of the solvent the residue was worked up in the usual way yielding 1-acetyl-2-hydroxyxanthone (37%).

3-Acetyl-2'-carboxy-4-hydroxydiphenyl ether

The sodium hydrogen carbonate extract of the previous experiment described under (a) gave on acidification a gum (5·2 g) which was separable into two components as follows: recrystallisation of the residue (aqueous ethanol) followed by extraction with petroleum ether (b.p. 100–120°) left a *2'-carboxydiacetyl-4-hydroxydiphenyl ether* (1·8%), m.p. 209° (Found: C, 65·2; H, 4·6. $C_{17}H_{14}O_6$ requires C, 65·0; H, 4·5%). It gave a green ethanolic ferric reaction and an orange precipitate with Brady's reagent. From the petroleum ether extract *3-acetyl-2'-carboxy-4-hydroxydiphenyl ether* (5·4%) was obtained as white crystals, m.p. 172°, identical with the hydrolysis product from the ethyl ester described above (Found: C, 66·2; H, 4·5. $C_{15}H_{12}O_5$ requires C, 66·2; H, 4·4%). It gave a positive reaction with Brady's reagent and a dark-green ethanolic ferric reaction.

Action of polyphosphoric acid on 3-acetyl-2'-carboxy-4-hydroxydiphenyl ether

(a) *Reaction temperature* 55°. The ether (0·68 g) and *poly*phosphoric acid (made from 1·9 g P_2O_5 and 1·6 ml syrupy phosphoric acid) were heated at 55° for 0·5 hr with occasional stirring. On diluting the reaction mixture with water (50 ml) only starting material was recovered.

(b) *Reaction temperature below* 80°. A reaction mixture similar to that under (a) was heated between 60–70° for 0·5 hr, water (50 ml) added and the precipitate extracted

several times with chloroform and sodium hydrogen carbonate. The insoluble residue proved to be 1-acetyl-2-hydroxyxanthone (31%). The sodium hydrogen carbonate extract yielded starting material. From the chloroform layer a yellow substance was obtained on evaporation which was not further investigated.

(c) *Reaction temperature above* 80°. A reaction mixture as described under (a) was heated for 1 hr between 90 110°. Extraction of the insoluble residue, obtained by addition of water, with sodium hydrogen carbonate left some 2-hydroxyxanthone. Acidification of the alkaline extract (hydrochloric acid) precipitated *phosphono-2-oxyxanthone* as small white needles (acetic acid) (Found: C, 53·0; H, 3·2; P, 10·5. $C_{13}H_9O_6P$ requires C, 53·4; H, 3·1; P, 10·6%). Its m.p. remained at 226–227° on admixture with a specimen prepared unambiguously by heating polyphosphoric acid and 2-hydroxyxanthone for 1 hr at 110°.

Action of polyphosphoric acid on 1-*acetyl-2-hydroxyxanthone*

A mixture of polyphosphoric acid (from P_2O_5 1·9 g, and syrupy phosphoric acid 1·6 ml) and the ketone (0·63 g) was heated at 110° for 1 hr. The precipitate obtained by pouring the reaction mixture into water yielded 2-hydroxyxanthone and phosphono-2-oxyxanthone separable with sodium hydrogen carbonate.

Reaction of 1-*formyl-2-hydroxyxanthone with diazomethane*

To an ice-cold solution of 1-formyl-2-hydroxyxanthone (0·60 g) in chloroform (ethanol free; 70 ml) an ethereal solution of diazomethane (0·11 g in 20 ml ether) was added in one portion and set aside for 24 hr in the dark. From the precipitate *2-hydroxy-9-oxo-1-xanthylethylene oxide* (0·1 g) was obtained as white needles (ethanol) m.p. 198–200° (Found: C, 70·5; H, 4·1. $C_{15}H_{10}O_4$ requires C, 70·9; H, 4·0%). A further quantity (0·4 g) of crude oxide resulted from evaporation of the filtrate. The substance had a negative ferric chloride reaction. Its *acetyl* derivative was prepared by the acetic anhydride-pyridine method as white needles, m.p. 211° (Found: C, 68·8: H, 4·1. $C_{17}H_{12}O_5$ requires C, 68·9; H, 4·1%).

Furano(3′:2′–1:2)*xanthone*

A suspension of the above hydroxyethylene oxide (0·02 g) in 2 N-sulphuric acid (10 ml) was refluxed for 5 min, cooled, and filtered. Removal of starting material from the precipitate by extraction with 2 N-sodium hydroxide left furano(3′:2′–1:2)xanthone (0·01 g) λ_{max} 233 (25,800), 250 (23,100), 305 (11,000), 351 (9800), m.p. 144°, undepressed on admixture with an authentic sample.[10]

2-Acetoxy-1-carboxyxanthone

To a solution of 2-acetoxy-1-formylxanthone[10] (1·4 g) in boiling acetone (200 ml) finely powdered potassium permanganate (2·5 g) was added over 1 hr. After addition of water (100 ml) sulphur dioxide was passed through the reaction mixture and the solvent was driven off. The residue was collected and taken up in chloroform (50 ml). Acidification of a sodium hydrogen carbonate extract gave *2-acetoxy-1-carboxyxanthone* (41%) as white needles (ethanol), m.p. 172–5° (decomp) (Found: C, 64·7; H, 3·3. $C_{16}H_{10}O_6$ requires C, 64·4; H, 3·4%). Hydrolysis (2 N-sodium hydroxide) furnished *1-carboxy-2-hydroxyxanthone* as yellow needles, (benzene) m.p. 185–186°

(decomp) (Found: C, 65·4; H, 3·2. $C_{14}H_8O_5$ requires C, 65·6; H, 3·1%). When 2-acetoxy-1-carboxyxanthone (0·5 g) was heated with thionyl chloride (1·0 g) in dry benzene (40 ml) at reflux temperature for 0·5 hr a crude, unstable acid chloride m.p. 160–165° (decomp) was obtained. It gave *2-acetoxy-1-ethoxycarbonylxanthone* when refluxed in ethanol as white needles, m.p. 190° (Found: C, 66·1; H, 4·3. $C_{18}H_{14}O_6$ requires C, 66·3; H, 4·3%). An unidentified pale-yellow solid, m.p. 175–190° was obtained when the acid chloride was made to react with diazomethane. From the reaction of the acid chloride with dimethyl cadmium only 1-carboxy-2-hydroxyxanthone could be isolated.

1-Carboxy-2-methoxyxanthone

1-Formyl-2-methoxyxanthone was prepared from dimethyl sulphate and 1-formyl-2-hydroxyxanthone as white needles, m.p. 207° (ethanol) (Found: C, 70·9; H, 3·9. $C_{15}H_{10}O_4$ requires C, 70·8; H, 4·0%). The methoxy-compound (0·1 g) was oxidised in refluxing acetone (25 ml) with powdered potassium permanganate (0·18 g) and worked up as described for 2-acetoxy-1-carboxyxanthone. *1-Carboxy-2-methoxyxanthone* was obtained as white needles (66%) m.p. 246° (decomp) (Found: C, 66·6; H, 3·9. $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7%).

Oxidation experiments with 1-acetyl-2-hydroxyxanthone

(a) Conventional Dakin reactions (in pyridine or aqueous sodium hydroxide), oxidation of the ketone in pyridine with iodine, or by hypobromite or treatment of 1-acetyl-2-methoxyxanthone with potassium permanganate in pyridine gave starting material only. In a modified hypobromite oxidation,[8] to a suspension of the ketone (0·27 g) in dioxan (8 ml) an ice-cold mixture of potassium hydroxide (0·5 g), water (2·5 ml) and bromine (0·5 g) was added dropwise and stirred at room temperature for 1 hr. Crystallisation (ethanol) of the resulting white precipitate afforded *1-tribromoacetyl-2-methoxyxanthone* (74%) as plates, m.p. 204° (Found: C, 38·4; H, 1·9; Br, 47·4. $C_{16}H_9O_4Br_3$ requires C, 38·0; H, 1·8; Br, 47·5%). Hydrolysis of the bromoketone (aqueous potassium hydroxide, 8%) gave mainly starting material.

(b) 1-Acetyl-2-methoxyxanthone (0·1 g) in concentrated sulphuric acid (3 ml) was oxidised with chromium trioxide (0·1 g) at 5° with stirring for 1 hr. The mixture was then diluted with water (50 ml) and the precipitate collected. Extraction of the residue with sodium hydrogen carbonate, followed by acidification of the extract, yielded 1-carboxy-2-methoxyxanthone, m.p. and mixed m.p. 244–245°.

4′:5′-Dihydro-4′-oxofurano(3′:2′-1:2)xanthone

To 1-acetyl-2-hydroxyxanthone (0·25 g) in acetic acid (25 ml) kept at 60° was added a solution of bromine (0·16 g) in acetic acid (10 ml) in one portion. When by raising the temperature to 75° the reaction mixture had become yellow, it was poured onto ice. The crude tribromoketone (0·27 g) m.p. 147–150°, which separated as a yellow precipitate was collected and dried but could not be purified. The bromo compound (0·8 g) was refluxed in ethanol (600 ml) in presence of sodium acetate (0·8 g) for 0·75 hr. After treatment with charcoal most of the solvent was removed and 4′:5′-dihydro-4′-oxofurano(3′:2′-1:2)xanthone (0·40 g) was precipitated by addition of water. It crystallised as needles (ethanol), m.p. 208°, λ_{max} 229 (29,500), 250 (30,900), 300 (3000),

358 (9500) (Found: C, 71·2; H, 3·4. $C_{15}H_8O_4$ requires C, 71·4; H, 3·2%). It gave a precipitate with Brady's reagent.

4′-Methylfurano(3′:2′–1:2)xanthone

1-Acetyl-2-hydroxyxanthone (1·02 g), ethyl bromoacetate (1·01 g) and anhydrous potassium carbonate (2·76 g) were boiled under reflux with acetone (30 ml) for 0·5 hr. The filtrate from the reaction mixture yielded after removal of the solvent a pasty residue which afforded *ethyl-1-acetyl-9-oxo-2-xanthyloxyacetate* (95%) as white needles from ethanol, m.p. 151° (Found: C, 67·1; H, 4·6. $C_{19}H_{16}O_6$ requires C, 67·0, H, 4·7%). Hydrolysis with 2 N-sodium hydroxide gave the *acid* m.p. 210° (decomp) (Found: C, 65·3; H, 3·7) $C_{17}H_{12}O_6$ requires C, 65·4; H, 3·9%). The acid (0·3 g) and sodium acetate (0·75 g) were boiled under reflux in acetic anhydride with stirring for 2 hr. The crude product obtained by the procedure described for the parent compound[10] gave *4′-methylfurano(3′:2′–1:2)xanthone* as white needles from ethanol, λ_{max} 235 (27,300), 318 (9600), 354 (10,600), m.p. 137° (Found: C, 76·8; H, 3·9. $C_{16}H_{10}O_3$ requires C, 76·8; H, 4·0%).

6′-Ethoxycarbonyl-4′-pyrono(3′:2′–1:2)xanthone

1-Acetyl-2-hydroxyxanthone (0·5 g), sodium ethoxide (0·3 g), diethyl oxalate (0·44 g) and xylene (40 ml) were heated and agitated on a steam-bath for 3 hr. Filtration of the reaction mixture gave a residue which was acidified (dilute hydrochloric acid) and then extracted with chloroform (25 ml). The chloroform layer was then repeatedly extracted with aqueous sodium hydrogen carbonate (3 × 10 ml). Acidification of the precipitate formed during this extraction yielded a white substance (0·16 g), m.p. 100–110°. On boiling it with a mixture of ethanol (8 ml) and concentrated hydrochloric acid (0·4 ml) for 10 min a pale-yellow precipitate was produced which gave *6′-ethoxycarbonyl-4′-pyrono(3′:2′ 1:2)xanthone* from ethanol, m.p. 252–253° (decomp) λ_{max} 218 (26,000), 273 (20,500), 346 (6500), 362 (6500) (Found: C, 67·8; H, 3·8. $C_{19}H_{12}O_6$ requires C, 67·8; H, 3·6%). Hydrolysis of the ester (hydrochloric acid and acetic acid) furnished the *acid hydrate*, m.p. 202–203° (decomp) λ_{max} 221 (24,600), 275 (20,700), 313 (6500), 345 (6000), 360 (6200) (Found: C, 63·0; H, 3·4. $C_{17}H_{10}O_7$ requires C, 62·5; H, 3·1%).

5′-Benzoyl-6′-phenyl-4′-pyrono(3′:2′–1:2)xanthone

1-Acetyl-2-hydroxyxanthone (0·51 g), benzoic anhydride (2·7 g) and sodium benzoate (0·58 g) were heated at 180–190° in an air-bath for 6 hr. The reaction product was then boiled with 2 N-sodium hydroxide (10 ml) for 0·5 hr and extracted with chloroform (15 ml). Evaporation of the solvent and repeated crystallisation (ethanol) of the resulting residue gave *5′-benzoyl-6′-phenyl-4′-pyrono(3′:2′–1:2)xanthone* as pale-pink needles, m.p. 280° (Found: C, 78·3; H, 4·2. $C_{29}H_{16}O_5$ requires C, 78·4; H, 3·6%).

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